INORGANIC COMPOUNDS

Polymeric triamminetetrakis(μ-cyano)-dicuprate(I)copper(II)

VIKTOR VRÁBEL,[a] JÁN GARAJ,[a] JÚLIUS SIVÝ[b] AND DRAHOMÍR OKTAVEC[a]

[a]*Faculty of Chemical Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Faculty of Pharmacy, Comenius University, Odbojarov 10, 832 32 Bratislava, Slovakia. E-mail: vrabel@cvt.stuba.sk*

Abstract

The crystal structure of the mixed-valence copper–cyanide complex $[Cu_2^I Cu^{II}(CN)_4(NH_3)_3]_\infty$ comprises infinite polymeric double chains. The geometry about the Cu^I centres is approximately trigonal pyramidal, and each Cu^{II} centre adopts a slightly distorted square-pyramidal coordination, with one NH_3 ligand disordered equally over two alternative sites. In contrast to previous reports, we find that the title compound crystallizes in the monoclinic space group $P2_1/n$.

Comment

There have been earlier reports of structure determinations of the title compound by Dunaj-Jurčo & Poraj-Kosic (1967) and Williams *et al.* (1972). Except for small differences in bond lengths and angles, the models appear to be the same in spite of the different space groups (*Abm2* and *Cmca*, respectively), with, in each case, two cyanide groups which are required by symmetry to be disordered, in the first case across a mirror plane and in the second across a twofold axis. To explain these discrepances, we repeated the synthesis and structure determination of the title compound, (I).

(I)
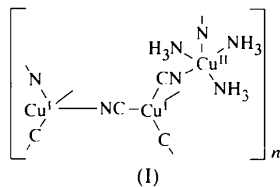
The present structure consists of infinite polymeric double chains orientated parallel to the crystallographic *b* direction (Fig. 1). The chains are linked by $Cu^I \cdots Cu^I$ interactions perpendicular to the direction of these double chains, with $Cu1 \cdots Cu1(1 - x, 1 - y, 1 - z)$ and

$Cu2 \cdots Cu2(1 - x, -y, 1 - z)$ distances of 2.807 (2) and 2.845 (2) Å, respectively, to give a three-dimensional infinite lattice. There are also short contacts between the ammine molecules and the cyanide N atoms. The chains consist of one Cu^{II} and four Cu^I centres linked by cyanide ligands to form pentagons (Fig. 2). Each pentagon is folded along the $Cu1 \cdots Cu2(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ vector to give two sections, each planar to within 0.038 Å and with a hinge angle of 27.4°. The infinite chains pack efficiently, with the Cu^{II} centre and its three ammine ligands of one layer lying over the centres of the pentagons in the next.

The coordination about the Cu^I centres is approximately trigonal pyramidal, the base of the pyramid being formed by the C or N atoms from the ordered cyanide groups. The deviations of the Cu1 and Cu2 atoms from this basal plane are 0.280 (1) and 0.261 (1) Å, respectively. The Cu1(1 - x, 1 - y, 1 - z) and Cu2(1 - x, -y, 1 - z) atoms complete this trigonal-bipyramidal arrangement *via* axial coordination; they lie 2.749 (1) and 2.752 (1) Å, respectively, from the basal plane. Each Cu^{II} centre adopts a slightly distorted square-pyramidal coordination consisting of three ammine ligands distributed over four positions (one of these is disordered over two positions of half occupancy), one N from a cyanide group approximately in the plane and one N from a second cyanide group at the apex. The two cyanide groups are mutually *cis*. The Cu^{II}—N
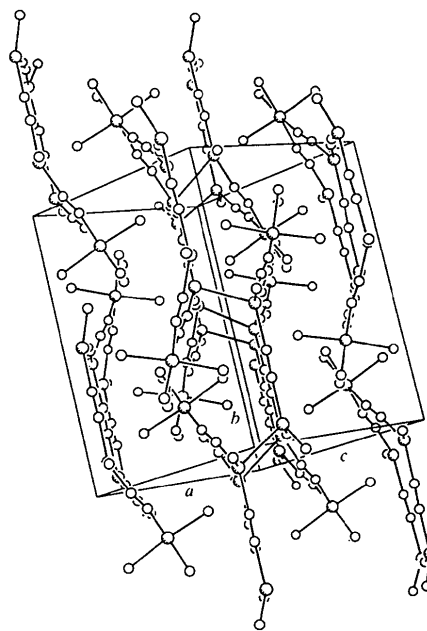

