Structures of [Ag(tcm)], [Ag(tcm)(phz)$_{1/2}$] and [Ag(tcm)(pyz)] (tcm = tricyanomethanide, C(CN)$_3^-$, phz = phenazine, pyz = pyrazine)

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The topologically unique sheet structure of [Ag(tcm)] [tcm = the tricyanomethanide ion, C(CN)$_3^-$] is retained in the derivative [Ag(tcm)(phz)$_{1/2}$] (phz = phenazine). The sheet structure is composite, consisting of two independent hexagonal grid nets which are corrugated so as to allow one to interpenetrate the other. The Ag^+ ion is three-coordinate and provides half the three-connecting nodes of the hexagonal grid net, the others being provided by the tcm central carbon. [Ag(tcm)(phz)$_{1/2}$] contains essentially the same composite double sheets linked together by phenazine units that bridge between silver centres which thereby become four-coordinate. The topology of [Ag(tcm)(pyz)] (pyz = pyrazine) is very different; in this case the Ag(tcm) component forms a planar, non-corrugated hexagonal grid and each such sheet is connected on both sides to neighbouring sheets by pyrazine bridging ligands whereby the silver becomes five-coordinate and trigonal bipyramidal. Two such 3,5-connected three-dimensional nets then interpenetrate.

There have been numerous recent reports in which N-donor bridging ligands,[1] in particular those with pyridyl[2] and nitrile[3] donor groups, have been used to construct coordination polymers showing novel structural features.

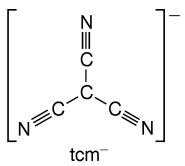
A number of new networks have been generated using three-connecting bridging ligands with a trigonal geometry. An example of this type is 2,4,6-tri(4-pyridyl)-1,3,5-triazine which provides several highly symmetrical, cubic three-dimensional (3D) nets.[4] An interesting hinged three-dimensional (10,3)b network is present in the coordination polymer formed by Ag^+ and 1,3,5-tris(4-cyanophenylethynyl) benzene,[5] while the related 3-ethynyl ligand[6] and 1,3,5-tricyanobenzene[5] with the same metal ion give two-dimensional (2D) hexagonal sheet structures.

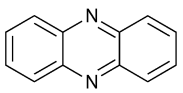
A particularly simple trigonal bridging ligand is the tricyanomethanide anion, tcm$^-$, C(CN)$_3^-$. With a range of octahedral divalent metal ions this gives an isostructural series of compounds of the simple 'binary' composition [M(tcm)$_2$] which consist of two independent but interpenetrating nets with the rutile topology.[1,7] The anion tcm$^-$, together with a variety of co-ligands, provides a number of other coordination networks.[8]

The present report is concerned with the structures of [Ag(tcm)] and two of its derivatives, namely [Ag(tcm)(phz)$_{1/2}$] (phz = phenazine) and [Ag(tcm)(pyz)] (pyz = pyrazine).

Results and Discussion

The crystal structure of [Ag(tcm)], determined from photographic data (R 0.0996) was described by Konnert and Britton in 1966.[9] This was a very significant paper reporting an entirely new type of interpenetrating structure, very few examples of which were known at that time. We have re-determined the structure to contemporary levels of precision to resolve uncertainties regarding the space group and the unusual silver environment. Our crystallographic study of [Ag(tcm)] confirms the earlier result. The structure consists of two identical and independent (6, 3) hexagonal grid sheets, interpenetrating in the manner shown in Fig. 1. Alternating three-coordinate silver and trigonal tcm carbon provide the three-connecting nodes from which the hexagonal grids are constructed. Individual sheets are corrugated so as to allow the interweaving which can be clearly seen in the 'edge-on' view in Fig. 1(*b*). The silver coordination environment is distinctly distorted towards trigonal-pyramidal geometry (sum of N-Ag-N angles = 349.4°); this together with significant bending at the nitrogens is responsible for the corrugation of the sheets. The tcm ligands internally remain essentially trigonal and planar. The silver makes two equivalent long contacts of 2.979(6) Å to nitrogen atoms in an adjoining layer. While these distances are too long for formal coordinative bonds to be assigned, they do represent significant interactions.





We were interested to see if it might be feasible to 'expand' the structure deliberately by intercalating bridging ligands between the layers without disrupting the interwoven sheet structure within the layers.

