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Bimetallic assemblies, $[Ni(en)_2]_3[M(CN)_6]_2{\cdot}3H_2O$ (en = $H_2NCH_2CH_2NH_2$; M = Fe, Co)

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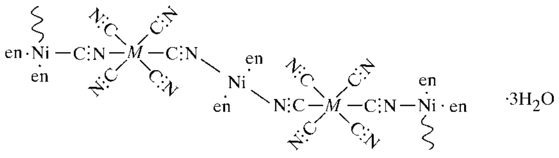
The reaction between tris(ethylenediamine)nickel(II) cations and hexacyanometallate(III) anions (M = Fe, Co) yields ordered bimetallic assemblies, *catena*-poly[[tris(ethylenediamine)nickel-bis(μ-hexacyanoiron-N,N')] trihydrate] and *catena*-poly[[tris(ethylenediamine)nickel-bis(μ-hexacyanocobalt-N,N')] trihydrate], $[\{Ni(C_2H_8N_2)_2\}_3\{M(CN)_6\}_2]{\cdot}3H_2O$, in which both *cis* and *trans* [Ni(en)$_2$] and [M(CN)$_6$] moieties are linked to give S-shaped Ni–NC–M–CN–Ni–NC–M–CN–Ni units which are crosslinked to give ribbons parallel to the *b* axis. The two compounds are isomorphous with mean metal–ligand distances Fe—C = 1.940 (3), Co—C = 1.844 (3) and Ni—N = 2.102 (2) Å for the iron, and 2.105 (3) Å for the cobalt compound. These compounds appear to be identical with those formulated as $[Ni(en)_2]_3[M(CN)_6]_2{\cdot}2H_2O$ [Ohba, Maruona, Okawa, Enoki & Latour (1994). *J. Am. Chem. Soc.* **116**, 11566–11567; Ohba, Fukita & Okawa (1997). *J. Chem. Soc. Dalton Trans.* pp. 1733–1737] which were indexed on a smaller unit cell and described as disordered.

Comment

Hexacyanometallate ions $[M(CN_6)]^{n-}$ have been shown (Dunbar & Heintz, 1997, and references therein) to act as building blocks to provide bimetallic assemblies exhibiting spontaneous magnetization. Kou *et al.* (1998) have reported the synthesis of the 2:1 compound $[Ni(en)_2]_2[Fe(CN)_6]$-$NO_3{\cdot}3H_2O$ which they obtained from the reaction between $[Ni(en)_3](NO_3)_2$ (en is ethylenediamine) and $K_3[Fe(CN)_6]$, but they were unable to obtain crystals suitable for X-ray diffraction. Our attempts at repeating their synthesis yielded crystals which diffracted well but were found to be $[Ni(en)_2]_3[Fe(CN)_6]_2{\cdot}3H_2O$, (I).

This compound contains both *cis*- and *trans*-$[Ni(en)_2]^{2+}$ cations linked to $[Fe(CN)_6]^{3-}$ anions (Fig. 1) *via* cyanide bridges to give S-shaped Ni–NC–Fe–CN–Ni–NC–Fe–CN–Ni units which are crosslinked by the terminal *cis*-Ni(en)$_2$ to give ribbons running along the *b* axis (Fig. 2). Distance ranges include: Fe—C 1.929 (2) to 1.960 (2) Å, mean value 1.941 (3) Å; Ni—N 2.071 (2) to 2.122 (2) Å, mean value 2.102 (3) Å; C—N (cyanide) 1.147 (2) to 1.157 (2) Å, mean value 1.152 (1) Å; C—N (ethylenediamine) 1.475 (3) to 1.488 (3) Å, mean value 1.480 (1) Å; and C—C 1.509 (3) to 1.522 (3) Å, mean value 1.518 (2) Å (the uncertainties given for the mean values are the sample standard deviations of the mean). Repeating the synthesis with an excess of $Ni(NO_3)_2$ still gave the 3:2 compound.



