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A cyanide-bridged bimetallic complex, $[CrPr(CN)_6(C_3H_7NO)_4(H_2O)_3]\cdot H_2O$

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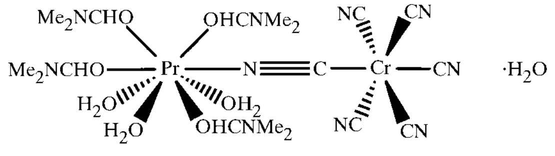
The crystal structure of the bimetallic cyanide-bridged title complex, triaqua-$1\kappa^3O$-μ-cyano-$1{:}2\kappa^2N{:}C$-pentacyano-$2\kappa^5C$-tetrakis(*N*,*N*-dimethylformamide)-$1\kappa^4O$-chromium(III)praseodymium(III) monohydrate, was obtained by single-crystal X-ray diffraction. The central praseodymium(III) ion is eight-coordinate, arranged in a square antiprism, while the chromium(III) ion is six-coordinate, oriented octahedrally. Molecules in the crystal lattice are held together by a network of hydrogen bonds.

Comment

Cyanometallate ions, $[M(CN)_x]^{n-}$, have been shown to act as building blocks for many cyanide-bridged rare earth/transition metal bimetallic assemblies. These complexes have proven useful in homogeneous and heterogeneous catalytic applications due to their electropositive nature, the retracted 4*f* orbitals, and the lability of ligands coordinated to the central lanthanide ion (Huskins *et al.*, 1995). Recently, a dinuclear cyano-bridged complex based on hexacyanoferrate and samarium nitrate was crystallographically studied (Kou *et al.*, 1998). The authors demonstrated that the compound $[(dmf)_4(H_2O)_4SmFe(CN)_6]\cdot H_2O$ [dmf is dimethylformamide (C_3H_7NO)] contained a nine-coordinate trivalent samarium ion in a distorted tricapped trigonal-prism geometry. Attempts to reproduce these synthetic results with chromium(III) hexacyanide and praseodymium(III) nitrate yielded crystals with the stoichiometry $[CrPr(CN)_6(C_3H_7NO)_4(H_2O)_3]\cdot H_2O$, (I).



(I)

Fig. 1 is a representation of the molecular structure of the title compound. The molecular units within the crystal lattice are separated by normal van der Waals contact distances. The Pr^{3+} ions exhibit a slightly distorted square-antiprism coordination geometry. The top face of the prism, comprised of atoms O71, O51, O21 and O61, is essentially planarity, with a mean deviation of 0.074 Å, while the bottom face, comprised of atoms N6, O31, O41 and O11, is slightly distorted from planarity, with a mean deviation of 0.220 Å. The dihedral angle between the two faces is 3.2°.

Selected geometric parameters for (I) are presented in Table 1. The mean $Pr-O_{dmf}$, $Pr-O_{H_2O}$ and $Pr-N$ bond lengths are 2.436 (15), 2.469 (15) and 2.569 (3) Å, respectively. When considering the Pr—O bond distances of the coordinated dmf ligands, it is observed that the Pr—O11 and Pr—O31 lengths are somewhat shorter than the Pr—O21 and Pr—O41 lengths. Also, the corresponding C—O—Pr bond angles described by the same sets of O atoms are significantly larger for the dmf ligands of O11 and O31 than those described by O21 and O41. This may be attributable to the fact that both dmf ligands corresponding to O11 and O31 are adjacent to the hexacyanochromate moiety, increasing the steric hindrance at those coordination sites. Other investigations on analogous compounds have shown similar results (Kou *et al.*, 1998; Mullica *et al.*, 2000). The geometry about the central Cr^{3+} ion is approximately octahedral, with C—Cr—C bond angles in the range 88.07 (13)–92.06 (13)°. The Cr—C bond lengths range from 2.062 (3) to 2.074 (4) Å [mean 2.068 (4) Å] and are normal when compared to the sum of the atomic radii for Cr and C. The overall mean C≡N bond length of 1.146 (2) Å is

