

- Siemens (1996). *SMART. Area Detector Control Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Yang, Y., Liu, Q.-T. & Wu, D.-X. (1993). *Inorg. Chim. Acta*, **208**, 85–89.
- Zimmermann, H., Hegetschweiler, K., Keller, T., Gramlich, V., Schmalte, H. W., Petter, W. & Schneider, W. (1991). *Inorg. Chem.* **30**, 4336–4341.

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Octakis(dimethyl sulfoxide-*O*)-gadolinium(III) Hexacyanoferrate(III)

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Abstract

In $[\text{Gd}(\text{C}_2\text{H}_6\text{OS})_8][\text{Fe}(\text{CN})_6]$, the central atom of the $[\text{Gd}(\text{C}_2\text{H}_6\text{OS})_8]^{3+}$ complex cation occupies a twofold axis, while in the $[\text{Fe}(\text{CN})_6]^{3-}$ anion, it is positioned on a centre of inversion. Gd—O bond lengths vary between 2.374 (5) and 2.417 (5) Å, but the Fe—C distances of 1.943 (8)–1.952 (8) Å are equal, within experimental error.

Comment

It is well known that hexacyanometallates can be successfully used as building blocks for constructing bimetallic assemblies which exhibit spontaneous magnetization. Two types of compounds have been prepared: (i) Prussian analogues, $A_kB(\text{CN})_6$, where *A* and *B* are either two transition metals or rare-earth ions (Verdaguer, 1996; Khan, 1995; Hulliger *et al.*, 1976), and (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ combined with transition metal complexes (Salah el Fallah *et al.*, 1996). In an attempt to prepare compounds of the latter type, a Gd^{III} complex of the Schiff base which is formed through the 2:1 condensation reaction of 2-pyridinecarboxaldehyde and ethylenediamine was combined with the $[\text{Fe}(\text{CN})_6]^{3-}$ ion. It is noteworthy that, in the reaction conditions used, the Schiff base ligand and the water molecules coordinated to the Gd^{III} atom were replaced by dimethyl sulfoxide (DMSO) molecules, and well developed yellow crystals of the compound $[\text{Gd}(\text{DMSO})_8][\text{Fe}(\text{CN})_6]$, (I), were formed after five days. We report here the structure of this last compound, which consists of discrete $[\text{Gd}(\text{DMSO})_8]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions. The Gd^{III} atom occupies a twofold axis, while the Fe^{III} atom is positioned on a centre of inversion.

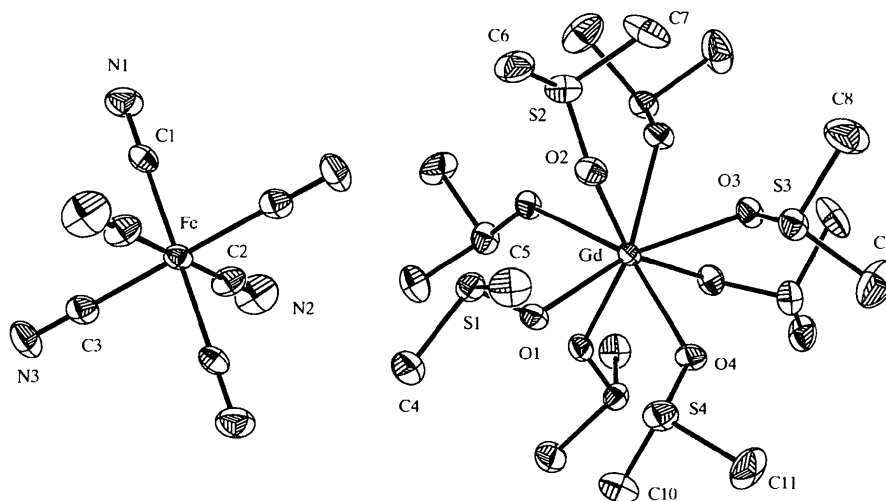
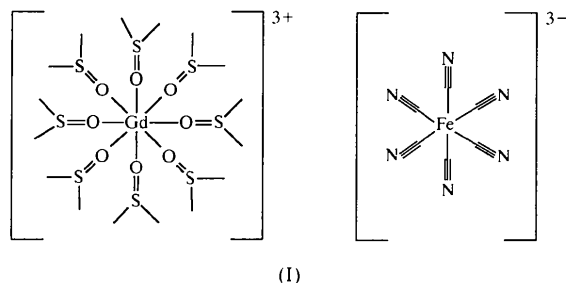


