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Tetraaqua-1κ^4O-bis(ε-caprolactam-1κO)-μ-cyano-1:2κ^2N:C-pentacyano-2κ^5C-iron(III)yttrium(III), a novel cyano-bridged dinuclear complex

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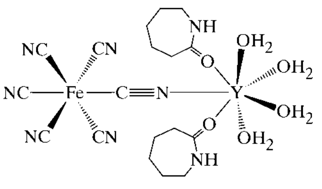
Using caprolactam as a ligand, the novel title cyano-bridged yttrium(III)–ferricyanide complex, $[\mathrm{Y(caprolactam)_2(H_2O)_4Fe(CN)_6}]$ or $[\mathrm{FeY(CN)_6(C_6H_{11}NO)_2(H_2O)_4}]$, has been synthesized and structurally characterized. The Y atom is seven-coordinate and has approximately pentagonal–bipyramidal stereochemistry, with water molecules occupying apical positions. Of the five ligands in equatorial positions, one is the *N*-bound bridging cyano group, and flanking this are two *O*-bound caprolactam moieties, which are markedly inclined towards the bridged ferricyanide moiety such that they partially envelop it. Water molecules occupy the remaining two equatorial positions. The Y—N—C—Fe—C—N sequence of atoms lies on a crystallographic twofold axis and is therefore perfectly linear, which has not been observed previously in cyano-bridged bimetallic complexes.

Comment

Cyano-bridged Prussian Blue complexes have been widely studied in the past. Recently, a growing trend in this field has been to prepare lanthanide–transition-metal complexes, because of their fascinating applications as catalysts (Amer & Alper, 1989) and semi-permeable solid membranes to desalinate sea water (Mullica & Sappenfield, 1991), as well as as precursors of electroceramic materials (Sadaoka *et al.*, 1996), and chemical sensor materials and oxide fuel cells (Minh, 1993). The most attractive property of lanthanide–transition-metal complexes is their magnetism. A series of cyano-bridged three-dimensional lanthanide hexacyanometallates, $[\mathrm{Ln}M(\mathrm{CN})_6]\cdot n\mathrm{H_2O}$ (M is $\mathrm{Fe^{III}}$ or $\mathrm{Cr^{III}}$, n = 4 or 5), were synthesized and the ferrimagnetic ordering observed in 1976 (Hulliger & Landolt, 1976). Very recently, many analogous Prussian Blue 4*f*–3*d* complexes with interesting zero- and three-dimensional structures have been synthesized by incorporating betaine (Yan *et al.*, 2001), 2,2′-bipyrimidine (Ma *et al.*, 2001), 2,2′-dipyridyl *N*,*N*′-dioxide (Gao *et al.*, 1999), dimethylformamide (Kou *et al.*, 1998; Kou, Gao & Jin, 2001; Kou, Gao, Sun & Zhang, 2001; Combs *et al.*, 2000; Figuerola *et al.*, 2001), dimethyl sulfoxide (Yang *et al.*, 2001), urea (Kou, Gao, Li *et al.*, 2002) and pyrrolidone (Kou, Gao & Wang, 2002; Sun *et al.*, 2002) as organic ligands.

Caprolactam (capro) has been shown to act as a useful ligand in the construction of 4*f*–3*d* complexes, for example, one-dimensional $[\mathrm{Gd(capro)_2(H_2O)_4Cr(CN)_6}]\cdot\mathrm{H_2O}$ (Kou, Gao, Li *et al.*, 2002). Bearing in mind that the introduction of larger numbers of ligands always leads to lower-dimensional complexes, we attempted to prepare a Y–capro–Fe complex with a Y:capro molar ratio of 1:4. Unexpectedly, however, we obtained the title cyano-bridged bimetallic complex, (I).



(I)

As shown in Fig. 1, the Y atom in (I) is seven-coordinate and has approximately pentagonal–bipyramidal stereochemistry, with water molecules O3 and O3$^{\rm i}$ [symmetry code: (i) $-x$, y, $\frac{1}{2} - z$] occupying apical positions. Of the five ligands in equatorial positions, one is the *N*-bound bridging cyano group, and flanking this are two *O*-bound caprolactam moieties,

