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Solvent control in the formation of mononuclear and dinuclear double-helical silver(I)-2,2′:6′,2″-terpyridine complexes

Gerhard Baum,[b] **Edwin C. Constable,***[a] **Dieter Fenske**[b] **Catherine E. Housecroft**[a] **and Torsten Kulke**[a]

[a] *Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland.*
E-mail: constable@ubaclu.unibas.ch
[b] *Institut für Anorganische Chemie, Universität Karlsruhe (TH), Engesserstraße, 76128 Karlsruhe, Germany*

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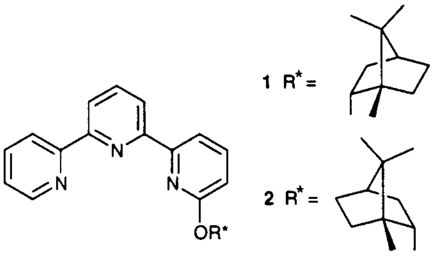
The coordination behaviour of chiral 2,2′:6′,2″-terpyridines with silver(I) is solvent dependent; in acetonitrile, mononuclear [Ag(L)(MeCN)]$^+$ complexes are formed, whereas in less coordinating solvents such as methanol or nitromethane, solid state tetranuclear bis(double helices) [{Ag_2L_2}$_2$]$^{4+}$ are obtained.

It is well established that oligopyridines and related ligands form helicates with a variety of metal centres.[1–3] Although copper(I) forms dinuclear double-helicates with 2,2′:6′,2″-terpyridines (tpy),[4,5] we have been unable to isolate analogous silver(I) species.[6] To date, the only oligopyridine system for which solution equilibria between {ML}$_n$ species have been established involves 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines and cobalt(II).[7] In the course of our studies on chiral helicates[5,8] we have revisited the 2,2′:6′,2″–terpyridine–silver(I) system and now show that both mononuclear and dinuclear double-helical species may be isolated and that the equilibrium between mono- and dinuclear species is solvent dependent.



The chiral ligands 1*S*-(−)-**1** and 1*R*-(+)-**2** (L)[8] reacted with Ag(O_2CMe) in MeOH to give colourless solutions from which white solids were precipitated by the addition of [NH_4][PF_6]. Both solutions and solids were photosensitive and turned yellow and then brown upon several hours exposure to sunlight. The electrospray mass spectra of these solids in MeOH or MeCOMe exhibited peaks assigned to {AgL}, {AgL_2} and {$Ag_2L_2(PF_6)$} whereas in acetonitrile, predominantly mononuclear species were observed. Recrystallisation from MeOH, $MeNO_2$ or MeCN gave solids with a 1 : 1 ratio of silver to L but which were qualitatively and quantitatively different. The ^1H NMR spectra of solutions of these solids were solvent dependent, although identical spectra were obtained in a given solvent for both crude and recrystallised materials. Reversible changes occurred upon adding CD_3CN to CD_3OD solutions. The magnitude of these changes suggested that different chemical species might be present in solvents of varying donor ability and the spectra in acetonitrile resembled those of the known [Ag(tpy)(MeCN)]$^+$.[6]

The ligands are chiral and CD spectroscopy proved useful. In [Ag(L)(MeCN)]$^+$, the only source of chirality is the ligand and the CD spectra of MeCN solutions of any of the solids are compatible with this formulation; the spectra exhibit $\Delta\varepsilon$ values of ± 2 mol^{-1} l cm^{-1} {$[\alpha]_D$ (MeCN) = ± 60°, $[M]_D$ (MeCN) = ± 420°}, similar to those of the free ligands and with equal and opposite responses for **1** and **2** compounds. We have previously shown that related dicopper(I) double helicates are formed with good diastereoselectivity for the *P* or *M* helicates and have CD responses with characteristic bands at 320 nm allowing the assignment of *P* or *M* helical chirality.[5,8,9] Solutions in MeOH or $MeNO_2$ of the crystals obtained from $MeNO_2$ showed equal and opposite responses at 329 nm {$\Delta\varepsilon \pm$ 20 mol^{-1} l cm^{-1}; $[\alpha]_D$ = ± 200°; $[M]_D$ = ± 2530°} for the compounds derived from **1** and **2**; addition of MeCN to the MeOH solution resulted in a decrease in the CD response and eventually the development of the same spectrum as observed for pure MeCN solutions (Fig. 1). Similar changes were observed upon adding MeOH to MeCN solutions. On the basis of these observations we propose the formation of mononuclear [Ag(L)(MeCN)]$^+$ species in MeCN but of double-helical complexes in $MeNO_2$ and MeOH; the sign of the CD response at 329 nm[5,8,10] and the observation of only a single solution species by NMR in MeOH suggest diastereoselective formation of *M*-[$Ag_2(\mathbf{1})_2$]$^{2+}$ and *P*-[$Ag_2(\mathbf{2})_2$]$^{2+}$.

