

5,5'-Dicyano-2,2'-bipyridine silver complexes: discrete units or co-ordination polymers through a chelating and/or bridging metal–ligand interaction

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The ambidentate ligand 5,5'-dicyano-2,2'-bipyridine (L) was found to function as a bi-, tri- or tetra-dentate chelate or chelate/bridging ligand in the co-ordination of silver ions. The mode of co-ordination depends on the anion and the crystallization conditions and was elucidated by single crystal X-ray diffractometry. With metal-co-ordinating anions such as NO₃⁻ and CF₃SO₃⁻ a tridentate co-ordination mode of L is observed which involves the two bipyridine nitrogen donor atoms and one cyano group. The latter bridges to a neighboring silver center so that a one-dimensional co-ordination polymer results. For NO₃⁻ this co-ordination polymer forms a 2₁ helix. With less co-ordinating anions such as BF₄⁻ and PF₆⁻ monomeric bis-chelate complexes are obtained, where L assumes a bidentate co-ordination mode involving only the bipyridine nitrogen donor atoms. In the case of the PF₆⁻ anion a variation in the solvent of crystallization also produced a two-dimensional hexagonal co-ordination polymer where L functions as a tetradentate ligand using all four nitrogen donor atoms in chelation and bridging to the silver centers.

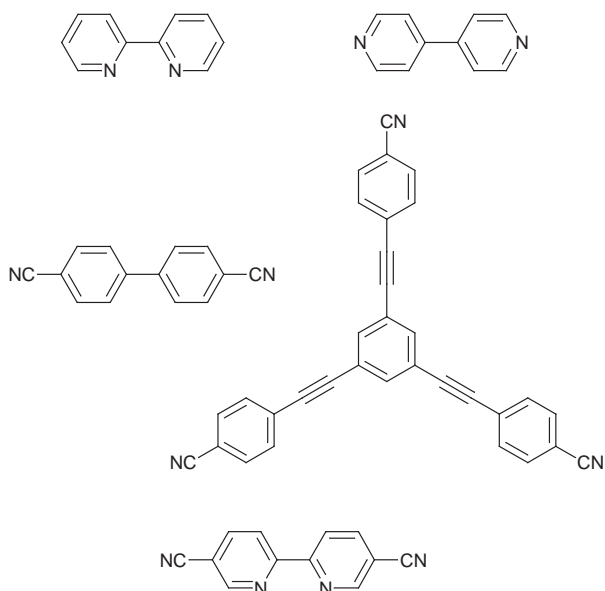
Introduction

Metal complexes of chelating 2,2'-bipyridine or bridging 4,4'-bipyridine or derivatives thereof are of constant and general interest in metal co-ordination chemistry.¹ 4,4'-Bipyridine has recently gained considerable interest in the synthesis of (rectangular) two-dimensional network structures.² The generation of such frameworks is a promising path in the search for stable microporous metal–organic networks that exhibit reversible guest exchange and possibly selective catalytic activity.^{3,4}

co-ordination polymers.⁵ A highlighted example is the co-ordination of TEB with AgSO₃CF₃ in benzene that led to the isolation of the compound [Ag(CF₃SO₃)(TEB)]·2C₆H₆,⁶ which exhibits 15 Å channels and is porous to benzene exchange.

We investigate here the co-ordination chemistry of 5,5'-dicyano-2,2'-bipyridine (L). This ambidentate ligand can be thought of as combining the ligating properties of the chelating 2,2'-bipyridine and the bridging 4,4'-dicyanobiphenyl ligand. The idea behind the use of such ambidentate ligands is to have cross-connecting blocks (tectons) for co-ordination polymers based on the *endo* chelation of two ligands with an appropriate metal center (**1**) or to supply functional donor atoms within the walls of the co-ordination polymer when the ligands are solely *exo* bridging (**2**).

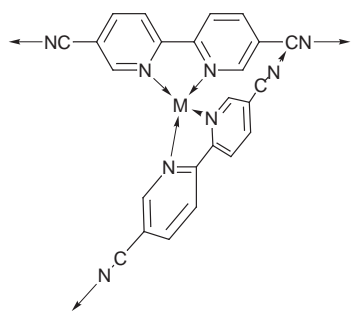
Our research has been concerned with the utilization of ambidentate *endo*-chelating/*exo*-bridging modified 2,2'-bipyridine ligands such as 5,5'-diamino-2,2'-bipyridine⁷ or 2,2'-dimethyl-4,4'-bipyrimidine⁸ and ligands of the tris(pyrazolyl)borate type for the assembly of metal co-ordination polymers.^{9,10} In this paper we describe the results of synthetic and structural studies of metal complexes with the ligand 5,5'-dicyano-2,2'-bipyridine (L) and try to elucidate the factors which lead to bridging, chelating or simultaneous bridging/chelating metal co-ordination. As a metal we have chosen silver(I) which together with copper(I) is a preferred ligand linker because of their favored tetrahedral co-ordination mode.^{5,11–13} In addition, silver can also assume a linear co-ordination¹³ and would thus be ideal for testing the formation of cross-linkers as depicted in **1**.



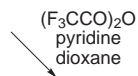
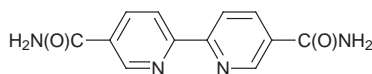
Ligands containing CN-donors such as 4,4'-dicyanobiphenyl, 1,3,5-tris(4-cyanophenylethynyl)benzene (TEB) and others are also excellent bridging ligands to synthesize porous

Results and discussion

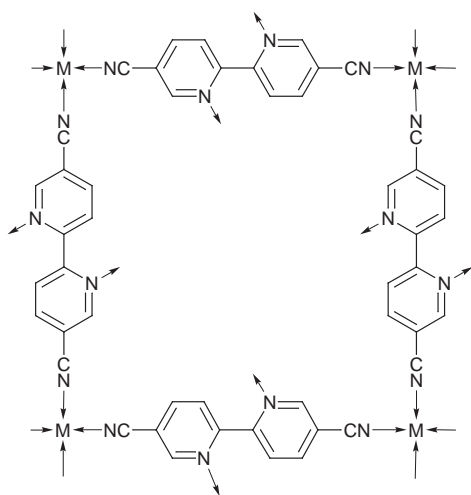
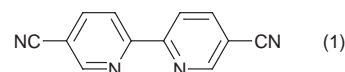
The synthesis of 5,5'-dicyano-2,2'-bipyridine as reported in the literature is the reaction of 2,2'-bipyridine-5,5'-dicarboxamide with POCl₃ in CHCl₃ under sonication (50 kHz) to give the product in 86% yield.¹⁴ Another method is the sublimation of a mixture of 2,2'-bipyridine-5,5'-dicarboxamide and P₄O₁₀



