

TABLE 2. Binding of adenine and guanine derivatives in square-planar (sq-pl) and octahedral (oct) complexes.<sup>a</sup>

Complex	Geometry	Adenine binding site	Guanine binding site
[Co(acac) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup>	oct	N(7)	—
[Rh <sub>2</sub> (acetate) <sub>4</sub> ]		N(7)	—
[Pt(acac)Cl <sub>2</sub> ] <sup>-</sup>	sq-pl	N(1),N(7)	N(7)
[RhCl <sub>3</sub> (dmsO) <sub>3</sub> ]	oct	N(7)	—
[RuCl <sub>2</sub> (dmsO) <sub>4</sub> ]	oct	N(7)	—
[PtCl <sub>2</sub> (dmsO) <sub>2</sub> ] <sup>-</sup>	sq-pl	N(1),N(7)	N(7)
[PtCl <sub>3</sub> (R <sub>2</sub> SO)] <sup>-</sup>	sq-pl	N(1),N(7)	N(7)

<sup>a</sup> The specific bases used and the complexes formed are omitted for clarity.

The effect of hydrogen-bonding interactions in the case where hydrogen-bond donor ligands are present, such as *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], can be expected to be different. The presence of more than one hydrogen in the ammine ligand allows for a considerably wider range of interaction, both intra- and inter-molecular. Whether these differences can explain the activity and specificity of the platinum complex in its antineoplastic activity is under investigation.

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## Quadridentate Nitrogen Donor Ligands acting as Bridging Di-bidentates; X-Ray Crystal and Molecular Structure of [Ag<sub>2</sub>{μ-(R)(S)-1,2-[(2-C<sub>5</sub>H<sub>4</sub>N)- C(H)=N]<sub>2</sub>-cyclohexane}<sub>2</sub>][O<sub>3</sub>SCF<sub>3</sub>]<sub>2</sub> and the Observation of <sup>3</sup>J(<sup>107,109</sup>Ag-<sup>1</sup>H) in the <sup>1</sup>H N.M.R. Spectrum of the Dinuclear [Ag<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> Cation

