Self-Assembly of Spheroidal Structures: The Coordination Chemistry of Pentacyanocyclopentadienide

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his retirement

Modelling studies show that the anion pentacyanocyclopentadienide, **1**, can complex linearly coordinating cations such as silver(I) and copper(I) to form a spheroidal complex $[M_{30}(\mathbf{1})_{12}]^{18+}$ with minimum distortion. The anion **1** complexes transition metal ions to give species which appear to be polymers in the solid state. The structure of Ag(**1**) was determined by powder diffraction and shows a one-dimensional polymeric structure with three coordinate Ag^I and two CN functions of the ligand **1** non-coordinated. No evidence for the formation of the spheroidal complex was found.

1. Introduction. – The use of the coordinate bond to assemble large structures has been the subject of great attention in recent years, encompassing both large but molecular entities [1], and coordination frameworks (or metal-organic frameworks, MOFs) [2–5]. The structures of these compounds are generally discussed in terms of networks. Thus, the metal ion may be considered as a node of the network, and is joined by suitable bridging ligands such as 4,4′-bipyridyl or benzene-1,4-dicarboxylic acid. The node may be a single metal ion, or may be a polynuclear unit: *Yaghi* and co-workers have used the Zn_4O unit as an octahedral node with great success in the synthesis of microporous solids such as Zn_4O(benzene-1,4-dicarboxylate)$_3$ [6]. Alternatively, the ligand may be considered as node, capable of binding several metals with a specific disposition in space, and the metal ion then acts as the linker between nodes. This approach has been used to generate cages by the groups of *Robson* and co-workers [7], *Stang* and co-workers [8], and most notably by *Fujita* and co-workers [9] who have shown recently that such cages may be used as containers for photochemical reactions [10]. Reactions inside metal-assembled cages have also been studied by *Raymond* and co-workers [11]. The use of network nomenclature has recently been reviewed by *O'Keefe* and *Yaghi*, and co-workers [12], and shown to be a powerful tool for the classification of structures, and the same authors have recently reviewed discrete polynuclear systems which they describe as metal-organic polyhedra, MOPs, [13].

Among the ligands capable of acting as nodes, there are currently none which show fivefold symmetry. Our interest in preparing a nodal ligand with D_{5h} symmetry is not merely academic, but is based on the well-known observation that fivefold symmetry is not possible for an extended network. This is shown in *Fig. 1*, where the reader will readily see that to form normal-length bonds between the five external pentagons (the bonds shown as dashed lines in *Fig. 1*), it will be necessary to bend them out of the plane of the central pentagon, thereby inducing a curvature.

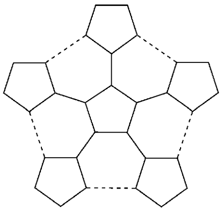
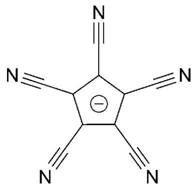


Fig. 1. *Scheme of a nodal ligand with* D_{5h} *symmetry*

An assembly of pentagons will thus automatically acquire a curvature and may be used to generate a spheroidal surface. The most famous example of this is, of course, the fullerene C_{60} which may be regarded as an assembly of twelve C_5 pentagons. There are, however, other examples of pentagonal units assembling into spheroidal structures: *Müller et al.* have synthesised some beautiful giant cages which use a $\{Mo(Mo)_5\}$ pentagons as building blocks [14][15], and *Scheer* and co-workers have shown recently how $[Cp^*Fe(P_5)]$ may be assembled into spheres using Cu^I [16][17]. The high symmetry of these systems containing a large number of chemically identical bonds makes them obvious targets for self-assembly reactions, and our aim in undertaking this work was to find a ligand L capable of acting as a roughly planar pentagonal node which could be assembled by complexation to a metal M into a spheroidal $[M_{30}L_{12}]$ unit.

