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The structures of Cu(I) and Ag(I) coordination polymers using the tricyanofluoroborate anion

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Received (in Purdue, IN, USA) 7th February 2002, Accepted 5th March 2002
First published as an Advance Article on the web 18th March 2002

The anion $BF(CN)_3^-$ forms isomorphous network polymers with Cu(I) and Ag(I) that exhibit one-dimensional channels along the *b* axis and demonstrate stability to air and light respectively.

The design of new molecular building blocks for the construction of coordination polymers continues to be an active area of research.[1] Molecular components that lead to specific topologies, generate open sites at metal centres, or modulate electronic structure in the solid could enable the generation of functional materials with designed properties.[2] In our recent work, we have begun to explore cyanoborates as anionic ligands for the synthesis of coordination polymers, and have found that they posses a number of desired attributes as materials components. In this report, we present the synthesis of materials based on the tricyanofluoroborate anion, $BF(CN)_3^-$ (Fig. 1), using Cu(I) and Ag(I) metal centres. The resultant two compounds, both having the empirical formula $M(BF(CN)_3)\cdot NCCH_3$, are isostructural, three-dimensional coordination polymers with solvent occupied sites at the metal centres. In both cases, the electron withdrawing nature of the bridging ligands results in stabilization of the +1 oxidation state for the metals and thus an air-stable Cu(I) compound and a light-stable Ag(I) material.

We uncovered the synthesis of these compounds while exploring reactions between the tetracyanoborate anion and Cu(I) and Ag(I). Two recent reports describe the preparation of the $B(CN)_4^-$ anion: one *via* a reaction using Me_3SiCN and a second involving boron halides and cyanide salts.[3] While working toward the preparation of $Cu[B(CN)_4^-]$, we found that the tetracyanoborate anion is unstable in the presence of fluoride in aqueous solution, forming the tricyanofluoroborate species. We can observe this anion *via* ^{19}F and ^{13}C NMR, which show resonances appearing at −29.6 and 101.2 ppm, respectively. Electrospray MS also demonstrates the formation of this anion, affording a negative ion peak at *m*/*z* 108.2. The cyanoborate anion $BF(CN)_3^-$ can be synthesized directly by reacting three equivalents of Me_3SiCN with the tetrafluoroborate anion. It is interesting to note that this anion is similar to other coordinating nitrile compounds presented in the literature, including $C(CN)_3^-$ and 4,4′,4″-tricyanotriphenylmethanol.[4]

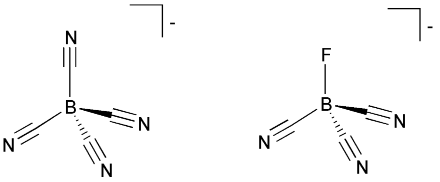

Fig. 1 Structures of $B(CN)_4^-$ and $BF(CN)_3^-$

The diffusion of an acetonitrile solution (5 mL 0.5 mmol), of $B(CN)_4^-$ into aqueous solutions of CuCl or $AgNO_3$ (5 mL, 0.5 mmol) with an equivalent of NaF by layering results in formation of crystals over several days of formula $M(BF(CN)_3)\cdot NCCH_3$. Both reactions form yellow, needle-like crystals that are stable to light and air. The structures of both compounds were elucidated from single crystal X-ray diffraction experiments.† The crystal system for both materials is orthorhombic, with a space group of *Pnma*. The coordination environment about the metal for the silver system is shown in Fig. 2(a), with the extended network structure along the *b* axis shown in Fig. 2(b). The morphology of $Cu(BF(CN)_3)\cdot NCCH_3$ is isostructural to that found in the silver compound. In each case, the metal centres are coordinated by three nitrile groups from different borate anions, with a fourth coordination site being occupied by a solvent acetonitrile. Selected bond distances and angles for the two compounds are shown in Table 1. Both the metals and the borates have nearly ideal tetrahedral geometries with angles close to 109.5°. In the silver compound, there is a greater deviation from the perfect tetrahedral geometry, exhibiting both larger (~115°) and smaller (~103°) angles. This divergence results from the increased radius of the Ag(I) cation relative to that of Cu(I). In addition, in both compounds the anions have virtually identical structures with the exception of minor bond length increases (B–C, C–N) in the silver

