ChemComm

A novel hybrid layer compound containing silver sheets and an organic spacer

C. N. R. Rao,* Anupama Ranganathan, V. R. Pedireddi and A. R. Raju

Chemistry & Physics of Materials Unit and CSIR Centre for Excellence in Chemistry, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in

Received (in Cambridge, UK) 12th October 1999, Accepted 23rd November 1999

A novel compound of the formula Ag_2·CA (CA = cyanuric acid) possessing Ag sheets and hydrogen-bonded CA chains, exhibits anisotropic conductivity and acts as an infinite parallel plate capacitor with a high dielectric constant.

Design of infinite two- and three-dimensional arrays of metal–ligand networks has attracted considerable attention in the last few years not only because of the structural and topological novelty of such engineered solids but also due to the potentially interesting electrical, magnetic and other properties.[1,2] Recently, interesting structures containing polymeric Ag(I) species and heterocyclic as well as aromatic compounds have been described.[2–4] For instance, Ag(I)–benzenesulfonate has a layered structure containing a planar hexagonal array of Ag(I) ions incorporating the anion.[4] A coordination network of dicyanodiphenylacetylene comprising Ag(I) sheets with an Ag···Ag separation of 3.39 Å has also been reported.[5] Equally interesting are the supramolecular Ag(I) complexes constructed with several aromatic compounds involving novel stacking of the aromatics such as the herringbone packing pattern.[6,7] Many of these compounds have Ag···Ag separation significantly shorter than the van der Waals contact distance, with Ag(I) having linear, trigonal, tetrahedral or hexagonal coordination,[8] however, the materials are generally either insulators or semiconductors with no unusual properties.

During the course of our investigations of supramolecular assemblies of cyanuric acid, $C_3H_3N_3O_3$ (CA), involving both hydrogen bonding and metal-ion coordination, we have isolated a novel silver compound possessing two-dimensional Ag sheets with the CA molecules in the interlayer space, forming linear hydrogen-bonded chains. This compound of composition Ag_2·CA, is a unique organic–inorganic hybrid with novel electrical properties, and is entirely different from the supramolecular assemblies described above, and from other Ag complexes and salts with short Ag···Ag distances.[9] Here, we describe the fascinating structure and properties of this Ag(I) compound.

Reaction of $AgNO_3$ with CA under hydrothermal conditions† gave single crystals of composition Ag_2·CA suitable for X-ray diffraction studies. The structure was determined‡ using the SHELXTL package,[10] with the intensity data collected on a Siemens smart diffractometer equipped with CCD area detector. The asymmetric unit of the compound is shown in Fig. 1. The structure viewed down the *b*-axis (Fig. 2) reveals the presence of two-dimensional sheets of Ag atoms separated by CA molecules, the inter-sheet separation being *ca*. 6 Å. The average Ag···Ag distance in the sheets is 2.95 Å, slightly longer than the Ag–Ag distance in metallic silver (2.89 Å). The dative Ag–O and Ag–N bond distances are in the range 2.22–2.76 and 2.09–2.12 Å, respectively, and the CA molecules are linked by relatively short N–H···O hydrogen bonds (H···O 1.90 Å, N···O, 2.75 Å), giving rise to a linear chain (Fig. 2). The arrangement of the CA molecules in the layers perpendicular to the Ag sheets is illustrated in Fig. 3. Another noteable feature of Ag_2·CA is that the organic spacer itself is the anion. Ag_2·CA can also be compared with Ag_3O with an *anti*-BiI_3 structure with the O atoms occupying 2/3 of the octahedral holes.[11] The Ag···Ag and Ag–O distances in Ag_2·CA are slightly longer than in Ag_3O, except for one Ag–O bond of 2.22 Å.