1



Crude product



2

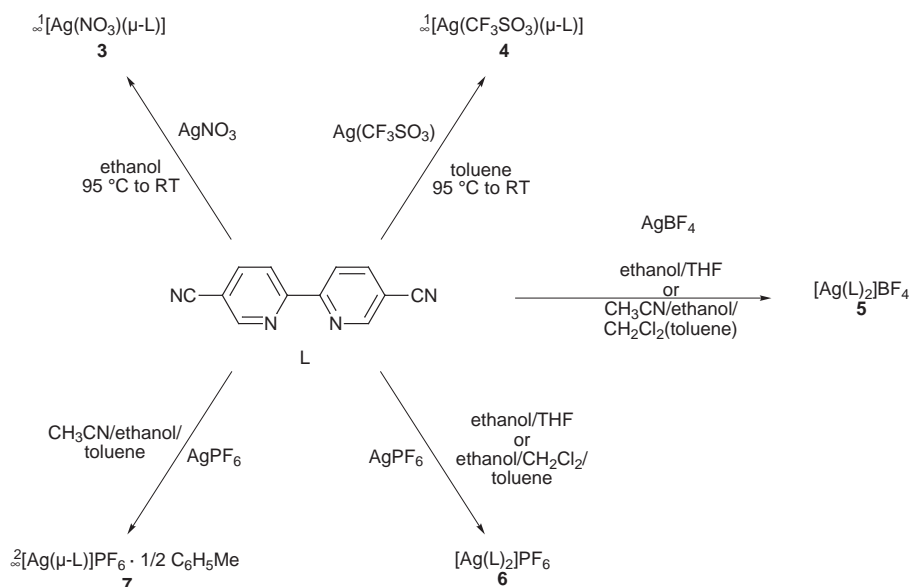
under vacuum at a temperature of 300 °C.¹⁵ However, a two-fold dehydration treatment and a two-fold sublimation of the crude (sublimed) product was found necessary to obtain the product in satisfactory purity. This finally gave the dicyanobipyridine in a low yield of only 29%. Furthermore, if more than 0.5 g of the dicarboxamide was used in the dehydration reaction with P_4O_{10} this resulted in a further decrease of the yield of the product. Thus, we report here a modified method which is based on a two-times dehydration treatment of the dicarboxamide, first with a trifluoroacetic anhydride–pyridine system and then with P_4O_{10} [eqn. (1)]. The initial dehydrated crude product

is obtained in high yield. This crude product was then again dehydrated with P_4O_{10} at 0.2 mbar/200 °C to give the final product in 43% yield. This method has the advantage of a higher yield (compared to the literature),¹⁵ the possibility of starting with an increased amount of the dicarboxamide, and the use of a lower sublimation temperature.

The reaction routes of 5,5'-dicyano-2,2'-bipyridine (L) with silver metal salts are summarized in Scheme 1. The reaction of silver nitrate or silver trifluoromethane sulfonate with L in a 2:1 metal-to-ligand stoichiometry in ethanol or toluene, respectively, led to the formation of compounds which feature a 1:1 metal-to-ligand ratio (3 and 4). Both reactions were carried out by heating the mixture of reactants to 95 °C for 24 h and then slowly cooling to room temperature (RT) at a rate of 1 °C h⁻¹.

Treating L with an excess of silver salts of less co-ordinating tetrafluoroborate or hexafluorophosphate anions (again with 2:1 metal-to-ligand stoichiometry) at room temperature gave silver complexes with a 1:2 (5 and 6) or a 1:1 metal-to-ligand ratio (7). The outcome of these latter reactions could be subtly affected by a change in solvents. For BF_4^- as the anion an ethanol–tetrahydrofuran mixture gave the same isostructural complex composition 5 as an acetonitrile–ethanol–methylene chloride or toluene mixture as shown by X-ray powder diffractometry. For PF_6^- as anion the inclusion of acetonitrile in the solvent mixture led to a 1:1 metal–ligand compound 7 instead of the 1:2 complex 6. All compounds were obtained in yields above 50%. Characterization was mainly based on X-ray diffraction studies.

The metal–ligand co-ordination modes elucidated from single-crystal structure determinations are depicted in Figs. 1,



Scheme 1

3, 5, and 7 for the 1-D co-ordination polymers **3** and **4**, the bis-chelate complexes **5** and **6**, and the 2-D framework **7**, respectively. The structural studies revealed that the anions

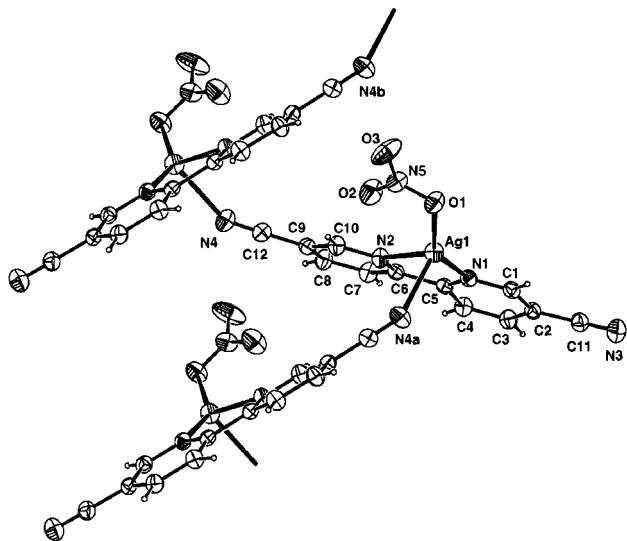


Fig. 1 Section of the one-dimensional co-ordination polymer of $\frac{1}{2}[\text{Ag}(\text{NO}_3)(\mu\text{-L})]$ **3**.

NO_3^- and CF_3SO_3^- in **3** and **4**, respectively, still co-ordinate to a metal center with one of the oxygen atoms (Figs. 1 to 4). They serve as terminal ligands and occupy one position in the distorted tetrahedral co-ordination sphere of the silver ions. At the same time, the dicyanobipyridine ligand chelates a silver atom in **3** and **4** through the bipyridine moiety and bridges to a neighboring silver center through one of the exodentate cyano groups. Hence, the silver co-ordination sphere consists of an oxygen atom, two bipyridine nitrogen atoms and a cyano nitrogen atom. The planes of the two pyridine rings within a bipyridine ligand deviate by $9.1(1)$ (**3**) and $16.9(3)^\circ$ (**4**) from coplanarity. The potentially tetradentate dicyanobipyridine group functions as a tridentate ligand only; the other cyano group is not involved in metal co-ordination even though a twofold excess of metal over ligand has been offered during the reaction. The bridging action of the ligand **L** gives rise to one-dimensional co-ordination polymers, $\frac{1}{2}[\text{Ag}(\text{NO}_3)(\mu\text{-L})]$ **3** and $\frac{1}{2}[\text{Ag}(\text{CF}_3\text{SO}_3)(\mu\text{-L})]$ **4**, whose metal-ligand arrangement is depicted in Figs. 1 and 3, respectively. While the chain in **4** is oriented rather straight with the metal and bipyridine ligands lying all in one plane, it is noteworthy that the strand for the silver nitrate complex **3** assumes a 2_1 -helical conformation. These chain conformations together with the packing of neighboring strands are further illustrated in Figs. 2 and 4 with the help of stereoplots. The chains run parallel in the