The recrystallisation of silver(I) complexes of simple 2,2′:6′,2″-terpyridines from MeCN leads to solvento species [Ag(L)(MeCN)]$^+$ [6] and this proved also to be the case with **1**. Fig. 2(a) shows the molecular structure of one of the two mononuclear [Ag(**1**)(MeCN)]$^+$ cations present in [Ag(**1**)(MeCN)][PF_6]·Et_2O. The silver is four coordinate and bonded to the three nitrogen donors of **1** and an acetonitrile molecule; the coordination geometry is distorted square planar and the silver lies 0.13–0.15 Å out of the plane defined by the three tpy nitrogen donors and the acetonitrile nitrogen donor lies 0.51–0.66 Å from this plane. The planar cations are stacked within the lattice [Fig. 2(b)] with a zigzag arrangement of silver centres (Ag···Ag = 5.277, 5.577 Å) resulting in efficient π-stacking of the tpy domains. The zigzag structure results in π-bonding interactions between silver and the central ring of the tpy in the adjacent cations to give a sandwich structure (Ag···centroid, 3.646, 3.514 Å).

X-Ray quality crystals of the product formed in $MeNO_2$ were obtained by the diffusion of Et_2O into an MeCOMe solution. The crystal structure of one of the cations found in the solid state

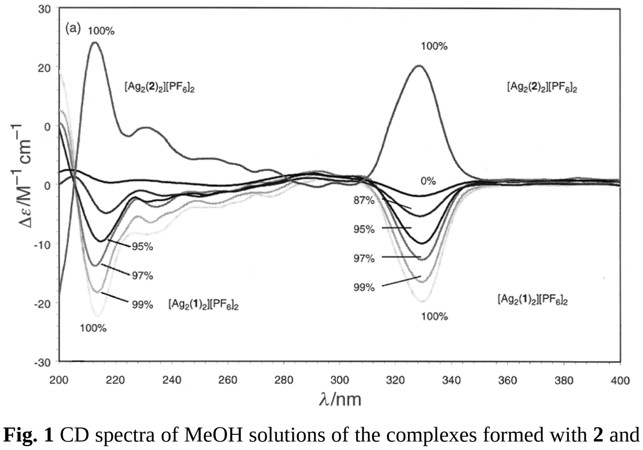


Fig. 1 CD spectra of MeOH solutions of the complexes formed with **2** and **1** and the effect of adding MeCN to the complex with **1**.

in the compound $[Ag_2(\mathbf{1})_2][PF_6]_2\cdot$MeCOMe is presented in Fig. 3. Firstly, a disilver head-to-head double helicate is present with Ag···Ag distances of 2.914–2.940 Å. Each silver is effectively two coordinate with short Ag–N bonds (2.146–2.616 Å) to terminal pyridine rings of each of two ligands and two longer Ag···N contacts to the central rings (3.1–3.2 Å). However, the structure is rather more complex; each of the double helicates forms a short (3.107, 3.156 Å) tail-to-tail Ag···Ag contact with a second dinuclear unit to give a tetranuclear unit. Each of the dinuclear subunits possesses the same helical chirality (both *M* in the case of Fig. 3). The tail-to-tail arrangement results in π-stacking of the terminal pyridine rings of the two dinuclear subunits (3.669–3.783 Å).

As discussed above, solution measurements indicated diastereoselective formation of *M*-$[Ag_2(\mathbf{1})_2]^{2+}$ and *P*-$[Ag_2(\mathbf{2})_2]^{2+}$ helicates; however, in the solid state, there are two tetranuclear units within the lattice, one of which has two *P* and the other two *M* helicates as dinuclear subunits–a diastereomeric excess of 0%! This illustrates the subtlety of the interactions controlling stereoselectivity in helicates. Although the formation of the tetranuclear units can be understood in terms of the favourable stacking and Ag···Ag interactions, the formation of both*P* and *M* helices in the solid state (but not in solution) is unexpected. A similar observation has been reported for mononuclear complexes[10] and it appears to be a consequence of a low energy barrier for the interconversion of diastereomers combined with crystal packing effects of the same order as the energy difference between the diastereomers. There are no short contacts between chiral substituents of adjacent tetranuclear subunits.