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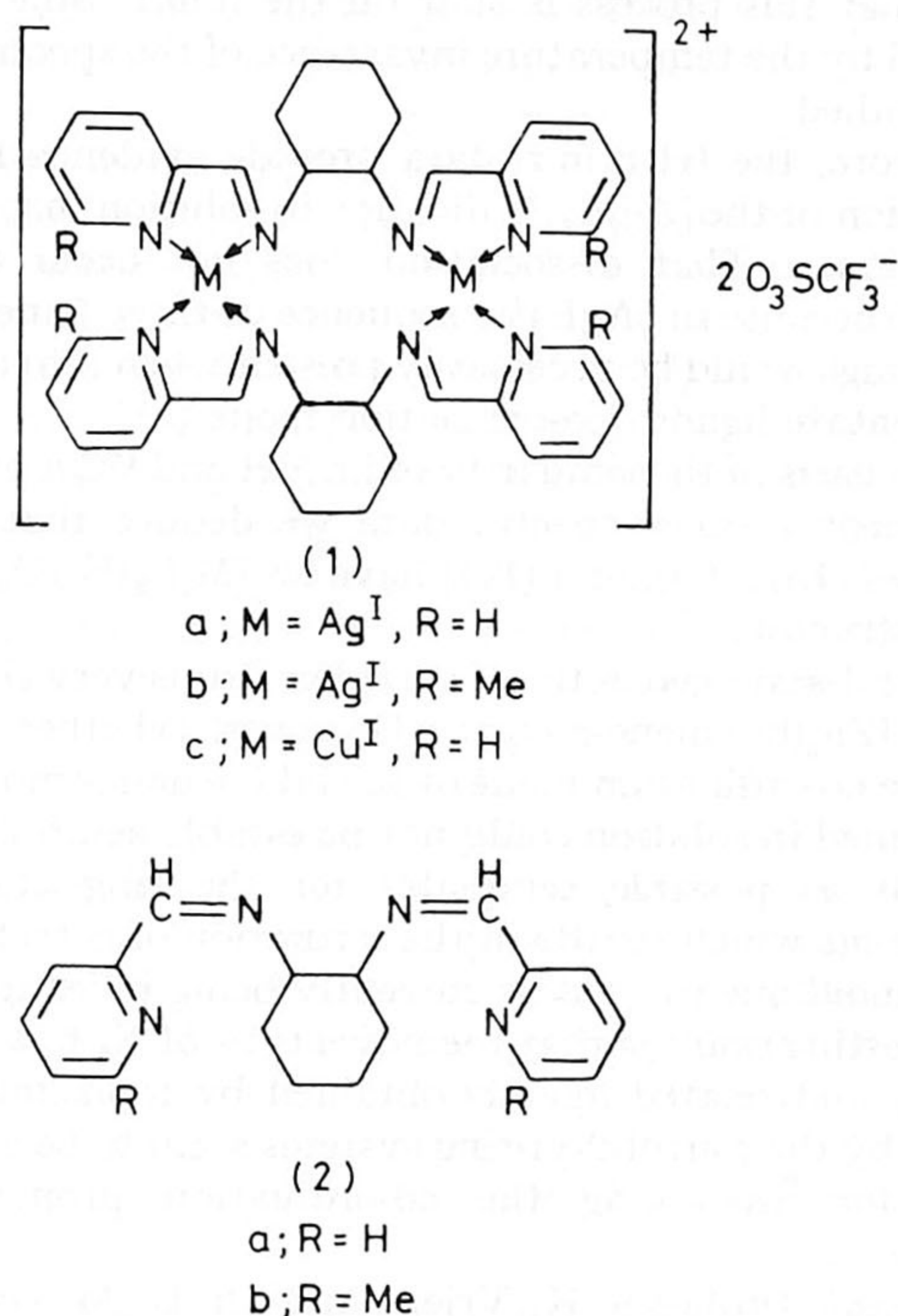
**Summary** The quadridentate N-donor ligands (R)(S)-1,2-[(6-R-2-C<sub>5</sub>H<sub>3</sub>N)C(H)=N]<sub>2</sub>-cyclohexane (R = H, Me), upon reaction with [M(O<sub>3</sub>SCF<sub>3</sub>)] (M = Ag<sup>I</sup> or Cu<sup>I</sup>), behave as bridging di-bidentate ligands to form dimeric complexes such as the title complex for which an X-ray crystal structure was obtained; <sup>3</sup>J(<sup>107,109</sup>Ag-<sup>1</sup>H) is observed in the <sup>1</sup>H n.m.r. spectra of the dinuclear [Ag<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> cations.

RECENTLY, it has been reported that 1,4-diazabuta-1,3-diene systems, R'-N=C(R)-C(R)=N-R', can function either in a σ-N-unidentate<sup>1</sup> or in a σσ-NN'-chelating<sup>2</sup> manner as well as in a variety of bridging modes.<sup>1,3</sup> The 2,5-diazahexa-1,5-diene derivatives [*p*-tolyl-C(H)=N]<sub>2</sub>-R' [R' = 1,2-ethane or (R)(S)-1,2-cyclohexane] are also capable of coordinating, in a bridging mode, to metal centres which have a preference for a square planar co-ordination geometry.<sup>4</sup>



Extension of the number of co-ordination sites by replacing the *p*-tolyl by 2-pyridyl groups results in the novel quadridentate ligands  $[(2-C_5H_4N)C(H)=N]_2-R'$ . Such  $N_4$ -ligands give rise either to dinuclear metal complexes, in which the ligand acts as a bridging di-bidentate (i), or to mononuclear metal complexes in which the  $N_4$ -ligand acts as a quadridentate ligand (ii).

During our studies of these quadridentate nitrogen donor ligands we have investigated the influence of the number of C-atoms and the conformation of the hydrocarbon chain ( $R'$ ) connecting the two  $-N=C-C=N-$  ligand sites on the mode of co-ordination, (i) or (ii).



We now report the synthesis and structural characterization of  $[Ag_2\{\mu-(R)(S)-1,2-[(6-R-2-C_5H_3N)C(H)=N]_2-cyclohexane\}_2][O_3SCF_3]_2$  [(1a) and (1b)] and the related Cu<sup>I</sup> complex (1c). In these complexes we have found that the quadridentate  $N_4$ -ligands prefer co-ordination mode (i); firstly because of the preference of 4-co-ordinate Ag<sup>I</sup> and Cu<sup>I</sup> for non-planar co-ordination geometries and secondly because of the higher strain in a cyclic monomeric structure in co-ordination mode (ii).

