Inorganica Chimica Acta, 53 (1981) L85–L87
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Cobalt(II) and Nickel(II) Complexes of 1-Methoxy-2-methylthioethane and 2-Methoxyethane thiol

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Received September 20, 1980

The complexing properties of some of the organic compounds which result from the decomposition of Technical Tinox, an insecticide, have been discussed in a previous paper [1]. Two further organic compounds containing sulphur and oxygen atoms as possible coordination centres, 1-methoxy-2-methylthioethane ($CH_3OCH_2CH_2SCH_3$; L) and 2-methoxyethane thiol ($CH_3OCH_2CH_2SH$; LsH) can be identified in the decomposition products [2]. The reaction of these compounds with cobalt(II) and nickel(II) halides is reported in this paper.

Experimental

The ligands were prepared by our own adaptation of established organic experimental methods. 1-Methoxy-2-methylthioethane was obtained by the action of sodium methoxide on 1-chloro-2-methylthioethane [3] in absolute methanol solution following the procedure of Williamson's reaction [4]. 2-Methoxyethane thiol was obtained by the reaction of 1-chloro-2-methoxyethane, thiourea and sodium hydroxide under conditions used by Miroslav [5] to prepare 2-methylthioethane thiol.

Complexes of 1-methoxy-2-methylthioethane. The hydrated metal salt (0.01 mol) was refluxed with 2,2-dimethoxypropane (30 ml) for twenty minutes. The product was evaporated to dryness at reduced pressure and then dissolved in butanol (50 ml). The ligand (0.03 ml) was added dropwise to a refluxing solution and the mixture refluxed for a further fifteen minutes. The product crystallised out slowly after halving the volume of the solution by boiling and cooling.

Complexes of 2-methoxyethane thiol. The hydrated metal salt (0.01 mol) was dissolved in ethanol (50 ml) and treated with the ligand (0.03 mol) dropwise. The compound which precipitated was filtered off, washed with ethanol and dried *in vacuo*.

Physical measurements were carried out as described previously [1].

Results and Discussion

1-Methoxy-2-methylthioethane (L)

Under strictly anhydrous conditions complexes of the type ML_2X_2 were obtained with the halides of both metals. However, the solubility in non-aqueous solvents differed for the complexes of each metal.

All the nickel complexes are soluble in nitromethane and acetone. Conductance measurements showed that in nitromethane at concentration 10^{-3} *M*, these compounds are essentially non-electrolytes, and molecular weight determinations indicated that they are monomeric with molecular weights corresponding to the stoichiometric formulae obtained from the elemental analysis.

The absorption spectra of the complexes in nitromethane were similar to the diffuse reflectance spectra thus showing that their symmetry was not altered in solution. These spectra are typical of nickel in coordination six and show three well defined transitions between the triplet states of O_h system with evidence of tetragonal distortion. As the symmetry is lowered to D_{4h} (since the in-plane ligands consists of two oxygen and two sulphur atoms the symmetry is strictly D_{2h}) the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ band of the O_h symmetry is split into ${}^3B_{1g} \rightarrow {}^3B_{2g}$ and ${}^3B_{1g} \rightarrow {}^3E_g$ [6]. Assuming that the halogens are lower in the spectrochemical series [7] than oxygen and sulphur ligands the former transition (*ca.* 8600 cm^{-1}) is assigned as 10 Dq^E and the latter (*ca.* 7900 cm^{-1}) as 10 $Dq^E - 35Dt/4$. The in-plane field strength of Dq^E of 860 cm^{-1} is compatible with the values recorded for the complexes [8] $Ni(O_4)X_2$ and $Ni(S_4)X_2$ which are in the range of 830–860 and 920–1020 cm^{-1}, and it differs little from the value recorded for a similar ligand, 2-methyl-thioethanol [1]. The axial strengths Dq^A calculated as 740, 725, and 717 cm^{-1} for Cl, Br, I, respectively, are similar to those recorded for the corresponding halogens in compounds ML_2X_2 [8]. The halogen sensitive bands in the far IR region recorded at 280, 220 and 155 cm^{-1} and assigned as $\nu(M–X)$ (X = Cl, Br, and I) for terminal position in 6-coordinated nickel complexes [9] support the assumption that O and S atoms are in the planar and the halogens in the axial positions.

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TABLE I. Electronic Spectra and Magnetic Moments and Stretching Frequencies in the Far IR Region of Ni(II) and Co(II) Halide Complexes with 1-Methoxy-2-methylthioethane and 2-Methoxyethane thiol (LsH).

