

A case of four-coordinate silver(I) adopting a high energy planar geometry. Experiment and theory

Shubhamoy Chowdhury,^a Michael G. B. Drew^b and Dipankar Datta^{*a}

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icdd@mahendra.iacs.res.in

^b Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

Received (in Montpellier, France) 29th November 2002, Accepted 8th January 2003

First published as an Advance Article on the web 7th April 2003

The ligands PhL and MeL are obtained by condensing 2-formylpyridine with benzil dihydrazone and diacetyl dihydrazone, respectively, in 2:1 molar proportion. With silver(I), PhL yields a double-stranded dinuclear cationic helicate **1** in which the metal is tetrahedral but MeL gives a cationic one-dimensional polymeric complex **2** where silver(I) is distorted square planar and the ligand backbone is nearly planar. In both complexes, metal:ligand ratio is 1:1. *Ab initio* calculations on the ligands at the HF/6-31+G* level reveal that while PhL strongly prefers a helical conformation, MeL has a natural inclination to remain in a planar conformation. Density functional theory calculations on model silver(I) complexes show that formation of the linear polymer in the case of MeL is also an important factor in imposing the planar geometry of Ag(I) in **2**.

In metallo proteins and enzymes, it is now known that to stabilise a high energy metal site (*i.e.*, one having an unusual geometry or configuration) the peptide backbone undergoes suitable compensatory conformational change(s).¹ In small metallo organic molecules, the conformation of the ligand is found to play a dominant role in determining the geometry of a metal ion. The most impressive example of this is possibly the stabilisation of square planar copper(I) by a stereochemically rigid tetradentate N-donor macrocycle.² Herein we describe a case of stabilisation of a planar geometry for a four-coordinate silver(I) by an acyclic N-donor ligand as a part of our continued studies on metal helicates.^{3–6}

Results and discussion

The ligands employed in this work are PhL and MeL (Chart 1), which are prepared by condensing two moles of 2-formylpyridine with one mole of benzil dihydrazone or diacetyl dihydrazone, respectively. The X-ray crystal structure of PhL, earlier reported elsewhere by us,⁷ reveals that it is a helical ligand. The helical twist in PhL is brought about mainly by the torsion angle N9–C10–C11–N12, which is –99.5(3)°. All our attempts to obtain single crystals of MeL suitable for X-ray diffraction have so far failed.

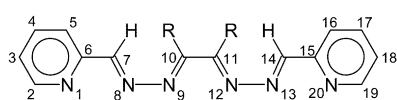
We have synthesised the silver(I) complexes of PhL and MeL by reacting them with hydrated AgClO₄ in methanol. PhL yields 1.5{[Ag₂(PhL)₂](ClO₄)₂}·3.5(CH₃OH) (**1**) and MeL gives [Ag(MeL)]ClO₄ (**2**).

X-Ray crystallography shows that **1** consists of a discrete dimeric cation [Ag₂(PhL)₂]²⁺ and perchlorate anions. There

are two independent cations in the crystal, one of which has crystallographic C₂ symmetry. The other cation, shown in Fig. 1, has approximate C₂ symmetry though this is not crystallographically imposed. In this structure the silver atoms are tetrahedral, being bonded to four nitrogen atoms from two PhL ligands. Although there is considerable variation in the Ag–N bond lengths it is clear that the Ag–N(pyridine) distances [range: 2.256(7)–2.299(7) Å] are significantly shorter than the Ag–N(imino) distances [range: 2.395(6)–2.479(7) Å]. The angles subtended at the silver atoms are very similar with two small chelate angles, N1–Ag–N8 and N13–Ag–N20 (72.2–73.4°), and four angles extending above the tetrahedral angle of which one is much larger (141.1–141.7°) than the other three (122.9–129.9°). The sum of the six angles around the metal lies in the range of 665.2–665.4° (for an ideal tetrahedron, this sum is 109.5° × 6 = 657°).