Fig. 1. View of $[\text{Gd}(\text{DMSO})_8][\text{Fe}(\text{CN})_6]$, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The Gd—O bond lengths vary between 2.374 (5) and 2.417 (5) Å. The Gd environment is quite crowded, due to the eight-coordination, and relatively low O—Gd—O angle values have been obtained, the minimum value being 69.0(2)°. In the coordinated DMSO molecules, the S—O distances range from 1.512 (5) to 1.525 (6) Å, and thus, the shortest ones do not deviate significantly from the corresponding distance of 1.495 (4) Å for a non-coordinated DMSO molecule (Kulikova *et al.*, 1989). Crystallographic data for [M(DMSO)₈]ⁿ⁺ complexes are very rare and, as far as we know, only the crystal structures of [ZrCl₄(DMSO)₈].DMSO (Kulikova *et al.*, 1989) and [La(DMSO)₈][Cr(SCN)₆] (Cherkasova, 1994) have been reported. In addition, a deuterated-DMSO (*d*-DMSO) complex, [Zr(*d*-DMSO)₈]Cl₄.2H₂O.*d*-DMSO (Klinga *et al.*, 1998), is known.

The geometry of the [Fe(CN)₆]³⁻ ion is quite normal (Morioka *et al.*, 1985). The coordination sphere of the Fe^{III} ion is very close to a regular octahedron, since the Fe—C distances are equal, within experimental error, and the C—Fe—C angles are close to 90 or 180°, owing to the symmetry.

Experimental

Two aqueous solutions, one containing [Fe(CN)₆]³⁻ ions and the other containing the Gd^{III} complex of the Schiff base from the 2:1 condensation of 2-pyridinecarboxaldehyde and ethylenediamine, were diffused into a U-tube with gelled DMSO at 273 K. Well developed yellow crystals of the title compound formed after five days.

Crystal data

[Gd(C₂H₆OS)₈][Fe(CN)₆]
M_r = 994.24
 Monoclinic
*P*2/*c*
a = 9.920 (2) Å
b = 10.631 (2) Å
c = 19.413 (4) Å
 β = 92.35 (3)°
V = 2045.6 (7) Å³
Z = 2
D_x = 1.614 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 21 reflections
 θ = 5.75–13.03°
 μ = 2.416 mm⁻¹
T = 193 (2) K
 Prismatic
 0.30 × 0.30 × 0.25 mm
 Yellow

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 ψ scan (North *et al.*, 1968)
T_{min} = 0.446, *T_{max}* = 0.547
 3500 measured reflections
 3315 independent reflections

2834 reflections with *I* > 2σ(*I*)
R_{int} = 0.056
 θ_{\max} = 25°
h = 0 → 12
k = 0 → 13
l = -24 → 24
 3 standard reflections every 200 reflections
 intensity decay: <2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.052
wR(*F*²) = 0.121
S = 1.169
 3315 reflections
 218 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 6.92P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 1.718 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.871 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

