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HYDROXYL ION AS A LIGAND

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CONTENTS

A. INTRODUCTION

A hydroxyl ion acts as a ligand if it participates in the inner coordination sphere of a central particle forming thus a hydroxo complex. It is necessary to distinguish between the terms "hydroxo complex" and "hydrolytic complex". Both these terms are very similar but are not identical since the former denotes all complexes with a hydroxyl group in the coordination sphere regardless of the mode of formation while the latter infers those hydroxo complexes which are formed in a hydrolytic reaction and/or which participate in the hydrolytic equilibrium. By the term "hydrolysis" one usually understands those reactions* which cause the acidity of aqueous solutions of certain electrolytes[1]. However, a sufficiently general and unambiguous definition of hydrolysis has not been presented as yet. This is caused by disagreement over the meaning of the general acid–base concept within which hydrolysis takes place[2–4].

Analyzing the large amount of published data on hydroxo complexes we emphasize the characteristic features of the hydroxyl component of these complexes, *e.g.* the role of the hydroxyl ligands in the formation of hydroxo complexes of various types, their adaptability to external conditions (mainly the effect of the central particle), their ability to form chemical bonds, *etc.*

The behaviour of the hydroxyl group will be naturally related to that of other ligands. The properties of non-hydroxyl ligands will therefore be briefly mentioned in certain parts of this review to indicate these more general relationships.

However, it seems useful to summarize first the properties of the free (uncoordinated) hydroxyl ion.

B. UNCOORDINATED OH^- ION

The gaseous OH^- ion can be experimentally produced by an electronic discharge in a gaseous mixture[5]. In agreement with theoretical predictions the dimensions found for OH^- differ insignificantly from those of the uncharged OH species. The electron affinity of OH is 1.83 ± 0.04 eV, and the energy of the valence vibration $\omega_e(OH^-) = 3735 \pm 560$ cm^{-1}. The index of refraction of the OH^- ion in the gas phase (at $\lambda = \infty$) is 4.61 and in the condensed phase it decreases to 4.28[6].

Solvated (hydrated) OH^- ion has already been put in chemical contact with a medium and from a general point of view can be thought of as a central particle. In aqueous solutions it is bound by rather strong hydrogen bonds to three water molecules (as proven by IR and NMR measurements[7,8]). The hydroxyl hydrogen hardly participates in the formation of these bonds[8,9], causing an asymmetric structure for the hydroxyl hydrate. Its effective radius calculated from spectroscopic data[10] is 1.63 Å roughly equal to its crystallographic radius**.

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* Substitution reactions of the type $R–X + OH^- = R–OH + X^-$ are sometimes denoted by the term "hydrolysis".

** The crystallographic radius of OH^-, 1.41 Å, was obtained by comparison with the radii of corresponding fluorides[11]. The value of 1.45 Å derived for the spherical model[12,13] and the values of Pauling's radii, $r_O = 1.36$ Å and $r_H = 1.325$ Å, for the di-spherical dumb-bell model[14,15] are in agreement with these results.

Electrolysis of tritium-labelled aqueous electrolyte solutions lead to the conclusion[16] that the hydroxyl ion, in a similar manner to Cl^- and SO_4^{2-} ions, transports only 0.176 moles H_2O per OH^-, *i.e.* this fraction of water molecules is considered to be bound firmly.

From extraction experiments with a series of tetraalkylammonium hydroxides in various organic solvents it follows that under these conditions trisolvates are formed in which the hydroxyl group offers three positions for a very strong hydrogen bond[17], analogous to its behaviour in water.

X-ray structural analysis of the solid $NaOH \cdot 4H_2O$ revealed[18] that the hydroxyl group is surrounded by six molecules of water in a strongly flattened octahedral arrangement, the hydroxyl oxygen being in five cases an acceptor for a strong hydrogen bond (bond length 2.68–2.73 Å) and in one case the donor for a very weak hydrogen bond (bond length 3.11 Å). There is therefore a pronounced difference in properties of the hydroxyl oxygen in the solid and liquid phases.

The properties of the hydroxyl ion are considerably modified in solids; for example, its radius in solid hydroxides varies in the range from 1.35 to 1.80 Å (*cf.* Ref. 11) or from 1.32 to 1.84 Å (*cf.* Ref. 10) depending on the nature of the corresponding cation. The electronegativity of the hydroxyl ion depends on the cation counterpart and varies from 3.1 to 2.15 from univalent to tetravalent cations[19], implying that the covalent character of the metal–OH bond increases with increasing valence of the cation.

On the contrary, in typical ionic compounds with spherical symmetry of the hydroxyl ion[20], *e.g.* RbOH and CsOH, its radius equals 0.957 and 0.960 Å, respectively[21], identical in fact with its radius in water (0.957 Å).

Theoretical considerations of the bonding abilities of the hydroxyl ion are based on the assumption of sp^3-hybridization of the valence orbitals of the hydroxyl oxygen oriented therefore towards the vertices of a tetrahedron[22]. One of these hybrid orbitals, together with the 1*s*-orbital of hydrogen and with certain participation of *p*-orbitals, forms the O–H bond, the other three hybrid orbitals being able to form bonds with other species. This is in very good agreement with the behaviour of hydroxyl ion in solution described above. Quantum-chemical calculations based on the above-mentioned assumptions gave the value of proton affinity of hydroxyl about 50% higher than the experimental value. The charges on oxygen and hydrogen were calculated to be $-0.8194\,e$ and $-0.1809\,e$, respectively, while the experimental values are $-0.79\ e$ and $-0.21\ e$ as measured in LiOH crystals by the NMR method[14]. The dipole moment was calculated to be 0.54 D (the values calculated by the same method for water and ammonia are 1.88 and 1.89 D, respectively: these results are close to the experimental values of 1.84 and 1.46 D, respectively).

The free hydroxyl group is diamagnetic, its molar magnetic susceptibility being -12×10^{-6} c.g.s. units[23]. The value persists in complexes with diamagnetic central ions forming an additive part of the overall susceptibility of the complex.

In complexes with paramagnetic central ions its role can be more complex. For example, in antiferromagnetic materials the appropriate cations can interact magnetically *via* bridge ligands (so-called "superexchange"), but it is more the question of solid state physics than that of coordination chemistry; to say nothing of the fact that in such cases the role of a ligand as such has not been as a rule expressed explicitly.

It seems indisputable[24–28] that the hydroxyl ion as a ligand is able to form both σ- and π-bonds with unoccupied and/or partially occupied orbitals of the central particle.

A model of hydroxyl ion as a ligand, having three electron pairs oriented towards the vertices of a tetrahedron available for the formation of bonds with central particles, follows thus from these theoretical assumptions and from experimental data.

C. COORDINATED HYDROXYL ION

The properties of the coordinated hydroxyl ion may conveniently be discussed in terms of its coordination number (*i.e.* the number of species coordinated directly thereto). A coordination number higher than 1 implies that it forms a bridge. It is possible that the same two central particles are bound by several OH-bridges. The basic characteristic of such ligands can be expressed by the symbol $_x(\mathrm{L})_y$ where L is the given ligand, x is its coordination number and y is the multiplicity of bridges; $x = 1$ and $y = 0$ stand for a terminal ligand.

(i) Hydroxyl ligands with coordination number 1 (type $_1(\mathrm{OH})_0$)

Ligands of this type appear in the inner coordination sphere of mononuclear as well as of polynuclear complexes (in the latter case along with bridging ligands of higher coordination numbers). The covalent character of a bond between the hydroxyl and the central particle can vary within certain limits. If the metal–OH bond is predominantly electrostatic, it manifests itself in the Raman spectrum only as a band of weak intensity (the hydroxyl behaves as an easily polarizable dipole of cylindrical symmetry[20,29]) while the covalent metal–OH bond gives rise to intense lines[30]. The covalent character of the bond can also be characterized by the energy of metal–OH valence vibrations in the IR spectrum, which is a measure of the shift of electrons along the bond towards the metal ion[31–33].

The energies of metal–OH valence vibrations in $3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2O}$ or $3\mathrm{SrO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2O}$ (containing two relatively isolated octahedrons $[\mathrm{Al(OH)_6}]^{3+}$ and therefore corresponding better to the formula[34] $\mathrm{M_3{}^{II}[Al(OH)_6]_2}$) fall in the region from 400 to 530 cm^{-1}. Similar vibrations in the hydroxo complexes $[\mathrm{M^{IV}(OH)_6}]^{2-}$ ($\mathrm{M^{IV}}$ = Pt, Pb and Sn[31]) fall in the range from 300 to 500 cm^{-1}.

Moreover, the energies of the M–O vibrations in a series of hydrated metal cations (Cu^{2+}, Zn^{2+}, Hg^{2+}, Mg^{2+}, In^{3+}, Ga^{3+}, Fe^{3+}, *etc.*) are found in a similar region[30,35] from 320 to 475 cm^{-1}. The values of these valence vibrations correspond to force constants from 0.8–1.9 mdyn/Å corresponding to bond orders[36] from 0.2–0.6.

The strength of the covalent bonds to OH^- and to H_2O as ligands in mononuclear complexes is evidently similar so that it is not surprising that in the one-dimensional spectroscopic series these ligands are located close together[37]. Spectroscopic and magnetochemical measurements confirm[37] the formulae for mononuclear hydroxo complexes $M'_2[M^{II}(OH)_6]$ and $Na_2[M^{II}(OH)_4]$ for $M' = Ba^{2+}$ or Sr^{2+} and M^{II} = Mn, Fe, Co, Ni, Cu and Zn.

(ii) Hydroxyl ligands with coordination number 2 (type ${}_2(OH)_y$)

It is obvious that a ligand forming a bridge must be part of a polynuclear complex. Simple bridges ${}_2(OH)_1$ and ${}_3(OH)_1$ as well as double bridges ${}_2(OH)_2$ and triple bridges ${}_2(OH)_3$ are observed in hydroxo complexes. Quadruple bridges ${}_2(OH)_4$ have not been characterised but are assumed[38] to occur in the hydrolytic products of thorium formed in ion-exchange resins under precisely defined conditions and to which the formula $[Th(OH)_4Th]_n{}^{4+}$ was ascribed. This conclusion needs verification.

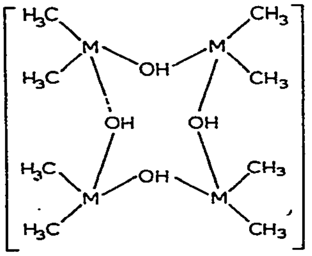
On the other hand quadruple acetate bridges ${}_2(Ac)_4$ have already been confirmed in anhydrous U^{IV}–acetate[39] and in hydrated acetates of copper, chromium and rhodium[40].