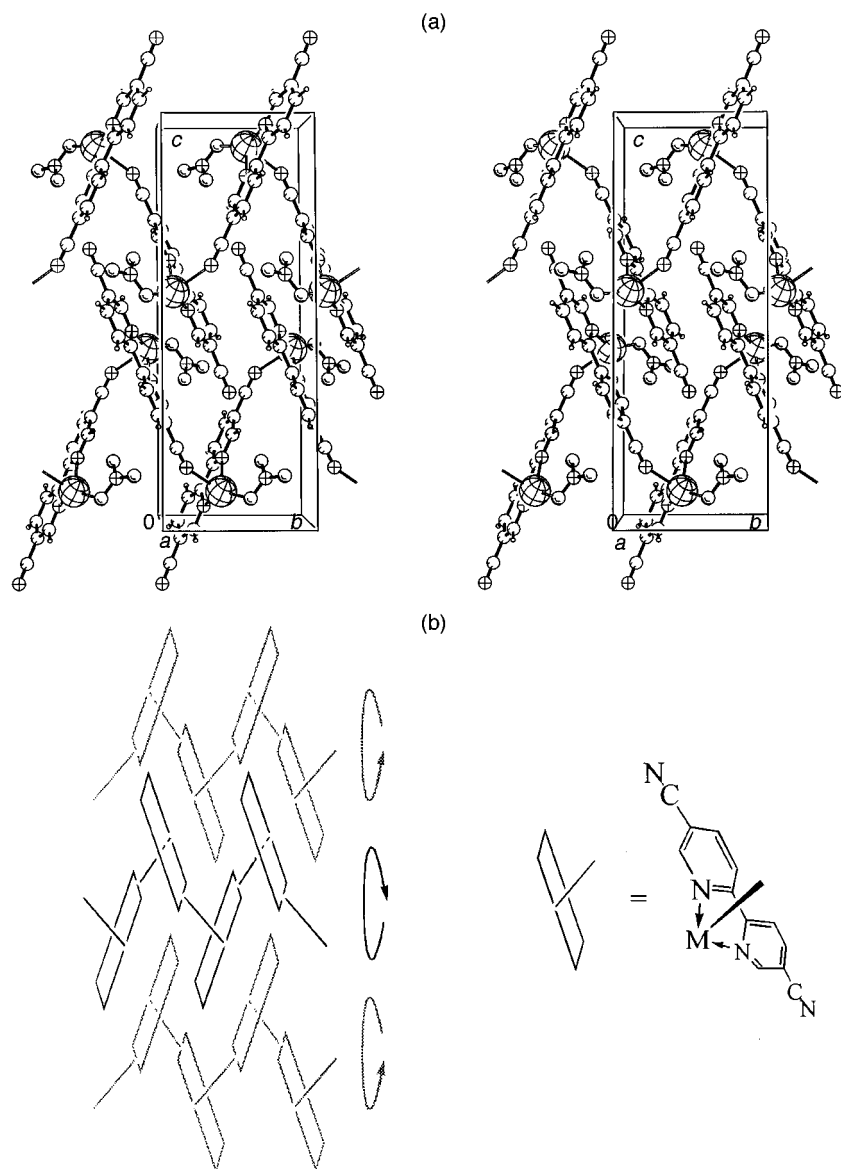


Fig. 2 (a) Stereoplot of the chain structure of $\frac{1}{2}[\text{Ag}(\text{NO}_3)(\mu\text{-L})]$ **3** illustrating the helical nature and the intertwining of neighboring 2_1 helices (view along *a*) and (b) schematic representation of the interdigitation of adjacent strands in **3**.

case of **4**. For **3** neighboring strands are of opposite helicity and interlock or interdigitate as is schematically depicted in Fig. 2(b). Bipyridine ligands from adjacent strands mutually intrude into the openings within the chain. The interdigitated bipyridine moieties form π - π stacks with an interplane distance of 3.47 Å. In the orientation of neighboring chains a weakly bridging mode of the NO_3^- and CF_3SO_3^- anions may play a role. Interchain non-bonding $\text{Ag}\cdots\text{O}$ contacts are 3.001 Å (to O1) in **3** and 3.370 and 3.590 Å (to O2 and O3, respectively) in **4**. In addition, an interchain silver-pyridine or electrostatic

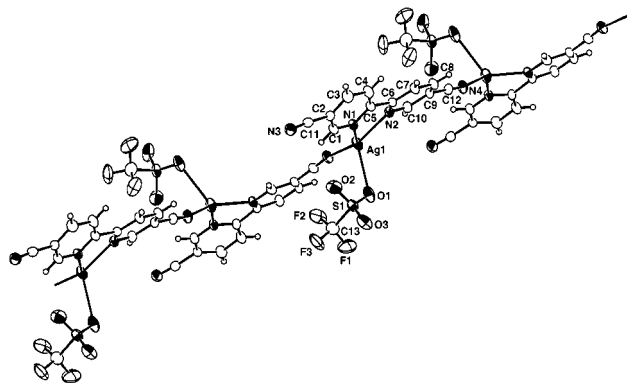


Fig. 3 Metal-ligand arrangement in a segment of the one-dimensional co-ordination polymer of $[\text{Ag}(\text{CF}_3\text{SO}_3)(\mu\text{-L})]$ **4**.

cation π contact might play a small role in **3**, as the $\text{Ag}\cdots\text{C}$ distances are 3.497 (to C3), 3.596 (to C4), and 3.716 Å (to C5). Silver is known to have a remarkably high affinity for some aromatic π -donor systems.¹⁶

When silver salts of only weakly co-ordinating anions such as BF_4^- and PF_6^- are employed, as in the isostructural compounds **5** and **6**, respectively,^{8,17} the metal co-ordination

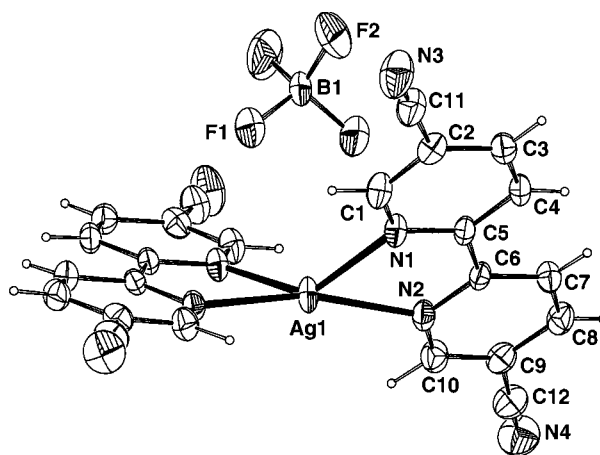


Fig. 5 Molecular structures of the bis-chelate complex $[\text{AgL}_2]\text{BF}_4$ **5** (shown) and of the isostructural $[\text{AgL}_2]\text{PF}_6$ **6**.

