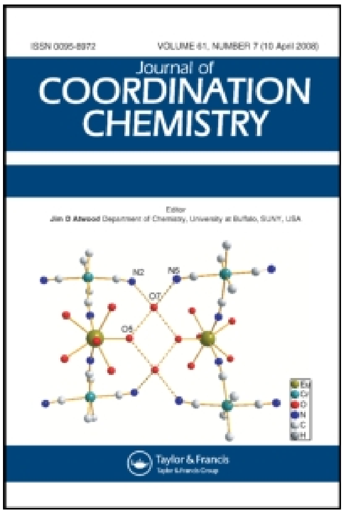

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# COPPER(II) COMPLEXES OF BIS-2,6-(METHYLTHIOMETHYL) PYRIDINE AND THE DITHIA(2,6)PYRIDINOPHANES[1]

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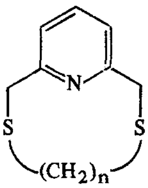
A series of tridentate macrocycles, the dithia(2,6)pyridinophanes, react with copper(II) to form five coordinate complexes of the form [Cu(tridentate)$X_2$] where X = $Cl^-$, $Br^-$, or $NCS^-$. Available evidence suggests that 2,9-dithia[10](2,6)pyridinophane coordinates in a folded manner while it is uncertain whether 2,10-dithia[11](2,6)pyridinophane and 2,11-dithia[12](2,6)pyridinophane coordinate in a folded or a planar fashion. These geometries result from the presence of varying lengths of the non-coordinating methylene chain present in each macrocycle. The effect of the methylene bridge on the structure and stability of the various complexes is discussed. The acyclic analogue, *bis*-2,6(methylthiomethyl)pyridine, also forms pentacoordinate complexes of the type [Cu(tridentate)$X_2$] as well as 2:1 ligand to metal complexes, [Cu(tridentate)$_2$]$(BF_4)_2$. Electronic spectra of the latter complex indicate that the copper(II) is in a slightly distorted octahedral environment in the solid state.

## INTRODUCTION

Developments in the area of pentacoordinate complexes of divalent first row transition metal ions have been summarized in recent review articles.[3] Formation of pentacoordinate complexes usually requires that the size and the orientation of the ligands be such that only five donor atoms are able to approach the central metal ion closely. Thus, five coordination is frequently achieved by the use of bulky and polydentate ligands which hinder six-coordination around the metal ion. In the case of the 3d metal(II) ions, this is achieved most readily by preparing complexes of the form: metal(tridentate)(*bis*-monodentate). The tridentate ligands that have been used in complexes of this type contained the following donor sets: NNN,[4–6] NNO,[7] NON,[8] SNN,[9,10] NSN,[11,12] and SNS.[13] The resulting stereochemistries may be based upon a trigonal bipyramid or a square pyramid, but in practice complexes usually possess structures which represent distortions from these two idealized geometries.

This report deals with the synthesis and properties of a series of copper(II) complexes containing macrocyclic tridentate dithia(2,6)pyridinophane ligands (**1**),



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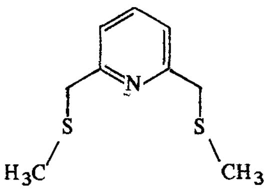

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abbreviated SNS-n. For example, SNS-6 refers to 2,9-dithia[10](2,6)pyridinophane. Copper(II) complexes of the acyclic analogue, *bis*-2,6(methylthiomethyl)pyridine (**2**), abbreviated SNS–$Me_2$, were prepared for comparison. All of the tridentate ligands described here form five coordinate copper(II) complexes which have a 1:1 ligand to metal ratio while SNS–$Me_2$ also forms 2:1 complexes. These complexes are of particular interest because they contain thioether sulphur atoms which are considered to have little affinity for copper(II).[14,15] The tridentate ligands (**1**) are unusual in that they are cyclic and contain a non-coordinating methylene bridge of $n$ members where $n = 6, 7$ or 8. This chain sterically prevents the formation of 2:1 ligand to metal complexes and effectively blocks an octahedral coordination site. The macrocycle SNS-6 is believed to coordinate in a folded fashion while it is uncertain whether SNS-7 and SNS-8 coordinate in a folded or a planar manner.

## EXPERIMENTAL SECTION

### *Reagents and Equipment*

All of the chemicals used were reagent grade unless otherwise noted. The 1,*n*-dichloro- and 1,*n*-dibromoalkanes and the 2,6-pyridinedimethanol were purchased from the Aldrich Chemical Co. and were used as received.

