Complexes of Nickel(III) with Biguanide and *N'*-Amidinoisoureas

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The following complexes of nickel(III) with biguanide (Hbg), *N'*-amidinoisourea (aiu), and *O*-alkyl-*N'*-amidinoisoureas [alkyl = Me (Hmaiu) or Et (Heaiu)] have been prepared and isolated: $[NiBr_2L_2]Br$ and $[NiCl_2L_2]X$ (L = Hbg, X = F or Cl); $[NiL_2]Cl$ (L = aiu); and $[NiL_2]_2[SO_4]\cdot 2H_2O$ (L = maiu or eaiu). Oxidimetric titrations and the values of the oxidation potentials indicate that the complexes are one-electron oxidizing agents, while polarographic reduction-potential studies suggest nickel(III) complexes rather than nickel(II)-stabilized radical-ligand compounds. Magnetic-susceptibility, e.s.r., and i.r. data also support the presence of Ni^{III} in these complexes.

A LARGE number of nickel(III) complexes have been described in the literature. These include dichlorobis(diarsine)nickel(III) chloride,[1] tribromobis(triethylphosphine)nickel(III),[2] and bis(ethylenediamine)dihalogenonickel(III) halides.[4] Some complexes of Ni^{III} with robust ligands such as dithiolate,[4] 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane,[5] and 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane [6] have been described. A very stable nickel(III) complex with a π-(3)-1,-2 and π-(3)-1,7 carbollyl system has been isolated by Hawthorne.[7] Recently a number of nickel(III) complexes with biuret and oxamide [8] have been prepared and characterized. Some nickel(III) complexes are also stabilized by pyridine oxime ligands.[9]

The e.s.r. spectral study of many of these complexes by Drago and Baucom [9] indicated that most of these ' nickel(III) ' complexes are actually nickel(II)-stabilized radical-ligand compounds. The $\langle g \rangle$ values and polarographic reduction-potential data of many of these complexes with ligands such as toluene-3,4-dithiol [10,11] suggest that the complexes are nickel(II) species with oxidized ligands. However, from a large amount of experimental evidence, it was suggested that nickel complexes having $\langle g \rangle > 2.1$ may be considered as nickel(III) species, while those having $\langle g \rangle < 2.1$ are better considered as nickel(II) complexes with oxidized ligands.[9] On this basis, it was concluded that nickel in TiO_2 [12] and $[Ni(pbo)_3]$, which possess comparatively high $\langle g \rangle$ values, are truly nickel(III) complexes. In cation-stabilized radical-ligand compounds the unpaired electron resides mainly on the ligand atoms rather than on the metal atom and $[Ni(pbo)_3]$ (pbo = α-2-pyridylbenzaldehyde oxime) is considered to be a nickel(III) complex rather than a nickel(II)-stabilized radical-ligand compound.

Biguanide, $H_2N\cdot C(NH_2)\colon N\cdot C(NH)\cdot NH_2$, is a very strong ligand and is capable of forming complexes with transition metals [13] and non-metals [14,15] having normal or high oxidation states.[16,17] In this respect biguanides and *O*-alkyl-*N'*-amidinoisoureas are very similar and can form complexes in which the ligand is neutral or unprotonated, while *N'*-amidinoisourea always forms complexes in which the ligand is unprotonated.* No metal complexes of Haiu have yet been prepared. This may be due to involvement of the central nitrogen atom in strong hydrogen bonding.

The π-electron delocalization in these metal chelates

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* Hbg = Biguanide, Haiu = *N'*-amidinoisourea, Hmaiu = *N'*-amidino-*O*-methylisourea, Heaiu = *N'*-amidino-*O*-ethylisourea.