The reaction of phenazine and [Ag(tcm)] in acetonitrile affords crystalline [Ag(tcm)(phz)$_{1/2}$] in the form of yellow rods; the structure is shown in Fig. 2. The phenazine rings, as anticipated, do bridge between interwoven double sheets which do retain their identity as we had hoped. The corrugations, however, are more pronounced than in the parent. Two independent interpenetrating 3D networks are thereby generated in contrast to the infinite number of independent 2D networks present in [Ag(tcm)].

Analogous reactions with the phenazine replaced by pyrazine, yield [Ag(tcm)(pyz)] as colourless crystals whose structure, shown in Fig. 3, is very different from the previous two. The Ag(tcm) still generates hexagonal grid sheets but these are now strictly planar and each such sheet is attached to two neighbouring sheets by pyrazine molecules that bridge between silver centres. The metal coordination environment therefore is trigonal bipyramidal and a 3,5-connected 3D net is formed. Two independent networks of this type interpenetrate with the bridging pyrazines of one net passing through

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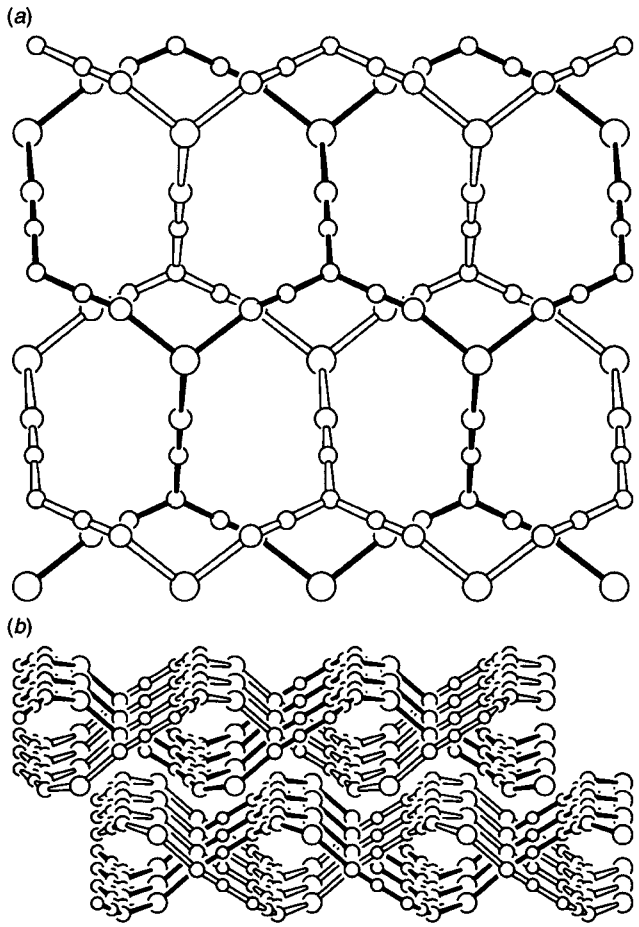

Fig. 1 (*a*) Two independent interwoven hexagonal grid networks viewed perpendicular to the sheets in the structure of [Ag(tcm)]. (*b*) Two layers of the internally interwoven double sheets viewed approximately 'edge-on'. The circles in order of decreasing size represent Ag, N and C atoms. Note the distortion of the silver atoms from trigonal geometry towards pyramidal geometry, and the approach of the N atoms of one layer to the Ag atoms of the adjacent layer [Ag—N = 2.979(6) Å]

the hexagonal windows in the Ag(tcm) sheets of the other as can be seen in Fig. 3.

We suggest that the differences in structure between [Ag(tcm)(pyz)] and [Ag(tcm)(phz)$_{1/2}$] arise from the differences in size of the two heterocyclic bridging ligands. The phz ligand is too large to be able to fit through the hexagonal windows of the planar Ag(tcm) sheets and yet when it bridges between the interwoven double sheets it fills the space between the sheets satisfactorily. If pyrazine were to play the same role as phenazine it is clear that a lot of empty space would be left between the double sheets; this could of course have been filled by solvent but this apparently does not happen. The interpenetrating structure observed for [Ag(tcm)(pyz)], with a density of 2.01 g cm^{-3}, provides much more efficient packing than the hypothetical [Ag(tcm)(pyz)$_{1/2}$] with a [Ag(tcm)(phz)$_{1/2}$]-like structure for which we calculate the density would be 1.56 g cm^{-3}.

