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ALCOHOLS AS LIGANDS. I.

Crystalline hexa-ethanol metal salts

BY

P. W. N. M. van LEEUWEN

Laboratorium voor Anorganische en Fysische Chemie, Leiden

The syntheses of approximately twenty coordination complexes with the ligand ethanol are reported. A new synthetical method is used to obtain these crystalline hexa-alcohol solvates. About ten perchlorates and fluoroborates of divalent metal ions are easily prepared by dissolving the corresponding hydrates in ethyl orthoformate. In the solid state, even the nitrates contain hexa-ethanol coordinated metal ions. The electronic and vibrational spectra, a summary of the proton magnetic resonance spectra and some X-ray powder patterns are given. The complexes of this very weak ligand are now easily obtainable and will be of great importance because ethanol may be replaced simply by many ligands.

Introduction

The solvating properties of alcohols have been extensively studied by several authors. The bonding tendencies of water and alcohols to coloured metal ions in water-ethanol mixtures have been described.^{1,2}

It was found that small amounts of water and certain anions in alcohol are strongly bound to transition metal ions. *Friedman*³ concluded from spectrophotometric studies that the Cu(II)-water bond is 25 times more stable than the Cu(II)-ethanol bond. *Jørgensen* found a factor of 18 in the case of divalent cobalt. Furthermore, it has been shown that alcoholic media containing $M(H_2O)_6^{2\oplus}$ (as appears from the electronic spectra) may contain strongly bound outer-sphere ion-pairs which lead to nonconducting solutions (Katzin effect).

Anhydrous magnesium perchlorate is solvated with nearly six methanol molecules as concluded from PMR measurements.⁴ No crystalline solvates have been prepared. *Drago*⁵ expected that alcoholic media containing hydrated metal salts would be dehydrated by 2,2-diethoxypropane and so

¹ L. I. Katzin, E. Gebert, C. K. Jørgensen and J. Bjerrum, *Nature*, **175**, 425 and 426 (1955).

² C. K. Jørgensen, *Acta Chim. Scand.*, **8**, 175 (1954).

³ N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963).

⁴ J. H. Swinehart and H. Taube, *J. Chem. Phys.*, **37**, 1579 (1962).

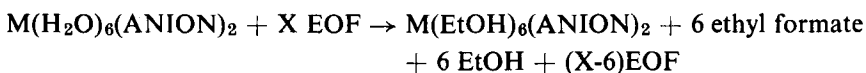
⁵ V. Imhoff and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965).

make it possible to obtain ethanol-metal salts. This appeared to be rather difficult; only in the case of nickel perchlorate was a pale yellowish green powder obtained and described as the hexa-ethanol complex.

Procedure

It is well known in organic chemistry that orthoformates react with water in the presence of acids as catalysts giving alcohols and esters.^{6,7}

In our laboratory ethyl orthoformate has been used in equivalent quantities as a dehydrating agent in ethanol, acetone or acetonitrile in order to prepare complexes of acetonitrile and sulfoxides,⁸ since these complexes could not be obtained by dehydration with dimethoxypropane. The reaction of the metallic hydrates with excess ethyl orthoformate (abbreviated EOF) was employed to synthesize the hexa-ethanol (EtOH) metal salts without addition of ethanol:



When 0.37 g of hydrated nickel perchlorate $\text{Ni}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ (0.01 mole), is dissolved in 15 g of EOF (0.1 mole) the separation of the EtOH complex as green hexagonal plates starts at once. In other cases crystals appeared after cooling, evaporation of alcohol, or addition of ether or ether-heptane mixtures.

Results and identification

The complexes which have been prepared so far are listed in Table I. Colours and metal analyses are also given. The numbers in the last column correspond to the several structural types found by X-ray powder analyses. Some X-ray powder data are tabulated in Table II.

In accordance with the metal analyses the compounds may contain either six EtOH molecules or two EOF molecules. Of course there are other possibilities which have to be taken into account. Other measurements were necessary therefore to show which organic molecules were present in the complexes. The isomorphous complexes (hexagonal plates) of type I were all expected to be hexa-EtOH compounds. When these extremely hygroscopic complexes were dissolved in a very small amount of water no separation of an organic layer (for instance ethyl formate) was observed. The complexes of magnesium and zinc perchlorates were dissolved in deuterium oxide and a PMR spectrum was recorded.*

* We are indebted to Drs. *T. J. Sekuur* and coworkers for measuring the PMR spectra.