The complexes (1a), (1b), and (1c) were synthesised by the reaction of  $(R)(S)-1,2-[(6-R-2-C_5H_3N)C(H)=N]_2-cyclohexane$  [(2a) and (2b)] with  $[M(O_3SCF_3)]$  (M = Ag<sup>I</sup> or Cu<sup>I</sup>) in methanol and were obtained in nearly quantitative yields. Pale yellow crystals of (1a) were formed by slow evaporation of a methanolic solution.

*Crystal data:*  $(C_{19}H_{20}AgF_3N_4O_3S)_2$ ,  $M = 1098.7$ , monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 10.412(2)$ ,  $b = 33.310-$

(8),  $c = 13.197(2)$  Å,  $\beta = 105.38(2)^\circ$ ;  $U = 4413.0$  Å<sup>3</sup>,  $D_{obs} = 1.65$  g/cm<sup>3</sup> (by flotation in 1,2-dibromoethane and CCl<sub>4</sub>),  $D_{calc} = 1.654$  g/cm<sup>3</sup>. The structure determination was carried out with 3092 independent reflexions  $I > 2.0\sigma(I)$ . Data were collected on an ENRAF-NONIUS CAD 4 diffractometer using Zr-filtered Mo- $K_\alpha$  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 program ILIAS† to a final  $R_F$  0.067 ( $R_{wF}$  0.07),  $w^{-1} = [\sigma^2(F) + 0.0027 F^2]/1.97$ . Hydrogen atoms were refined in the riding mode on their neighbouring carbon atom.‡ Figure 1

