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Transition Metal Ion Complexes of 2-Thio-6-picoline *N*-Oxide

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Abstract

Complexes of the anion 2-thio-6-picoline *N*-oxide (6MOS) have been isolated with the following stoichiometry: $M(6MOS)_3$ (M = Cr, Fe, and Co) and $M(6MOS)_2$ (M = Co, Ni, Cu and Zn). The spectral properties of these complexes are compared with those of 2-thiopyridine *N*-oxide in order to determine the stereochemical effect of the 6-methyl substituent. The nature of the Ni(I) species formed on exposure to high energy radiation, and the nature of the heterocyclic amine adducts to both the Ni(II) and Cu(II) complexes are also reported.

Introduction

Since the preparation [1] of 2-mercaptopyridine *N*-oxide (its tautomer, 1-hydroxy-2-pyridinethione, is the stable form [2]), there have been several reports concerned with its metal complexes. The first report was a study of the metal complexes' bactericidal and fungicidal properties [3], and little attention was given to their chemical properties. Robinson [4] prepared the first-row transition metal ion complexes and reported their molecular weights, molar conductivities, magnetic susceptibilities, electronic spectra, and a few bands of their IR spectra. In a report [5] of some lanthanide complexes of this ligand, the bands in the IR spectrum most useful for establishing the mode of coordination were assigned for the chromium(III) and lanthanide complexes. More recently we have communicated an ESR study of the heterocyclic amine adducts of the copper(II) complex of this ligand [6] and the spectral and thermal studies of the analogous adducts of the Ni(II) complex [7]. Also, the Ni(I) complex has been formed by exposure of the Ni(II) compound to ionizing radiation in different solvents, and the various species have been studied by ESR [8].

In a study of the related 2-aminopyridine *N*-oxides [9] we included the various 2-aminopicoline *N*-oxides [10] and have found considerable variation in both the stoichiometry and stereochemistry of the complexes formed. A similar study has been initiated based on 2-mercaptopyridine *N*-oxide, which has been shown to coordinate exclusively as the anion, 2-thiopyridine *N*-oxide [4, 5], in order to establish whether ring methyl groups alter the nature of these metal complexes. We report here the spectral and thermal characterization and the chemical properties of the metal ion complexes of 2-mercapto-6-picoline *N*-oxide (6MOSH). This ligand has been tested as an analytical reagent for Fe(III) [11], and the chromatographic behavior of its complexes has been studied [12] along with those of other 2-thiopicoline *N*-oxides. However, we know of no report of the various transition metal complexes of this ligand.

Experimental

6-Methyl-2-chloropyridine (Aldrich) was oxidized with 30% hydrogen peroxide in acetic acid following the method of Katritzky [13]. The resulting *N*-oxide was refluxed with thiourea to form 6MOSH (melting point 44 °C) which was worked up according to the reported procedure [2] for 1-hydroxy-2-pyridinethione. The complexes were isolated from aqueous solution with preparative mole ratios of metal salt: 6MOSH:sodium hydroxide of 1:2:2 or 1:3:3. The resulting solids were filtered and dried in a vacuum oven at *ca.* 50 °C. Elemental analyses were carried out by Micro-analysis, inc. of Wilmington, Del.

IR spectra were recorded on a Perkin-Elmer 783 Spectrometer, UV–Vis–NIR spectra on a Perkin-Elmer 330 Spectrometer, ESR spectra on Varian E-104 and E-109 Spectrometers and NMR on a Perkin-Elmer R-24 Spectrometer. Magnetic susceptibilities were measured with a Johnson-Matthey, Inc. balance and thermal data were obtained with Perkin-Elmer DSC-2C and TGA systems. $Ni(6MOS)_2$ was irradiated in a ^{60}Co Vickrad γ-ray source for up to 1 h at a dose rate of *ca.* 1 rad h^{-1}.