(a) Type ${}_2(OH)_1$

Hydroxo complexes with an open (noncyclic) structure contain bridges of this type in dimers [M–OH–M]. A metal–OH bond of weak covalent character is supposed[41] to be most favourable for these complexes. The stability of these dimers is not very high[42]. They usually appear in a hydrolyzed system together with a higher or predominating complex, *e.g.* $[(UO_2)_2OH]^{3+}$ together with the trimer at high concentrations of uranyl ions[43], Pb_2OH^{3+} together with the predominating complex $Pb_4(OH)_4{}^{4+}$ in a wide range of concentrations[44], Be_2OH^{3+} together with the cyclic trimer $(BeOH)_3{}^{3+}$ (again in wide range of concentrations[45–48]), Cd_2OH^{3+} as the most important complex from the low number of soluble hydroxo complexes of cadmium at high concentrations of Cd[49], Hg_2OH^{3+} appears together with $[Hg_2(OH)_2]^{2+}$ at high concentrations of mercury[50]; similar hydrolytic complexes of Cu^{II} have been observed[51]. The same bridge also appears in the ammine–hydroxo complexes of Cr^{III} [52,53] of the type $[Cr_2(OH)(NH_3)_{10}]Cl_5$ which (according to spectroscopic measurements) contain the group $\mathrm{Cr}\diagup^{\mathrm{OH}}\diagdown\mathrm{Cr}$ with an angle of about 135°. On steric grounds alone this angle should be at least 140° (*cf.* Ref. 54).

In the case of analogous oxygen bridges $_2(O)_1$ the angle M–O–M is affected by the participation of π-bonds[55–57], being 110° if their contribution is negligible and 180° if π-bonds participate highly in these bonds.

The trimer $(BeOH)_3{}^{3+}$ with an assumed[45,46,58] hexagonal ring structure belongs to the hydroxo complexes with a closed (cyclic) structure. Another type of a cyclic hydroxo complex includes for example the undissociated tetramers $[(CH_3)_2AuOH]_4$ and $[(CH_3)_2GaOH]_4$ (Refs. 59, 60) which form eight-membered rings with $_2(OH)_1$ bridges; schematically:



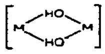
These compounds have a flat but not strictly planar structure. The mean value of M–OH–M angle is 111° in the case of the gold compound (which is very near to the tetrahedral angle 109.5°) and 135° in the case of the Ga complex. On the other hand, the mean value of the C–Me–C angle is 84° and 129°, respectively.

The hydroxo complex $[Bi_6(OH)_{12}]^{6+}$ is interesting from the point of view that the octahedron of central ions is bound partly by direct metal–metal bonds and partly by $_2(OH)_1$ bridges over edges of this octahedron[61]. A similar geometric structure was also found in the complexes $[PtCl_2]_6 \equiv Pt_6Cl_{12}$ (Ref. 62, p. 152) and $[M_6Cl_{12}]^{2+}$ in Nb_6Cl_{14} and Ta_6Cl_{14} (Ref. 63); it is not known whether together with the $_2(Cl)_1$ bridges there are also metal–metal bonds in these complexes. The IR spectra of M_6X_{12} systems (M = Pd, Pt; X = Cl, Br) have been discussed[64].

We can conclude that mere $_2(OH)_1$ bridges do not form a sufficiently strong linkage between central particles. The presence of an additional stabilizing factor (*e.g.* formation of π-bonds, cyclic configuration of the complex or binding of central ions by metal–metal bonds) is necessary if a more stable complex is to be formed.

(b) *Type $_2(OH)_2$*

Bridges of this type are very common appearing in the hydrolytic complexes of many cations (Cu^{2+}, Zn^{2+}, Sn^{2+}, Pb^{2+}, $UO_2{}^{2+}$, Al^{3+}, Sc^{3+}, Y^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Fe^{3+}, Ce^{4+}, U^{4+}, Th^{4+}, etc.)[65–68]. The simplest complex with $_2(OH)_2$ bridges is



which is often the most well established polynuclear hydroxo complex of the given cation.

TABLE 1

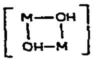
STRUCTURAL DATA ON $_2(OH)_2$ BRIDGES IN DIMERS

Coordination compound	*M–O bridged*		*M–O terminal (non-bridged)*	*M–M*	*Angle*		*Coord. No.*	*Central ion and its polyhedron*	*Ref.*
	I	*II*			$M\diagup^{OH}\diagdown M$	$OH\diagup^{M}\diagdown OH$			
$[\{(NH_2)_2CO\}_3UO_2(OH)_2UO_2\{OC(NH_2)_2\}_3]$[a]	2.38	2.38	2.35–2.42	3.928	111	69	5	UO_2^{2+}, plane pentagon	69
$[(H_2O)_2ClUO_2(OH)_2UO_2Cl(OH)_2]_2$[b]	2.32[c] 2.40[c]	2.39[c] 2.35[c]	2.37–2.53	3.944	113.6 112.4	66.2 67.2	5	UO_2^{2+}, plane pentagon	70
$[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4 \cdot 4H_2O$	1.88	1.99	—	2.97	100	80	6	Co^{3+}, octahedron	71
$[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4 \cdot 4H_2O$	1.911	1.913	—	2.932	100.1	79.7	6	Co^{3+}, octahedron	54
$[Al_2(OH)_2(H_2O)_8](SO_4)_2 \cdot 2H_2O$	1.85	1.87	1.88–1.95	2.86	100.4	79.6	6	Al^{3+}, octahedron	72
$[Al_2(OH)_2(H_2O)_8](SeO_4)_2 \cdot 2H_2O$	1.87	1.87	1.88–1.92	2.88	100.7	79.3	6	Al^{3+}, octahedron	72
$Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SeO_4)_4 \cdot xH_2O$	1.86	1.86	1.94[d]	2.88	102.0	78.0	6	Al^{3+}, octahedron	73
$[Zr_4(OH)_6(CrO_4)_5(H_2O)_2]$[e,f]	2.21	2.21	1.97–2.21	3.595	109	71	7	Zr^{4+}, pentagonal bipyramid	74
$K_6[Zr_2(OH)_2(CO_3)_6] \cdot 6H_2O$[g]	2.07	2.13	2.16–2.29[h]	3.47	111.5	68.5	8	Zr^{4+}, distorted dodecahedron[i]	75
$[Zr_2(OH)_2(SO_4)_3(H_2O)_4]$	2.09	2.16	2.17–2.26[j]	3.547	113.0	67.0	8	Zr^{4+}, dodecahedron[i]	76
$[Zr_4(OH)_8(H_2O)_{16}]^{8+}$[e,k]	2.13	2.23	2.09–2.35[l]	3.57	113.0	67.0	8	Zr^{4+}, distorted square antiprism	77
$[Th_2(OH)_2(NH_3)_6(H_2O)_8]^{6+}$[m]	2.33	2.39	2.49–2.76	3.988	115.5	64.5	11	Th^{4+}, see note[n]	78

[a] Formal composition $UO_2(OH)_2 \cdot 3.2CO(NH_2)_2 \cdot I^- \cdot 0.73I^\circ$; preparation and some properties see Ref. 79. [b] Formal composition $UO_3 \cdot HCl \cdot 2H_2O$. [c] Average value 2.37 Å. [d] An average value. [e] Does not contain dimers, merely $_2(OH)_2$ bridges. [f] Formal composition $4ZrO_2 \cdot 5CrO_3 \cdot 5H_2O$. [g] IR spectra of that and many other related complexes discussed in paper[80] (see p. 77). [h] Average value 2.19 Å. [i] Of the type $Mo(CN)_8^{4-}$. [j] Average value 2.22 Å. [k] Formal composition $ZrOCl_2 \cdot 8H_2O$. [l] Average value 2.26 Å. [m] Practically the same Th–Th separations were found in soluble hydrolytic Th complexes; a more soluble complex, probably a tetramer, is composed of dimers[81]. [n] If each bidentate nitrate group is considered as a single ligand, the coordination polyhedron may be described as a somewhat distorted dodecahedron.

Structural data on coordination compounds, within which the binuclear complex $[M(OH)_2M]$ can be identified are given in Table 1. Complexes with coordination number 6 seem to differ markedly from the other complexes both with respect to the dimer bond angles and M–M separations. The reason could be found in the smaller geometric suitability of an octahedron for formation of four-membered rings (see p. 85 and Table 3). Relatively great structural similarity exists in the basic dinuclear unit of the other complexes despite great differences in the coordination numbers of the central ion. The angles found at the hydroxyl bridge correspond well with the supposition of a tetrahedral arrangement of its bonding orbitals. In view of the relatively high M–M separation it seems unlikely that a direct interaction exists between the central ions. The apparent radius of the zirconium central ion is rather smaller than that of uranium within the uranyl ion (*e.g.*, if the apparent radius of a hydroxyl bridge were equal to 1.30 Å, the apparent Zr^{4+} radius would be 0.80 Å and that of uranium on the equator of the UO_2^{2+} group 1.08 Å).

The configuration of a four-membered ring is very favourable from the point of view of stability[42,82]. This is supported by the fact that polynuclear complexes with less stable bridges $_2(L)_2$ — where L is *e.g.* a halide atom (the lower stability following from the less effective donor properties of these elements[25]) — often exist only in the configuration of these dimers (*e.g.* Ref. 83). Moreover calculations based on the electrostatic model show[84] that the planar structure



is more stable than the linear structure [M–OH–M–OH]*. The stability would also increase if the M–OH bond were covalent.

The published data for the dimerization constants $K_D = [\text{dimer}] \cdot [\text{monomer}]^{-2}$, corresponding to the equation: $2MOH^{z+} = [M(OH)_2M]^{2z+}$, are all greater than one (usually of the order of 10^2–10^5)[1,65,68,85–87]. Therefore, the free energy change of dimerization is negative. Since entropy decreases as a consequence of the formation of a dimer, dimerization should be an exothermic reaction and the value of the dimerization constant should therefore decrease with increase of temperature[84]. Similar considerations were also published in connection with the hydrolytic behaviour of certain heavy metal ions[88]. Unfortunately, these considerations do not take into account the simultaneous change of entropy of the solvent. Nevertheless the few experimental results which are available are in agreement with the abovementioned conclusion (*cf.* Table 2).

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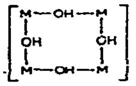
* If MOH is the basic entity then the configuration



is even more stable than the dimer.

TABLE 2

DEPENDENCE OF DIMERIZATION CONSTANT, K_D, ON TEMPERATURE AND IONIC STRENGTH

Central ion	*Ref.*	*$\log_{10}K_D$ (at °C)*			*μ*
UO_2^{2+}	85	5.49(25)	4.28(40)	—	0.0347, ClO_4^-
		4.97(25)	—	—	0.347, ClO_4^-
	86	5.48(25)	3.88(94)	—	0.5M KNO_3
Fe^{3+}	89	1.67(18)	1.56(25)	1.42(32)	0(extrapol)
		2.43(18)	2.34(25)	2.23(32)	0.103
		2.62(18)	2.51(25)	2.38(32)	0.203
		2.70(18)	2.59(25)	2.48(32)	0.303
		2.99(18)	2.86(25)[a]	2.71(32)	1.000
Sc^{3+}	90	3.53(10)	3.33(40)[b]	—	1M $NaClO_4$
Ce^{4+}	91	2.04(5)	1.62(15)	1.22(25)[c]	2M $NaClO_4$
Th^{4+}	66	3.04(0)	3.63(25)	1.93(95)	1M $NaClO_4$

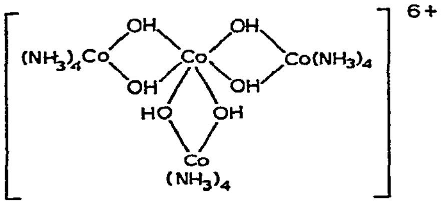
[a] From data obtained in 3M $NaClO_4$ at 25 °C log K_D = 3.18 which seems to be adequate[92]. [b] There is some uncertainty in these data[90]. [c] Log K_D (at 35 °C) = 0.49.