(I) = Fe
(II) = Co

The structure is remarkably similar to that described by Ohba *et al.* (1994) for $[Ni(en)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$, except that we found a unit cell twice as large as theirs, the small cell being obtained from ours by the transformation (1,0,0,1,0.5,1,0,0.5,0), and we believe the two compounds to be identical. We also found three waters of crystallization instead of two. Doubling the cell removes the apparent disorder of the *trans*-Ni(en)$_2$ moiety which had previously been observed and explains the very anisotropic displacement parameters previously observed for one of the monodentate cyanide groups. The analogous Co(CN)$_6$ compound was described by Ohba *et al.* (1997) as being isomorphous with the Fe(CN)$_6$ compound. We have prepared the cobalt compound and find that it too should be described on the doubled unit cell, *i.e.* it is isomorphous with (I) and should be formulated as $[Ni(en)_2]_3[Co(CN)_6]_2{\cdot}3H_2O$, (II).

Distance ranges include: Co—C 1.884 (3) to 1.917 (3) Å, mean value 1.899 (3) Å; Ni—N 2.077 (2) to 2.128 (2) Å, mean value 2.105 (3) Å; C—N (cyanide) 1.143 (4) to 1.159 (3) Å, mean value 1.151 (1) Å; C—N (ethylenediamine) 1.476 (4) to 1.486 (4) Å, mean value 1.481 (1) Å; and C—C 1.507 (4) to 1.523 (4) Å, mean 1.514 (2) Å. For both structures, there is a wide spread in the values obtained for the Ni—N distances; for each *cis*-Ni(en)$_2$ moiety, one of the Ni—N(cyanide) bonds is short, 2.086 (2) and 2.072 (2) Å for the iron, and 2.088 (2) and 2.077 (2) Å for the cobalt complex. The Ni—N(cyanide) distances for the *trans*-Ni(en)$_2$ are also short. The curvature of the S-shaped fragments is achieved largely through the relatively large deviations from linearity at the N atoms of the cyanide groups; the Ni—N—C angles are in the range 149.7 (2)–154.4 (2)° for the iron compound and 149.9 (2)–154.6 (2)° for the cobalt compound. Similar values are also found in Ni(en)$_2$Ni(CN)$_4$ (Černác *et al.*, 1988) and in Ni(en)$_2$Ni(CN)$_4{\cdot}$2.18H$_2$O (Černác *et al.*, 1990), a structure which also contains both *cis*- and *trans*-Ni(en)$_2$ moieties. The Ni—N—C—M groups linking the S's are closer to linearity with Ni—N—C angles of 168.1 (2) and 168.6 (2), and 168.0 (2) and 169.1 (2)° for the iron and cobalt complexes, respectively, and it is for these crosslinkages that the shortest Ni—N bonds occur. As expected (Sharpe, 1981), the CN stretching