The structure of **2** consists of a 1-dimensional polymer of [Ag(MeL)]⁺ units, shown in Fig. 2, with discrete perchlorate anions. The silver atom occupies a crystallographic centre of symmetry and is bonded to two nitrogen atoms from each of two MeL ligands. The bite angle of the MeL ligand is 70.9(2)°. The coordination sphere is perforce planar. But the unique bond lengths are very different, being 2.247(5) Å for N(imino) and 2.543(6) Å for N(pyridine). It should be noted that the difference between the lengths of the two types of Ag–N bonds is significantly more than that observed in **1** and that the structure can be considered as distorted square planar.^{8–10}

Four-coordinate silver(I) complexes are usually tetrahedral, as expected on the basis of the fact that there is no ligand field stabilisation for a d¹⁰ configuration. Distorted tetrahedral coordination has been observed at times.¹¹ Examples of square planar silver(I) complexes are indeed rare. Our complex **2** provides, most possibly, the third example of a square planar silver(I) complex. The other two examples have been reported by Munakata and co-workers very recently.^{12,13} Interestingly, these two complexes, one containing a Ag₂N₄ core and the other a Ag₂S₄ core, are also polymeric like **2**. It is not understood why in Munakata's complexes silver(I) assumes a square



PhL: R = Ph; MeL: R = Me

Chart 1 The ligands with the numbering scheme, which is the same as that used in Figs. 1 and 2, for the skeletal atoms.