The decrease of the numerical value of the constant K_D with temperature is caused by the relatively great increase in the monomer concentration compared with the concentration of dimer. However, absolute values of the concentration of dimer increase, too, in agreement with the overall enhancement of hydrolytic equilibria (*i.e.* in agreement with the increase of acidity and of the total concentration of hydrolytic complexes accompanied by the decrease of the concentration of the free cation) at higher temperatures.

As regards the effect of ionic strength on dimerization, it is assumed that the constant K_D increases with ionic strength[84,87]. This conclusion is in agreement with the experimental data for the ferric ion but was not confirmed in the case of the uranyl ion (Table 2). It would be premature to make any conclusions because there are few experimental data and the conclusion is, strictly speaking, valid only for sufficiently dilute solutions because it was derived from the Debye–Hückel theory[87].

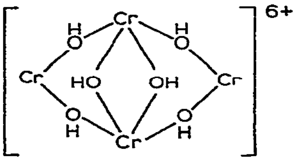
A very interesting complex is the tetramer $[Co_4(OH)_6(NH_3)_{12}]^{6+}$, *i.e.* $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$. It is assumed[93] that its central cobalt atoms are not equivalent, but form a triangle with one central ion in the centre (see the scheme).

Magnetochemical measurements[94] at temperatures above 77 °K for an



analogous complex of the Cr^{III}-ion, $[Cr_4(OH)_6(en)_6]^{6+}$, show that central atoms are not equivalent (in agreement with the assumed structure of the cobalt complex). However, an alternative treatment of the same results[95], on the contrary, states that these measurements prove the equivalence of central ions and that, accordingly, their configuration is tetrahedral.

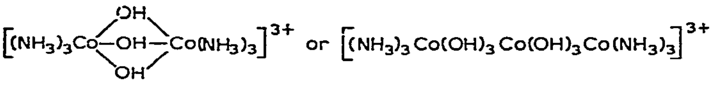
New magnetochemical measurements[96] down to 4.2 °K did not resolve the question; although the results could not be adequately explained on the basis of the plane triangular arrangement, neither could they be interpreted on the basis of the tetrahedral model. A structural study of the crystal $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ shows that the chromium atoms are linked by means of four $_2(OH)_1$ bridges with a Cr–OH–Cr angle of 131°, to form a rhombus with diagonals of 2.921 and 6.554 Å in which the nearer atoms are, in addition, linked by $_2(OH)_2$ bridges with Cr–OH–Cr angles equal to 95°. The basic skeleton is given in the following scheme.



Additional ligands (not sketched in the scheme), confer an octahedral coordination about the chromium atoms. The central chromium atoms are not equivalent and are arranged in a plane but in an entirely different manner than supposed originally.

(c) *Type* $_2(OH)_3$

Complexes with triple hydroxyl bridges of the $_2(OH)_3$ type are, in contrast to the preceding types, rather rare. They can be represented by cobaltiammine complexes



$$\left[(NH_3)_3Co\overset{OH}{\underset{OH}{-OH-}}Co(NH_3)_3\right]^{3+} \text{ or } \left[(NH_3)_3Co(OH)_3Co(OH)_3Co(NH_3)_3\right]^{3+}$$

The geometry of the triple bridge in the first of these two complexes is as follows[97]: the Co–Co distance is 2.54 Å, the average Co–OH distance is 1.97 Å (in one bridge it is 1.96 and 2.03 Å, in the other two 1.98 Å and 1.90 Å). The corresponding Co$\diagup^{OH}\diagdown$Co angles are 79° and 82°, respectively, substantially lower than the tetrahedral angle 109.5°. Hydroxyl bridges of this complex do not reveal any acid–base properties in aqueous solutions. In spite of the similarity of coordination behaviour[98,99] of Co^{3+} and Cr^{3+} ions, complexes of this type with Cr^{3+} central ions are not known[100].

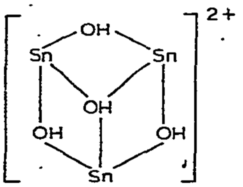
Cobaltiammine hydroxo complexes cannot be regarded as hydrolytic complexes because they are not formed in any hydrolytic equilibrium in a solution of the central ions but they must be prepared by special preparative methods starting from a lower oxidation form[2,101].

(iii) Hydroxyl ligand with coordination number 3 (type ${}_3(OH)_y$)

If the tetrahedral model of the bond orbitals of oxygen in the hydroxyl ion corresponds adequately to reality, then the maximum coordination number of a hydroxyl group is 3*. Simple bridges with this coordination number were found in several complexes with 4 or 6 central atoms. In the latter case these atoms are arranged in an octahedral configuration, over the faces of which there are 8 ligands of the type ${}_3(L)_1$. This configuration can be considered relatively stable because it was found[102] in basic salts of uranium(IV) and cerium(IV) as $[M_6(O)_4(OH)_4]^{12+}$ entities, moreover it occurs in solutions and in the solid phase of hydrolyzed systems of lead[103,104] (*e.g.* the complex ion $[Pb_6(OH)_8]^{4+}$ with direct metal–metal bonds)† and it is also typical of many complexes of bivalent molybdenum[107,108] which contain the basic entity $[Mo_6Cl_8]^{4+}$ with ${}_3(Cl)_1$ ligands. In the case of the tetramer $[M_4L_4]^{(4z-4)+}$ both central ions and ligands form two mutually penetrating tetrahedra involving the coordination type ${}_3(OH)_1$. This assumption was confirmed in the case of hydroxo complexes of lead, both in liquid and solid phases[103,104,109] in which the basic entity $[Pb_4(OH)_4]^{4+}$ was found.

The arrangement of trimethyl platinum hydroxide, $[(CH_3)_3PtOH]_4$, is entirely analogous[110]. The Pt–OH–Pt angle within the complex is equal to 101.2°, *i.e.* close to the tetrahedral angle.

The ${}_3(OH)_1$ bridge, together with three ${}_2(OH)_1$ bridges, also appears in the oligomer $[Sn_3(OH)_4]^{2+}$ with the following structure:



The formation of a triangular pyramid with three ligands at the apices of its base is typical[111] for Sn^{2+}. The ${}_3(OH)_1$ bridges have recently been found in $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ [112].

The existence of a bridge of the ${}_3(OH)_2$-type can be formally anticipated. This would need a configuration of three central atoms at the vertices of a triangle bound by two hydroxyls from each side of the triangle forming thus a triangular

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* The maximum coordination number 4 of oxygen is valid *e.g.* for the isomorphous oxides CeO_2, ThO_2 and UO_2 which have cubic symmetry of the fluorite type. These compounds cannot, however, be considered to be complexes comparable with the ones discussed.

† According to recent measurements[105,106], the molecular structure of this complex in solution as well as in the solid should be modified a little, the correct formula being $Pb_6O(OH)_6(ClO_4)_4$.

bipyramid. It is obvious that the likelihood of such a configuration will be low because of the unusual angular correlations of the orbitals of the central atoms.

(iv) Methods for determination of the coordination mode of the hydroxyl ligand

An unambiguous determination of the coordination mode of a ligand by one single method is rather exceptional, usually it is determined by a combination of the results of several methods. The situation is still more complicated in hydrolyzed systems because individual complexes cannot normally be isolated and directly analyzed.

Together with chemical methods vibrational spectroscopy is very useful in the case of $_1(L)_0$ ligands. Vibrational frequencies of M–L bonds for coordinated hydroxyl and water molecules lie roughly in the region from 300 to 500 cm^{-1} (*cf.* pp. 68, 69). Corresponding frequencies for other simple ligands (*e.g.* halides) are lower because of their heavier weight and poorer donor properties relative to oxygen[25].

Bridges of the $_2(L)_1$ type in linear or angular arrangement M–L–M can also be identified from IR spectra[55]. The antisymmetric frequency, ν_3, of this configuration is somewhat lowered when bent (for the $_2(O)_1$ bridges the absorption occurs near 800 cm^{-1}) whilst the symmetric frequency, ν_1, on the contrary, increases (in the mentioned case to values around 500 cm^{-1}). Values of these stretching frequencies depend not only on the M–L–M– angle but also on the strength of the M–L bond.

The correct assignment of this frequency as arising from a bridge can be confirmed by comparison with the spectrum of a suitable monomer complex, where the corresponding band cannot appear, or by deuteration, which causes a decrease in the value of ν_3 (depending on the M–L–M angle). Bridges $_2(OH)_1$ in ammine complexes of chromium[55] of the type $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ are bent and exhibit a strong absorption band, ν_3, with an energy of about 570 cm^{-1}. $_2(OH)_1$ bridges in the hydroxo complex $[Bi_6(OH)_{12}]^{6+}$, which also contains metal–metal bonds, exhibit frequencies in the region above 400 cm^{-1} (Refs. 61, 113).

In the IR spectrum[114] of dimethylgallium(III) hydroxide, $[(CH_3)_2GaOH]_4$, containing only $_2(OH)_1$ bridges, the deformation vibrations, $\delta_{OH}{}^b$, exhibit sharp and intense bands at 1013 and 1030 cm^{-1} shifting after deuteration to about 730 cm^{-1}. Sharp bands due to the valence vibrations, $\nu_{OH}{}^b$, are shifted from 3601 cm^{-1} to 2656 cm^{-1}.

$_2(L)_2$ bridges also reveal themselves spectroscopically. Empirically it was found[115,116] that in the IR spectra of hydroxo complexes of copper and chromium with $_2(OH)_2$ bridges, strong absorption bands can be found in the region from 400 to 600 cm^{-1}. Many other compounds[117–120] containing these $_2(OH)_2$ bridges also absorb in this region. These bands are very probably caused by skeletal stretching modes. Similar behaviour was also observed in complexes with $_2(Cl)_2$

bridges, *e.g.* absorption at 420 cm^{-1} by the gaseous dimer Al_2Cl_2 (Ref. 121), somewhat lower values were found in gallium chloride[122], titanium(IV) chloride[123], titanium(III), vanadium(III) and chromium(III) chlorides[124]. More general relations in systems with halide bridges ${}_2(L)_2$ are discussed in Refs. 125, 126.

In a series of related dihydroxocarbonate complexes of zirconium, ${}_2(OH)_2$ bridges manifested themselves by intense deformation vibration bands, $\delta_{OH}{}^b$, near 1000 cm^{-1}; the corresponding band in the hafnium analogue occurs at 1018 cm^{-1}, a little above the preceding ones[80]. These observations are in agreement with results of the IR analysis[127] of the so-called zirconium oxychloride with contains $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ tetramer units with four ${}_2(OH)_2$ bridges — their $\delta_{OH}{}^b$ frequencies lie in the region 1000–1100 cm^{-1}, their stretching frequencies at 3530 cm^{-1}. $\delta_{OH}{}^b$ frequencies in silica gel found in the region 900–1100 cm^{-1} are mentioned below, p. 79.

In complexes $(NH_4)_2Fe_2(OH)_4(CO_3)_2 \cdot nH_2O$, $n = 1$ or 3, in which dihydroxo bridges seem to be very likely, bands at 912 and 752 cm^{-1} ($n = 1$) and at 980 cm^{-1} ($n = 3$) were identified as δ_{OH}; the ν_{OH} frequencies were observed at 3295 cm^{-1} and in the region 3030–3350 cm^{-1}, respectively[128].