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Results and Discussion

Elemental analyses indicate that all the complexes involve the anionic 2-thio-6-picoline *N*-oxide ligand, 6MOS. All are non-electrolytes and have colors and stoichiometries similar to the complexes formed with 2-thiopyridine *N*-oxide [4]. The values for the magnetic susceptibility of $Fe(6MOS)_3$ and $Co(6MOS)_3$ indicate the former to be high spin and the latter low spin, $Co(6MOS)_2$ to be high spin, and $Ni(6MOS)_2$ to be diamagnetic.

The infrared bands most useful for establishing the coordination mode of 6MOS behave as follows: ν(NO) undergoes a much smaller shift than is observed for most pyridine *N*-oxides upon coordination of the *N*-oxide oxygen [14] because the thione tautomer is the dominant form of the free ligand. However, the ν(NO) bands of the complexes are found in the range expected for *N*-oxide ligands [9, 10]. In the spectrum of 6MOSH we have assigned δ(NO) at an energy higher than that of other pyridine *N*-oxides [9, 10] (*i.e.* 876 cm^{-1}), which is again consistent with the hydroxy tautomer being the dominant form of the ligand [15]. However, all the complexes, as well as the sodium salt, have this band in the 820 cm^{-1} region consistent with the complexes of 2-thiopyridine *N*-oxide studied previously [5–7]. We have assigned the ν(MO) bands in the 440–460 cm^{-1} region of the spectra based on our earlier assignment for the lanthanide complexes of 2-thiopyridine *N*-oxide [5] as well as the knowledge that the deprotonated 2-alkylaminopyridine *N*-oxide complexes of copper(II) have ν(CuO) at higher energy than do the corresponding neutral ligands [16]. ν(CS) is assigned to a strong band at 802 cm^{-1} in agreement with the range suggested for thioamides [17]. In the spectra of the complexes this band cm^{-1} is absent, and new bands in the 650 cm^{-1} region are assigned to this mode indicating coordination via the sulfur atom. A band near 400 cm^{-1} is assigned to ν(MS) in agreement with the 395–400 cm^{-1} range for Ni(II) complexes of deprotonated thioamides [18].

$Cr(6MOS)_3$

This green solid possesses a broad ESR feature with $g_{iso} = 1.970$, but we have not been able to achieve sufficient solubility in any solvent to record a solution spectrum. Bands in the electronic spectrum due to intraligand and charge transfer transitions obscure $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ as is often the situation with Cr(III) complexes. However, both $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ as well as a spin forbidden transition are observed, and the calculated values of the highest energy d–d band and the ligand field parameters are included in Table I. Compared to the Cr(III) complex of 2-thiopyridine *N*-oxide, $Cr(OS)_3$, the present solid has both a higher value of $10Dq$ and more covalent character to its bonding. Although the differences are relatively small as would be expected because of the weak electron donor ability of a methyl group, this donor ability appears to be more important than a steric effect.

$Fe(6MOS)_3$

This dark violet solid is a high spin d^5 complex and possesses an extremely broad, isotropic solid state ESR spectrum. Its electronic spectrum consists of a strong band located at 19 050 cm^{-1} which we assign to a S → Fe(III) transition, a weak band at *ca.* 13 700 cm^{-1} which is likely a spin forbidden $^6S \rightarrow {}^4T_{1g}(G)$ transition [18], and a shoulder at *ca.* 26 320 cm^{-1} which is assignable to O → Fe(III) [19]. This solid is soluble in chloroform, and the molar absorptivity of the band at 19 050 cm^{-1} is greater than 4000 M^{-1} cm^{-1}. Also, it should be noted that 6MOSH, like 2-thiopyridine *N*-oxide, gives a blue solution with Fe(III) when the ratio of ligand-to-Fe(III) is about 1:1 rather than 3:1, which suggests the existence of a second species in solution.