Fig. 1. View of the double chains of $Cu_3(CN)_4(NH_3)_3$ running along the *b* axis. H atoms have been omitted for clarity.
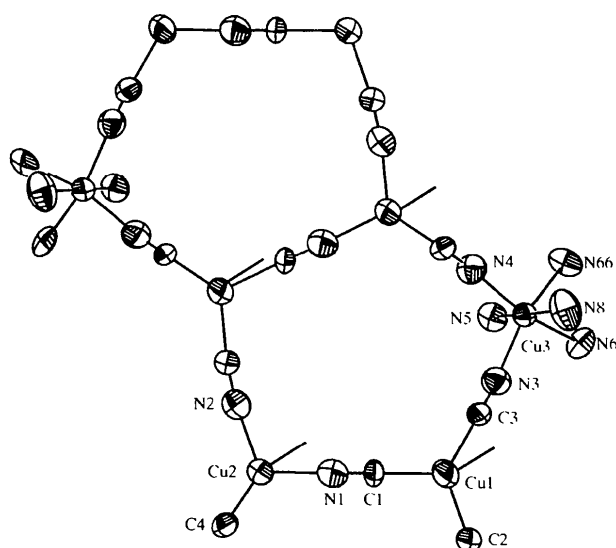
Fig. 2. View of a segment of the polymeric chains showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

bond distances range from 2.000 (6) to 2.070 (6) Å and agree well with earlier results (Williams *et al.*, 1972; Vrábel *et al.*, 1979). The Cu^{II} centre lies 0.124 (1) and 0.122 (1) Å from the planes defined by N4/N5/N6/N8 and N3/N5/N66/N8, respectively, on opposite sides from the cyanide N3 and N4 atoms.

Experimental

Dark blue–green crystals of $Cu_3(CN)_4(NH_3)_3$ were prepared according to the method of Cooper & Plane (1966).

Crystal data

$[Cu_3(CN)_4(NH_3)_3]$	Mo $K\alpha$ radiation
$M_r = 345.80$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 9.435$ (6) Å	$\theta = 7.3–18.6°$
$b = 12.605$ (4) Å	$\mu = 5.663$ mm^{-1}
$c = 9.481$ (5) Å	$T = 293$ (2) K
$\beta = 99.82$ (5)°	Block
$V = 1111.0$ (10) Å^3	$0.3 \times 0.2 \times 0.2$ mm
$Z = 4$	Blue–green
$D_x = 2.067$ Mg m^{-3}	
$D_m = 2.08$ (1) Mg m^{-3}	
D_m measured by flotation in bromoform–trichloroethane	

Data collection

Syntex $P2_1$ diffractometer	1332 reflections with
$\theta/2\theta$ scans	$I > 2\sigma(I)$

Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{min} = 0.258$, $T_{max} = 0.322$
2581 measured reflections
2581 independent reflections

$\theta_{max} = 27.6°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.085$
$S = 1.144$
2581 reflections
140 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0140P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction coefficient: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—C1	1.947 (7)	Cu3—N3	2.066 (6)
Cu1—C2	1.928 (7)	Cu3—N4	2.070 (6)
Cu1—C3	1.954 (7)	Cu3—N5	2.000 (6)
Cu2—N1	1.970 (7)	Cu3—N6	2.003 (9)
Cu2—N2	1.932 (7)	Cu3—N66	2.045 (10)
Cu2—C4	1.925 (7)	Cu3 N8	2.025 (6)
N5—Cu3—N6	88.0 (3)	N6—Cu3—N4	166.2 (4)
N5—Cu3—N8	175.7 (2)	N66—Cu3—N4	95.4 (4)
N6—Cu3—N8	88.7 (3)	C1—N1—Cu2	176.8 (6)
N5—Cu3—N66	89.0 (3)	C2'—N2 —Cu2	172.2 (7)
N8—Cu3—N66	87.4 (4)	N1 —C1 Cu1	177.6 (7)
N6—Cu3—N3	94.7 (4)	N3—C3 Cu1	175.4 (7)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

One ammine ligand was disordered over two equally occupied sites (N6 and N66). H atoms were refined as part of rigid NH$_3$ groups which were allowed to rotate but not tip or distort.