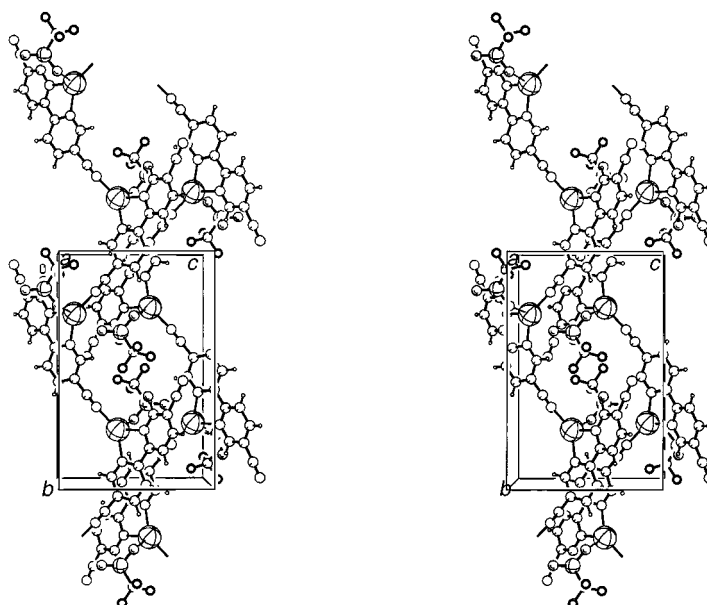


Fig. 4 Stereoplot of the chain structure of $[\text{Ag}(\text{CF}_3\text{SO}_3)(\mu\text{-L})]$ **4** to show the parallel alignment of the chains in contrast to those of **3**. View along *a*.

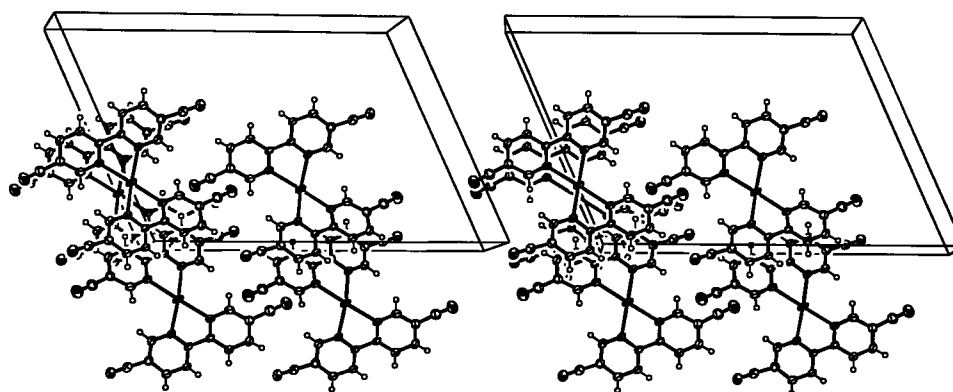


Fig. 6 Stereoscopic partial cell plot of complex **5** to illustrate the packing of the bis-chelate complexes. The BF_4^- anion has been omitted for clarity. View approximately along *b*.

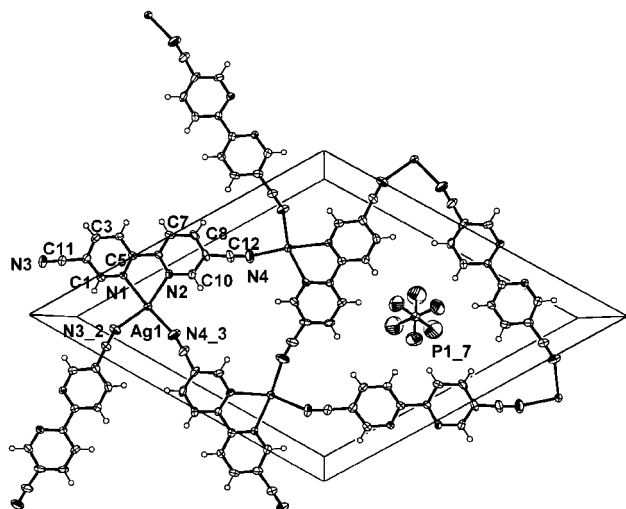


Fig. 7 Section of the two-dimensional framework of ${}^2_2[\text{Ag}(\mu\text{-L})]\text{PF}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{Me}$ **7**. View along c . The toluene molecule and two of the three crystallographically different PF_6^- anions are not shown for clarity (see Fig. 8 for these remaining moieties and Fig. 9 for the complete ensemble). Owing to space requirements the ligand is not fully labelled. Symmetry equivalent positions: $-2 = -y + 1, x - y - 1, z; -3 = -x + y + 1, -x + 1, z; -7 = -x + 1, -y + 1, -z$.

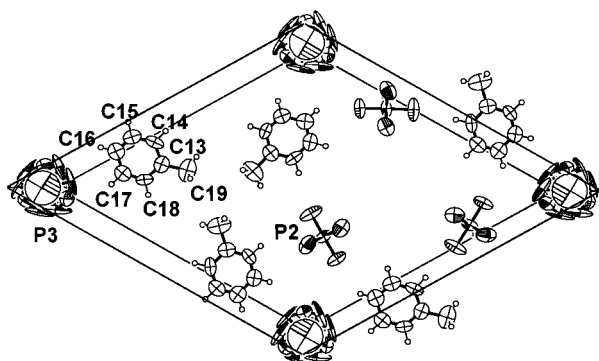


Fig. 8 The toluene- PF_6 layer in the crystal structure of ${}^2_2[\text{Ag}(\mu\text{-L})]\text{PF}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{Me}$ **7** which contains two of the three crystallographically different PF_6^- sites. One of these anions **P3** sits on a special position and is disordered. View along c as in Fig. 7.

