

Fig. 2. Packing view of the crystal. View direction along $-b^*$, a horizontal, c vertical.

The compact crystal packing described above and the tight fit between the Pb atom and tren molecule could be the reason why the title compound is easily separated from the trien solution. On the other hand, isomorphous compounds have not been crystallized from the reaction of trien solution with $PbBr_2$ or PbI_2 , because of expectations of size differences in the anions.

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Acta Cryst. (1988). **C44**, 1530–1533

The Structure of an Intensely Coloured Fe^{II} Complex, Diaquabis(2-nitro-1,3-indandionato)iron(II) Dihydrate

BY OLE SIMONSEN AND HANS TOFTLUND

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

(Received 11 February 1988; accepted 20 April 1988)

Abstract. $[Fe(C_9H_4NO_4)_2(H_2O)_2] \cdot 2H_2O$, $M_r = 508.18$, monoclinic, $P2_1/c$, $a = 8.763(3)$, $b = 15.006(5)$, $c = 15.680(5)$ Å, $\beta = 105.56(2)^\circ$, $V = 1986(3)$ Å³, $Z = 4$, $D_m = 1.72(1)$, $D_x = 1.699$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 8.36$ cm⁻¹, $F(000) = 1040$, $T = 295$ K, $R = 0.040$ for 3579 observed reflections. The Fe^{II} ions are placed on a general position and coordinated to six oxygen atoms in a slightly distorted octahedral configuration. Each 'nitronate' ligand has two different C–O and N–O bond distances. The cause of the dark colour of the title compound is discussed. A Mössbauer spectrum of the title compound has been recorded.

Introduction. During work with 2-nitro-1,3-indandione (Simonsen & Jacobsen, 1977) we became aware of the title coordination compound (*A*), first described by Wanag (1936). The structure of (*A*) was determined as part of a study of nitro compounds and their salts and especially to investigate the 2-nitro-1,3-indandionato ion as a ligand and to look for a structural explanation of the deep purple colour of (*A*). The colour of (*A*) is so characteristic that 2-nitro-1,3-indandionato has been suggested as a reagent for Fe^{II} (Wanag, 1936).

Experimental. The crystals used in the structure determination were prepared by allowing aqueous solutions of $(NH_4)_2Fe^{II}(SO_4)_2$ and 2-nitro-1,3-indandione to diffuse slowly into each other in the horizontal part of an H-shaped tube. D_m by flotation in a mixture of CCl_4 and CH_2BrCl . Crystal $0.36 \times 0.13 \times 0.08$ mm. The crystals are black, with a violet lustre. Thin crystals are red-violet in transmitted light. Diffractometer: Enraf–Nonius CAD-4F, graphite-monochromatized $Mo K\alpha$ radiation, lattice parameters from Guinier–Hägg photographs with $Cu K\alpha_1$ ($\lambda = 1.54051$ Å), 19 reflections with $5.23 < \theta < 16.68^\circ$, Si used as an internal standard. 5750 unique reflections ($h0 \rightarrow 12$, $k0 \rightarrow 21$, $l-21 \rightarrow 20$) with $2.0 < \theta < 30.0^\circ$, 3579 with $I > 2.5\sigma(I)$ used in refinement process together with 'less-than' reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (5034 contributing reflections). $\omega/2\theta$ -scan technique, scan angle $\Delta\omega = (1.00 + 0.35\tan\theta)^\circ$. Standard reflections 354, 327, 361 and $\bar{2}1\bar{6}$ used for orientation control every 100 reflections, 353 used for intensity check every third hour of exposure time, standard intensity variations $< 3.0\%$ of mean value. L_p correction, absorption

ignored. Structure solved with direct methods using *SHELX76* (Sheldrick, 1976); full-matrix least-squares refinement of anisotropic non-H atoms. Positional H parameters from $\Delta\rho$ map. Refinements of $H(x, y, z)$ with $(\sin\theta)/\lambda < 0.40 \text{ \AA}^{-1}$, fixed isotropic H temperature factor $U = 0.038 \text{ \AA}^2$. One of the H atoms which binds to a water oxygen atom [O(83)] could not be located. $\sum w(\Delta|F|)^2$ minimized, final $R = 0.040$, $wR = 0.043$. Average $(w\Delta|F|)^2$ was almost independent of $|F_o|$ by using $w = 1$ when $|F_o| < 60$ else $w = (60/F_o)^2$. $S = 2.49$, $(\Delta/\sigma)_{\max} = 0.66$. Minimum and maximum in final $\Delta\rho$ map: -0.47 and 0.78 e \AA^{-3} . Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs from *SHELX76* (Sheldrick, 1976) and *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The positional and isotropic thermal parameters are given in Table 1.*

Discussion. (A) contains four molecules of water in each formula unit. According to Wanag (1936) two molecules of water are easily lost by heating to about 323 K. This observation is in agreement with the crystal structure in which two molecules of water are ligands to Fe^{II} and the other water molecules have weaker bonding relationships through hydrogen bonds (see Figs. 1 and 2).