The cyclopentadienyl unit is the obvious choice for the nucleus of such a ligand. For the binding unit, we initially chose the CN function which is a simple monodentate ligand for many metals. Dicyanamide is well-established as a bridging ligand, and tricyanomethanide has been used as a threefold node [18]. TCNQ was recently shown to act as a fourfold node [19]. This suggested the ligand pentacyanocyclopentadienide $[C_5(CN)_5]^-$ (**1**), which was reported many years ago by *Webster* [20], to be a potential fivefold node. The crystal structure of the anion in salts with organic cations shows it to possess the required pentagonal symmetry [21–23], but very little has appeared on its coordination chemistry. *Christopher* and *Venanzi* reported $[M(\mathbf{1})(CO)_3]$ (M = Mn, Re) and $[Fe(\mathbf{1})_2]$, and concluded on the basis of IR studies that the ligand was bound by N coordination, but no crystal structure was published [24]. More recently *Nalawajek et al.* have shown that 1,2-dicyanocyclopentadienide can act as a bridging ligand between transition metals [25].



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The choice of metal to link the ligands is straightforward: a metal is required that has a basically linear coordination, and which can support a slight degree of distortion to allow curvature. The group 11 ions Cu^{I} and Ag^{I} are obvious choices and have been shown to form polymeric species with CN ligands [26]. Other possibilities would be square planar ions such as Pt^{II} and Pd^{II} with two *trans*-sites occupied by monodentate blocking ligands, or an octahedral metal with two bidentate blocking ligands in *trans*-configuration. In the present manuscript, we report the results of our studies on the coordination chemistry of ligand **1**.

2. Results and Discussion. – 2.1. *Modelling Studies.* It seemed appropriate to model the proposed cage structure to identify any obvious stereochemical problems. The molecular mechanics package in *Hyperchem*® [27] was used. We began by placing five previously optimised molecules of **1** around a central molecule of **1** as shown in *Fig. 1*. The ligands were then connected *via* N–Ag–N bonds to give a $[Ag_{10}(\mathbf{1})_6]^{4+}$ fragment. This minimised easily and showed the expected curvature, giving a bowl-shaped structure. The final molecule was constructed by placing an inverted bowl above the first and linking them by another ten N–Ag–N units. Structure minimisation was again easily carried out and gave the molecule shown in *Fig. 2*, which shows the expected icosahedral I_h symmetry. The diameter of the resulting structure is *ca.* 20 Å. We consider it would be imprudent to place too much weight on these models, but it is nonetheless significant that the spheroidal structure requires no major distortion of bond lengths or angles.

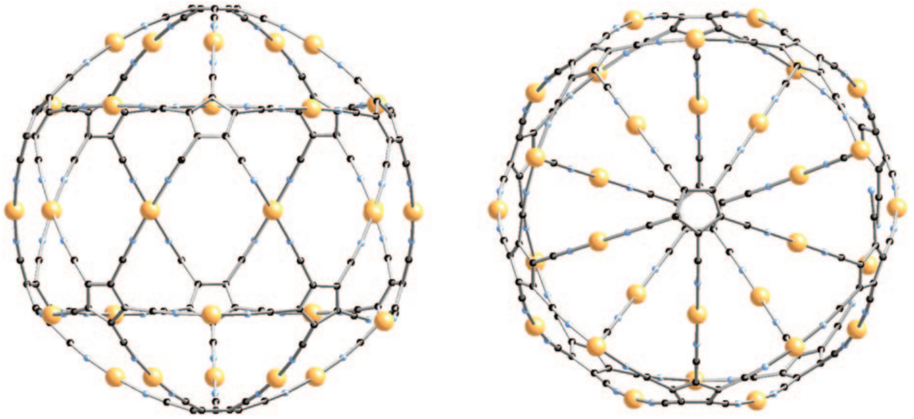

Fig. 2. *View of the minimised structure for* $[Ag_{30}(\mathbf{1})_{12}]^{18+}$. The left view is perpendicular to, and the right along, a C_5 axis.

2.2. *Reaction of Ligand* **1** *with Silver(I) and Copper(I).* Treatment of solutions of Ag^{I} or Cu^{I} in MeCN with solution of $(Et_4N)(\mathbf{1})$ gave precipitates of the salts $M(\mathbf{1})$, with or without MeCN of solvation (see *Exper. Part*). The IR spectra of these compounds show that the CN IR absorption (2219 cm^{-1} for **2a**, 2220 cm^{-1} for **2b** and 2220 cm^{-1} for **3**) was shifted to slightly higher energy compared with $Et_4N^{+}\mathbf{1}^{-}$ at 2216 cm^{-1}. The precipitate is slightly soluble in MeCN or DMSO to give colourless solutions whose ESI mass spectra indicate only the component ions $\mathbf{1}^-$ and $[M(CH_3CN)_3]^+$ ($M = Cu$, Ag) indicating that complete dissociation had occurred. No trace of the self-assembled polynuclear species was seen. The ^{13}C-NMR spectra of **2b** and **3** were recorded in DMSO and are given in *Table 1*. The absence of shifts for the Ag salt suggests dissociation in solution, but for Cu there is some sign of a bonding interaction, which must, however, be labile for all five cyanides to be equivalent.

