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## COBALT(II), NICKEL(II), AND COPPER(II) HALIDE COMPLEXES OF 7-OXA-2,12-DITHIA(13)(2,6)PYRIDINOPHANE<sup>1</sup>

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A new macrocyclic ligand, 7-oxa-2, 12-dithia (13) (2, 6)-pyridinophane (*I*, SNSO) was synthesized and characterized by its elemental analytical data, nmr, ir, and mass spectra. Its cobalt(II), nickel(II), and copper(II) halide complexes (MLX<sub>2</sub>, where X = Br and Cl) were investigated. Probable structures of these complexes are proposed on the basis of electrical conductivity measurements, magnetic susceptibility data, electronic and infrared spectra. The nickel(II) bromide complex is five coordinate and the other complexes are six-coordinate. The electronic spectral bands due to selected d-d transitions are tentatively assigned.

### INTRODUCTION

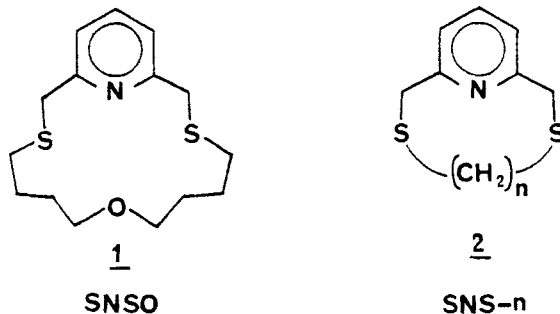
Numerous organic ligands containing oxygen, sulphur, nitrogen and/or phosphorus donor atoms have been used to prepare complexes of first row transition metal ions.<sup>3</sup> Macrocyclic polydentate ligands have been designed with specific ring sizes and fixed geometries in attempts to generate specific ligand fields in their complexes.<sup>4</sup> The recent confirmation of the presence of thioether and thiol sulphur atoms, and imidazole nitrogen atoms in the inner coordination sphere of "blue" copper proteins has stimulated interest in synthetic complexes with similar structures.<sup>5,6</sup> In a previous report, the synthesis and characterization of pentacoordinate complexes of dithiapyridinophanes 2 (SNS-*n*, where *n* equals the number of methylene groups in the bridge) were presented.<sup>7</sup> On the basis of spectral, magnetic and conductivity data, we concluded that the copper(II) complexes of SNS-8 were pentacoordinate with *trans*-monodentate ligands. The methylene bridge in SNS-8 effectivity blocked the sixth coordination site, and thus led to the pentacoordinate structure.

We describe here the synthesis and characterization of the divalent cobalt, nickel, and copper halide complexes of a new potentially tetradentate ligand, 7-oxa-2,12-dithia (13) (2,6) pyridinophane, (*I*, SNSO). These complexes are of particular interest because they contain thioether sulphur atoms and an aromatic nitrogen atom; atoms of this type form the inner coordination sphere of "blue" copper proteins.<sup>5</sup> Secondly, thioether sulphur atoms have been reported to have little affinity for copper(II).<sup>8,9</sup> and ether oxygens and thioether sulphur atoms have been reported to be weak donors toward cobalt(II).<sup>9,10</sup> A comparison of properties of the divalent transition metal complexes derived from SNSO with those reported previously for SNS-8 allow us to assess the effect of oxygen on structural features.

### EXPERIMENTAL

All chemicals used were reagent grade, except 2,6-pyridinedimethanol (Aldrich) and 4-chlorobutyl ether (Pfaltz and Bauer). Melting points are uncorrected. Proton nmr

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spectra were recorded on an EM-360A (60 MHz) nmr spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined in Nujol mulls between sodium chloride plates on a Beckmann IR-10 spectrophotometer. Solution electronic spectra were recorded on a Beckmann DK-2 spectrophotometer over a 10-30 kK range. Electrolytic conductivities were measured at 25.0° on approximately  $2 \times 10^{-4}$  molar nitromethane solutions using a YSI Model 31 Conductivity Bridge. The equivalent conductance of  $(\text{CH}_3)_4\text{NI}$  is  $100.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  under these conditions.

