Inorganica Chimica Acta, 34 (1979) L197–L198

Nickel(II) and Cobalt(II) Halide Complexes of O,O-Dimethyl-S-(2-Methyl-Thicethyl)Phosphoro-Thiolato $[(CH_3O)_2P(O)SCH_2CH_2SCH_3]$

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Received January 30, 1979

Technical Tinox, an insecticide [1], consists mainly of O,O-dimethyl-O-(2-methylthioethyl)phosphorothionate (the thiono form) and O,O-dimethyl-S-(2-methylthioethyl)phosphorothiolate (the thiolo form). On standing, it decomposes slowly forming a range of compounds [2] which do not exhibit insecticidal activity. This behaviour will affect, to some extent, the potency of Tinox formulations when these have to be stored over relatively long periods.

Our investigations of the way in which metal chelation might influence the stability of Tinox led us to the study of the chelating properties of the more stable of the two isomers, the thiolo form.

Experimental

Technical Tinox obtained by the manufacturing process [3] was submitted to various solvent extractions until the pure thiolo isomers was isolated [4]. The complexes were prepared by reacting the anhydrous metal salt (0.01 mol) dissolved in a minimum volume of dichloromethane with an excess of a solution of the liquid in the same solvent added dropwise over 2 to 3 hours at 50 °C. Precipitation was effected by the addition of a small amount (*ca.* 25 ml) of dried light petroleum. After cooling, the precipitated solid was filtered off under nitrogen in a dry box, washed with dry light petroleum and stored in a vacuum desiccator.

All the nickel complexes were dark green in colour and the cobalt complexes dark blue. No pure complex with cobalt iodide could be isolated and vacuum concentration of the solvent yielded a gummy product which could not be crystallised.

Physical measurements were carried out as described previously [5].

Results and Discussion

The isolated complexes (Table I) are very hygroscopic and are decomposed by most of the common organic solvents. Elemental analysis led to the stoichiometry of MLX_2 for all the complexes, and conductance measurements indicated that these are essentially non-electrolytes in dichloromethane. Determination of the molecular weights of the complexes by the ebulluoscopic method yielded inconclusive results.

TABLE I. Analytical Data for Ni(II) and Co(II) Halide Complexes with O'O-Dimethyl-S-(2-methylthioethyl)phosphorothiolate (L).

Compound	Found (calc.) %			
	M	C	H	X
$NiLCl_2$	17.2(16.8)	16.6(17.3)	3.7(3.7)	20.2(20.5)
$NiLBr_2$	13.2(13.5)	13.5(13.8)	3.0(2.9)	35.2(36.8)
$NiLI_2$	11.4(11.0)	11.2(11.4)	2.5(2.4)	45.2(47.9)
$CoLCl_2$	16.2(16.8)	16.7(17.3)	3.6(3.7)	20.2(20.5)
$CoLBr_2$	13.2(13.6)	12.9(13.8)	2.7(2.9)	35.2(36.8)

Identification of the d–d bands (Table II) was restricted to the region below 20,000 cm^{-1} by the more intense parity allowed bands at higher energy. However, the consideration of the band maxima, their characteristic splitting, and calculations following Konig's method [6], of the B and β values related to the field strength, led to the conclusion that in all the complexes, both metals are in a pseudotetrahedral environment. Thus, for the nickel

TABLE II. Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) Halide Complexes.

Compound	μ_{eff} (B.M.)^a	ν(cm^{-1} × 10^3)^b	10 Dq (cm^{-1})	β
$NiLCl_2$	3.45	14.5, 11.5sh, 7.3, 5.0sh	4020	0.75
$NiLBr_2$	3.47	14.4, 11.6sh, 7.3, 5.2sh	4000	0.75
$NiLI_2$	3.5	14.9, 7.3	3980	0.73
$CoLCl_2$	4.62	15.8, 14.9, 13.5, 7.2, 6.2, 5.1	3810	0.76
$CoLBr_2$	4.71	16.1, 14.7, 13.8, 7.5, 6.4, 5.2	3812	0.71

^{a}At room temperature. ^{b}Diffuse reflectance spectra against $MgCO_3$; sh = shoulder.

TABLE III. Some of the Important Infrared Bands (cm^{-1}) of Ni(II) and Co(II) Halide Complexes.

Compound	ν(P–O)	ν(M–L)	ν(M–X)
L	1250		
$NiLCl_2$	1220	432s, 362m	320s
$NiLBr_2$	1220	434s, 367m	270s
$NiLI_2$	1220	435s, 364w	240s
$CoLCl_2$	1220	430s, 385m	315s
$CoLBr_2$	1220	435s, 390m	260s

complexes the transitions are $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) and $^3T_1(F) \rightarrow {}^3A_2(\nu_2)$ at *ca.* 15000 and 7300 cm^{-1}, respectively, and in the case of cobalt complexes, $^4A_2 \rightarrow {}^4T_1(P)$ (ν_3) and $^4A_2 \rightarrow {}^4T_1(F)$ (ν_2) in the regions of 13000–16000 and 5000–7500 cm^{-1}, respectively. In each case, the values of B (*ca.* 4000 as compared to 3950 cm^{-1} for Ni and 3800 cm^{-1} as compared to 3700 cm^{-1} for Co) are somewhat just higher than those obtained for the complexes of the corresponding metal halides with triphenyl phosphate ML_2X_2 [7].

Far infrared spectra and magnetic measurements support the assignment of tetrahedral structure to the complexes. The values recorded for the halogen sensitive bands are in the regions diagnostic of ν(M–X) modes of tetrahedrally co-ordinated metal atoms [8]. Furthermore, the spectra do not contain bands which could be related to halogen-bridged complexes. The room temperature magnetic moments are for all complexes in the region expected for tetrahedral symmetry of these metals.

Since the halogens are non-bridging, the complexes will be tetrahedral only if the ligand is bidentate. There are three possible co-ordination sites on the ligand, namely, the two sulphur atoms and the phosphoryl oxygen. Although thioethers of the type $R-SCH_2CH_2S-R$ can act as chelating ligands, their complexing ability is sensitive to the bulkiness of the groups R [9].

It is therefore unlikely that the atom attached directly to the phosphorus could act as a co-ordination centre. Thus co-ordination takes place through the thio-ether sulphur of the side group and the phosphoryl oxygen. This would explain the significant shift of ν(P=O) from 1250 cm^{-1} in the free ligand to *ca.* 1220 cm^{-1} in the complexed ligand. However, it is unlikely that the ligand is chelating since this would necessitate the formation of a rather unstable seven-member ring. By contrast, a polymeric structure in which the O and S atoms on the same ligand molecule are attached to different metal atoms would lead to better agreement with the observed stoichiometry and it would also, to some extent, explain the instability of the complexes and their low solubility in most organic solvents.

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