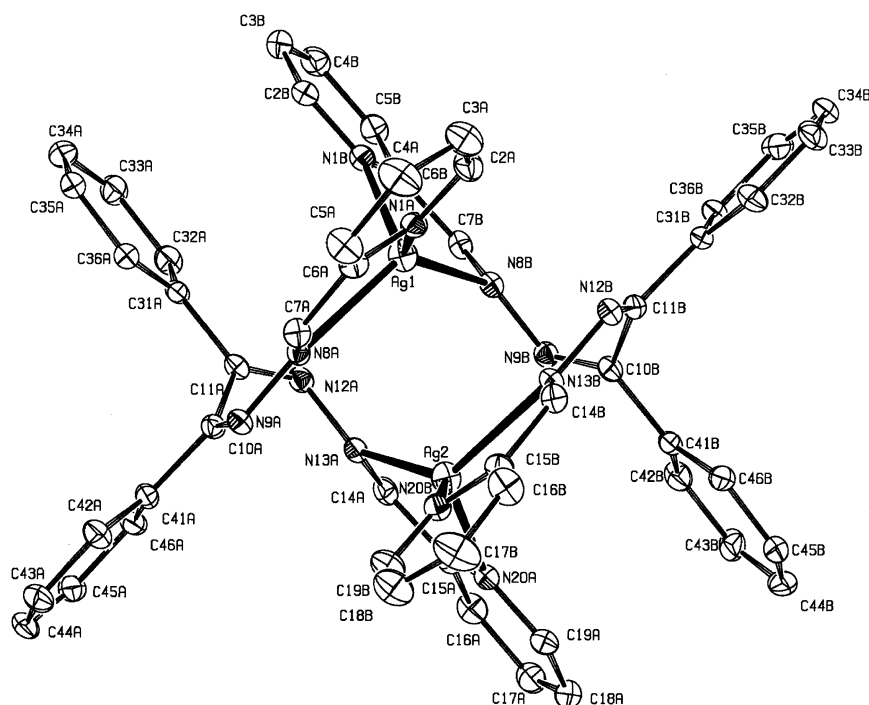


Fig. 1 The structure of $[\text{Ag}_2(\text{PhL})_2]^{2+}$ found in **1** with ellipsoids at 15% probability. The structure of a second cation, which has crystallographic C_2 symmetry, is similar and not shown. Selected bond distances (Å) and angles ($^\circ$): Ag1–N1A 2.256(7), Ag1–N8A 2.476(7), Ag1–N1B 2.295(8), Ag1–N8B 2.395(6), Ag2–N20A 2.296(7), Ag2–N13A 2.397(7), Ag2–N20B 2.272(7), Ag2–N13B 2.473(6), Ag3–N1C 2.299(7), Ag3–N8C 2.403(7), Ag3–N13CS1 2.479(7), Ag3–N20CS1 2.266(8), N1A–Ag1–N8A 72.8(2), N1A–Ag1–N1B 125.4(2), N1A–Ag1–N8B 141.1(2), N8A–Ag1–N1B 123.5(2), N8A–Ag1–N8B 129.6(2), N1B–Ag1–N8B 73.0(2), N13A–Ag2–N20A 73.4(2), N13A–Ag2–N13B 129.9(2), N13A–Ag2–N20B 141.2(2), N20A–Ag2–N13B 123.1(2), N20A–Ag2–N20B 125.2(3), N13B–Ag2–N20B 72.4(2), N1C–Ag3–N8C 73.4(3), N1C–Ag3–N13CS1 122.9(2), N1C–Ag3–N20CS1 125.2(3), N8C–Ag3–N13CS1 129.9(2), N8C–Ag3–N20CS1 141.7(2), N13CS1–Ag3–N20CS1 72.2(2). \$1 refers to the symmetry element $1 - x, y, -z$.

planar geometry. Here we try to provide a rationale for our case.

From Figs. 1 and 2, it is found that the ligand backbone in PhL and MeL adopts two different conformations in the complexes **1** and **2**; the conformation in **1** is clearly helical while it is nearly planar in **2** (Fig. 3). This is illustrated by the torsion angles listed in Table 1. The ligand in **2** contains a centre of symmetry. Of the five independent torsion angles all are trans apart from C7–N8–N9–C10, which is $111.7(6)^\circ$. This distortion from 180° is necessary to twist the methyl group away so that the metal can bind to the two nitrogens in the ligand. However, for the three independent ligands (named A and B in one cation and $C \times 2$ in the other) in the structure of **1**, all have approximate C_2 symmetry. The four outer torsion angles C5–C6–C7–N8, C6–C7–N8–N9, N12–N13–C14–C15 and N13–C14–C15–C16 are all trans but the C7–N8–N9–C10 and C11–N12–N13–C14 torsion angles are significantly

distorted from trans to 144.7 – 158.4° while N8–N9–C10–C11 and C10–C11–N12–C13 are cis (less than 10°) rather than trans as found in **2**, and the central N9–C10–C11–N12 torsion angle is intermediate at 91.5 – 95.3° . The two pyridine rings at the ends of the ligand in **2** are parallel because the ligand contains a crystallographic centre of symmetry but no symmetry restrictions apply in **1** where the three pairs of pyridine rings in ligands A, B, C are almost perpendicular, intersecting at angles of 89.2 , 89.3 and 86.0° , respectively. It is thus apparent that a change of tetrahedral geometry in **1** to a square planar one for the metal in **2** is accompanied by a conformational change in the ligand backbone.

We have carried out conformational analyses on the two ligands using the grid search method available in Cerius2.¹⁴ In each ligand 5 backbone torsion angles (τ_1 , τ_3 , τ_5 , τ_3' and τ_1' in Table 1) were considered as variable, along with 2 additional torsion angles in PhL for the orientation of the phenyl

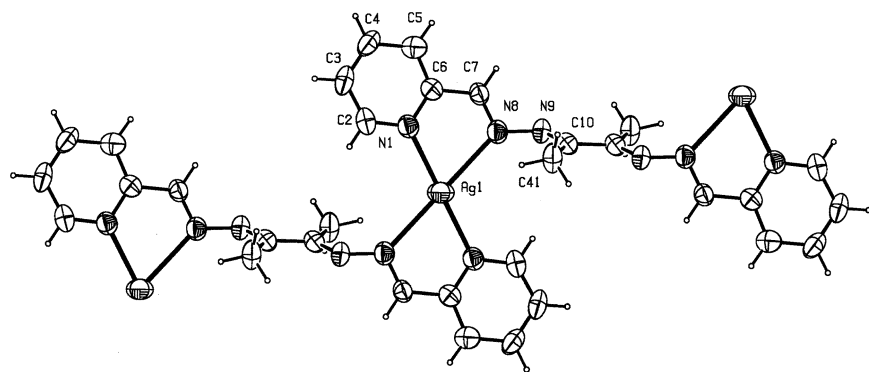


Fig. 2 The polymeric structure of $[\text{Ag}(\text{MeL})]^+$ in **2** with ellipsoids at 15% probability. Selected bond distances (Å) and angles ($^\circ$): Ag1–N1 2.247(5), Ag1–N8 2.543(5), N1–Ag1–N8 $70.9(2)$, N1–Ag1–N8* $109.1(2)$.

