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Metal Complexes of Hydroxylamine

M. N. HUGHES and K. SHRIMANKER

Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH, U.K.

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The following complexes with hydroxylamine or deprotonated hydroxylamine as a ligand have been prepared and characterised: $[NiL_6]X_2$, $X = Cl, Br, ClO_4$; NiL_4X_2, $X = Cl, Br, NO_3, ClO_4$; NiL_3Cl_2; NiL_2X_2, $X = Cl, Br$; $NiLX_2$, $X = Cl, NO_3$; $Ni_2L_6(L–H)X_3$, $X = Cl, Br$; $NiL_4(L–H)_2$; ZnL_2X_2, $X = Cl, Br, {}^1/_2SO_4$; $Zn_2L_3(L–H)X_3$, $X = Cl, Br$; CdL_2X_2, $X = Cl, Br$; CoL_2X_2, $X = Cl, {}^1/_2SO_4$. *A few complexes with O-methylhydroxylamine have been obtained, but there is no evidence for complex formation in solution between metal halides and N-methylhydroxylamine. All the nickel compounds are six coordinate, the ligand is nitrogen bonded to the metal and present as* NH_2OH, *with* Δ_o *(in* $[NiL_6]X_2$*)* $= 12.6$ *kK. The product from* $Ni(OH)_2$ *and* $N\overset{+}{H}_3OHCl^-$ *has the hydroxylamine present in a different form, probably the N-oxide, as evidenced by infrared spectroscopy. Two forms of* ZnL_2X_2 *have been prepared, the course of the reaction being solvent dependent. Cd(II) and Co(II) 1:2 complexes contain the ligand in the N-oxide form,* $M(ONH_3)X_2$.

Introduction

As part of our work[1] on models for the metalloenzyme hydroxylamine oxidase and other biological systems involving hydroxylamine, we have been studying the reactivity of metal-bound hydroxylamine.

TABLE I. Analytical Data.

Complex	Found %					Calculated %				
	N	H	X	M	NH_2OH	N	H	X	M	NH_2OH
$[NiL_6]Cl_2$	25.2	5.65	21.7	17.9		25.6	5.49	21.7	17.9	
$[NiL_6]Br_2$	20.2	4.29		14.5		20.2	4.32		14.3	
$[NiL_6](ClO_4)_2$	19.9	4.20			43.1	18.4	4.00			43.5
NiL_4Cl_2	21.3	5.18	26.5	22.4		21.4	4.59	27.1	22.5	
NiL_4Br_2	16.6	4.40	44.9			16.0	3.40	45.4		
$NiL_4(NO_3)_2$	19.1[c]	3.91		18.0		26.7	3.81		18.6	
$NiL_4(ClO_4)_2$	13.8	3.30			34.1	14.3	3.08			33.9
$NiL_3Cl_2 \cdot 2H_2O$	16.3	5.10				15.8	4.91			
NiL_3Br_2	13.5	3.38		18.6		13.2	2.83		18.5	
NiL_2Cl_2	12.9	3.21	36.3	30.6	33.0	14.3	3.07	36.3	30.1	33.7
NiL_2Br_2	10.4	2.15	56.2	20.3	23.4	9.84	2.10	56.2	20.6	23.3
$NiLCl_2$				35.7					36.1	
$NiL(NO_3)_2$				27.1					27.2	
$NiL_4(L–H)_2 \cdot 2H_2O$[a]	28.1	5.63		22.3		28.9	6.90		23.1	
$NiL_4(L–H)_2 \cdot 2H_2O$[b]	28.8	5.70		22.0		28.9	6.90		23.1	
$Ni_2L_6(L–H)Cl_3$			22.8	26.0				23.4	25.9	
CdL_2Cl_2 } *ex* CdO	11.1	2.22				11.2	2.41			
CdL_2Br_2			47.2					47.3		
CdL_2CL_2	10.6	2.48				11.2	2.41			
ZnL_2Cl_2 (*ex* ZnO)			34.8	32.3				35.0	32.3	
$Zn_2L_3(L–H)Cl_3$	14.1	3.20	28.5	35.0		15.2	3.20	29.0	35.5	
$Zn_2L_3(L–H)Br_3$	11.1	2.10				11.2	2.20			
CoL_2Cl_2	13.4	3.27	36.3			14.3	3.05	36.2		

[a] *ex* $Ni(NO_3)_2$. [b] *ex* $Ni(SCN)_2$. [c] If NH_2OH nitrogen only is analysed for expected %N = 17.8%.