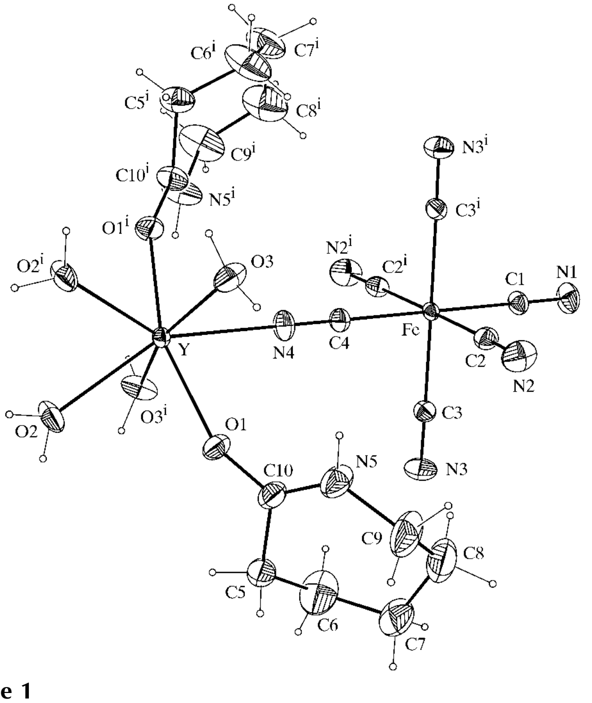


Figure 1
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Only the major component of the disordered atom C5 is shown. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

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which are markedly inclined towards the bridged ferricyanide moiety such that they partially envelop it. Water molecules occupy the remaining two equatorial positions. The two monodentate caprolactam molecules are in *cis* positions, with an O1—Y—O1^i angle of 159.24 (10)°. The Y—N4—C4—Fe—C1—N1 sequence of atoms lies on a crystallographic twofold axis. To our knowledge, this perfectly linear cyano-bridging linkage has not been observed previously in other cyano-bridged complexes.

The Y—O$_{water}$ bond lengths (Y—O2 and Y—O3) are a little longer than the Y—O$_{capro}$ bond length (Y—O1; Table 1). The Y—N4 bond length is a little shorter than the Gd—N bonds in [Gd(capro)$_2$(H$_2$O)$_4$Cr(CN)$_6$]·H$_2$O (2.505 and 2.501 Å; Kou, Gao, Li *et al.*, 2002), which may be due to the difference in the radii of the two lanthanide ions.

The geometry of the [Fe(CN)$_6$]$^{3-}$ ion in (I) is approximately octahedral, with Fe—C bond distances in the range 1.930 (3)–1.937 (3) Å and C—Fe—C angles in the range 89.09 (8)–90.91 (8)°. The average C≡N bond length of 1.143 Å is in accord with the sum of the triple-bond radii of C and N atoms (0.603 and 0.55 Å, respectively; Pauling, 1960). The Fe—C—N angles are almost linear and range from 178.1 (3) to 180°.

Experimental

Since K$_3$[Fe(CN)$_6$] has a tendency to decompose on heating and under irradiation, the synthesis of (I) was performed at room temperature and the crystallization was carried out in the dark. A solution of K$_3$[Fe(CN)$_6$] (65.8 mg, 0.2 mmol) in water (5 ml) was added to an aqueous solution (5 ml) of YCl$_3$·6H$_2$O (60.7 mg, 0.2 mmol) and caprolactam (90.4 mg, 0.8 mmol). The mixture was filtered and slowly evaporated, producing yellow single crystals of (I) (yield 30%).

Crystal data

[FeY(CN)$_6$(C$_6$H$_{11}$NO)$_2$(H$_2$O)$_4$]
M_r = 599.26
Monoclinic, $C2/c$
a = 14.006 (3) Å
b = 12.951 (3) Å
c = 15.011 (3) Å
β = 104.15 (3)°
V = 2640.3 (10) Å^3
Z = 4

D_x = 1.508 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4518 reflections
θ = 2.4–32.0°
μ = 2.78 mm^{-1}
T = 293 (2) K
Block, yellow
0.30 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.445, T_{max} = 0.606
12 364 measured reflections