$Co(6MOS)_2$ and $Co(6MOS)_3$

As with other sulfur containing ligands such as thiosemicarbazones [20], 2-thiopyridine *N*-oxide is capable of oxidizing the preparative Co(II) salt to form $Co(OS)_3 \cdot 2H_2O$. However, the first complex that we isolated with 6MOSH was the dull green Co(II) complex, $Co(6MOS)_2$. For this reason we decided to attempt a preparation of a cobalt(II) complex using sodium 2-thiopyridine *N*-oxide and isolated the brown $Co(OS)_2$. [Calc. (found): C, 38.59(38.54); H, 2.59(2.59); N, 9.00(8.98)% with μ = 4.0 BM.] Also, upon refluxing an aqueous solution containing a 6:1 mole ratio excess of sodium 2-thiopyridine *N*-oxide to cobalt(II) chloride, we have isolated a dark green solid with $\mu = 0$ consistent with $Co(OS)_3$ stoichiometry found by Robinson [4]. A similar preparative procedure was attempted with 6MOS and resulted in the dark green $Co(6MOS)_3$.

A comparison of the infrared spectra of $Co(OS)_2$ and $Co(OS)_3$ shows a significant difference in the energy of ν(NO), 1182 and 1169 cm^{-1}, respectively, indicating stronger bonding of the ligand to Co(III). However, the two cobalt complexes of 6MOSH have smaller differences in their spectra. The electronic spectral parameters in Table I show that $Co(6MOS)_3$ has a stronger ligand field and is more covalent than $Co(OS)_3$, as was found for the analogous Cr(III) compounds. A comparison of the spectral properties of the two Co(II) solids shows the opposite trend; that is, OS has the stronger ligand field and also has the most covalent character in its bonding. As expected, the Racah parameter β shows the Co(III) complexes to have greater covalent character in their bonding than the Co(II) complexes.

TABLE I. Band Assignments and Ligand Field Parameters (cm^{-1}) of the Metal Ion Complexes of 2-Thio-6-picoline *N*-Oxide (6MOS) and 2-Thiopyridine *N*-Oxide (OS)

Compound	Band assignments				Ligand field parameters			
	${}^4A_{2g} \rightarrow {}^2T_{2g}, {}^2E_g$	$\rightarrow {}^4T_{2g}$	$\rightarrow {}^4T_{1g}(F)$	$\rightarrow {}^4T_{1g}(P)$ (calc.)	*Dq*	*B*	*β*	
$Cr(6MOS)_3$	12550	17920	25710	40105	1792	804	0.88	
$Cr(OS)_3$	12900	16030	24100	37490	1603	899	0.98	
	${}^1A_{1g} \rightarrow {}^3T_{1g}$	$\rightarrow {}^3T_{2g}$	$\rightarrow {}^1T_{1g}$	$\rightarrow {}^1T_{2g}$	*Dq*	*C*	*B*	*β*
$Co(6MOS)_3$	8330	15580	20830	23260	2180	3987	529	0.48
$Co(OS)_3$	6720	15780	19920	22990	2000	3807	658	0.60
	${}^4A_2 \rightarrow {}^4T_1(F)$	$\rightarrow {}^4T_1(P)$	$\rightarrow {}^4T_2$ (calc.)		*Dq*	*B*	*β*	
$Co(6MOS)_2$	5990	16000	3430		343	779	0.80	
$Co(OS)_2$	6940	16080	4020		402	731	0.75	
			${}^1A_{1g} \rightarrow {}^1A_{2g}$	$\rightarrow {}^1B_{1g}$				
$Ni(6MOS)_2$		13930	18520	22220				
$Ni(OS)_2$		13760	18450	23930				
		${}^3B_1 \rightarrow {}^3E$	$\rightarrow {}^3A_2$ $\rightarrow {}^3B_2$	$\rightarrow {}^3E$				
$Ni(6MOS)_2 \cdot (3,4Lut)$		5920	8620	14040				
	${}^2B_{1g} \rightarrow {}^2B_{2g}$	$\rightarrow {}^2E_g$						
$Cu(6MOS)_2$	12590	17290						
$Cu(OS)_2$	12200	18120						

[a] Average of two bands.

