A molecular tetraamminecopper(II)-trans-diamminecopper(II) tetracyanonickelate(II) coordination compound†

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Abstract

The title complex, $[\text{Ni}_2\text{Cu}_2\text{(CN)}_6\text{(NH}_3\text{)}_2]_2$ or $[[\text{Cu}_2\text{(CN)}_4\text{(NH}_3\text{)}_2]_2\text{cis}-\text{Ni(CN)}_2\text{(NH}_3\text{)}_2\text{]}_2$, is a dimeric $C_{2v}$ symmetrical entity built from square-planar $[\text{Ni(CN)}_4]^{2-}$ anions as cis bridging ligands and (distorted) square-pyramidal copper centres. All of the atoms, except those of the three independent ammine groups, lie on a mirror plane. Copper is coordinated by ammine and tetracyanonickeiate ligands. This is a rare example of a discrete molecular cyano–copper–nickel complex.

Comment

The interest in coordination polymers formed from metal ions and bridging ligands is fuelled by expectations of developing new materials with unique electronic properties (Robson et al., 1992; Gardner et al., 1995; Janiak, Scharmann, Albrecht et al., 1996). Polynuclear CuII complexes have been studied intensely because they form diverse novel structural networks, including chains, sheets and matrices (Chui et al., 1999; Smith, 1998; Janiak, Scharmann, Günther et al., 1996).

Hoffman-type clathrates, $M\text{(NH}_3\text{)}_2M'\text{(CN)}_4\text{2C}_6\text{H}_6$ (guest), have a layered structure of square-meshed trans-diamminemetal $[M'\text{II}]$ tetra-catena-$\mu$-cyanometallate $[M'\text{II}]$ sheets, with $M' = \text{Ni, Pd or Pt}$ (Dunbar & Heintz, 1997). Only one of these structures is known where $M = \text{Cu}$ (Miyoshi et al., 1973). We therefore attempted crystallization of a discrete units of tetracyanonickeiate–copper compounds. Ni is the predominant $M'$ metal in these framework structures (Park & Iwamoto, 1992, 1993; Yuge & Iwamoto, 1994; Yuge et al., 1995, 1997).

From the reaction of $\text{Cu}^{2+}$ in $\text{NH}_3$ with $[\text{Ni(CN)}_4]^{2-}$, a molecular copper–nickel complex was isolated, i.e bis{tetraamminecopper(II)[$\text{cis}$-(dicyano)$\mu$-dicyano]nickelate(II)}-cyano-bis{trans-diammine[$\text{cis}$-(dicyano)$\mu$-dicyano]nickelate(II)}copper(II), (I). The formation of a discrete complex rather than a coordination polymer was unexpected in view of the known coordination chemistry of $[\text{Ni(CN)}_4]^{2-}$ anions. Normally, two-dimensional frameworks result (Park & Iwamoto, 1992, 1993; Yuge & Iwamoto, 1994; Yuge et al., 1995, 1997).

As shown in Fig. 1, the discrete units of (I), which display $C_{2v}$ symmetry, are octanuclear and built up from four amminecopper and four tetracyanonickeiate moieties. The arrangement may also be viewed as a dimer, with the two molecular parts related by a $C_2$ axis or a centre of inversion. Intermolecular contacts between the discrete units are provided by weak hydrogen bonds of the form N–H⋯N (Table 2).

The $\text{Ni/Cu}$ assignment is based on the established stability of the $[\text{Ni(CN)}_4]^{2-}$ species; this in turn determines the $C/N$ identity. We note that otherwise the neighbouring $\text{Ni/Cu}$ and $C/N$ elements cannot be distinguished easily by crystallographic means alone.