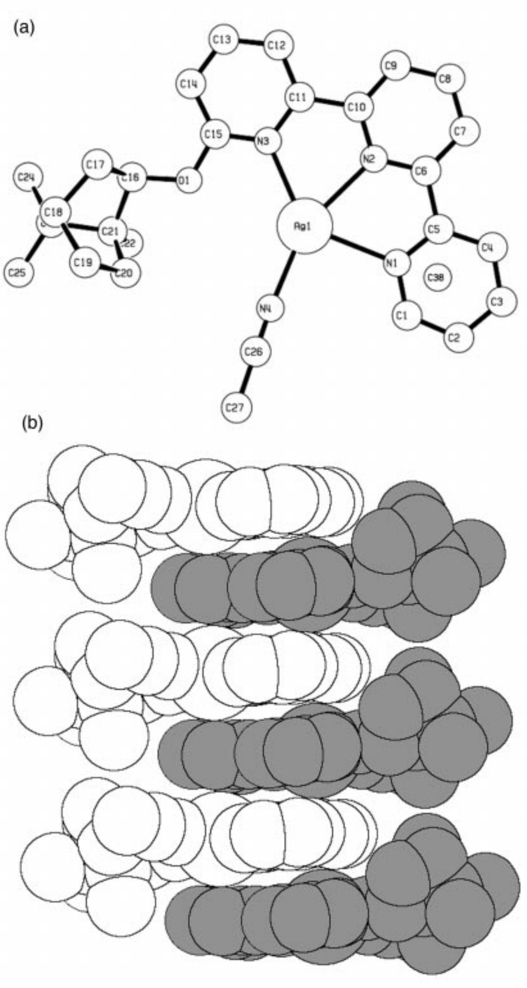


Fig. 2 (a) One of the $[Ag(\mathbf{1})(MeCN)]^+$ cations and (b) the packing of cations in the lattice of $[Ag(\mathbf{1})(MeCN)][PF_6]\cdot Et_2O$. H-atoms omitted for clarity.

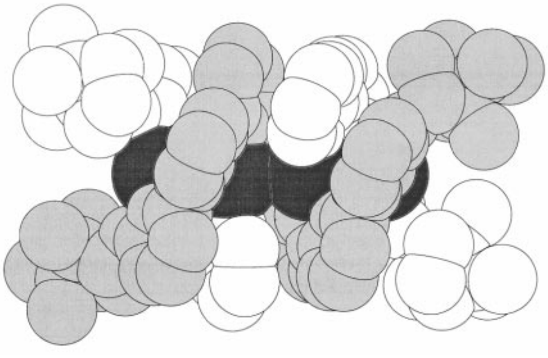


Fig. 3 The structure of the tetranuclear *M,M*-$[Ag_2(\mathbf{1})_2]^{2+}$ cation in $[Ag_2(\mathbf{1})_2][PF_6]_2\cdot$MeCOMe. H-atoms omitted for clarity.

In conclusion, we have now established that silver(I) behaves in a similar manner to copper(I) and forms double helical complexes with tpy ligands. However, the tendency for the formation of Ag···Ag interactions results in a subsequent aggregation process to give tetranuclear species.

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Notes and references

‡ *Crystal data*: for $C_{31}H_{40}AgF_6N_4O_2P$, M = 753.52, triclinic, space group $P1$ (no. 1), a = 7.1000(10), b = 12.170(2), c = 19.907(5) Å, α = 106.09(2), β = 90.72(2), γ = 93.40(2)°, U = 1649.1(6) Å^3, θ range 3.2–28.1°), Z = 2, D_c = 1.518 Mg m^3, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 7.3 cm^{-1}, F(000) = 772, T = 173 K, 11 593 independent reflections [11 008, $I > 2.0\sigma(I)$]. Refinement converged at a final R = 0.0264, 0.0282 (all data) $wR2$ = 0.0696, 0.0716 (all data). Minimum and maximum final electron density 0.51 and 0.24 e Å^3.

For $C_{26.5}H_{30}AgF_6N_3O_{1.5}P$, M = 667.38, monoclinic, space group $P2$, (no. 4), a = 13.831(3), b = 33.071(6), c = 25.147(6) Å, β = 91.34(2), U = 11 499(4) Å^3, θ range 2.1–26.0°, Z = 16, D_c = 1.542 Mg m^3, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 8.22 cm^{-1}, F(000) = 5408, T = 183 K, 55 171 independent reflections [39 367, $I > 2.0\sigma(I)$]. Refinement converged at a final R = 0.0492 , 0.0694 (all data), $wR2$ = 0.1278, 0.1403 (all data). Minimum and maximum final electron density 0.493 and 0.840 e Å^3.

Data collected were measured on a STOE IPDS Image Plate diffractometer; structure solution SHELXL-97, SHELXS-97. CCDC 182/1080. See http://rsc.org/suppdata/cc/1998/2659/for crystallographic files in .cif format.

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