sphere is fully constructed from the ligand donor atoms (Figs. 5 and 6). However, only the endodentate bipyridine nitrogen atoms serve as donor atoms towards silver; the exodentate cyano groups are not involved in metal co-ordination even though a twofold molar excess of metal over ligand has again been offered during the reaction. The results are cationic bis-chelate complexes of the type $[\text{AgL}_2]^+$ with BF_4^- (**5**) and PF_6^- (**6**) as the anion. The non-involvement of the cyano groups is remarkable in view of their known high affinity towards Ag^+ ions.¹⁸ The cyano nitrogen atom is perhaps a somewhat weaker donor atom when compared with a pyridine nitrogen atom. The co-ordination of the latter is definitely enhanced further through the chelate effect of the bipyridine unit. Two chelating ligands construct a strongly distorted environment, almost halfway between tetrahedral and square planar as is evident from the graphical presentation in Figs. 5 and 6. The interplane angle between the two five-membered chelate rings formed by Ag-N1-C5-C6-N2 and their symmetry equivalent atoms is $55.34(5)^\circ$ for **5** and $56.31(5)^\circ$ for **6**. The origin of this distortion is not clearly apparent as the nearest non-co-ordinating atoms are fluorine atoms, which are, however, 3.12 (**5**) and 3.16 Å (**6**) away. The two pyridine rings of the bipyridine ligand remain essentially coplanar to within 3° for **5** or 5° for **6** (based on the torsion angles N1-C5-C6-N2 and C4-C5-C6-C7). A stereoscopic cell plot of **5** in Fig. 6 serves to illustrate the packing of

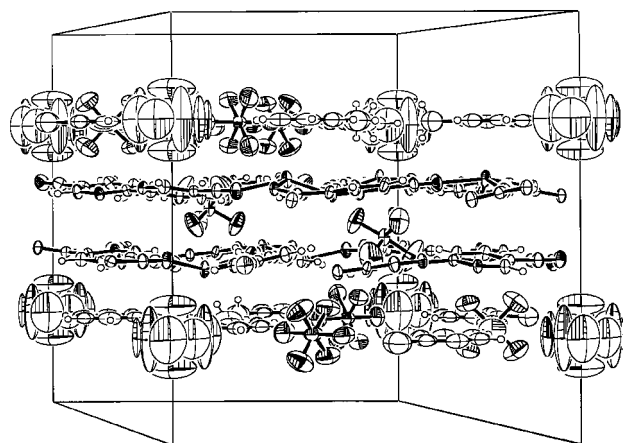


Fig. 9 Partial cell plot of ${}^2_2[\text{Ag}(\mu\text{-L})]\text{PF}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{Me}$ **7** viewed along the ab plane to show the ... BAABAA... sequence of the metal-ligand (A) and toluene- PF_6 (B) layers which were separately depicted in Figs. 7 and 8.

the ionic bis-chelate complexes through a bipyridine π - π interaction of neighboring molecules with an interplane distance of 3.76 Å.

The working hypothesis that the co-ordination of the exodentate cyano nitrogen atoms would be exercised only when the simultaneous endodentate co-ordination of two chelating bipyridine moieties was not possible, was proven wrong with the structure elucidation of complex **7**. In this two-dimensional co-ordination polymer of formula ${}^2_2[\text{Ag}(\mu\text{-L})]\text{PF}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{Me}$ the dicyanobipyridine ligand chelates a silver ion and bridges to two other metal centers with both of the exodentate cyano groups (Fig. 7). Two types of C_3 -symmetrical triangular openings are thus created in this framework. In the larger ones one of the three crystallographically different PF_6 anions is partly immersed. The other two PF_6 anion sites lie within a layer together with the toluene solvent molecules (Fig. 8). The metal-ligand layer (A, together with one PF_6) and the toluene- PF_6 layer (B) are stacked along the c direction in a ... BAABAA... sequence as is illustrated in Fig. 9. Clearly, a silver-toluene or electrostatic cation π contact is present in **7**, as rather short $\text{Ag} \cdots \text{C}$ distances of 2.815 (to C18) and 2.830 Å (to C17) are encountered.¹⁶ The remaining silver-toluene contacts are 3.381 (to C16), 3.771 (to C15), 3.769 (to C14), and 3.335 Å (to C13). The two pyridine rings are strongly twisted by $21.0(1)^\circ$ in **7**, more than in the other compounds **3-6**. The metal environment is again almost halfway between tetrahedral and square planar. The interplane angle between the five-membered chelate ring and the plane formed by the cyano nitrogen atoms with the silver center is $25.5(2)^\circ$.

Selected bond distances and angles for compounds **3-6** are summarized in Table 1.

Conclusion

In the ambidentate ligand 5,5'-dicyano-2,2'-bipyridine (L) both the bipyridine nitrogen and the exodentate cyano nitrogen atoms can function as donors towards a silver metal center. The choice of metal co-ordination was found to depend on the counter anion^{8,19} or the solvent of crystallization. When a co-ordinating anion was present in the silver co-ordination sphere L acted as a tridentate ligand, chelating through the bipyridine moiety and bridging through one of the cyano groups. With non-co-ordinating anions the silver co-ordination sphere was solely constructed from the ligand nitrogen donors. Either the formation of bis-chelate silver complexes through bis-bipyridine nitrogen co-ordination could be observed with L as a bidentate ligand, or, with a slight change in the solvent mixture for crystallization, L could also become tetradentate

Table 1 Selected bond distances (Å) and angles (°) for complexes 3–7

Compound	$\frac{1}{2}[\text{Ag}(\text{NO}_3)(\mu\text{-L})] \mathbf{3}$	$\frac{1}{2}[\text{Ag}(\text{CF}_3\text{SO}_3)(\mu\text{-5})] \mathbf{4}$	$[\text{AgL}_2]\text{BF}_4 \mathbf{5}$	$[\text{AgL}_2]\text{PF}_6 \mathbf{6}$	$\frac{2}{3}[\text{Ag}(\mu\text{-L})]\text{PF}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5\text{Me} \mathbf{7}$	
Ag1–N1 _{bipy}	2.339(2)	2.349(6)	2.356(2)	2.325(2)	2.377(6)	
Ag1–N2 _{bipy}	2.453(2)	2.322(4)	2.312(2)	2.378(3)	2.444(6)	
Ag1–N3 _{CN}					g: 2.375(7)	
Ag1–N4 _{CN}	a: 2.425(3)	c: 2.156(5)			h: 2.294(7)	
Ag1–O1	2.371(2)	2.689(5)				
N3–C11	1.143(4)	1.139(7)	1.139(4)	1.140(5)	1.134(10)	
N4–C12	1.148(4)	1.116(8)	1.137(4)	1.144(5)	1.146(10)	
Within the anions						
	O1–N5 1.277(3)	O1–S1 1.438(5)	B1–F1 1.389(4)	P1–F1 1.596(2)	P1–F 1.539(7)–1.569(9)	
	O2–N5 1.236(3)	O2–S1 1.438(5)	B1–F2 1.374(4)	P1–F2 1.599(3)	P2–F 1.576(10)–1.601(11)	
	O3–N5 1.240(3)	O3–S1 1.430(5)		P1–F3 1.596(2)	P3–F 1.40(4)–1.54(4)	
N1–Ag1–N2	68.42(7)	70.6(2)	N1–Ag1–N2	71.12(8)	70.75(9)	68.38(19)
N1–Ag1–O1	148.69(8)	105.5(2)	N1–Ag1–N1	e: 136.5(1)	f: 170.5(1)	
N2–Ag1–O1	129.38(8)	118.3(2)	N2–Ag1–N2	e: 165.7(1)	f: 135.3(1)	
N1–Ag1–N4	a: 106.44(8)	c: 129.2(2)	N1–Ag1–N2	e: 114.57(8)	f: 113.12(9)	
N2–Ag1–N4	a: 90.32(8)	c: 144.3(2)	N1–Ag1–N3			g: 88.4(2)
O1–Ag1–N4	a: 99.54(9)	c: 87.3(2)	N1–Ag1–N4			h: 164.6(3)
C12–N4–Ag1	b: 148.4(2)	d: 168.3(6)	N2–Ag1–N3			g: 144.9(3)
X–O1–Ag1	X = N5; 103.0(2)	X = S1; 110.8(3)	N2–Ag1–N4			h: 101.7(3)
			N3f–Ag1–N4g			94.5(3)