TABLE II. Infrared Spectra (cm^{-1}) of Ni(II) Complexes.[a]

	NiL_6Cl_2	NiL_6Br_2	NiL_4Cl_2	NiL_4Br_2	$NiL_4(ClO_4)_2$	$NiL_4(NO_3)_2$	NiL_2Cl_2
ν_{OH}	3350m	3330m	3370sh 3330m	3370m 3300m	3400m	3400m	3360m
ν_{NH}(as)	3265m 3245m	3250m	3260m	3245m 3195m	3250s	3250s	3240m 3200m
ν_{NH}(s)	3190w	3190w	3190m 3160m	3110m	3130sh	3130sh	3120m 3100m
δ_{NH_2} $+\delta_{HNO}$ $+\delta_{HNM}$	1592w 1572s 1562w, sh	1590sh 1575s 1562sh	1590s, sp 1567s 1530w	1605w, sh 1575s 1520w	1585s	1585s	1570br
δ_{NOH} $+\delta_{HNO}$ $+\delta_{HNM}$	1410w 1305w 1294m	1310sh 1294w	1402w 1315m 1285m	1410w 1310m 1288w	–	–	1305sh 1295sh
δ_{NH_2} $+\delta_{HNO}$ $+\delta_{NOH}$	1265m 1240sh 1220m	1265sh 1252s 1235sh	1252m 1245m 1225m	1250sh 1225s 1215sh	1238s	1240br	1240s 1225sh
		1025s	1175w, sp 1165w, sp 1020s	1173w 1163w 1020s	1000w	1000w	1165sh 1000s
ν_{NO} $+\delta_{NHM}$ $+\delta_{HNO}$	940s, sh 932s 920sh	938s	936sh 929s	935s 928sh	935s	932s	935s
		642					
δ_{HNM}	600m		635s	640s			
δ_{HNO}	532m	550m	560m	550m, br			
ν_{MN}	495m, sh	500sh	500sh	490m, br	495m 450s	495sh 450s	470s 420sh
	385m 355m	385m 355m	385m 358sh	385m 355m	375sh 350sh	375sh 350sh	380m 356sh
	270m 250m	275m 250sh	280m	275m 240m	250sh	250sh	280m
δ_{M-N}	230s	–	230m	210m	230m	230m	230m 210m

[a] Anion bands not given. [b] Identical spectra for products derived from $Ni(NO_3)_2$ and $Ni(SCN)_2$.

However, surprisingly little information is available on the hydroxylamine molecule as a ligand, and so we have prepared and examined a number of hydroxylamine complexes. A number of these have been reported, particularly in the older literature[2]. In recent years most attention has been paid to the infrared spectra of the Zn(II) and Pt(II) species[3,4]. The spectrum of ZnL_2Cl_2 (L = hydroxylamine, prepared by the action of hydroxylamine hydrochloride on zinc oxide) has been interpreted in terms of an N-oxide structure for the ligand, $Zn(ONH_3)Cl_2$, although the spectra of other complexes are consistent with the presence of nitrogen linked $M \leftarrow NH_2OH$. The following complexes have been reported; CoL_6Cl_3, $[Coen_2ClL]Cl_2$, NiL_4X_2[5,6], CoL_2X_2, MnL_2Cl_2[7], NiL_6Cl_2[8] and NiL_4Cl_2[9], where $X^- = Cl^-, Br^-$. In a few cases, magnetic moments and *d–d* spectra have been detailed.

We have prepared a range of complexes of Ni(II), Zn(II), Co(II) and Cd(II), and have attempted to prepare complexes of O- and N-substituted hydroxylamines. We have found that coordinated hydroxylamine undergoes ready deprotonation, and have also prepared isomeric pairs in which the ligand is present either as $\bar{O}N\overset{+}{H}_3$ or NH_2OH.

