

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

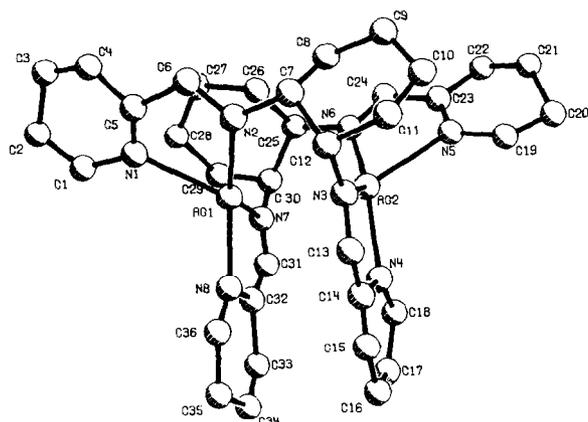


Fig. 2. PLUTO drawing of the  $[Ag_2(N_4)_2]^{2+}$  unit.

$[M_2(N_4)_2]^{2+} 2O_3SCF_3^-$  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*  $150^\circ$  [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  $CO$  ( $\nu_{CO} = 2092\text{ cm}^{-1}$ ). An X-ray study is underway.

The X-ray structures of the mononuclear  $[M(N_2S_2)_2]^+ O_3SCF_3^-$  complexes have been resolved for  $M =$

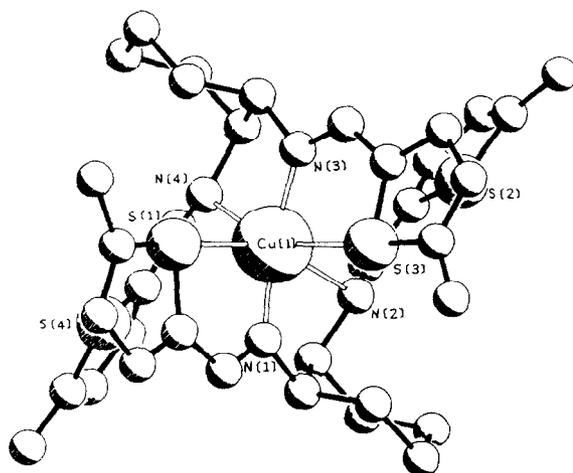


Fig. 3. PLUTO drawing of the  $[Cu^I(N_2S_2)_2]^+$  cation. The  $[Ag^I(N_2S_2)_2]^+ O_3SF_3^-$  complex has a similar geometry.

$Cu^I$  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

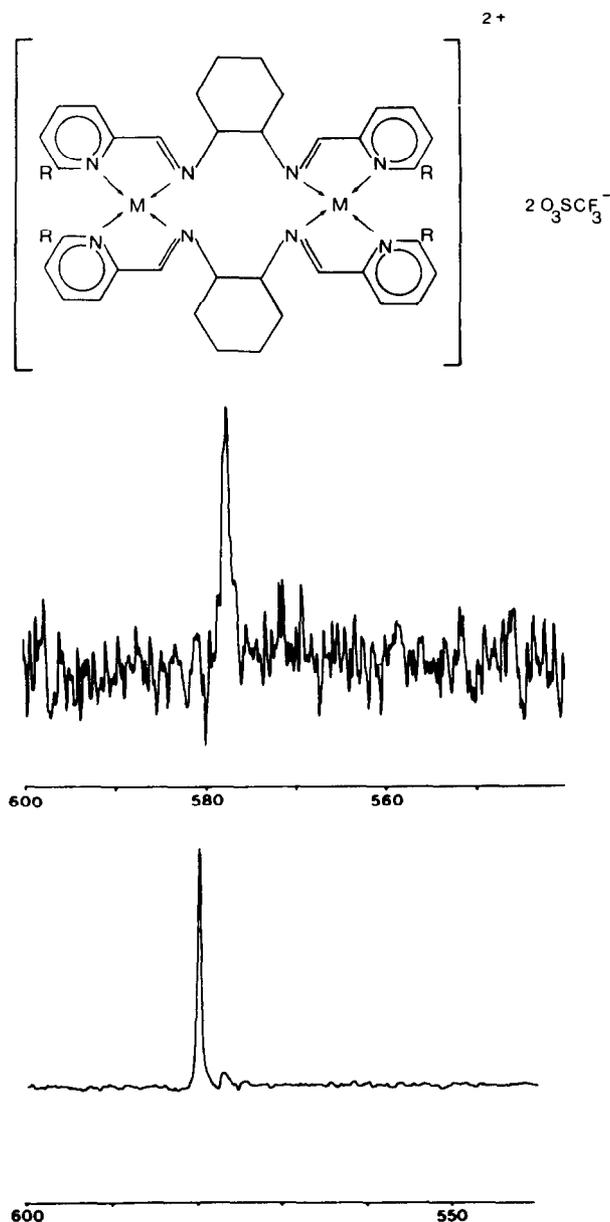


Fig. 1.  $^{109}\text{Ag}$  NMR spectra of  $[\text{Ag}_2(\text{N}_4)_2]^{2+} 2\text{O}_3\text{SCF}_3^-$  ( $\text{R} = \text{H}$ ) in  $\text{CD}_3\text{OD}$ . Left, direct observation, 15 mm probe, 55,000 scans; right, INEPT sequence, 10 mm probe, 10,000 scans, same solution ( $^1\text{H}$  decoupled).

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  $^{107}\text{Ag}$  or  $^{109}\text{Ag}$  NMR spectroscopy (natural abundances 50%,  $I = \frac{1}{2}$ ) using the recently developed polarization transfer sequence INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) [1] provides an excellent tool for studying the metal-ligand interactions.

$^1\text{H}$  NMR studies show that the analogous copper(I) and silver(I) complexes of potentially quadridentate  $\text{N}_4$  ( $R$ )( $S$ )-1,2-(6- $R$ -pyridine-2- $\text{CH}=\text{N}$ ) $_2$ -cyclohexane ( $\text{R} = \text{H}$  or  $\text{Me}$ ) as well as the  $\text{N}_2\text{S}_2$  donor ligand ( $R$ )( $S$ )-1,2-(5- $R$ -thiophene-2- $\text{CH}=\text{N}$ ) $_2$ -cyclohexane ( $\text{R} = \text{H}$  or  $\text{Me}$ ) 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  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  (natural abundances 70 and 30% respectively,  $I = 3/2$ ).

We have measured directly  $^{109}\text{Ag}$  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  $^{109}\text{Ag}$  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  $^{109}\text{Ag}$  NMR, but also INEPT  $^{15}\text{N}$  NMR spectroscopy. In particular the  $^{15}\text{N}$  NMR (INEPT) spectra of the silver(I) complexes  $[\text{M}_2(\text{N}_4)_2]^{2+} 2\text{O}_3\text{SCF}_3^-$  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  $^1J(^{15}\text{N}-^{107,109}\text{Ag})$  coupling constants the relative bond strengths of the various Ag–N interactions can be deduced.

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

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