Symmetry transformations apply to the last atom in the bond or angle definition if not assigned otherwise: a = $-x + 0.5$, $y - 0.5$, $-z + 0.5$; b = $-x + 0.5$, $y + 0.5$, $-z + 0.5$; c = $-x + 1$, $y + 0.5$, $-z + 1.5$; d = $-x + 1$, $y - 0.5$, $-z + 1.5$; e = $-x$, y , $-z + 0.5$; f = $-x + 1$, y , $-z + 1.5$; g = $-y + 1$, $x - y - 1$, $z = -2$ in Fig. 7; h = $-x + y + 1$, $-x + 1$, $z = -3$ in Fig. 7.

utilizing all four nitrogen donor atoms in chelating and bridging co-ordination between three metal centers. Pyridine π – π interactions and silver–pyridine or –toluene cation π contacts were controlling factors in the non-bonded crystal organization.

Experimental

The NMR spectra were collected on a Varian O-300 spectrometer (300.0 MHz for ^1H , 75.4 MHz for ^{13}C) and calibrated against the solvent signal (d_8 -THF: ^1H , δ 1.73; ^{13}C , δ 25.2), IR spectra on a Perkin-Elmer 783 spectrophotometer as KBr disks or as Nujol mulls. Elemental analyses were carried out with a Perkin-Elmer Elemental Analyzer E 240 C. X-Ray powder diffractograms were obtained with a Siemens powder diffractometer D5000 using Cu-K α radiation. All crystallizations of the silver complexes were carried out in the dark.

Preparations

2,2'-Bipyridine-5,5'-dicarboxamide. A mixture of 3.0 g of diethyl 2,2'-bipyridine-5,5'-dicarboxylate, 100 ml of ethanol and 100 ml of ethylene glycol was saturated with ammonia and heated in a sealed round bottom flask in an oil-bath at 95 °C for 48 h. The precipitate formed was collected and washed with hot ethanol and ethylene glycol. 1.9 g (79%) of 2,2'-bipyridine-5,5'-dicarboxamide was obtained, mp >280 °C (lit.¹⁵ >310 °C). IR: 3375s, 3170s, 1660s, 1634s, 1599s, 1548m, 1480w, 1410s, 1370m, 1285w, 1252m, 1165w, 1132m, 1118w, 1055w, 1028m, 955w, 860m, 810w, 790m, 760w, 720m, 665m, 659m, 638m, 600w and 535w cm^{-1} .

5,5'-Dicyano-2,2'-bipyridine (L). This compound was prepared by two methods.

*Literature method.*¹⁵ 2,2'-Bipyridine-5,5'-dicarboxamide (0.2 g, 0.8 mmol) and 0.5 g (1.7 mmol) of P_4O_{10} were placed into a sublimator and kept at 0.2 mbar/300 °C until the sublimation had ceased. The crude product which easily absorbs water from the air was resublimed to obtain 0.1 g of a colorless solid. This was repurified with 0.2 g of P_4O_{10} in a sublimator at 0.2 mbar/300 °C followed by resublimation to give 0.05 g of L (29% yield), mp 275.9–276.6 °C (lit. 269–271,¹⁵ 284–285 °C¹⁴). IR: 3420w, 3070w, 2240s, 1985w, 1898w, 1796w, 1720s, 1597s,

1540m, 1468s, 1373s, 1292m, 1240s, 1170w, 1130w, 1053w, 1030s, 948w, 850s, 795w, 776w, 751m, 726m, 652m and 554m cm^{-1} .

Modified method. Trifluoroacetic anhydride (2.5 ml, 18.4 mmol) was added dropwise to a stirred ice-cooled suspension of 2,2'-bipyridine-5,5'-dicarboxamide (2.0 g, 8.4 mmol) in anhydrous 1,4-dioxane (150 ml) and anhydrous pyridine (1.5 ml, 18.4 mmol). Over the period of the addition the temperature was kept below 5 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 10 h. Then 100 ml of distilled water were added, the solid product was removed by filtration and washed with water to obtain 1.5 g of crude product. A 0.2 g amount of this was heated together with 0.5 g of P_4O_{10} in a sublimator at 0.2 mbar/180 °C until sublimation had ceased. The solid was purified by resublimation to obtain 0.12 g of a colorless solid (L) (43% yield), mp 275.4–276.2 °C. The IR spectrum was identical to that of the above sample. ^1H NMR (d_8 -THF): δ 8.34 (dd, 2 H, H4, H4', $J = 8.3, 2.1$), 8.57 (dd, 2 H, H3, H3', $J = 8.2, 0.8$ Hz) and 8.9 (br, 2 H, H6, H6'). ^{13}C NMR (d_8 -THF): δ 111.63 (C5, C5'), 117.49 (CN), 122.38 (C3, C3'), 142.33 (C4, C4'), 153.40 (C6, C6') and 157.75 (C2, C2').

(μ -5,5'-Dicyano-2,2'-bipyridine)nitrat silver(I), $\frac{1}{2}[\text{Ag}(\text{NO}_3)(\mu\text{-L})] \mathbf{3}$. In a 50 ml round bottom flask an ethanolic solution (10 ml) of L (21 mg, 0.10 mmol) was added to an ethanolic solution (15 ml) of silver nitrate (34 mg, 0.20 mmol). A yellow precipitate immediately formed. The flask was sealed and heated to 95 °C for 24 h. The reaction mixture was then cooled to room temperature at a rate of 1 °C h^{-1} . Well formed yellow rod-like crystals were produced, collected by filtration, washed with water and ethanol and dried under vacuum. Yield: 28 mg (76%, based on L) (Found: C, 38.07; H, 1.56; N, 17.92. Calc. for $\text{C}_{12}\text{H}_6\text{AgN}_5\text{O}_3$: C, 38.30; H, 1.60; N, 18.60%). IR: 3440m, 3110w, 3062w, 3030w, 2240m, 1725w, 1598s, 1540w, 1478s, 1468m, 1387s, 1316m, 1240m, 1249w, 1030m, 849m, 735m, 651s and 555w cm^{-1} .

