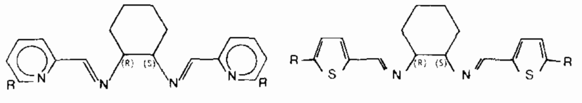

Fig. 1. The N_4 and N_2S_2 ligand system (R = H or Me).

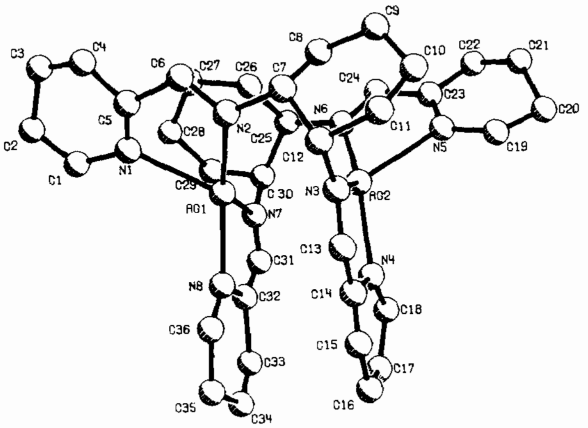

Fig. 2. PLUTO drawing of the $[Ag_2(N_4)_2]^{2+}$ unit.

$[M_2(N_4)_2]^{2+}$ $2O_3SCF_3^-$ complexes. The X-ray structure of the silver(I) complex showed that each ligand acts in a di-bidentate manner bridging the two metal centres (see Fig. 2). The silver ions have distorted tetrahedral geometries with each Ag^I centre taking part in two short Ag–N (2.25 Å) and two long Ag–N (2.43 Å) interactions. The N–Ag–N bond angle between the two short Ag–N bonds is *circa* 150° [1].

The copper(I) and silver(I) complexes are very stable and do not react further either with excess N_4 ligand or with H_2O, O_2 and CO. However, detailed ^1H studies have shown that inter- and intramolecular exchange (*e.g.* metal-ion or ligand exchange) occurs. These will be discussed. In contrast to these results reactions of the N_2S_2 ligand system with $M(O_3SCF_3)$ (M = Cu^I or Ag^I) give rise to two different types of complexes, *i.e.* a dimeric $[M_2(N_2S_2)_2]^{2+}2O_3SCF_3^-$ and a monomeric $[M(N_2S_2)_2]^+O_3SCF_3^-$ complex. According to ^1H and ^{109}Ag NMR data the dimeric complex has a structure similar to that found for the $[M_2(N_4)_2]^{2+}$ $2O_3SCF^{3-}$ complex. However, in the $[M_2(N_2S_2)_2]^{2+}$ dication the imine-N atoms of the N_2S_2 ligands have strong interactions with the metal centres, while the thiophene-S atoms coordinate only weakly with the metal-IB centre. This coordination behaviour is reflected by the reactivity of the copper(I) complex, which reacts rapidly with CO (ν_{CO} = 2092 cm^{-1}). An X-ray study is underway.

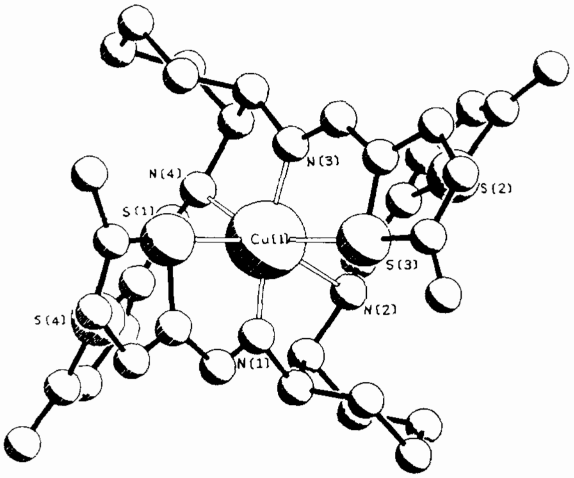

Fig. 3. PLUTO drawing of the $[Cu^I(N_2S_2)_2]^+$ cation. The $[Ag^I(N_2S_2)_2]^+O_3SF_3^-$ complex has a similar geometry.

The X-ray structures of the mononuclear $[M(N_2S_2)_2]^+$ $O_3SCF_3^-$ complexes have been resolved for M = Cu^I and M = Ag^I to establish the exact molecular conformations and to test the validity of the assumption that copper(I) can be replaced by silver(I) with retention of the structural features [2]. As a result of the constraint of the N_2S_2 system, each ligand is primarily bonded to the metal centre (M = Cu or Ag) by one imine-N atom [N(1) and N(3)] with the remaining three hetero-atoms being held in close proximity to the metal centre (see Fig. 3: M = Cu). These complexes do not react with H_2O, O_2 and CO.