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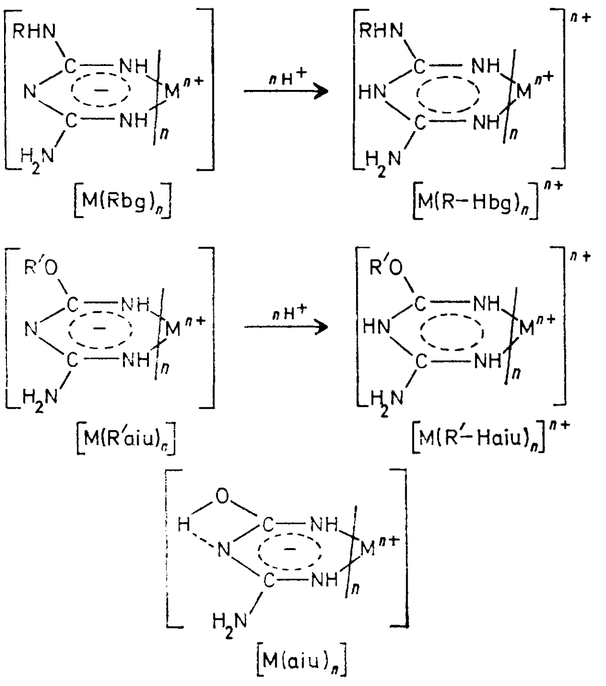
has been supported by LCAO MO calculations,[18] by a number of electrophilic-substitution reactions,[19] and by ^1H n.m.r. studies of nickel(II) complexes.[20] This type of electron delocalization will produce stronger metal chelates and raise some of the metal *d* electrons to antibonding orbitals from which they can be removed by oxidation, and the isolation of stable complexes with metals having higher oxidation states may be possible. We have prepared some nickel(III) complexes of these ligands by oxidizing the corresponding nickel(II) complexes.



EXPERIMENTAL

Instrumentation.—Infrared spectra were recorded on a Beckman IR-12 spectrophotometer in Nujol mulls. Conductance measurements were made with a Phillips conductivity bridge. Standard conductivity cells with platinum electrodes were used. The magnetic measurements were carried out with a Gouy balance at ordinary temperatures and at two field strengths using $Hg[Co(SCN)_4]$ as calibrant. The magnetic susceptibilities were corrected for the diamagnetism of the ligands by using Pascal's constants. Optical spectra and the polarographic reduction potentials were recorded with a Beckman DB-G grating spectrophotometer and an LP7 polarograph (against the saturated calomel electrode) respectively. E.s.r. studies were made with a Varian E-4 *X*-band spectrometer using polycrystalline samples held in quartz tubes at 77 K.

Materials.—All the reagents were of analytical grade. The liquids were distilled and gases were purified before use.

Bis(biguanide)dichloronickel(III) *Chloride*, $[NiCl_2(Hbg)_2]Cl$.—Finely ground $[Ni^{II}(Hbg)_2]Cl_2\cdot 2H_2O$ [13] was suspended in carbon tetrachloride (50 cm^3) and chlorine gas was passed through the mixture at a rate of 80 bubbles per minute for 1 h. The colour of the suspension turned from orange-red to maroon-red. The suspension was filtered and the residue, after drying *in vacuo*, was again finely powdered and subjected to chlorination as before. The whole process was repeated three times. The complex was then filtered off, washed with carbon tetrachloride (3 × 20 cm^3), and finally dried *in vacuo* over calcium chloride. The complexes bis(biguanide)dichloronickel(III) fluoride, $[NiCl_2(Hbg)_2]F$ and bis(amidinoisoureido)nickel(III) chloride, $[Ni(aiu)_2]Cl$, were similarly prepared by chlorination of $[Ni^{II}(Hbg)_2]F_2\cdot 4H_2O$ [13] and $[Ni^{II}(aiu)_2]\cdot 2H_2O$ [13] respectively.

Bis(biguanide)dibromonickel(III) *Bromide*, $[NiBr_2(Hbg)_2]Br$.—A mixture of air and bromine vapour was passed through a suspension of $[Ni^{II}(Hbg)_2]Br_2\cdot 1.5H_2O$ (5 g) [13] in carbon tetrachloride (100 cm^3) for 12 h. The rate of bubbling was kept at 4—5 bubbles per second. Deep red shiny crystals were formed which after filtration were dried in a vacuum desiccator over potassium hydroxide pellets.