NiL_2Br_2	$NiL_4(L-H)_2$[b]	$Ni_2(L-H)L_6Cl_3$	$Ni_2(L-H)L_6Br_3$	NiL_3Cl_2	$Ni(OH)_2$+LHCl	$Ni(L-d_3)_4Cl_2$
3360m		3360m 3310m	3330m	3340m		2440m
3240m 3180m	3200sh 3180s	3240m 3200m	3240m 3200m	3250vbr	3170s	2340sh 2300m
3110m 3095m	3100m	3100m	3100br		3052s	2190m
					2705w	
					1895w	
	1600m	1605sh	1605sh		1625sh	1162m 1155sh
1570br		1575s	1575s	1565s	1580m 1155sh	
		1555sh	1555sh	1515m		
				1370s		
1300sh	1310m 1295m	1310w	1310w	1315m		1105m 1100m
			1240sh	1290w		
1240br	1270m 1248m	1250sh 1225s 1215sh 1205w	1250s 1225s 1215sh 1200sh	1265sh 1245sh 1235m 1200m	1190s	1015s 980m 955sh 945m
					1160s	
1165sh	1152m					
1000s		1024s	1020s	1025s		
					995s	
932s	940m	936s 930sh	935s	935s		910m
	830w			800sh		
	660m	645m	645m	680m		410m
		565m	560m	570m		
470s		480m	480m	495sh		485m
420sh		435m	435m	435m		
380sh 360sh		385m 350m	370m 350m	385m 360m		
		272m	272m	265br		
250m						
		240m	240w	240m		
230m			230m			
210m		215m				

Results and Discussion

Complexes have been prepared by two methods: (a) by treating[10] a metal carbonate, oxide or hydroxide with a hydroxylammonium compound, so forming 1:2 products with M^{2+} ions, and (b) by adding solutions of the free hydroxylamine, in varying ratios, to metal salts. These methods give identical 1:2 complexes with cadmium(II), cobalt(II), and zinc(II) bromide, but give different products in other cases. This has been confirmed over many preparations over a four year period. Thus method (a) with $ZnCl_2$ gives a 1:2 complex with the ligand in the N-oxide form, while method (b) gives a 1:2 complex with the ligand N-coordinated in the normal form, NH_2OH. The latter 1:2 complex on standing or in solution gives a product containing deprotonated hydroxylamine, as evidenced by analytical data showing Zn^{2+} and Cl^- to be present in 2:3 ratio. In general the presence of free hydroxylamine in ratio greater than 1:2 tended to give complexes with deprotonated hydroxylamine, the excess ligand acting as a base to remove a proton from coordinated hydroxylamine, reflecting the enhanced acidity of the ligand. Thus treatment of nickel(II)

TABLE III. Infrared Spectra (cm^{-1}) of Co(II), Zn(II) and Cd(II) Complexes.

ZnL_2Cl_2 *ex* ZnO	ZnL_2Cl_2[a] *ex* $ZnCl_2$	ZnL_2Cl_2[b] *ex* $ZnCl_2$	ZnL_2Br_2[c] *ex* $ZnBr_2$	$Zn_2(L-H)L_3Cl_3$	$ZnSO_4$ + NH_2OH	ZnO + $(LH)_2SO_4$	CdL_2Cl_2 *ex* CdO	CdL_2Cl_2 *ex* $CdCl_2$	CdL_2Br_2 *ex* CdO	CdL_2Br_2 *ex* $CdBr_2$	CoL_2Cl_2 *ex* $CoCO_3$	$CoCl_2$ + NH_2OH(xs)	$CoCO_3$ + $(LH)_2SO_4$
	3500s		3380s	3400s,br	3390s							3400br	
3185sh	3250m	3240m	3240s,br										
3165s	3200m	3180m,br	3100sh	3180s	3200s	3100m	3190sh	3190sh	3170sh	3175sh	3160s	3150s,br	3230br
3072sh	3120sh						3170s	3170s	3140m	3140m			3180s
2710s	2720w	2710m	2700w	2705s	2740m	2725m	2700m	2700m	2660m	2670m	2705m	2705m	2705w
1620m		1621m		1625sh	1650m	1635m	1630m	1635m	1615m	1620sh	1615sh		1650m
1597m		1585m		1588m	1590m	1615m	1600s	1600m	1590s	1585s	1590m		1586m
	1570m		1565s									1575m	
1550m		1548m		1552m	1530m	1550m	1549s	1551m	1530m	1542m	1550m		1540m
1530m		1530m		1535m		1535m	1535m	1535m	1515m	1525m	1535m		
			1490s						1505sh	1505sh			
	1255s	1242m	1240s	1245m	1240s						1300w	1245m	
1200s		1198m		1200m		1200m	1200s	1195s	1205s	1180m	1200m		1200m
		1180w											
		1165w										1160w	
			1005s		1000s							995sh	
980s		982m		985s		975sh,w	972s	978s	960s	968s	975s		985m
	950m	942m	940s	950m					925m			940s	
	650m		570w	570w	625m							560w	
430m	440m	425m	448m	430s	450m	430m	400m	405m			440m	440s	
			418m		420m, br								
390m		390m		390s		400m	366s	360s	370s		390m		
300s	300m	300s	300s	300s	325m	312m	280s	280s	335s		300s		
					250m,br				230s				