Data collection: $P2_1$ *Diffractometer Control Software* (Syntex, 1973). Cell refinement: $P2_1$ *Diffractometer Control Software*. Data reduction: *XP21* (Pavelčík, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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sites of space group $C2/m$, the magnetic moments in the antiferromagnetic ground states are aligned parallel to [100] for the $4i$ site and to [010] for the $4h$ site in α-FeMoO₄, but parallel to [001] for both sites in α-CoMoO₄. Therefore, highly competing interactions with respect to the orientation of the magnetic moments are expected for the mixed compositions.
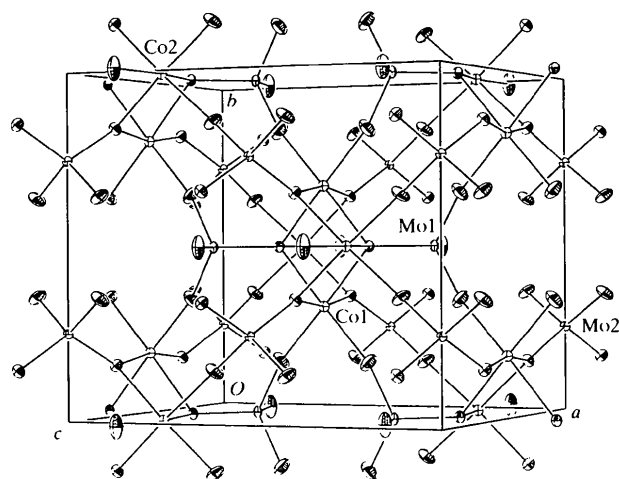
A mixed transition metal molybdate, β-(Co₀.₇Fe₀.₃)MoO₄

HELMUT EHRENBERG, INGRID SVOBODA, MARC WIESMANN AND HANS WEITZEL

Strukturforschung, FB Materialwissenschaft, Technische Universität Darmstadt, Petersenstraße 23, 64287 Darmstadt, Germany. E-mail: helmut@steno.st.mw.tu-darmstadt.de

Abstract

The high-temperature modification of the title mixed compound, cobalt iron molybdate, a transition metal molybdate of type β-AMoO₄, with $A = (Co_{0.7}Fe_{0.3})$, is metastable at room temperature. The distribution of Fe and Co is different for the two non-equivalent A sites: only 18 (9)% of all atoms on the $4i$ site are Fe, compared with 43 (9)% on the $4h$ site.

Comment

For the transition metal molybdates $AMoO_4$, with $A =$ Fe or Co, three different modifications were reported by Sleight & Chamberland (1968), i.e. the high-pressure form $AMoO_4$-II, the standard modification α-$AMoO_4$ and the high-temperature phase β-$AMoO_4$. The reversible phase transition between the α- and β-phases takes place at about 673 K for $A =$ Fe and at about 773 K for $A =$ Co. Motivated by the very different magnetic behaviour of α-FeMoO₄ and α-CoMoO₄ (Ehrenberg et al., 1994), we have studied compounds of mixed composition. For the Co:Fe ratio of 0.7:0.3, we have obtained the title β-modification at room temperature, which is at least metastable under ambient conditions. The crystal structure of this β-modification is only known from α-MnMoO₄ (Abrahams & Reddy, 1965). It has not been refined for β-FeMoO₄ and β-CoMoO₄.

The Co:Fe ratio is different for the two non-equivalent A sites: 18 (9)% of all atoms on the $4i$ site are Fe, compared with 43 (9)% on the $4h$ site. This is of importance for the magnetic properties of the mixed compounds. In the case of the α-phases, in which the transition metal ions also occupy the $4h$ and $4i$

Fig. 1. The crystal structure of the title β-AMoO₄ compound. All cations within one unit cell are shown with their complete coordination sphere, i.e. [MoO₄] tetrahedra and [AO₆] octahedra. For brevity, the mixed A sites are labelled Co1 and Co2. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound was prepared by subsolidus reaction of a mixture of MoO₃ (99.99%, Aldrich), Co₃O₄ (99.99%, Aldrich), CoO (99.9%, Aldrich), Fe₂O₃ (99.98%, Aldrich) and Fe (99.9%, Aldrich) in the ratio 1:0.175:0.175:0.1:0.1. The reactants were mixed intimately in an agate mortar under acetone, sealed in an evacuated silica tube and heated to 1273 K at a rate of 300 K h⁻¹. After 10 h, the reaction product was cooled down, first at a rate of 40 K h⁻¹ to 873 K, then at a rate of 15 K h⁻¹ to 723 K and finally to room temperature at a rate of 18 K h⁻¹.

Crystal data

Co₀.₇Fe₀.₃MoO₄	Mo $K\alpha$ radiation
$M_r = 217.54$	$\lambda = 0.71093$ Å
Monoclinic	Cell parameters from 25
$C2/m$	reflections
$a = 10.221\,(3)$ Å	$\theta = 6.04–16.69°$
$b = 9.275\,(3)$ Å	$\mu = 8.79$ mm⁻¹
$c = 7.024\,(2)$ Å	$T = 299\,(2)$ K
$\beta = 106.87\,(2)°$	Prism
$V = 637.2\,(3)$ Å³	$0.075 \times 0.050 \times 0.037$ mm
$Z = 8$	Dark brown
$D_x = 4.546$ Mg m⁻³	
D_m not measured	