(μ -5,5'-Dicyano-2,2'-bipyridine)(trifluoromethanesulfonato) silver(I), $\frac{1}{2}[\text{Ag}(\text{CF}_3\text{SO}_3)(\mu\text{-L})] \mathbf{4}$. In a 50 ml round bottom flask a solution of $\text{Ag}(\text{CF}_3\text{SO}_3)$ (56 mg, 0.22 mmol) in 5 ml of toluene was added to 15 ml of a toluene solution of L (21 mg,

0.1 mmol). A white precipitate immediately formed. The flask was sealed and heated to 95 °C for 24 h, followed by cooling to room temperature at 1 °C h⁻¹. The well formed colorless to pale green crystals were collected by filtration, washed with ethanol and dried under vacuum. Yield 31 mg (67%) (Found: C, 33.37; H, 1.26; N, 11.86. Calc. for C₁₃H₆AgF₃N₄O₃S: C, 33.69; H, 1.29; N, 12.10%). IR: 3440m, 3120w, 3070w, 3138w, 2270w, 2240m, 1598s, 1540m, 1480m, 1468s, 1374m, 1260s, 1240m, 1188w, 1160s, 1035s, 1030s, 945w, 850s, 705m, 650m, 634m, 580w, 555m and 520m cm⁻¹.

Bis(5,5'-dicyano-2,2'-bipyridine)silver(I) tetrafluoroborate, [AgL₂]BF₄ 5. A solution of AgBF₄ (21 mg, 0.10 mmol) in 10 ml of ethanol was carefully overlaid in a test-tube with a solution of L (10 mg, 0.05 mmol) in 10 ml of tetrahydrofuran. After 10 d at room temperature, well formed orange crystals had appeared at the boundary between ethanol and THF. They were collected, washed with water and ethanol and dried under vacuum. Yield 8 mg (66% based on L) (Found: C, 47.40; H, 1.97; N, 18.38. Calc. for C₂₄H₁₂AgBF₄N₈: C, 47.54; H, 1.98; N, 18.48%). IR: 3440m, 3124w, 3064w, 3235w, 2239m, 1725w, 1598s, 1560w, 1540w, 1478s, 1467m, 1388s, 1376m, 1320m, 1241m, 1126m, 1088m, 1070s, 1050s, 1030s, 1000m, 946w, 938w, 869m, 850w, 735m, 670w, 650w, 560w and 522w cm⁻¹.

When a solution of AgBF₄ (10 mg, 0.05 mmol) in 0.5 ml of acetonitrile and 4 ml of ethanol was carefully overlaid in a test-tube with a solution of L (21 mg, 0.10 mmol) in 10 ml of dichloromethane (or toluene) orange crystals were obtained after 5 d. Yield 15 (18) mg [49% (58%)]. The crystals were identified as complex **5** based on an identical IR spectrum. Furthermore, they were shown to be isotypic from their X-ray powder diffractograms which in addition matched the calculated pattern from the single crystal data.

Bis(5,5'-dicyano-2,2'-bipyridine)silver(I) hexafluorophosphate, [AgL₂]PF₆ 6. A solution of AgPF₆ (28 mg, 0.11 mmol) in 10 ml of ethanol was carefully overlaid in a test-tube with a solution of L (10 mg, 0.05 mmol) in 10 ml of tetrahydrofuran. After 12 d at room temperature, the well formed orange crystals were collected, washed with water and ethanol and dried under vacuum. Yield 19 mg (57% based on L) (Found: C, 42.81; H, 1.59; N, 16.51. Calc. for C₂₄H₁₂AgF₆N₈P: C, 43.31; H, 1.80; N,

16.85%). IR: 3435m, 3139w, 3064w, 3036w, 2238m, 1728w, 1600s, 1560w, 1540w, 1480s, 1466m, 1388s, 1380m, 1323m, 1250m, 1150w, 1033m, 947w, 860m, 850w, 830m, 788w, 733w, 670w, 650w and 562w cm⁻¹.

Slow concentration of a mixture of solutions of AgPF₆ in ethanol and of L in THF (or dichloromethane and toluene) in the mole ratio of 1:1 (or 2:1) also gave complex **6**, with the yield being about 57%. The identity was based on IR spectroscopy and X-ray powder diffractometry.

(μ₃-5,5'-Dicyano-2,2'-bipyridine)silver(I) hexafluorophosphatehemitoluene solvate, ²[Ag(μ₃-L)]PF₆·¹/₂C₇H₅Me 7. A solution of 27 mg (0.11 mmol) of AgPF₆ in a mixture of 1 ml of acetonitrile and 2 ml of ethanol was overlaid in a test-tube with a solution of 10 mg (0.05 mmol) of L in 6 ml of toluene. After 8 d at room temperature (in the dark) pale yellow crystals had formed. Yield 16 mg (64% based on L) (Found: C, 36.66; H, 1.93; N, 11.40. Calc. for C_{15.5}H₁₀AgF₆N₄P: C, 36.8; H, 1.98; N, 11.90%). IR: 3440m, 3108w, 3070w, 2240m, 1730w, 1598s, 1550w, 1540s, 1478s, 1467s, 1374m, 1280w, 1240s, 1088s, 1054w, 1030s, 950m, 850s (br), 776m, 734m, 695m, 650m, 565s and 555m cm⁻¹.

Even when stored in the dark, compound **7** slowly turned dark and appeared to be more sensitive to decomposition than the other four complexes **3–6**.

Structure determinations

Data were collected on a Bruker Smart CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and the use of a graphite monochromator. The crystal specimens were cooled to 173(2) K. Structure solution was performed by direct methods (SHELXL 97).²⁰ Refinement: full-matrix least squares on F² (SHELXL 97); all non-hydrogen positions found and refined with anisotropic thermal parameters. The hydrogen atoms of complexes **3**, **5** and **6** were found and refined, including the thermal parameter. Calculated hydrogen positions were added in the structures of **4** and **7**, refined as riding atoms on the bonded carbon atom position. With respect to data quality it should be noted that the crystal of **4** was very small. The refinement of the heavily disordered fluorine atoms in the third hexafluorophosphate anion of **7** (P3, cf. Fig. 8) is a rough approximation, the electron density related to the fluorine