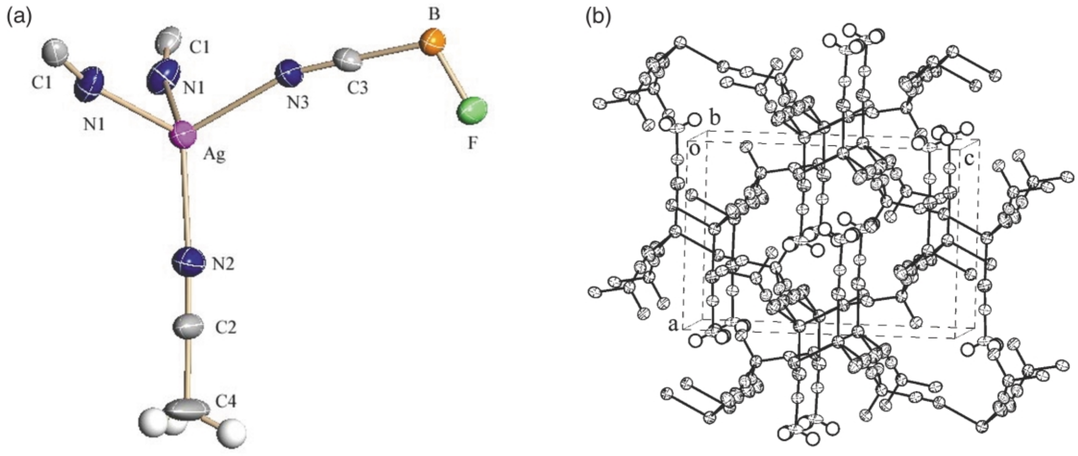

Fig. 2 Structures of the extended network solid $Ag(BF(CN)_3)\cdot NCCH_3$: (a) the local structure about the silver metal centre with 50% thermal ellipsoids and (b) the extended structure viewed along the *b* axis. The copper analogue has an essentially identical structure.

DOI: 10.1039/b201442d

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compound due to increased backbonding from the metal relative to copper.

These two materials are networked solids where the borates bridge the metal centres to form three-dimensional coordination polymers. As can be seen in Fig. 2, this material is not as efficiently packed as an adamantine-type structure, and there are one-dimensional channels along the *b* axis. These channels are identical in the two materials with the exception of their diameters; the channels have dimensions of ~ 6.3 × 5.8 Å in the copper compound and ~ 7.7 × 5.9 Å in the silver material. In both cases, the coordinated acetonitrile solvent molecules interlace into the void spaces of these channels. The increase in channel diameter as one goes from Cu(I) to Ag(I) corresponds to the increase in bond distances observed in the asymmetric units of the two materials. As can be seen in Table 1, the metal–nitrogen bond distances lengthen approximately 0.25–0.3 Å in the silver compound relative to the copper material. We are currently investigating these materials to investigate if the three-dimensional structure remains intact upon liberation of the acetonitrile solvent molecules. While both compounds show channel topologies, it is still unclear whether or not there is access to the metal-bound solvent molecules.

By using a bridging ligand with a non-coordinating moiety (fluorine), the resultant network polymers have potentially open sites at the metal centres. The presence of only three coordinating groups on the $BF(CN)_3^-$ species requires that either the metal adopt a lower coordination number structure or that solvent occupy the open sites at the metal in the extended solid. Both Cu(I) and Ag(I) metal centres frequently exhibit tetrahedral geometries in network solids, however lower coordination number complexes are occasionally observed.[1,5] In a network with a tetrahedral ligand, one would expect the formation of a diamond-like adamantane structure with metals that form tetrahedral complexes. This is observed in the structure of the salt $LiB(CN)_4$, since lithium also frequently forms tetrahedral complexes.[3] With only three cyano groups present on the borate, the fourth coordination site on the metal is likely to be filled by a solvent molecule, which is an acetonitrile in both cases. We are currently attempting to grow crystals of these materials in non-coordinating solvents, in the hope that we can isolate compounds with three-coordinate metals.

