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

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Abstract

The title complex, [Ni₄Cu₄(CN)₁₆(NH₃)₁₂] or {[Cu(NH₃)₄][*cis*-Ni(CN)₂(μ-CN)₂]-*cyclo*-[*trans*-Cu(NH₃)₂]-[*cis*-Ni(CN)₂(μ-CN)₂]}₂, is a dimeric C_{2h} symmetrical entity built from square-planar [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 tetracyanonickelate ligands. This is a rare example of a discrete molecular cyano-copper-nickel complex.

Comment

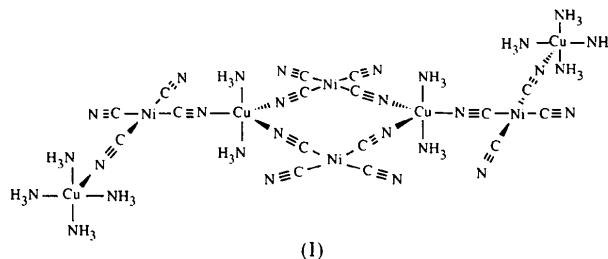
The interest in coordination polymers formed from metal ions and bridging ligands is fuelled by expectations of developing new materials with unique electronic properties (Robson *et al.*, 1992; Gardner *et al.*, 1995;

† Systematic name: dodecaammine-5κ⁴N,6κ²N,7κ²N,8κ⁴N-octa-μ-cyano-1:5κ²C:N;1:6κ²C:N;2:6κ²C:N;2:7κ²C:N;3:6κ²C:N;3:7κ²C:N;-4:7κ²C:N;4:8κ²C:N-octacyano-1κ²C,2κ²C,3κ²C,4κ²C-tetracopper(II)-tetranickel(II).

Janiak, Scharmann, Albrecht *et al.*, 1996). Polynuclear Cu^{II} 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(NH₃)₂M'(CN)₄·2(guest), have a layered structure of square-meshed *trans*-diamminemetal [M^{II}] tetra-*catena*-μ-cyanometallate-[M'^{II}] sheets, with M' = Ni, Pd or Pt (Dunbar & Heintz, 1997). Only one of these structures is known where M = Cu (Miyoshi *et al.*, 1973). We therefore attempted crystallization of additional cyano-bridged tetracyanonickelate-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 Cu²⁺ in NH₃ with [Ni(CN)₄]²⁻, a molecular copper-nickel complex was isolated, *i.e.* bis{tetraamminecopper(II)[*cis*-(dicyano)(μ-dicyano)-nickelate(II)]}-*cyclo*-bis{*trans*-diammine[*cis*-(dicyano)(μ-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 [Ni(CN)₄]²⁻ anions. Normally, two-dimensional frameworks result (Park & Iwamoto, 1992, 1993; Yuge & Iwamoto, 1994; Yuge *et al.*, 1995, 1997). A two-dimensional network was also found in the closely related compound Cu(NH₃)₂Ni(CN)₄·2C₆H₆ (Miyoshi *et al.*, 1973).



As shown in Fig. 1, the discrete units of (I), which display C_{2h} symmetry, are octanuclear and built up from four amminecopper and four tetracyanonickelate moieties. The arrangement may also be viewed as a dimer, with the two molecular parts related by a C₂ 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 Ni/Cu assignment is based on the established stability of the [Ni(CN)₄]²⁻ species; this in turn determines the C/N identity. We note that otherwise the neighbouring Ni/Cu and C/N elements cannot be distinguished easily by crystallographic means alone.