Table 1. *^{13}C-NMR Data* (δ in ppm) *of* $Et_4N^+\mathbf{1}^-$, *and Complexes* **2b** *and* **3**

	C_5 Unit	CN Group	CN (MeCN)	Me (MeCN)
$Et_4N^+\mathbf{1}^-$	124.0	113.1	–	–
2b	124.1	113.1	116.2	1.2
3	115.5	101.4	118.4	1.2

2.3. *Crystal Structure of* **2a**. Our many attempts to grow crystals of these compounds were unsuccessful, but a reasonable X-ray powder diffraction diagram could be obtained. Since the structure of the anion is known from previous single-crystal studies, a satisfactory description of the structure requires relatively few parameters, and powder diffraction is thus interesting. The observed reflections of **2a** could be indexed with a primitive monoclinic unit cell $a = 6.666(3)$, $b = 13.765(3)$, $c = 11.222(2)$ Å, $\beta = 116.61(1)°$ with extinction symbol $P12_1/c1$. The structure was solved in the space group $P2_1/c$ with one Ag-atom in a general position and one planar rigid anion $[C_5(CN)_5]^-$ within the unit cell. The structure was refined ($\chi^2 = 11.1$, $R_{Bragg} = 0.03$ for main phase) keeping the $[C_5(CN)_5]^-$ anion planar and semi-rigid with three refined distances as given in *Table 2*. The anti-bump restraint Ag–N of 2.2(1) Å was used to stabilize the refinement. The *s.u.* of the translation parameters of the anion is 0.001, the *s.u.* of the rotation parameters (*Euler* angles) of the anion is 0.2°. All atoms of the anion were refined with the same isotropic displacement factor. Significant bond lengths are reported in *Table 2*, and full atomic coordinates are available as *Supplementary Material*. The bond lengths found for the anion are equal within experimental error to those reported in previous structure determinations of the anion **1** [21–23]. The *Rietveld* plot (*Fig. 3*) shows the presence of three phases, **2a** (63 wt.-%), and two impurities: Ag (34 wt.-%) and AgCl (3 wt.-%).

The structure shows the anion **1** to bind to three Ag ions using three adjacent CN functions. The Ag–N bond distances agree with the values found in the *Cambridge*

Table 2. *Selected Bond Distances* [Å] *for Ag(***1***)*

Ag–N13	2.32(1)	
Ag–N14	2.27(1)	
Ag–N15	2.45(1)	
C–C	1.38(3)	within C_5 ring
C–C	1.40(3)	between C_5 ring and CN C-atom
C≡N	1.14(5)	CN group

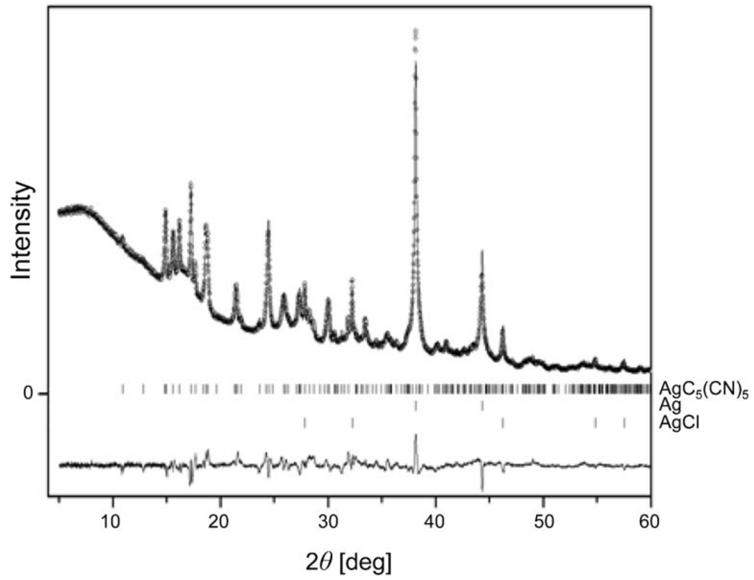

Fig. 3. Rietveld *plot of laboratory X-ray powder diffraction data* (Cu$K\alpha_1$) *of* $AgC_5(CN)_5$, $\chi^2 = 11.1$, $R_{Bragg} = 0.03$ *for main phase.* The position of reflections of $AgC_5(CN)_5$ (63 wt.-%), Ag (34 wt.-%), and of AgCl (3 wt.-%) are shown by vertical bars.