Considering vibrations of ${}_3(OH)_1$ bridges, which are the only bridges in $[(CH_3)_3PtOH]_4$ (see p. 75), the $\delta_{OH}{}^b$ frequencies were found[129] at 724 and 706 cm^{-1}, their $\nu_{OH}{}^b$ at 3595 cm^{-1}. The low values of the former and the high value of the latter, along with the sharpness of these bands, indicate absence of hydrogen bonding in this complex. Similarly, in $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2$-$(H_2O)_2$ with ${}_3(OH)_1$ bridges, the $\nu_{OH}{}^b$ frequency was identified[112] as a weak but sharp absorption band at 3560 cm^{-1}.

It is evident that in a spectroscopic determination of the mode of coordination of the hydroxyl ligand the regions in which different types of hydroxyl group manifest themselves very often overlap. A more extensive discussion of the energies of individual types of bridges and their vibrational modes, seems to be premature.

Recently[130,131] the dimer $[Cu_2Cl_6]^{2-} = [Cl_2Cu(Cl)_2CuCl_2]^{2-}$ was identified by its electronic absorption spectrum; this complex has an electronic absorption band at 19.000 cm^{-1} polarized in the direction Cu–Cu, which does not appear in the perpendicular direction. The generality of this procedure is not known, certain limitations follow from the difficulty in getting single crystals (with exception of complexes of Co^{3+} or, perhaps, even Cr^{3+}) of the hydroxo complexes.

If the central ion is paramagnetic, the formation of dimers may be indicated by a decrease in the magnetic susceptibility of the bound ion in comparison with its hydrated form[52,132,133]. The decrease of paramagnetism can be explained by the partial compensation of spins of the central ions via bridges[134], but it can also be caused by direct bonding between the ions[40,135].

An absolute method for the determination of the configuration of complexes, and therefore also of the mode of coordination of ligands, is structural analysis. The necessary single crystals of hydroxo complexes were mostly prepared in the form of basic salts[102,136,137], the preparation of hydroxides is very difficult.

Individual complexes participating in hydrolytic equilibria in aqueous solutions cannot be isolated. The formulae of these complexes are usually derived from certain analytical and potentiometric data[138]; a most excellent formal approach for the treatment of these data was formulated by Sillén[139,140]. Of course, the conclusions are indirect and depend, among other things, on the type of model complex chosen for interpretation of the experimental data (*e.g.* Sillén's "core-links complexes") so that it is desirable to use more direct measurement ("fingerprint methods")[1,141], if possible. Among the most important are vibrational spectroscopy [hydroxo systems of Bi^{3+} (Ref. 61) and Pb^{2+} (Ref. 103)], X-ray diffraction in solutions [hydroxo systems of Pb^{2+} (Refs. 137, 142) and Zr^{4+} (Ref. 120)], ultracentrifugation [*e.g.* hydroxo systems of Pb^{2+} (Ref. 109), $UO_2{}^{2+}$ (Ref. 143), Ta^V (Ref. 144)], light scattering [systems of Pb^{2+} (Ref. 145)], to some extent, absorption spectroscopy [hydroxo systems of $UO_2{}^{2+}$ (Ref. 146) and U^{4+} (Ref. 147)], *etc.* Naturally, it is desirable to compare the conclusions derived by different methods so that our knowledge of the configuration of complexes and, accordingly, of the coordination modes of ligands can be more reliable.

D. REACTIONS OF COORDINATED HYDROXYL IONS

(i) Dissociation of the bridge hydrogen (oxolation)

One of the possible reactions of the hydroxyl bridge is dissociation of its hydrogen in the form of an ion into solution accompanied by the formation of an oxygen or oxo bridge. This reaction is called oxolation[148] and can be expressed by the scheme

$$[M(OH)_nM]^{y+} \rightleftharpoons [M(O)_nM]^{(y-n)+} + nH^+$$

There is experimental support of this scheme, *e.g.* solutions of basic chromium(III) salts become more acidic if heated, whereas the reestablishment of the former acidity after cooling takes a very long time.

On the other hand it is well known that aqueous solutions of cobalt(III) complexes with double[149] or triple[97] hydroxyl bridges do not exhibit acid–base properties. Decreased reactivity of hydroxyl bridges can probably be taken as a general property[148]. The assumption of oxolation in the above mentioned sense is however not convincing (*cf.* Ref. 42, page 157). The behaviour of the chromium(III) systems can be explained without introducing a new term by a shift of the hydrolytic equilibrium at a higher temperature (*i.e.* by an increase of the total amount of hydrolytic products together with an increase in the acidity of the solution); the decrease of acidity during the period of cooling can be explained by a slow re-establishment of the former equilibrium.

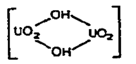
On the other hand it is experimentally proven that some hydrolytic precipitates (essentially electrically neutral hydroxides) are able to release H^+ ions into supernatant solution, if the solution contains some electrolytes. This is especially so in the case of iron(III)[150] and manganese(IV)[151] hydroxides, and of silica gel[152,153], *etc.* This process also proceeds very easily in the case of the uranyl ion[154,155]. In contrast to oxolation this case is a substitution reaction of the type

$$[UO_2(OH)_2UO_2]\,(OH)_2+2Na^+ = [UO_2(ONa)_2UO_2]\,(OH)_2+2H^+$$

which proceeds only in the solid phase[156]. The substituted hydroxyl bridge $>$ONa is thermally very stable, in contrast to the unsubstituted $>$OH, which decomposes at temperatures between 300° and 400 °C[157].

From general considerations it follows[158] that the formation of an oxonium oxygen in the hydroxyl bridge is connected with a shift of electrons from this oxygen towards the central atoms. This shift increases the covalency of the M–OH bond and simultaneously, decreases the bond strength of O–H because of weakening of its electrostatic component. This is the reason for potential acidity of the hydroxyl bridge. Their gradual substitution can be followed in the IR spectra of uranates[159] by the linear dependence of the uranyl antisymmetric frequency ν_3 (reflecting the increasing covalent character of the U–OH bond) on the relative amount of sodium, Na/U.

If the solid phase of uranates were formed from isolated dimers



there should be three coordination states of uranyl, dependent on the number of substituted hydroxyls, and therefore three different values of the ν_3 frequency, corresponding to none, one or two substituted bridges, respectively. The intensities of these bands would be proportional to the number of corresponding states. However, the energy of the ν_3 frequency actually decreases continuously with increasing Na/U ratio, preserving its rather high intensity. This means that the dimers in the solid phase are mutually interconnected in one giant molecule and the measured value of ν_3 characterizes the average state of substitution.

Direct observation of these processes by shifts in the M–O frequencies as a consequence of the change in covalent character of the metal-bridged oxygen bond is unfortunately not possible. The probable reason is a lower sensitivity of these vibrations to the detailed structure, compared to the sensitivity of $O=U=O$ bonds in the uranyl ion to changes of coordination in its equatorial plane. Moreover, the corresponding bands are rather diffuse so that frequency determination cannot be precise[159]. However, a decrease in the intensity of two absorption bands ascribed to the hydroxyl deformation vibration, δ_{OH}, has been observed in the region 900–1100 cm^{-1} caused by the substitution of cations into silica gel (a similar effect is observed upon dehydration of unsubstituted silica gel[152]). It follows that these frequencies must be derived from bridging hydroxyl groups (*cf.* p. 77).

(ii) Depolymerization and dehydroxylation

Many cations (*e.g.* Zn^{2+}, Cu^{2+}, Co^{2+}, Sn^{2+}, Cd^{2+}, Cr^{3+}, Al^{3+}, *etc.*) exhibit amphoterism whereby in solution it is possible to precipitate an insoluble hydroxide by alkali and to redissolve this in excess alkali[148]. In this review we would like to discuss one special feature of these processes, namely that soluble hydroxo complexes in acidic solutions and insoluble hydroxo complexes (basic salts) at roughly neutral pH values usually form polynuclear (oligomeric) entities, while after dissolution in excess alkali the same central ions form only mononuclear complexes. In other words, depolymerization occurs with increasing OH^- concentration. This can be typically represented by aluminium ions. In a hydrolyzed solution aluminium forms hexamers as dominant entities[160], in solid hydrolytic phase (basic salts) complicated entities with 13 aluminium atoms were identified[161] (their existence was also assumed in solution[162]) while in alkaline solution $Al(OH)_4^-$ anions are present[163–165]. Moreover, in strongly alkaline solutions ($pH > 13$) AlO_2^- anions are formed by dehydroxylation as indicated by Raman spectra[166] and by NMR[165]. Along with depolymerization a process of dehydroxylation proceeds until a simple oxo ion is achieved.

Lead hydroxo complexes can serve as a similar example. In acidic solutions and in hydrolytic solid phase they form predominantly tetramers and hexamers[104,137,167] whereas in alkaline solutions $Pb(OH)_3^-$ anions were identified polarographically[168,169] (Lingane[168] regards these ions as $HPbO_2^-$). The monomer character of these ions is also corroborated by the results of ultracentrifugation[170] as well as by the fact that the diffusion coefficients of the free ions and the complex particles differ only by about 5%[168]. In the case of zinc the existence of an anion $Zn(OH)_4^{2-}$ was proven by Raman spectra[163,171] and by NMR spectra[172] while binuclear complexes Zn_2OH^{3+} exist in acidic solutions[173–175].

Even though hydrolytic complexes of Ga^{3+} ion in acidic medium are polynuclear[65] the $[Ga(OH)_4]^-$ anion was proven[176] by an ion-exchange technique in aqueous alkaline solutions. Similarly, stannic ions form the mononuclear complex $Sn(OH)_6^{2-}$ in alkaline solution[177], although their hydroxo complexes in acidic solutions are very probably polynuclear. At the present time complete data about complexes of other ions are not available but the formulae given for the well-crystalline salts of amphoteric elements[148] indicate that the basic tendency would be the same.

A similar tendency can be observed in the case of uranyl fluoride complexes[178]. A small excess of fluoride to uranyl ion leads to the separation of oligomer, $M^I_2[(UO_2)_3F_8(H_2O)_4]$, from solution. With additional fluoride there are a diminishing number of central ions per complex and a progressive substitution of water molecules (*i.e.* to complexes $M^I_3[(UO_2)_2F_7(H_2O)_2]$ and $M^I_5(UO_2)_2F_9]$). At $[F^-]:[UO_2^{2+}] \geq 7$ the mononuclear complex, $M^I_3[UO_2F_5]$, is formed.

The above mentioned behaviour of hydroxyl and fluoride complexes can be summarized as follows: many central ions in aqueous solution prefer more to bind hydroxyl or fluoride ions than water molecules. With sufficient excess of these anions mononuclear complexes are formed in which the number of ligands per cation equals the coordination number of the central ion. Decrease of the excess is compensated by increase of the coordination number of the ligands so that oligomers (with bridged ligands) result, possibly also containing coordinated water. Accordingly, hydrated metal cations only form mononuclear complexes, $M(H_2O)_4^{z+}$, because of the great excess of water molecules in water solution. Formation of bridges of the type $_2(H_2O)_y$ is not excluded in non-aqueous solvent systems where solvent molecules might bind the central particles less strongly than the water molecules present. The extra two free electron pairs of the molecular water oxygen would technically allow this possibility. The existence of $_2(H_2O)_2$ bridges, in $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$, has been claimed[112].

