Copper(I) and Silver(I) Ions in Unusual poly Donor-atom Environments; X-ray Crystal and Molecular Structures of $[M\{(R)(S)\text{-}1,2\text{-}(5\text{-Me-thiophene-2-CH=N})_2\text{-cyclohexane}\}_2](O_3SCF_3)$, M = Cu^I or Ag^I

GERARD C. VAN STEIN, GERARD VAN KOTEN*

Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

ANTHONY L. SPEK, ALBERT J. M. DUISENBERG and ENNO A. KLOP

Department of Structural Chemistry, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

Received February 23, 1983

Coordination properties of Cu^I and Cu^{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*)-1,2-(6-R-py-2-CH=N)$_2$-cyclohexane (R = H or Me), in which the inner two N-donor sites are connected by the (*R*)(*S*)-1,2-cyclohexanediyl ring, act as di-bidentate ligands binding two Cu^I or Ag^I atoms (see Fig. 1) [2]. The application of INEPT ^{15}N and ^{109}Ag NMR spectroscopy revealed that the structural features found for the silver(I) complex $[Ag_2\{(R)(S)\text{-}1,2\text{-}(py\text{-}2\text{-}CH{=}N)_2\text{-cyclohexane}\}_2]\text{-}(O_3SCF_3)_2$ in the solid, with characteristic alternating two short and two long Ag–N distances around the distorted tetrahedral silver centres [2], are retained in solution [3]. Attempts to form mononuclear Cu^I or Ag^I complexes with these N_4-donor ligands, using ½ Cu^I- or Ag^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 N_2S_2 ligand system (*R*)(*S*)-1,2-(5-R-thiophene-2-CH=N)$_2$-cyclohexane (R = H or 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.

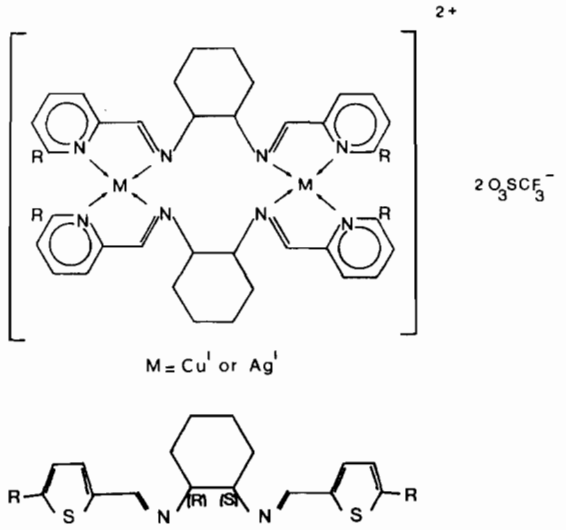

Fig. 1. Schematic representations of: structure of the complexes $[M_2\{(R)(S)\text{-}1,2\text{-}(6\text{-R-py-2-CH=N})_2\text{-cyclohexane}\}_2]\text{-}(O_3SCF_3)_2$ (R = H or Me) (top); the N_2S_2 ligand system (*R*)(*S*)-1,2-(5-R-thiophene-2-CH=N)$_2$-cyclohexane (R = H or Me)** (bottom).

In this paper is shown that *i*) in striking contrast with the N_4-donor ligand, the N_2S_2 system produces both dinuclear and mononuclear copper(I) and silver(I) complexes having $[M_2(N_2S_2)_2]^{2+}$ and $[M(N_2S_2)_2]^+$ stoichiometries and *ii*) according to X-ray crystal and molecular structures of $[M(N_2S_2)_2]^+\text{-}O_3SCF_3^-$ each N_2S_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 $[M_2(N_2S_2)_2]^{2+}(O_3SCF_3^-)_2$ (*1a*, M = Cu^I; *1b*, M = Ag^I) complexes were obtained in quantitative yields from the 1/1 molar reactions of (*R*)(*S*)-1,2-(5-Me-thiophene-2-CH=N)$_2$-cyclohexane with $[Cu^I(O_3SCF_3)]$. ½ C_6H_6 and $[Ag(O_3SCF_3)]$ in benzene and methanol, respectively. Based on the Field-Desorption mass spectra and the ^1H and INETP ^{109}Ag solution NMR data of the complexes *1a* and *1b*, a dinuclear structure is proposed similar to that shown for the copper(I) and silver(I) complexes of the N_4 ligand system in Fig. 1 [3b]. Accordingly, it may be concluded that the N_2S_2 ligand is likewise capable of acting as a di-bidentate ligand using

*Author to whom correspondence should be addressed.

