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Structure of Bis(ethylenediamine)copper(II) Tetracyanonickelate(II)

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Abstract. $[Cu(C_4H_{16}N_4)][Ni(CN)_4]$, $M_r = 346{\cdot}5$, triclinic, $P\bar{1}$, $a = 6{\cdot}460\ (9)$, $b = 7{\cdot}230\ (10)$, $c = 7{\cdot}864\ (15)$ Å, $\alpha = 106{\cdot}81\ (13)$, $\beta = 91{\cdot}51\ (14)$, $\gamma = 106{\cdot}94\ (12)°$, $V = 333{\cdot}9\ (9)$ Å^3, $Z = 1$, $D_m = 1{\cdot}71\ (1)$, $D_x = 1{\cdot}723$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}55$ mm^{-1}, $F(000) = 177$, $T = 293$ K, final $R = 0{\cdot}056$ for 1212 unique observed reflections. The structure consists of centrosymmetric $[Cu(en)_2]^{2+}$ (en = ethylenediamine) cations and $[Ni(CN)_4]^{2-}$ anions linked together by two of the CN groups (the remaining two act as unidentate ligands) to form infinite chains running along the [111] direction. Bridging by the CN groups is clearly unsymmetrical [Ni—C = 1·850 (4) and Cu—N = 2·533 (4) Å], leading to four-coordinate Ni^{II} species alternating with axially distorted octahedral Cu^{II} groups along the chain [the equatorial Cu—N distances are 1·997 (3) and 2·001 (3) Å].

Experimental. The title compound, (I), was prepared by mixing equimolar amounts of $K_2Ni(CN)_4$ and $CuSO_4.5H_2O$ (dissolved in H_2O). The resulting precipitate was collected by filtration, washed with H_2O and dissolved in ethylenediamine/ethanol. Finally, 4–5 volumes of C_6H_6 (or C_6D_6) were added and allowed to stand until crystals appeared.

Crystal size: 1·0 × 0·6 × 0·4 mm, D_m by flotation in bromoform–cyclohexane, Weissenberg photographs consistent with Laue symmetry $\bar{1}$. Syntex $P2_1$ diffractometer; unit-cell parameters by least-squares refinement of 22 reflections, $7 < 2\theta < 26°$; intensity data ($h = 0$ to 8, $k = -9$ to 8, $l = -10$ to 9) collected with graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode, variable scan speed, scan width 2° (in 2θ) plus $\alpha_1 - \alpha_2$ dispersion. Two standard reflections measured every 100 reflections, these varied by less than 5%; intensities corrected for Lorentz–polarization effects but not for absorption; 1550 unique reflections, $2\theta \leq 55°$, 1212 with $I \geq 2\sigma(I)$ considered observed and included in the refinement. Structure solved by the heavy-atom method using *XFPS* (Pavelčík, 1986) and refined by block-diagonal least-squares methods, anisotropic thermal parameters for non-H atoms, H atoms fixed at calculated positions with isotropic thermal parameters set to B_{eq} of the bonded atoms; in final cycle $R = 0{\cdot}056$, $wR = 0{\cdot}073$ for observed reflections only, $S = 1{\cdot}51$, $(\Delta/\sigma)_{max} = 0{\cdot}03$, function minimized $\sum w(\Delta F)^2$, where $w^{-1} = \sigma^2(F_o) + (C|F_o|)^2$ [$\sigma(F_o)$ derived from pulse statistics and $C = 0{\cdot}018$, in order to make $w(\Delta F)^2$ approximately independent of $|F_o|$ and $\sin\theta/\lambda$], max. and min. heights in final $\Delta\rho$ synthesis 0·86 and $-0{\cdot}77$ e Å^{-3}. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV); all calculations except *XFPS* performed with local version of *NRC* (1973).