Dehydroxylation, leading to oxo–hydroxo or up to pure oxo compounds, is a special ability of hydroxyl ligands. For instance, the oxo–hydroxide geothite, FeOOH, or haematite, Fe_2O_3, can be formed from a colloidal solution of amphoteric $Fe(OH)_3$ as well as from feebly alkaline solutions containing Fe^{3+} ions and their hydroxo complexes[179–183]. This process proceeds at room temperature but elevated temperatures are favourable; α-FeOOH can be prepared by boiling in alkaline solution for several hours[181]. The same is true for deuterated hydroxide which in alkaline suspension changes into α-FeOOD after a long time even at low temperatures (at 35 °C in about 20 days)[184], *cf.* hydroxo systems of aluminium[185].

Oxo–hydroxo complexes are also fundamental components of some basic salts of U^{IV} and Ce^{IV} which under mild hydrothermal conditions (100–150 °C, 0.1–0.5M H_2SO_4) form chains $[M(OH)_2]_n^{2+}$, at higher temperatures (175–200 °C, 0.5–1.0M $H_2SO)_4$ they form $[M_6(OH)_4O_4]^{12+}$ entities (Ref. 102). Both dehydroxylation with preservation of the coordination number of the central atom and increase in the coordination number of ligands from 2 to 3 [*i.e.* the change of type $_2(OH)_2$ to the types $_3(OH)_1$ and $_3(O)_1$] proceed with the formation of oligomers. Ultimately even oxides MO_2 can be obtained so that the genetic series reaches its limit, *i.e.* it proceeds to complete dehydroxylation and to the maximum number of chemical bonds of oxygen equal to 4 [the coordination type $_4(O)_1$].

It seems therefore that dehydroxylation can proceed in acidic (in the case of U^{IV} and Ce^{IV}) as well as in alkaline (in the case of Fe^{III} and Al^{III}) aqueous solutions so that it follows that this reaction is not directly connected with the presence or absence of hydrogen or hydroxyl ions. Its course is after all determined by the state of coordinated hydroxyls so that it is influenced also by the properties of central ions and therefore also by the type of the complex.

One of the conditions for the dehydroxylation

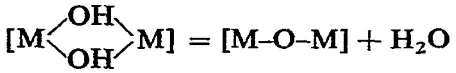
$$M(OH)_2 \rightarrow MO + H_2O$$

is the sufficiently close proximity of condensing particles. From the point of view of coordination it is important whether the hydroxyls $_1(\mathrm{OH})_0$ are condensed from the inner coordination sphere of the same cation or from spheres of different cations. In the first case (*cf.* the equation given above) there would be a decrease in the coordination number of the metal cation of one unit, in the second case the coordination number of both cations would be preserved and the oxygen bridge $_2(\mathrm{O})_1$ would be formed

$$2\mathrm{M{-}OH} = \mathrm{M{-}O{-}M} + \mathrm{H_2O}.$$

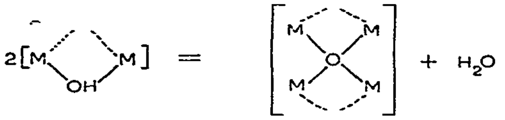
The second reaction would possibly change the M–M distance so that there would be a corresponding change of structure, along with the change of physical (color, density) as well as chemical properties (solubility, reactivity *etc.*).

This would also be valid in the case of the dehydroxylation of bridge hydroxyl groups. Condensation from the inner coordination sphere of the same polynuclear complex would lead to a decrease of the coordination number of the central ions in one unit



$$[\mathrm{M}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{M}] = [\mathrm{M{-}O{-}M}] + \mathrm{H_2O}$$

while condensation between different complexes would not change the coordination number of the central ions:



Any of these possibilities cannot be a priori excluded but the coordination number of the central ions is usually preserved (*cf.* the above mentioned examples of $\mathrm{Al^{III}}$, $\mathrm{Fe^{III}}$, $\mathrm{Ce^{IV}}$ and $\mathrm{U^{IV}}$) which support the second possibility.

As for the hydroxyl ligands, the processes mentioned lead to increase of their coordination number, in addition to their possible change into O-ligands with maximum coordination number 4. In the case of dehydroxylation of the bridges, the sum of coordination numbers of which exceeds 4 [*e.g.* bridges of the $_3(\mathrm{OH})_y$ type mutually or between $_3(\mathrm{OH})_y$ and $_2(\mathrm{OH})_y$ bridges], a more substantial molecular and structural rearrangement should be expected. As an example of this behaviour, the final steps in the rearrangement of the hydroxo complexes of $\mathrm{U^{IV}}$ and $\mathrm{Ce^{IV}}$ can serve, where the oxygen and hydroxyl bridges of the $_3(\mathrm{L})_1$ type in oligomers $[\mathrm{M_6(OH)_4O_4}]^{12+}$ gradually change into $\mathrm{MO_2}$ with $_4(\mathrm{O})_1$ bridges. The coordination number of the metal in the hydroxo complexes cited remains 8 in the arrangement of a square antiprism[102].

Dehydroxylation initiated hydrothermally should be distinguished from dehydroxylation initiated by elevated temperatures in solid samples (*e.g.*in hydroxides $\mathrm{Cd(OH)_2}$ and $\mathrm{Ni(OH)_2}$ at 140–200, or at 210–330 °C, respectively[186], in the hydrolytic precipitate $SnO(OH)_2$ at about 200–600 °C[187], in aluminium hydroxide[188] at 250–425 °C, in the oxo–hydroxide of scandium[117] $Sc_2O(OH)_4$ at 120–440 °C, in the natural oxo–hydroxide crocidolith[189] between 570 and 700 °C, in hydroxo complexes of uranyl of different types[157,190] in the range 300–400 °C, *etc.*). A theoretical attempt to explain the behaviour of hydroxyl groups at elevated temperatures has been made[191]. It is based on purely physical principles (the form of lattice potential functions, Debye temperature, bond vibrations, polarizability, *etc.*), and does not consider the chemical description of dehydroxylation applied in the present paper. Undoubtedly, no sharp limit exists between these two approaches. Their principal difference lies in the cause of the changes which in the former case is physical, in the latter one chemical. Moreover, in the hydrothermal preparation there is, at least approximately, reached an equilibrium during the chemical reaction while in the dehydroxylation at elevated temperatures one has a non-equilibrium decomposition.

E. CHEMICAL BONDS IN HYDROXO COMPLEXES

(i) Classification of central ions according to their ability to form mono- or polynuclear hydroxo complexes

Central ions can be characterized by their behaviour to selected ligands. In hydroxo complexes we can therefore recognize central ions forming in their genetic series predominantly and/or characteristically polynuclear complexes, and central ions forming predominantly mononuclear complexes (*cf. e.g.*, Ref. 1. p. 151 and Ref. 192, p. 397). It is necessary to emphasize that this classification is merely a convenience because experimental conditions substantially influence the formation of mono- or poly-nuclear hydroxo complexes of a given central ion. For instance, polynuclear hydroxo complexes cannot be formed if the concentration of the central ion is sufficiently low (in uranyl systems the concentration limit is at about 10^{-3}M[192–194], in thorium systems at concentrations lower than 10^{-6}M only mononuclear complexes are formed[195], *etc.*). This is, of course, a consequence of the mass action law so that increasing the concentration of the central ions* causes formation of polynuclear complexes where they would not be formed under normal conditions (*i.e.* at metal concentrations 10^{-1}–10^{-3}M).

There are, however, several central ions which cannot be easily classified because their behaviour does not correspond strictly to either group. This is the case, for instance, of Mn^{2+}, Co^{2+} and Ni^{2+} ions[199,200], the thermodynamic data of which are very similar[201,202].

Having this in mind we can, nevertheless, state that most metal cations

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* Such media are sometimes called "self-media"[196]; *e.g.* Hg^{2+} and Cd^{2+} ions[197,198] form polynuclear complexes only in a "self-medium"[49,50].

prefer to form polynuclear hydroxo complexes[1,65]. Cations which do not[1], include Fe^{2+}, Cd^{2+}, $Hg_2{}^{2+}$, Hg^{2+} and Tl^{3+}.

It is noteworthy that central ions, if classified according to the relative stability of their halide complexes[203–205] (*i.e.* according to the increase or decrease of their stability in the series $F^- - Cl^- - Br^- - I^-$), can be divided into two groups which are similar to those obtained if classified according to their hydroxo complexes. To the first, more numerous, group which favours coordination by F^- belong[203] H^+, Ce^{3+}, U^{4+}, $UO_2{}^{2+}$ Zr^{4+}, Fe^{3+} and In^{3+} and very probably Be^{2+}, Th^{4+}, Pu^{4+}, Cu^{2+}, Zn^{2+}, Al^{3+} and Sn^{2+} (called class A acceptors). To the second group, favouring the heavier halides (class B), belong Pt^{II}, Cu^+, Ag^+, Cd^{2+}, Hg^{2+} and Pb^{2+} and very probably Pd^{II}, Pd^{IV}, Pt^{IV}, Au^{III} and Tl^{3+}.

Omitting non-ionic forms we see that, with the exception of Pb^{2+} ions*, this classification of central ions is identical with their classification according to the hydroxo complexes. This is not easy to explain. The physical basis for the classification of central ions according to the stability of their halide complexes depends upon the fact that ions of the first group form essentially electrostatic bonds[203] with halides so that their stability is highest in the case of the smallest ligand F^- and decreases for heavier halides. On the other hand, the second group favours a covalent bond to the halide ligands[203] so that the fluoride complexes are the least stable[25].

In the case of hydroxo complexes differences between the behaviour of the two groups of central ions cannot be explained by electrostatic or covalent bonding because it was confirmed by spectroscopic measurements (p. 68) that the M–OH bond is predominantly covalent in both polynuclear and mononuclear complexes. This is readily understood because oxygen has a very high donor ability[25]. The distinction in behaviour between these two groups of elements should therefore be looked for in the framework of the chemical covalent bond itself, *i.e.* among the factors which influence its formation.

The stability of the polynuclear hydroxo complexes of many cations is sufficiently high. The M–OH bond strength is of primary importance for the stability of such hydroxo complexes since only simple entities could occur if these bonds were weak. Weak bonds are formed *e.g.* in hydroxo complexes of Fe^{2+} and Cd^{2+} (ions of the second group). Their equilibrium constants K_M for monomer formation

$$M^{z+} + OH^- \rightleftharpoons MOH^{(z-1)+}$$

do not exceed 10^6 (depending on conditions)[65]. This is, however, not true for other ions where the values of K_M vary in the range from 10^9–10^{13}, yet these do not necessarily form polynuclear complexes to any significant degree. We shall

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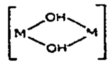
* Hydrogen ion is not a metal ion so that its properties cannot be included into the discussion dealing with metal ions. It would be completely formal to classify the ion $H_3O^+ = H^+\text{–}OH^-\text{–}H^+$ as its polynuclear hydroxo complex.

therefore discuss the geometry of hydroxo complexes as another important factor determining their stability.

(ii) Geometry of the complexes as a stabilizing factor

Four-membered rings



are very abundant among hydroxo complexes and are very stable. We shall therefore discuss more deeply their geometric configuration. This ring is considered as planar with angles 2φ(M–OH–M) and 2ε(OH–M–OH); $2\varphi+2\varepsilon = 180°$. Under the assumption that the spatial orientation of valence orbitals of hydroxyls is not perturbed by their bonds with central ions, the angle 2φ would be the tetrahedral angle* 109,5° so that the angle 2ε should be equal to 70.5°. The data (see Table 1) in general confirm the tetrahedral geometry of valence orbitals of the hydroxyl group, disregarding, for the moment, the approximate 10° deviation from theoretical predictions in the case of octahedral coordination.

