

## METAL COMPLEXES OF AMINO ACIDS AND DERIVATIVES—XIII

### SOME NICKEL(II) COMPLEXES OF *L*-ARGININE ZWITTERIONS OR *L*-ARGININATE ANIONS. A NOVEL IONIC $\rightarrow$ BIDENTATE PERCHLORATE REARRANGEMENT BROUGHT ABOUT BY PRESSURE[1-5]

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**Abstract**—Nickel(II) complexes have been isolated in which the ligand coordinates as an anion ( $\text{Arg}^-$ ) or a zwitterion ( $\text{ArgH}$ ). These complexes,  $\text{Ni}(\text{Arg})X \cdot n\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4$ ) and  $\text{Ni}(\text{ArgH})_2X_2 \cdot n\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{NO}_3, \text{ClO}_4, \text{OH}$ ), are six-coordinate and contain a  $\text{NiN}_2\text{O}_4$  coordination moiety. Only in the cases of  $\text{Ni}(\text{ArgH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{ArgH})(\text{OH})_2 \cdot \text{H}_2\text{O}$  are  $X^-$  groups coordinated. However, it has also been found that the complexes containing ionic perchlorate, when put under pressure, rearrange to form complexes containing bidentate perchlorato groups. The complexes have been characterised by magnetic measurements and by infrared and visible reflectance spectral methods.

#### INTRODUCTION

IT HAS long been known that amino acids may bind to a metal ion through either or both the amino and carboxylate groups, depending upon the nature of the metal ion[6]. Among amino acid complexes those of nickel(II) have received much attention as their electronic spectra can be used to elucidate bonding sites[7, 8]. With potentially tridentate amino acids investigations have not been as exhaustive as those of simple amino acids. Apart from histidine[9] basic amino acids such as ornithine, lysine, and arginine, though of immense biological importance[10], have not yet attracted much attention from inorganic chemists.

From potentiometric measurements Albert[11] has proposed that lysine and arginine function predominantly as bidentate ligands, binding metal ions through the  $\alpha$ -amino and carboxylate groups, whereas ornithine may be bidentate or tridentate with the  $\epsilon$ -amino as the additional donor group forming a six-membered ring under different pH conditions. The latter observations on lysine have been corroborated by Brubaker and Busch[7] and by Clark and Martell[12].

The omission of any studies of solid complexes of arginine has prompted us to embark on the present investigation. Arginine, incorporated into peptide chains in protein, is a constituent of many metalloenzymes[13], and a study of actual metal-arginine interactions seemed to be worthwhile and of interest at the present time. We were primarily interested in the elucidation of the ligand binding sites and of the general behaviour of this unusual type of ligand; we have recently observed some novel reactions resulting from the complexation of amino acids containing formal charge separation in the ligand.

Quagliano *et al.*[14] have also reported unusual coordination behaviour with ligands containing a formal positive charge removed from the donor site. We were thus not altogether surprised to discover that, not only does arginine have the ability to coordinate as either a neutral or a zwitterionic species, but that some of the complexes undergo interesting rearrangements when put under pressure in the solid state.

#### EXPERIMENTAL

##### Starting materials

*L*-Arginine (Koch-Light Laboratories Ltd.) and analytical grade nickel(II) salts were used without further purification.

##### Complex preparation

The nickel(II) complexes were prepared by the following methods. Yields were of the order of 60-75 per cent, based on *L*-arginine.

##### Method A

*L*-Arginine (0.0028 mole) and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (0.0028 mole) were dissolved in ethanol (30 ml) by refluxing for 20 min, after which the solution was filtered to remove any insoluble materials. This solution was then slowly added to a solution of the hydrated nickel(II) salt (0.0028 mole) in ethanol (10 ml) with stirring. The green precipitate which formed immediately was filtered, washed with ethanol and acetone and dried *in vacuo* over  $\text{CaCl}_2$ .