In addition to generating a porous network solid, the tricyanofluoroborate anion also stabilizes the low oxidation states of the copper and silver metal sites in these solids. Frequently, both Cu(I) and Ag(I) compounds are unstable to atmospheric dioxygen and light, respectively, but the electron withdrawing (p acceptor) character of the cyanide groups bound to the metals significantly alter the potential of both metals to favour the lower oxidation state.[6] We can observe the backbonding in the weakened CN stretching vibrations at 2241 cm^{-1} for $Cu(BF(CN)_3)\cdot NCCH_3$ and 2257 cm^{-1} for $Ag(BF(CN)_3)\cdot NCCH_3$ relative to that found for $B(CN)_3NCSiMe_3$ at 2310 cm^{-1} or for $B(CN)_4^-$ at 2271 cm^{-1}.[3] The preference for the +1 oxidation state results in materials that are air stable in the case of the copper material and light stable for the silver compound. This apparent delocalisation of electron density onto the ligand bodes well for the use of this coordinating anion for use in magnetic materials, such as Prussian blue analogues.[7]

Table 1 Selected bond lengths and angles for $M(BF(CN)_3)\cdot NCCH_3$

	Cu	Ag
M–N(1)	1.993(2)	2.296(3)
M–N(2)	1.989(4)	2.224(4)
M–N(3)	1.990(3)	2.286(4)
C(1)–N(1)	1.138(3)	1.143(4)
C(2)–N(2)	1.123(5)	1.126(6)
C(3)–N(3)	1.137(5)	1.126(6)
B–C(1)	1.606(4)	1.615(5)
B–C(3)	1.617(6)	1.626(7)
B–F	1.408(5)	1.402(6)
N(2)–M–N(3)	109.09(15)	115.97(15)
N(2)–M–N(1)	111.83(8)	115.43(9)
N(1)–M–N(3)	107.15(8)	102.04(9)
N(1)–M–N(1)	109.55(13)	103.99(15)
F–B–C(1)	109.6(2)	110.8(3)
F–B–C(3)	109.5(4)	110.2(4)
C(1)–B–C(1)	110.1(3)	109.6(4)
C(1)–B–C(3)	109.1(2)	107.7(3)

The ability to tune the attributes of the solid by changing the metal ion is also encouraging for the design of other ordered solids. By altering the metal centre, we can obtain two isomorphous compounds that differ only in their unit cell dimensions and channel diameter. We are currently examining these materials to determine if changing the metal cation in these networks can also affect observed reactivity, such as loss of acetonitrile at high temperatures or affinity for soft ligand guests, such as thiols.

This work was supported by the University of Akron. C. J. Z. acknowledges the University of Akron for a faculty research grant (FRG-1524).

Notes and references

† *Crystallographic summary* for **1** and **2**: data was collected at 150 K on a P(2)1 Syntex diffractometer. $CuBC_5H_3N_4F$ **1**; $M = 212.46$, yellow needles 0.2 × 0.2 × 0.1 mm, orthorhombic, space group *Pnma*, $Z = 4$ in a cell of dimensions $a = 8.476(2)$, $b = 7.7715(19)$, $c = 12.519(3)$ Å, $V = 824.6(4)$ Å^3, $D_c = 1.711$ Mg m^{-3}, μ(Mo-Kα) = 2.608 mm^{-1}, $F(000) = 416$, final *R* indices on 781 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0257$, $wR_2 = 0.0447$.

$AgBC_5H_3N_4F$; $M = 256.79$, yellow needles 0.5 × 0.2 × 0.2 mm, orthorhombic, space group *Pnma*, $Z = 4$ in a cell of dimensions $a = 8.7909(18)$, $b = 8.1413(16)$, $c = 12.743(3)$ Å, $V = 912.0(3)$ Å^3, $D_c = 1.870$ Mg m^{-3}, μ(Mo-Kα) = 2.174 mm^{-1}, $F(000) = 488$, Final *R* indices on 864 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0247$, $wR_2 = 0.0500$.

CCDC reference numbers 178955 and 178956. See http://www.rsc.org/suppdata/cc/b2/b201442d/ for crystallographic data in CIF or other electronic format.

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