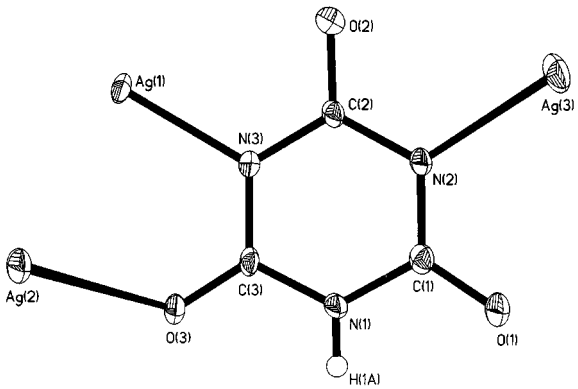


Fig. 1 ORTEP drawing showing the asymmetric unit of Ag_2·CA.

The presence of multipoint recognition patterns between CA and Ag in Ag_2·CA is of interest. For instance, the hydrogen bonding motif (a) in Scheme 1, found in the structure of CA,[12] is replaced by the motif (b) in Ag_2·CA by the substitution of Ag for H. Motif (b) is similar to that present in Ag carboxylates, except that two of the O atoms are replaced by N atoms. In addition, there are three-point recognition patterns (c) and (d) in Ag_2·CA, comparable to the hydrogen bonding pattern (e) found in the adduct of CA with melamine.[13]

Ag_2·CA crystals are mica-like and are readily cleaved because of the layer structure and the presence of weakly bound Ag sheets. The presence of two-dimensional Ag sheets is expected to give rise to anisotropic conductivity. Accordingly, the values of the dc conductivity parallel and perpendicular to the Ag sheets (*bc* plane) are *ca*. 5×10^{-3} and *ca*. 2×10^{-5} S cm^{-1}, respectively, at 300 K. The conductivity along the sheets is temperature-independent down to 15 K. Ag_2·CA, in which the conducting Ag sheets are separated by the organic spacer molecules, can be considered as an infinite parallel plate capacitor. In accord with this, the crystals possess a high static dielectric constant of *ca*. 22 000 at 300 K, a phenomenally high value which promises potential applications. This value of the

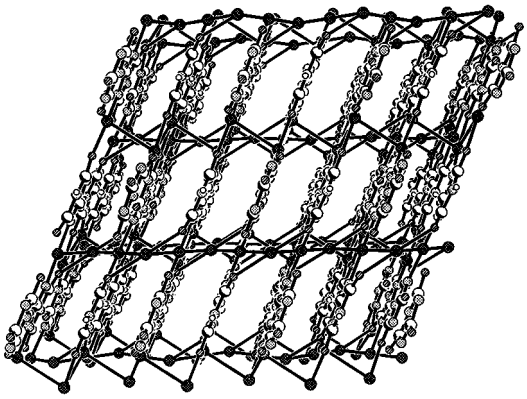


Fig. 2 Structure of Ag_2·CA showing Ag sheets and linear CA chains.

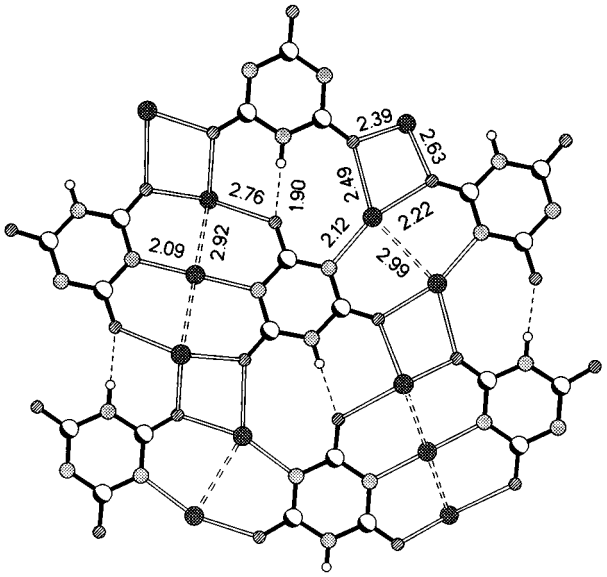
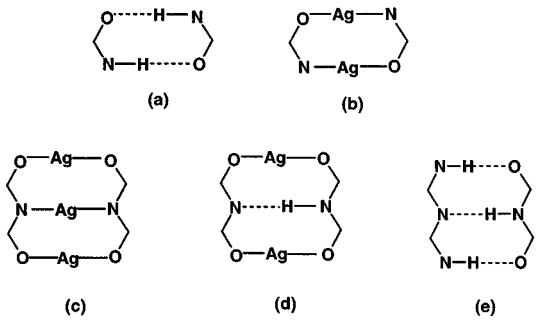