⁶ *R. H. de Wolfe* and *R. M. Roberts*, *J. Am. Chem. Soc.*, **76**, 4379 (1954).

⁷ *J. W. Scheeren* and *W. Stevens*, *Rec. Trav. Chim.*, **85**, 793 (1966).

⁸ *P. W. N. M. van Leeuwen* and *W. L. Groeneveld*, to be published.

Table I
Alcohol complexes, syntheses and properties

| | Metal analyses | | Colour | Synthetical method * | X-ray type ** |
|---|----------------|-------|--------------|----------------------|---------------|
| | found | calc. | | | |
| Mg(EtOH) ₆ (ClO ₄) ₂ | 4.88 | 4.87 | White | B | I |
| Mn(EtOH) ₆ (ClO ₄) ₂ | 10.4 | 10.4 | White | A | I |
| Fe(EtOH) ₆ (ClO ₄) ₂ | 10.2 | 10.5 | Yellow | A | I |
| Co(EtOH) ₆ (ClO ₄) ₂ | 11.0 | 11.0 | Purplish-red | A | I |
| Ni(EtOH) ₆ (ClO ₄) ₂ | 10.8 | 11.0 | Green | A | I |
| Cu(EtOH) ₆ (ClO ₄) ₂ | 12.0 | 11.8 | Pale green | C | — |
| Zn(EtOH) ₆ (ClO ₄) ₂ | 12.1 | 12.1 | White | A | I |
| Mn(EtOH) ₆ (BF ₄) ₂ | 10.9 | 10.9 | White | B | I |
| Co(EtOH) ₆ (BF ₄) ₂ | 11.4 | 11.6 | Purplish-red | A | I |
| Ni(EtOH) ₆ (BF ₄) ₂ | 11.4 | 11.5 | Green | A | I |
| Zn(EtOH) ₆ (BF ₄) ₂ | 13.3 | 12.7 | White | A | I? |
| Mg(EtOH) ₆ (NO ₃) ₂ | 5.77 | 5.73 | White | B | II |
| Ca(EtOH) _{3,5} (NO ₃) ₂ | 12.4 | 12.3 | White | B | III |
| Co(EtOH) ₆ (NO ₃) ₂ | 12.8 | 12.8 | Purplish-red | D | (II)? |
| Ni(EtOH) ₆ (NO ₃) ₂ | 12.7 | 12.8 | Green | B | II |
| Zn(EtOH) ₆ (NO ₃) ₂ | 13.5 | 14.0 | White | D | — |
| Ca(EOF) ₂ (ClO ₄) ₂ | 7.56 | 7.5 | White | C | IV |

* See Experimental part.

** See Identification.

It was established that the complexes contained only ethanol as ligand. From this fact and the X-ray diagrams it is concluded that all other complexes of X-ray type I are hexa-EtOH compounds.

The complex of calcium perchlorate initially gave a cloudy aqueous solution, which cleared up after a few seconds. The PMR spectrum of this complex in deuterium oxide solution showed the presence of two kinds of ethyl groups and the formate proton. EOF reacts with deuterium oxide giving EtOD and ethyl formate. Therefore no XOH peak should be found in this spectrum; the small observed XOH peak was always present in the pure solvent. Comparison and integration of the spectra led to the conclusion that ethyl formate and EtOD were present in a ratio of about 1 : 2. The complex is most likely formulated as Ca(EOF)₂(ClO₄)₂. It is noted that the complex was obtained after evaporation of the solution (procedure C) and in this case probably all EtOH has been removed.**

** Mr. G. J. Alsema in our laboratory has prepared in this way, a few other complexes of metal perchlorates which also contain about two moles of EOF. — Private communication.

