A Silver Co-ordination Polymer bridged by a Conjugated Ligand

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The crystallographic characterization of the first well defined co-ordination polymer in which silver ions are linked by a bridging conjugated organic ligand is reported.

Although metal containing polymers may have unusual physical, electronic, or optical properties compared to wholly organic materials,[1] progress in this field has been hampered by difficulties in the synthesis and characterization of well defined materials.[2] The silver(I) ion is known to form co-ordination polymers with a number of inorganic[3] and organic[4,5] ligands capable of bridging two metal centres. In this work, we report the synthesis and structural characterization of a polymeric silver complex in which the metal centres are linked by a conjugated bridging ligand, 1,4-di-t-butyldiazabuta-1,3-diene (Bu^{t}-DAB). Although the ability of DAB ligands to bridge two metal centres has been noted previously,[6] to our knowledge this work represents the first structural characterization of a polymeric system with this class of conjugated ligands.

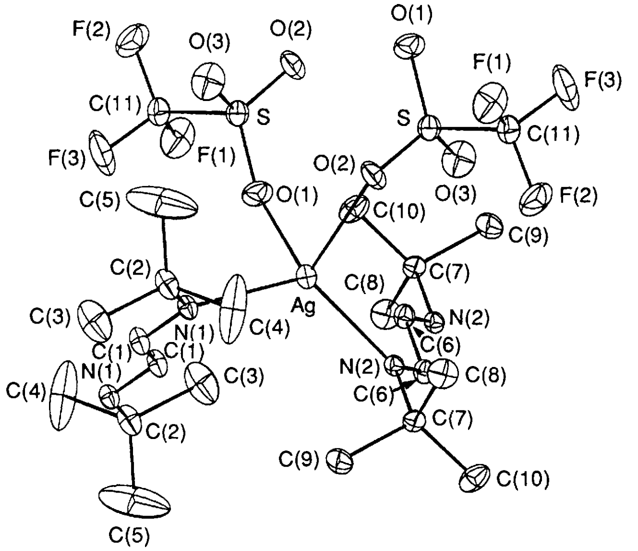

Figure 1. Computer generated ORTEP diagram of Ag(Bu^{t}-DAB)OTf showing atom labelling scheme with atoms depicted as 20% probability thermal ellipsoids.

Addition of Bu^{t}-DAB (1 equiv.) to a tetrahydrofuran (THF) solution of AgOTf (OTf = O_3SCF_3) results in a light yellow solution from which precipitation of the white somewhat light-sensitive complex Ag(Bu^{t}-DAB)OTf takes place within minutes in essentially quantitative yield.† Solid state IR spectra show a slight decrease in the $\nu_{C=N}$ stretching band from 1632 cm^{-1} in the free ligand to 1624 cm^{-1} in the co-ordination complex. In addition strong bands at 1285, 1235, 1162, 1022, and 628 cm^{-1} indicate the presence of co-ordinated [OTf]$^-$.[7]

Crystals suitable for an *X*-ray structural analysis‡ were

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† Satisfactory elemental analyses were obtained.

‡ *Crystal data* for Ag(Bu^{t}-DAB)OTf: space group $P\bar{1}$, $a = 9.020(1)$, $b = 10.065(2)$, $c = 11.374(1)$ Å, $\alpha = 111.96(1)$, $\beta = 96.48(1)$, $\gamma = 114.19(1)°$, $U = 829.3$ Å^3, $Z = 2$, $D_c = 1.702$ g cm^{-3}. Of 2814 unique reflections measured (Cu-$K_{\alpha 1}$ radiation, $4.0 < 2\theta > 130.0$), 2560 had $I > 3\sigma(I)$ and were used in the solution and refinement with an empirical absorption correction ($\mu = 114.9$ cm^{-1}) applied. Final refinement with hydrogen atoms located and included as fixed isotropic contributions and all other atoms as anisotropic contributions, 191 variables) gave $R = 0.0354$, $R_w = 0.0379$ and g.o.f. = 1.12. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