Compound	μ_{eff} (BM)[a]	Λ	ν (cm^{-1} × 10^3)[b]	Dq		β	ν (M–X)	ν (M–O)	ν (M–S)
				Dq^E	Dq^A				
NiL_2Cl_2	3.4	12.1	23.9(6.1), 15.1(3.2), 9.1, 7.9	860	740	0.78	280vs	424m	320m
NiL_2Br_2	3.4	13.5	22.8(11), 14.8(4.2), 9.1, 7.9	861	725	0.77	220vs	410m	312m
NiL_2I_2	3.5	15.0	c 14.9(5.1), 9.2, 7.6	859	717	0.76	155vs	415m	315m
CoL_2Cl_2	4.5	280	18.0(250), 15.4, 14.5, 8.16		420	0.72	–	438s	390m
CoL_2Br_2	4.5	275	17.8(200), 15.1, 13.7, 7.6, 5.8		410	0.72	–	435s	376m
CoL_2I_2	4.4	260	17.1(220), 15.2, 13.9, 7.2, 5.6		400	0.72	–	437s	380m
$Ni_2Ls_2Cl_2$	0	–	27.0(2000), 22.3sh, 17.5(200), 12.5(24)				370s	435m	342m
$Ni_2Ls_2Br_2$	0	–	27.2(2100), 22.0sh, 17.5(250), 13.0(26)				340s	434m	348m
$Ni_2Ls_2I_2$	0	–	27.1(2000), 22.4sh, 17.4(280), 13.2(30)				290s	440m	341m
$Co_2Ls_2Cl_2$	2.1	–	26.4(1200), 20.0, 7.4, 4.6(31)				380s	428m	364m
$Co_2Ls_2Br_2$	2.2	–	26.3(1300), 19.8, 7.2, 4.6(25)				345s	430m	361m
$Co_2Ls_2I_2$	2.1	–	26.4(1200), 19.8, 7.3, 4.5(20)				300s	425m	359m

[a] At room temperature; ohm^{-1} cm^{-2} mole^{-1}; conc. 10^{-3} M in nitromethane $(Et_4N)^+Br^-$ has a value of 110 at conc. 10^{-3} *M*. [b] Diffuse reflectance spectra against $MgCO_3$; sh, shoulder. [c] Solution spectra at concentration *ca.* 10^{-3} *M* in nitromethane. Obscure by the charge transfer band.

The cobalt complexes are sufficiently soluble in nitromethane for conductance measurements, but their solubility in chloroform is too low to yield reliable results for molecular weight determination by ebullioscopic method.

Conductivity measurements, indicating the complexes to be $[CoL_2]^{2+}[2X^-]$ and the similarity of the far IR showing the absence of halogen sensitive bands support the view that the halogens are not covalently bonded to the metal. The diffuse reflectance spectra (Table I) show characteristic absorption bands for cobalt(II) in a tetrahedral environment [13] with two intense, split bands assignable to the $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions of the d^7 high spin ion in the regions of 16000 and 6000 cm^{-1} respectively. The values for crystal field splitting, the electronic repulsion B and the ratio β have been calculated using the method suggested by König [11] while assuming that the centre of gravity of the transition $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ as ν_2 and ν_3 values (Table I). Again these values lie between those reported for CoO_4 [12] and CoS_4 [13] chromophores. The room temperature magnetic moments *ca.* 4.5 BM are as expected for Co(II) in tetrahedral environment [14].

Thus the ligand gives 6-coordinated complexes with nickel but tetrahedral with cobalt; in both cases the S and O atoms act as the coordination centres of the chelating ligand. A similar behaviour has been observed for the ligand 2-methylthioethanol. Similar complexes of nickel salts have been obtained with 2,5-dithiahexane [15] but cobalt complexes of the type CoL_2X_2 were also 6-coordinated; the latter type of symmetry was not observed with the ligand studied in this work.

2-Methoxyethane thiol (LsH)

No complexes could be isolated with this ligand under stringent anhydrous conditions: but when hydrated salts were treated with the ligand in alcoholic solution then complexes corresponding to the formula MLsX were formed. Thus, this ligand reacts only when the acidic hydrogen can be lost from the thiol group. Conductance measurements show that the complexes of both metals behave as non-electrolytes in organic solvents. Molecular weight determinations in chloroform suggest a molecular formula $M_2Ls_2X_2$.

The nickel complexes are diamagnetic. The diffuse reflectance spectra, though poorly resolved, are characteristic of nickel in square planar environment [16]. The solubility of the complexes in nitromethane is sufficiently high, to yield spectra which allow the band at 13000 cm^{-1} to be clearly assigned as $^1A_{1g} \rightarrow {}^1A_{2g}$ and that at 17500 cm^{-1} as $^1A_{1g} \rightarrow {}^1B_{1g}$. A high intensity band *ca.* 27000 cm^{-1} is probably a charge transfer; it has a high extinction coefficient, and is also present in the spectra of the complexes of the same ligand with Co(II). The high values for the stretching frequencies M–X (Table I) are within the region recorded for terminal ν(Ni–X) in square planar complexes [17]. Furthermore the disappearance of ν(S–H) band, present in the free ligand, in the infrared spectra of the complexes leads to the conclusion that coordination takes place *via* the thiolate sulphur and oxo-ether group. The thiolate acts as a bidentate but evidence for this cannot be obtained from the mid IR spectra.

Similar conclusions are reached on the chelating properties of the ligand in the cobalt complexes. A low magnetic moment of *ca.* 2.2 BM is consistent with the square planar structure suggested by the diffuse reflectance spectra.

The solution spectra in nitromethane show low intensity bands at *ca.* 4600 ($^2A_{1g} \rightarrow {}^2E_g$) 7400 ($^2A_{1g} \rightarrow {}^2B_{1g}$) and 20000 cm^{-1} ($^2A_g \rightarrow {}^2E_g{}^1$) which can be related to transitions pertaining to square stereochemistry for cobalt(II) complexes [18]. The metal–halogen stretching frequencies in the far IR are very similar to those given by the nickel complexes and they are compatible with those recorded for terminal ν(M–X) for square planar complexes. This ligand is very similar in behaviour to 2-methylthioethane thiol and forms complexes of similar structure [1].

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