The $[\text{Ni(CN)}_4]^{2-}$ anions act as cis bridges between the Cu centres, thereby utilizing two CN groups as donors. There are two types of Cu centres and two types of tetracyanonickeiate anions. One type of Cu centre (Cu2) seems at first sight to possess a trigonal-
bipyramidal coordination polyhedron of two trans-ammine ligands and three equatorial [Ni(CN)₄]²⁻ ligands. Two of these Cu centres form a tetranuclear ring, together with two cis bridging tetracyanonickelate groups (around Ni2). A third [Ni(CN)₄]²⁻ group (around Ni1) completes the coordination sphere in the equatorial plane. This exocyclic tetracyanonickelate ligand also bridges to a terminal Cu centre. However, a closer inspection reveals that the coordination polyhedron around Cu2 may be better described as strongly distorted square pyramidal. We use the angular structure parameter \( \tau = (\beta - \alpha)/60 \) as a general descriptor of five-coordinate metal centres (\( \beta \) and \( \alpha \) are the two largest angles; \( \tau = 1 \) for an ideal trigonal bipyramid and \( \tau = 0 \) for an ideal square pyramid; Addison et al., 1984). For Cu2, a value of \( \tau = 0.32 \) is obtained from the angles of N03--Cu2--N03 ii = 171.2(2)° and of N12 i--Cu2--N22 = 152.3(2)° [symmetry codes: (i) 1-x, -y, -z; (ii) x, y, -z]. From this model, the Cu--N11 bond would, however, be predicted to be elongated with respect to the other four bonds. This is not the case. None of the five Cu2--N bonds appears to be elongated when compared with their expected range (see below), but the Cu2--N22 bond is peculiar. The Cu2--N22--C22 linkage is strongly bent [128.1(4)°] so that the orbital overlap from the nitrogen lone pair to Cu becomes rather small. This reflects a weak covalent interaction. Unlike the Cu1--N31 bond, however, where the Cu1--N31--C31 linkage is bent to 140.0(4)°, the Cu2--N22 bond remains short. This might be due to either a stronger ionic bonding contribution or an unusual CN--Cu2 π overlap. On the other hand, in the structural chemistry of CuII, the potential surface for Cu linkages is known to be very soft and much determined by the crystal environment (Gazo et al., 1976; Jean et al., 1988; Wijnands et al., 1996; Janiak, Scharmann, Günter et al., 1996).

The terminal Cu centre possesses a square-pyramidal coordination polyhedron. The nearest CN groups pointing to the open coordination site of Cu1 are over 4 Å away. The base of the square pyramid is formed from four ammine ligands and \( \mu\)-NC—Ni occupies the apical site. This Cu1—NC linkage is considerably longer [2.309(4) Å] than the Cu2—NC bonds (between 2.02 and 2.13 Å). This reflects the expected tetragonal distortion of a square-pyramidal coordination sphere for CuII. The expected range for Cu—\( \mu\)-NC is 2.05±0.13 Å or 1.99±0.05 Å when excluding those above 2.3 Å (Orpen et al., 1989). Hence, the tetracyanonickelate group around Ni1 bridges quite unsymmetrically between different Cu centres. The ligand arrangements in both [Ni(CN)₄] groups are very close to square planar. Any angular deviations are within 2° of 90 or 180°, respectively. Other metal-ligand distances in (I) are usual. For Cu—NH₃, the expected range is 1.99±0.02 Å, and for terminal Ni—CN and for Ni—\( \mu\)-CN, it is 1.86±0.02 Å (Orpen et al., 1989).

**Experimental**

The title compound was synthesized from a solution of CuCl₂·2H₂O (36 mg, 0.21 mmol) in water (7.5 ml) which was overlayed with concentrated ammonia (2 ml) and a solution of NiCl₂·6H₂O (50 mg, 0.21 mmol) together with KCN (55 mg, 0.84 mmol) in water (2.5 ml). After three weeks,
blue crystals were collected by filtration and washed with cold water and ethanol (yield 28 mg, 48%). Crystal analysis, IR (KBr): 3368 (m), 3278 (w), 3190 (w), 2170 (m), 2114 (s), 1642 (br, w), 1285 (w), 1267 (s), 1255 (m), 1225 (w), 693 (br, s), 428 (s) cm⁻¹; calculated for Cu₄H₅CN₅N₇: C 18.068, H 13.367, N 28.893. The H atoms of the ammine groups were located in difference syntheses and refined using a common displacement parameter of 0.068 (6) Å² and a common restrained N–H distance, which refined to 0.805 (15) Å. There are difference densities of about 1.5 e Å⁻³ close to Cu and Ni despite a numerical absorption correction.


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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1356). Services for accessing these data are described at the back of the journal.

