

**Copper(I) and Silver(I) Ions in Unusual poly Donor-atom Environments; X-ray Crystal and Molecular Structures of  $[M\{(R)(S)\text{-}1,2\text{-}(5\text{-Me-thiophene-}2\text{-CH=N})_2\text{-cyclohexane}\}_2](\text{O}_3\text{SCF}_3)_2$ ,  $M = \text{Cu}^{\text{I}}$  or  $\text{Ag}^{\text{I}}$**

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Coordination properties of  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  with ligand systems containing N and S donor atoms as potential coordinating sites continue to be of interest as models for the redox active sites in the 'blue' proteins [1].

The conformation and rigidity of the carbon skeleton connecting the hetero-atoms, as well as the types and number of hetero-atoms in the model ligand systems, are important with respect to both the number of metal atoms which can be bonded and the ultimate configuration at the metal centres. Recently we have shown that the quadridentate N-donor ligands  $(R)(S)\text{-}1,2\text{-}(6\text{-R-py-}2\text{-CH=N})_2\text{-cyclohexane}$  ( $R = \text{H}$  or  $\text{Me}$ ), in which the inner two N-donor sites are connected by the  $(R)(S)\text{-}1,2\text{-cyclohexanediyl}$  ring, act as di-bidentate ligands binding two  $\text{Cu}^{\text{I}}$  or  $\text{Ag}^{\text{I}}$  atoms (see Fig. 1) [2]. The application of INEPT  $^{15}\text{N}$  and  $^{109}\text{Ag}$  NMR spectroscopy revealed that the structural features found for the silver(I) complex  $[\text{Ag}_2\{(R)(S)\text{-}1,2\text{-}(py\text{-}2\text{-CH=N})_2\text{-cyclohexane}\}_2](\text{O}_3\text{SCF}_3)_2$  in the solid, with characteristic alternating two short and two long  $\text{Ag-N}$  distances around the distorted tetrahedral silver centres [2], are retained in solution [3]. Attempts to form mononuclear  $\text{Cu}^{\text{I}}$  or  $\text{Ag}^{\text{I}}$  complexes with these  $\text{N}_4$ -donor ligands, using  $1/2$   $\text{Cu}^{\text{I}}$ - or  $\text{Ag}^{\text{I}}$ -to-ligand ratios were unsuccessful. Interpretation of these results requires more information concerning the influence of the donor sites on the coordination properties of these types of potentially quadridentate ligands. For this purpose we have now investigated the bonding features of the  $\text{N}_2\text{S}_2$  ligand system  $(R)(S)\text{-}1,2\text{-}(5\text{-R-thiophene-}2\text{-CH=N})_2\text{-cyclohexane}$

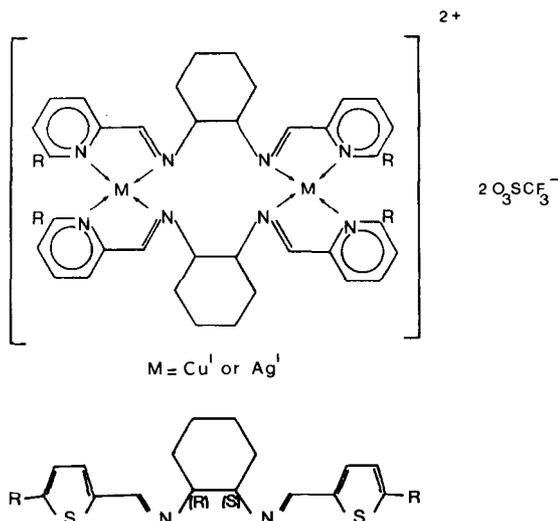


Fig. 1. Schematic representations of: structure of the complexes  $[M_2\{(R)(S)\text{-}1,2\text{-}(6\text{-R-py-}2\text{-CH=N})_2\text{-cyclohexane}\}_2](\text{O}_3\text{SCF}_3)_2$  ( $R = \text{H}$  or  $\text{Me}$ ) (top); the  $\text{N}_2\text{S}_2$  ligand system  $(R)(S)\text{-}1,2\text{-}(5\text{-R-thiophene-}2\text{-CH=N})_2\text{-cyclohexane}$  ( $R = \text{H}$  or  $\text{Me}$ )\*\* (bottom).