[a] From butanol. [b] From ethanol. [c] From butanol, similar spectrum for product from $NH_3^+OHBr^-$ + ZnO.

TABLE IV. Electronic Spectra (kK) and Magnetic Moments.

$[NiL_6]Cl_2$	30.0(s);	19.0(m);	12.6(m)	
$[NiL_6]Br_2$	30.0(s);	19.0(m);	12.6(m)	
$[NiL_6](SCN)_2$[a]	30.0(s);	19.3(m);	12.6(m)	
$[Ni(NH_2OCH_3)_6]Cl_2$[b]	29.4(m);	18.6(m);	13.0(sh), 11.5(m)	
$Ni(NH_2OCH_3)_4Cl_2$[b]	27.0(m);	17.0(m);	10.3(m)	
NiL_4Cl_2	28.6(m);	18.4(m);	12.7, 10.2(m)	
NiL_4Br_2	28.8(m);	18.6, 16.5(m);	12.7, 10.42(m)	
$NiL_4(SCN)_2$[a]	26.7(m);	16.6(m);	10.7(m)	
$NiL_4(ClO_4)_2$	26.0(m);	16.0(m);	10.6(sh,?), 9.40(m)	
NiL_2Cl_2	25.0(m);	15.2(m);	8.75(m)	
NiL_2Br_2	25.2(m);	15.5(m);	9.0(m)	
$NiLCl_2$	25.1(m);	14.7(m);	8.55(m)	
$NiL(NO_3)_2$	26.2(m);	16.4(m);	10.0(m)	
$NiL_4(L{-}H)_2$[c]	30.0(s);	19.1(m);	12.7(m)	
$NiL_4(L{-}H)_2$[d]	30.0(s);	19.0(m);	12.5(m)	
$Ni_2L_6(L{-}H)Cl_3$	27.0(m);	17.3(m);	10.2(m)	
$Ni_2L_6(L{-}H)Br_3$	27.0(m);	17.2(m);	10.0(m)	
CoL_2Cl_2	20.15(s);	19.5(sh);	15.1(s);	9.15(m), 7.7(sh)
CoL_2SO_4[e]	20.5(s);	19.6(sh);	16.5(sh);	8.3(m), 6.9(sh)

Magnetic moments (B.M. room temperature): NiL_2Cl_2, 2.92; NiL_2Br_2, 3.25; CoL_2Cl_2, 4.90.

[a] Measured in aqueous solution. [b] Measured in methanolic solution. [c] *ex* $Ni(SCN)_2$. [d] *ex* $Ni(NO_3)_2$. [e] *ex* $(NH_3^+OH)_2SO_4$.

nitrate or thiocyanate with a twelvefold excess of ligand gives an identical product in both cases, the anion being lost completely. A further complication is that higher complexes tend to lose ligand until the 1:2 product is reached (or one with deprotonated ligand). All measurements usually had to be carried out shortly after preparation,while complexes lost ligand, giving gummy products, on grinding so that magnetic moments were difficult to measure.

The complexes are noted in Table I, with analytical data for N, H, M^{2+}, halide and hydroxylamine, where appropriate. Infrared spectra are given in Tables II and III, and electronic spectra and magnetic moments in Table IV. The infrared spectra were of particular value in showing the form of the ligand, the spectra of the N-oxide and NH_2OH forms showing characteristic bands at 1200 and 970 cm^{-1}, and 3,400, 1245, and 940 cm^{-1} respectively (as reported previously) and also in the far infrared region as detailed later.