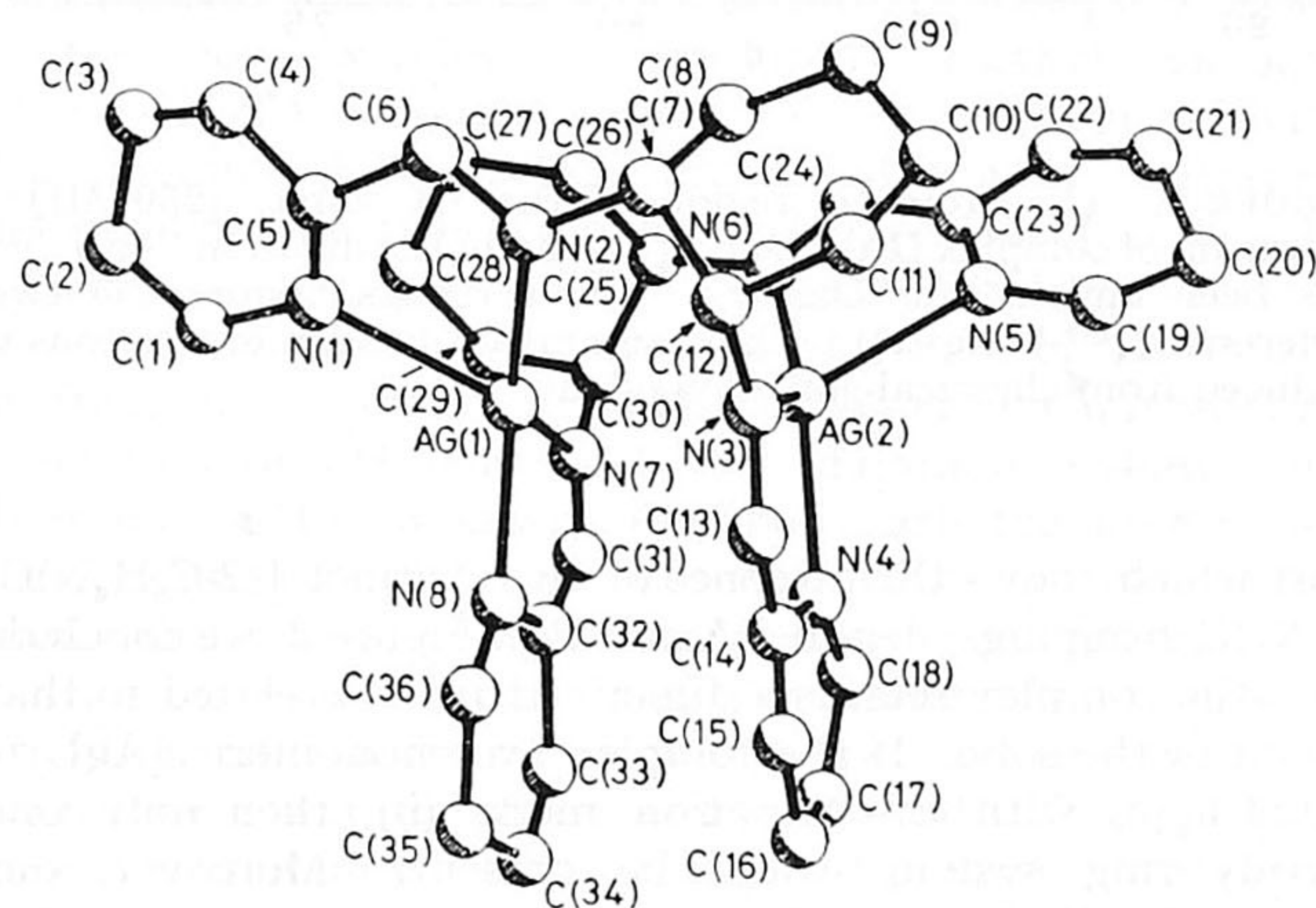


FIGURE 1. PLUTO drawing of  $[Ag_2L_2]^{2+}$  unit of  $[Ag_2\{\mu-(R)(S)-1,2-[(2-C_5H_4N)C(H)=N]_2-cyclohexane\}_2][O_3SCF_3]_2$ . Hydrogen atoms are omitted for clarity.

shows the molecular structure of the dication (1a) which consists of two Ag<sup>I</sup> centres, at a non-bonding distance of 3.254(2) Å, each co-ordinated by the N-atoms of two  $[(2-C_5H_4N)C(H)=N]$  units from the separate ligands (2a). Accordingly, each ligand bridges between 2 Ag<sup>I</sup> cations and thus acts as a di-bidentate (i). The Ag<sup>I</sup> cations have an irregular non-planar 4-co-ordinate geometry partly imposed by the small bite-angles of the bidentate  $[(2-C_5H_4N)C(H)=N]$  system of 71.1(4)—73.6(4)°. Such values are in the range generally found for related bidentates participating in 5-membered metal-chelate rings.<sup>1</sup> Each Ag<sup>I</sup> cation takes part in two short Ag-N [Ag(1)-N(2) 2.25(1), Ag(1)-N(8) 2.24(1), Ag(2)-N(4) 2.25(1), and Ag(2)-N(6) 2.24(1) Å] and two long Ag-N interactions [Ag(1)-N(1) 2.46(1), Ag(1)-N(7) 2.44(1), Ag(2)-N(3) 2.43(1), and Ag(2)-N(5) 2.43(1) Å] while the N-Ag-N angle between the two strongest bonded N-sites is *ca.* 150° [N(2)-Ag(1)-N(8) 149.5(4) and N(4)-Ag(2)-N(6) 144.3(4)°].

The dimeric nature of the complexes in solution could not be established directly with certainty, because (1a), (1b), and (1c) are only soluble in solvents such as methanol which are not suitable for accurate molecular-weight determinations. However, on the basis of solution <sup>1</sup>H n.m.r. data of

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

‡ The atomic co-ordinates of this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