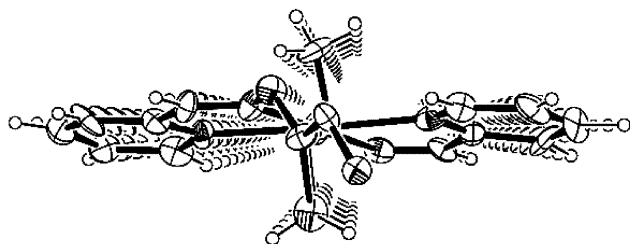


Fig. 3 A view of the cation in **2** along ten silver atoms showing the centrosymmetric, near planar conformation of the ligand backbone.

rings; all these angles were allowed to vary at 60° intervals. We also included τ_4 , τ_4' as variable torsion angles, with permitted values of 0 or 180°. All resulting structures were energy minimised using molecular mechanics with the Dreiding forcefield available in Cerius2. The six lowest energy conformations for each ligand were then subjected to geometry optimisation at the HF/6-31+G* level. Common features emerged from the conformational analyses of both ligands. The overall conformation of each ligand is dependent only upon the values of τ_4 , τ_5 and τ_4' , as τ_2 , τ_3 , τ_2' , and τ_3' are always close to 180° in each low energy conformation; then independently the values of τ_1 , τ_1' determine whether the ligand can chelate to a metal ($\tau_1 = \tau_1' = 0^\circ$) or are in the lower energy trans ($\tau_1 = \tau_1' = 180^\circ$) conformation.

The two lowest energy conformations for MeL are planar and helical with τ_4 , τ_5 , τ_4' angles of 180°, 180°, 180° (energy = -941.84459 a. u.) and -3.1°, 102.1°, -3.1° (energy = -941.84055 a. u.), respectively. By contrast the lowest energy conformation for PhL is helical with τ_5 , τ_4 , τ_5' torsion angles of -0.8°, 94.3°, -0.9° (energy = -1322.87396 a. u.). The next lowest energy conformation is asymmetrical with torsion angles of 0.1°, -103.5°, -176.9° and an energy of -1322.86543 a. u. while the symmetrical planar conformation is only the fourth lowest energy conformation at -1322.86308 a. u. Thus, in MeL there is a favourable energy difference of 2.53 kcal mol⁻¹ for the planar form over the helical while in PhL the energy difference is of 6.83 kcal mol⁻¹ in favour of the helical form over the planar (and of 5.35 kcal mol⁻¹ over other low energy conformations).

It will be noted that the values of the τ_4 torsion angles are of crucial importance to the conformation of the ligand. In order to obtain a planar conformation these angles need to be trans, but to provide a helical conformation these angles need to be cis. It can be argued that these τ_4 torsion angles are not likely to change easily and therefore that these ligands must have these conformations in the free state with a predisposition therefore for MeL to be planar and PhL to be helical. It is interesting in this regard to note that the crystal structure of PhL determined previously has a conformation very similar

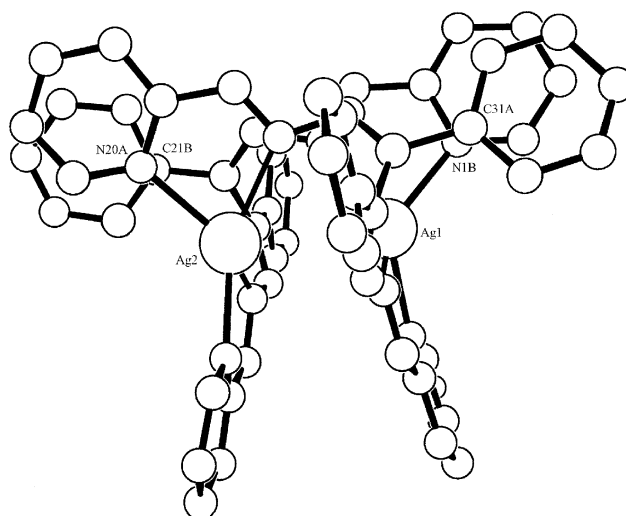
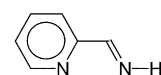