*Bis(*O*-methyl-*N′*-amidinoisoureido)nickel*(III) *Sulphate Hydrate*, $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$.—(a) *Peroxodisulphate oxidation.* An aqueous solution (1 l) of $[Ni^{II}(Hmaiu)_2]Cl_2\cdot 3H_2O$ (5 g) was treated with saturated sodium hydrogencarbonate solution (200 cm^3). The mixture was filtered and the orange-red filtrate was cooled to 10 °C. Saturated potassium peroxodisulphate solution (200 cm^3) was added to the filtrate and the resulting solution was kept at 0 °C for 30 min. A deep blue precipitate appeared and was filtered off and washed with ice-cold water (10 cm^3), methanol (10 cm^3) at 0 °C, and finally cold dry carbon tetrachloride (10 cm^3). The residue was dried under high vacuum at 0 °C over calcium chloride. The complex is moderately soluble in methanol, undergoing slow decomposition.

(b) *Anodic oxidation.* A platinum basin containing a solution (100 cm^3) of $[Ni(Hmaiu)_2][SO_4]\cdot 3H_2O$ was cooled to 0 °C. The solution was then electrolyzed with a platinum strip as the cathode and the basin as the anode, keeping the anodic potential at *ca.* 0.82 V. The current was passed for 1 h and the temperature of the solution was kept at 0 °C throughout. A deep blue precipitate was formed on the anode surface and was filtered off, washed, and dried as in (a).

*Bis(*O*-ethyl-*N′*-amidinoisoureido)nickel*(III) *Sulphate Hydrate*, $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$.—An aqueous solution of $[Ni^{II}(Heaiu)_2]Cl_2\cdot 3H_2O$ [13] was subjected to the same treatment as in (a) above and a deep blue precipitate was obtained. This was filtered off and washed with ice-cold water (10 cm^3), dry methanol (2 × 5 cm^3) at −5 °C, and finally dry diethyl ether at −5 °C (10 cm^3). The complex was dried *in vacuo* over calcium chloride at 0 °C. It is sparingly soluble in water, moderately in methanol and acetone, and decomposes in solution (slowly even in a dry atmosphere).

RESULTS AND DISCUSSION

Orange-red solutions of $[Ni^{II}(Hbg)_2]Cl_2\cdot 2H_2O$ in various solvents (water, methanol, dioxan, *etc.*) changed to deep red on treatment with various oxidizing agents, chlorine, bromine, peroxodisulphate, *etc.* This deep red solution changed rapidly to light green, indicating that the oxidized species is unstable in solution. The oxidation of $[Ni^{II}(Hbg)_2]Cl_2\cdot 2H_2O$ was therefore

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attempted in suspension. Chlorination of the complex in suspension in carbon tetrachloride produced a deep red complex which was characterized as $[NiCl_2(Hbg)_2]Cl$. Oxidation of $[Ni^{II}(R\text{-}Hbg)_2]Cl_2$ (R = alkyl group) with chlorine in aqueous solution produced a deep red solution indicating formation of a nickel(III) complex, but in suspension in carbon tetrachloride there was apparently no reaction. Oxidation of $[Ni^{II}(R\text{-}Haiu)_2]Cl_2$ (R = alkyl group) with chlorine or bromine in aqueous solution resulted in the formation of a blue colouration which faded very quickly in the presence of excess of the oxidizing agents. However, peroxodisulphate or anodic oxidation of $[Ni^{II}(Hmaiu)_2][SO_4]\cdot 3H_2O$ gave an insoluble sulphate characterized as $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$. Anodic oxidation of $[Ni^{II}(Hbg)_2]Cl_2\cdot 2H_2O$ alone or in the presence of perchlorate ion produced only a blue solution which underwent rapid decomposition.

