metal-organic compounds

A ferric-cyanide-bridged one-dimensional dirhodium complex with (18-crown-6)potassium cations

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The crystal structure of the title compound, *catena*-poly[bis-[aqua(18-crown-6)potassium] diaqua(18-crown-6)potassium [[tetra-μ-benzoato-2:3$\kappa^8 O:O'$-μ-cyano-1:2$\kappa^2 C:N$-tetracyano-1κC-irondirhodium($Rh-Rh$)]-μ-cyano-1κC:3'κN] octahydrate], [K(18-crown-6)(H$_2$O)]$_2$[K(18-crown-6)(H$_2$O)$_2$][FeRh$_2$-(C$_7$H$_5$O$_2$)$_4$(CN)$_6$]·8H$_2$O, where (18-crown-6) is 1,4,7,10,13,16-hexaoxacyclooctadecane (C$_{12}$H$_{24}$O$_6$), has been determined. Ferric cyanides connect the dirhodium units to form a one-dimensional chain compound. [K(18-crown-6-ether)(H$_2$O)$_2$] cations (with inversion symmetry) and [K(18-crown-6-ether)(H$_2$O)] cations (in general positions) are located between the chains.

Comment

Metal cyanide compounds have been used to synthesize coordination polymers (Ward, 1995; Vahrenkamp *et al.*, 1997, and references therein). Hexacyanometallate ions [M(CN)$_6$]$^{n-}$ can provide one- (Colacio *et al.*, 2000), two- (Miyasaka *et al.*, 1997) and three-dimensional polymers (Miyasaka *et al.*, 1998*a,b*; Langenberg *et al.*, 1997) since cyano groups are directed to all three axes. Dirhodium acetate units are connected by [Co(CN)$_6$]$^{3-}$ to form a two-dimensional sheet
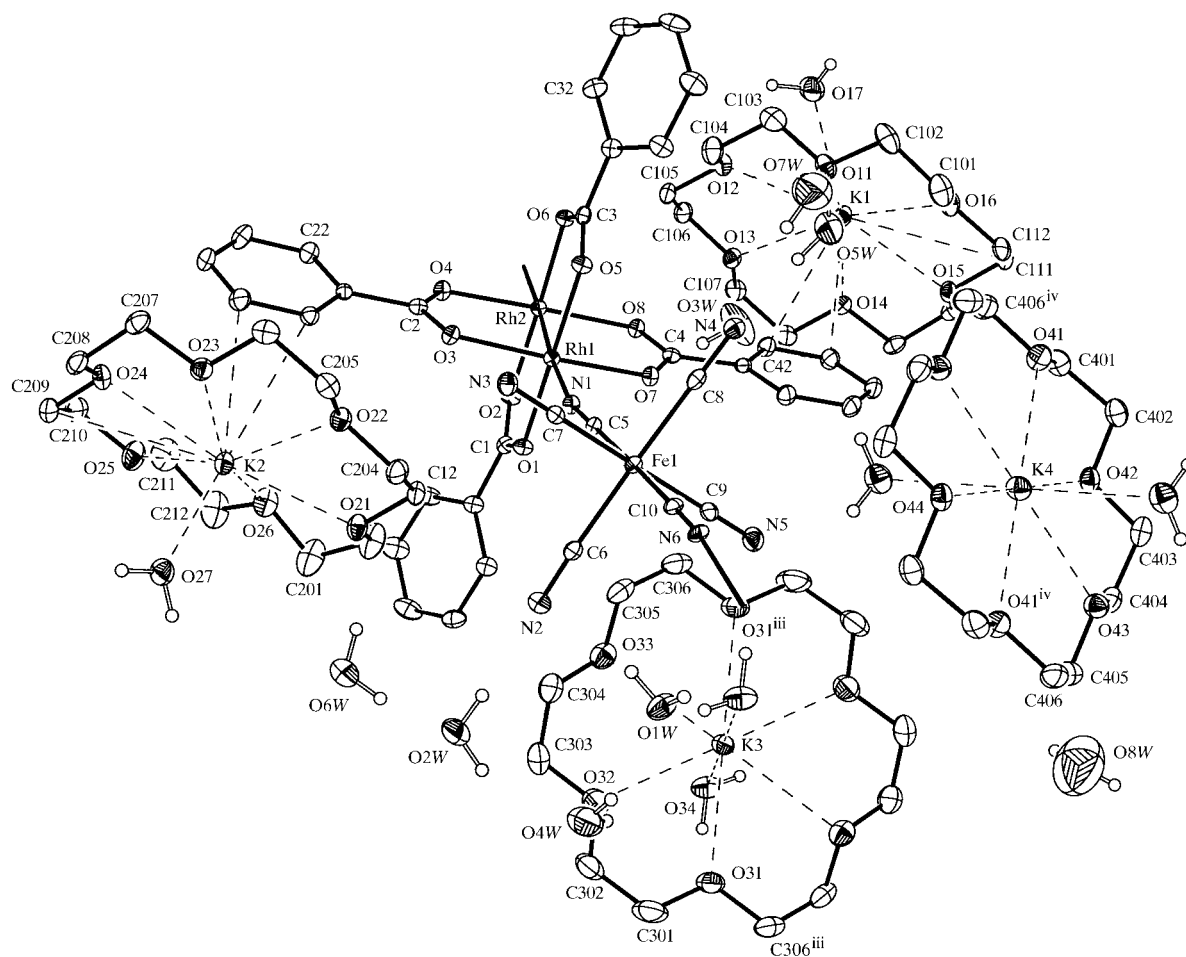
Figure 1
*ORTEP*II (Johnson, 1976) drawing of compound (I). All H atoms have been omitted, except for the water H atoms. [Symmetry codes: (iii) $-x, 2-y, 1-z$; (iv) $1-x, 2-y, 1-z$.]