Fig. 3 Structure of a layer (*ab* plane) perpendicular to the Ag sheets: Solid lines, covalent bonds; double lines, dative bonds; dashed lines, hydrogen bonds; double dashed lines, Ag–Ag bonds.



Scheme 1

dielectric constant is comparable with that of barium titanate (*ca*. 12000 at 300 K).

Notes and references

† A solution (10 mL) consisting of a mixture of $AgNO_3$ (0.170 g) and CA (0.129 g) in water in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 180 °C for 24 h and then cooled to room temperature (25 °C) over a period of 3 h. Good quality off-white plate-like single crystals, were obtained and the composition of the product was established as Ag_2·CA, consistent with that derived from X-ray crystallography. There were no other products in the reaction.

‡ *Crystal data* for Ag_2·CA($Ag_2C_3N_3HO_3$): crystal dimensions, 0.35 × 0.25 × 0.20 mm, monoclinic, space group, *C*2/*c*, a = 12.726(1), b = 13.064(1), c = 6.623(1) Å, β = 97.35(1)°, V = 1092.0(2) Å^3, Z = 8, D_c = 4.170 Mg m^{-3}, μ(Mo-Kα) = 7.11 mm^{-1}, F(000) = 1264, λ = 0.71073 Å, ω–2θ scan, 2 < θ < 24° (−13 ⩽ h ⩽ 14, −11 ⩽ k ⩽ 14, −6 ⩽ l ⩽ 7), 2266 total reflections, 785 independent reflections which were used in the refinement. The structure was solved to $R1$ = 0.035 and $wR2$ = 0.083. Hydrogen atoms were placed in calculated positions.

CCDC 182/1491. See http://www.rsc.org/suppdata/cc/a9/a908171b/ for crystallographic files in .cif format.

1 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecutre*, ACS Symp. Ser., Washington, D.C., 1992, vol. 449, 1992, ch. 19.
2 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895 and references therein.
3 G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, J. A. Ripmeester and D. D. M. Wayner, *Angew. Chem., Int. Ed.*, 1998, **37**, 1407.
4 G. K. H. Shimizu, G. D. Enright, C. I. Ratcliffe, K. F. Preston, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 1999, 1485.
5 K. A. Hirsch, S. R. Wilson and J. S. Moore, *Inorg. Chem.*, 1997, **36**, 2960.
6 M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, G. L. Ning and T. Kojima, *J. Am. Chem. Soc.*, 1998, **120**, 8610.
7 G. L. Ning, L. P. Wu, K. Sugimoto, M. Munakata, T. Kuroda-Sowa and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1999, 2529.
8 D. Venkataraman, Y. Du, S. R. Wilson, P. Zhang, K. Hirsch and J. S. Moore, *J. Chem. Educ.*, 1997, **74**, 915.
9 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 5th edn., 1995, p. 1099.
10 G. M. Sheldrick, SHELXTL, Users Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1993.
11 W. Beesk, P. G. Jones, H. Rumpel, E. Schwarzmann and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1981, 664.
12 P. Coppens and A. Vos, *Acta Crystallogr., Sect. B*, 1971, **27**, 146.
13 A. Ranganathan, V. R. Pedireddi and C. N. R. Rao, *J. Am. Chem. Soc.*, 1999, **121**, 1752.

Communication a908171b