$\text{-}2\text{-CH=N})_2\text{-cyclohexane}$  ( $R = \text{H}$  or  $\text{Me}$ )\*\* (see Fig. 1) with copper(I) and silver(I) since in this system the two outer coordinating sites, *i.e.* the S-donor atoms may or may not coordinate.

In this paper is shown that *i*) in striking contrast with the  $\text{N}_4$ -donor ligand, the  $\text{N}_2\text{S}_2$  system produces both dinuclear and mononuclear copper(I) and silver(I) complexes having  $[M_2(\text{N}_2\text{S}_2)_2]^{2+}$  and  $[M(\text{N}_2\text{S}_2)]^+$  stoichiometries and *ii*) according to X-ray crystal and molecular structures of  $[M(\text{N}_2\text{S}_2)]^+\text{-O}_3\text{SCF}_3^-$  each  $\text{N}_2\text{S}_2$  ligand is bonded monodentate *via* one N-donor atom. The remaining N and two S-donor atoms are surrounding the  $M^+$  centre as a result of the constraining ligand skeleton.

The  $[M_2(\text{N}_2\text{S}_2)_2]^{2+}(\text{O}_3\text{SCF}_3)_2$  (*Ia*,  $M = \text{Cu}^{\text{I}}$ ; *Ib*,  $M = \text{Ag}^{\text{I}}$ ) complexes were obtained in quantitative yields from the 1/1 molar reactions of  $(R)(S)\text{-}1,2\text{-}(5\text{-Me-thiophene-}2\text{-CH=N})_2\text{-cyclohexane}$  with  $[\text{Cu}^{\text{I}}(\text{O}_3\text{SCF}_3)] \cdot \frac{1}{2} \text{C}_6\text{H}_6$  and  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  in benzene and methanol, respectively. Based on the Field-Desorption mass spectra and the  $^1\text{H}$  and INEPT  $^{109}\text{Ag}$  solution NMR data of the complexes *Ia* and *Ib*, a dinuclear structure is proposed similar to that shown for the copper(I) and silver(I) complexes of the  $\text{N}_4$  ligand system in Fig. 1 [3b]. Accordingly, it may be concluded that the  $\text{N}_2\text{S}_2$  ligand is likewise capable of acting as a di-bidentate ligand using

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\*\*In this paper we restrict ourselves to a discussion of the  $R = \text{Me}$  complexes.

the N as well as the S donor sites for coordinating to these metal ions.

Reactions of the  $[M(O_3SCF_3)]$  salts with the  $N_2S_2$  ligand system in  $\frac{1}{2}$  molar ratios resulted in the formation of the  $[M(N_2S_2)_2]^+(O_3SCF_3)^-$  complexes ( $2a$ ,  $M = Cu^I$ ;  $2b$ ,  $M = Ag^I$ ) in nearly quantitative yields.

In particular the isolation of the silver(I) complexes  $1b$  and  $2b$  is surprising since Ho and Livingstone [4] did not observe formation of silver(I) complexes with similar quadridentate  $N_2S_2$  systems.

In order to establish the exact molecular conformations in the  $[Cu(N_2S_2)_2]^+$  cation and to test the validity of the assumption that  $Cu^I$  can be replaced by  $Ag^I$  with retention of the structural features (cf.  $^{109}Ag$  NMR studies in ref. 3), the X-ray crystal structure determination of both complexes has been carried out.