##### Method B

To a refluxing solution of *L*-arginine (0.0028 mole) and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (0.0028 mole) in ethanol (30 ml) was slowly added a solution of the hydrated nickel(II) salt (0.0014 mole) in ethanol (10 ml) with stirring. The green precipitate which formed immediately was filtered, washed with ethanol and acetone, and dried *in vacuo* over  $\text{CaCl}_2$ .

**Method C**

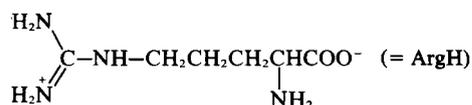
L-Arginine (0.0028 mole) dissolved in water (10 ml) was treated with  $\text{Na}_2\text{CO}_3$  (0.0014 mole) and warmed to  $40^\circ$ . To this solution was added a solution of the hydrated nickel(II) salt (0.0014 mole) in water (5 ml) with stirring. The resulting green solution was warmed to  $40^\circ$  and stirred for 2 hr, after which it was placed in the refrigerator until precipitation took place. The precipitate was filtered, washed with acetone and dried *in vacuo* over  $\text{CaCl}_2$ .

**Physical measurements**

I.R. spectra were obtained using a Perkin-Elmer 621 double beam spectrophotometer in the range  $4000\text{--}200\text{ cm}^{-1}$ ; samples were prepared either as KBr discs or as Nujol mulls. The electronic reflectance spectra were obtained on a Beckman DK2A spectrophotometer using MgO as dilutant. Melting or decomposition points were determined on a Gallenkamp melting apparatus, and magnetic measurements were carried out by the Gouy method.

**RESULTS AND DISCUSSION**

Arginine exists as a zwitterion both in solution [15] and in the solid state [16]. It differs from other simple amino acids in that the protonated site is the guanido group and not the  $\alpha$ -amino group. Thus, because of the large charge separation between the positive and negative centres in the molecule, arginine may be expected to complex either



as the neutral zwitterionic species (ArgH) or, by deprotonation of the guanido group, as an anion ( $\text{Arg}^-$ ).

Table 1 contains a list of the complexes prepared together with some physical properties. Table 2 lists the solid state electronic absorption frequencies (see Fig. 1) and some electronic parameters derived from these data. The magnetic moments and visible spectra indicate that all the complexes have an essentially octahedral stereochemistry.

There are essentially two types of complexes which have been isolated: the  $\text{Ni}(\text{Arg})\text{X}\cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4$ ) derivatives which contain anionic ligands, and the  $\text{Ni}(\text{ArgH})_x\text{X}_2\cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{NO}_3, \text{ClO}_4, \text{OH}$ ) complexes which contain the zwitterionic ligands.

Jorgensen [17] has observed that the spectra of nickel(II) complexes are similar for any given combination of  $n$  amine and  $6-n$  oxygen donors, a phenomenon he has named the rule of average environment. Using this rule it is possible to estimate the number of each type of donor atom. The complexes containing the anionic ligands