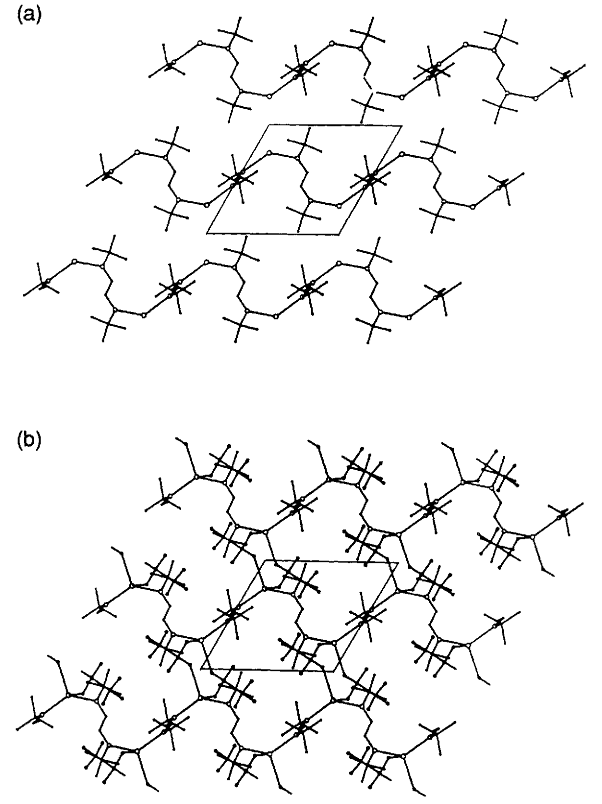

Figure 2. PLUTO unit cell representation of Ag($\mathrm{Bu^t}$-DAB)OTf view down the *z*-axis with the *y*-axis to the right, showing (a) the bridging [$\mathrm{OTf^-}$] anions removed for clarity; and (b) the complete structure.

obtained by diffusion of $\mathrm{Et_2O}$ into a saturated 1,2-dichloroethane solution of Ag($\mathrm{Bu^t}$-DAB)OTf. As illustrated in Figure 1, the polymer crystallizes with an inversion centre at the midpoint of the C–C backbone of the $\mathrm{Bu^t}$-DAB ligand which is in the *E-s-trans-E* conformation. Although several carbons of the $\mathrm{Bu^t}$ groups have elevated thermal parameters, the overall quality of the structural model is high. Consistent with the IR data presented above, the C–N and C–C bond lengths of the ligand are essentially unchanged upon co-ordination.[6,8] Each silver cation is bridged by two trifluoromethanesulphonate anions to form eight-membered $\mathrm{Ag_2(OTf)_2}$ rings [Ag–O(1) 2.444(3), Ag–O(2) 2.424(3) Å]. The remaining two co-ordination sites on the pseudo-tetrahedral silver ion are occupied by a nitrogen donor of a different $\mathrm{Bu^t}$-DAB ligand with Ag–N(1) 2.330(3) Å and Ag–N(2) 2.313(4) Å. The silver–nitrogen distances are reasonable for four-co-ordinate silver and significantly longer than the Ag–imine nitrogen bonds in a related dico-ordinate complex.[5]

The unit cell diagram given in Figure 2 provides a more complete picture of the solid state structure of this material. The infinite Ag–($\mathrm{Bu^t}$-DAB)–Ag–($\mathrm{Bu^t}$-DAB) chain propagates through the lattice with a kink at silver defined by the N(1)–Ag–N(2) angle of 123.9(1)°. These chains are cross-linked into sheets by pairs of bridging trifluoromethanesulphonate anions. Thus a two-dimensional network polymer is formed with layers in the (x, y) plane.

This work demonstrates that co-ordination chemistry can play a significant role in the generation of new types of solid state materials.[9] Although the structural parameters of Ag($\mathrm{Bu^t}$-DAB)OTf indicate that extensive delocalization over the π-system is not important in the ground state structure, exploration of the photochemical behaviour of this material is in progress. Variation of the metal centre, bridging ligand, or counterion provide opportunities for rational control of the structures and properties of this class of materials.[10]

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