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_{eq}</i>
Gd	1/2	0.02457 (5)	1/4	0.0187 (2)
Fe	0	1/2	0	0.0211 (4)
S1	0.3668 (2)	0.2340 (2)	0.11973 (10)	0.0267 (5)
S2	0.2459 (2)	-0.1069 (2)	0.13710 (11)	0.0325 (5)
S3	0.7021 (2)	-0.1908 (2)	0.15499 (11)	0.0285 (5)
S4	0.7560 (2)	0.1810 (2)	0.15840 (11)	0.0324 (5)
O1	0.4677 (5)	0.2057 (5)	0.1791 (3)	0.0264 (12)
O2	0.3777 (5)	-0.0367 (5)	0.1478 (3)	0.0282 (12)
O3	0.6191 (5)	-0.1628 (5)	0.2167 (3)	0.0281 (13)
O4	0.7177 (5)	0.0809 (5)	0.2099 (3)	0.0285 (13)
N1	-0.2798 (7)	0.3880 (7)	0.0311 (4)	0.036 (2)
N2	0.0677 (8)	0.4969 (8)	0.1564 (4)	0.049 (2)
N3	-0.1139 (7)	0.7700 (7)	0.0125 (4)	0.037 (2)
C1	-0.1763 (8)	0.4296 (7)	0.0191 (4)	0.024 (2)
C2	0.0424 (8)	0.4986 (8)	0.0986 (4)	0.030 (2)
C3	-0.0705 (8)	0.6698 (8)	0.0076 (4)	0.027 (2)
C4	0.3850 (10)	0.3976 (8)	0.1063 (5)	0.042 (2)
C5	0.4447 (10)	0.1821 (9)	0.0434 (4)	0.039 (2)
C6	0.1932 (9)	-0.0775 (9)	0.0501 (4)	0.039 (2)
C7	0.2904 (11)	-0.2649 (8)	0.1308 (5)	0.048 (3)
C8	0.6705 (11)	-0.3508 (10)	0.1357 (6)	0.058 (3)
C9	0.8711 (9)	-0.2101 (12)	0.1898 (5)	0.056 (3)
C10	0.7797 (10)	0.3210 (8)	0.2078 (5)	0.043 (2)
C11	0.9279 (9)	0.1459 (10)	0.1411 (6)	0.049 (3)

Table 2. Selected geometric parameters (Å, °)

Gd—O2	2.374 (5)	S1—O1	1.525 (6)
Gd—O1	2.381 (5)	S2—O2	1.512 (6)
Gd—O4	2.401 (5)	S3—O3	1.512 (5)
Gd—O3	2.417 (5)	S4—O4	1.519 (5)
Fe—C3	1.943 (8)	N1—C1	1.151 (10)
Fe—C2	1.944 (9)	N2—C2	1.138 (11)
Fe—C1	1.952 (8)	N3—C3	1.155 (10)
C3—Fe—C2	89.8 (3)	S3—O3—Gd	131.5 (3)
C3—Fe—C1	90.8 (3)	S4—O4—Gd	129.9 (3)
C2—Fe—C1	88.2 (3)	N1—C1—Fe	179.3 (7)
S1—O1—Gd	131.7 (3)	N2—C2—Fe	179.5 (8)
S2—O2—Gd	131.3 (3)	N3—C3—Fe	179.1 (7)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1014). Services for accessing these data are described at the back of the journal.

References

- Cherkasova, T. G. (1994). *Zh. Neorg. Khim.* **39**, 1316–1319.
- Hulliger, F., Landolt, M. & Vertch, H. (1976). *J. Solid State Chem.* **18**, 307–312.
- Khan, O. (1995). *Nature*, **378**, 667–668, and references therein.
- Klinga, M., Jany, G., Repo, T. & Leskelä, M. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 317–318.
- Kulikova, N. N., Troyanov, S. I., Nikitin, K. N. & Gerasimova, S. O. (1989). *Zh. Neorg. Khim.* **34**, 2693–2696.
- Molecular Structure Corporation (1993a). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993b). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Morioka, Y., Toriumi, K., Ito, T., Saito, A. & Nakagawa, I. (1985). *J. Phys. Soc. Jpn.* **54**, 2184–2189.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Salah el Fallah, M., Rentschler, E., Caneschi, A., Sessoli, R. & Gatteschi, D. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1947–1949, and references therein.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Verdaguer, M. (1996). *Science*, **272**, 698–699, and references therein.