Fig. 4 A view of the cation in **1** showing π - π interactions between pairs of pyridine and phenyl rings. The structure of the second cation is equivalent. The atom labelling is identical to that given in Fig. 1.

to the lowest energy form established here. However, for the ligands to form complexes some changes in conformation are inevitable. Clearly τ_1 , τ_1' must change from trans to cis to form the five-membered chelate ring. Calculations show that this cis form is higher in energy by ca. 12.5 kcal mol⁻¹ for both ligands, independently of the values of τ_4 , τ_5 and τ_4' . It is therefore to be expected that the crystal structure of the free ligand PhL would be trans, thus avoiding steric contacts between the NH and the ortho hydrogen atom in the pyridine ring. For MeL a further change is necessary to move the methyl groups away from the coordination sphere and therefore τ_3 and τ_3' change from 180 to 111°. For PhL, these torsion angles also change on complexation but only to ca. 150° to move the phenyl rings away from the coordination sphere, a much smaller change being required compared to MeL because the helical conformation already moves the phenyl rings away from the metal.

These calculations are remarkably consistent with the experimental results that MeL adopts a planar conformation and PhL a helical conformation, which is retained on metal complexation. An additional stabilising feature of the helical dimer observed in **1** is the presence of strong π - π interactions between a pyridine ring of one ligand and a phenyl ring of the other ligand (Fig. 4). There are two such pairs of interacting aromatic rings in each molecule in **1**. These are parallel to each other within experimental error (angle of intersection: 0.5°, 0.6° in one molecule and twice 0.2° in the other) with distances of two times 3.45 Å in one molecule and two times 3.43 Å in the other, resulting in extremely short π - π interactions.¹⁵ It may be noted that such interactions are not possible in the case of MeL and in the near planar conformation of PhL. The π - π interactions present in **1** are likely to increase the stabilisation of the helical dimer with tetrahedral silver(I) centres with regards to other possible products.

We then estimated the difference in energy between square planar and tetrahedral silver for this type of coordination sphere. Because one complex was a dimer and the other a polymer, and also because we wished to neglect differences between MeL and PhL, it was decided to consider the model compound [Ag(L')₂]⁺ where L' is:



Two models of [Ag(L')₂]⁺ were built, one tetrahedral with no imposed symmetry and the other square planar with C_i

Table 1 Torsion angles (°) in the ligand backbones in complexes **1** and **2** and in the free ligand PhL

	2	1A	1B	1C	PhL ^a
N1-C6-C7-N8 (τ_1)	3.1	-4.6	-7.4	-6.3	-165.6
C6-C7-N8-N9 (τ_2)	178.3	178.2	175.1	173.3	176.5
C7-N8-N9-C10 (τ_3)	111.7	156.8	146.6	144.7	-169.4
N8-N9-C10-C11 (τ_4)	177.0	-1.0	-9.5	-7.1	0.3
N9-C10-C11-N12 (τ_5)	180.0	91.5	95.3	94.0	99.5
C10-C11-N12-C13 (τ_4')	-177.0 ^b	-6.8	-3.3	-3.7	1.6
C11-N12-N13-C14 (τ_3')	-111.7 ^b	144.8	158.3	158.4	-178.1
N12-N13-C14-C15 (τ_2')	-178.3 ^b	173.7	179.0	179.0	-178.2
N13-C14-C15-N20 (τ_1')	-3.1 ^b	-6.3	-6.0	-5.2	-175.5

^a The data are taken from ref. 7. ^b The ligand in **2** contains a crystallographic centre of symmetry.

symmetry, and these were subjected to density functional calculations. The final energies after geometry optimisation were -7.09825 , -7.11617 a. u. with a difference of $11.2 \text{ kcal mol}^{-1}$. This is only an approximate measure of the energy required to force Ag(I) to become square planar rather than tetrahedral in the presence of MeL, but it is considerably larger than the difference in energy of the two ligand conformations, suggesting that the formation of the linear polymer is also an important factor in the stabilisation of the square planar structure for silver(I).