4853 independent reflections
3691 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 33.5°
$h = -19 \rightarrow 20$
$k = -16 \rightarrow 19$
$l = -22 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.087
S = 1.06
4853 reflections
161 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 5.7178P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Y—O1	2.211 (2)	Fe—C3	1.936 (2)
Y—O2	2.3359 (19)	Fe—C4	1.930 (3)
Y—O3	2.321 (2)	N1—C1	1.146 (4)
Y—N4	2.401 (3)	N2—C2	1.145 (4)
Fe—C1	1.933 (3)	N3—C3	1.143 (3)
Fe—C2	1.937 (3)	N4—C4	1.140 (5)
O1^i—Y—O1	159.24 (10)	O3—Y—N4	80.00 (5)
O1—Y—O2	79.43 (8)	C1—Fe—C2	90.91 (8)
O1—Y—O3	84.89 (8)	C1—Fe—C3	90.24 (7)
O3—Y—O2	124.84 (8)	C3—Fe—C2	89.43 (11)
O1—Y—O2^i	118.71 (8)	C4—Fe—C2	89.09 (8)
O1—Y—O3^i	91.52 (8)	C4—Fe—C3	89.76 (7)
O3—Y—O2^i	73.44 (8)	C2^i—Fe—C2	178.17 (16)
O2^i—Y—O2	69.09 (10)	C3^i—Fe—C3	179.52 (14)
O3^i—Y—O3	159.99 (11)	C10—O1—Y	153.9 (2)
O1—Y—N4	79.62 (5)	N2—C2—Fe	178.1 (3)
O2—Y—N4	145.46 (5)	N3—C3—Fe	179.2 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H21···N3^i	0.85	2.07	2.823 (3)	148
O2—H20···N1^{ii}	0.85	2.01	2.809 (3)	157
O3—H30···N3^{iii}	0.85	2.03	2.861 (3)	167
O3—H31···N2^{iv}	0.85	1.90	2.739 (3)	168
N5—H5A···N2^{iv}	0.86	2.36	3.098 (4)	144

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

The coordinates of the H atoms of the water molecules were found from difference Fourier maps and were normalized to have an O—H distance of 0.85 Å. H atoms bound to C and N atoms were also visible in difference maps, and were placed using the *HFIX* command in *SHELXL*97 (Sheldrick, 1997) and refined as riding atoms, with C—H distances of 0.96–0.97 Å and N—H distances of 0.86 Å. During the refinement, there was a high peak (2.0 e Å^{-3}) in the vicinity of atom C5 (1.2 Å), indicating the presence of a degree of disorder about this C atom. A treatment for disorder was applied and the refinement gave occupancies for C5 and C5′ of 0.82 and 0.18, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1385). Services for accessing these data are described at the back of the journal.

References

Amer, I. & Alper, H. (1989). *J. Am. Chem. Soc.* **111**, 927–930.
Bruker (2000). *SMART* and *SAINT* (Versions 5.6), and *SADABS* (Version 2.01). Bruker AXS Inc., Madison, Wisconsin, USA.
Combs, R. A., Farmer, J. M. & Kautz, J. A. (2000). *Acta Cryst.* C**56**, 1420–1422.

Figuerola, A., Diaz, C., ElFallah, M. S., Ribas, J., Maestro, M. & Mahia, J. E. (2001). *Chem. Commun.* pp. 1204–1205.
Gao, S., Ma, B. Q., Wang, Z. M., Yi, T., Liao, C. S., Yan, C. H. & Xu, G. G. (1999). *Mol. Cryst. Liq. Cryst.* **335**, 201–210.
Hulliger, F. & Landolt, M. (1976). *J. Solid State Chem.* **18**, 283–291.
Kou, H. Z., Gao, S. & Jin, X. (2001). *Inorg. Chem.* **40**, 6295–6300.
Kou, H. Z., Gao, S., Li, C. H., Liao, D. Z., Zhou, B. C., Wang, R. J. & Li, Y. (2002). *Inorg. Chem.* In the press.
Kou, H. Z., Gao, S., Sun, B. W. & Zhang, J. (2001). *Chem. Mater.* **13**, 1431–1433.
Kou, H.-Z., Gao, S. & Wang, R.-J. (2002). *Acta Cryst.* C**58**, m325–m326.
Kou, H. Z., Yang, G. M., Liao, D. Z., Cheng, P., Jiang, Z. H., Yan, S. P., Huang, X. Y. & Wang, G. L. (1998). *J. Chem. Crystallogr.* **28**, 303–307.
Ma, B. Q., Gao, S., Su, G. & Xu, G. X. (2001). *Angew. Chem. Int. Ed.* **20**, 434–437.
Minh, N. Q. (1993). *J. Am. Ceram. Soc.* **76**, 563–588.
Mullica, D. F. & Sappenfield, E. L. (1991). *Acta Cryst.* C**47**, 2433–2435.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.
Sadaoka, Y., Traversa, E. & Sakamoto, M. (1996). *J. Mater. Chem.* **6**, 1355–1360.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Verson of 2002. University of Utrecht, The Netherlands.
Sun, X. R., Chen, Z. D., Yan, F., Gao, S., Cheung, K. K., Che, C. M. & Zhang, X. X. (2002). *J. Cluster Sci.* **13**, 103–117.
Yan, B., Wang, H. D. & Chen, Z. D. (2001). *Polyhedron*, **20**, 591–591.
Yang, C., Guo, G. C., Ma, H. W., Liu, J. C., Zhang, X., Zheng, F. K., Lin, S. H., Zhou, G. W., Mao, J. G. & Huang, J. S. (2001). *Chin. J. Struct. Chem.* **20**, 229–232.