**Crystal data** for the copper(I) complex  $2a$  ( $C_{37}H_{44}CuF_3N_4O_3S_5$ ):  $M = 873.6$ , monoclinic, space group  $P2_1/n$ ,  $Z = 4$ ,  $a = 13.934(5)$ ,  $b = 19.34(1)$ ,  $c = 16.127(5)$  Å,  $\beta = 97.90^\circ(2)$ ,  $U = 4305.8(1)$  Å<sup>3</sup>;  $D_{calc} = 1.348$  g/cm<sup>3</sup>,  $D_{obs} = 1.347$  g/cm<sup>3</sup> (by flotation in 1,2-dibromo-ethane and n-heptane)  $\mu(Cu-K\alpha) = 33.33$  cm<sup>-1</sup>. All crystals of the sample were twinned. Diffractometer data were collected for a specimen with an approximate 0.63:0.37 twinning ratio. The current  $R$  value is 11.9% for 2983 unique reflections and further refinement is in progress. In view of the status of this refinement of the  $Cu^I$  structure only the data of  $[Ag(N_2S_2)_2]^+(O_3SCF_3)^-$  ( $2b$ ) will be discussed further.

**Crystal data** for the silver(I) complex  $2b$  ( $C_{37}H_{44}AgF_3N_4O_3S_5$ ):  $M = 917.9$ , triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ,  $a = 9.900(4)$ ,  $b = 11.465(4)$ ,  $c = 19.423(6)$  Å,  $F(000) = 944$ ,  $U = 2082.7$  Å<sup>3</sup>,  $D_{calc} = 1.464$  g/cm<sup>3</sup>,  $D_{obs} = 1.459$  g/cm<sup>3</sup> (by flotation in 1,2-dibromo-ethane and n-heptane)  $\alpha = 106.10^\circ(3)$ ,  $\beta = 99.95^\circ(3)$ ,  $\gamma = 90.38^\circ(3)$ . The structure determination of  $2b$  was carried out with 5124 unique reflections. Data were collected on an ENRAF: NONIUS CAD 4 diffractometer using Zr-filtered  $MoK\alpha$  ( $\mu = 7.7$  cm<sup>-1</sup>) radiation in the  $\omega/2\theta$  scan mode. The structure was solved by standard Patterson and Fourier techniques and refined by anisotropic blocked full-matrix least-squares techniques with the programme ILIAS\* to a final  $R$  value of 3.8%. Hydrogen atoms were refined in the riding mode on their neighbouring carbon atom\*\*.

The molecular geometries of both  $[M(N_2S_2)_2]^+$  cations  $2a$  and  $2b$  may be considered to be similar. The differences in bond lengths and bond angles

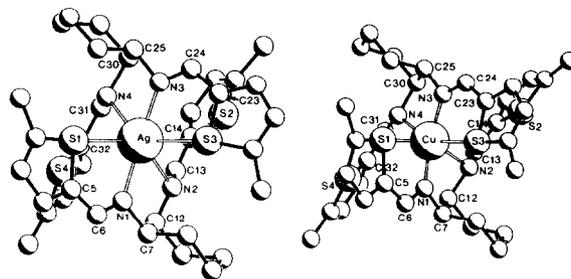


Fig. 2. PLUTO drawing of the  $[M\{(R)(S)\text{-}1,2\text{-}(5\text{-Me-thiophene-}2\text{-CH=N)}_2\text{-cyclohexane}\}_2]^+$  cations,  $[M = Cu^I, 2a; M = Ag^I, 2b]$ . Hydrogen atoms are omitted for clarity. Relevant bond distances (Å) and bond angles are (values for  $M = Cu^I, 2a$  between brackets):  $M-N(1)$ , 2.273(3) [1.891(2)];  $M-N(2)$ , 2.551(3) [2.513(2)];  $M-N(3)$ , 2.279(3) [1.929(2)];  $M-N(4)$ , 2.516(3) [2.255(3)];  $M-S(1)$ , 3.058(1) [2.959(6)];  $M-S(2)$ , 3.637(1) [4.055(6)];  $M-S(3)$ , 3.106(1) [3.152(6)];  $M-S(4)$ , 3.475(1) [3.735(6)];  $N(1)-M-N(3)$ ,  $153.3^\circ(1)$  [ $156.8^\circ(1)$ ];  $N(2)-M-N(4)$ ,  $97.6^\circ(1)$  [ $91.6^\circ(1)$ ];  $S(1)-M-S(3)$ ,  $98.5^\circ(1)$  [ $74.8^\circ(2)$ ];  $N(1)-M-S(1)$ ,  $70.2^\circ(1)$  [ $77.6^\circ(6)$ ];  $S(2)-M-S(4)$ ,  $114.7^\circ(1)$  [ $138.6^\circ(2)$ ];  $N(1)-M-S(2)$ ,  $123.8^\circ(1)$  [ $117.0^\circ(6)$ ].