Table 1. Physical properties and analytical data of the nickel(II) complexes

Compound	Prep.	Color	Decomposition point ( $^\circ\text{C}$ )	Magnetic moment (B.M.)	% Carbon		% Hydrogen		% Nitrogen	
					Calcd	Found	Calcd	Found	Calcd	Found
$\text{Ni}(\text{Arg})\text{ClO}_4\cdot 2\text{H}_2\text{O}$	A	Pale green	230	3.22	19.6	19.9	4.6	4.8	15.2	15.2
$\text{Ni}(\text{Arg})\text{NO}_3\cdot 3\text{H}_2\text{O}$	A	Pale green	200	3.44	20.7	21.0	5.5	5.2	20.1	20.2
$\text{Ni}(\text{Arg})\text{Cl}\cdot 4\text{H}_2\text{O}$	A	Pale green	210	3.47	21.2	21.6	6.2	5.7	16.5	16.4
$\text{Ni}(\text{Arg})\text{Br}\cdot 2\text{H}_2\text{O}$	A	Pale green	210	3.34	21.9	22.5	4.6	5.4	17.0	16.7
$\text{Ni}(\text{ArgH})_2(\text{NO}_3)_2\cdot \text{H}_2\text{O}$	B	Pale green	205	3.05	26.3	26.7	5.5	6.4	25.6	25.6
$\text{Ni}(\text{ArgH})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$	B	Pale green	195	3.54	28.1	28.7	6.3	6.5	21.8	21.6
$\text{Ni}(\text{ArgH})_3(\text{ClO}_4)_2\cdot 4\text{H}_2\text{O}$	B	Pale green	210	3.43	25.4	25.7	5.9	5.9	19.7	19.4
$\text{Ni}(\text{ArgH})(\text{OH})_2\cdot \text{H}_2\text{O}$	C	Pale green	200	2.90	25.3	25.4	6.3	5.9	19.6	19.7

Table 2. Visible spectra\* ( $\text{cm}^{-1}$ ) of the nickel(II) complexes and some spectral parameters†

Compound	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	${}^3\text{A}_g \rightarrow {}^3\text{T}_{1g}(\text{P})$	$Dq$	$B'$	$\beta$
$\text{Ni}(\text{Arg})\text{ClO}_4\cdot 2\text{H}_2\text{O}$	9600		15,500	26,900	960	975	0.906
‡	9750		15,500	26,300	975	905	0.858
$\text{Ni}(\text{Arg})\text{NO}_3\cdot 3\text{H}_2\text{O}$	9550		15,800	26,400	955	886	0.839
$\text{Ni}(\text{Arg})\text{Cl}\cdot 4\text{H}_2\text{O}$	9400		15,300	26,500	940	916	0.851
$\text{Ni}(\text{Arg})\text{Br}\cdot 2\text{H}_2\text{O}$	9700		15,900	26,300	970	864	0.803
$\text{Ni}(\text{ArgH})_2(\text{NO}_3)_2\cdot \text{H}_2\text{O}$	10,500	13,100	16,600	27,700	1050	948	0.881
$\text{Ni}(\text{ArgH})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$	9500		16,200	26,900	950	929	0.863
$\text{Ni}(\text{ArgH})_3(\text{ClO}_4)_2\cdot 4\text{H}_2\text{O}$	9700		16,600	26,600	970	953	0.885
‡	10,000		16,100§	27,100	1000	885	0.839
$\text{Ni}(\text{ArgH})(\text{OH})_2\cdot \text{H}_2\text{O}$	9500		15,700	27,000	950	870	0.808

\*Reflectance spectra in MgO as dilutant.

† $\beta$  = Racah parameter.  $B$ , the  ${}^3\text{F}_3\text{--}{}^3\text{P}$  term separation for the free  $\text{Ni}^{2+}$  ion was taken as  $15,840\text{ cm}^{-1}$  [32].  $B'$ , the  ${}^3\text{F}_3\text{--}{}^3\text{P}$  term separation for the  $\text{Ni}^{2+}$  complexes were calculated by an empirical method [33].

‡Reflectance spectra of KBr disks.

§An absorption also appears at  $17,400\text{ cm}^{-1}$ .