$Ni(6MOS)_2$

Like $Ni(OS)_2$ [4], $Ni(6MOS)_2$ is brown and diamagnetic, and there is little difference in their electronic spectra (Table I). The absence of bands at lower energy than 10000 cm^{-1} is consistent with planar stereochemistry for both. Although a crystal structure has not yet been solved for either solid, it is likely that the planar arrangement of the four donor atoms is *trans*, similar to NiE_2 (E = anion of 2-ethylaminopyridine *N*-oxide) [21]. In support of the *trans* arrangement is the observation of only one absorption band assignable to both $\nu(MO)$ and $\nu(MS)$.

Green, heterocyclic amine adducts of $Ni(OS)_2$ were reported [7] and similarly, the brown chloroform solution of $Ni(6MOS)_2$ changes to green on addition of these bases. The best crystals were obtained with 3,4-lutidine, and its electronic spectral bands are included in Table I. The presence of the broad band below 6000 cm^{-1} is consistent with a 1:1 adduct, while 3,4-lutidine formed a 2:1 adduct with $Ni(OS)_2$ [7]. This base is lost on standing for a week in the refrigerator. This difference in the nature of the adducts may be due to a steric effect of the 6-methyl group.

On exposure to ${}^{60}Co$ γ-rays, $Ni(6MOS)_2$, like $Ni(OS)_2$ [8], can be reduced to a Ni(I) center. Both have a small rhombic character to their spectra like the corresponding Cu(II) solids. The presence of the ring methyl group causes a small decrease in the *g* values, which is probably due to a more tetrahedral stereochemistry or simply a strengthening of the metal–ligand bonds within the square-planar geometry because of the small inductive effect of the methyl group.

$Cu(6MOS)_2$

The band at 25770 cm^{-1} is due to an O → Cu(II) charge transfer and is at a comparable energy found for other 2-substituted pyridine *N*-oxides [19]. The electronic spectrum of this solid also features two distinct d–d transitions, which often occurs for 4-coordinate Cu(II) complexes approaching planarity.

TABLE II. ESR Parameters for the Metal Ion Complexes of 2-Thio-6-picoline *N*-Oxide (6MOS) and 2-Thiopyridine *N*-Oxide

Compound	Sample	Temperature					g_{iso}	Reference
$Cr(6MOS)_3$	solid	RT	pk–pk = 450 G				1.970	a
			g_1	g_2	g_3	A_1(G)	g_{av}	
$Ni(6MOS)_2^-$	MeTHF	77 K on anneal:	2.247	2.087 $g_\parallel = 2.180$	2.061 $g_\perp = 2.080$	60	2.132 2.113	a
$Ni(OS)_2^-$	MeTHF	77 K on anneal:	2.257	2.086 $g_\parallel = 2.214$	2.066 $g_\perp = 2.101$	61	2.136 2.138	8
$Cu(6MOS)_2$	solid	RT	2.172	2.071	2.030		2.091	a
$Cu(OS)_2$	solid	RT	2.164	2.069	2.024		2.086	6
			$A_\parallel(^{65}Cu)$	$A_\parallel(^{63}Cu)$	$g_\parallel$	$g_\perp$	g_{av}	
$Cu(6MOS)_2$	1% Cu/Ni	RT	196 G	182 G	2.148	2.043	2.078	a
$Cu(OS)_2$	1% Cu/Ni	RT	207 G	194 G	2.150	2.040	2.077	8
			$A_\parallel(^{63}Cu)$	$A_\perp$	$g_\parallel$	$g_\perp$	g_{av}	
$Cu(6MOS)_2$	CH_3NO_2	77 K RT	189 $A_o = 86$ G	44	2.140	2.037	2.071 $g_o = 2.068$	a
$Cu(OS)_2$	CH_3NO_2	77 K RT	190 $A_o = 84$ G	43	2.145	2.042	2.076 $g_o = 2.076$	6
$Cu(6MOS)_2 \cdot Py$	CH_3NO_2	77 K	173	20	2.174	2.034	2.081	a
$Cu(OS)_2 \cdot Py$	CH_3NO_2	77 K	166		2.182	2.028	2.079	6
$Cu(6MOS)_2 \cdot 2Py$	CH_3NO_2	77 K	165	b	2.188	b	b	a
$Cu(OS)_2 \cdot 2Py$	CH_3NO_2	77 K	163	b	2.199	b	b	6

[a]This work. [b]These features are hidden by those of the 1:1 adduct.