Table 2. Hydrogen-bonding geometry (Å, °)

<table>
<thead>
<tr>
<th>D···H···A</th>
<th>D–H</th>
<th>H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N02–H12···N32w</td>
<td>1.12 (7)</td>
<td>1.82 (6)</td>
</tr>
<tr>
<td>N02–H22···N31</td>
<td>1.13 (7)</td>
<td>1.73 (6)</td>
</tr>
<tr>
<td>N03–H22···N41</td>
<td>1.12 (7)</td>
<td>1.73 (6)</td>
</tr>
<tr>
<td>N03–H32···N42w</td>
<td>1.13 (7)</td>
<td>1.73 (6)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, y, z; (ii) x, -y, z; (iii) 1/2 - x, -y, 1/2 - z; (iv) -x, -y, -z. Data are 99.4% complete to θ = 27.95°. The H atoms of the ammine groups were located in difference syntheses and refined using a common displacement parameter of 0.068 (6) Å² and a common restrained N–H distance, which refined to 0.805 (15) Å. There are difference densities of about 1.5 e Å⁻³ close to Cu and Ni despite a numerical absorption correction.

References
Trierbium digallide trigermanide

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Abstract

The synthesis and single crystal structure of Er$_3$Ga$_2$Ge$_3$ (analysed as Er$_3$Ga$_{2.21}$Ge$_{2.79}$) are reported. Er$_3$Ga$_2$Ge$_3$ is isotypic with Pu$_3$Pd$_5$.

Comment

The title compound, Er$_3$Ga$_2$Ge$_3$, is isotypic with Pu$_3$Pd$_5$ (Cromer, 1976). Until now, this structural type has been mainly reported for R$_3$In$_5$ and R$_3$TI$_5$ compounds (R = lanthanide elements; Villars & Calvert, 1991). In the Er–Ga–Ge system investigated by us at 1173 K, Er$_3$Ga$_2$Ge$_3$ is in equilibrium with the Tm$_3$Ga$_5$-type compound Er$_3$Ga$_3$Ge$_2$ (Yatsenko et al., 1983) and with the defect AIB$_2$-type compound Er$_{3.8}$Ga$_{1.7}$Ge$_{4.7}$. The Pu$_3$Pd$_5$ structure is closely related to the Tm$_3$Ga$_5$-type structure (Yatsenko et al., 1983). The evolution of the structure as a function of the Ga content is not well understood.

Experimental

Crystals of the title compound were extracted from an Er$_{25}$Ga$_{20}$Ge$_{55}$ ingot annealed at 1173 K for one week. The microprobe analysis of the crystals gives the following composition: Er 37 (1), Ga 27 (1) and Ge 36 (1) atom%.

Crystal data

Er$_3$Ga$_{2.21}$Ge$_{2.79}$

$M_r = 858.99$

Orthorhombic

Cmcm

$a = 9.2880 (6)$ Å

$b = 7.4180 (7)$ Å

$c = 9.3830 (4)$ Å

$V = 646.47 (8)$ Å$^3$

$Z = 4$

$D_r = 8.826$ Mg m$^{-3}$

$D_m$ not measured

Ag $K\alpha$ radiation

$\lambda = 0.56090$ Å

Cell parameters from 176 reflections

$\theta = 0.64$–23.58°

$\mu = 32.069$ mm$^{-1}$

$T = 293$ (2) K

Parallelepiped

0.08 × 0.07 × 0.07 mm

Metallic grey

Data collection

Nonius KappaCCD diffractometer

358 reflections with $I > 2\sigma(I)$

Oscillations scan

$R_m = 0.063$

Absorption correction: empirical (SORTAV; Blessing, 1987)

$h = -11 \rightarrow 12$

$k = -9 \rightarrow 9$

$l = -12 \rightarrow 12$

3631 measured reflections

423 independent reflections

The refinement of the occupancy factors of the Ga and Ge sites leads us to assume that the Ga$_5$ and Ge$_6$ sites are fully occupied by Ga and Ge atoms, respectively. The occupancy factor of the (Ge$_3$,Ga$_4$) site suggests a mixture of Ge and Ga atoms on this site. In spite of the close scattering factors of Ge and Ga atoms, the chemical formula deduced from the results of the refinements (Er$_{3.7}Ge_{3.4}Ga_{2.7}$) is in good agreement with that measured by microprobe analysis.

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