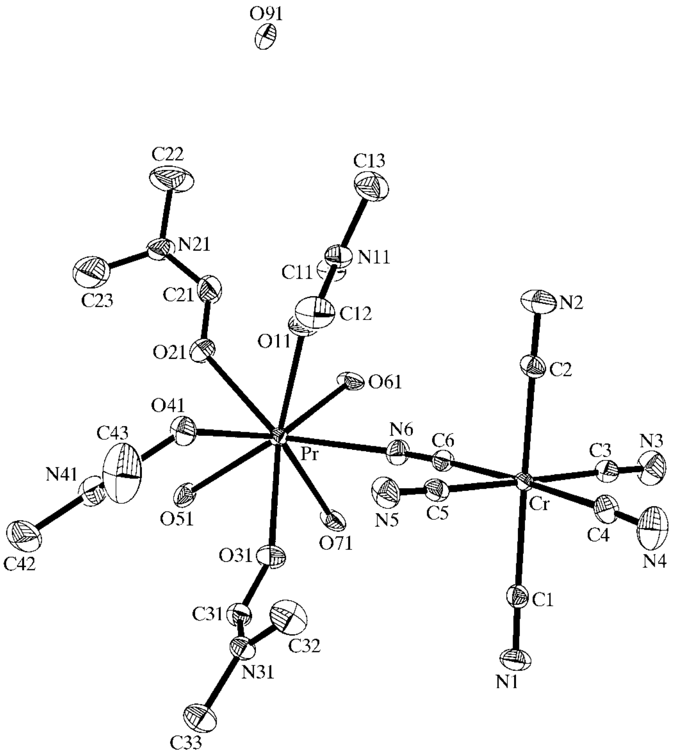


Figure 1
Displacement ellipsoid plot (40% probability) of (I) with the atom labels. H atoms have been omitted for clarity.

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also in accord with the sum of the triple bond radii of C and N atoms (0.603 and 0.55 Å, respectively) found in the work of Pauling (1960). The Cr—C—N bond angles are almost linear and range from 176.7 (5) to 179.7 (4)° for (I), indicative of strong directional bonding as the π orbitals of the cyano ligands interact with the d orbitals of the metal center. However, the isocyanide linkage to the central praseodymium(III) ion deviates significantly from linearity. The Pr—N—C bond angle for (I) is 164.1 (4)°. This phenomenon has been shown to occur in similar compounds containing Ln—NC—*R* linkages. Darensbourg (1985) has proposed that the angular position of the metal cation may facilitate interaction with the lone pairs or π orbitals of the ligand. However, it may simply be that the change in energy by bending the ligands is insignificant, thus allowing steric factors to promote the deviation from linearity in the Pr—NC—Cr linkages.

Hydrogen bonding is paramount in the intermolecular network in the crystal lattice of this complex. According to the work of Hamilton & Ibers (1968), hydrogen bonding of the O—H···N and O—H···O types may be present when O···N and O···O contact distances are within 3.2 Å. Such is the case in the crystal lattice of (I) where the free water of hydration, O91, along with the coordinated water molecules and the nitrogen ends of the cyano ligands are involved in a hydrogen-bonding network. Specific intermolecular interactions are included in Table 2. An IR spectroscopic study of (I) supports the X-ray evidence of varying degrees of hydrogen bonding with broad peaks in the 3100 to 3500 cm^{-1} region.

Interest in lanthanide cyanide-bridged complexes will continue due to their possible ability to function as models for evaluating molecule–membrane interactions and molecular transport in permselective membranes. Both selectivity and permeation rates of the species of interest can be strongly influenced by the molecular structure of the exchange host. Furthermore, studies have shown that compounds containing both lanthanide and transition metals may serve as bimetallic catalysts or as precursors to bimetallic particles on oxide surfaces (White *et al.*, 1994; Deng & Shore, 1991). Of course, compounds containing direct lanthanide–transition metal bonds would be ideal for these purposes. Unfortunately, very few of these materials have been characterized as their synthesis has proven quite challenging. Nevertheless, the development of new materials with such possibilities is always of interest to this research laboratory.

Experimental

The title complex was prepared by the addition of a $Pr(NO_3)_3$ hexahydrate (0.44 g, 1.0 mmol) solution in *N*,*N*-dimethylformamide (dmf) to an equivalent of anhydrous $K_3Cr(CN)_6$ (0.32 g, 1.0 mmol) dissolved in a minimal amount of distilled deionized water. The Pr^{3+}/dmf solution was layered onto the separately prepared chromium(III) hexacyanide solution. Light-green crystals of (I) large enough for single-crystal X-ray analysis were obtained after 24 h. IR spectroscopy (KBr disc, Mattson–Cygnus 100 FT–IR spectrometer): ν(OH)/hydrogen bonding 3390 (*br*), 3306 (*br*), 3094 (*br*); ν(CN) 2148, 2136; ν(CO) 1670, 1650; δ(HCO) 1381; δ(NCO) 671 cm^{-1}.