The [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 tetracyanonickelate anions. One type of Cu centre (Cu2) seems at first sight to possess a trigonal-

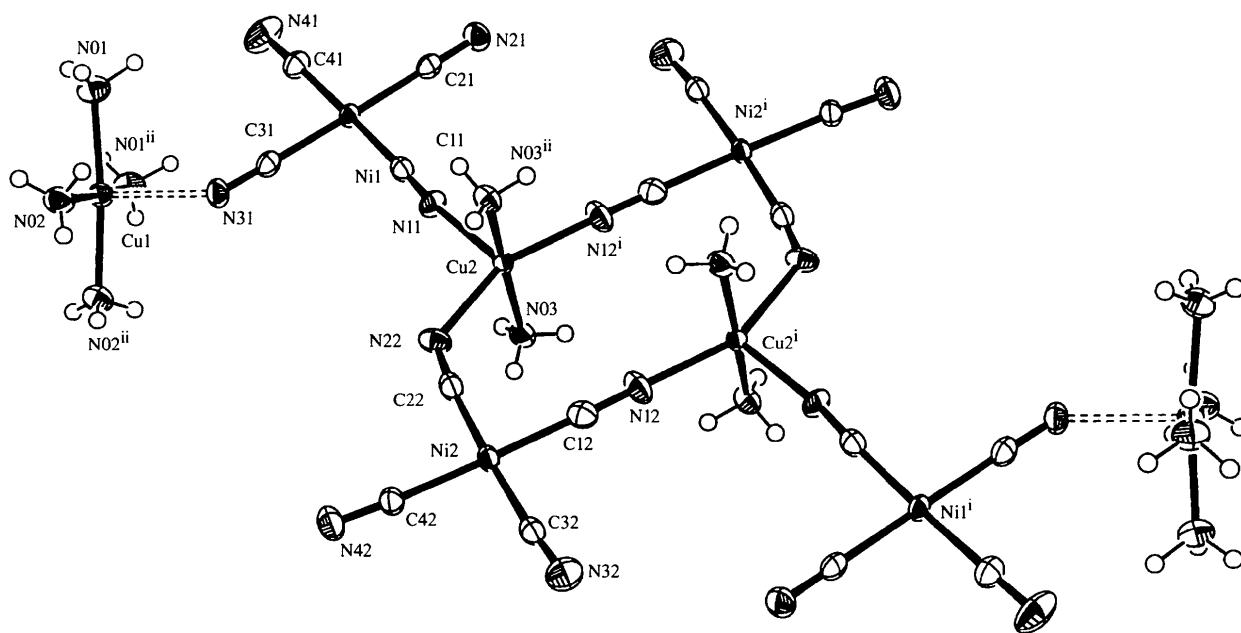


Fig. 1. An ORTEP-3 (Farrugia, 1997) view of the title compound showing the atom-labelling scheme [symmetry codes: (i) $1-x, -y, -z$; (ii) $x, y, -z$]. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

bipyramidal coordination polyhedron of two *trans*-ammine ligands and three equatorial $[\text{Ni}(\text{CN})_4]^{2-}$ ligands. Two of these Cu centres form a tetranuclear ring, together with two *cis* bridging tetracyanonickelate groups (around Ni2). A third $[\text{Ni}(\text{CN})_4]^{2-}$ 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 (β and α 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 $\text{N03}-\text{Cu2}-\text{N03}^{\text{ii}} = 171.2(2)^\circ$ and of $\text{N12}^{\text{i}}-\text{Cu2}-\text{N22} = 152.3(2)^\circ$ [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 [$128.1(4)^\circ$] 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 $140.0(4)^\circ$, 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 Cu^{II}, 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, Günther *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 $\mu\text{-NC-Ni}$ occupies the apical site. This Cu1—NC linkage is considerably longer [$2.309(4)\text{Å}$] 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 Cu^{II}. The expected range for Cu— $\mu\text{-NC}$ is $2.05 \pm 0.13\text{Å}$ or $1.99 \pm 0.05\text{Å}$ 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 $[\text{Ni}(\text{CN})_4]$ 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 $1.99 \pm 0.02\text{Å}$, and for terminal Ni—CN and for Ni— $\mu\text{-CN}$, it is $1.86 \pm 0.02\text{Å}$ (Orpen *et al.*, 1989).

Experimental

The title compound was synthesized from a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (36 mg, 0.21 mmol) in water (7.5 ml) which was overlaid with concentrated ammonia (2 ml) and a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (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 C₄H₉CuN₇Ni: C 17.32, H 3.27, N 35.35%; found C 17.54, H 2.89, N 34.64%.

