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Hexakis[tris(ethylenediamine-κ^2N,N')nickel(II)] tricyanocuprate(I) bis{μ-cyano-bis[tricyanocuprate(I)]} nonahydrate

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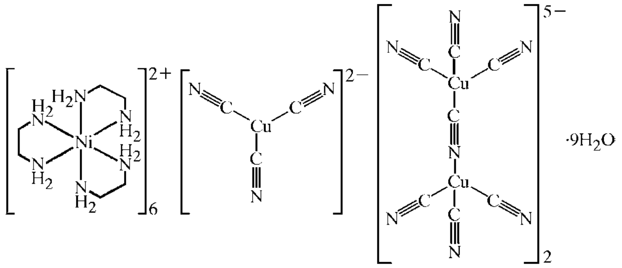
The title compound, $[Ni(C_2H_8N_2)_3]_6[Cu(CN)_3][Cu_2(CN)_7]_2\cdot9H_2O$, was formed upon dissolution of a freshly prepared precipitate of $CuNi(CN)_4$ in ethylenediamine (en) as a result of complex redox and complexation equilibriums in the presence of air. The compound exhibits an ionic structure and contains three crystallographically independent chiral $[Ni(en)_3]^{2+}$ cations, planar $[Cu(CN)_3]^{2-}$ and chiral $[(NC)_3Cu–(\mu\text{-}CN)–Cu(CN)_3]^{5-}$ anions, and water molecules of crystallization. All metal atoms are situated on special positions. One of the Ni atoms lies on a twofold axis, whereas all other metal atoms are located on threefold axes.

Comment

Magneto-structural correlations are being studied intensively at present (Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Dunbar & Heintz, 1997; Mukherjee *et al.*, 2004; Chandramouli *et al.*, 2003; Boča, 2004). Literature data show that the magnetic dimensionality of a system may differ from the structural dimensionality governed by covalent bonds. For example, $Cu(en)_2Ni(CN)_4$ (en is ethylenediamine) exhibits a one-dimensional crystal structure displaying composition $[–Cu(en)_2–(\mu\text{-}NC)–Ni(CN)_2–(\mu\text{-}CN)–Cu–]$ (Seitz *et al.*, 2001), but at low temperatures it behaves as a two-dimensional magnet with short-range ordering at 230 K. It was proposed that N—H···N hydrogen bonds may serve as additional exchange paths for magnetic interactions in this compound (Orendáč *et al.*, 1995). In order to understand better the role of the hydrogen bonds in mediating magnetic interactions and to avoid the possibility of mediation of magnetic interactions *via* bridging cyano ligands, we tried to prepare a tetracyanonickellate compound with the $[Cu(en)_3]^{2+}$ cation; this cation has already been structurally characterized, for example, in $[Cu(en)_3]SO_4$ (Cullen & Lingafelter, 1970). Instead, we unexpectedly obtained in low yield (15%) a new compound, $[Ni(en)_3]_6[Cu_2(CN)_7]_2[Cu(CN)_3]\cdot9H_2O$, (I); the synthetic procedure is reproducible. Our attempts to prepare (I) from the aqueous system Ni^{II}–en–Cu^{I}–CN^- were unsuccessful.

The structure of (I) is built up of $[Ni(en)_3]^{2+}$ cations, $[Cu(CN)_3]^{2-}$ and $[(NC)_3Cu(\mu\text{-}CN)Cu(CN)_3]^{5-}$ anions, and water molecules of crystallization. It is isostructural with the analogous zinc compound described by Černák *et al.* (1994). The structures of the analogous Cu^I/Cu^{II} mixed-valence compounds $[Cu(en)_2(H_2O)Cu_2(CN)_4]$ and $[Cu(en)_3][Cu(CN)_3]\cdot2H_2O$ have also been described (Williams *et al.*, 1972; Wicholas & Wolford, 1975).



(I)

In the unit cell there are three crystallographically independent chiral $[Ni(en)_3]^{2+}$ cations; the Ni^{II} atoms lie on special positions, *viz.* Ni1 on the threefold axis, Ni2 on the intersection of the twofold and threefold axes, and Ni3 on the twofold axis. All Ni^{II} atoms are coordinated in a pseudo-octahedral manner by three chelating molecules of ethylenediamine (Figs. 1*a*–1*c*). The chelate rings exhibit a *gauche* conformation. There are three types of enantiomorphs; the configurations of the $[Ni1(en)_3]^{2+}$ and $[Ni3(en)_3]^{2+}$ cations are $\Lambda\delta\delta\delta$ and $\Lambda\delta\delta\lambda$, respectively, and the configuration of the $[Ni2(en)_3]^{2+}$ cation (the same mean as in the case of atom Ni1) is $\Delta\lambda\lambda\lambda$. The average values of the Ni—N bonds and N—Ni—N angles within the metallocycle [2.129 (1) Å and 81.75 (2)°; Table 1] are as observed in octahedral complexes of Ni^{II}; for example, in $[Ni(en)_3]SO_4$, the corresponding values are 2.125 (2) Å and 80.9 (2)°, respectively (Jameson *et al.*, 1982).