Crystal data

$[CrPr(CN)_6(C_3H_7NO)_4(H_2O)_3]\cdot H_2O$
M_r = 713.48
Monoclinic, $P2_1/n$
a = 17.940 (3) Å
b = 8.9381 (8) Å
c = 19.8691 (16) Å
β = 96.121 (10)°
V = 3167.9 (6) Å^3
Z = 4
D_x = 1.496 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 20–24°
μ = 1.915 mm^{-1}
T = 186 (2) K
Block, light green
0.85 × 0.54 × 0.46 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–5/3θ scans
Absorption correction: numerical (*SHELXTL*/*PC*; Sheldrick, 1995)
$T_{\min}$ = 0.292, $T_{\max}$ = 0.474
5760 measured reflections
5538 independent reflections
5024 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\max}$ = 25°
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 10$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity decay: 10.49%

Table 1
Selected geometric parameters (Å, °).

Pr—O11	2.413 (2)	Pr—N6	2.569 (3)
Pr—O31	2.435 (2)	Cr—C2	2.062 (3)
Pr—O41	2.445 (2)	Cr—C4	2.065 (4)
Pr—O21	2.453 (2)	Cr—C1	2.069 (3)
Pr—O61	2.457 (2)	Cr—C3	2.069 (4)
Pr—O51	2.461 (2)	Cr—C6	2.070 (3)
Pr—O71	2.490 (3)	Cr—C5	2.074 (4)
O11—Pr—O31	127.51 (10)	O51—Pr—O71	73.18 (9)
O11—Pr—O41	77.34 (9)	O11—Pr—N6	72.46 (9)
O31—Pr—O41	73.00 (9)	O31—Pr—N6	75.36 (9)
O11—Pr—O21	73.82 (9)	O41—Pr—N6	105.87 (10)
O31—Pr—O21	139.19 (9)	O21—Pr—N6	143.11 (9)
O41—Pr—O21	80.65 (10)	O61—Pr—N6	83.32 (10)
O11—Pr—O61	79.20 (9)	O51—Pr—N6	146.03 (9)
O31—Pr—O61	136.11 (9)	O71—Pr—N6	82.19 (10)
O41—Pr—O61	150.66 (9)	N1—C1—Cr	178.5 (3)
O21—Pr—O61	76.06 (9)	N2—C2—Cr	178.9 (3)
O11—Pr—O51	140.44 (9)	N3—C3—Cr	177.8 (3)
O31—Pr—O51	75.01 (9)	N4—C4—Cr	177.0 (3)
O41—Pr—O51	80.79 (9)	N5—C5—Cr	177.8 (3)
O21—Pr—O51	70.36 (9)	N6—C6—Cr	176.1 (3)
O61—Pr—O51	107.35 (9)	C6—N6—Pr	163.5 (3)
O11—Pr—O71	139.97 (9)	C11—O11—Pr	167.4 (3)
O31—Pr—O71	72.05 (9)	C21—O21—Pr	133.1 (3)
O41—Pr—O71	140.63 (8)	C31—O31—Pr	155.0 (2)
O21—Pr—O71	116.11 (10)	C41—O41—Pr	128.7 (2)
O61—Pr—O71	67.30 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O51—H51A···N1$^{\rm i}$	0.83 (4)	2.03 (3)	2.849 (4)	169 (4)
O51—H51B···O91$^{\rm ii}$	0.83 (4)	1.81 (3)	2.641 (3)	174 (4)
O61—H61A···N2$^{\rm iii}$	0.84 (3)	1.88 (3)	2.711 (4)	173 (4)
O61—H61B···N5$^{\rm iv}$	0.83 (4)	2.12 (3)	2.908 (4)	159 (4)
O71—H71A···N5$^{\rm iv}$	0.83 (3)	1.95 (3)	2.785 (4)	174 (3)
O71—H71B···N1$^{\rm i}$	0.83 (4)	2.03 (3)	2.828 (4)	161 (5)
O91—H91A···N4$^{\rm iii}$	0.84 (3)	1.97 (3)	2.807 (4)	170 (4)
O91—H91B···N3$^{\rm v}$	0.83 (3)	2.04 (3)	2.873 (4)	177 (4)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 6.8116P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$(\Delta/\sigma)_{\max} = 0.002$
$wR(F^2) = 0.071$	$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$S = 1.097$	$\Delta\rho_{\min} = -0.90$ e Å^{-3}
5538 reflections	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
376 parameters	Extinction coefficient: 0.00086 (12)
H atoms treated by a mixture of independent and constrained refinement	

All H atoms, except those on the various water molecules, were included in calculated positions and allowed to ride on their parent carbon or O atoms with fixed isotropic displacement parameters ($U_{\rm iso} = 1.2U_{\rm iso}$ of the parent atom, except for methyl H atoms where $U_{\rm iso} = 1.5U_{\rm iso}$). The water H atoms were located in Fourier syntheses. The positional parameters of these H atoms were allowed to refine with fixed isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm iso}({\rm O})$].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1006). Services for accessing these data are described at the back of the journal.

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