Solution absorption spectra were recorded using a Cary 14 spectrophotometer. Room temperature solid-state mull spectra (4.3–30 kK) were obtained using filter paper impregnated with Halocarbon 25-5S grease and the compound. The mull spectra were also recorded at 77°K by using a dewar flask with quartz windows which contained liquid nitrogen as described by Busch *et al.*[16]

Infrared spectra were obtained as Nujol mulls between KBr discs or as KBr pellets using a Perkin-Elmer 257 spectrophotometer. Electrolytic conductivities at 25.0° were obtained using a Model 1605-A General Radio Impedance Comparator. Magnetic moment measurements were done on 10–20 mg of sample in the solid state using the Faraday method.[17] The diamagnetic corrections for the ligands were determined as being $-264 \times 10^{-6}$ cgs for SNS-6 and $-304 \times 10^{-6}$ cgs for SNS-8. Diamagnetic corrections for SNS-$Me_2$ and the counterions were made using Pascal's constants.[18]

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., Instranal Laboratories, Rensselaer, N.Y., and Heterocyclic Chemical Corporation, Harrisonville, Mo. Mass spectra were obtained at the University of Minnesota, Minneapolis, Mn., and were determined at 70 ev. The $^1H$ nmr spectra were recorded on a Jelco HL-60 nmr spectrometer.

### *Preparation of Cyclic Ligands*

*[n]Dithia(2,6)pyridinophanes* (**1**) The pyridinophanes were synthesized by adapting the procedure that was developed by Vogtle.[19] Thus, 1,*n*-alkanedithiouronium dihalides were prepared by treatment of an ethanolic solution of thiourea with the appropriate 1,*n*-alkanedihalide in a 2:1 molar ratio, respectively. The dithiouronium dihalides were hydrolyzed with four molar equivalents of aqueous sodium hydroxide to yield the corresponding 1,*n*-alkanedimercaptides.[20] An aqueous solution (200 ml) of 1,*n*-alkanedimercaptides (0.039 mole) and 0.040 mole of 2,6-*bis*-(chloromethyl)pyridine[21] in 200 ml of benzene were added simultaneously to 1.5 liters of refluxing ethanol over a four hour period. After refluxing for an additional 18 hours, the pyridinophanes (**1**) were isolated by evaporation of the solvent under reduced pressure and extraction of the residue with dichloromethane, followed by a second evaporation. The yellow oils obtained in this manner were chromatographed on alumina, using chloroform as eluent.[19] The desired product was recovered in the first 300 ml of eluent. Recrystallization from methanol yielded white crystalline solids. Physical data for the dithiapyridinophanes are summarized in Tables I–II.

### *Mass Spectral Data for Ligands*

All masses having relative intensities of *ca* 5% or more of the base peak are listed for SNS-7 and SNS-8. The first mass listed in each series is the M + 1 ion. The parent ion follows, and masses are given in decreasing order. Each mass is followed by its relative intensity in parenthesis. SNS-7: 268(6.1), 267(32), 234(28.4), 208(6.9), 161(5.9), 140(100), 139(84), 138(5.2), 137(23), 136(7.6), 107(95), 106(32), 93(6.8), 79(5.8), 78(8.4), 77(7.4), 41(7.9), and 39(7.4). SNS-8: 282(1.4), 281(5.2), 248(11), 222(4.7), 140(3.5), 139(27), 138(17), 137(6.7), 108(10), 107(100), 106(16), 78(5.8), 77(4.5), 65(4.6), 45(5.9), 41(4.8), and 39(4.7). SNS-6 gave a mass spectrum similar to those observed for SNS-7 and SNS-8. Spectra were scanned for higher masses corresponding to dimeric and trimeric species at low voltage. In each case the highest mass observed was the one corresponding to the calculated molecular weight for the monomeric species.

*Bis-2,6-(methylthiomethyl)pyridine* (**2**) *Bis*-2,6-(chloromethyl)pyridine[21] (17.6 g, 0.10 mole) and thiourea (15.2 g, 0.20 mole) were dissolved in 100 ml of ethanol with heat and allowed to react at reflux temperature for 4 hours. A concentrated aqueous solution (20 g, 0.50 mole, in 25 ml of water) of sodium hydroxide was added to the cooled solution and the mixture was allowed to react for 18 hours at room temperature. The solution was treated with iodomethane (46 g, 0.30 mole) in small portions and allowed to react with stirring for 24 hours. The

TABLE I
Analytical data for ligands and complexes

| Compound | Calculated, % | | | | Found, % | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Halide | C | H | N | Halide |
| SNS–Me$_2$ | 32.39 | 4.20 | 3.93 | | 32.14 | 4.45 | 3.96 | |
| SNS-6 | 61.61 | 7.56 | 5.53 | | 61.79 | 7.67 | 5.51 | |
| SNS-7 | 62.87 | 7.91 | 5.23 | | 62.99 | 8.06 | 5.30 | |
| SNS-8 | 64.01 | 8.26 | 4.98 | | 64.25 | 8.13 | 4.85 | |
| Cu(SNS–Me$_2$)Cl$_2$ | 32.39 | 4.20 | 3.93 | | 32.14 | 4.45 | 3.96 | |
| Cu(SNS-6)Cl$_2$ | 40.20 | 4.94 | | 18.30 | 40.58 | 5.16 | | 18.11 |
| Cu(SNS-7)Cl$_2$ | 41.84 | 5.27 | | 17.64 | 41.63 | 5.27 | | 17.87 |
| Cu(SNS-8)Cl$_2$ | 43.32 | 5.57 | | 17.05 | 43.46 | 5.73 | | 17.40 |
| Cu(SNS–Me$_2$)Br$_2$ | 25.57 | 3.10 | | 37.81 | 25.39 | 3.11 | | 38.51 |
| Cu(SNS-6)Br$_2$ | 32.75 | 4.02 | | 33.52 | 32.90 | 4.04 | | 32.75 |
| Cu(SNS-8)Br$_2$ | 35.69 | 4.59 | | 31.66 | 35.60 | 4.52 | | 31.90 |
| Cu(SNS–Me$_2$)(NCS)$_2$ | 34.86 | 3.46 | 11.09 | | 34.25 | 3.40 | 11.04 | |
| Cu(SNS-8)(NCS)$_2$ | 44.27 | 5.03 | 9.11 | | 43.67 | 4.92 | 9.20 | |
| [Cu(SNS–Me$_2$)$_2$](BF$_4$)$_2$ | 34.00 | 4.12 | 4.41 | | 34.02 | 4.11 | 4.43 | |
| [Cu(SNS–Me$_2$)(dien)](BF$_4$)$_2$ | 28.93 | 4.86 | 10.38 | | 28.77 | 5.07 | 10.43 | |