The positive charges of the cations are compensated by two structurally different anions in the unit cell. The planar $[Cu(CN)_3]^{2-}$ anion has already been described, for example, in $Na_2[Cu(CN)_3]\cdot3H_2O$ (Kappenstein & Hugel, 1977) and $[Cu(en)_3][Cu(CN)_3]\cdot2H_2O$ (Wicholas & Wolford, 1975). The symmetry of this anion is D_{3h} (Fig. 1*d*) and the geometrical parameters correspond to those described previously.

The second chiral anion, $[(NC)_3Cu(\mu\text{-}CN)Cu(CN)_3]^{5-}$ (symmetry C_3), has previously been described only in the analogous zinc compound (Černák *et al.*, 1994); it also forms a part of the polymeric anion in $[H_{31}O_{14}][CdCu_2(CN)_7]$ (Nishikiori & Iwamoto, 1993). In this anion there exist two different coordination spheres, *viz.* CuC_4 and CuC_3N, with tetrahedrally coordinated Cu^I atoms (Fig. 1*e*). The dihedral angle between the Cu5/Cu6/C51/N51 and Cu6/Cu5/C61/N61 least-squares planes is 26.6 (1)°, which means that the conformation of the anion is staggered. The corresponding value in the isostructural zinc compound is 23.8 (1)° (Černák *et al.*, 1994). The Cu—C bond lengths in the CuC_4 chromophore are shorter