Magnetic susceptibilities were determined by the Evans method<sup>11</sup> (in methanol-chloroform solution for the nickel and cobalt complexes and in dimethyl sulfoxide-chloroform solution for the copper complexes) at 37.0°. The diamagnetic correction for the ligand (SNSO) was estimated as  $-309 \times 10^{-6}$  cgs based on the previously determined value<sup>7</sup> of  $-304 \times 10^{-6}$  cgs for SNS-8 and Pascal's constants. The magnetic moment of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was determined in methanol-chloroform for reference, and the observed effective magnetic moment of 3.3 BM compares favorably with the value reported in the literature.<sup>12</sup>

Elemental analyses were performed by Instranal Laboratory, Inc., Rensselaer, New York. Mass spectra were obtained on a Hewlett Packard 5985 GC-MS spectrometer at Louisiana State University, Baton Rouge, Louisiana.

#### *Preparation of the Cyclic Ligand (SNSO)*

The oxadithiapyridinophane (SNSO) was prepared by adapting the high dilution method of Vogtle.<sup>13</sup> Thus, treatment of 0.50 mole of 1,9-dichloro-5-oxanonane with 1.0 mole thiourea in 300 cm<sup>3</sup> of refluxing ethanol for 24 hours yielded nonane-1,9-diisothiouronium dichloride, quantitatively. A 0.020 mole sample of this salt was hydrolyzed with four molar equivalents of aqueous sodium hydroxide to yield the corresponding disodium dimercaptide.<sup>14</sup> Subsequently, an aqueous solution (200 cm<sup>3</sup>) of 0.020 mole of disodium dimercaptide and a benzene solution (200 cm<sup>3</sup>) of 0.020 mole of 2,6-bis-(chloromethyl)pyridine<sup>15</sup> were added simultaneously and dropwise to 1.5 dm<sup>3</sup> of refluxing ethanol over a two hour period. After refluxing for two days, the product was isolated by evaporation of the ethanol solution under reduced pressure, extraction with chloroform (200 cm<sup>3</sup>) followed by a second evaporation. The yellow viscous oil that was obtained in this manner was chromatographed on an alumina column, using carbon tetrachloride (80 cm<sup>3</sup>), chloroform (100 cm<sup>3</sup>) and methanol (140 cm<sup>3</sup>), in succession, as eluents. The first 200 cm<sup>3</sup> of eluents were combined and evaporated. Recrystallization of the solid from methanol yielded 7.0 g (59%) of a white crystalline solid, mp 48-49°.

#### *General Preparation of M(SNSO)<sub>2</sub> Complexes*

The cyclic ligand (SNSO) was allowed to react with either  $\text{CuBr}_2$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in hot methanol to form the corresponding

TABLE I  
Analytical data for ligand and complexes.

Compound	Calculated, %			Found, %			% Yield
	C	H	Halide	C	H	Halide	
SNSO	60.56	7.79		60.56	7.82		59
Cu(SNSO)Cl <sub>2</sub>	41.80	5.38	16.45	41.15	5.27	16.80	91
Cu(SNSO)Br <sub>2</sub>	34.65	4.45	30.73	34.54	4.33	30.40	92
Ni(SNSO)Cl <sub>2</sub>	42.19	5.43	16.90	41.51	5.41	17.16	37
Ni(SNSO)Br <sub>2</sub>	33.59	4.45	30.68	33.99	4.31	30.53	56
Co(SNSO)Cl <sub>2</sub>	42.19	5.43	16.59	41.72	5.36	16.60	61

complex.<sup>16</sup> In general a 0.5 m mole sample of the ligand dissolved in 10 cm<sup>3</sup> of hot methanol was mixed with a hot solution of 1.0 m mole of the metal halide in 10 cm<sup>3</sup> of methanol. Immediate colour changes were observed, except for the case of cobalt(II) chloride. Colour changes were followed by immediate precipitate formation. Reaction mixtures were heated and stirred for ten minutes, cooled and filtered to collect the crystalline product. After drying at 90° for two hours, the physical properties of the crystalline complexes were determined. Results of the syntheses and physical properties of the complexes are summarized in Tables I and IV, respectively.