Table II

d-Values calculated from the X-ray powder patterns and visually estimated relative intensities of some alcohol complexes.

| Mg(EtOH) ₆ (ClO ₄) ₂ | | | | Zn(EtOH) ₆ (ClO ₄) ₂ | | | | Mg(EtOH) ₆ (NO ₃) ₂ | | | |
|--|-----|------|-----|--|-----|------|-----|---|-----|------|-----|
| d | int | d | int | d | int | d | int | d | int | d | int |
| 9.18 | 60 | 2.01 | 20 | 9.18 | 60 | 2.01 | 10 | 9.48 | 20 | 1.91 | 30 |
| 7.67 | 50 | 1.93 | 40 | 7.67 | 50 | 1.93 | 40 | 7.12 | 90 | 1.83 | 30 |
| 5.88 | 90 | 1.88 | 40 | 5.88 | 90 | 1.88 | 40 | 6.56 | 50 | 1.82 | 20 |
| 4.67 | 20 | 1.83 | 10 | 4.67 | 20 | 1.81 | 20 | 5.07 | 30 | 1.77 | 20 |
| 4.44 | 80 | 1.77 | 20 | 4.44 | 70 | 1.79 | 10 | 4.22 | 30 | 1.75 | 10 |
| 4.01 | 70 | 1.74 | 20 | 4.01 | 70 | 1.77 | 20 | 3.88 | 100 | 1.68 | 30 |
| 3.94 | 30 | 1.73 | 30 | 3.93 | 40 | 1.74 | 20 | 3.56 | 60 | 1.67 | 10 |
| 3.91 | 30 | 1.68 | 60 | 3.89 | 40 | 1.73 | 30 | 3.26 | 50 | 1.64 | 20 |
| 3.85 | 70 | 1.65 | 60 | 3.87 | 40 | 1.68 | 60 | 3.16 | 20 | 1.62 | 20 |
| 3.55 | 100 | 1.54 | 10 | 3.55 | 100 | 1.65 | 60 | 2.96 | 10 | 1.60 | 50 |
| 3.12 | 10 | 1.52 | 20 | 3.12 | 10 | 1.53 | 20 | 2.78 | 70 | 1.58 | 50 |
| 2.95 | 50 | 1.48 | 10 | 2.98 | 50 | 1.51 | 20 | 2.58 | 40 | 1.52 | 20 |
| 2.90 | 50 | 1.46 | 10 | 2.90 | 40 | 1.47 | 10 | 2.50 | 40 | 1.46 | 40 |
| 2.85 | 50 | 1.44 | 30 | 2.82 | 50 | 1.46 | 10 | 2.45 | 30 | 1.44 | 30 |
| 2.77 | 60 | 1.38 | 20 | 2.78 | 60 | 1.43 | 30 | 2.38 | 30 | 1.38 | 30 |
| 2.57 | 20 | 1.32 | 30 | 2.57 | 20 | 1.38 | 20 | 2.30 | 10 | 1.36 | 20 |
| 2.46 | 40 | 1.28 | 10 | 2.45 | 40 | 1.32 | 30 | 2.20 | 20 | 1.35 | 20 |
| 2.39 | 10 | 1.28 | 20 | 2.39 | 20 | 1.28 | 10 | 2.17 | 20 | 1.31 | 30 |
| 2.24 | 30 | 1.27 | 20 | 2.24 | 30 | 1.28 | 10 | 2.11 | 20 | 1.29 | 10 |
| 2.14 | 10 | 1.25 | 10 | 2.13 | 20 | 1.27 | 20 | 2.03 | 40 | 1.25 | 10 |
| 2.12 | 20 | 1.23 | 20 | 2.11 | 20 | 1.25 | 10 | 2.01 | 50 | 1.20 | 20 |
| 2.08 | 40 | 1.21 | 20 | 2.08 | 40 | 1.23 | 20 | 1.95 | 30 | | |
| | | | | | | 1.21 | 20 | | | | |

As a representative of the isomorphous nitrate compounds, the magnesium nitrate complex was dissolved in deuterium oxide and a PMR spectrum was recorded. Only the resonances of EtOH were found. The metal analyses indicated that the complexes contained six moles of ethanol.

Additional notes to Table I

Co(EtOH)₆(NO₃)₂ melted slightly above room temperature. We were not able to record a satisfactory X-ray powder pattern of this compound. Large needles of the compound Zn(EtOH)₆(NO₃)₂ melted at 10-11°.

Zn(EtOH)₆(BF₄)₂ showed some extra lines besides the lines of a typical pattern I.