The related $Cu(OS)_2$ solid has comparable bands at 18 120 and 12 200 cm^{-1}, suggesting that the present solid may be slightly more distorted from a planar arrangement of the four donor atoms around the Cu(II) center.

The ESR spectral results of the solid powders show that the present solid has a somewhat higher value for $g_\parallel$ as well as g_{av} (Table II), which is consistent with weaker in-plane bonding found for the Ni(I) species of the two ligands. Also, like their Ni(I) analogs, both solids have a rhombic ESR spectrum, which is presumably caused by the longer Cu–S bonds compared to Cu–O bonds. When doped into their corresponding diamagnetic, planar Ni(II) complexes, both Cu(II) centers are evidently forced to assume a more square-planar conformation based on their lower g values. However, the hyperfine coupling constants, $A_\parallel$, measured for both copper(II) isotopes show that $Cu(OS)_2$ has the stronger planar bonding in the Ni(II) host as well as in nitromethane.

The covalency parameters for the two solids were calculated [22] to be the following: $k_\parallel = 0.57$ and $k_\perp = 0.72$ for $Cu(6MOS)_2$ and $k_\parallel = 0.55$ and $k_\perp = 0.70$ for $Cu(OS)_2$ (g_1 was taken as $g_\parallel$ and g_2 and g_3 were averaged to determine $g_\perp$). Both complexes have considerably more in-plane than out-of-plane π-bonding. When compared to the copper(II) complex of the anion of 2-aminopyridine *N*-oxide, which has $k_\parallel = 0.60$ and $k_\perp = 0.75$ [23], there is little difference. This suggests a lack of interaction by the Cu(II) d electrons with the empty d orbitals of the sulfur donor atom. Further, the covalency parameter α^2 is in the 0.72–0.73 range for both of the sulfur containing ligands as well as the aminopyridine *N*-oxide anion complex, CuA_2.

In nitromethane solution the ESR spectrum of $Cu(6MOS)_2$ shows two different Cu(II) centers, one having very sharp features and the other relatively broad features. However, both have $A_{iso} = 86$ G and $g_{iso} = 2.068$, which are similar to the parameters for the new species found in a nitromethane solution of $Cu(OS)_2$ [6]. The species having the broader features, which are typical of most solution spectra of Cu(II) complexes, is most likely solvated in the axial positions, while the species with the sharp features must involve little solvent interaction. In frozen solution only one species is observable, and its ESR parameters correlate with those found for $Cu(OS)_2$ in frozen nitromethane solution [6].

Addition of heterocyclic amines such as pyridine to nitromethane solutions of $Cu(OS)_2$ followed by freezing yielded ESR spectra consistent with two new species in the case of pyridine and most of the other heterocyclic amines studied (*i.e.* 1:1 and 2:1 adducts). Sterically hindered amines such as 2,6-lutidine showed parameters consistent with the formation of only a 1:1 adduct. The parameters for the 1:1 and 2:1 pyridine adducts of both $Cu(OS)_2$ and $Cu(6MOS)_2$ are included in Table II. A spectrum of the 2:1 adduct alone could not be obtained with either complex even in pure pyridine. The differences in the $A_{\|}$ and $g_{\|}$ values for the 4-coordinate Cu(II) center and the two adducts are consistent with increased axial bonding. The somewhat higher values for $A_{\|}$ and lower values of $g_{\|}$ for the adducts of $Cu(6MOS)_2$ compared to those of $Cu(OS)_2$ are consistent with weaker axial bonding. The weaker axial bonding is likely due to some steric repulsion between the ring methyl groups of the bidentate *N*-oxide ligands and the heterocyclic amine.

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