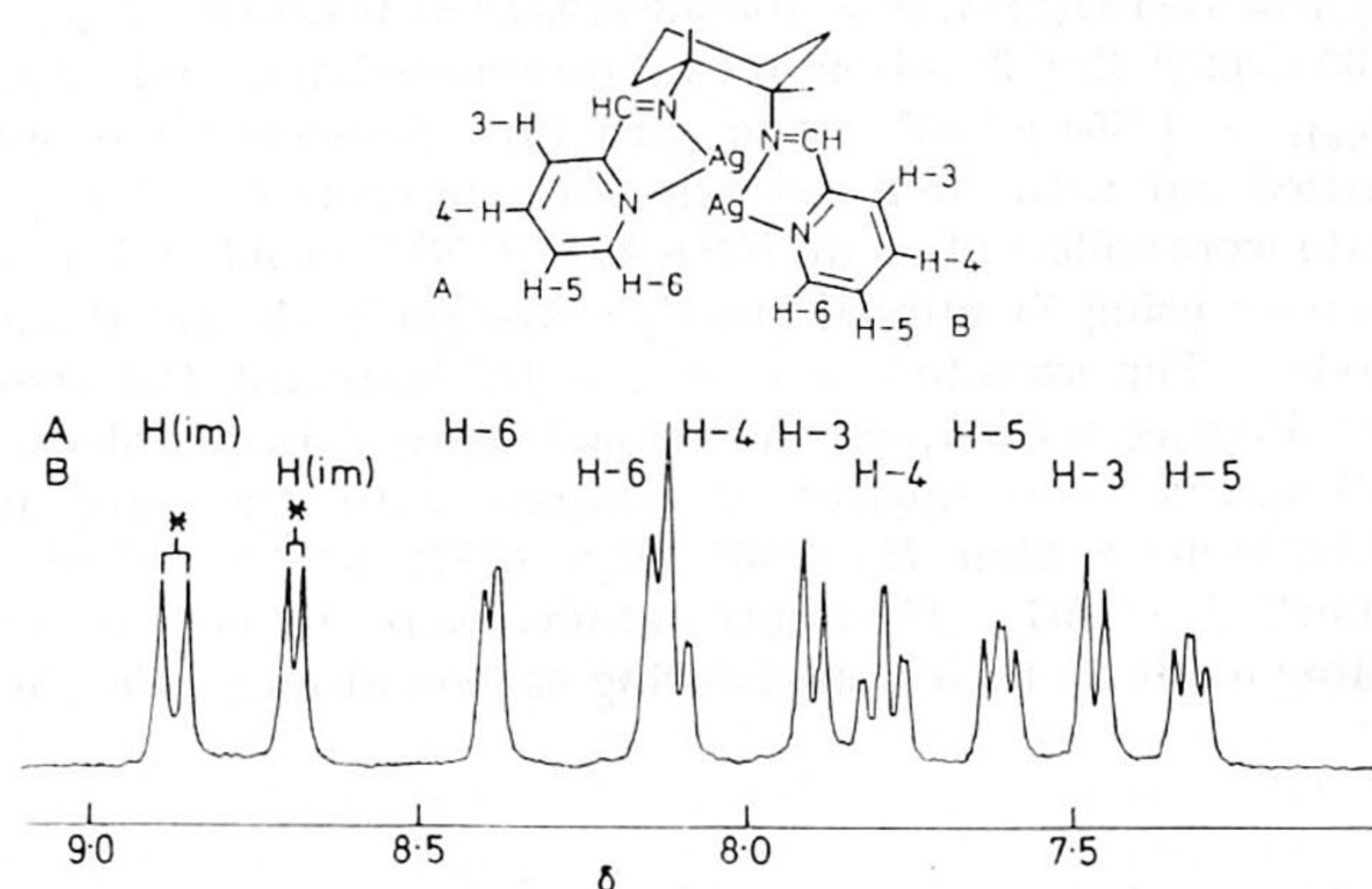


FIGURE 2. The aromatic region of the  $^1\text{H}$  n.m.r. (250 MHz) spectrum of complex (**1a**). (One  $\text{N}_4$ -ligand in the dication  $[\text{Ag}_2\text{L}_2]^{2+}$  has been omitted for clarity.) The asterisks denote the two different  $^3J(^{107,109}\text{Ag}-^1\text{H})$ . The assignment of the imine protons is deduced from chemical-shift behaviour.

(**1a**) which shows the presence of two distinct  $[(2-\text{C}_5\text{H}_4\text{N})\text{C}(\text{H})=\text{N}]$  groupings, denoted A and B in Figure 2, we conclude that the complex retains a dimeric structure related to that found in the solid. If the complex was monomeric  $[\text{AgL}]^+[\text{O}_3\text{SCF}_3]^-$ , with co-ordination mode (ii), then only one pyridyl-ring system would be present. Moreover, our chemical-shift data are also not in accordance with a possible 3-co-ordinate monomeric species containing a non-co-ordinated pyridyl-ring system. In both the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra we observe resonance patterns for two co-ordinated pyridyl-ring systems. The appropriate part of the  $^1\text{H}$  n.m.r. (250 MHz) spectrum of (**1a**) is shown in Figure 2. Interestingly, two imine-proton resonances are observed, both of which appear as doublets. The constancy of these splittings in the  $^1\text{H}$  n.m.r. (60, 100, and 250 MHz) spectra $\S$  suggests that these lines arise from spin-spin couplings.