To study the effect of a given coordination number of a central particle or of various geometric configurations of a given coordination number** on the formation of the above-mentioned four-membered ring, we have calculated the angle $2\varepsilon'$ with the assumption that the bonds are oriented from the centre to the vertices of the given polyhedron. The results are given in Table 3 together with the values of $\Delta 2\varepsilon = 2\varepsilon' — 70.5°$ characterizing the deviation from the most favourable configuration under the supposed geometry.

From this Table it follows that the most favourable angular correlation for the overlapping of orbitals of bridges and central atoms in the direction of their connecting line in the configuration of a four-membered ring, should be for central atoms with the cubic geometry of valence orbitals. However, such complexes are not found because of unfavourable energetic conditions[206]. The pentagonal configuration of orbitals (the pentagonal bipyramid or planar pentagon with the coordination numbers 7 or 5, respectively) fulfils these conditions very well but is not too abundant. On the other hand, the configuration of a square antiprism with the coordination number 8 is very common. In this configuration the value of $\Delta 2\varepsilon$ is sufficiently small that central ions with this orbital geometry can easily form these dimers. The formation of a four-membered ring is possible, even in the case of the octahedral geometry with $\Delta 2\varepsilon = 19.5°$, but distinct deviations of the

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* The remaining two orbitals would lie out of the ring plane in a plane perpendicular to it. One may form a bond to a hydroxyl hydrogen (Ref. 7, p. 94), whilst the other may form another bond[54].

** Differences between individual idealized geometrical configurations are surprisingly small at high coordination numbers and they further decrease by distortion within real structures (Ref. 62, p. 114; Refs. 206, 207).

TABLE 3

CALCULATED VALUES OF THE BOND ANGLES FOR VARIOUS ORBITAL GEOMETRIES OF THE CENTRAL IONS (SEE TEXT)

$2\varepsilon'(^\circ)$	$\Delta 2\varepsilon(^\circ)$	*Geometry of orbitals*	*Coord. number*	*Note: $2\varepsilon'$ calculated for center of the polyhedron and...*
70.5	0	cube	8	.... two vertices joined by an edge
75.0	4.5	square antiprism	8	.... two vertices joined by an edge
72.0	1.5	pentagonal bipyramid	7	.... two adjacent vertices of the base
90.0	19.5	regular octahedron	6	.... two adjacent vertices
72.0	1.5	plane pentagon	5	Plane figure, the angle $2\varepsilon'$ holds for adjacent vertices
109.5	39	tetrahedron	4	.... arbitrary two vertices[a]
90.0	19.5	square	4	Plane figure, the angle $2\varepsilon'$ holds for adjacent vertices
180	109.5	linear L–M–L	2	No polyhedron is formed

[a] Tetrahedron is derived from a cube therefore all its elements can be found in the cube. In the case of the cube the angle cited holds true for two vertices joined by a face diagonal.

order of 10° from the ideal configuration towards the value of $2\varepsilon = 70.5^\circ$ were found.

The same value of $\Delta 2\varepsilon = 19.5^\circ$ is also valid for the square-planar geometry with coordination number 4. Of all the hydrolyzing cations only the Be^{2+} ion has this coordination number but its typical geometry is tetrahedral[208,209]. The corresponding value of $\Delta 2\varepsilon = 39^\circ$ is too high for the formation of a four-membered ring and the ion Be^{2+} does not readily form such a configuration. On the other hand, central atoms like Pt^{II}[*], Pd^{II} and Au^{III} with a typical square-planar coordination can form four-membered rings with halide or other $_2(L)_2$ bridges[125,126,210]. It is possible that this fact is affected by the differences between the behaviour of OH^- and Cl^- bridges.

The coordination number 2 is evidently entirely unfavourable for the formation of four-membered rings.

These considerations support the assumption of the important role of the geometry of the valence orbitals of the central atoms in the formation of a four-membered ring. Already these partial results indicate that there will be a large number of cations capable of forming polynuclear hydroxo complexes because there is certainly a larger number of central ions with orbital geometry suitable for the formation of dimers with $_2(OH)_2$ bridges than of ions which are unable to form them.

The question arises as to what type of complexes may be formed by central ions which do not easily form four-membered rings according to the above men-

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[*] It is supposed that $[PtCl_2]_6$ contains an octahedron of Pt atoms with twelve $_2(Cl)_1$ bridges (Ref. 62, p. 152).

tioned criteria. They can, of course, form mononuclear complexes because there is no geometric restriction for their formation; to a certain degree this is also true of binuclear complexes with $_2(OH)_1$ bridges so that this type of dimer is also possible. They may also form complexes with a higher number of central ions (3,4,6, *etc.*, so-called oligomers) which will play an important role in the hydrolytic genetic series if they are sufficiently stable.

However, it is very difficult to give any general conditions, even if only geometric, for the stability of oligomers so that we shall describe here only a few examples. Assuming that the spatial orientation of orbitals of both Be^{2+} ion and the hydroxyl ligand is the same, *i.e.* that it is tetrahedral, the formation of the six-membered planar ring[45,46,58] $[BeOH]_3^{3+}$ requires that the angles 2ε (OH–Be–OH) and 2φ (Be–OH–Be) would be 120°, differing thus by only about 10.5° from the theoretical value. In the tetramer $[(CH_3)_2AuOH]_4$ with a square configuration of central atoms (p. 70, this complex is not a hydrolytic one) the necessary angular correlation is achieved by a spatial distortion of the ring, *i.e.* the bridges and central atoms do not form a strictly planar* configuration; the angle 2φ is equal to 111° in good agreement with theoretical predictions. In a similar tetramer $[(CH_3)_2GaOH]_4$ the angle 2φ is equal to 133°; this may be caused because a tetrahedral configuration is typical of Ga^{III} while a square-planar configuration of ligands is more typical for Au^{III}.

These examples indicate the possibility of stabilization of oligomers with $_2(OH)_1$ bridges by formation of planar six- or eight-membered rings. The hydrolytic complexes $[Pb_4(OH)_4]^{4+}$, $[Pb_6(OH)_8]^{4+}$ and $[Bi_6(OH)_{12}]^{6+}$ with $_3(OH)_1$ bridges in the first two cases and with $_2(OH)_1$ bridges in the third case (*cf.* p. 75 and 70) are the best studied of all oligomers with a regular spatial configuration of central ions. The stability of the tetrahedra or octahedra of central ions is significantly enhanced by the participation of direct metal–metal bonds. The problem of these bonds in other oligomers of this type should be subjected to further research.

Linear polymers with a very high (theoretically infinite) number of central particles connected by multiple bridges are very probably only a theoretical alternative formalism used for the interpretation of experimental data[211].

From these considerations it is obvious that there will be few central ions unable to form polynuclear hydroxo complexes†. Alkali metal or alkaline earth metal ions reveal typically low ability to form bonds with hydroxyl ions (values of log K_M are lower than 1.3). Included with these are such ions as Ag^+ (typical coordination number 2, log $K_M = 2$–4), Cu^+ and Au^+ with an unsuitable geometry of orbitals (there are no reliable data for their affinity for hydroxyl), Cd^{2+}

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* In these tetramers the central atoms do not lie precisely in a plane, the bridges are alternately above and below the pair of adjacent central atoms. The structure of the trimer $[BeOH]_3^{3+}$ is not known but could be planar according to these considerations.

† The numerical data quoted in this paragraph are taken from Refs. 58, 63, 65.

(predominantly tetrahedral geometry, log K_M = 4–6) and the group of ions Fe^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} (log K_M does not exceed 6), the group having nevertheless a *potential ability* to form polynuclear complexes in octahedral configuration. Further, the ions Hg^{2+} and $Hg_2{}^{2+}$ have a rather high affinity for the hydroxyl group (log $K_M > 9$) but their orbitals are in linear or tetrahedral configuration[212]. The Tl^{3+} ion is an interesting example because it has a high affinity for hydroxyl (log K_M = 13) and its coordination number is 4 or 6[213]. Nevertheless, *it does not* form polynuclear hydroxo complexes[1,136,214] but is able to form the complex[215] $[Cl_3Tl(Cl)_3TlCl_3]$. With the assumption that this entity is formed from two octahedra sharing a face, the angle 2φ (Tl–Cl–Tl) would be theoretically equal to 77.5°, which is, however, substantially lower than the tetrahedral angle (in the ammine Co^{III} complex with $_2(OH)_3$ bridges the same angle has a value close to 80°, *cf.* p. 74).

Regardless of the remarkable agreement *in the grouping of central ions* according to our criteria and according to the stability of their halide complexes, it is evidently not possible to use the electrostatic *vs.* covalent bonding arguments to explain the hydroxo series even if the approach has been used with great success (but see Ref. 216) with the halides.

It seems likely that the linking of central ions by a single bridge, $_2(OH)_1$ or $_3(OH)_1$, is not very strong. Dimers with $_2(OH)_1$ bridges only accompany other more dominant complexes in the genetic series and entities with higher numbers of central particles connected merely by $_2(OH)_1$ bridges are not known. The complexes are significantly stabilized by a cyclic planar (or at least flat) configuration; four-membered rings are very abundant. In several oligomers with a regular *spatial* arrangement of central ions linked by $_3(OH)_1$ or $_2(OH)_1$ bridges further stabilization arises from additional metal–metal bonds, in addition to the closed configuration.

F. SUMMARY

From the data it follows that the hydroxyl ion can form complexes with most metal cations. Its bond to central ions is predominantly covalent regardless of the type of complexes (mono- or poly-nuclear). The hydroxyl ligands very easily form bridges, the properties of which correspond to theoretical predictions of the tetrahedral geometry of the valence orbitals in the hydroxyl ligand. Single bridges are probably not very strong but multiple bridges [most often $_2(OH)_2$], together with other factors such as the spatial arrangement of the complex, direct metal–metal bonds, π-bonds, *etc.*, substantially enhance the stability of hydroxo complexes.

The chemical properties of the hydroxyl group are changed by coordination so that *e.g.* the hydroxyl bridge could be acidic and in some cases substitution of the type $> OH + M^+ = \; > OM + H^+$ is possible. Under certain conditions the coordination sphere could be dehydroxylated forming thereby oxo–hydroxo or, finally, oxo products. In sufficiently alkaline media, insoluble polynuclear complexes of some (amphoteric) cations depolymerize into soluble mononuclear ones.

The overwhelming majority of the available data on the composition of hydroxo complexes was obtained by indirect methods (principally by potentiometry combined with special evaluation procedures), only recently have methods been successfully applied to study directly the properties of a given hydroxo complex (*e.g.* vibrational spectroscopy). No doubt their further application will present new and more precise data for the determination of properties of hydroxo complexes and thus even for the hydroxyl ligand itself.

In the future one might also expect further development of our knowledge from studies of the behaviour of hydroxo complexes in non-aqueous media combined with the general development of coordination chemistry in non-aqueous solvents.