**In this paper we restrict ourselves to a discussion of the R = Me complexes.

0020-1693/83/$3.00

© Elsevier Sequoia/Printed in Switzerland

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 ½ 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, β = 97.90°*(2)*, U = 4305.8(1) Å^3; D_{calc} = 1.348 g/cm^3, D_{obs} = 1.347 g/cm^3 (by flotation in 1,2-dibromo-ethane and n-heptane) $\mu(Cu\text{-}K_\alpha)$ = 33.33 cm^{-1}. All crystals of the sample were twined. 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^3, D_{calc} = 1.464 g/cm^3, D_{obs} = 1.459 g/cm^3 (by flotation in 1,2-dibromo-ethane and n-heptane) α = 106.10°(3), β = 99.95°(3), γ = 90.38°(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 Mo-K_α (μ = 7.7 cm^{-1}) 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 can be accounted for by the differences in the Cu^I an Ag^I ionic radii (see Fig. 2).

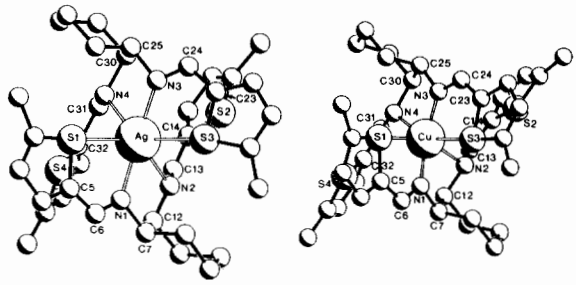

Fig. 2. PLUTO drawing of the $[M\{(R)(S)\text{-}1,2\text{-}(5\text{-Me-thiophene-2-CH=N})_2\text{cyclohexane}\}_2]^+$ cations, [M = Cu^I, *2a*; M = Ag^I, *2b*]. Hydrogen atoms are omitted for clarity. Relevant bond distances (Å) and bond angles are (values for M = Cu^I, *2a* between brackets): M–N(1), 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°(1) [156.8°(1)]; N(2)–M–N(4), 97.6°(1) [91.6°(1)]; S(1)–M–S(3), 98.5°(1) [74.8°(2)]; N(1)–M–S(1), 70.2°(1) [77.6°(6)]; S(2)–M–S(4), 114.7°(1) [138.6°(2)]; N(1)–M–S(2), 123.8°(1) [117.0°(6)].

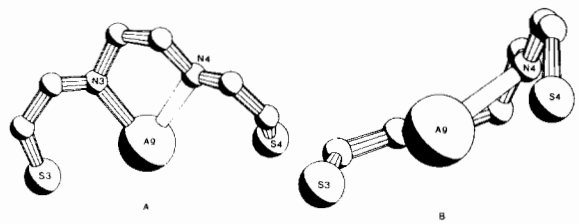

Fig. 3. The S(3) C(23) C(24) N(3) C(25) C(30) N(4) C(31) C(32) S(4) chain: a) viewed perpendicular on the N(3)–Ag–C(24) plane, b) projection down the Ag–N(3) bond.

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°(4) [55.4°(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°(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.

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

Acknowledgement

We thank Dr. D. M. Grove and Prof. K. Vrieze for helpful discussions, Prof. N. M. M. Nibbering and coworkers for the Field-Desorption mass spectrometric measurements, and the Netherlands Foundation for Chemical Research (SON) (in part) and the Netherlands Organization of Pure Research (ZWO) (A.L.S.) for financial support.

References

1 (a) L. Casella and J. A. Ibers, *Inorg. Chem., 20,* 2438 (1918);
(b) M. H. Schilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem., 21,* 2637 (1982).
2 G. C. van Stein, H. van der Poel. G. van Koten, A. L. Spek, A. J. M. Duisenberg and P. S. Pregosin, *J. Chem. Soc., Chem. Commun.,* 1016 (1980).
3 (a) C. Brevard, G. C. van Stein and G. van Koten, *J. Am. Chem. Soc., 103,* 6746 (1981).
(b) G. C. van Stein, G. van Koten, A. L. Spek, A. J. M. Duisenberg and C. Brevard, to be submitted.
4 R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem., 18,* 659 (1965).
5 (a) P. G. Beckingsale, A. T. Morcom, C. E. F. Rickard and T. N. Waters, *J. Chem. Soc., Dalton,* 2135 (1977).
(b) B. M. Cressey, E. D. McKenzie and S. Yates, *J. Chem. Soc. (A),* 2677 (1971).
6 F. J. Rietmeyer, P. J. M. W. L. Birker, S. Gorter and J. Reedijk, *J. Chem. Soc., Dalton,* 1191 (1982).