Experimental

Computations

Density functional calculations on $[\text{Ag}(\text{L}')_2]^+$ were performed by using the ADF programme.¹⁶ Slater-type orbital basis sets of triple zeta quality for the valence orbitals were employed with polarisation functions on the ligand atoms (2p for H, and 3d for C and N). The Generalised Gradient Approximation was used with Becke88 exchange and Perdew86 correlation gradient corrections. The cations were given +1 charges and the input symmetry was maintained. *Ab initio* calculations on PhL and MeL were carried out using the Gaussian98 programme.¹⁷

Syntheses

CAUTION! Though while working with **1** and **2** we have not met with any incident, care should be taken in handling them as perchlorates are potentially explosive. These should not be prepared and stored in large amounts.

PhL. This was synthesised as reported elsewhere by us.⁷

MeL. Diacetyl dihydrazone (1.25 g, 11 mmol), synthesised by a literature procedure,¹⁸ was dissolved in 50 ml of anhydrous methanol, to which 2 ml (22 mmol) of freshly distilled 2-formylpyridine was added. The resulting yellow mixture was stirred for 4 h while maintaining a dry atmosphere. The yellow compound that precipitated was filtered, washed with 15 ml of diethyl ether and stored *in vacuo* over fused CaCl_2 . Yield, 2.0 g (62%); mp 152°C . Anal. found (calcd): C, 64.68 (65.72); H, 5.49 (5.52); N, 28.79 (28.75)%. FTIR (KBr) ν/cm^{-1} : 1615vs (C=N). UV/VIS (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 267sh (23 557), 302 (36 642).

$1.5\{\text{Ag}_2(\text{PhL})_2(\text{ClO}_4)_2\} \cdot 3.5(\text{CH}_3\text{OH})$ (1**).** $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$ (0.21 g) was added to 0.42 g (1 mmol) of PhL dissolved in 20 ml of methanol and stirred for 30 min at room temperature. The yellow compound that precipitated was filtered, washed with 10 ml of diethyl ether and dried *in vacuo* over fused CaCl_2 . It was recrystallised from a 1:3 dichloromethane-*n*-hexane mixture to obtain deep yellow microcrystals of **1**. Yield, 0.40 g (77%). Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. found (calcd.): C 49.37 (49.33), H 3.71 (3.76), N 12.69 (12.71)%. FTIR (KBr) ν/cm^{-1} : 1630s (C=N), 1083 vs (ClO_4). UV/VIS (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 267sh (34 400), 299 (55 300).

$[\text{Ag}(\text{MeL})]_n(\text{ClO}_4)_n$ (2**).** $\text{AgClO}_4 \cdot x\text{H}_2\text{O}$ (0.21 g) was added to 0.29 g (1 mmol) of MeL dissolved in 20 ml of methanol and stirred for 30 min at room temperature. The yellow compound that precipitated was filtered, washed with 10 ml of diethyl ether and dried *in vacuo* over fused CaCl_2 . It was recrystallised from a 1:3 acetonitrile-diethyl ether mixture to obtain a deep yellow powder of **2**. Yield, 0.40 g (80%). Single crystals were grown by direct diffusion of diethyl ether into a dilute acetonitrile solution of the complex. Anal. found (calcd): C 38.53

(38.43), H 3.19 (3.23), N 16.76 (16.81)%. FTIR (KBr) ν/cm^{-1} : 1613s (C=N), 1083vs (ClO_4). UV/VIS (CH_3CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 197 (20 300), 267sh (25 850), 297 (38 100).