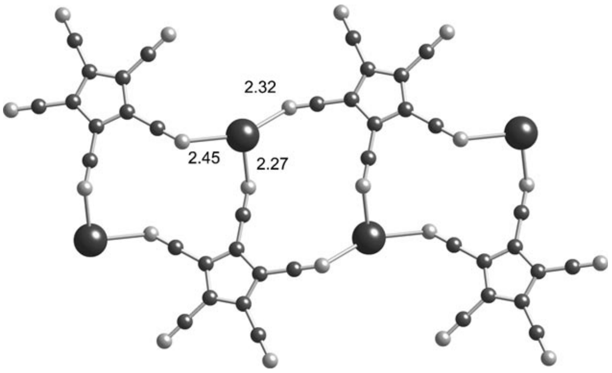

Fig. 4. *The* $\{Ag(\mathbf{1})\}_n$ *tapes running along the* c*-axis*

Structural Database. The Ag ions have an approximately T-shaped geometry, and the resulting structure (*Fig. 4*) may be regarded as a tape running along the crystallographic *c*-axis.

Neighbouring tapes are inclined to each other at an acute angle to form a corrugated sheet in the crystallographic *bc*-plane. The two non-coordinated CN functions of each ligand dovetail neatly into those of the neighbouring tape (*Fig. 5*). The packing coefficient as calculated by *Platon* [28] is 0.769.

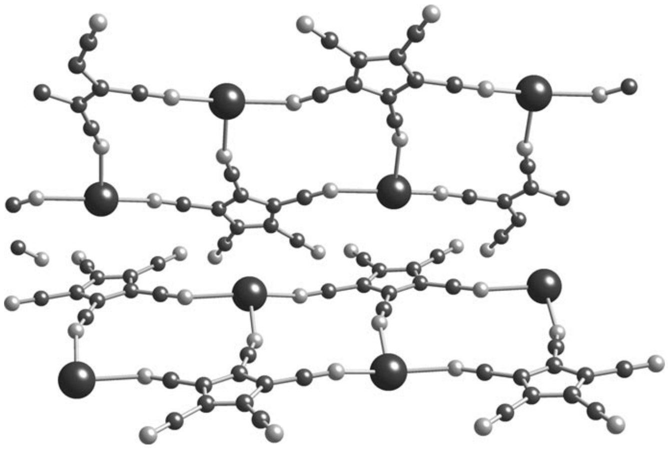

Fig. 5. *The dovetailing of the non-coordinated CN groups of different chains in Ag(***1***)*

2.4. *Reaction of Ligand* **1** *with Other Metal Ions.* Many attempts were made to isolate complexes with other metal ions. $(C_6H_{11}CN)AuCl$ gave no reaction with Et_4N(**1**). Several attempts were made using Pd compounds or complexes including $Pd(NO_3)_2$, $Pd(CH_3CN)_2Cl_2$, and $(phen)Pd(NO_3)_2$. In some cases, precipitates were obtained, in others solid samples were obtained by evaporation of the solvent. The results, as assessed by the IR spectra and elemental analysis, were poorly reproducible. The most significant observation was the change in the CN band at 2216 cm^{-1}: a new band at higher frequency (typically 2240–2260 cm^{-1}) was observed beside the original band. Following *Christopher* and *Venanzi* [24], we assume the higher-energy band to be associated with complexion of the metal to **1**, the uncoordinated CN bands appearing around 2216 cm^{-1}. We also reacted **1** with $M(CF_3SO_3)_2$ (M = Co and Ni). On evaporating the solution and washing the residue with MeOH, we obtained an orange red powder with Co and a red powder with Ni. The IR spectrum showed new bands at 2262 cm^{-1} and 2267 cm^{-1}, respectively, for the Co and the Ni compounds, as well as bands due to uncoordinated CN.