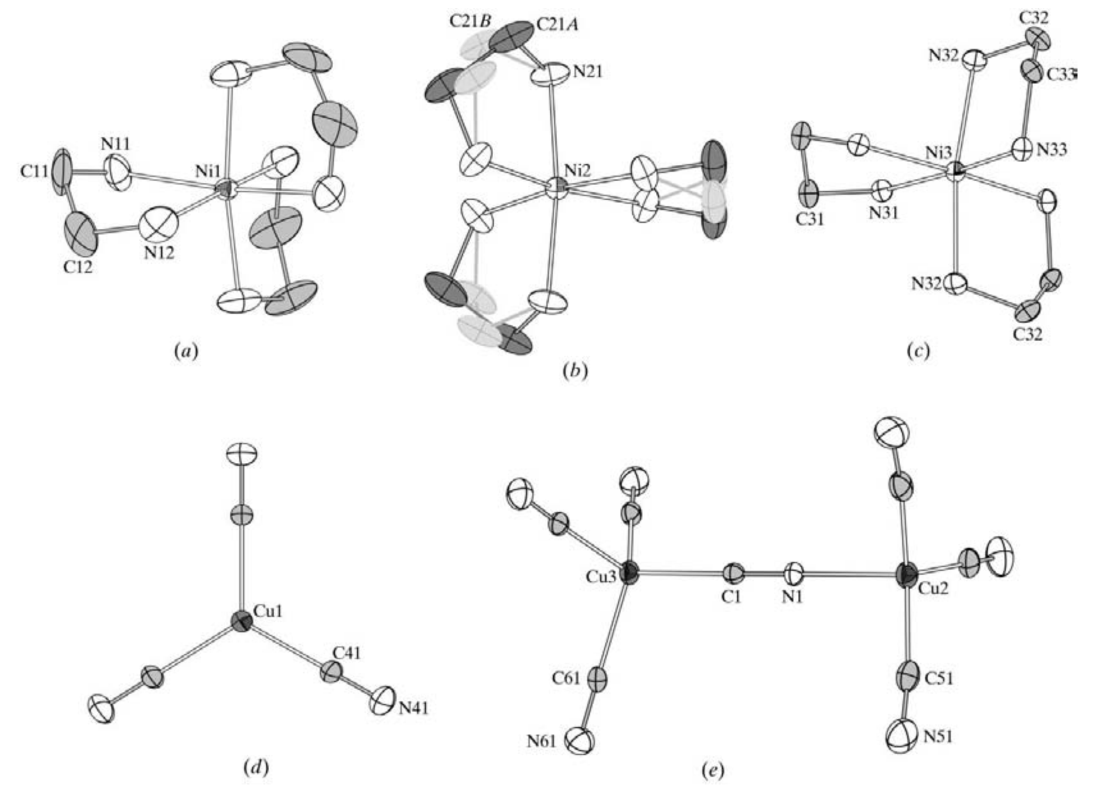


Figure 1

Views of the ions of the title compound, with displacement ellipsoids drawn at the 30% probability level; H atoms have been omitted. (*a*) $[Ni(en)_3]^{2+}$ (Ni1, internal symmetry 3), (*b*) $[Ni(en)_3]^{2+}$ (Ni2, internal symmetry 32), (*c*) $[Ni(en)_3]^{2+}$ (Ni3, internal symmetry 2), (*d*) $[Cu(CN)_3]^{2-}$ (Cu4, internal symmetry 3) and (*e*) $[Cu_2(CN)_7]^{5-}$ (Cu5 and Cu6, internal symmetry 3).

than the equivalent bonds in $K_3[Cu(CN)_4]$ (Roof *et al.*, 1968), and the bond lengths for CuC_3N are similar to those in $[Cu(en)_2Cu_2(CN)_4]\cdot H_2O$ (Williams *et al.*, 1972).

There are two crystallographically different water molecules of crystallization in the unit cell; these are involved in the hydrogen-bond system (Table 2) and contribute to the stability of the packing as well as to the configuration of the cations.

The formation of (I) means that during preparation the central atoms exchanged their ligands and, moreover, reduction of Cu^{II} to Cu^{I} occurred. One of the reasons behind such an exchange could be the (partial) instability of Cu^{II} in the presence of cyano ligands, leading to various cyanocuprate anions and/or Cu^{II}/Cu^{I} mixed-valence compounds (Dunaj-Jurčo *et al.*, 1988). The higher stability of the $[Ni(en)_3]^{2+}$ cation with respect to the $[Cu(en)_3]^{2+}$ cation forced by the very high concentration of the en ligand may also play an important role.

Experimental

To a warm solution (10 ml, 0.1 *M*) of $CuSO_4$ (1 mmol) was added slowly a warm solution (10 ml, 0.1 *M*) of $K_2[Ni(CN)_4]\cdot H_2O$ (1 mmol) (333 K). The resulting glaucous precipitate was filtered off, washed several times with water until producing a negative reaction with barium chloride and then dissolved in liquid en (large excess). The resulting clear blue solution was left to crystallize in a refrigerator (277 K). Single crystals of (I) appeared after one week (yield 0.348 g, 15%). Analysis calculated: C 27.74, H 6.74, N 31.84, Ni 14.93, Cu 13.48%; found: C 27.28, H 6.77, N 31.68, Ni 14.2, Cu 15.73%. FT–IR (KBr, cm^{-1}): 3333 (*vs*), 3282 (*vs*), 2962 (*s*), 2935 (*s*), 2885 (*s*), 2089 (*vs*), 2079 (*vs*), 1664 (*m*), 1587 (*s*), 1570 (*vs*), 1470 (*s*), 1396 (*m*), 1335 (*m*), 1281 (*m*), 1149 (*w*), 1113 (*m*), 1024 (*vs*), 972 (*m*), 947 (*w*), 669 (*s*), 640 (*s*), 517 (*s*), 490 (*w*).

Crystal data

$[Ni(C_2H_8N_2)_3]_6[Cu(CN)_3]$-$[Cu_2(CN)_7]_2\cdot 9H_2O$
$M_r = 2356.32$
Trigonal, *R*32
$a = 15.3025$ (5) Å
$c = 38.2467$ (17) Å
$V = 7756.2$ (5) $Å^3$
$Z = 3$
$D_x = 1.513$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.14$ mm^{-1}
$T = 193$ (2) K
Block, blue
0.24 × 0.22 × 0.12 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (*WinGX*; Farrugia, 1999; Spek, 2003)
$T_{min} = 0.623$, $T_{max} = 0.813$
27795 measured reflections
4597 independent reflections
3287 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 29.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.083$
$S = 0.89$
4597 reflections
207 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e $Å^{-3}$
$\Delta\rho_{min} = -0.62$ e $Å^{-3}$
Absolute structure: Flack (1983), 2050 Friedel pairs
Flack parameter: 0.00 (2)

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Table 1
Selected geometric parameters (Å, °).