Table 2 Crystal data for compounds **3–7**

	3	4	5	6	7
Formula	C ₁₂ H ₆ AgN ₅ O ₃	C ₁₃ H ₆ AgF ₃ N ₄ O ₃ S	C ₂₄ H ₁₂ AgBF ₄ N ₈	C ₂₄ H ₁₂ AgF ₆ N ₈ P	C _{15.5} H ₁₀ AgF ₆ N ₄ P
<i>M</i>	376.09	463.15	607.10	665.26	505.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 6 ₃ / <i>m</i>
Crystal size/mm	0.4 × 0.2 × 0.1	0.15 × 0.1 × 0.02	0.3 × 0.15 × 0.1	0.3 × 0.2 × 0.05	0.4 × 0.3 × 0.3
2θ range/°	4–62.1	4.3–57.8	4.0–62.3	4.1–57.5	2.6–60.4
<i>h</i> ; <i>k</i> ; <i>l</i> range	–10, 11; –10, 7; –29, 24	–11, 12; –5, 21; –9, 12	–17, 31; –10, 9; –21, 22	–28, 25; –4, 10; –10, 10	–24, 17; –8, 24; –27, 9
<i>a</i> /Å	8.2230(2)	9.4946(5)	21.9430(3)	21.8760(1)	17.8017(3)
<i>b</i> /Å	7.5328(2)	15.8010(8)	7.5298(1)	8.2210(2)	17.8017(1)
<i>c</i> /Å	20.3896(5)	10.3381(5)	15.7431(2)	15.8848(3)	19.6142(1)
β/°	93.308(1)	92.242(2)	112.676(1)	115.277(1)	90
<i>V</i> /Å ³	1260.87(5)	1549.78(14)	2400.10(5)	2583.24(8)	5383.0(1)
<i>Z</i>	4	4	4	4	12
<i>D</i> _c /g cm ⁻³	1.981	1.985	1.680	1.711	1.870
<i>F</i> (000)	736	904	1200	1312	2964
μ/cm ⁻¹	16.17	14.91	9.02	9.17	12.80
Measured reflections	9319	5664	7335	4895	22491
Unique reflections	3703 (0.0586)	2813 (0.0836)	3420 (0.0416)	2649 (0.0298)	5094 (0.0538)
(<i>R</i> _{int})					
Observed reflections	3269	1634	2561	2286	3491
[<i>I</i> > 2σ(<i>I</i>)]					
Parameters refined	214	226	197	206	277
Δρ/e Å ⁻³ ^a	0.537; –1.361	0.616; –0.960	0.562; –0.808	0.369; –0.593	1.694; –2.171
<i>R</i> 1; <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0337; 0.0796	0.0522; 0.0874	0.0440; 0.0925	0.0384; 0.0852	0.0753; 0.1882
(all reflections)	0.0403; 0.0839	0.1188; 0.1094	0.0693; 0.1035	0.0486; 0.0907	0.1104; 0.2037

^a Largest difference peak and hole.

atoms forming an almost perfect shell around P3. Crystal data are listed in Table 2. Graphics were prepared with ORTEP 3 and PLATON/PLUTON 97 for Windows.²¹

CCDC reference numbers 186/1235.

See <http://www.rsc.org/suppdata/dt/1999/183/> for crystallographic files in .cif format.

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References

- 1 A. E. Martell and R. D. Hancock, *Metal Complexes in Aqueous Solutions*, Plenum Press, New York, 1996; A. v. Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, 1996; J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
- 2 See for example: M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; L. R. MacGillivray, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676; A. J. Blake, S. J. Hill, P. Hubberstey and W.-S. Li, *J. Chem. Soc., Dalton Trans.*, 1998, 909; M.-L. Tong, X.-M. Chen, X.-L. Yu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1998, 5; K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, 1998, 177; P. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; O. M. Yaghi, H. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**, 4292; J. Lu, T. Paliwala, S. C. Lim, C. Yu, T. Niu and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 923; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; P. Lossier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1079.
- 3 C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431; O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.
- 4 P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, 1997, **119**, 2737.
- 5 K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. Eur. J.*, 1997, **3**, 765; *Inorg. Chem.*, 1997, **36**, 2960; D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.
- 6 G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature (London)*, 1995, **374**, 792.
- 7 C. Janiak, H.-P. Wu, S. Deblon, M. J. Kolm, P. Klüfers and H. Piotrowski, *Eur. J. Inorg. Chem.*, submitted for publication.
- 8 C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *Inorg. Chem.*, submitted for publication.
- 9 See for example: C. Janiak, T. G. Scharmann, J. C. Green, R. P. G. Parkin, M. J. Kolm, E. Riedel, W. Mickler, J. Elguero, R. M. Claramunt and D. Sanz, *Chem. Eur. J.*, 1996, **2**, 992; C. Janiak, T. G. Scharmann, W. Günther, F. Girgsdies, H. Hemling, W. Hinrichs and D. Lentz, *Chem. Eur. J.*, 1995, **1**, 637.
- 10 See for example: F.-Q. Liu and T. D. Tilley, *Chem. Commun.*, 1998, 103; H. Li, C. E. Davis, T. L. Groy, D. G. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1998, 31; B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2752; R. W. Saalfrank, O. Struck, M. G. Davidson and R. Snaith, *Chem. Ber.*, 1994, **127**, 2489.
- 11 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 920; P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153; K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. Commun.*, 1998, 13; L. Carlucci, G. Ciani, D. W. v. Gudenberg, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1997, 631; A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393; C. Janiak, T. G. Scharman, P. Albrecht, F. Marlow and R. Macdonald, *J. Am. Chem. Soc.*, 1996, **118**, 6307; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.
- 12 See I. M. Müller, T. Röttgers and W. S. Sheldrick, *Chem. Commun.*, 1998, 823; Y. Suenaga, S. G. Yan, L. P. Wu, I. Ino, T. Kuroda-Sowa, M. Maekawa and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 1998, 1121; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401.
- 13 J. A. R. Navarro, J. M. Salas, M. A. Romero and R. Faure, *J. Chem. Soc., Dalton Trans.*, 1998, 901; C. B. Aakeröy and A. M. Beatty, *Chem. Commun.*, 1998, 1067.
- 14 P. N. W. Baxter and J. A. Connor, *J. Organomet. Chem.*, 1988, **355**, 193.
- 15 C. P. Whittle, *J. Heterocycl. Chem.*, 1977, **14**, 191.
- 16 O. Struck, L. A. J. Christoffels, R. J. W. Lugtenberg, W. Verboom, G. J. van Hummel, S. Harkema and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 2487; J. Gross, G. Harder, F. Vögtle, H. Stephan and K. Gloe, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 481; A. Ikeda, H. Tsuzuki and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2073; H. C. Kang, A. W. Hanson, B. Eaton and V. Boekelheide, *J. Am. Chem. Soc.*, 1985, **107**, 1979.
- 17 S. Lopez, M. Kahraman, M. Harmata and S. W. Keller, *Inorg. Chem.*, 1997, **36**, 6138.
- 18 *Gmelin Handbook of Inorganic Chemistry, Silver*, Part B6, Springer, Berlin, 1975, pp. 346–353.
- 19 J. A. R. Navarro, J. M. Salas, M. A. Romero and R. Faure, *J. Chem. Soc., Dalton Trans.*, 1998, 901; M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.
- 20 G. M. Sheldrick, SHELXL 97, Programs for Crystal Structure Analysis, University of Göttingen, 1997.
- 21 ORTEP 3 for Windows, L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565; PLATON/PLUTON 97, A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

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