3. Conclusions. – Although the anion **1** has been considered to be a very weak base [23], it does complex transition metal ions as evidenced by the structure reported here, and the shift of the CN band in the IR spectrum. It seems reasonable to assume that the complexes formed are generally polymers in the solid state, and dissociate in solution: we found no evidence for complexation in solution. In all the compounds studied here, a band in the IR spectrum around 2216 cm^{-1} due to uncoordinated CN was always seen, implying that the full coordination potential of **1** was never observed. This leads to the question why the Ag(**1**) does not dissolve in presence of excess Ag^I to form the cage $[Ag_{30}(\mathbf{1})_{12}]^{18+}$ which would allow saturation of the coordination sites. Dissolution of the salt will be favoured by the formation of coordinate bonds but will involve the loss of the lattice energy of the salt Ag(**1**). The crystal structure shows this to be quite closely packed, and we presume this leads to the salt to be the thermodynamically most stable form. Recently, we have reported on the coordination chemistry of a pentapyridylcyclopentadienyl species and given evidence that it does indeed form a spherical aggregate with Ag^I; in this case, however, the ligand is neutral, so that no neutral salt can precipitate.

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Experimental Part

General Solvents and starting materials were purchased from *Fluka AG* (CH-Buchs) and were used without further purification unless otherwise stated. IR Spectra: *Perkin-Elmer Spectrum-One* or *883* instruments, KBr discs; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Gemini-300* spectrometer at 300 (^1H) and 74.44 MHz (^{13}C) at 22°; in (D_6)DMSO; chemical shifts δ in ppm with respect to Me_4Si, J in Hz. ESI-MS: *Finnigan Mat-SSQ7000* instrument of the Mass Spectrometry Laboratory, University of Geneva; in *m*/*z* (rel. %). Elemental analyses were performed by Dr. *H. Eder,* University of Geneva.

Tetraethylammonium pentacyanocyclopentadienide (Et_4N^+**1**$^-$) was prepared as described in [20] from 1,1,2,2-tetracyanoethylene. IR: 2996*m*, 2216*s* (CN), 1488*m*, 1467*m*, 1441*m*, 1393*m*, 1368*w*, 1173*m*, 1145*w*, 1052*w*, 999*m*, 784*m*. ^1H-NMR: 3.25 (*q*, $J = 7.2$, 4 CH_2); 1.20 (*t*, $J = 7.2$, 4 Me). ^{13}C-NMR: 124.0 (C_5); 113.1 (CN); 51.4 (CH_2); 7.1 (Me). ES-MS ($2 \cdot 10^{-3}$ M, MeCN): 190.3 (100, $[C_5(CN)_5]^-$).

Silver Pentacyanocyclopentadienide (**2a**). $AgNO_3$ (271.0 mg, 1.60 mmol) was added to a soln. of tetraethylammonium pentacyanocyclopentadienide (511.3 mg, 1.60 mmol) in MeOH (70 ml). After stirring 10 min at r.t., a dark brown microcrystalline solid formed, and the mixture was stirred for 1 h at r.t. After filtration, the product was washed with MeOH (2 × 20 ml) and Et_2O (2 × 15 ml) to give a brown-orange product which was dried *in vacuo* (303.3 mg, 55%) . IR: 2219 (CN), 1622*m*, 1575*m*, 1485*s*, 1463*s*, 1407*m*, 1361*m*, 1181*w*, 1159*w*, 824*w*, 624*w*, 513*m*, 495*m*, 483*m*, 472*m*. ^{13}C-NMR: 124.1 (C_5); 113.1 (CN). Anal. calc. for $C_{10}AgN_5 \cdot 2.5\, H_2O$: C 35.01, H 1.47, N 20.41; found: C 34.94, H 1.25, N 20.52.

Silver Pentacyanocyclopentadienide Trisacetonitrile (**2b**). *Method A.* $AgNO_3$ (145.9 mg, 0.86 mmol) was added to a soln. of tetraethylammonium pentacyanocyclopentadienide (275.2 mg, 0.86 mmol) in MeOH (50 ml). After stirring 10 min at r.t., a dark brown microcrystalline solid formed. After filtration, the product was dissolved in MeCN (10 ml)). Et_2O (20 ml) was added to the MeCN soln. to precipitate [Ag(**1**)$(CH_3CN)_3$] as a brown powder, which was collected and dried *in vacuo* (173.2 mg, 48%).