solution was diluted with 200 ml of water and extracted with three 150 ml portions of dichloromethane. The combined dichloromethane solution was washed with a 100 ml portion of 5% sodium hydroxide, dried ($K_2CO_3$) and the solvent evaporated to yield a yellow oil. The oil was dissolved in 150 ml of carbon tetrachloride, 10 g of neutral alumina was added and the mixture was allowed to stand for an hour. The solution was filtered and the solvent removed under reduced pressure. The clear yellow oil (18.3 g, 92%) gave ir and nmr spectra that are consistent with the assigned structure (Tables I and II).

*General preparation of Cu(SNS)X$_2$ complexes (X = Cl$^-$ or Br$^-$)* The appropriate ligand (0.002 mole) dissolved in 20 ml of hot methanol was added to a heated solution of copper halide (0.002) mole in methanol. The instantaneous color change observed was followed in most cases by immediate precipitate formation. The solution was heated and stirred for ten minutes, cooled and filtered. Yields of the pure complexes were generally 80–90%.

TABLE II
Ligand properties and spectral data

| Compound | mp (°C) | Yield | nmr absorptions[a] (δ) |
|---|---|---|---|
| SNS-6 | 97 | 71 | 1.35(m), 2.35(t), 3.80(s), 7.25(m) |
| SNS-7 | 57 | 53 | 1.30(m), 2.50(t), 3.83(s), 7.40(m) |
| SNS-8 | 77 | 54 | 1.30(m), 2.50(t), 3.82(s), 7.40(m) |
| SNS–(CH$_3$)$_2$ | oil | 92 | 2.02(s), 3.70(s), 7.15(m) |

[a] m = multiplet, t = triplet, s = singlet.

*General preparation of Cu(SNS)(NCS)$_2$ complexes* The appropriate ligand (0.002 mole) dissolved in 20 ml of hot methanol was added to a heated solution of $[Cu(CH_3CN)_4](BF_4)_2$ [22] (0.002 mole) in methanol which effected an instantaneous color change to dark green. After five minutes the addition of a hot solution of lithium thiocyanate (0.008 mole) in methanol caused the formation of a precipitate. The solution was heated and stirred for five minutes, cooled and filtered. Yields were about 70%.

*[Cu(SNS–Me$_2$)$_2$](BF$_4$)$_2$* A 2.0 g sample (0.010 mole) of *bis*-2,6(methythiomethyl) pyridine dissolved in 25 ml of hot methanol was treated with 1.3 g of copper tetrafluoroborate hydrate in 25 ml of hot methanol. The resulting dark green solution deposited 1.8 g (75%) of dark green crystals upon cooling.

*[Cu(SNS–Me$_2$)(dien)](BF$_4$)$_2$* A 0.70 g sample of copper tetrafluoroborate hydrate in 30 ml of hot methanol was treated with 0.39 g (0.002 mole) of *bis*-2,6(methylthiomethyl)pyridine. After stirring for five minutes, 0.20 g (0.002 mole) of freshly distilled diethylenetriamine (technical grade) was added. The resulting deep blue solution was stirred for 10 minutes, cooled and filtered. The yield was 0.45 g (45%) of solid.

## RESULTS AND DISCUSSION

### *Ligand Preparation and Properties*

The general procedure used for the preparation of the dithia(2,6)pyridinophanes was developed by Vogtle.[19] The synthesis of SNS-3 and a series of pyridinophane N-oxides, including examples corresponding to the dithiapyridinophanes (**1**) reported here, have been reported previously.[23] The preparation of the tridentate macrocycles involves a high dilution reaction of 2,6-*bis*-(chloromethyl)pyridine with the appropriate 1,*n*-alkanedimercaptide. Some polymer formation is observed in the reaction, but it is removed via column chromatography. The dithia(2,6)pyridinophanes are white crystalline solids which decompose slowly upon standing, but they can be purified easily by recrystallization from methanol before use. The macrocycles (**1**) show parent peaks in their mass spectra which correspond to the respective calculated molecular weights, and fragmentation patterns are consistent with the assigned structures. Nmr spectral data for **1** and **2** are summarized in Table II. The nmr spectrum of SNS-8 consists of a multiplet for pyridine protons at $\delta$ 7.40 (3H), a singlet for protons alpha to the pyridine ring at $\delta$ 3.82 (4H), a triplet for methylene protons alpha to the sulphur atoms at $\delta$ 2.50 (4H), and a multiplet for the remaining methylene protons at *ca* $\delta$ 1.3 (10H). The relatively high field for the latter protons suggests that the methylene bridge is folded above the pyridine nucleus. The proton assignments for SNS-6 and SNS-7 are directly analogous to those described above for SNS-8. The infrared spectra of the pyridinophanes contain a sharp pair of peaks at 1590 and 1570 cm$^{-1}$ that arise from stretching vibrations of the pyridine nucleus.