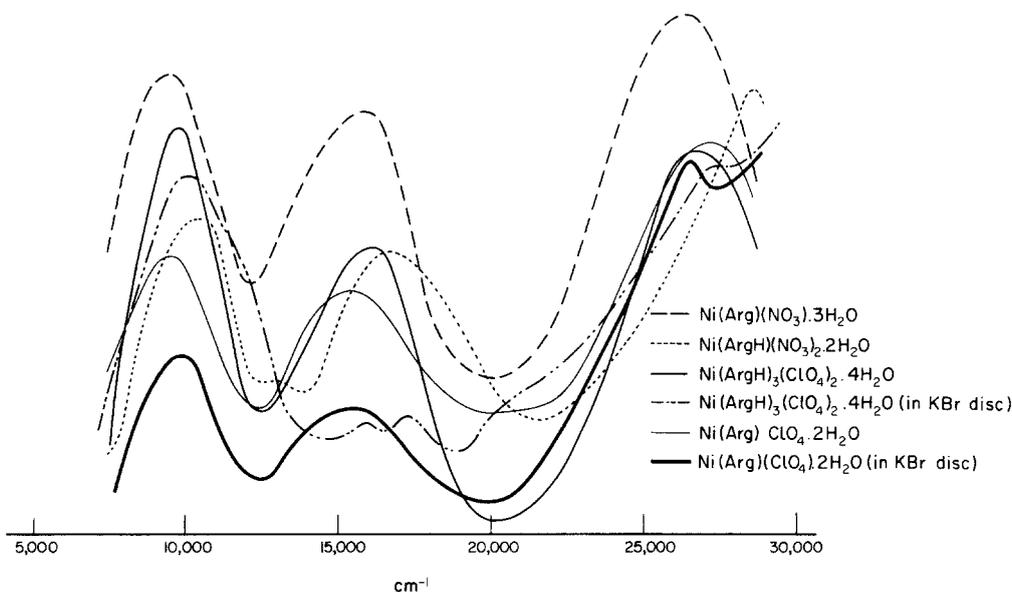


Fig. 1. Solid reflectance spectra of some nickel(II)-L-Arginine complexes.

exhibit spectra indicative of a 2N,4O environment around the nickel atom [7, 8, 17]. Moreover, the complexes exhibit almost identical spectra irrespective of the other anion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ), which is evidence that the coordination sphere of nickel does not contain these anions. The i.r. spectra of perchlorate ion is very susceptible to the physical state of the ion, i.e. whether coordinated or non-coordinated [18], and the Nujol mull spectrum of  $\text{Ni}(\text{Arg})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  exhibits bands at

$1095 \text{ cm}^{-1}$  and  $620 \text{ cm}^{-1}$  (Table 3, Fig. 2) which are indicative of ionic perchlorate. It is reasonable to suggest, therefore, that the coordination environment of nickel derives from the carboxylato, the  $\alpha$ -amino, an amino group of the deprotonated guanido group, and three water molecules (even though the complexes were synthesised in alcohol, absolute alcohol was not employed and hydrated nickel(II) salts were used).

The i.r. spectra of metal-amino acid complexes have

Table 3. Some significant infrared frequencies of the Ni(II) complexes of L-arginine\*

Compound	$\nu(\text{NH}_2)$	$\nu(\text{CN})$	$\nu(\text{COO}^-)_{\text{asym}}$	$\nu(\text{COO}^-)_{\text{sym}}$	$\delta(\text{NH}_2)$	Anion	$\Delta$
ArgH	3350(3340) 3290(3290)	1670(1674)	1610(1614)	1415(1418)	1550(1555)		195(196)
$\text{Ni}(\text{Arg})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$	3350(3330) 3290 3185(3165)	1660(1660)	1620(1618)	1402(1401)	1582(1570)	1095(1142, 1120, 1109, 1089) 620(636, 626)	218(217)
$\text{Ni}(\text{Arg})\text{NO}_3 \cdot 3\text{H}_2\text{O}$	3340(3320) 3280 3180(3160)	1662(1660)	1622(1620)	1405(1400)	1570(1575)	1380(1380) 824(831)	217(220)
$\text{Ni}(\text{Arg})\text{Cl} \cdot 4\text{H}_2\text{O}$	3330(3325) 3160(3160)	1655(1655)	1616(1618)	1403(1400)	1580(1580)		213(218)
$\text{Ni}(\text{Arg})\text{Br} \cdot 2\text{H}_2\text{O}$	3320 3160	1660	1620	1404	1570		216
$\text{Ni}(\text{ArgH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	3340 3170	1660	1628	1402	1500	1380 821	226
$\text{Ni}(\text{ArgH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3335(3330) 3160(3160)	1660(1658)	1620(1620)	1402(1402)	1570(1575)		218(218)
$\text{Ni}(\text{ArgH})_3(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$	3350(3330) 3285 3165(3160)	1670(1660)	1634(1625)	1405(1405)	1575(1575)	1090(1140, 1120, 1110, 1090) 623(638, 628)	229(220)
$\text{Ni}(\text{ArgH})(\text{OH})_2 \cdot \text{H}_2\text{O}$	330 3165	1665	1633	1404	1572		229