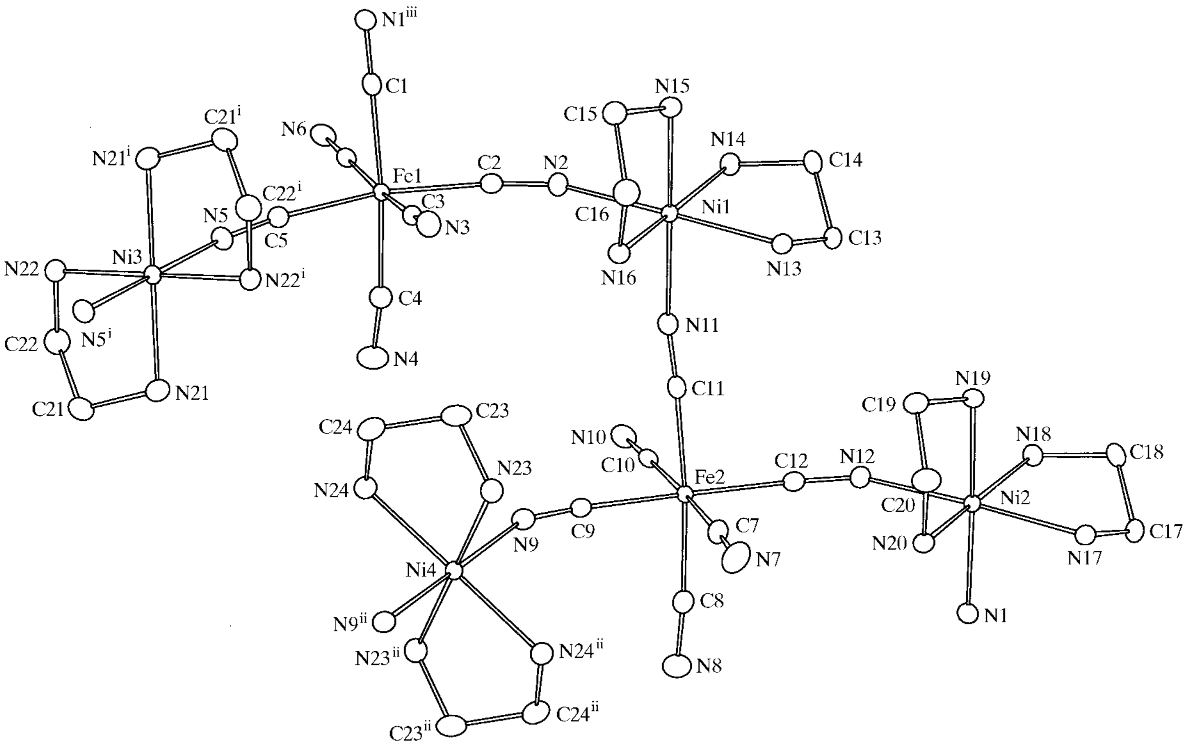


Figure 1
View of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms have been omitted [symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, -z$; (iii) $x, 1 + y, z$].

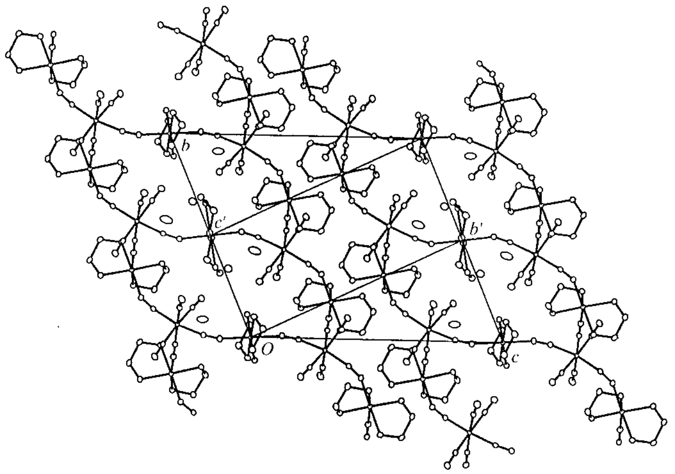


Figure 2
The structure viewed parallel to the *a* axis. The cell chosen by Ohba *et al.* (1994) is shown as *b*′ and *c*′.

frequencies are slightly lower for the iron than for the cobalt compound. We could not, however, observe any significant difference in the C—N bond distances.

Experimental

For the preparation of (I), $K_3Fe(CN)_6$ (0.825 g, 2.5 mmol) was added to $Ni(NO_3)_2{\cdot}6H_2O$ (1.454 g, 5 mmol) and ethylenediamine (0.901 mg, 15 mmol) in water (100 ml). The colour changed from violet to yellow and then brown. Black crystals appeared after 3–4 d. IR spectra (KBr disc, Perkin Elmer FT–IR spectrometer): ν(CN) 2106, 2128, 2153 cm^{-1}. Complex (II) was prepared as for (I) except that $K_3Fe(CN)_6$ was replaced by $K_3Co(CN)_6$. The solution remained violet and violet crystals appeared after a few days. IR spectra (KBr disc): ν(CN) 2118, 2141, 2164 cm^{-1}.

Compound (I)

Crystal data

$[\{Ni(C_2H_8N_2)_2\}_3\{Fe(CN)_6\}_2]{\cdot}3H_2O$
$M_r = 1014.72$
Triclinic, $P\overline{1}$
$a = 9.6424$ (9) Å
$b = 14.861$ (2) Å
$c = 17.021$ (2) Å
$\alpha = 107.604$ (3)°
$\beta = 101.474$ (2)°
$\gamma = 106.528$ (2)°
$V = 2117.6$ (4) $Å^3$
$Z = 2$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.3$–30.4°
$\mu = 2.037$ mm^{-1}
$T = 120$ K
Block, black
0.40 × 0.20 × 0.20 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frame
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.505$, $T_{max} = 0.650$
19 479 measured reflections
10 994 independent reflections
7683 reflections with $I > 3\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 29°$
$h = -9 \rightarrow 13$
$k = -20 \rightarrow 20$
$l = -23 \rightarrow 23$

Table 1
Selected bond lengths (Å) for (I).