Ni1—N12	2.126 (4)	Cu4—C41	1.958 (6)
Ni1—N11	2.134 (4)	Cu5—C51	1.970 (5)
Ni2—N21*A*	2.123 (3)	Cu5—N1	2.152 (4)
Ni3—N33	2.115 (3)	Cu6—C1	1.990 (5)
Ni3—N31	2.131 (3)	Cu6—C61	1.991 (4)
Ni3—N32	2.148 (3)	N1—C1	1.145 (6)
N12—Ni1—N11	81.33 (18)	N32—Ni3—N33	82.23 (12)
N21*A*^{i}—Ni2—N21*A*^{ii}	81.7 (2)	N31—Ni3—N32	96.88 (12)
N31—Ni3—N33	175.74 (14)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*B*···O3	0.92	2.09	2.937 (11)	152
N12—H12*B*···O3^{i}	0.92	2.10	2.98 (8)	160
N12—H12*B*···O1^{i}	0.92	2.15	2.998 (8)	153
N31—H31*A*···N61^{iii}	0.92	2.63	3.478 (5)	154
N32—H32*B*···N51^{iv}	0.92	2.48	3.346 (5)	157
N33—H33*B*···N41^{v}	0.92	2.37	3.225 (6)	156
N21*A*—H21*A*···O2^{iv}	0.92	2.34	2.96 (7)	125
O1—H1O1···N61^{vi}	0.85	2.35	2.905 (7)	124
O1—H2O1···N12^{iii}	0.85	2.55	2.998 (8)	114
O2—H1O2···O3	0.85	2.22	2.842 (12)	130
O2—H1O2···O1	0.85	2.36	2.806 (10)	113
O2—H2O2···N51	0.85	2.00	2.773 (9)	151

Symmetry codes: (i) $-y, x-y, z$; (iii) $-x+y, -x, z$; (iv) $\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{2}{3}-z$; (v) $-\frac{1}{3}-y, \frac{1}{3}+x-y, \frac{1}{3}+z$; (vi) $\frac{1}{3}-y, \frac{2}{3}+x-y, z-\frac{1}{3}$.

H atoms were treated as riding, with C—H distances of 0.96 or 0.99 Å, O—H distances of 0.85 Å and N—H distances of 0.92 Å.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3005). Services for accessing these data are described at the back of the journal.

References

Boča, R. (2004). *Coord. Chem. Rev.* **248**, 757–815.
Černák, J., Chomič, J., Kappenstein, C. & Dunaj-Jurčo, M. (1994). *Z. Kristallogr.* **209**, 430–436.
Chandramouli, G. V. R., Kundu, T. K. & Manoharan, P. T. (2003). *Aust. J. Chem.* **56**, 1239–1248.
Crystal Impact (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Cullen, D. L. & Lingafelter, E. C. (1970). *Inorg. Chem.* **9**, 1858–1864.
Dunaj-Jurčo, M., Ondrejovič, G. & Melník, M. (1988). *Coord. Chem. Rev.* **83**, 1–28.
Dunbar, K. R. & Heintz, R. A. (1997). *Prog. Inorg. Chem.* **45**, 283–391.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jameson, G. B., Schneider, R., Dubler, E. & Oswald, H. R. (1982). *Acta Cryst.* B**38**, 3016–3020.
Kappenstein, C. & Hugel, R. (1977). *Inorg. Chem.* **17**, 1945–1949.
Mukherjee, S., Weyhermuller, T., Bill, E. & Chaudhuri, P. (2004). *Eur. J. Inorg. Chem.* **21**, 4209–4215.
Nishikiori, S. & Iwamoto, T. (1993). *J. Chem. Soc. Chem. Commun.* **20**, 1555–1556.
Ohba, M. & Okawa, H. (2000). *Coord. Chem. Rev.* **198**, 313–328.
Orendáč, M., Orendáčová, A., Černák, J. & Feher, A. (1995). *Solid State Commun.* **94**, 833–835.
Roof, R. B., Larson, A. C. & Cromer, D. T. (1968). *Acta Cryst.* B**24**, 269.
Seitz, K., Peschel, S. & Babel, D. (2001). *Z. Anorg. Allg. Chem.* **627**, 929–934.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (1999). *IPDS Sotware*. Version 2.92. Stoe & Cie, Darmstadt, Germany.
Verdaguer, M., Bleuzen, A., Marvaud, V., Vaissermann, J., Seuleiman, M., Desplanches, C., Scuiller, A., Train, C., Garde, R., Gelly, G., Lomenech, C., Rosenman, I., Veillet, P., Cartier, C. & Villain, F. (1999). *Coord. Chem. Rev.* **192**, 1023–1047.
Wicholas, M. & Wolford, T. (1975). *Inorg. Nucl. Chem. Lett.* **11**, 157–159.
Williams, R. J., Larson, A. C. & Cromer, D. T. (1972). *Acta Cryst.* B**28**, 858.

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