Experimental

Syntheses

[Ag(tcm)]. The complex [Ag(tcm)] was prepared and crystals grown using the previously published procedures.[9]

[Ag(tcm)(phz)$_{1/2}$]. A solution obtained by combination of [Ag(tcm)] (75 mg, 0.38 mmol) in acetonitrile (15 mL) and phenazine (34 mg, 0.19 mmol) in acetonitrile (5 mL) gave yellow rods of [Ag(tcm)(phz)$_{1/2}$] (24 mg, 0.083 mmol, 22%) after 3 d. IR(KBr): 556, 595, 658, 759, 825, 908, 1004, 1070, 1120, 1152, 1206, 1250, 1338, 1365, 1435, 1468, 1514, 2190, 2500, 3445 (br) cm^{-1}. Analysis: Calcd.: C 41.7, N 19.5, H 1.4. Found: C 41.9, N 19.7, H 1.0%.

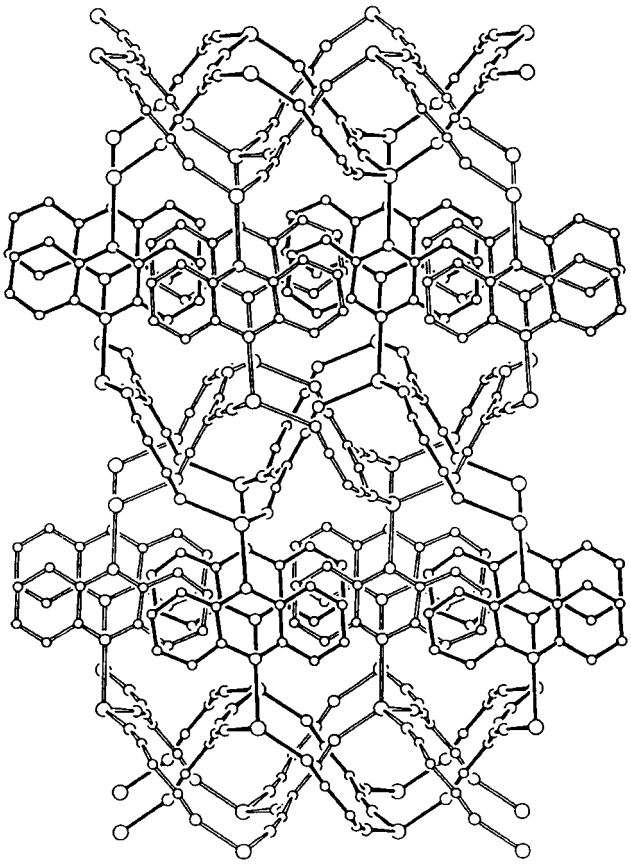

Fig. 2 The two interpenetrating 3D frameworks of [Ag(tcm)(phz)$_{1/2}$], showing the phz ligands bridging between layers of doubly interpenetrating Ag(tcm) sheets. The Ag atoms now have tetrahedral geometry. The circles in order of decreasing size represent Ag, N and C atoms

[Ag(tcm)(pyz)]. A solution obtained by combination of [Ag(tcm)] (75 mg, 0.38 mmol) in acetonitrile (15 mL) and pyrazine (30 mg, 0.38 mmol) in acetonitrile (5 mL) gave colourless plates of [Ag(tcm)(pyz)] (42 mg, 0.15 mmol, 39%). IR(KBr): 402 (sh), 430, 550, 565, 797, 915, 940, 1022, 1035, 1068, 1104, 1125, 1154, 1180, 1240, 1268, 1340, 1415, 1482, 1706, 1762, 1894, 1945, 2150, 2160, 2210, 2470, 2820, 3020,

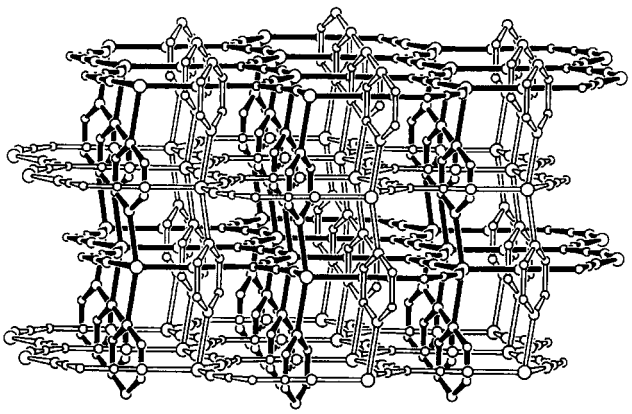

Fig. 3 The two interpenetrating 3D frameworks of [Ag(tcm)(pyz)]. The Ag atoms now have five-coordinate, trigonal-bipyramidal geometry. The circles in order of decreasing size represent Ag, N and C atoms

3070, 3400 (br) cm^{-1}. Analysis: Calcd.: C 34.6, N 25.2, H 1.5. Found: C 34.7, N 25.4, H 1.3%.

