A cyano-bridged dinuclear 4f–3d array

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A cyano-bridged bimetallic 4f–3d complex, triaqua-1$\kappa^3 O$-μ-cyano-1:2$\kappa^2 N$:C-pentacyano-2$\kappa^5 C$-tetrakis(2-pyrrolidone-1κO)chromium(III)dysprosium(III) dihydrate, [CrDy(C$_4$H$_7$NO)$_4$(CN)$_6$(H$_2$O)$_3$]·2H$_2$O, has been prepared and characterized by X-ray crystallographic analysis. The structure consists of a neutral cyano-bridged Dy–Cr dimer. A hydrogen-bonded three-dimensional architecture is formed through N—H···O, O—H···N and O—H···O hydrogen bonds.

Comment

Recently, there has been considerable interest in lanthanide(III) hexacyanoferrates, and the analogous cobalt(III) and chromium(III) complexes, because of their potential as catalytic, semiconductor and magnetic materials (Hulliger *et al.*, 1976). Also, some of these cyanides can form semipermeable membranes, which are very important in connection with the desalination of sea water. In particular, a series of three-dimensional cyano-bridged 4f–3d complexes, Ln[M(CN)$_6$]·nH$_2$O (M is Cr^{III} or Fe^{III}), exhibit magnetic ordering (Hulliger *et al.*, 1976). Incorporation of organic ligands into these three-dimensional 4f–3d adducts may reduce the dimensionality of the parent complexes and give various molecular structures. In this regard, we have employed the simple ligand dimethylformamide (dmf) to prepare cyano-bridged 4f–3d dimers, [Ln(dmf)$_4$(H$_2$O)$_4$Fe(CN)$_6$]·H$_2$O (Kou *et al.*, 1998; Kautz *et al.*, 2000) and [Pr(dmf)$_4$(H$_2$O)$_3$Cr(CN)$_6$]·H$_2$O (Combs *et al.*, 2000), a one-dimensional zigzag chain, [Sm(dmf)$_4$(H$_2$O)$_2$Cr(CN)$_6$]·H$_2$O (Kou, Gao & Jin, 2001), and two-dimensional brick-wall-like complexes, [Ln(dmf)$_2$(H$_2$O)$_3$Cr(CN)$_6$]·H$_2$O (Ln is Sm or Gd; Kou, Gao & Jin, 2001; Kou, Gao, Sun & Zhang, 2001). In the present study, we used 2-pyrrolidone (pyr) to synthesize the cyano-bridged bimetallic complex [Dy(pyr)$_4$(H$_2$O)$_3$Cr(CN)$_6$]·2H$_2$O, (I).

A perspective view of (I) is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The crystal structure of (I) consists of a neutral cyano-bridged bimetallic

fragment. The lanthanide ion is eight-coordinate and the coordination polyhedron can be described as a distorted square antiprism. Seven O atoms from three water molecules and four pyr molecules, and one N atom from the bridging CN ligand coordinate to Dy^{III}. The bridging cyanide coordinates to the Dy^{III} ion in a bent fashion, with a bond angle of 162.4 (3)° for C1—N1—Dy. The Cr···Dy metal–metal distance is 5.592 (2) Å.

(I)
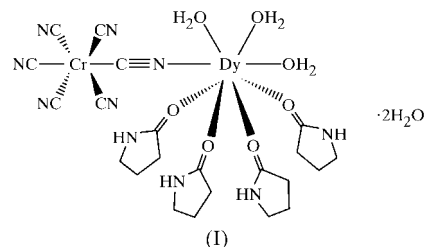
The N1—Dy—O$_{H_2O}$ angles range from 83.68 (13) to 141.33 (11)°, compared with the range for N1—Dy—O$_{pyr}$ of 72.28 (12)–149.59 (12)°. This reflects the fact that small water molecules are more polar than the bulky 2-pyrrolidone ligand, and the electrostatic repulsion force may be significant.
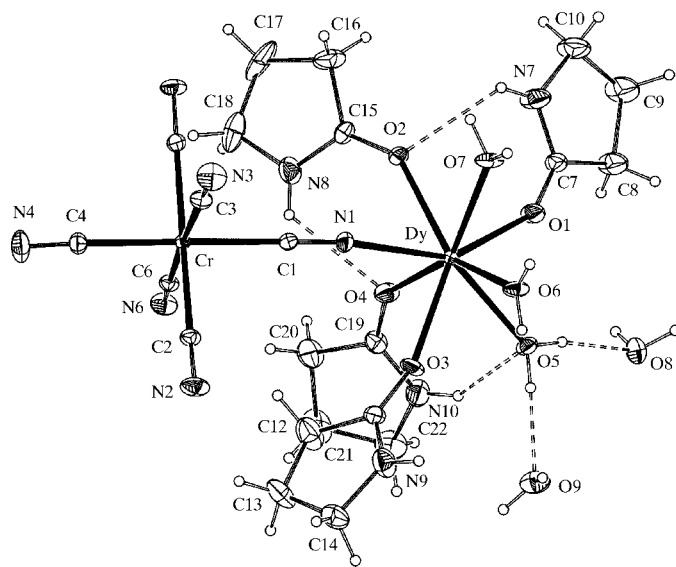

Figure 1
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen bonds within the asymmetric unit are indicated by dashed lines.

The Cr—C—N bond angles are nearly linear and range from 174.2 (4) to 179.5 (5)°, indicative of directional bonding involving the π orbitals of the metal centre. The Cr—C bond distances are in the range 2.061 (4)–2.088 (4) Å, consistent with the corresponding literature values (Combs *et al.*, 2000; Kou, Gao & Jin, 2001; Kou, Gao, Sun & Zhang, 2001).

