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Aqua(hexacyanoferrato-*N*)bis(μ -glycine)-glycinecerium(III) Monohydrate

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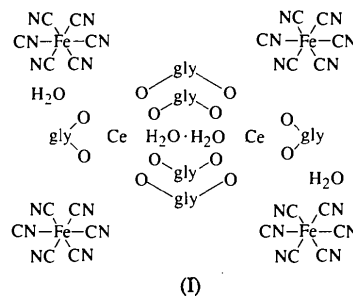
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Abstract

The structure of the title compound, $[\text{Ce}\{\text{Fe}(\text{CN})_6\}-(\text{C}_2\text{H}_5\text{NO}_2)_3(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, consists of FeC_6 octahedra linked to an eight-coordinate cerium ion *via* two cyanide bridging $\text{Ce}-\text{N}-\text{C}-\text{Fe}$ groups. The rest of the coordination polyhedron of the cerium is formed by six O atoms: one from a molecule of water and five from glycine molecules. The three-dimensional framework is formed through $\text{N}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen-bonding interactions. Two glycine molecules form bifurcated hydrogen bonds. An additional uncoordinated molecule of water is within hydrogen-bonding distance of two glycine molecules.

Comment

In a previous paper, we reported the synthesis and the characterization, by X-ray powder diffraction, thermal analysis and Mössbauer and IR spectroscopy, of the hexacyanocobaltate(III) and the hexacyanoferrate(III) of lanthanum and glycine (Fernández-Bertrán, Reguera, Dago & López, 1996). We found that glycine takes the neutral zwitterion form. As a continuation of our studies of the metal–ligand bond interactions in this type of complex, the crystal structure of the isotopic cerium analogue, (I), was determined.



The low spin Fe^{3+} ion is octahedrally coordinated to six cyano groups. The average $\text{Fe}-\text{C}$ and $\text{C}-\text{N}$ bond distances are 1.941 (3) and 1.143 (4) Å, respectively, which compare well with literature values (Mullica, Herbert, Sappenfield & David, 1988). The Ce^{3+} ion is eight-coordinate. This is fairly common in molecular complexes of the lanthanide series (Hulliger, Landolt & Vetsch, 1976). Only two cyano groups are coordinated to cerium ($\text{Ce}-\text{N}1$ and $\text{Ce}-\text{N}2$), which is in accordance with IR and Mössbauer results (Fernández-Bertrán *et al.*, 1996), with an average $\text{Ce}-\text{N}$ bond length of 2.623 (3) Å. The rest of the coordination polyhedron is formed by six O atoms, one from water (O7) and five from glycine moieties. The average $\text{Ce}-\text{O}$ bond length is 2.502 (2) Å. The structure consists of FeC_6 octahedra linked to cerium *via* two cyanide bridging $\text{Ce}-\text{N}-\text{C}-\text{Fe}$ linkages. The three-dimensional framework is completed through hydrogen-bonding interactions (Table 3). Among these, the most significant are the $\text{N}-\text{H}\cdots\text{N}$ interactions that link glycine NH_3 groups with the N atoms of the cyano groups not bonded to the Ce ion. The uncoordinated O atom of the glycine (O6) forms three hydrogen bonds, of which two are strong (to the water molecule coordinated to the cerium ion, O7—

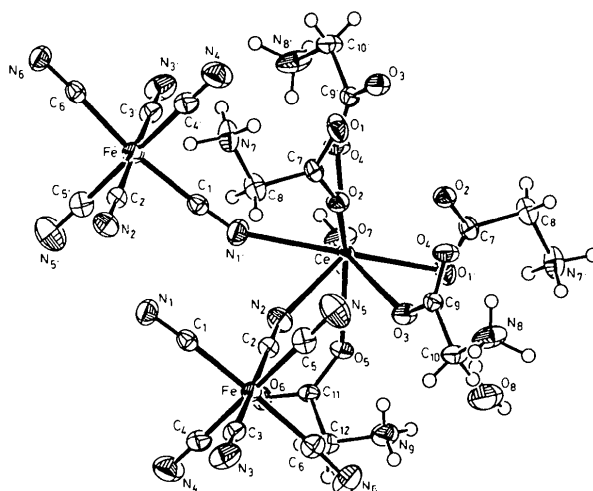


Fig. 1. *EUCLID* (Spek, 1982) plot, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are represented by spheres of arbitrary radii.

H7D···O6, and to a glycine molecule, N7—H7A···O6) and one weaker (N8—H8D···O6 to another glycine molecule). Two molecules of glycine form bifurcated hydrogen bonds: N9—H9A···N6, N9—H9A···O8 and N8—H8D···O4, N8—H8D···O6. An additional uncoordinated molecule of water is within hydrogen-bonding distance of two glycine molecules: N9—H9A···O8, N9—H9C···O8.

Experimental

Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous equimolecular solution of cerium trichloride, potassium ferrocyanide and a fivefold excess of glycine.