Method B. Silver triflate (14.1 mg, $5.5 \cdot 10^{-2}$ mmol) was added to a soln. of tetraethylammonium pentacyanocyclopentadienide (17.5 mg, $5.5 \cdot 10^{-2}$ mmol) in MeOH (50 ml). After stirring 10 min at r.t., a brown microcrystalline solid formed. After filtration, the product was washed with MeOH (2 × 5 ml). The solid was dissolved in MeCN (5 ml). Evaporation of the solvent under reduced pressure gave a brown powder (13.2 mg, 57%). IR: 2237 (Me*CN*), 2220 (CN), 1639*w*, 1482*m*, 1466*m*, 1405*m*, 1388*m*, 1367*m*, 1293*m*, 1180*w*, 1155*w*, 1030*w*, 812*w*, 628*w*, 513*m*, 499*m*, 476*m*. ^{13}C-NMR: 124.1 (C_5); 116.2 (Me*C*N); 113.1 (CN); 1.2 (*Me*CN). ES-MS ($8 \cdot 10^{-4}$ M, DMSO): 230.0 (64, $[Ag(MeCN)_3]^+$), 189.3 (100, $[Ag(MeCN)_2]^+$), 190.3 (100, $[C_5(CN)_5]^-$). Anal. calc. for $C_{16}H_9AgN_8$: C 45.63, H 2.15, N 26.61; found: C 45.14, H 1.99, N 26.07.

Copper Pentacyanocyclopentadienide Trisacetonitrile (**3**). $[Cu(MeCN)_4][PF_6]$ [29] (140.8 mg, 0.38 mmol) was added to a soln. of tetraethylammonium pentacyanocyclopentadienide (121.0 mg, 0.38 mmol) in THF (40 ml). The mixture was stirred overnight at r.t. The red-orange powder which precipitated was collected and dried *in vacuo* (92.4 mg, 65%). IR: 2238 (Me*CN*), 2221 (CN), 1487*m*, 1464*m*, 1407*m*, 1361*m*, 1169*m*, 1033*m*, 833*s*, 738*m*, 559*s*. ^{13}C-NMR: 118.4 (Me*C*N); 115.8 (C_5); 101.4 (CN); 1.2 (*Me*CN). ES-MS ($4 \cdot 10^{-4}$ M, DMSO): 186.4 (60, $[Cu(MeCN)_3]^+$), 145.63 (100, $[Cu(MeCN)_2]^+$), 190.4 (100, $[C_5(CN)_5]^-$). Anal. calc. for $C_{16}H_9CuN_8$: C 51.00, H 2.41, N 29.73; found: C 51.82, H 2.27, N 30.14.

Reaction of $PCCP^-$ *with* $M(CF_3SO_3)_2$ (M = Co, Ni). Five equiv. of $M(CF_3SO_3)_2$ (M = Co or Ni) were added to a soln. of 1 equiv. of tetraethylammonium pentacyanocyclopentadienide in MeCN. The mixture was stirred overnight at r.t. The solvent was evaporated to dryness, and the residue was treated with MeOH to give a red-orange powder for 'Co complex' and red for 'Ni complex', which were collected, washed with MeOH and dried *in vacuo.* Reaction with $Co(CF_3SO_3)_2$: IR: 2262*m*, 1657*s*, 1483*w*, 1438*w*, 1379*w*, 1252*s*, 1173*s*, 1116*w*, 1034*s*, 768*w*, 693*w*, 647*s*, 581*m*, 519*m*. Reaction with $Ni(CF_3SO_3)_2$: IR: 2267*m*, 1660*m*, 1625*s*, 1259*s*, 1174*s*, 1034*s*, 765*w*, 646*s*, 579*m*, 520*m*.

X-Ray Powder Diffraction. Powder diffraction data (PXD; sample AgPCCP 17.2.2005) were collected on the *Bruker-D8-Advance* diffractometer in reflection mode using Cu$K\alpha_1$ radiation¹). The sample was placed in a spinning plastic sample holder with diameter of 1 cm. The observed reflections of $AgC_5(CN)_5$ were indexed with DICVOL04 [30], the structure was solved with the direct space method program *Fox* [31] and refined with the *Rietveld* method by using the program *Topas* [32].

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¹) The crystallographic data for Ag(**1**) have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 732108. Copies of the data may be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road Cambridge, CB21EZ (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).