A complete set of  $^1\text{H}$ - $^1\text{H}$  decoupling experiments (recorded at 250 MHz on a Bruker WM 250 spectrometer) established the assignments shown and indicated that each of the imine-protons couples with one Ag atom $\P$  [ $\delta$  8.69,  $^3J(^{107,109}\text{Ag}-^1\text{H})$  6.3 Hz and 8.87,  $^3J(^{107,109}\text{Ag}-^1\text{H})$  9.3 Hz]. Furthermore, this conclusion is confirmed by the absence of these splittings in the  $^1\text{H}$  n.m.r. of the related  $\text{Cu}^{\text{I}}$  complex (**1c**). More-

over, these decoupling experiments revealed that the exchange occurs between the two types of pyridyl-rings, A and B. For example, irradiation at the chemical-shift position of H-5 in the B ring ( $\delta$  7.33) strongly reduces the intensity of the corresponding H-5 multiplet ( $\delta$  7.62) in the A ring. The fact that the  $^3J(^{107,109}\text{Ag}-^1\text{H})$  remains unaffected over the whole temperature range studied (210–310 K) indicates that this process occurs intramolecularly. Studies on molecular models of (**1a**) suggest that exchange of ring A and B is possible by Ag-N(pyridine) bond-dissociation with retention of the Ag-N(imine) bond. This process must occur concertedly at both Ag centres and re-coordination then regenerates either of the two enantiomers of (**1a**). That this process is slow on the n.m.r. time scale is indicated by the temperature invariance of the spectra in the range studied.

Therefore, the  $^1\text{H}$  n.m.r. data provide evidence for non-dissociation of the  $[\text{Ag}_2\text{L}_2]^{2+}$  dication in solution into  $[\text{AgL}]^+$  monocations. That dissociation does not occur is most probably because in  $[\text{AgL}]^+$  a sequence of three 5-membered chelate rings would be necessarily present when (**2a**) acts as a quadridentate ligand [co-ordination mode (ii)].

On the basis of the similarity of i.r.,  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r., and field-desorption mass-spectra data we deduce that all the complexes (**1a**), (**1b**), and (**1c**) have an  $[\text{M}_2\text{L}_2]^{2+}[\text{O}_3\text{SCF}_3^-]_2$  type of structure.

The solid-state geometry of complex (**1a**) is very similar to that of  $[\text{Zn}_2(\text{biladiene-}a,c)_2]$ .<sup>5</sup> However, whether the didentate co-ordination mode of the biladiene-*a,c* molecule is also retained in solution could not be established.<sup>5</sup> The role of metals as possible templates for the ring closure of biladiene-*a,c* which results in the formation of corrinoid and porphyrinoid macrocycles is currently being investigated.<sup>5,6</sup> An interesting point is that the novel type of  $\text{N}_4$ -ligands (**2a**) and (**2b**) and related ligands obtained by replacing the 2-pyridyl- by the pyrrol-2-yl-ring systems seem to be excellent models for mimicking the co-ordination properties of biladiene-*a,c*.

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$\S$   $^1\text{H}$  n.m.r. (60 MHz) spectra were recorded in  $\text{CD}_3\text{OD}$  with  $\text{SiMe}_4$  as internal standard,  $^1\text{H}$  (90 and 250 MHz) and  $^{13}\text{C}$  n.m.r. (20 MHz) spectra were recorded in  $\text{CD}_3\text{OD}$  which was used as the internal reference.

$\P$  So far only a few  $^3J(^{107,109}\text{Ag}-^1\text{H})$  values have been reported (e.g. G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *Inorg. Chem.*, 1977, **16**, 1782 and references cited therein; H. Schmidbaur, J. Adlkofer, and W. Buchner, *Angew. Chem.*, 1973, **85**, 448). The  $^1\text{H}$  n.m.r. spectra of (**1b**) reveals  $^3J(^{107,109}\text{Ag}-^1\text{H})$  values of 7.5 ( $\delta$  8.79) and 10.5 Hz ( $\delta$  8.89).

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