Crystal data

[Ni₄Cu₄(CN)₁₆(NH₃)₁₂]
M_r = 1109.604
 Orthorhombic
Pnmm
a = 16.8265 (13) Å
b = 15.7626 (13) Å
c = 7.2886 (5) Å
V = 1933.2 (3) Å³
Z = 2
D_x = 1.906 Mg m⁻³
D_m not measured

Mo *Kα* radiation
 λ = 0.71073 Å
 Cell parameters from 5000 reflections
 θ = 2.5–27.9°
 μ = 4.113 mm⁻¹
T = 200 (2) K
 Needle
 0.50 × 0.06 × 0.04 mm
 Blue

Data collection

Stoe IPDS diffractometer
 Area-detector scans
 Absorption correction:
 numerical (*X-RED*; Stoe
 & Cie, 1995a)
 T_{\min} = 0.624, T_{\max} = 0.838
 18 058 measured reflections
 2493 independent reflections

1630 reflections with
 $I > 2\sigma(I)$
 R_{int} = 0.064
 θ_{\max} = 27.95°
 h = -22 → 22
 k = -20 → 20
 l = -9 → 9
 Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.033
 $wR(F^2)$ = 0.073
 S = 0.854
 2493 reflections
 177 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0408P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.683 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.477 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—N02	2.023 (4)	C21—N21	1.139 (6)
Cu1—N01	2.034 (4)	C31—N31	1.137 (7)
Cu1—N31	2.309 (4)	C41—N41	1.150 (7)
Cu2—N03	1.976 (3)	Ni2—C22	1.860 (5)
Cu2—N12 ¹	2.026 (4)	Ni2—C32	1.870 (5)
Cu2—N11	2.124 (4)	Ni2—C42	1.875 (5)
Cu2—N22	2.128 (4)	Ni2—C12	1.880 (5)
Ni1—C41	1.856 (5)	C12—N12	1.134 (7)
Ni1—C31	1.861 (5)	C22—N22	1.153 (7)
Ni1—C11	1.869 (5)	C32—N32	1.153 (7)
Ni1—C21	1.874 (5)	C42—N42	1.136 (6)
C11—N11	1.135 (6)		
N02 ² —Cu1—N02	92.2 (2)	N12 ¹ —Cu2—N11	103.37 (18)
N02 ² —Cu1—N01	173.43 (13)	N03—Cu2—N22	87.35 (9)
N02—Cu1—N01	89.42 (14)	N12 ¹ —Cu2—N22	152.25 (19)
N01 ¹ —Cu1—N01	88.3 (2)	N11—Cu2—N22	104.39 (18)
N02—Cu1—N31	94.52 (12)	C11—N11—Cu2	172.2 (4)
N01—Cu1—N31	91.71 (13)	C31—N31—Cu1	140.0 (4)
N03—Cu2—N03 ¹	171.24 (18)	C12—N12—Cu2 ¹	179.9 (5)
N03—Cu2—N12 ¹	90.72 (9)	C22—N22—Cu2	128.1 (4)
N03—Cu2—N11	94.03 (9)		

Symmetry codes: (i) 1 - *x*, -*y*, -*z*; (ii) *x*, *y*, -*z*.

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

D—H...A	D—H	H...A	D...A	D—H...A
N02—H12...N32 ⁱⁱⁱ	0.81 (5)	2.41 (5)	3.203 (5)	165 (4)
N02—H22...N21 ^{iv}	0.81 (4)	2.49 (5)	3.219 (4)	151 (4)
N03—H23...N41 ^v	0.82 (4)	2.28 (5)	3.068 (5)	162 (5)
N02—H32...N31 ^{vi}	0.80 (4)	2.61 (5)	3.313 (5)	147 (4)
N03—H33...N42 ^{vii}	0.80 (4)	2.40 (4)	3.201 (5)	170 (4)

Symmetry codes: (iii) $\frac{1}{2} - x, y - \frac{1}{2}, -z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -\frac{1}{2} - y, -\frac{1}{2} - z$; (v) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} - z$; (vi) $-x, -y, z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data are 99.4% complete to $\theta = 27.95^\circ$. 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.