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Structural Investigation of Nickel(II) Complexes. XIII. μ -[2,3,5,6-Tetra-(2-pyridyl)pyrazine]-bis[bis(acetato)aqua-nickel(II)]-Formaldehyde (1/1)

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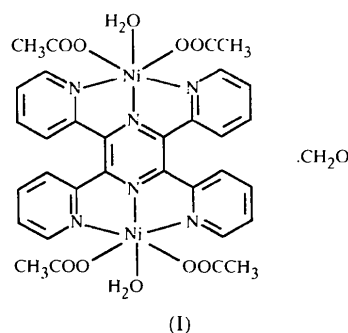
Abstract

In the title compound, $[\text{Ni}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_{24}\text{H}_{16}\text{N}_6)(\text{H}_2\text{O})_2] \cdot \text{CH}_2\text{O}$, the coordination polyhedron of each Ni^{II} centre is a distorted octahedron formed by three N-atom donors from a tetra(2-pyridyl)pyrazine molecule and an aqua O atom in the equatorial positions, and by two O atoms from different acetate anions in the axial positions. The formaldehyde molecule is not coordinated; it

is disordered over two sites related by a crystallographic twofold axis.

Comment

Despite the steric repulsion between its adjacent pyridine rings, the ligand tetra(2-pyridyl)pyrazine (tppz) can act as a bis-tridentate ligand with Cu^{II} (Graf *et al.*, 1993; Valigura *et al.*, 1998), thus forming dinuclear complexes containing two metal atoms bridged by a pyrazine ring. Removal of this steric repulsion was achieved by a twisting deformation of the central pyrazine ring and allowing the Cu^{II} atoms to adopt pentacoordination. Similar deformations of the central pyrazine ring were also found for mononuclear $[\text{Zn}(\text{tppz})\text{Cl}_2]$ (Graf *et al.*, 1993) and $[\text{Cu}(\text{tppz})\text{Cl}_2]$ (Kožišek *et al.*, 1997). We have now extended this work to Ni^{II} complexes and report herein the structure of the title compound, (I).



The crystal structure of the title complex consists of $[\text{Ni}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2(\text{tppz})]$ and CH_2O molecules (Fig. 1) held together by van der Waals interactions and weak intermolecular hydrogen bonds $[\text{O}2 \cdots \text{H}11(-x, 1-y, -z) 2.372 \text{ \AA}]$. The coordination polyhedron of the Ni^{II} atom is a distorted octahedron with nickel-to-donor atom distances within the range 2.001 (4)–2.119 (4) Å. The greatest deviation from ideal octahedral angles is for $\text{N}1-\text{Ni}1-\text{N}3$ $[156.41(15)^\circ]$ and is attributed to the shape of the tppz ligand. The tendency of the Ni^{II} central atom to adopt the octahedral polyhedron seems to be greater than for Zn^{II} , for which pentacoordinate complexes are found. A *catena*-nickel(II) complex containing pyrazine (Travníček *et al.*, 1996) contains octahedral polyhedra with pyrazine N-atom donors in axial positions and $\text{Ni}-\text{N}$ distances of 2.150 (2) Å. On the other hand, the nickel(II) bromide complex with 2,5-dimethylpyrazine (Ayres *et al.*, 1964) exhibits a square-planar configuration with an $\text{Ni}-\text{N}$ distance of 1.85 Å. The anion and/or dianion of 2,3-pyrazinedicarboxylic acid (Mao *et al.*, 1996) gives nickel(II) complexes which are nearly octahedral, with $\text{Ni}-\text{N}$ distances of 2.048 (1) and 2.074 (1) Å, respectively. The title complex exhibits a similar twisting deformation of the central pyrazine ring, characterized by a dihedral angle of 12.8° between the C–N–C planes.