Treatment of the disodium salt of 2,6-pyridinedithiomethanol with two molar equivalents of methyl iodide produced 2,6-*bis*(methylthiomethyl)pyridine, SNS–Me$_2$ (**2**), in excellent yield. The nmr spectrum of the yellow oil consists of a multiplet at $\delta$ 7.15 (3H) for the pyridine protons, a singlet for the methylene protons at $\delta$ 3.70 (4H), and a singlet for the methyl hydrogens at $\delta$ 2.02 (6H). Similar to its cyclic analogues, SNS–Me$_2$ displays a characteristic doublet in the infrared spectrum for the substituted pyridine nucleus.

### *Five Coordinate Copper(II) Complexes*

Both SNS–Me$_2$ and the series of SNS-*n* ligands react with Cu(II)X$_2$ (X = Cl$^-$, Br$^-$) in methanol to yield complexes with the empirical formula CuLX$_2$ where L represents a tridentate ligand. Formation of the analogous thiocyanate complexes required anhydrous conditions. Attempts to prepare these complexes using copper tetrafluoroborate hydrate and the ligands in methanol followed by addition of lithium thiocyanate in methanol led to products of variable composition. The thiocyanate complexes were successfully synthesized by using anhydrous [Cu(CH$_3$CN)$_4$](BF$_4$)$_2$ as a copper(II) source. However, this method failed to produce an uncontaminated complex containing SNS-6.

Some of the physical properties of the copper complexes are listed in Table III. Conductivity measurements of approximately 10$^{-3}$ M solutions of the complexes in nitromethane indicate that all of the CuLX$_2$ (X = Cl$^-$, Br$^-$, NCS$^-$) complexes are nonelectrolytes.[24] Thus, in nitromethane solution the complexes appear to be five coordinate. Although five coordination in general is unusual, it is fairly typical of metal(II) complexes containing an uncharged tridentate ligand and two halide ions.

TABLE III
Physical properties of Cu(II) complexes

| Complex | Colour | mp (°C) | $\mu_{eff}$ (BM) | $\Lambda^a$ |
|---|---|---|---|---|
| Cu(SNS–Me$_2$)Cl$_2$ | green | 159 | 1.84 | 5.1 |
| Cu(SNS-6)Cl$_2$ | green | 174 | 1.84 | 6.7 |
| Cu(SNS-7)Cl$_2$ | green | 182 | 1.88 | 5.0 |
| Cu(SNS-8)Cl$_2$ | green | 181 | 1.84 | b |
| Cu(SNS–Me$_2$)Br$_2$ | dark green | 188 | 1.92 | 4.8 |
| Cu(SNS-6)Br$_2$ | yellowish green | 197 | 1.83 | 11 |
| Cu(SNS-8)Br$_2$ | yellowish green | 187 | 1.86 | b |
| Cu(SNS–Me$_2$)(NCS)$_2$ | brownish green | 136 | 1.88 | 9.3 |
| Cu(SNS-8)(NCS)$_2$ | brown | 141 | 1.73 | 15 |
| [Cu(SNS–Me$_2$)$_2$](BF$_4$)$_2$ | dark green | 188 | 1.99 | 170 |
| [Cu(SNS–Me$_2$)(dien)](BF$_4$)$_2$ | blue violet | 162 | – | 173 |

[a] ohm$^{-1}$ cm$^2$ mole$^{-1}$, in nitromethane.
[b] Insoluble.