Fe1—C1	1.941 (2)	Ni1—N14	2.120 (2)
Fe1—C2	1.946 (2)	Ni1—N15	2.107 (2)
Fe1—C3	1.939 (2)	Ni1—N16	2.110 (2)
Fe1—C4	1.947 (2)	Ni2—N1	2.071 (2)
Fe1—C5	1.934 (2)	Ni2—N12	2.119 (2)
Fe1—C6	1.933 (2)	Ni2—N17	2.117 (2)
Fe2—C7	1.937 (2)	Ni2—N18	2.122 (2)
Fe2—C8	1.960 (2)	Ni2—N19	2.100 (2)
Fe2—C9	1.929 (2)	Ni2—N20	2.115 (2)
Fe2—C10	1.930 (2)	Ni3—N5	2.079 (2)
Fe2—C11	1.947 (2)	Ni3—N21	2.103 (2)
Fe2—C12	1.945 (2)	Ni3—N22	2.104 (2)
Ni1—N2	2.117 (2)	Ni4—N9	2.081 (2)
Ni1—N11	2.086 (2)	Ni4—N23	2.105 (2)
Ni1—N13	2.113 (2)	Ni4—N24	2.107 (2)

Table 2
Selected bond lengths (Å) for (II).

Co1—C1	1.898 (3)	Ni1—N14	2.120 (2)
Co1—C2	1.907 (3)	Ni1—N15	2.110 (2)
Co1—C3	1.893 (3)	Ni1—N16	2.110 (2)
Co1—C4	1.904 (3)	Ni2—N1	2.077 (2)
Co1—C5	1.897 (3)	Ni2—N12	2.123 (2)
Co1—C6	1.891 (3)	Ni2—N17	2.121 (2)
Co2—C7	1.893 (3)	Ni2—N19	2.105 (2)
Co2—C8	1.917 (3)	Ni2—N20	2.116 (2)
Co2—C9	1.884 (3)	Ni2—N18	2.128 (2)
Co2—C10	1.893 (3)	Ni3—N5	2.091 (2)
Co2—C11	1.906 (3)	Ni3—N21	2.102 (2)
Co2—C12	1.903 (3)	Ni3—N22	2.103 (2)
Ni1—N2	2.127 (2)	Ni4—N9	2.090 (2)
Ni1—N11	2.088 (2)	Ni4—N23	2.102 (3)
Ni1—N13	2.111 (2)	Ni4—N24	2.104 (2)

Refinement

Refinement on F
$R = 0.024$
$wR = 0.033$
$S = 1.139$
7456 reflections
509 parameters
H-atom parameters constrained
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$

$(\Delta/\sigma)_{max} = 0.0015$
$\Delta\rho_{max} = 0.52$ (7) e Å^{-3}
$\Delta\rho_{min} = -0.37$ (7) e Å^{-3}
Extinction correction: type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 19 (4)

Compound (II)

Crystal data

$[\{Ni(C_2H_8N_2)_2\}_3\{Co(CN)_6\}_2]\cdot 3H_2O$
$M_r = 1020.90$
Triclinic, $P\overline{1}$
$a = 9.6303$ (8) Å
$b = 14.787$ (1) Å
$c = 16.951$ (1) Å
$\alpha = 107.500$ (2)°
$\beta = 101.464$ (2)°
$\gamma = 106.652$ (2)°
$V = 2095.6$ (3) Å^3

$Z = 2$
$D_x = 1.618$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7727 reflections
$\theta = 1.6$–29.6°
$\mu = 2.159$ mm^{-1}
$T = 120$ K
Needle, violet
0.52 × 0.18 × 0.18 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frame
Absorption correction: multi-scan (*SADABS*: Sheldrick, 1996)
$T_{min} = 0.382$, $T_{max} = 0.678$
17341 measured reflections

9897 independent reflections
6342 reflections with $I > 3\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 28°$
$h = -13 \rightarrow 13$
$k = -20 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F
$R = 0.028$
$wR = 0.040$
$S = 1.385$
6342 reflections
509 parameters
H-atom parameters constrained
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$

$(\Delta/\sigma)_{max} = 0.0011$
$\Delta\rho_{max} = 1.16$ (8) e Å^{-3}
$\Delta\rho_{min} = -0.63$ (8) e Å^{-3}
Extinction correction: type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 18 (5)

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR*97 (Cascarano *et al.*, 1996) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1101). Services for accessing these data are described at the back of the journal.

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