Final atomic coordinates of non-H atoms and equivalent isotropic B's are listed in Table 1,* bond

* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54285 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\Sigma\Sigma\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cu(1)	0	0	0	2·12 (2)
Ni(1)	5000	5000	5000	1·96 (2)
N(1)	−898 (5)	−2645 (5)	526 (4)	2·67 (9)
N(2)	−1604 (5)	923 (5)	2057 (4)	2·81 (10)
N(3)	3520 (6)	1081 (5)	2048 (5)	3·38 (10)
N(4)	1617 (6)	6152 (6)	3252 (5)	3·85 (13)
C(1)	−2698 (7)	−2654 (7)	1622 (6)	3·67 (13)
C(2)	−2139 (8)	−607 (7)	2975 (6)	3·85 (15)
C(3)	4101 (6)	2539 (6)	3188 (5)	2·51 (11)
C(4)	2882 (6)	5754 (6)	3960 (5)	2·65 (12)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1)—N(1)	1·997 (3)	Ni(1)—C(3)	1·850 (4)
Cu(1)—N(2)	2·001 (3)	Ni(1)—C(4)	1·864 (4)
N(1)—C(1)	1·465 (6)	C(3)—N(3)	1·123 (5)
C(1)—C(2)	1·487 (7)	C(4)—N(4)	1·125 (6)
C(2)—N(2)	1·455 (6)		

N(1)—Cu(1)—N(2)	84·6 (1)	N(2)—C(2)—C(1)	108·7 (4)
Cu(1)—N(1)—C(1)	107·9 (3)	C(3)—Ni(1)—C(4)	88·1 (2)
Cu(1)—N(2)—C(2)	108·7 (3)	Ni(1)—C(3)—N(3)	177·2 (4)
N(1)—C(1)—C(2)	107·3 (4)	Ni(1)—C(4)—N(4)	176·6 (4)

distances and angles in Table 2. A stereoview of the structure and the numbering scheme is given in Fig. 1.

Related literature. Following the report (Williams, Larson & Cromer, 1972) that the mixed-valence copper cyanide ethylenediamine complex, $Cu^I_2(CN)_4$-$Cu^{II}(en)_2.H_2O$ (II), forms a three-dimensional network in the solid state, we attempted to prepare a

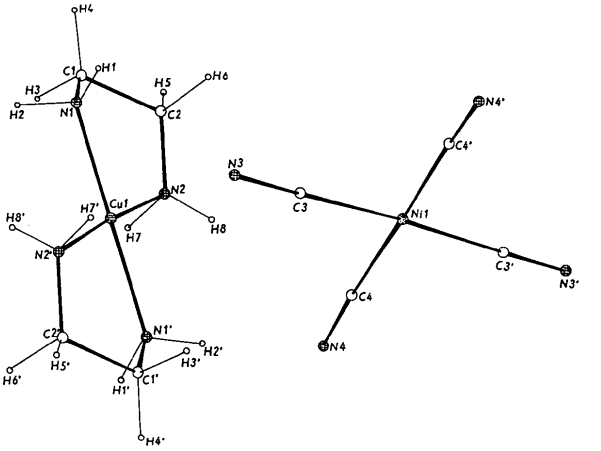

Fig. 1. A perspective view of the cation and anion and the numbering of the atoms.

C_6H_6 (or C_6D_6) clathrate of the stoichiometrically related system $Ni(CN)_4$–$Cu(en)_2$. However, as revealed by this crystal-structure determination, the replacement of the $[Cu^I_2(CN)_4]^{2-}$ by $[Ni^{II}(CN)_4]^{2-}$ anion causes a conversion of the three-dimensional framework into a chain structure. Consequently, in contrast to (II), there is no hole formation in the present structure (I) and, as a result, no clathrate formation was observed.

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Structure of Tetracarbonyl[3,6-bis(pyridin-2-yl)-2,5-dihydro-1,2,4,5-tetrazine]-tungsten(0)

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Abstract. $[W(C_{12}H_{10}N_6)(CO)_4]$, $M_r = 534·14$, monoclinic, $P2_1/c$, $a = 15·327$ (2), $b = 13·993$ (2), $c = 18·526$ (2) Å, $\beta = 114·00$ (1)°, $V = 3629·7$ (9) Å^3, $Z = 8$, $D_x = 1·95$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 6·535$ mm^{-1}, $F(000) = 2032$, $T = 298$ K, R (wR) = 0·023 (0·030) for 5538 unique observed reflections [I

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