The hexagonal plates of Cu(EtOH)₆(ClO₄)₂ decomposed rapidly. The complexes were not only very hygroscopic but they also showed affinity towards nearly every polar organic solvent. The nitrates especially are extremely deliquescent and even soluble in anhydrous ether.

Electronic spectra

The solid reflectance spectra and the transmission spectra were measured on the complexes of Ni(II), Fe(II) and Co(II). The results are listed in Table III. The solid reflectance spectra are almost the same for all anions. Special attention has been paid to the vibrational overtones in the near infrared. Besides the absorptions caused by the modes of the ethyl group an absorption was found between 6250-6770 cm^{-1} , which was assigned to an overtone of hydroxyl modes. This mode appeared to be nearly independent of the character of the central ion, but showed great dependency on the anion. In complexes of the various anions the absorptions were found respectively: ClO_4^\ominus at 6750, BF_4^\ominus at 6760, NO_3^\ominus at 6300 cm^{-1} .

The determination of the maxima of the lowest energy transitions were hampered by the occurrence of vibrational overtones in this region. This was also the case with the transmission spectra. The transmission spectra were recorded in super dry ethanol containing 2% of EOF. It is possible that even under these conditions the last traces of water have not been removed. Whereas the reflection spectra of the complexes of the various anions were almost identical, the transmission spectra of the nitrates differed from the spectra of the complexes of the other anions. The molar extinction coefficients of the nitrates are noticeably higher and the peaks are shifted towards lower energies. The nitrate ions take part in the coordination of the metal in solution; in the solid state $\{\text{M}(\text{EtOH})_6(\text{NO}_3)_2\}$ we propose they do not.

Table III

Absorption maxima of electronic spectra of ethanol complexes
(wavenumber in units $\text{cm}^{-1} \times 10^3$) (24-26 °C) (shoulders in parentheses)
Solid reflectance spectra

| | | | | | |
|--|--------|--------|--------|------|-----|
| $\text{Fe}(\text{EtOH})_6(\text{ClO}_4)_2$ | 10.15 | (8.0) | | | |
| $\text{Co}(\text{EtOH})_6(\text{ClO}_4)_2$ | (21.2) | 19.7 | (16.0) | 8.3 | |
| $\text{Co}(\text{EtOH})_6(\text{BF}_4)_2$ | (21.2) | 19.7 | (15.6) | 8.3 | |
| $\text{Co}(\text{EtOH})_6(\text{NO}_3)_2$ | (21.2) | 19.8 | (15.4) | 8.4 | |
| $\text{Ni}(\text{EtOH})_6(\text{ClO}_4)_2$ | (24.8) | (21.5) | (14.9) | 13.6 | 8.4 |
| $\text{Ni}(\text{EtOH})_6(\text{BF}_4)_2$ | 25.0 | (21.5) | (14.9) | 13.6 | 8.3 |
| $\text{Ni}(\text{EtOH})_6(\text{NO}_3)_2$ | 25.0 | (21.5) | (14.9) | 13.5 | 8.4 |

Transmission spectra in EtOH-2% EOF

The molar extinction coefficients in $1 \text{ mole}^{-1} \text{ cm}^{-1}$ (*in italics*)

| | | | | | |
|--|------------|-------------|-----------|------------|------------|
| $\text{Fe}(\text{EtOH})_6(\text{ClO}_4)_2$ | 10.2, 2.1 | (8.6), 1.6 | | | |
| $\text{Co}(\text{EtOH})_6(\text{ClO}_4)_2$ | (21.0) | 19.6, 6.0 | (15.5) | 8.0, 1.5 | |
| $\text{Co}(\text{EtOH})_6(\text{NO}_3)_2$ | — | 19.1, 17.6 | (15.5) | 8.0, 3.1 | |
| $\text{Ni}(\text{EtOH})_6(\text{ClO}_4)_2$ | 24.9, 6.5 | (21.5), 0.5 | 15.0, 1.8 | 13.7, 2.14 | 8.35, 2.36 |
| $\text{Ni}(\text{EtOH})_6(\text{BF}_4)_2$ | 25.0, 6.4 | (21.5), 0.6 | 15.0, 1.9 | 13.7, 2.2 | 8.35, 2.38 |
| $\text{Ni}(\text{EtOH})_6(\text{NO}_3)_2$ | 24.7, 15.5 | — | 14.6, 4.7 | 13.3, 5.0 | 8.23, 3.0 |