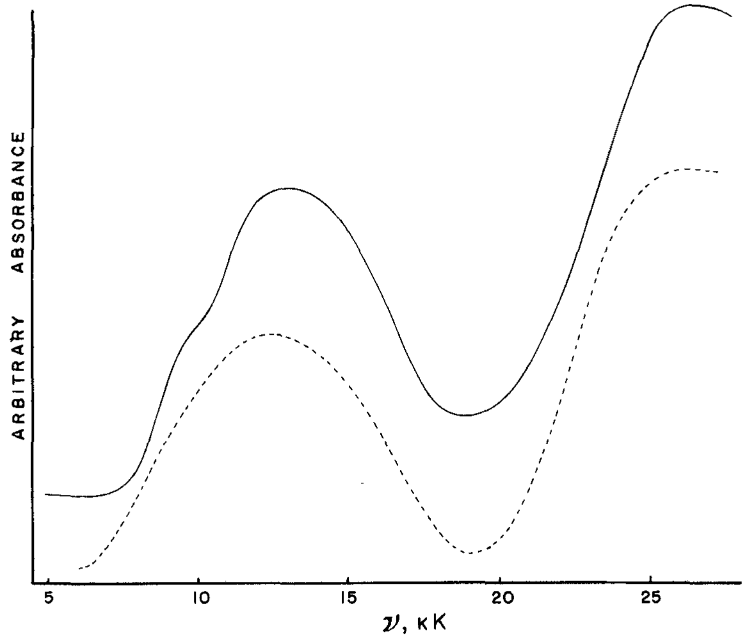

FIGURE 1 Solid state mull spectra of Cu(SNS-6)$Cl_2$ at room temperature (dotted line) and at 77°K (solid line)

The two idealized pentacoordinate geometries are the trigonal bipyramid and square pyramid. In most cases, however, neither of these geometries is observed in pure regular form and distortions from these idealized geometries are the rule.[25] For example, Cu(TTDA)$Cl_2$ where TTDA = $S[CH_2CON(CH_3)_2]_2$ has a slightly distorted square pyramidal structure,[26] whereas [Cu($Me_6$tren)Br]Br where $Me_6$tren = $N[CH_2CH_2N(CH_3)_2]_3$ has a slightly distorted trigonal bipyramidal structure.[27] Although these complexes have different structures, the electronic spectra of pentacoordinate copper(II) complexes do not provide sufficient information to distinguish between the two.[28] In both cases the spectra contain a broad band in the 12 kK region which contains several transitions. These spectra are very similar in appearance to those shown in Figure 1 for Cu(SNS-6)$Cl_2$, which are typical of all the spectra for the five coordinate complexes presented here.

The band positions measured in solution and as solid state mulls are given in Table III. At 77°K the band maxima shift to higher energies (loss of red tail)[29] and some resolution of the band envelope occurs as shown in Figure 1. The spectra also contain intense bands at higher energies which are attributed to charge transfer transitions. The molar extinction coefficients indicate that the broad lower energy band is of the d-d type, while the intense band at higher energies is of the charge transfer type.

The magnetic moments measured at room temperature (Table III) are typical of mononuclear copper(II) complexes.[30] However, it has been pointed out that no stereochemical information about copper(II) complexes can be obtained from the measurement of room-temperature magnetic moments.[31] The infrared spectra of all the complexes display sharp doublets at about 1595 and 1570 $cm^{-1}$ associated with the substituted pyridine ring.

The relationship between ring size and stereochemistry in transition metal complexes containing macrocyclic ligands has been clarified primarily through investigations during the last decade.[32] For example, it is known that in a saturated macrocycle containing four nitrogen donors a 13-membered ring is able to encircle a first-row transition metal ion in a planar fashion,[33] but reducing the number of ring members to 12 results in a folding of the ligand.[34] Recent work with macrocyclic ligands containing only sulphur donor atoms has shown that a 13-membered ring coordinates to nickel(II) in a folded manner[35] while a 14-membered ring exhibits planar coordination.[36] The increased size of S relative to N is probably responsible for this observation. It was also observed that in one case a 14-membered cyclic tetradentate thioether formed a folded structure with Co(III).[37] These observations make it possible to predict the likely stereochemistry of the copper complexes containing the cyclic dithia(2,6)pyridinophanes.

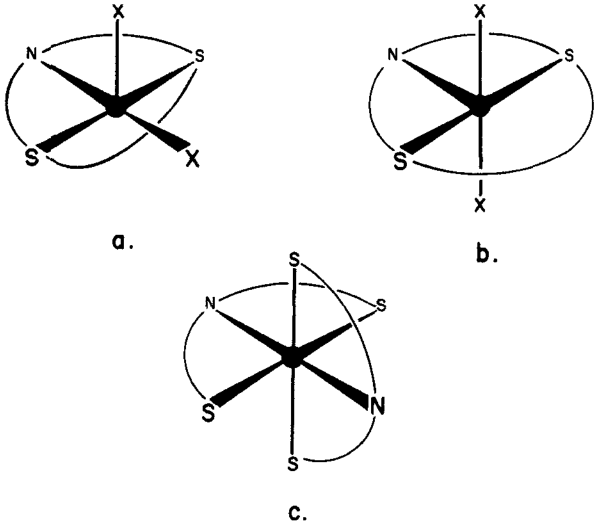

FIGURE 2 Schematic diagrams of the proposed structures of the copper complexes: (a) folded ring (*cis*-monodentates); (b) planar ring (*trans*-monodentates); (c) *bis*–SNS–$Me_2$.

For tridentate coordination of the SNS-*n* ligands the SNS donor atoms must lie in the same plane. By analogy to cyclic tetradentate thioether complexes, the 13-membered SNS-6 ligand is most likely to bond to a metal in a folded manner. The methylene bridge blocks one of the coordination sites of an octahedron producing a five-coordinate complex. This gives rise to an approximately square pyramidal structure schematically shown in Figure 2a. Drieding models of the complex support the geometry illustrated in Figure 2a.