\*Frequencies in  $\text{cm}^{-1}$ ; data from Nujol mull, figures in parentheses from KBr discs.

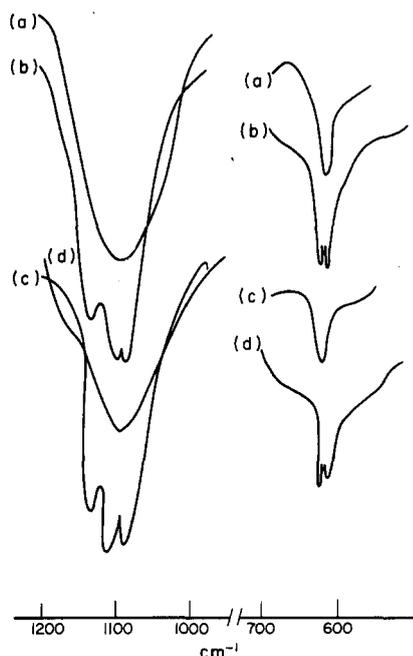
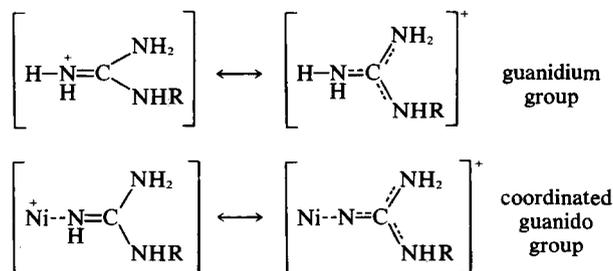
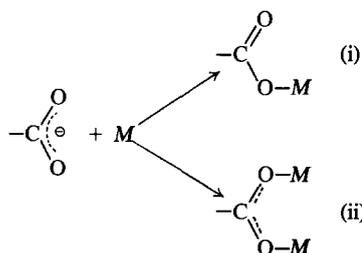


Fig. 2. Infrared spectra of the nickel(II) perchlorate complexes of *L*-arginine. (a)  $\text{Ni}(\text{Arg})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Nujol mull), (b)  $\text{Ni}(\text{Arg})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (KBr disc), (c)  $\text{Ni}(\text{ArgH}_3)(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Nujol mull), (d)  $\text{Ni}(\text{ArgH}_3)(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (KBr disc).

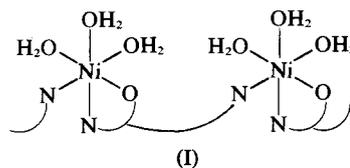
been well investigated [8, 19, 20], and a good deal of information about bonding sites may be thus obtained. All the complexes contain a broad absorption centred *ca.*  $3500\text{ cm}^{-1}$  which can be assigned to a combination of the  $\nu(\text{OH})$  modes of coordinated and lattice water. The other significant infrared frequencies are listed in Table 3 and assignments have been made by comparison with other amino acid [21] and guanidium [22] spectra. In certain cases deuterated complexes were obtained to aid in band assignments. In the  $3\mu$  region peaks observed for the ligand at  $3350\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  are not considerably changed upon complexation, but a new peak *ca.*  $3180\text{ cm}^{-1}$  was observed for all the complexes. This new peak is at a frequency indicative of  $\nu(\text{NH})$  of a coordinated amino group [20]. The similar absorption at  $3350\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  for the complexes as well as for the guanidium ion in the ligand seems to suggest that the symmetry of the guanido group is not appreciably altered, and this could be true for the deprotonated guanido group only if it is involved in coordination to the nickel:



This reasoning also would rule out any possibility of two nitrogen atoms of the guanido group being involved in coordination, and molecular models reinforce this view. It also seems that the ligand, acting as a tridentate, bridges two nickel atoms, as a nine-membered chelate ring would result from the guanido group coordinating to the same metal atom as the  $\alpha$ -amino acid groups. Table 3 also contains the  $\nu(\text{COO}^-)_{\text{asym}}$  and  $\nu(\text{COO}^-)_{\text{sym}}$  frequencies, and  $\Delta$ , the difference between them. It can be seen that  $\Delta$  increases upon complexation of the ligand, which implies a monodentate acido group as distinct from a bridging acid group [5, 23].  $\Delta$  is a measure of the asymmetry of the C-O bonds in the acidato group, and an increase in  $\Delta$  of  $20\text{--}25\text{ cm}^{-1}$ , found in the complexes as compared with the free ligand, implies [23] a structure of type (i).

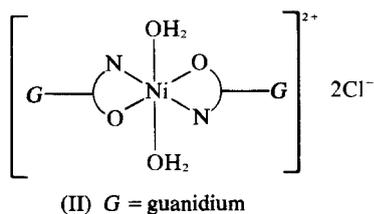


Thus, the i.r. and visible spectral evidence suggest a structure *similar* to that of (I), and it should be emphasised that this structure has many different possible isomers. The deviation from strictly  $\text{O}_h$  symmetry in these complexes is reflected in the high magnetic moments,  $\mu_{\text{eff}} = 3.22\text{--}3.47\text{ B.M.}$  [24]. The relative insolubility of the complexes in most solvents would also seem to verify a polymeric structure.



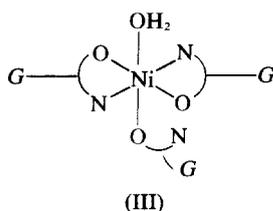
The group of complexes containing the neutral, zwitterionic ligand are diverse inasmuch as the metal has formed bonds with one, two or three ligands, and the stoichiometry of the complexes is often independent of the ratio of starting materials (see Experimental section).

The  $\text{Ni}(\text{ArgH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complex has an i.r. spectrum containing evidence for both amino and carboxylato coordination, and the electronic spectrum suggests a 2N,4O donor group. The obvious structure of this complex is (II).



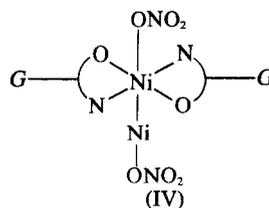
The magnetic moment of this complex is 3.54 B.M., which suggests considerable tetragonal distortion.

The most difficult structure to assign is that of  $\text{Ni}(\text{ArgH})_3(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Its electronic spectrum is quite typical of a 2N,4O environment, and so a complex containing three bidentate  $\alpha$ -amino acid groups is excluded. The  $\nu(\text{COO}^-)$  frequencies appear to be quite typical of the other complexes described in this work, but it is apparent that the  $\nu(\text{NH})$  region is more complicated. These facts would seem to indicate that the coordination around nickel is similar to structure (III), i.e. a complex containing two bidentate and one monodentate arginine ligand.\* The i.r. spectrum in Nujol contains evidence of only ionic perchlorate groups.