Complexes of Nickel(II) Halides

The addition of the free ligand in methanol to solutions of nickel halides in methanol in a 6:1 ratio gave a grey–blue precipitate and a purple–red supernatant solution. After filtration and standing overnight this solution deposited purple–red needle-like crystals, analysing as $[NiL_6]X_2$ (X = Cl, Br). These were stable if kept in a dessicator containing free hydroxylamine but otherwise decomposed over a few days to give fairly stable 1:4 species. This took place more readily for the chloride. The electronic spectra of both 1:6 species are identical, the $^3A_{2g}$–$^3T_{2g}$ transition (in O_h symmetry) appearing at 12.6kK. This value for Δ_o places hydroxylamine at the strong end of the spectrochemical series, close to nitrite. The colour of the 1:6 species is very similar to that of the well known hexanitronickelate(II) cation. Jørgensen[11] quotes a significantly lower value of Δ_o (11.3kK) for hydroxylamine.

The blue 1:4 complexes are of D_{4h} symmetry, as shown by the splitting of the two lowest energy bands. Parameter values, calculated[12] from these splittings at 77° K, are shown below. The in-plane crystal field value confirms the result from the 1:6 species. An attempt was made to prepare the 1:4 complexes by reaction between NiX_2 and NH_2OH in 1:4 ratio. This initially gave light blue precipitates, which did not correspond to an exact stoicheiometry, but these underwent a colour change to bright blue giving a crystalline compound that analysed as a 1:3 species. Reaction in a 1:2 stoicheiometry gave 1:2 complexes NiL_2X_2, X = Cl, Br, of magnetic moments 2.92 and 3.25 BM respectively. Their electronic spectra may be assigned in O_h symmetry, band splitting being absent, but the energies of the three bands are higher for the bromo complexes than the chloro complexes, an interesting observation. The most reasonable structure for these compounds involves bridging halide groups with axial hydroxylamine ligands. This is confirmed by their far-infrared spectra, which are

	Dq^{xy}	D_q^z	D_s	D_t	d_σ	d_π
NiL_4Br_2	1266	818	398	256	–1077	+43
NiL_4Cl_2	1266	829	278			

identical to 200 cm^{-1} in accord with the fact[13] that metal–halogen (bridge) frequencies lie below this value. These compounds decompose over a period of one year. Repetitive analysis over this period shows that the percentage of nickel increases, while that of halide decreases, suggesting the loss of a hydrogen halide with the formation of a deprotonated ligand. A 1:1 green complex $NiLCl_2$ has also been prepared on a small scale, but not studied.

The grey–blue precipitate originally isolated from the 1:6 preparation loses weight readily on standing, finally giving a product for chloride and bromide in which the metal/halide ration is 2/3, and with overall analysis corresponding to $Ni_2(L\text{–}H)(L)_6X_3$. Electronic spectra show these to be six–coordinate.

Complexes of Other Nickel(II) Salts

Blue $NiL_4(NO_3)_2$ has been prepared from a 1:6 reaction stoicheiometry, the presence of the coordinated nitrate group being shown by its infrared spectrum. Blue–green $NiL(NO_3)_2$, prepared by a 1:2 reaction, also has coordinated (bidentate) nitrate. Both compounds are six–coordinate, the 1:4 species being of D_{4h} symmetry. The purple product obtained from the filtrate of the attempted 1:6 preparation showed no nitrate absorption in the infrared, analysing as $NiL_4(L\text{–}H)_2$.

An attempt to prepare a 1:6 complex with nickel thiocyanate gave a gray–green precipitate (of approximate 1:2 stoicheiometry) and a purple solution, whose colour was temperature-dependent going blue on warming and reverting to purple on cooling. Electronic spectra show that this involves an equilibrium with the 1:4 species, in which the thiocyanate is N-bonded.

$$[NiL_6](NCS)_2 \rightleftharpoons NiL_4(NCS)_2 + 2NH_2OH$$

On adding a further excess of hydroxylamine (giving a 1:12 ratio) and standing, purple crystals were deposited, which analysed as $NiL_4(L\text{–}H)_2$ and were identical to the product obtained from nickel nitrate. The absence of thiocyanate was confirmed by infrared measurements and by the ferric ion test.