Crystal data

[CeFe(CN)₆(C₂H₅NO₂)₃·(H₂O)].H₂O

M_r = 613.33

Triclinic

P $\bar{1}$

a = 10.004 (3) Å

b = 10.168 (2) Å

c = 12.166 (4) Å

α = 75.02 (3)°

β = 88.21 (3)°

γ = 61.36 (3)°

V = 1043.0 (6) Å³

Z = 2

D_x = 1.953 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer

ω -2 θ scans

Absorption correction:

ψ scan (North, Phillips & Mathews, 1968)

*T*_{min} = 0.899, *T*_{max} = 1.000

3843 measured reflections

3656 independent reflections

Refinement

Refinement on *F*²

R [*F*² > 2 σ (*F*²)] = 0.0188

wR(*F*²) = 0.0486

S = 1.083

3656 reflections

356 parameters

All H-atom parameters refined

w = 1/[$\sigma^2(F_o^2) + (0.0224P)^2 + 0.4228P$]

where *P* = (*F*_o² + 2*F*_c²)/3

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 15–18°

μ = 2.910 mm⁻¹

T = 293 (2) K

Prismatic

0.3 × 0.1 × 0.1 mm

Green

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ce	0.20210 (2)	0.34200 (2)	0.45283 (1)	0.01680 (6)
Fe	0.36460 (4)	0.78054 (4)	0.21788 (3)	0.02176 (9)
C1	0.4653 (3)	0.7803 (3)	0.3505 (2)	0.0244 (6)
C2	0.3575 (3)	0.5966 (3)	0.3064 (2)	0.0246 (6)
C3	0.3661 (3)	0.9698 (3)	0.1344 (2)	0.0279 (6)
C4	0.5678 (4)	0.6504 (4)	0.1782 (3)	0.0304 (7)
C5	0.1616 (4)	0.9055 (4)	0.2596 (3)	0.0334 (7)
C6	0.2746 (4)	0.7762 (3)	0.0802 (3)	0.0308 (7)
N1	0.5331 (3)	0.7761 (3)	0.4269 (2)	0.0336 (6)
N2	0.3483 (3)	0.4915 (3)	0.3597 (2)	0.0334 (6)
N3	0.3670 (4)	1.0813 (3)	0.0837 (2)	0.0432 (7)
N4	0.6870 (4)	0.5701 (4)	0.1571 (3)	0.0489 (8)
N5	0.0429 (4)	0.9771 (4)	0.2839 (3)	0.0545 (8)
N6	0.2267 (4)	0.7737 (4)	-0.0030 (3)	0.0508 (8)
O1	-0.0931 (2)	0.4228 (2)	0.4783 (2)	0.0272 (4)
O2	0.0197 (2)	0.2750 (3)	0.3641 (2)	0.0371 (5)
C7	-0.0900 (3)	0.3379 (3)	0.4169 (2)	0.0237 (6)
C8	-0.2241 (4)	0.3100 (4)	0.4116 (3)	0.0346 (7)
N7	-0.2214 (3)	0.2534 (4)	0.3096 (3)	0.0383 (7)
O3	0.0408 (2)	0.5621 (2)	0.2803 (2)	0.0312 (5)
O4	-0.1638 (2)	0.7381 (2)	0.3414 (2)	0.0310 (5)
C9	-0.0785 (3)	0.6908 (3)	0.2677 (2)	0.0225 (6)
C10	-0.1224 (4)	0.8004 (4)	0.1485 (3)	0.0307 (7)
N8	-0.2669 (4)	0.9433 (4)	0.1400 (3)	0.0456 (8)
O5	0.3250 (2)	0.2419 (2)	0.2958 (2)	0.0257 (4)
O6	0.5723 (2)	0.1552 (2)	0.2719 (2)	0.0293 (4)
C11	0.4320 (3)	0.2427 (3)	0.2402 (2)	0.0221 (6)
C12	0.3902 (4)	0.3614 (4)	0.1236 (3)	0.0285 (6)
N9	0.2236 (3)	0.4471 (4)	0.0912 (3)	0.0417 (7)
O7	0.3070 (3)	0.0506 (3)	0.5159 (2)	0.0378 (6)
O8	0.0154 (4)	0.3215 (4)	0.1092 (3)	0.0604 (8)

Table 2. Selected geometric parameters (Å, °)