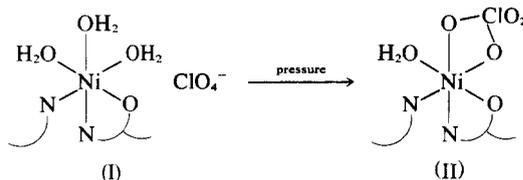
Method C described in the Experimental section produces only one type of complex,  $\text{Ni}(\text{ArgH})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , irrespective of the nickel(II) salt (perchlorate, nitrate, halide) used. An intense i.r. absorption at  $3410 \text{ cm}^{-1}$  may be assigned to a combination of  $\nu(\text{OH})$  of hydroxide and water. It is probably significant that this absorption is much stronger than the  $\nu(\text{OH})$  bands in the complexes which do not contain hydroxide. No attempt is made here to postulate a structure for this complex, other than to point out that the electronic spectrum is once again typical of a  $\text{NiN}_2\text{O}_4$  coordination moiety.

The  $\text{Ni}(\text{ArgH})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  complex is extremely interesting, as the available evidence suggests that it contains coordinated nitrate groups (IV). The electronic spectrum of this complex (Table 2, Fig. 1) exhibits a much higher energy  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition than any other complex studied here, and the  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) transitions are also at higher energy. (Also, this is the only



complex in which the  ${}^3A_{2g} \rightarrow {}^1E_g$  band is distinguishable). This therefore would seem to exclude a structure of type (II) in which the coordination is 2N,4O and in which anions are non-coordinating. The nitrate complex must thus contain coordinated anions. The position of  $\text{NO}_3^-$  in the spectrochemical series is significantly higher than  $\text{H}_2\text{O}$ [26] and this accounts for the high energy bands. Although the i.r. spectra of ionic and coordinated nitrate have been well investigated[27, 28] the i.r. spectrum of the complex prepared here did not, unfortunately, yield conclusive evidence for either ionic or coordinated nitrate groups.

When  $\text{Ni}(\text{Arg})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  is pressed in a KBr die the resulting i.r. spectrum (Table 3, Fig. 2) indicates that the perchlorate group has become coordinated and, moreover, is bidentate[18]. The perchlorate bands in the original complex at  $1095 \text{ cm}^{-1}$  and  $620 \text{ cm}^{-1}$  are no longer present and a series of absorptions at 1142, 1120, 1109 and  $1089 \text{ cm}^{-1}$  and at 636 and  $626 \text{ cm}^{-1}$  appear. The following change can be envisaged:



It may be pointed out that the vibrational spectrum due to the ligand has not changed when the KBr disc is prepared and this indicates that the ligand is attached to the metal atom in the same way. Moreover, although the reflectance spectrum of the KBr disc complex is slightly changed from that of  $\text{Ni}(\text{Arg})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  (Table 2) (due to the higher ligand field strength of perchlorate over water[26]) it is still indicative of a 2N,4O environment around the nickel. This process should be contrasted with the usual effect of KBr under pressure on even coordinated perchlorate, which is to displace the perchlorate in favour of bromide ion[29]. We have investigated this unique phenomenon carefully, though we admit to a lack of apparatus to measure the exact pressure needed to induce rearrangement. Simple mixing of KBr and  $\text{Ni}(\text{Arg})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  does not bring about the rearrangement; neither does heating to  $100^\circ$  *in vacuo* for some hours. Only after the mixture has been put under pressure in the die does the complex rearrangement occur. This pressure effect seems to us to be a novel application of the theorem of Le Chatelier to coordination systems. We have observed a similar rearrangement when  $\text{Ni}(\text{ArgH})_3(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  was put under pressure in a KBr

\*Evidence has also been found in copper(II) complexes of L-arginine of monodentate ligands.

die, when the ionic perchlorate groups have become bidentate (Table 3). There has been some considerable interest recently in the effect of pressure on chemical systems: spectral studies of stereochemical changes of metal complexes in solution[30, 31], and the interesting observations of Ferraro *et al.* that high external pressure can convert the distorted tetrahedral (spin-free)  $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{Ph})_2\text{Br}_2$  into a planar (spin-paired) complex [31]. The latter results set a precedent for the type of pressure reaction we report here.

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