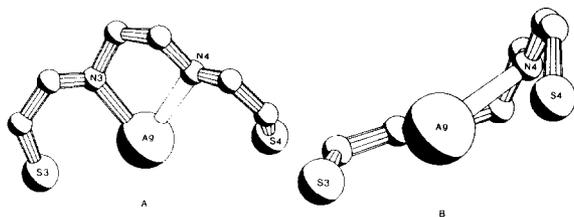


Fig. 3. The  $S(3) C(23) C(24) N(3) C(25) C(30) N(4) C(31) C(32) S(4)$  chain: a) viewed perpendicular on the  $N(3)-Ag-C(24)$  plane, b) projection down the  $Ag-N(3)$  bond.

can be accounted for by the differences in the  $Cu^I$  and  $Ag^I$  ionic radii (see Fig. 2).

When the conformations of the two ligand skeletons surrounding the  $Ag^I$  centre are analyzed (see Fig. 3) it is surprising to find that each  $N_2S_2$  ligand is bonded *via* only one N atom (short  $Ag-N(1)$  2.273(3) Å and  $Ag-N(3)$  2.279(3) Å). The extent of interaction of the remaining three donor sites of each  $N_2S_2$  ligand with the metal centre, positioned at distances 2.551(3) Å for  $N(2)$  [2.516(3) Å for  $N(4)$ ], 3.058(1) for  $S(1)$  [3.106(1) for  $S(3)$ ] and 3.637(1) for  $S(2)$  [3.475(1) for  $S(4)$ ], can be deduced from the orientation of the N and S lone pairs. It is observed that (see Fig. 3):

i, Each 5-Methiophene-2-CH=N grouping in the  $N_2S_2$  ligand has the E configuration around the C=N bonds (with distances which are within the range expected for C=N double bonds),

ii, the thiophene rings and the CH=N moieties are coplanar, and

\*ILIAS-A DG-Eclipse/S 230-minicomputer crystallographic programme package derived from G. Sheldrick's SHELX-76.

\*\*The atomic coordinates of this work are available on request from the author (A.L.S.).

iii, the N(1) C(7) C(12) N(2) [N(3) C(25) C(30) N(4)] dihedral angle, *i.e.* the conformation of the C–C bond connecting the two 5-Me-thiophene-2-CH=N groupings, is  $56.7^\circ(4)$  [ $55.4^\circ(4)$ ].

As a consequence the lone pairs of these three donor atoms are hardly (N(2) [N(4)] and S(1) [S(3)] or not at all (S(2) [S(4)]) directed towards the  $M^+$  centre. Accordingly, it may be concluded that the  $N_2S_2$  ligand is primarily bonded via one imine N atom. The two strong M–N ( $M = Cu^I$  or  $Ag^I$ ) interactions are almost linearly arranged [*e.g.* N(1)–Ag–N(3)  $153.3^\circ(1)$ ], a fact which is in line with the preference of IB metal centres for a linear coordination geometry [1b]. In addition to this two coordination, the other N and S donor sites are positioned in the metal cations environment as a result of the constraint of the  $N_2S_2$  ligand\* and thus mimics to some extent the influence of the rigidity of protein skeletons on the coordination geometry of the copper sites in for instance 'blue' proteins.

Further studies, which involve a detailed structural study of the  $Cu^{II}$  complexes of the  $N_2S_2$  donor ligand systems as well as measurements of the  $Cu^I/Cu^{II}$  redox potential by cyclic voltammetry, are now in progress.

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\*NMR results show that when the cyclohexanediyl group is replaced by a  $CH_2-CH_2$  bridge the ligand skeleton becomes more flexible.

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