The coordinated and uncoordinated water molecules are hydrogen bonded to the non-bridging cyanide N atom and to water molecules to produce a hydrogen-bonded three-dimensional network; details are available in Table 2.

Experimental

Complex (I) was obtained as yellow crystals by the reaction between an aqueous solution (10 ml) of $K_3[Cr(CN)_6]$ (0.2 mmol), 2-pyrrolidone (0.4 mmol) and an aqueous solution (10 ml) of $[Dy(H_2O)_6]Cl_3$ (0.2 mmol) at room tempetature.

Crystal data

$[CrDy(C_4H_7NO)_4(CN)_6\text{-}(H_2O)_3]\cdot 2H_2O$	$Z = 2$
$M_r = 801.12$	$D_x = 1.612$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.1442\ (18)$ Å	Cell parameters from 5798
$b = 12.448\ (3)$ Å	reflections
$c = 14.518\ (3)$ Å	$\theta = 3.5$–$25.0°$
$\alpha = 90.19\ (3)°$	$\mu = 2.64$ mm^{-1}
$\beta = 92.40\ (3)°$	$T = 293\ (2)$ K
$\gamma = 91.10\ (3)°$	Platelet, yellow
$V = 1650.8\ (6)$ Å^3	$0.20 \times 0.10 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	5798 independent reflections
	5457 reflections with $I > 2\sigma(I)$
CCD scans	$R_{int} = 0.046$
Absorption correction: empirical (Blessing, 1995, 1997)	$\theta_{max} = 25.0°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.625$, $T_{max} = 0.812$	$k = -14 \rightarrow 14$
9078 measured reflections	$l = 0 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 3.8796P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.001$
5798 reflections	$\Delta\rho_{max} = 2.25$ e Å^{-3}
389 parameters	$\Delta\rho_{min} = -0.95$ e Å^{-3}
H-atom parameters constrained	

The coordinates of the water H atoms were found from difference Fourier maps and were normalized to have O—H distances of 0.88 Å.

Table 1
Selected geometric parameters (Å, °).

Dy—O1	2.326 (3)	Dy—N1	2.458 (4)
Dy—O3	2.337 (3)	Cr—C3	2.061 (4)
Dy—O4	2.354 (3)	Cr—C5	2.064 (4)
Dy—O2	2.373 (3)	Cr—C4	2.066 (4)
Dy—O7	2.374 (3)	Cr—C2	2.081 (4)
Dy—O6	2.383 (3)	Cr—C1	2.088 (4)
Dy—O5	2.394 (3)	Cr—C6	2.088 (4)
O1—Dy—O3	136.65 (12)	O7—Dy—O6	67.39 (10)
O1—Dy—O4	88.05 (14)	O1—Dy—O5	68.44 (11)
O3—Dy—O4	77.80 (14)	O3—Dy—O5	69.05 (11)
O1—Dy—O2	76.31 (11)	O4—Dy—O5	81.61 (12)
O3—Dy—O2	135.47 (12)	O2—Dy—O5	137.63 (11)
O4—Dy—O2	74.29 (11)	O7—Dy—O5	123.17 (12)
O1—Dy—O7	79.61 (13)	O6—Dy—O5	76.14 (11)
O3—Dy—O7	132.63 (13)	O1—Dy—N1	149.59 (12)
O4—Dy—O7	144.12 (11)	O3—Dy—N1	72.28 (12)
O2—Dy—O7	70.10 (10)	O4—Dy—N1	90.87 (13)
O1—Dy—O6	103.88 (13)	O2—Dy—N1	74.17 (12)
O3—Dy—O6	73.53 (13)	O7—Dy—N1	83.68 (13)
O4—Dy—O6	148.46 (11)	O6—Dy—N1	92.71 (13)
O2—Dy—O6	136.60 (10)	O5—Dy—N1	141.33 (11)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N7—H7$\cdots$O2	0.86	2.46	3.075 (6)	129
N7—H7$\cdots$N5^{i}	0.86	2.46	3.183 (7)	142
N8—H8$\cdots$O4	0.86	2.44	3.028 (6)	126
N9—H9$\cdots$N2^{ii}	0.86	2.51	3.290 (7)	152
N10—H10$\cdots$O5	0.86	2.38	3.096 (6)	141
N10—H10$\cdots$O9^{iii}	0.86	2.55	3.147 (6)	127
O5—H51$\cdots$O8	0.88	1.85	2.724 (4)	170
O5—H52$\cdots$O9	0.88	1.88	2.754 (5)	169
O6—H61$\cdots$N6^{iv}	0.88	2.01	2.861 (5)	162
O6—H62$\cdots$N2^{ii}	0.88	1.91	2.792 (5)	178
O7—H71$\cdots$N6^{iv}	0.88	2.07	2.890 (5)	154
O7—H72$\cdots$N5^{i}	0.88	1.96	2.762 (5)	152
O8—H81$\cdots$N3^{v}	0.88	1.96	2.792 (6)	157
O8—H82$\cdots$N4^{vi}	0.88	2.02	2.855 (6)	159
O9—H91$\cdots$N2^{ii}	0.88	2.47	3.294 (6)	156
O9—H92$\cdots$O8^{iii}	0.88	2.12	2.945 (5)	155

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, -y, -z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 + x, y, z$; (v) $x, 1 + y, z$; (vi) $1 + x, 1 + y, z$.

H atoms bound to C and N atoms were also visible in difference maps and were placed using the *HFIX* commands in *SHELXL*97 (Sheldrick, 1997). All H atoms were allowed for as riding atoms (C—H = 0.97 Å and N—H = 0.86 Å). Residual peaks in the final Fourier map were adjacent (1.12 Å) to the Dy atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

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