TABLE 1

Analytical data

Complex	Colour	Analysis (%)[a] M *d*	*e*		N	C	Cl or Br	SO$_4$ or F	λ[b] S cm^2 mol^{-1}	μ$_{eff.}$ B.M.
$[NiCl_2(Hbg)_2]Cl$	maroon-red	15.85	(16.0)	15.8	38.7 (38.15)	13.0 (13.05)	28.85 (29.0)		140[f]	1.87
$[NiCl_2(Hbg)_2]F$	red	16.65	(16.75)	16.4	39.9 (39.95)	13.6 (13.7)	19.8 (20.2)	5.45 (5.40)	145[f]	1.95
$[Ni(aiu)_2]Cl$	deep brown	19.65	(19.8)	19.55	37.8 (37.8)	16.2 (16.2)	12.15 (12.25)			1.80
$[NiBr_2(Hbg)_2]Br$	deep red	11.7	(11.75)	11.7	27.9 (28.0)	9.55 (9.60)	47.85 (47.9)			1.72
$[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$	deep blue	16.4	(16.45)	16.4	31.35 (31.4)	20.15 (20.2)		13.4 (13.45)	68[g]	1.91
$[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$	deep blue	15.25	(15.25)	15.2	29.05 (29.1)	24.1 (24.55)		12.45 (12.45)	68[g]	1.90

[a] Calculated values are given in parentheses. [b] At 0 °C. [c] At 303 K; 1 B.M. ≈ 9.27×10^{-24} A m^2. [d] Gravimetric. [e] Oxidimetric. [f] In water. [g] In methanol.

TABLE 2

Oxidation-potential, polarographic reduction-potential, and e.s.r. data

Complex	Oxidation potential V	Polarographic reduction potential[a] V	λ$_{max.}$[a] nm	g_1	g_2	g_3	$\langle g \rangle$
$[NiCl_2(Hbg)_2]Cl$	0.86[b]	−0.40[b]	375s	2.27	2.25	2.01	2.18
$[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$	0.81[b]	−0.35[c]	620s 750(sh)	2.31	2.11	2.01	2.14
$[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$	0.84[b]	−0.36[c]	620s 755(sh)	2.29	2.10	2.01	2.13

[a] At 0 °C. [b] In water. [c] In methanol.

All the new complexes are strong oxidizing agents. Nickel(III) complexes are one-electron oxidizing agents toward acidified potassium iodide or iron(II) sulphate solution. The complexes $[NiCl_2(Hbg)_2]Cl$, $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$, and $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$ (Table 1) are sufficiently stable for most of the physical and chemical investigations. Anodic-oxidation, polarographic-reduction, and optical-absorption measurements were made on these three complexes at 0 °C in either water or methanol. The results are shown in Table 2. The oxidation potentials were measured in aqueous solution with reference to the saturated calomel electrode (s.c.e.) and the values range from 0.81 to 0.86 V. These values are much higher than the corresponding values for copper(II) biuret complexes.[8] The polarographic reduction potentials were determined for the Hbg complex in water with 0.5 mol dm^{-3} KCl and for the maiu and eaiu complexes in methanol with 0.25 mol dm^{-3} LiCl as supporting electrolyte, all at 0 °C. The reactions were reversible one-electron transfers at $E_{\frac{1}{2}}$ in the range −0.35 to −0.4 V. These values are comparable with those obtained for other nickel(III) complexes.[8] The optical-absorption spectra of the complexes were recorded for very dilute solutions at 0 °C. The complex $[NiCl_2(Hbg)_2]Cl$ showed a sharp band at 375 nm while $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$ and $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$ showed sharp bands at *ca.* 620 nm with shoulders at 755 nm. The molar absorption coefficients could not be measured due to slow decomposition in solution.