## RESULTS AND DISCUSSION

### *Spectral Properties of the Ligand*

The structure of the ligand SNSO was assigned on the basis of spectral and analytical data. The nmr spectrum of SNSO consists of a multiplet for pyridine protons at  $\delta$  7.4 (3H), a singlet for protons *alpha* to the pyridine ring at  $\delta$  3.8 (4H), a triplet for methylene protons *alpha* to the oxygen atom at  $\delta$  3.2 (4H), a triplet for methylene protons *alpha* to the sulphur atoms at  $\delta$  2.5 (4H), and a multiplet for the remaining methylene protons at  $\delta$  1.6 (8H). In the mass spectrum of SNSO, the four higher mass peaks with their relative intensities in parentheses are as follows: 300 (0.2), 299 (0.7), 298 (1.2), and 297 (8.1). The latter peak corresponds to the calculated molecular weight. The four largest peaks in the mass spectrum appear at  $m/e$  170 (100.0), 138 (31.0), 139 (22.7), and 106 (19.7) and may be accounted for by a monomeric structure. The infrared spectrum of SNSO has a strong pair of bands at 1597 and 1575 cm<sup>-1</sup> arising from stretching vibration of the pyridine nucleus. A medium intensity band in the range 670-765 cm<sup>-1</sup> and a weak band at 820-935 cm<sup>-1</sup> are assigned to stretching vibrations of the thioether group -CH<sub>2</sub>-S-CH<sub>2</sub>-, and a strong band in the 1060-1170<sup>-1</sup> region arises from the ether group -CH<sub>2</sub>-O-CH<sub>2</sub>-. The infrared spectral data confirm the existence of these three functional groups in the cyclic ligand molecule. Additionally, analytical data for the ligand, SNSO, support the assigned structure (Table I).

### *Infrared Spectra of Complexes*

When the ligand SNSO reacts with the metal ions, copper(II), nickel(II), or cobalt(II), each heteroatom (S, N, S, and O) in the ligand molecule is expected to provide a lone pair of electrons to form a coordination bond with the metal ion. As a result, the characteristic infrared frequencies of the functional group containing the donor atom would be expected to change. Comparison of the ir spectra of these complexes with that of the

TABLE II  
 Partial IR spectral data of ligand and complexes.<sup>a</sup>

Compound	Characteristic frequencies (cm <sup>-1</sup> ) of functional groups				New bands						
	-CH <sub>2</sub> -O-CH <sub>2</sub>	-CH <sub>2</sub> -S-CH <sub>2</sub>	Pyridine nucleus								
SNSO	628(W)	1080(S)	748(M)	982(W)	1575(S)	1597(S)	720	925	1020	1170	1405
Cu(SNSO)Cl <sub>2</sub>	1100(S)	1100(S)	888(W)	888(W)	1577(S)	1605(S)	720	923	1020	1170	1400
Cu(SNSO)Br <sub>2</sub>	1103(S)	1103(S)	753(W)	886(W)	1578(S)	1604(S)	720	923	1015	1170	1402
Ni(SNSO)Cl <sub>2</sub>	1102(S)	1102(S)	755(W)	870(M)	1578(S)	1603(S)	720	923	1015	1170	1402
Ni(SNSO)Br <sub>2</sub>	1110(S)	1110(S)		893(W)	1580(S)	1610(S)	723	930	1020	1177	1398
Co(SNSO)Cl <sub>2</sub>	1100(S)	1100(S)	890(W)	890(W)	1577(S)	1600(S)	720	1011	1032	1170	1403

<sup>a</sup>Spectra were determined in nujol mulls. The strong nujol band at 1465 cm<sup>-1</sup> served as an internal reference, and frequencies were calibrated against polystyrene; S = strong, M = medium, W = weak.

ligand are shown in Table II. Slight shifts in the characteristic frequencies of functional groups are inconclusive regarding whether the oxygen, sulphur, and nitrogen atoms in the ligand molecule coordinate with the metal ion. However, the appearance of several new bands at about 720, 925, 1020, 1170, and 1405  $\text{cm}^{-1}$  suggests structural changes in the ligand.