(Lu *et al.*, 1996); this was the first example of a dimetal unit connected by a metal cyanide. Dirutheium units are also bridged by $[Co(CN)_6]^{3-}$ to form a pentanuclear complex (Kim *et al.*, 1998).

(I)
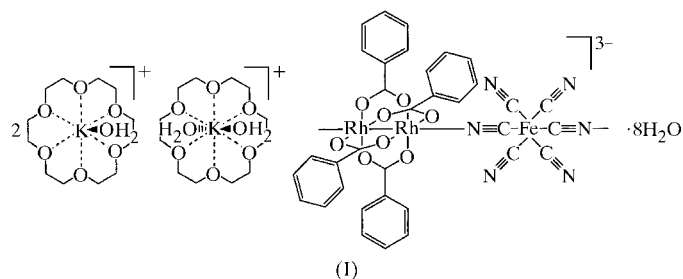
Ferric cyanide can also be used as a metal cyanide to connect dimetal units to form one-, two- or three-dimensional compounds. Only the potassium salt among the ferric cyanides is water soluble. 18-Crown-6-ether can help increase the solubility of a ferric cyanide (Miyasaka *et al.*, 1998*a*).

Only *trans*-cyano groups of the ferric cyanide connect the dirhodium units to form a one-dimensional chain compound. The Rh—Rh distance is 2.4109 (4) Å which is a little longer than the typical Rh—Rh distance in tetracarboxylatodirhodium(II,II) complexes. Rh—N(bridging cyano group) distances are 2.208 (3) and 2.200 (3) Å. The chain is not linear, with angles of 168.1 (3) and 170.7 (3)° for C5—N1—Rh1 and C10—N6—Rh2^{ii}, respectively [symmetry code: (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$]. The benzoate groups of a dirhodium unit are staggered with those of the next dirhodium unit, and also twisted with respect to the four Fe—CN bonds. The Fe—CN bonds are eclipsed with those of the next ferric cyanide. Actually, ferric cyanide is capable of forming three-dimensional network structures since all six cyano groups can connect complex units. However, a benzoate bridging ligand of a dirhodium complex is too bulky to make a two- or three-dimensional compound. Potassium cations encapsulated by crown ether are located between anion chains. Two K atoms, K1 and K2, are on general positions, whereas K3 and K4 are on inversion centres. Each K1 and K2 has a water molecule on one axial site and the other axial site interacts with the phenyl group of the benzoate bridging ligand. K3 and K4 have water molecules on both axial sites since they have inversion centres on the K atom. There are hydrogen bonds between H atoms of water molecules bonded to the potassium, K3 and K4, and N atoms N2, N3, N4 and N5 of free cyano groups.