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R14

Application of INEPT ^{109}Ag and ^{15}N NMR Spectroscopy for the Study of Metal–Ligand Interactions of Silver Analogues of Copper(I) Model Compounds

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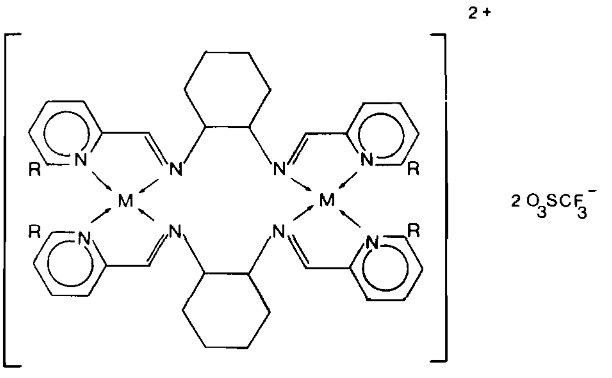
Because of the presence of copper (in its reduced state) at active sites in proteins it has become very



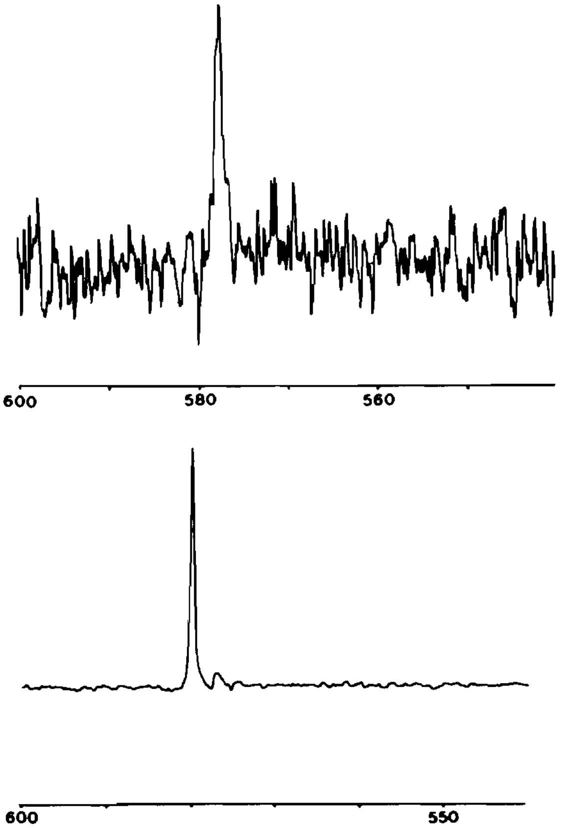


Fig. 1. ^{109}Ag NMR spectra of $[Ag_2(N_4)_2]^{2+}2O_3SCF_3^-$ (R = H) in CD_3OD. Left, direct observation, 15 mm probe, 55.000 scans; right, INEPT sequence, 10 mm probe, 10.000 scans, same solution (^{1}H decoupled).

important to study copper(I) model compounds by spectroscopic techniques.

We now report that if copper(I) in model complexes can be substituted by silver(I) with retention of the structural features then ^{107}Ag or ^{109}Ag NMR spectroscopy (natural abundances 50%, I = ½) using the recently developed polarization transfer sequence INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) [1] provides an excellent tool for studying the metal IB–ligand interactions.

^{1}H NMR studies show that the analogous copper(I) and silver(I) complexes of potentially quadridentate N_4 (*R*)(*S*)-1,2-(6-R-pyridine-2-CH=N)$_2$-cyclohexane (R = H or Me) as well as the N_2S_2 donor ligand (*R*)-(*S*)-1,2-(5-R-thiophene-2-CH=N)$_2$-cyclohexane (R = H or Me) have similar structures (confirmed by X-ray studies [2]). However, study of the direct coordination sphere and copper(I)–ligand interactions in these model complexes by Cu NMR is hampered by the large quadrupole moments of both ^{63}Cu and ^{65}Cu (natural abundances 70 and 30% respectively, I = 3/2).

We have measured directly ^{109}Ag NMR (INEPT) spectra with large enhancements in signal to noise and enormous experimental time saving (a factor 400–500) as compared to the conventional methods (see Fig. 1) [3]. The influence of the nature of the hetero-atoms coordinating the metal centre is directly reflected in the chemical shift differences of the ^{109}Ag resonances.

It is shown that for silver(I) coordination complexes information about the ligand-to-metal interactions can be obtained by using not only direct ^{109}Ag NMR, but also INEPT ^{15}N NMR spectroscopy. In particular the ^{15}N NMR (INEPT) spectra of the silver(I) complexes $[M_2(N_4)_2]^{2+}$ $2O_3SCF_3^-$ show that the structure of these complexes, as found in the solid by X-ray methods, in which each metal ion has a distorted tetrahedral coordination geometry of four N-atoms, is fully retained in solution. From different $^1J(^{15}N-^{107,109}Ag)$ coupling constants the relative bond strengths of the various Ag–N interactions can be deduced.

Where Cu^I can be substituted by Ag^I either in coordination (model) complexes or biological systems (bovine superoxide dismutase [4]) INEPT ^{109}Ag NMR spectroscopy has potential as a novel technique for the study of the coordinating properties of the metal centres.

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