Crystallography

The intensity data for all three structures were measured at 295(1) K with MoKα radiation (graphite monochromator, λ = 0.710 69 Å) using an Enraf-Nonius Cad-4F diffractometer and employing the ω/2θ scan method; corrections for Lorentz, polarization and absorption effects were applied.

Crystal data for [Ag(tcm)]: $M = 197.94$, orthorhombic, space group *I*2*cm* (no. 46), $a = 6.200(1)$, $b = 10.147(2)$, $c = 7.977(2)$ Å, $U = 501.8$ $Å^3$, $Z = 4$, crystal dimensions $0.12 \times 0.07 \times 0.01$ mm, $\rho_{calc} = 2.62$ g cm^{-3}, $\rho_{meas} = 2.64(1)$ g cm^{-3}, $F(000) = 368$, 1060 reflections measured, 714 unique reflections, $2\theta_{max} = 70°$, $\mu(MoK\alpha) = 38.19$ cm^{-1}, min./max. transmission = 0.7763/0.9462. The position of the silver atom was determined using the Patterson function of SHELXS-86, and all other atoms were found in subsequent full-matrix least-squares refinements (SHELX-76, refined against $|F|$). Anisotropic thermal parameters were applied to all atoms. At convergence $R = 0.0307$ and $R_w = 0.0288$ for the 449 observed reflections [$I \geqslant 3\sigma(I)$] with 51 parameters; max. residual electron density = 0.77 e $Å^{-3}$.

Crystal data for [Ag(tcm)(phz)$_{1/2}$]: $M = 288.08$, monoclinic, space group $P2_1/a$ (no. 14), $a = 8.391(2)$, $b = 10.152(3)$, $c = 24.115(6)$ Å, $\beta = 100.01(2)°$, $U = 2022.9$ $Å^3$, $Z = 8$, crystal dimensions $0.22 \times 0.15 \times 0{\cdot}05$ mm, $\rho_{calc} = 1.89$ g cm^{-3}, $\rho_{meas} = 1.92(1)$ g cm^{-3}, $F(000) = 1112$, 4827 reflections measured, 3760 unique reflections, $2\theta_{max} = 50°$, $\mu(MoK\alpha) = 19.14$ cm^{-1}, min./max. transmission = 0.8571/0.9148. The structure was solved using the Patterson routine of SHELXS-86. A full-matrix least-squares refinement (SHELX-76, refined against $|F|$) was then employed. The poor quality of the data required the bond lengths of the phenazine to be fixed to chemically sensible values [1.40(2) Å], as were the C—C [1.40(2) Å] and C—N [1.15(2) Å] bond lengths of the tcm anions. Anisotropic thermal parameters were applied to both unique silver atoms; all other atoms were refined with isotropic thermal parameters. The phenazine hydrogens were assigned to calculated positions and refined with a common isotropic thermal parameter. At convergence $R = 0.0670$ and $R_w = 0.0666$ for the 1394 observed reflections [$I \geqslant 3\sigma(I)$] with 133 parameters; max. residual electron density = 0.95 e $Å^{-3}$.

Crystal data for [Ag(tcm)(pyz)]: $M = 278.04$, orthorhombic, space group *Pmcn* (no. 62), $a = 7.445(1)$, $b = 9.175(2)$, $c = 13.466(2)$ Å, $U = 919.9$ $Å^3$, $Z = 4$, crystal dimensions $0.05 \times 0.02 \times 0.02$ mm, $\rho_{calc} = 2.01$ g cm^{-3}, $\rho_{meas} = 2.01(1)$ g cm^{-3}, $F(000) = 536$, 2536 reflections measured, 1417 unique reflections, $2\theta_{max} = 60°$, $\mu(MoK\alpha) = 21.06$ cm^{-1}, min./max. transmission = 0.9469/0.9668. The structure was solved using the Patterson routine of SHELXS-86. A full-matrix least-squares refinement (SHELX-76, refined against $|F|$) was then employed. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Both unique pyrazine hydrogens were assigned to calculated positions and refined with a common isotropic thermal parameter. At convergence $R = 0.0406$ and $R_w = 0.0390$ for the 916 observed reflections [$I \geqslant 3\sigma(I)$] with 81 parameters; max. residual electron density = 1.53 e $Å^{-3}$ (1.00 Å from Ag).

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