X-ray crystallography

The data were collected with Mo-K α radiation using the MARresearch Image Plate System at 293(2) K. The crystals were positioned at 70 mm from the image plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.¹⁹ The structures were solved using direct methods with the SHELXS-86 program.²⁰ In **1** there are four independent perchlorate anions, one in a general position and one on a 2-fold axis, both ordered, and also one in a general position and one on a 2-fold axis, both disordered with the oxygen atoms occupying two sets of tetrahedral sites. There are also 7 solvent methanol molecules, each refined with 50% occupancy. In **2** the perchlorate anions are disordered with the oxygen atoms occupying two sets of tetrahedral sites. Apart from disordered atoms, non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out using DIFABS.²¹ The structures were refined on F^2 using SHELXL-93.²² Final R values: for **1** with observed data [$I > 2\sigma(I)$] $R_1 = 0.0684$, $wR_2 = 0.1867$ and for all data $R_1 = 0.0897$, $wR_2 = 0.2069$; for **2** with observed data [$I > 2\sigma(I)$] $R_1 = 0.0675$, $wR_2 = 0.2010$ and for all data $R_1 = 0.1061$, $wR_2 = 0.2705$. The relatively high R values are due to poor spot shapes in the diffraction pattern.

CCDC reference numbers 201371 and 201372. See <http://www.rsc.org/suppdata/nj/b2/b211898j/> for crystallographic data files in CIF or other electronic format.

1. $\text{C}_{81.5}\text{H}_{74}\text{N}_{18}\text{O}_{15.5}\text{Ag}_3\text{Cl}_3$, $M_w = 1983.55$, monoclinic, space group $C2/c$, $a = 26.66(4)$, $b = 15.40(2)$, $c = 21.64(3) \text{ \AA}$, $\beta = 90.06(1)^\circ$, $U = 8885(23) \text{ \AA}^3$, $d_c = 1.483 \text{ g cm}^{-3}$, $Z = 4$, $\mu = 0.817 \text{ mm}^{-1}$, 28 146 reflections collected, 16 892 independent, $R_{\text{int}} = 0.0501$.

2. $\text{C}_{16}\text{H}_{16}\text{N}_7\text{O}_4\text{AgCl}$, $M_w = 499.67$, monoclinic, space group $C2/c$, $a = 18.46(3)$, $b = 5.612(11)$, $c = 18.46(3) \text{ \AA}$, $\beta = 100.17(1)^\circ$, $U = 1882(5) \text{ \AA}^3$, $d_c = 1.763 \text{ g cm}^{-3}$, $Z = 2$, $\mu = 1.249 \text{ mm}^{-1}$, 4974 reflections collected, 1785 independent, $R_{\text{int}} = 0.0867$.

Acknowledgements

M. G. B. D. thanks EPSRC and the University of Reading for funds for the Image Plate system. D. D. thanks the Department of Science and Technology, New Delhi, India for financial support.

References

- P. Ghosh, D. Shabat, S. Kumar, S. C. Sinha, F. Grynszpan, J. Li, L. Noodleman and E. Keinan, *Nature*, 1996, **382**, 339.
- R. R. Gagne, J. L. Allison and D. M. Ingle, *Inorg. Chem.*, 1979, **18**, 2767.
- M. Zimmer, D. A. Tocher, G. K. Patra, J. P. Naskar and D. Datta, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor., Anal. Chem.*, 1999, **38**, 1087.
- P. K. Pal, S. Chowdhury, P. Purkayastha, D. A. Tocher and D. Datta, *Inorg. Chem. Commun.*, 2000, **3**, 585.
- G. K. Patra, I. Goldberg, S. K. Chowdhury, B. C. Maiti, A. Sarkar, P. R. Bangal, S. Chakravorti, N. Chattopadhyay, D. A. Tocher, M. G. B. Drew, G. Mostafa, S. Chowdhury and D. Datta, *New J. Chem.*, 2001, **25**, 1371.