#### *Magnetic Properties, Conductivity and Electronic Spectral Data*

A summary of room temperature effective magnetic moments for the complexes in solution<sup>11</sup> is given in Table III. Effective magnetic moments ( $\mu_{\text{eff}} \approx 1.7$  BM) of  $\text{Cu}(\text{SNSO})\text{Cl}_2$  and  $\text{Cu}(\text{SNSO})\text{Br}_2$  fall within the expected range for mononuclear octahedral copper(II) complexes.<sup>17</sup> The nickel(II) complexes,  $\text{Ni}(\text{SNSO})\text{Cl}_2$  and  $\text{Ni}(\text{SNSO})\text{Br}_2$ , exhibit similar effective magnetic moments at room temperature. The effective magnetic moment for  $\text{Ni}(\text{SNSO})\text{Cl}_2$  is close to the expected range for octahedral complexes of nickel(II),<sup>18</sup> while the observed moment ( $\mu_{\text{eff}} = 3.8$  BM) of  $\text{Ni}(\text{SNSO})\text{Br}_2$  is consistent with a high-spin five-coordinate species (see conductivity data).<sup>19</sup> The structure of the ligand and electronic spectra point to a square-pyramidal structure as the most probable geometry for the latter complex.<sup>20</sup> The observed effective magnetic moments for  $\text{Ni}(\text{SNSO})\text{Cl}_2$  and for  $\text{Ni}(\text{SNSO})\text{Br}_2$  rule out square-planar coordinated nickel(II) in these species. Also, square-planar coordination of cobalt(II) in  $\text{Co}(\text{SNSO})\text{Cl}_2$  is ruled out on the basis of its observed magnetic moment ( $\mu_{\text{eff}} = 5.4$  BM). The high magnetic moment for  $\text{Co}(\text{SNSO})\text{Cl}_2$  suggests a high-spin octahedral species.<sup>21</sup>

Conductivity data indicate that  $\text{Cu}(\text{SNSO})\text{Cl}_2$  and  $\text{Ni}(\text{SNSO})\text{Cl}_2$  are non-electrolytes in nitromethane solution (Table III), and therefore each central cation has two chloride ions in its inner coordination sphere. The low equivalent conductances ( $\sim 24 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ) of  $\text{Cu}(\text{SNSO})\text{Br}_2$  and  $\text{Co}(\text{SNSO})\text{Cl}_2$  indicate that these complexes are non-electrolytes and may contain minor amounts of 1:1 dissociated species. For these complexes, major species in nitromethane solution are either five- or six-coordinate, depending on whether the ether oxygen is coordinated to the metal cation. We conclude that  $\text{Ni}(\text{SNSO})\text{Br}_2$  is a 1:1 electrolyte on the basis of an equivalent conductance of  $85.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  in nitromethane, indicating a five-coordinate species wherein one of the bromide ions is outside the coordination sphere.

Solution spectra of  $\text{Cu}(\text{SNSO})\text{Cl}_2$  and  $\text{Cu}(\text{SNSO})\text{Br}$  display broad unsymmetrical bands at about 14.3 kK corresponding to d-d transitions, in either nitromethane or acetonitrile. The appearance of the low energy band at 14.3 kK is consistent with an octahedral environment for copper(II).<sup>22,25</sup> This would require coordination of copper(II) to the ether oxygen, in addition to coordination to nitrogen, two sulphur atoms and two halide ions. The 14.3 kK band for  $\text{Cu}(\text{SNSO})\text{Br}_2$  is less symmetrical than the correspond-

TABLE III  
Physical properties of the transition metal(II) complexes.

Compound	Colour	Mp ( $^{\circ}$ )	$\Lambda^a$	$\mu_{\text{eff}}$ (BM) <sup>b</sup>
$\text{Cu}(\text{SNSO})\text{Cl}_2$	blue-green	182–183	6.7	1.7 <sup>d</sup>
$\text{Cu}(\text{SNSO})\text{Br}_2$	green	192–193	23.8	1.7 <sup>d</sup>
$\text{Ni}(\text{SNSO})\text{Cl}_2$	brown	> 360	12.3	3.8
$\text{Ni}(\text{SNSO})\text{Br}_2$	gold	309–310 <sup>c</sup>	85.4	3.8
$\text{Co}(\text{SNSO})\text{Cl}_2$	bright purple	285–287 <sup>c</sup>	24.4	5.4

<sup>a</sup>  $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ , in nitromethane. <sup>b</sup> Bohr magnetons. <sup>c</sup> Decomposed. <sup>d</sup> Approximate value due to limited solubility.

TABLE IV  
 Electronic spectra of transition metal(II) complexes.