The Fe^{II} ions are in a general position and coordinated to six oxygen atoms in a slightly distorted octahedral configuration (Fig. 3). The three diagonal $\text{O}\cdots\text{Fe}^{\text{II}}\cdots\text{O}$ coordination angles are O(1) $\cdots\text{Fe}^{\text{II}}\cdots$ O(11) $179.7(2)$, O(21) $\cdots\text{Fe}^{\text{II}}\cdots$ O(121) $176.6(1)$ and O(81) $\cdots\text{Fe}^{\text{II}}\cdots$ O(82) $172.5(2)^\circ$. The rest of the $\text{O}\cdots\text{Fe}^{\text{II}}\cdots\text{O}$ coordination angles have values between $85.5(1)$ and $96.9(1)^\circ$. The $\text{Fe}^{\text{II}}\cdots\text{O}$ coordination distances (Fig. 1) range from $2.062(3)$ to $2.184(3) \text{ \AA}$, in good agreement with the $\text{Fe}^{\text{II}}\cdots\text{O}$ distances found in some related compounds: aqua(citrato)iron(II) hexa-aquairon(II) dihydrate $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6][\text{Fe}^{\text{II}}\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (Strouse, Layten & Strouse, 1977), $\text{Fe}\cdots\text{O} 2.085(2)$ to $2.178(2) \text{ \AA}$; hexakis(pyridine *N*-oxide)iron(II) perchlorate $[\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5\text{NO})_6][\text{ClO}_4]_2$ (Taylor, 1978), $\text{Fe}\cdots\text{O} 2.112(2) \text{ \AA}$.

A comparison between (A) and (B): 2-nitro-1,3-indandione dihydrate (Table 2) (Selenius & Lundgren, 1980; Simonsen, 1988) reveals shifts in the bond lengths, corresponding to an increased difference between the two $>\text{C}-\text{O}$ and $\text{C}-\text{CNO}_2$ bonds in each

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters of non-H atoms with *e.s.d.*'s in parentheses; O(83) and O(84) are the oxygen in the crystal water

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i, \mathbf{a}_j)$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}} (\text{\AA}^2)$
Fe^{II}	3101.7 (7)	4476.7 (3)	7804.1 (4)	2.66 (4)
O(1)	4535 (3)	3799 (2)	8863 (2)	3.1 (2)
O(3)	3693 (3)	683 (2)	8442 (2)	3.3 (2)
O(11)	1657 (3)	5151 (2)	6742 (2)	2.9 (2)
O(13)	2633 (3)	8259 (2)	7143 (2)	3.2 (2)
O(21)	1895 (3)	3257 (2)	7483 (2)	3.3 (2)
O(22)	1467 (4)	1842 (2)	7337 (2)	3.6 (2)
O(81)	1727 (4)	27 (2)	3600 (2)	4.1 (2)
O(82)	4609 (3)	4141 (2)	6945 (2)	3.2 (2)
O(83)	8532 (4)	10 (2)	3153 (2)	4.1 (2)
O(84)	2708 (5)	4837 (3)	358 (3)	3.3 (4)
O(121)	4417 (3)	5681 (2)	8087 (2)	3.1 (2)
O(122)	4887 (3)	7105 (2)	8213 (2)	3.1 (2)
N(2)	2295 (3)	2460 (2)	7725 (2)	2.5 (2)
N(12)	4016 (3)	6483 (2)	7854 (2)	2.3 (2)
C(1)	4588 (4)	2972 (2)	8949 (2)	2.4 (2)
C(2)	3605 (4)	2303 (2)	8424 (2)	2.3 (2)
C(3)	4174 (4)	1417 (2)	8741 (2)	2.5 (2)
C(4)	6546 (5)	969 (3)	73 (3)	3.2 (3)
C(5)	7787 (5)	1310 (3)	746 (3)	3.5 (3)
C(6)	8043 (5)	2216 (3)	861 (2)	3.2 (3)
C(7)	7048 (5)	2828 (3)	10302 (3)	3.0 (3)
C(11)	1603 (4)	5980 (2)	6692 (2)	2.3 (2)
C(12)	2630 (4)	6646 (2)	7199 (2)	2.2 (2)
C(13)	2066 (4)	7530 (2)	6883 (2)	2.3 (2)
C(14)	9653 (5)	7988 (3)	5582 (3)	3.0 (3)
C(15)	8410 (5)	7657 (3)	4903 (3)	3.4 (3)
C(16)	8159 (4)	6746 (3)	4789 (3)	3.2 (3)
C(17)	9133 (4)	6138 (3)	5342 (2)	2.8 (2)
C(31)	5563 (4)	1580 (2)	9524 (2)	2.5 (2)
C(71)	5807 (4)	2495 (2)	9642 (2)	2.4 (2)
C(131)	627 (4)	7383 (2)	6135 (2)	2.3 (2)
C(171)	368 (4)	6467 (2)	6019 (2)	2.2 (2)