The molar conductance values in aqueous solution for complexes $[NiCl_2(Hbg)_2]Cl$ and $[NiCl_2(Hbg)_2]F$ (Table 1) and in methanol solution for $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$ and $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$ indicate them to be 1 : 1 electrolytes. The difference from the value of an ideal 1 : 1 electrolyte may be attributed to slight decomposition of the complexes in solution. On decomposition in aqueous solution complexes $[NiCl_2(Hbg)_2]Cl$ and $[NiCl_2(Hbg)_2]F$ produce water-soluble $[Ni^{II}(Hbg)_2]X_2$ and HX, which will result in increase in conductance, while with complexes $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$ and $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$ such decomposition in methanol gives rise to insoluble $[Ni^{II}(R\text{-}Haiu)_2][SO_4]$ or its corresponding base leading to a decrease in conductance. The complexes $[Ni^{II}(R\text{-}Haiu)_2]^{2+}$ (R = Me or Et) were oxidized by peroxodisulphate solution to the nickel(III) complexes in the presence of hydrogencarbonate solution, but even without hydrogencarbonate the complex in solution (pH 5.0) can be oxidized to $[Ni^{III}(Raiu)_2]_2[SO_4]\cdot 2H_2O$ which precipitates out as a blue complex. At this pH, all the bases of the R-Haiu complexes of Ni^{III} are converted into the corresponding normal salts. From this it appears that in the complex $[Ni(Raiu)_2]_2[SO_4]\cdot 2H_2O$, the flow of electrons from the ligand towards the Ni^{III}, required for its stabilization, decreases the electron density on the ligand and thus prevents its protonation even in a slightly acidic medium. The difference in colour of these two series of nickel(III) complexes may be due to a difference in the co-ordination number, due to chelation by neutral and unprotonated ligands or to charge transfer bands involving the ligands.

The assignment of the formula $[Ni(Hbg)_2Cl_2]F$ in Table 1 is based on the molar conductance value and on the fact that a freshly prepared aqueous solution of the complex does not give any precipitate with silver(I) nitrate solution. From the properties of the complex $[NiCl_2(Hbg)_2]Cl$, the Ni^{III} is also suggested to have a co-ordination number of six. The co-ordination number of Ni^{III} in all the other complexes could not be determined, however, due to their instability in solution.

The i.r. spectra of some of the complexes were recorded and compared with those of the corresponding nickel(II) complexes.[19] No significant differences in the band positions were observed. It was not possible to isolate a single crystal suitable for e.s.r. measurements. However, sharp signals were observed for the undiluted polycrystalline materials at liquid-air temperature. The e.s.r. spectra for complexes $[NiCl_2(Hbg)_2]Cl_2$ $[Ni(maiu)_2]_2[SO_4]\cdot 2H_2O$, and $[Ni(eaiu)_2]_2[SO_4]\cdot 2H_2O$ are typical for polycrystalline solids with $S = \frac{1}{2}$. From the three transitions for each complex, g_1, g_2, and g_3, values of $\langle g \rangle$ were calculated. No hyperfine splitting was observed. The $\langle g \rangle$ values (Table 2) clearly indicate that these complexes are of nickel(III) rather than of nickel(II)-stabilized radical ligand compounds.

Attempts to prepare complexes of higher oxidation states other than those reported here were unsuccessful. The absence of such complexes also suggests the present complexes contain nickel(III) species rather than nickel(II) with oxidized ligands.[10,11] From LCAO MO calculations [18] it was shown that for square-planar complexes some of the filled metal *d* orbitals are above the highest filled ligand orbitals, and oxidation of the metal atom will take place in preference to that of the ligands especially in the present case. The increased positive charge on nickel may then be partially shared by the ligand atoms through π-electron delocalization. The metal complexes with biguanide and amidinoisourea have degrees of π-electron delocalization over the metal chelate ring as shown by electrophilic-substitution reactions [19] and n.m.r. spectra.[20]

From the physical and chemical properties of these complexes, and especially from the $\langle g \rangle$ values, it is concluded that the complexes described above contain nickel in the oxidation state III.

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