The only well characterised complexes prepared from nickel perchlorate were $[NiL_6](ClO_4)_2$ and $NiL_4(ClO_4)_2$, the latter species having coordinated perchlorate groups.

Infrared Spectra of Nickel(II) Complexes

These are given in Table II. The identification of metal–halogen vibrations hat not been straightforward in view of the presence of a number of metal–hydroxylamine bands in the appropriate region assigned to $\nu_{M\text{–}N}$ and $\delta_{M\text{–}N}$, (Table II). The absorptions due to hydroxylamine are particularly interesting. These may be assigned readily (some complexes have been deuteriated), although the bands probably do not represent pure vibrational modes. The various stoicheiometries (1:6, 1:4, 1:2) show characteristic band shapes and splittings, while the deprotonated species show reduced intensity in the $\nu_{O\text{–}H}$ region. In all cases the ligand is present as NH_2OH. However, this is not the case with products obtained by reacting solutions of nickel hydroxide with hydroxylammonium salts. These reactions gave gummy products but their infrared spectra were of good quality and were identical with those assigned to the N-oxide form of the ligand for ZnO + LH^+X^-.

Attempted Preparation of Complexes with O- and N-methyl Hydroxylamine

With $NiCl_2$: NH_2OCH_3 in 1:6 ratio in methanol, a purple solution was obtained but no grey–blue precipitate was formed. The spectrum of this solution had absorptions at slightly lower energies than $[NiL_6]Cl_2$. A 1:6 species could not be isolated, the colour of the solution changing to blue, with shifts to lower energy, probably reflecting the formation of a 1:4 species. This behaviour is similar to that of hydroxylamine, but deprotonated complexes could not be formed, reflecting the inability of NH_2OCH_3 to lose a proton. No evidence could be obtained for complex formation with N-methylhydroxylamine. This behaviour confirms that the coordination mode of hydroxylamine to nickel is through the nitrogen atom. In contrast the reaction between nickel hydroxide and N-methylhydroxylamine did result in complex formation in solution, the infrared spectrum of the product confirming the N-oxide O-linked structure.

Complexes with Zinc(II)

The action of $\overset{+}{N}H_3OHCl^-$ on ZnO or $ZnCO_3$ gives a 1:2 complex, having an identical infrared spectrum to that reported in the literature and assigned an N-oxide structure, $Zn(ONH_3)Cl_2$. The reaction of free hydroxylamine with $ZnCl_2$ in 2:1 ratio is solvent dependent. The use of butanol gives a product with the ligand in the NH_2OH form, as clearly shown in the infrared spectrum. The use of ethanol gives a product that appears to be a mixed $NH_2OH/\overset{-}{O}\overset{+}{N}H_3$ system, the infrared spectrum showing bands characteristic of both forms. This behaviour has been confirmed for many preparations over a four year period. In contrast the action of hydroxylammonium bromide on zinc oxide and that between free hydroxylamine and zinc bromide both give a product with the ligand in the NH_2OH form. An N-oxide product could not be obtained. In no example where the ligand is in the NH_2OH form could a pure 1:2 product be obtained. Both $Zn(NH_2OH)_2X_2$ species, assumed to be formed initially, lose weight on standing giving $Zn_2(L\text{–}H)L_3X_3$, *i.e.* with deprotonated ligand and loss of hydrogen halide. This must reflect the enhanced acidity of the coordinated ligand. One problem with ZnL_2Cl_2 and related species is that ν_{Zn-Cl} bands cannot be assigned readily, although there is an hydroxylamine absorption at 300 cm^{-1} which may mask it. This may mean that the N-oxide complexes contain six-coordinate zinc with halogen bridges.

Sulphate complexes have been prepared by the zinc oxide and the zinc sulphate methods, giving the N-oxide and NH_2OH forms of the ligand respectively. In the N-oxide case the sulphate group is clearly bidentate, the ν_4 mode of the sulphate group at 613 cm^{-1} being split into three components as is the ν_3 mode at ~ 1100 cm^{-1}. This suggests a six coordinate structure in this case, $Zn(ONH_3)_2SO_4$, as well as in $Zn(ONH_3)_2X_2$. In contrast the other sulphate with NH_2OH ligand has unidentate sulphate and appears to be four-coordinate.