The vibrational spectra

The infrared spectra can only be interpreted in a qualitative way. The alcohol complexes containing perchlorate anions show a broad absorption at about 3400 cm^{-1} (shoulders at $3300\text{-}3500\text{ cm}^{-1}$) assigned to O - H stretch. The O - H bending frequencies are observed at 1625 cm^{-1} and sometimes a weaker one at 1675 cm^{-1} . The perchlorate ν_3 absorption coincides with EtOH frequencies but ν_1 is observed as a very weak absorption at 938 cm^{-1} . A slight distortion of the T_d symmetry may be caused by hydrogen bonding giving rise to some ν_1 absorption. We assume that perchlorate ions do not take part in the coordination.

In the fluoroborate compounds the large broad O - H stretching frequency has its maximum at $3480\text{ - }3500\text{ cm}^{-1}$. The bending O - H occurs at 1670 cm^{-1} with some shoulders at lower wavenumbers. At 772 cm^{-1} the ν_1 absorption of BF_4^\ominus is observed as a very weak and sharp peak.

The O - H stretching frequencies are markedly shifted towards lower energies in the complexes with nitrate anions. The O - H stretch is observed at $3200\text{ - }3400\text{ cm}^{-1}$. The O - H bendings occur at 1600 cm^{-1} and the shoulders at 1500 cm^{-1} in the C - H bending are possibly also caused by O - H bendings. The infrared inactive ν_1 nitrate absorption cannot be observed since EtOH obscures the $1030\text{ - }1050\text{ cm}^{-1}$ region. A very weak and sharp absorption at 839 cm^{-1} may be assigned to ν_2 . The intense and broad ν_3 absorption at $1300\text{ - }1400\text{ cm}^{-1}$ coincides with C - H bendings, so we were not able to estimate the exact character of the absorption. The infrared spectra do not give information on the coordination in this case. But from the similarity of the solid reflectance spectra it was concluded that the nitrates also contained hexaethanol metal groups.

Thus we may state that the anions have considerable influence on the hydroxyl frequencies of ethanol. The magnitudes of the influences of the three anions can be arranged in the same order as the tendencies of the anions to take part in the coordination: $\text{NO}_3^\ominus \gg \text{ClO}_4^\ominus > \text{BF}_4^\ominus$.

Experimental

Synthetical Procedures

A. The appropriate hydrated salt was dissolved in a twofold excess of EOF. The ethanol complexes of Co(II) and Ni(II) with the anions ClO_4^\ominus and BF_4^\ominus separated immediately. The other complexes crystallized upon standing.

B. An equal amount of anhydrous ether was added to the warm solution of salts in EOF. Upon standing at -20° crystals were formed.

C. The solutions of hydrated salts in EOF were gently refluxed at 40° at diminished pressure and the solution was somewhat concentrated by evaporation. An equal amount of ether was added. Crystals appeared at -20° .

D. To the warm solution obtained by the foregoing method sodium-dried heptane was added. Upon cooling crystals separated.

General

In an extremely dry glove-box the crystals were filtered with suction through a sintered glass funnel and washed with ether, ether-heptane 1 : 1 or heptane. The preparation of the samples for the various measurements were also carried out in a dry-box.

IR spectra

The IR spectra were recorded with a Beckman IR-10 spectrometer on Nujol mulls between rock salt windows.

Visible spectra

The visible spectra were obtained with a Beckman DK-2A spectrofotometer.

X-ray spectra

The X-ray powder patterns were obtained from vaseline mulls between dried tapes with an evacuated (10 mm Hg) Nonius Guinier camera using Cu-K α radiation.

Conclusion and applications

The existence of complexes of alcohol has been proved. The syntheses of several divalent metal perchlorate- and fluoroborate-ethanol complexes may be carried out with commercially available EOF in a few hours. If moisture is thoroughly excluded these complexes show very attractive properties as starting materials for the synthesis of coordination compounds of weak ligands or water-sensitive ligands.

The orthoformates of methanol, butanol and pentanol gave the complexes of the respective alcohols. The properties of these various compounds are now being studied.

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