nitronate anion, when a coordination to Fe^{II} occurs. This could be interpreted as an electron-density shift from O(3)/O(13) to O(1)/O(11) through the fragment O(3)–C(3)–C(2)–C(1)–O(1)/O(13)–C(13)–C(12)–C(11)–O(11). Fe^{II} apparently coordinates strongest to the carbonyl oxygen as the $\text{Fe}^{\text{II}}\cdots\text{OC}$ coordination distances are significantly shorter than those of $\text{Fe}^{\text{II}}\cdots\text{ON}$.

Whereas Fe^{III} forms dark-coloured complexes with a series of oxygen donor ligands, similar complexes of Fe^{II} are quite unusual (Feigl & Anger, 1972). In order to clarify the nature of the electronic transition responsible for the colour, we have recorded the electronic absorption spectrum in acetonitrile (λ_{\max} : 495 nm, ϵ_{\max} : $420 \text{ l mol cm}^{-1}$) and measured the Mössbauer spectrum (δ : 1.19 nm s^{-1} ; ΔE_Q : 2.41 mm s^{-1}).

The Mössbauer parameters are (Gütlich, Link & Trautwein, 1978) typical for a high-spin Fe^{II} complex in an octahedral geometry. This result is in agreement with the structural data, but gives no clue to the nature of the observed electronic absorption.

Because of the intensity, the electronic transition responsible for the colour is suggested to be a charge-transfer type. The oxidizing nature of the ligand would suggest that the metal to ligand transfer mode would occur at lower energy than the ligand to metal variety.

* Lists of powder diffraction data (JCPDS Diffraction File No. 39-1995), structure factors, anisotropic thermal parameters and H-atom coordinates of the title compound and of structure factors, positional and thermal parameters, and bond distances and angles of 2-nitro-1,3-indandione dihydrate (Simonsen, 1988; cf. Table 2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44973 (60 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