In contrast to the SNS-6 stereochemistry, analogy to cyclic tetradentate thioether complexes suggests that the 14-membered SNS-7 and 15-membered SNS-8 macrocycles could bond in a planar fashion as shown in Figure 2b. Dreiding models suggest that the SNS-7 complex is more stable in the folded configuration (Figure 2a) whereas the SNS-8 complex appears to be more stable in the planar configuration (Figure 2b). Attempts to provide evidence for these structures by growing single crystals suitable for X-ray analysis have thus far been unsuccessful, but these structures will be investigated using complexes containing other first-row transition metal ions.

Although direct evidence is lacking, certain observations suggest that the structures indicated by the models are correct. For example, the SNS-8 complexes are insoluble in nitromethane while those of the other two cyclic ligands are soluble. The solubility differences might be due to the presence of *trans* monodentate ions in the SNS-8 case (Figure 2b) as compared to the more polar structures containing *cis* monodentate ions in the SNS-6 and SNS-7 complexes (Figure 2a). These geometries are also suggested by the behaviour of the complexes in the presence of water. It is well known that water displaces thioether ligands from copper(II) ions.[38] The dissolution of Cu(SNS-*n*)$Cl_2$ complexes in water resulted in the immediate displacement of SNS-6 and SNS-7. These water insoluble ligands were displaced intact as confirmed by their physical properties. In contrast to this behaviour, Cu(SNS-8)$Cl_2$ is stable in water for several days at room temperature. Both Busch[39] and Margerum[40] have discussed the enhanced stability of tetraaza macrocyclic complexes as compared to their acyclic analogues. Suggested models for the dissociation of macrocyclic complexes indicate that the ring folds before the first bond between the ring and the metal is broken. This observation is consistent with the behaviour observed above. Since the structure in Figure 2a is already folded, ligand replacement should be facile. Ligand displacement of a planar macrocycle as in Figure 2b should be slower. Thus, the differences observed suggest that the complexes containing SNS-6 and SNS-7 have a folded structure while those containing SNS-8 have a planar configuration. In summary, steric restrictions require the complexes containing SNS-6 to be folded, but further work is necessary to determine the geometries of the SNS-7 and SNS-8 complexes with certainty.

Although the presence of the methylene bridge in the cyclic complexes makes it possible to discuss their probable geometries, this is not true for the five coordinate complexes of the acyclic ligand, SNS–$Me_2$.

### *Six Coordinate Copper(II) Complexes*

Attempts to prepare *bis*-tridentate complexes with SNS-*n* ligands were unsuccessful. Dreiding models indicate that the presence of non-coordinating methylene chain in the cyclic ligands makes it impossible for two of these ligands to bond to the metal because of steric limitations. However, in the corresponding acyclic analogue, SNS–$Me_2$, treatment of copper tetrafluoroborate hydrate with two equivalents of the ligand resulted in a *bis*-tridentate complex, $[Cu(SNS–Me_2)_2](BF_4)_2$. Some of the physical properties of the complex are listed in Table III. Conductivity measurements in nitromethane indicate that the complex is a 2:1 electrolyte.[24] Thus, the complex appears to be octahedral. Since tridentate coordination for each ligand requires that the SNS donor atoms lie in the same plane, the structure is expected to be as schematically shown in Figure 2c. If only the

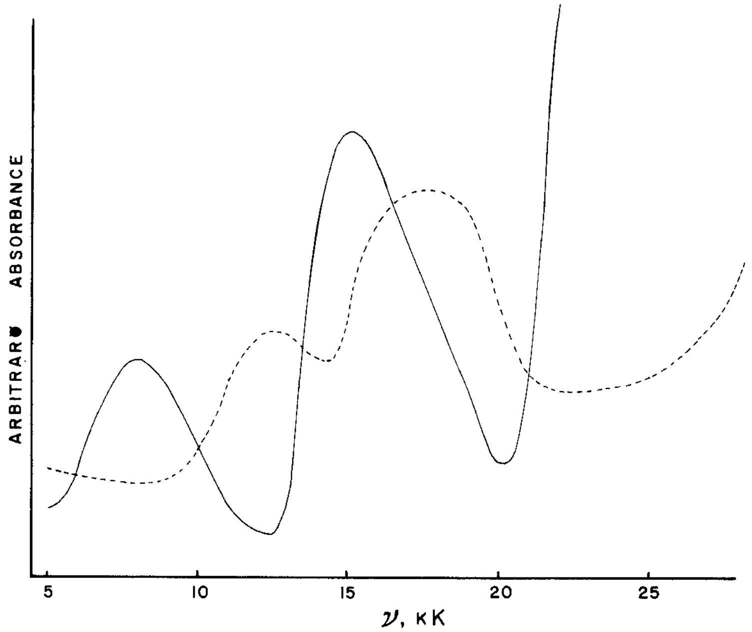

FIGURE 3 Solid state mull spectra (77°K) of $[Cu(SNS{-}Me_2)_2](BF_4)_2$ (solid line) and $[Cu(SNS{-}Me_2)(dien)](BF_4)_2$ (dotted line).

donor atoms are considered, a $D_{4h}$ crystal field is generated which represents a tetragonal distortion of an octahedron. The magnitude of this distortion depends upon the differences of the ligand field strengths of the planar S atoms versus the axial N atoms.