REFERENCES

1 L. G. Sillén, *Quart. Rev.*, 13 (1959) 146.
2 A. A. Grinberg, *An Introduction to the Chemistry of Complex Compounds*, Pergamon, New York, 1962.
3 G. Jander, H. Spandau and C. C. Addison, *Chemistry in Nonaqueous Ionizing Solvents, A Series of Monographs*, Wiley–Interscience, New York–London, 1966.
4 V. Baran, *Chem. Listy*, 62 (1968) 280.
5 L. M. Branscomb, *Phys. Rev.*, 148 (1966) 11.
6 S. S. Batsanov, *Zh. Strukt. Khim.*, 8 (1967) 736.
7 Y. V. Moiseyev and M. I. Vinnik, *Zh. Strukt. Khim.*, 4 (1963) 336.
8 R. Grahn, *Acta Chem. Scand.*, 19 (1965) 153.
9 R. W. Busing and D. F. Hornig, *J. Phys. Chem.*, 65 (1961) 284.
10 J. Jortner, B. Raz and G. Stein, *J. Chem. Phys.*, 34 (1961) 1455.
11 S. S. Batsanov and G. B. Bokii, *Zh. Strukt. Khim.*, 3 (1962) 716.
12 J. A. A. Ketelaar, *Chemical Constitution*, Elsevier, Amsterdam, 1958, p. 29.
13 J. Goubeau and W. Klemm, *Z. Phys. Chem.*, 36 (1937) 362.
14 I. D. Campbell and C. K. Coogan, *J. Chem. Phys.*, 42 (1965) 2738.
15 C. K. Coogan, *J. Chem. Phys.*, 43 (1965) 823.
16 I. N. Maksimova and N. N. Zatsepina, *Zh. Fiz. Khim.*, 43 (1969) 1023.
17 B. R. Agarwal and R. W. Diamond, *J. Phys. Chem.*, 67 (1963) 2785.
18 G. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, 41 (1964) 924.
19 A. F. Clifford, *J. Phys. Chem.*, 63 (1959) 1227.
20 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, 1962.
21 D. R. Lide, Jr. and Ch. Matsumura, *J. Chem. Phys.*, 50 (1969) 3080.
22 R. Grahn, *Arkiv Fysik*, 28 (1964) 85.
23 P. W. Selwood, *Magnetochemistry*, Interscience, New York, 2nd ed., 1956.
24 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958, p. 15.
25 B. Jeżowska-Trzebiatowska, in W. Schneider, G. Anderegg and R. Gut (Eds.), *Essays in Coordination Chemistry*, *Exp. Suppl.*, Verlag Birkhäuser, Basel–Stuttgart, 1964, p. 128.
26 D. W. Cruickshank, *J. Chem. Soc.*, (1961) 5486.
27 A. B. Blake, F. A. Cotton and J. S. Wood, *J. Amer. Chem. Soc.*, 86 (1964) 3024.

28 A. A. Vlček, *Structure and Properties of Coordination Compounds* (in Czech), Academia, Praha, 1966, p. 16.
29 J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc. (A)*, 151 (1935) 384.
30 R. E. Hester, *Coord. Chem. Rev.*, 2 (1967) 319.
31 M. Maltese and W. J. Orville-Thomas, *J. Inorg. Nucl. Chem.*, 29 (1967) 2533.
32 E. Hartert and O. Glemser, *Z. Elektrochem.*, 70 (1956) 746.
33 O. Glemser, *Angew. Chem.*, 73 (1961) 785.
34 P. Tarte, *Spectrochim. Acta*, 23A (1967) 2127.
35 R. E. Hester and W. E. L. Grossman, *Spectrochim. Acta*, 23A (1967) 1945.
36 L. Jenšovský, *Z. Chem.*, 3 (1963) 453.
37 W. E. Hatfield, J. F. Anders and L. J. Rivela, *Inorg. Chem.*, 4 (1965) 1088.
38 A. I. Zhukov, N. V. Onosov, V. J. Kydyakov and B. M. Sergeyev, *Zh. Neorg. Khim.*, 8 (1963) 871.
39 I. Jelenić, D. Grdenić and A. Bezjak, *Acta Crystallogr.*, 17 (1964) 758.
40 J. Lewis, *Pure Appl. Chem.*, 10 (1965) 11.
41 G. Mattock, *Acta Chem. Scand.*, 8 (1954) 777.
42 L. Pokras, *J. Chem. Educ.*, 33 (1956) 152.
43 S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 13 (1959) 1828.
44 I. Pajdovski and Å. Olin, *Acta Chem. Scand.*, 16 (1962) 983.
45 H. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, 10 (1956) 895.
46 S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 18 (1964) 1015.
47 B. Carell and Å. Olin, *Acta Chem. Scand.*, 15 (1961) 1875.
48 F. Bertin, G. Thomas and J.-Cl. Merlin, *Bull. Soc. Chim. Fr.*, (1967) 2393.
49 G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, 16 (1962) 2221.
50 I. Ahlberg, *Acta Chem. Scand.*, 16 (1962) 887.
51 K. J. Pedersen, *Danske Videnskab. Selskab. Math.-fys. Medd.*, 20 (1943) No. 7.
52 A. Earnshaw and J. Lewis, *J. Chem. Soc.*, (1961) 396.
53 *Gmelin's Handbuch der Anorganischen Chemie*: *Chrom.*, *S.N.52*, *Tl.C.*, Verlag Chemie, Weinheim, 1965, p. 294.
54 C. K. Prout, *J. Chem. Soc.*, (1962) 4429.
55 D. J. Hewkin and W. P. Griffith, *J. Chem. Soc. (A)*, (1966) 472.
56 Y. K. Syrkin, *Uspekhi Khimii*, 28 (1959) 903.
57 G. A. Barclay, E. G. Cox and H. Lynton, *Chem. Ind.*, (1956) 178.
58 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962, p. 174.
59 G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton and R. S. Tobias, *J. Amer. Chem. Soc.*, 90 (1968) 1131.
60 G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, 81 (1959) 3907.
61 V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, 7 (1968) 183.
62 E. L. Muetterties and G. M. Wright, *Quart. Rev.*, 21 (1967) 109.
63 M. N. Jones, *Elementary Coordination Chemistry*, Prentice-Hall, Englewood Cliffs, 1964, p. 85.
64 R. Mattes, *Z. Anorg. Allgem. Chem.*, 364 (1969) 279, 290.
65 L. G. Sillén and A. E. Martell, *Stability Constants*, The Chemical Society, London, 1964, Spec. Publ. No. 17.
66 C. F. Baes, Jr., N. J. Meyer and C. E. Roberts, *Inorg. Chem.*, 4 (1965) 518.
67 G. Biedermann and L. Ciavatta, *Arkiv Kemi*, 22 (1964) 253.
68 J. Aveston, *J. Chem. Soc. (A)*, (1966) 1599.
69 Y. N. Mikhaylov, V. G. Kuznetsov and E. S. Kovaleva, *Zh. Strukt. Khim.*, 9 (1968) 710.
70 M. Åberg, *Acta Chem. Scand.*, 23 (1969) 791.
71 N.-G. Vannerberg, *Acta Chem. Scand.*, 17 (1963) 85.
72 G. Johansson, *Acta Chem. Scand.*, 16 (1962) 403.
73 G. Johansson, *Arkiv Kemi*, 20 (1963) 305.
74 G. Lundgren, *Arkiv Kemi*, 13 (1958) 59.
75 Y. E. Gorbunova, V. G. Kuznetsov and E. S. Kovaleva, *Zh. Strukt. Khim.*, 9 (1968) 918.
76 D. B. McWhan and G. Lundgren, *Inorg. Chem.*, 5 (1966) 284.

77 A. Clearfield and P. Vaughan, *Acta Crystallogr.*, 9 (1956) 555.

78 G. Johansson, *Acta Chem. Scand.*, 22 (1968) 389.

79 I. V. Tsapkina and G. V. Ellert, *Zh. Neorg. Khim.*, 13 (1968) 1393.

80 Y. Y. Kharitonov, L. A. Pospelova and L. M. Zajtsev, *Zh. Neorg. Khim.*, 12 (1967) 2635.

81 G. Johansson, *Acta Chem. Scand.*, 22 (1968) 399.

82 J. Bjerrum, Dissertation, Copenhagen, 1941, see Ref. 92.

83 I. R. Beattie, T. R. Gilson and G. A. Ozin, *J. Chem. Soc. (A)*, (1968) 2765.

84 K. B. Yatsimirskii, *Zh. Neorg. Khim.*, 8 (1963) 811.

85 J. A. Hearne and A. G. White, *J. Chem. Soc.*, (1957) 2168.

86 C. V. Baes, Jr. and N. J. Meyer, *Inorg. Chem.*, 1 (1962) 780.

87 L. Pokras, *J. Chem. Educ.*, 33 (1956) 223.

88 K. A. Kraus, *Proc. Int. Conf. Peaceful Uses Atom. Energy, Geneva, 1955*, 7 (1956) 245.

89 R. M. Milburn, *J. Amer. Chem. Soc.*, 79 (1957) 537.

90 M. Kilpatrick and M. Pokras, *J. Electrochem. Soc.*, 101 (1954) 39.

91 T. J. Hardwick and E. Robertson, *Can. J. Chem.*, 29 (1951) 818.

92 B. O. A. Hedström, *Arkiv Kemi*, 6 (1953) 1.

93 *Gmelin's Handbuch der Anorganischen Chemie: Kobalt, S.N.58., Tl. B., Lfg.* 2, Verlag Chemie, Weinheim, 1964, pp. 615–634.

94 R. A. D. Wentworth and E. Saillant, *Inorg. Chem.*, 6 (1967) 1436.

95 C. D. Barraclough, H. B. Gray and L. Dubicki, *Inorg. Chem.*, 7 (1968) 844.

96 M. T. Flood, R. E. Marsh and H. B. Gray, *J. Amer. Chem., Soc.*, 91 (1969) 193.

97 P. Anderson, *Acta Chem. Scand.*, 21 (1967) 243.

98 F. A. Cotton and G. Wilkinson,*Advanced Inorganic Chemistry*, Interscience, New York, 1962, p. 726.

99 R. L. Carlin (Ed.), *Transition Metal Chemistry*, Part I, Marcel Dekker, New York, 1965.

100 *Gmelin's Handbuch der Anorganischen Chemie: Chrom, S.N. 52, Tl. C.*, Verlag Chemie, Weinheim, 1965, p. 311.

101 M. N. Jones, *Elementary Coordination Chemistry*, Prentice–Hall, Englewood Cliffs, 1964, pp. 23–26.

102 G. Lundgren, *Svensk Kem. Tidskr.*, 71 (1956) 200.

103 V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, 7 (1968) 188.

104 V. A. Maroni and T. G. Spiro, *J. Amer. Chem. Soc.*, 89 (1967) 45.

105 G. Johansson and Å. Olin, *Acta Chem. Scand.*, 29 (1969) 3197.

106 T. G. Spiro, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 8 (1969) 856.

107 Ref. 98, pp. 792–793.

108 J. E. Ferguson, B. M. Robinson and C. J. Wilkins, *J. Chem. Soc. (A)*, (1967) 486.

109 E. O. Esval and J. S. Johnson, Jr., *J. Phys. Chem.*, 69 (1965) 959.

110 T. G. Spiro, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 7 (1968) 2165.

111 J. D. Donaldsen, in F. A. Cotton (Ed.), *Progress in Inorganic Chemistry*, Vol. 8, Interscience, New York, 1967, pp. 297, 320f.