Data collection: *IPDS* (Stoe & Cie, 1995b). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SIR97* (Casarano *et al.*, 1996). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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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.

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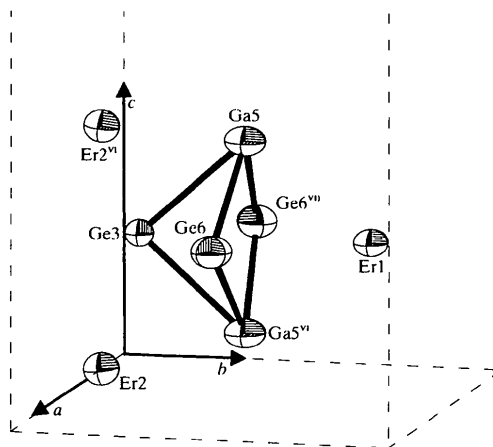


Fig. 1. View of the asymmetric unit of $\text{Er}_3\text{Ga}_2\text{Ge}_3$. Displacement ellipsoids are shown at the 99% probability level.

The refinement of the occupancy factors of the Ga and Ge sites leads us to assume that the Ga5 and Ge6 sites are fully occupied by Ga and Ge atoms, respectively. The occupancy factor of the (Ge3,Ga4) 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 ($\text{Er}_{37.5}\text{Ge}_{34.9}\text{Ga}_{27.6}$) is in good agreement with that measured by microprobe analysis.

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Trierbium digallide trigermanide

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Abstract

The synthesis and single crystal structure of $\text{Er}_3\text{Ga}_2\text{Ge}_3$ (analysed as $\text{Er}_3\text{Ga}_{2.21}\text{Ge}_{2.79}$) are reported. $\text{Er}_3\text{Ga}_2\text{Ge}_3$ is isotopic with Pu_3Pd_5 .

Comment

The title compound, $\text{Er}_3\text{Ga}_2\text{Ge}_3$, is isotopic with Pu_3Pd_5 (Cromer, 1976). Until now, this structural type has been mainly reported for $R_3\text{In}_5$ and $R_3\text{Tl}_5$ compounds (R = lanthanide elements; Villars & Calvert, 1991). In the Er–Ga–Ge system investigated by us at 1173 K, $\text{Er}_3\text{Ga}_2\text{Ge}_3$ is in equilibrium with the Tm_3Ga_5 -type compound $\text{Er}_3\text{Ga}_3\text{Ge}_2$ (Yatsenko *et al.*, 1983) and with the defect AlB_2 -type compound $\text{Er}_{36}\text{Ga}_{17}\text{Ge}_{47}$. The Pu_3Pd_5 structure is closely related to the Tm_3Ga_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 $\text{Er}_{25}\text{Ga}_{20}\text{Ge}_{55}$ 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

$\text{Er}_3\text{Ga}_{2.21}\text{Ge}_{2.79}$
 $M_r = 858.99$
 Orthorhombic
Cmcm
 $a = 9.2880(6) \text{ \AA}$
 $b = 7.4180(7) \text{ \AA}$
 $c = 9.3830(4) \text{ \AA}$
 $V = 646.47(8) \text{ \AA}^3$
 $Z = 4$
 $D_x = 8.826 \text{ Mg m}^{-3}$
 D_m not measured

Ag $K\alpha$ radiation
 $\lambda = 0.56090 \text{ \AA}$
 Cell parameters from 176 reflections
 $\theta = 0.64\text{--}23.58^\circ$
 $\mu = 32.069 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Parallelepiped
 $0.08 \times 0.07 \times 0.07 \text{ mm}$
 Metallic grey

Data collection

Nonius KappaCCD diffractometer
 Oscillations scan
 Absorption correction: empirical (SORTAV; Blessing, 1987)
 $T_{\min} = 0.090$, $T_{\max} = 0.109$
 3631 measured reflections
 423 independent reflections

358 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 21.34^\circ$
 $h = -11 \rightarrow 12$
 $k = -9 \rightarrow 9$
 $l = -12 \rightarrow 12$