In order to investigate the effect of tetragonal distortion, it was of interest to prepare a mixed ligand complex for comparison, that is $[Cu(SNS{-}Me_2)(dien)](BF_4)_2$ where dien = diethylenetriamine. Physical data (Table III) indicate that it is also an octahedral complex. Considering only the donor atoms and assuming equal ligand field strengths for the pyridine and amine N's, a $D_{4h}$ crystal field is also generated. In this case, there are four planar N donor atoms and two axial sulphur atoms.

The solid state electronic spectra at 77°K of the two octahedral complexes are shown in Figure 3. Both spectra display an intense band at higher energies and a less intense band at lower energy. The latter bands, 7.9 kK for $[Cu(SNS{-}Me_2)_2]^{2+}$ and 12.5 kK for $[Cu(SNS{-}Me_2)(dien)]^{2+}$, are the most interesting features of the spectra and this type of band has been observed previously in the spectra of $[Cu(dien)_2]^{2+}$ at 8.8 kK and $[Cu(NO_2)_6]^{4-}$ at 8.6 kK.[41,42] It has been assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition in these cases and is considered to be related to the amount of tetragonal distortion in the complexes. The appearance of this band at low energies is indicative of a small amount of tetragonal distortion. As the tetragonal distortion increases, this band moves to higher energy and eventually is included under the broad envelope of the higher energy band. For example, the corresponding $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for $Cu(NH_3)_4(NCS)_2$ occurs at high energy, i.e., 14.3 kK.[30]

Although no definite assignments of the spectra can be made from the data presented here (Table IV), it is possible to compare the spectra of the complexes with those of the well studied $[Cu(dien)_2]^{2+}$ and $[Cu(NO_2)_6]^{4-}$ systems.[41,42] These two cases involve a $d_{z^2} \rightarrow d_{x^2-y^2}$ low energy band assignment which indicates $Dq(xy) > Dq(z)$. For the case where $Dq(xy) < Dq(z)$, the low energy band assignment would be $d_{x^2-y^2} \rightarrow d_{z^2}$, but the frequency observed would still be indicative of the tetragonal distortion.

Since the spectrum of $[Cu(SNS{-}Me_2)_2](BF_4)_2$ has a low energy band which indicates a small degree of tetragonal distortion, a similarity in the ligand field strengths of the N and S donors is suggested. Although the placement of thioethers in the spectrochemical series is not certain, it has been pointed out that a thioether donor ligand has a ligand field strength comparable to that of a nitrogen donor ligand.[43,44] The data for the mixed ligand complex are helpful in pursuing this further. Hathaway has shown that an

TABLE IV
Absorption spectra of copper(II) complexes

| | Absorptions (kK) | | | |
|---|---|---|---|---|
| | Solution spectra | | Solid state | |
| Compound | $CH_3NO_2$ | $CH_3CN$ | R.T. | 77°K |
| $Cu(SNS{-}Me_2)Cl_2$ | 12.8 (449) | 12.6 (417)<br>24.9 (2380) | 12.5<br>25.5 | 12.9<br>26.1 |
| $Cu(SNS\text{-}6)Cl_2$ | 11.7 (446) | | 12.6<br>26.2 | 13.1<br>26.5 |
| $Cu(SNS\text{-}7)Cl_2$ | 11.4 (449) | | 12.5<br>25.1 | 13.0<br>25.1 |
| $Cu(SNS\text{-}8)Cl_2$ | insoluble | | 13.2<br>25.3 | 13.7<br>25.8 |
| $Cu(SNS{-}Me_2)Br_2$ | 12.8 (572) | 12.7 (606)<br>28.9 (4450) | 13.4<br>26.9 | 13.8<br>25.6 |
| $Cu(SNS\text{-}6)Br_2$ | 12.4 (584) | | 12.1<br>28.0 | 12.9<br>28.4 |
| $Cu(SNS\text{-}8)Br_2$ | insoluble | | 13.1<br>28.5 | 13.6<br>28.2 |
| $Cu(SNS{-}Me_2)(NCS)_2$ | 13.8 (564) | 13.7 (458)<br>25.8 (3190) | 13.6<br>25.5 | 13.9<br>26.4 |
| $Cu(SNS\text{-}8)(NCS)_2$ | 13.3 (482) | | 12.4<br>broad | 13.5<br>26.7 |
| $[Cu(SNS{-}Me_2)_2](BF_4)_2$ | 15.4 (348) | 16.1 (542)<br>25.2 (5960) | 14.9<br>23.6 | 7.9<br>15.1<br>24.3 |
| $[Cu(SNS{-}Me_2)(dien)](BF_4)_2$ | | | | 12.5<br>17.7 |

approximate value for $10D_q$ can be obtained by subtracting one-half of the energy value of the lower energy band from the higher energy band.[45] Values obtained for $[Cu(dien)_2]^{2+}$, $[Cu(SNS{-}Me_2)(dien)]^{2+}$, and $[Cu(SNS{-}Me_2)_2]^{2+}$ are, respectively, 11.6, 11.4, and 11.1 kK. This indicates that the ligand field strength of dien is slightly greater than that of $SNS{-}Me_2$. This further suggests that the field in $[Cu(SNS{-}Me_2)_2]^{2+}$ is best represented by $Dq(xy) < Dq(z)$ since the S donors appear to have a slightly smaller ligand field strength than the pyridine N donor atoms.