- 6 S. Chowdhury, P. B. Iveson, M. G. B. Drew, D. A. Tocher and D. Datta, *New J. Chem.*, 2003, **27**, 193.
- 7 P. K. Pal, S. Chowdhury, M. G. B. Drew and D. Datta, *New J. Chem.*, 2000, **24**, 931.
- 8 A referee has suggested that the differences in the Ag–N bond lengths indicate that in **2** we have a two-coordinate system with associated third and fourth ligands in the plane. To resolve this, we took recourse to the bond valence sum (BVS) model,^{9,10} which relates the bond distances around a metal ion with its oxidation state. In the method introduced by Pauling and developed later by Brown and co-workers,^{9,10} the valence v_{ij} of a bond between two atoms i and j is given empirically by eqn. (1):
- $$v_{ij} = \exp[(r_0 - r_{ij})/0.37] \quad (1)$$
- where r_{ij} is the length (expressed in Å) and r_0 a parameter characteristic of the bond. The oxidation number V_i of an atom i is a simple algebraic sum of the v values of all the bonds formed by the atom [eqn. (2)]; it is also known as BVS.
- $$V_i = \sum_j v_{ij} = \sum_j \exp[(r_0 - r_{ij})/0.37] \quad (2)$$
- Thus, if r_0 is known for a particular bond type, then the BVS can be calculated from the crystallographically determined r_{ij} values. The bond valence parameter r_0 for the Ag(I)–N bond calculated by us by following the method described in ref. 10 is 1.859 (estimated standard deviation, 0.043) Å. We have found that with this r_0 , the BVS values calculated for a number of silver(I) complexes of N-donor ligands containing AgN₂, AgN₃, AgN₄ and AgN₆ cores are found to lie in the range of 1.00 ± 0.20 unit, i.e. the oxidation numbers of Ag in these complexes are reproduced within ± 0.20 unit. When we apply this method to **2** with two Ag(I)–N(imino) bond lengths of 2.247 Å it yields a BVS of 0.70 unit, which is outside the stipulated error limit of 0.20 unit. This means that the silver(I) atom in **2** is not a two-coordinate system—additional coordinating atoms are needed to satisfy its valence. When the other two Ag–N bonds (with the pyridyl N atoms) are included in the coordination sphere of silver in **2**, the BVS increases to 1.02. Thus, we conclude that the silver atom in **2** is essentially four-coordinate.
- 9 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.
- 10 S. Hati and D. Datta, *J. Chem. Soc., Dalton Trans.*, 1995, 1177 and references therein.
- 11 E. C. Constable, C. E. Housecroft, B. M. Kariuki, N. Kelly and C. B. Smith, *Inorg. Chem. Commun.*, 2002, **5**, 199 and references therein.
- 12 I. Ino, J. C. Zhong, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and Y. Kitamori, *Inorg. Chem.*, 2000, **39**, 4273.
- 13 Y. Suenaga, K. Kitamura, T. Kuroda-Sowa, M. Maekawa and M. Munakata, *Inorg. Chim. Acta*, 2002, **328**, 105.
- 14 Cerius2, v. 3.5, Molecular Simulations Inc, San Diego, Calif., USA, 1999.
- 15 I. G. Dance, *New J. Chem.*, 2003, **27**, 22.
- 16 ADF2000 program: E. J. Baerends, A. Berces, C. Bo, P. M. Boerrigter, L. Cavallo, L. Deng, R. M. Dickson, D. E. Ellis, L. Fan, T. H. Fisher, C. Fonseca-Guerra, S. J. A. van Gisbergen, J. A. Groeneveld, O. V. Gritsenko, F. E. Harris, D. van Hoek, P. H. Jacobson, G. van Kessel, F. Kootstra, E. van Lenthe, V. E. Osinga, P. H. T. Philipson, D. Post, C. C. Pye, W. Ravenek, P. Ros, P. R. T. Schipper, G. Schreckenback, J. G. Snijders, M. Sola, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. Woo and T. Ziegler, SCM Inc, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, 2000.
- 17 Gaussian98 program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Latham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- 18 D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, 1956, **78**, 1137.
- 19 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
- 20 SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 21 DIFABS: N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 22 G. M. Sheldrick, SHELXL-93, A Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1993.