Compound	Absorptions, kK ( $\epsilon$ )		Transition <sup>a</sup>
	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	
Cu(SNSO)Cl <sub>2</sub>	14.4 (307) b	14.3 (57) b	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>
Cu(SNSO)Br <sub>2</sub>	14.3 (537) 27.0 (1324) b	14.3 (92) b	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>
Ni(SNSO)Cl <sub>2</sub>	14.3 (56) 18.1 (79) 21.9 (189) 27.2 (118)	13.9 (59) 18.1 (76) 21.7 (157) > 30 <sup>c</sup>	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)
Ni(SNSO)Br <sub>2</sub>	14.5 (61) 21.5 (237) 26.7 (928)	14.1 (91) 21.3 (221) 27.0 (821)	<sup>3</sup> B <sub>1g</sub> → <sup>3</sup> E <sub>2g</sub> <sup>3</sup> B <sub>1g</sub> → <sup>3</sup> B <sub>2g</sub> d
Co(SNSO)Cl <sub>2</sub>	15.2 (146) 16.9 (204) 26.7 (367)	15.2 (234) 16.9 (214) > 30 <sup>c</sup>	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P) d

<sup>a</sup>Assignments based on literature data, see references 19, 20, 25 and 26. <sup>b</sup>High intensity bands above 27 kK. <sup>c</sup>Intensity and exact position were not determined. <sup>d</sup>Contains d-d and charge-transfer transitions.

ing band in the spectrum of Cu(SNSO)Cl<sub>2</sub>, suggesting that the Jahn-Teller effect is greater in Cu(SNSO)Br<sub>2</sub> than in Cu(SNSO)Cl<sub>2</sub>.<sup>23</sup> The spectra of the copper(II) complexes contain intense high energy bands which are attributed to charge transfer transitions (Table IV).

The solution spectra of Ni(SNSO)Cl<sub>2</sub> consist of four bands that may arise from d-d transitions. When nitromethane is the solvent, the four bands appear at 14.6, 18.1, 21.9 and 27.2 kK, but in acetonitrile solution the bands appear at 13.9, 18.1, 21.7 and above 30 kK. Thus the frequencies of the second and third bands are independent of solvent, while the energies of the first and fourth bands are solvent dependent. We propose that Ni(SNSO)Cl<sub>2</sub> has approximate *D*<sub>4h</sub> symmetry (assuming equal ligand fields of nitrogen, sulphur and oxygen). The equatorial molecular orbitals, b<sub>1</sub>(dx<sup>2</sup>-y<sup>2</sup>) and b<sub>2</sub>(d<sub>xy</sub>), are surrounded by the cyclic ligand, and the energies of these orbitals are not affected by the solvent. In contrast, the spectra of Ni(SNSO)Br<sub>2</sub> contain only three bands attributable to d-d transitions, and in either nitromethane or acetonitrile, these bands appear at approximately 14, 21, and 27 kK. The effect of solvent on energies of the d-d transitions is small, while the effect of halogen anion (bromide versus chloride) on spectral properties is remarkable. Available data indicate that Ni(SNSO)Cl<sub>2</sub> has an approximate octahedral structure, while Ni(SNSO)Br<sub>2</sub> is either square-pyramidal or trigonal-bipyramidal.

An elongated (along the metal to halogen axis) octahedral structure with approximate *D*<sub>4h</sub> symmetry (assuming equal ligand field strengths of nitrogen, oxygen and sulphur atoms) is proposed for Co(SNSO)Cl<sub>2</sub>. The solution electronic spectra of this complex consist of only three bands in the 10-30 kK range. However, single bands may represent mergers of bands arising from more than one d-d transition, and bands for low energy d-d transitions were not recorded.<sup>24</sup> A summary of observed electronic spectra, and tentative assignments of d-d transitions<sup>20,25,26</sup> are presented in Table IV.

The complexes of nickel(II) and cobalt(II) are labile in aqueous solution. Thus, Ni(SNSO)Cl<sub>2</sub>, Ni(SNSO)Br<sub>2</sub> and Co(SNSO)Cl<sub>2</sub> dissolve readily in water with immediate

decolouration, which is precipitation of the ligand. In contrast,  $\text{Cu}(\text{SNSO})\text{Cl}_2$  and  $\text{Cu}(\text{SNSO})\text{Br}_2$  are slightly soluble in water, and displacement of the ligand from the green complexes is slow. The green complexes yield blue solutions of hydrated copper(II) ion upon prolonged standing in water. Electronic spectral data, the inertness of the copper(II) complexes in water, and their low solubility in polar organic solvents suggest a nonpolar octahedral structure with a high degree of symmetry. Since the cobalt(II) and nickel(II) complexes dissolve readily in common polar organic solvents, polymeric structures seem unlikely.