The coordination properties of the SNS-*n* ligands toward other first row transition metal ions are under investigation.

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## REFERENCES

1. Presented in part before the 169th American Chemical Society National Meeting, Philadelphia, Pa., 1975.
2. (a) Colgate University, Hamilton, N.Y.; (b) Macalester College, St. Paul, Minn.
3. (a) L. Sacconi, *Pure Appl. Chem.*, 17, 95 (1968); (b) M. Ciampolini, *Structure and Bonding*, 6, 52 (1969);
   (c) P. L. Orioli, *Coor. Chem. Rev.*, 6, 285 (1971).
   (d) B. F. Hoskins, *Coor. Chem. Rev.*, 9, 365 (1972).
4. L. Sacconi, I. Bertini and R. Morassi, *Inorg. Chem.*, 6, 1548 (1967).
5. Z. Dori and H. B. Gray, *Inorg. Chem.*, 7, 889 (1968).
6. M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 5, 45 (1966).
7. L. Sacconi and I. Bertini, *Inorg. Chem.*, 7, 1178 (1968).
8. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5, 445 (1967).

9. L. Sacconi and G. P. Speroni, *Inorg. Chem.*, 7, 259 (1968).
10. P. S. K. Chia and S. E. Livingstone, *Aust. J. Chem.*, **22**, 1613 (1969).
11. E. Uhlig and G. Heinrich, *Z. Anorg. Allg. Chem.*, **330**, 40 (1964).
12. M. Ciampolini and J. Gelsomini, *Inorg. Chem.*, **6**, 1821 (1967).
13. S. E. Livingstone and J. D. Nolan, *Aust. J. Chem.*, **22**, 1817 (1969).
14. C. A. McAuliffe, J. V. Quagliano and L. M. Vallarino, *Inorg. Chem.*, **5**, 1996 (1966).
15. R. H. Fish, J. J. Windle, W. Gaffield and J. R. Scherer, *Inorg. Chem.*, **12**, 855 (1973).
16. J. C. Dabrowski, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, **11**, 1979 (1972).
17. V. Katovic, L. Lindoy and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).
18. J. Lewis and R. G. Wilkins, *Modern Coordination Chemistry*, Interscience, New York, N.Y., 1960, p. 403.
19. F. Vogtle, *Tetrahedron*, **25**, 3231 (1969).
20. A. Speziale, *Org. Syn., Coll. Vol. 4*, 401 (1963)
21. W. Baker, K. Buggle, J. McOmie and D. Watkins, *J. Chem. Soc.*, 3594 (1958).
22. B. J. Hathaway, D. G. Holah and A. E. Underhill, *J. Chem. Soc.*, 2444 (1962).
23. F. Vogtle, *Angew. Chem. Internat. Edit.*, **11**, 727 (1972).
24. W. J. Geary, *Coor. Chem. Rev.*, 7, 81 (1971).
25. C. Furlani, *Coor. Chem. Rev.*, **3**, 141 (1968).
26. L. Ackerman, J. G. H. duPreez and M. L. Gibson, *Inorg. Chim. Acta*, **5**, 539 (1971).
27. M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).
28. B. J. Hathaway and D. E. Billing, *Coor. Chem. Rev.*, **5**, 143 (1970).
29. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, N.Y., 1968, p. 146 ff.
30. B. J. Hathaway and D. E. Billing, *Coor. Chem. Rev.*, **5**, 143 (1970).
31. B. J. Hathaway and A. A. G. Tomlinson, *Coor. Chem. Rev.*, **5**, 1 (1970).
32. L. Y. Martin, L. J. DeHayes, L. J. Zompa and D. H. Busch, *J. Amer. Chem. Soc.*, **96**, 4046 (1974), and references therein.
33. D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, **86**, 1331 (1964).
34. J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).
35. W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970).
36. W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).
37. K. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974).
38. S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).
39. D. H. Busch, K. Farmery, V. Goedkin, V. Katovic, A. C. Melnyk, C. R. Sperati and N. Tokel, *Advan. Chem. Ser., No. 100*, **44** (1971).
40. D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **91**, 6540 (1969).
41. B. J. Hathaway, M. J. Bew, D. E. Billings, R. J. Dudley and P. Nicholls, *J. Chem. Soc. (A)*, **2312** (1969).
42. B. J. Hathaway, R. J. Dudley and P. Nicholls, *J. Chem. Soc. (A)*, **1845** (1969).
43. R. L. Carlin and E. Weissberger, *Inorg. Chem.*, **3**, 611 (1964).
44. C. D. Flint and M. Goodgame, *J. Chem. Soc. (A)*, **2178** (1968).
45. H. Elliott, B. J. Hathaway and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).