112 F. A. Cotton and B. H. C. Winquist, *Inorg. Chem.*, 8 (1969) 1304.

113 V. A. Maroni and T. G. Spiro, *J. Amer. Chem. Soc.*, 88 (1966) 1410.

114 R. S. Tobias, M. J. Sprague and G. E. Glass, *Inorg. Chem.*, 7 (1968) 1714.

115 R. G. Inskeep and M. Benson, *J. Inorg. Nucl. Chem.*, 20 (1961) 290.

116 J. R. Ferraro and W. R. Walker, *Inorg. Chem.*, 4 (1965) 1382.

117 I. V. Arkhangelskii, L. N. Komissarova, T. J. Puskhina and E. G. Terenin, *Zh. Neorg. Khim.*, 12 (1967) 1756.

118 P. Tarte, *Spectrochim. Acta*, 13 (1957) 107.

119 Y. Y. Kharitonov, Y. A. Buslayev, *Izv. Akad. Nauk S.S.S.R., Otd. Khim. Nauk*, (1962) 293.

120 W. P. Griffith and T. D. Wickins, *J. Chem. Soc. (A)*, (1967) 675.

121 W. Klemperer, *J. Chem. Phys.*, 24 (1956) 353.

122 I. R. Beattie, T. Gibson and P. Cocking, *J. Chem. Soc. (A)*, (1967) 702.

123 S. C. Jain and R. Rivest, *Can. J. Chem.*, 45 (1967) 139.

124 R. J. H. Clark, *Spectrochim. Acta*, 21 (1965) 955.

125 D. M. Adams, P. J. Chandler and R. G. Churchill, *J. Chem. Soc. (A)*, (1967) 1272.

126 D. M. Adams and R. G. Churchill, *J. Chem. Soc. (A)*, (1968) 2141.
127 A. N. Yermakov, A. V. Karyakin, G. A. Muradova, I. N. Marov and L. P. Kazanski, *Zh. Neorg. Khim.*, 13 (1968) 2985.
128 V. Dvořák and W. Feitknecht, *Helv. Chim. Acta*, 52 (1969) 515, 522.
129 P. A. Bulliner and T. G. Spiro, *Inorg. Chem.*, 8 (1969) 1023.
130 R. D. Willett, *J. Inorg. Nucl. Chem.*, 29 (1967) 2482.
131 R. D. Willett and O. L. Liles, Jr., *Inorg. Chem.*, 6 (1967) 1666.
132 B. Jeżowska-Trzebiatowska, *Rocz. Chem.*, 41 (1967) 453.
133 L. Pajdovski, B. Jeżowska-Trzebiatowska, *J. Inorg. Nucl. Chem.*, 28 (1966) 443.
134 B. Jeżowska-Trzebiatowska, *Coord. Chem. Rev.*, 3 (1968) 255.
135 F. A. Cotton, *Quart. Rev.*, 20 (1966) 389.
136 G. Johansson, *Svensk Kem. Tidskr.*, 2 (1963) 41.
137 G. Johansson and Å. Olin, *Acta Chem. Scand.*, 22 (1968) 3197.
138 Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Fall 1950, rotaprint paper.
139 L. G. Sillén, *Acta Chem. Scand.*, 8 (1954) 299.
140 L. G. Sillén, *Acta Chem. Scand.*, 8 (1954) 318.
141 L. G. Sillén, *J. Inorg. Nucl. Chem.*, 8 (1958) 176.
142 O. E. Esval, Ph. D. Thesis, University of North Carolina, Chapel Hill, 1963.
143 R. M. Rush, J. S. Johnson and K. A. Kraus, *Inorg. Chem.*, 1 (1962) 378.
144 J. Aveston and J. S. Johnson, *Inorg. Chem.*, 3 (1964) 1051.
145 F. C. Hentz, Jr. and S. Y. Tyree, *Inorg. Chem.*, 3 (1964) 844.
146 V. Baran, *Coll. Czech. Chem. Commun.*, 31 (1966) 2093.
147 V. Baran and M. Tympl, *Coll. Czech. Chem. Commun.*, 34 (1969) 756.
148 C. L. Robbinson, in J. C. Bailar, Jr. and D. H. Busch (Eds.), *The Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, pp. 448–471.
149 A. Werner, *Ber.*, 40 (1907) 4436.
150 Z. Kolařík, *Coll. Czech. Chem. Commun.*, 27 (1962) 938.
151 Z. Kolařík, *Coll. Czech. Chem. Commun.*, 27 (1962) 1333.
152 A. Kozawa, *J. Inorg. Nucl. Chem.*, 21 (1961) 315.
153 V. V. Strelko, M. B. Micyuk, A. I. Kazantseva and Z. Z. Vysockii, *Dokl. Akad. Nauk S.S.S.R.*, 179 (1968) 1392.
154 V. Baran, *Z. Chem.*, 5 (1965) 56.
155 V. Baran and M. Tympl, *J. Inorg. Nucl. Chem.*, 28 (1966) 89.
156 V. Baran and M. Tympl, *Coll. Czech. Chem. Commun.*, 27 (1962) 709.
157 V. Baran and M. Tympl, *Z. Anorg. Allg. Chem.*, 347 (1966) 184.
158 O. Wichterle, *Organic Chemistry* (in Czech), Czechoslov. Acad. Sci. Publ. House, Praha, 1955.
159 V. Baran and M. Tympl, *Z. Anorg. Allgem. Chem.*, 347 (1966) 175.
160 C. Brosset, G. Biedermann and L. G. Sillén, *Acta Chem. Scand.*, 8 (1954) 1917.
161 G. Johansson, G. Lundgren, L. G. Sillén and R. Söderquist, *Acta Chem. Scand.*, 14 (1960) 769.
162 J. Aveston, *J. Chem. Soc.*, (1965) 4438.
163 E. R. Lippincott, J. A. Psellas and M. C. Tobin, *J. Chem. Phys.*, 20 (1952) 536.
164 P. Lanaspere and C. Euraud, *Bull. Soc. Chim. Fr.*, (1960) 313.
165 G. Z. Maltsev, G. V. Malinin, V. P. Mashovec, *Zh. Strukt. Khim.*, 6 (1965) 378.
166 L. A. Carreira, V. A. Maroni, J. W. Swain, Jr. and R. C. Plumb, *J. Chem. Phys.*, 45 (1960) 2216.
167 Å. Olin, *Acta Chem. Scand.*, 14 (1960) 126.
168 J. J. Lingane, *Chem. Rev.* 29 (1941) 1; I. M. Kolthoff and J. J. Lingane, *Polarography I.*, Interscience, New York–London, 1952.
169 A. A. Vlček, *Coll. Czech. Chem. Commun.*, 20 (1955) 400.
170 J. S. Johnson, Jr. and K. A. Kraus, *J. Amer. Chem. Soc.*, 81 (1959) 1569.
171 J. S. Fordyce and R. L. Baum, *J. Chem. Phys.*, 43 (1965) 843.
172 G. H. Newman and C. E. Blomgren, *J. Chem. Phys.*, 43 (1965) 2744.
173 E. Matijević, J. P. Couch and M. Kerker, *J. Phys. Chem.*, 66 (1962) 111.

174 T. Sékine, *Acta Chem. Scand.*, 19 (1965) 1526.
175 G. Schorsch, *Bull. Soc. Chim. Fr.*, (1964) 1449.
176 A. Chretien and D. Bizot, *Compt. Rend.*, 266C (1968) 1688.
177 R. S. Tobias and C. E. Freidline, *Inorg. Chem.*, 4 (1965) 215.
178 R. L. Davidovych and T. A. Kalacheva, *Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk* (Proc. Siberian Dept. Acad. Sci. USSR, Ser. Chem. Sci.), 12/45 (1968) 44.
179 W. Feitknecht and W. Michaelis, *Helv. Chim. Acta*, 45 (1962) 212.
180 T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils and P. Saltman, *J. Amer. Chem. Soc.*, 88 (1966) 2721.
181 U. Schwartmann and W. R. Fischer, *Z. Anorg. Allgem. Chem.*, 246 (1966) 137.
182 A. N. Christensen and S. Fregerslev, *Acta Chem. Scand.*, 22 (1968) 1043.
183 A. N. Christensen, *Acta Chem. Scand.*, 22 (1968) 1487.
184 W. Wolski, A. Burewicz and J. Skrzypczak, *Z. Anorg. Allg. Chem.*, 351 (1967) 63.
185 P. W. Schmidt and W. O. Miligan, *J. Elec. Micr. Jap.*, 10 (1961) 238.
186 I. F. Hazell and R. J. Irving, *J. Chem. Soc. (A)*, (1966) 669.
187 E. W. Giesekke, H. S. Gutowsky, P. Kirsov and H. A. Laitinen, *Inorg. Chem.*, 6 (1967) 1294.
188 J. Beretka and M. J. Ridge, *J. Chem. Soc. (A)*, (1967) 2106.
189 M. W. Clark and A. G. Freeman, *Trans. Faraday Soc.*, 63 (1967) 2051.
190 M. Fodor, Z. Pokó and J. Mink, *Mikrochim. Acta.*, (1966) 865.
191 F. Freund, *Fortschr. Chem. Forsch.*, 10 (1968) 347.
192 S. Ahrland, *Acta Chem. Scand.*, 3 (1949) 374.
193 S. Ahrland, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 8 (1954) 1907.
194 J. Rydberg, *Arkiv Kemi*, 8 (1955) 113.
195 M. Beran, *Coll. Czech. Chem. Commun.*, 32 (1967) 1368.
196 S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 13 (1959) 1533.
197 D. Dyrsen and P. Lumme, *Acta Chem. Scand.*, 16 (1962) 1785.
198 S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 6 (1952) 747.
199 K. A. Burkov, L. S. Lilič and L. G. Sillén, *Acta Chem. Scand.*, 19 (1965) 14.
200 K. A. Burkov and L. V. Ivanova, *Vestnik Leningr. Univ. (Bull. Leningr. Univ.)*, 16 (1966) 120.
201 D. D. Perrin, *J. Chem. Soc.*, (1962) 2197.
202 D. D. Perrin, *J. Chem. Soc.*, (1964) 3644.
203 S. Ahrland, *Acta Chem. Scand.*, 10 (1956) 723.
204 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, 10 (1958) 265.
205 S. Ahrland, in *Structure and Bonding*, Vol. I., Springer Verlag, Heidelberg–New York, 1966, pp. 207–212.
206 R. V. Parish, *Coord. Chem. Rev.*, 1 (1966) 439.
207 R. J. Gillespie, *Can. J. Chem.*, 39 (1961) 2336.
208 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, 1962, pp. 169–170.
209 M. N. Jones, *Elementary Coordination Chemistry*, Prentice-Hall, Englewood Cliffs, 1964, p. 67.
210 D. M. Adams and P. J. Chandler, *J. Chem. Soc. (A)*, (1969) 588.
211 L. G. Sillén, *Acta Chem. Scand.*, 16 (1962) 1051.
212 K. Aurivillius, *Arkiv Kemi*, 24 (1965) 151.
213 L. K. Chuchalin, I. A. Kuzin, K. F. Obzherina, T. T. Omarov and L. S. Chuchalina, *Zh. Neorg. Khim.*, 12 (1967) 1175.
214 G. Biedermann, *Arkiv Kemi*, 5 (1952) 441.
215 Ref. 208, pp. 341–342.
216 S. Ahrland, in M. Cais (Ed.), *Chemistry of Coordination Compounds*, Elsevier, Amsterdam, 1968, p. 539.