Ce—O1 ⁱ	2.468 (2)	C3—N3	1.147 (4)
Ce—O2	2.580 (2)	C4—N4	1.145 (4)
Ce—O3	2.518 (2)	C5—N5	1.135 (4)
Ce—O4 ⁱ	2.502 (2)	C6—N6	1.144 (4)
Ce—O5	2.420 (2)	O1—C7	1.269 (3)
Ce—O7	2.523 (2)	O2—C7	1.233 (3)
Ce—N1 ⁱⁱ	2.624 (3)	C7—C8	1.506 (4)
Ce—N2	2.622 (3)	C8—N7	1.490 (4)
Fe—C1	1.928 (3)	O3—C9	1.253 (3)
Fe—C2	1.935 (3)	O4—C9	1.244 (3)
Fe—C3	1.937 (3)	C9—C10	1.507 (4)
Fe—C4	1.951 (3)	C10—N8	1.460 (4)
Fe—C5	1.948 (3)	O5—C11	1.250 (3)
Fe—C6	1.947 (3)	O6—C11	1.254 (3)
C1—N1	1.147 (4)	C11—C12	1.520 (4)
C2—N2	1.141 (4)	C12—N9	1.471 (4)
O5—Ce—O1 ⁱ	142.49 (7)	C1—Fe—C2	89.74 (12)
O5—Ce—O2	74.32 (7)	C1—Fe—C3	88.88 (12)
O5—Ce—O3	77.53 (7)	C1—Fe—C4	87.48 (13)
O5—Ce—O4 ⁱ	143.29 (7)	C1—Fe—C5	92.61 (13)
O5—Ce—O7	72.75 (8)	C1—Fe—C6	176.57 (13)
O5—Ce—N1 ⁱⁱ	91.90 (8)	C1—N1—Ce ⁱⁱ	148.5 (2)
O5—Ce—N2	71.48 (8)	C2—N2—Ce	154.9 (2)

Symmetry codes: (i) -*x*, 1 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*.

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N7—H7A···O6 ⁱ	0.98 (7)	1.82 (7)	2.781 (5)	168 (6)
N7—H7B···N4 ⁱ	0.96 (5)	2.06 (6)	2.973 (5)	158 (5)
N7—H7C···N5 ⁱⁱ	1.07 (4)	1.85 (5)	2.875 (4)	160 (4)
N8—H8C···N3 ⁱ	1.01 (6)	2.54 (5)	3.254 (6)	127 (4)
N8—H8D···O6 ⁱⁱⁱ	0.82 (7)	2.38 (7)	2.848 (4)	118 (6)

N8—H8D···O4	0.82 (7)	2.09 (5)	2.622 (4)	123 (6)
N9—H9A···O8 ^{iv}	0.84 (4)	2.36 (4)	3.034 (4)	138 (4)
N9—H9A···N6	0.84 (4)	2.64 (6)	3.236 (6)	129 (4)
N9—H9B···O3	0.87 (5)	2.20 (5)	3.014 (4)	155 (4)
N9—H9C···O8	0.99 (7)	2.01 (7)	2.897 (7)	147 (5)
O7—H7E···N1 ⁱⁱ	0.79 (5)	2.39 (4)	3.072 (4)	146 (4)
O7—H7D···O6 ^v	0.79 (4)	1.96 (4)	2.735 (3)	165 (4)
O8—H8F···O2	0.73 (7)	2.29 (7)	3.012 (4)	176 (7)

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

The structure was solved by Patterson and Fourier methods. Non-H atoms were refined anisotropically by full-matrix least-squares techniques. All H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *CAD-4-Express Software* (Enraf–Nonius, 1994). Cell refinement: *CRYSDA* in *DIRDIF* (Beurskens *et al.* 1992). Data reduction: *REFLEX* (local program). Program(s) used to solve structure: *DIRDIF*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983). Molecular graphics: *EUCLID* (Spek, 1982). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Arsanilic Acid, a Redetermination

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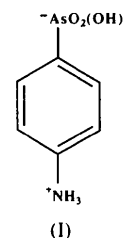
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Abstract

The title compound, *p*-arsanilic acid, C₆H₈AsNO₃, contains an As atom tetrahedrally coordinated to three O atoms and a C atom of the substituted benzene ring. The molecules are linked by an array of hydrogen bonds arising from three separate interactions formed between N and O atoms and one involving two O atoms. The molecule is in the zwitterionic form (*i.e.* *p*-ammoniophenylarsonate).

Comment

Interest in the structure of arsenicals has in part been stimulated by their biomedical applications. For example, some are still used against trypanosomal infection despite their toxicity (Dhubhghaill & Sadler, 1991; Zwegarth & Kaminsky, 1990). Shimada (1961) previously characterized the structure of *p*-arsanilic acid, (I), using Weissenberg and oscillation photography and visual estimation of intensities. The original publication omitted details pertaining to the precision of the structure. For example, no standard deviations are given. Our analysis improves the precision and fully documents the structure. Shimada (1961) concluded from his analysis that the sample is a mono-acid; this proposal is reassessed.



The As—O bond distances indicate one As—O bond of length 1.737 (8) Å and two As=O bonds of length 1.656 (6) and 1.669 (5) Å. As—O bond distances have been assigned in the *ortho*-acid structure by Chatterjee & Gupta (1977); one As=O bond of length 1.64 Å and two As—O single bonds of length 1.73 Å were observed. For comparative purposes, an analysis of bond lengths observed in the compounds stored in the Cambridge Structural Database (Allen *et al.*,