Experimental

A methanol solution of $[Rh_2(O_2CC_6H_5)_4(CH_3OH)_2]$ was added to a methanol solution of $[K(18\text{-crown-6-ether})(H_2O)_2][Fe(CN)_6]\cdot 3H_2O$. The solution was allowed to stand for several days in the dark room until almost all the solvent had evaporated. Small brown block crystals for suitable X-ray data collection were obtained. IR(KBr): $\nu(C\equiv N)$ 2112.77 cm^{-1}.

Crystal data

$[K(C_{12}H_{24}O_6)(H_2O)]_2$- $[K(C_{12}H_{24}O_6)(H_2O)]$- $[FeRh_2(C_7H_5O_2)_4(CN)_6]\cdot 8H_2O$
$M_r = 2028.66$
Monoclinic, $P2_1/c$
$a = 16.0884 (4)$ Å
$b = 23.1083 (5)$ Å
$c = 25.8233 (6)$ Å
$\beta = 104.090 (1)°$
$V = 9311.6 (4)$ Å^3

$Z = 4$
$D_x = 1.447$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 75 952 reflections
$\theta = 2.59–27.00°$
$\mu = 0.724$ mm^{-1}
$T = 150 (1)$ K
Block, brown
$0.25 \times 0.15 \times 0.14$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.840$, $T_{max} = 0.906$
75 952 measured reflections

20 305 independent reflections
13 576 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.00°$
$h = -21 \rightarrow 20$
$k = -30 \rightarrow 29$
$l = -32 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.116$
$S = 1.022$
20 305 reflections
1156 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 9.4629P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 1.33$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh1—O7	2.034 (2)	Rh2—O8	2.058 (2)
Rh1—O5	2.038 (2)	Rh2—N6^i	2.200 (3)
Rh1—O1	2.054 (2)	Fe1—C7	1.944 (4)
Rh1—O3	2.059 (2)	Fe1—C10	1.944 (4)
Rh1—N1	2.207 (3)	Fe1—C8	1.944 (4)
Rh1—Rh2	2.4109 (4)	Fe1—C9	1.946 (4)
Rh2—O4	2.031 (2)	Fe1—C6	1.947 (4)
Rh2—O2	2.032 (2)	Fe1—C5	1.950 (3)
Rh2—O6	2.048 (2)	N6—Rh2^{ii}	2.200 (3)
O7—Rh1—O5	87.05 (10)	O6—Rh2—N6^i	92.99 (10)
O7—Rh1—O1	91.85 (10)	O8—Rh2—N6^i	95.35 (10)
O5—Rh1—O1	175.56 (9)	N6^i—Rh2—Rh1	177.71 (8)
O7—Rh1—O3	175.69 (9)	C7—Fe1—C10	89.76 (14)
O5—Rh1—O3	91.78 (10)	C7—Fe1—C8	90.06 (15)
O1—Rh1—O3	89.00 (10)	C10—Fe1—C8	90.34 (14)
O7—Rh1—N1	87.84 (10)	C7—Fe1—C9	179.26 (15)
O5—Rh1—N1	90.23 (10)	C10—Fe1—C9	90.90 (14)
O1—Rh1—N1	94.03 (10)	C8—Fe1—C9	89.61 (15)
O3—Rh1—N1	96.32 (9)	C7—Fe1—C6	90.89 (15)
N1—Rh1—Rh2	176.38 (8)	C10—Fe1—C6	88.85 (14)
O4—Rh2—O2	86.45 (10)	C8—Fe1—C6	178.74 (15)
O4—Rh2—O6	91.10 (10)	C9—Fe1—C6	89.44 (15)
O2—Rh2—O6	175.17 (9)	C7—Fe1—C5	89.54 (13)
O4—Rh2—O8	175.77 (9)	C10—Fe1—C5	178.66 (15)
O2—Rh2—O8	93.46 (10)	C8—Fe1—C5	90.81 (14)
O6—Rh2—O8	88.67 (10)	C9—Fe1—C5	89.81 (14)
O4—Rh2—N6^i	88.88 (10)	C6—Fe1—C5	90.02 (14)
O2—Rh2—N6^i	91.12 (10)		

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

All H atoms, except water H atoms, were inserted at calculated positions and treated as riding with isotropic displacement parameters.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1112). Services for accessing these data are described at the back of the journal.

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