#### Summary and Conclusions

Cobalt(II), nickel(II) and copper(II) halide complexes of the tetradentate ligand, SNSO, have been synthesized and characterized. Six-coordinate structures with *trans*-monodentate halide ions are proposed for the copper(II) complexes (Figure 1a). Similar approximately octahedral structures are proposed for  $\text{Ni}(\text{SNSO})\text{Cl}_2$  and  $\text{Co}(\text{SNSO})\text{Cl}_2$ , although the alternate approximately, square-bipyramidal structure (Figure 1b) cannot be

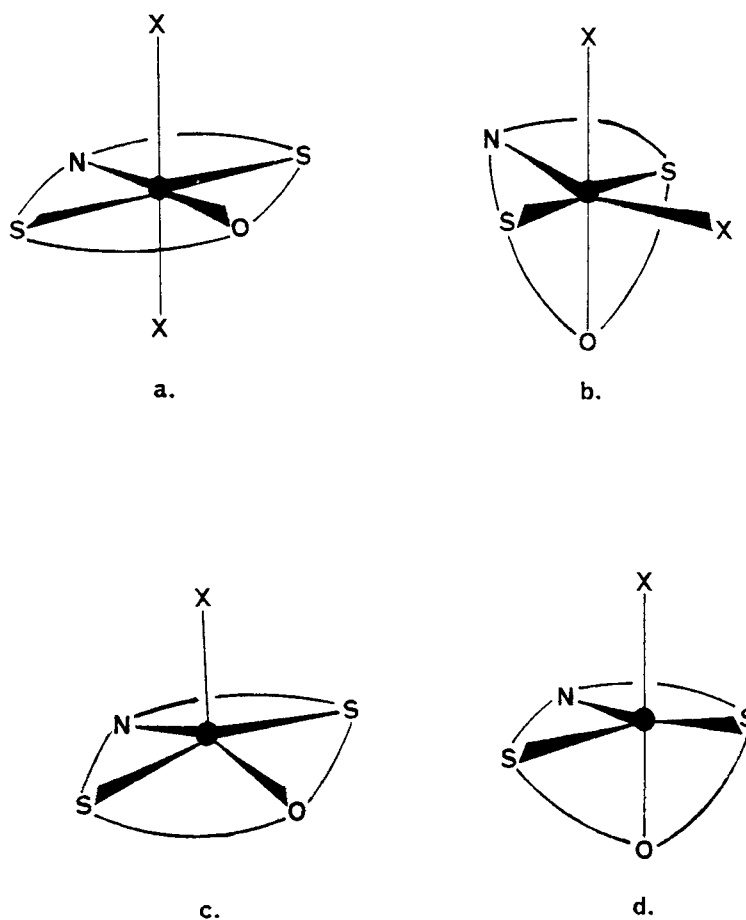


FIGURE 1 Schematic diagrams of the proposed structures of the transition metal (II) complexes. a. square bipyramidal, *trans*-monodentate ligands. b. approximate square bipyramidal, *cis*-monodentate ligands. c. square pyramidal. d. trigonal bipyramidal.



excluded. Electronic spectral data for Ni(SNSO)Cl<sub>2</sub> and for Co(SNSO)Cl<sub>2</sub> can be rationalized in terms of approximately octahedral structures. Additionally, the electronic spectra are similar to those reported previously for octahedral cobalt(II)<sup>24</sup> and octahedral nickel(II)<sup>26</sup> complexes. Nickel(II) is pentacoordinate in the Ni(SNSO)Br<sub>2</sub> complex. On the basis of conductivity data, electronic spectral data and ligand geometry, a square-pyramidal structure is proposed for Ni(SNSO)Br<sub>2</sub>, wherein nickel(II) lies above the base formed by the four donor atoms of the cyclic ligand (Figure 1c).<sup>27</sup> The trigonal-bipyramidal structure (Figure 1d) seems less likely since a folded aliphatic bridge would be required. The realities of the proposed structures must await x-ray crystallographic analysis of selected examples of the complexes reported here.

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