N-methylhydroxylamine gave no product with $ZnCl_2$, but it did give a solid product when reacted as the onium chloride salt with zinc oxide. This confirms the different nature of the products from these two reactions.

Complexes with Cadmium(II)

Both preparative methods give 1:2 products with the ligand in the N-oxide form, $Cd(ONH_3)_2X_2$, X = Cl, Br. Their infrared spectra show shifts from the corresponding $ZnCl_2$ complex, due to the presence of the heavier cadmium atom. They are not isomorphous with $Zn(ONH_3)_2\,Cl_2$.

Complexes with Cobalt(II)

The 1:2 species CoL_2Cl_2 prepared by the action of hydroxylammonium chloride on cobalt carbonate is identical to that obtained by Simmons and Wendlandt[7]. Its infrared spectrum, not previously reported, shows the ligand to be in the N-oxide form. The N-oxide form is also present in bright pink CoL_2SO_4, obtained similarly from $(NH_3OH)_2SO_4$, and containing bidentate sulphate groups. In contrast the reported infrared spectrum of CoL_6Cl_3 clearly shows the ligand to be in the NH_2OH form. In view of the high value of Δ_0 for hydroxylamine, an attempt was made to prepare the 1:6 species to ascertain whether this, like the hexanitrocobaltate(II) anion is low spin. However the action of excess free hydroxylamine on $CoCl_2$ gave a brown product that was clearly high spin from susceptibility measurements, and which analysed approximately as a 1:4 species, the ligand being present in the NH_2OH form.

Conclusions

As expected, hydroxylamine as NH_2OH is a ligand at the strong end of the spectrochemical series. It is unfortunate that a comparison cannot be made with the N-oxide form of the ligand. The differentiation between the two forms of the ligand is clear cut from the infrared spectra of their complexes (3400, 1250–1240, 980–940 cm^{-1}) as noted earlier. But it is noteworthy that the distinction between the two forms is maintained in the far infrared spectrum. For Co(II) and Zn(II) there is a band at ~390 cm^{-1} present in all cases where the N-oxide form is postulated. In the Cd(II) compounds this is present at ~365 cm^{-1}. This is probably a metal–oxygen mode. In contrast the NH_2OH species have an absorption at 570 cm^{-1}, although this seems rather high for ν_{M-N}.

It does not seem possible to simply rationalise the conditions under which the different forms of the ligand result. Clearly the use of methods (a) and (b) require acidic and basic conditions respectively, which may be important in determining the final product in cases where stoicheiometric pairs exist, but in other cases where only one type of product is formed irrespective of the method used (*e.g.* Cd(II); $ZnBr_2$) other factors such as solid state effects must be important.

Experimental

Preparation of Complexes

Preparations involving the use of hydroxylammonium salts and metal carbonates/oxides/or hydroxides were based on the literature method[10]. Solutions of the free base were made up by adding sodium alkoxide in alcohol to solutions of hydroxylamine hydrochloride in alcohol and filtering off the precipitated sodium chloride. The resulting free base was not isolated but used in solution. The solutions of sodium alkoxide were prepared by the careful addition of sodium to alcohol. Solutions of the appropriate metal salt were then added to the solution of the free base in appropriate ratio, usually based upon 1g of the metal salt. Detailed reference to the complexes obtained by the addition of excess hydroxylamine to nickel salts has already been made in the text.

Analysis

Compounds were analysed for N, H and C (where relevant). Halide analyses were carried out by conductometric titrations with silver nitrate, or gravimetrically as the silver salt, metals by *edta* or by atomic absorption analysis (Hilger and Watts Atomspek), and hydroxylamine by the addition of excess bromate and back titration.

Instrumentation

The following instruments were used. Infrared spectroscopy, Perkin Elmer 325 and 237 spectrometers as nujol/hexachlorobutadiene mulls; reflectance and solution spectroscopy, Unicam SP700/SP735 and Beckman DK4 spectrometers; conductivity, Doran bridge, 10^{-3} mol dm^{-3} solutions; magnetic moments, by Gouy method. X-ray powder photographs were measured on the University of London Intercollegiate Research Service.

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