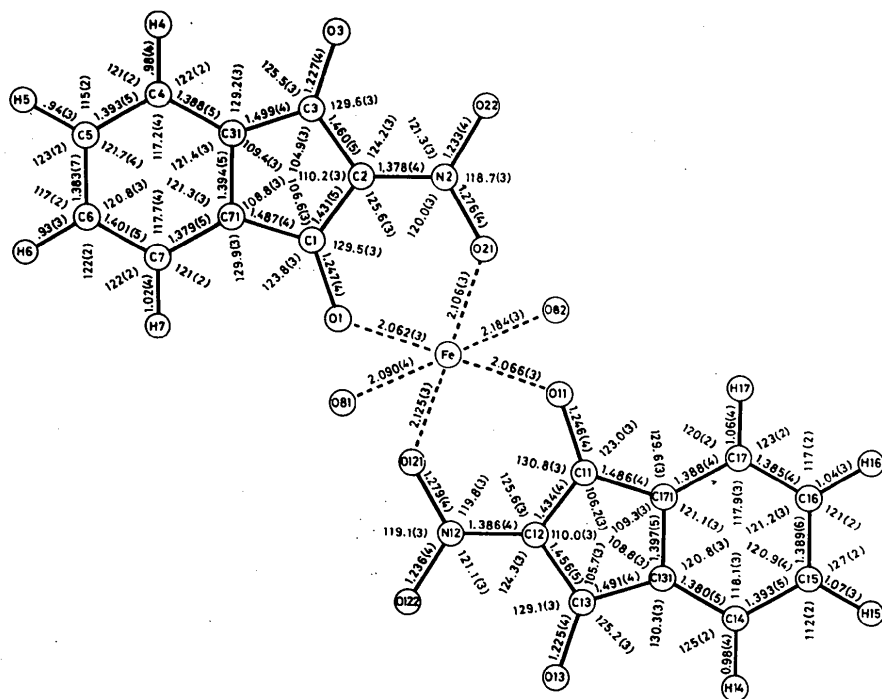


Fig. 1. Bond distances (Å), angles (°) and the atom-numbering scheme for (A).

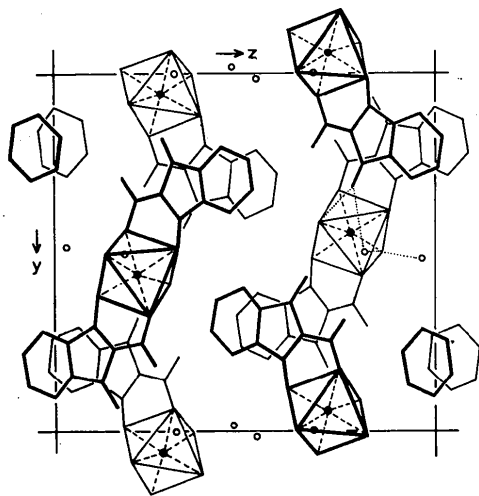


Fig. 2. The crystal structure of (A) projected down the x axis. The Fe atoms are symbolized by black circles and the surrounding 6 O atoms by octahedra. Open circles: O atoms in the crystal water. The four shortest hydrogen bonds in one asymmetric unit are drawn as dotted lines.

Following the procedure suggested by Beyers, Chou, Lever & Parish, (1969), the optical electronegativity of the nitronate ligand can be estimated. The transition at $20.2 \times 10^3 \text{ cm}^{-1}$ (495 nm) is assumed to be due to the excitation from a t_{2g} orbital at the Fe^{II} to an empty π^*

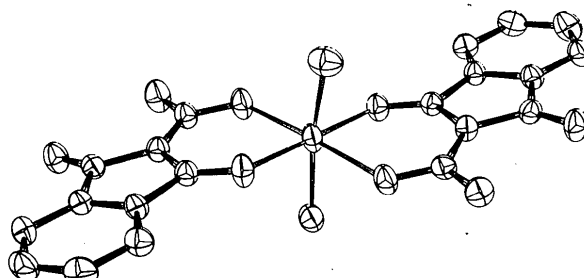


Fig. 3. Perspective view of (A) (ORTEP). The atoms are represented by thermal ellipsoids enclosing 50% probability.

Table 2. A comparison of selected bond distances (Å) for the title compound (A) and for (B) (2-nitro-1,3-indandione dihydrate) (Selenius & Lundgren, 1980; Simonsen, 1988)

	(A)	(B)
C(1)—C(2)	1.431 (5)	1.446 (1), 1.443 (3)*
C(11)—C(12)	1.434 (4)	
C(2)—C(3)	1.460 (5)	1.451 (1), 1.452 (2)*
C(12)—C(13)	1.456 (5)	
C(1)—O(1)	1.247 (4)	1.226 (1), 1.230 (2)*
C(11)—O(11)	1.246 (4)	
C(3)—O(3)	1.227 (4)	1.228 (1), 1.227 (2)*
C(13)—O(13)	1.225 (4)	
C(2)—N(2)	1.378 (4)	1.370 (1), 1.369 (2)*
C(12)—N(12)	1.386 (4)	
N(2)—O(21)	1.276 (4)	1.261 (1), 1.270 (2)*
N(12)—O(121)	1.279 (4)	
N(2)—O(22)	1.233 (4)	1.237 (1), 1.243 (2)*
N(12)—O(122)	1.236 (4)	

* Simonsen (1988); see deposition footnote.

orbital at the 2-nitro-1,3-indandionato ligand. If the optical electronegativity of Fe^{II} is chosen to be 1.95 then an optical electronegativity of 1.2 is found for the nitronate ligand. This is a reasonable result considering that a nitronate ligand is expected to be more oxidizing than a pyridine *N*-oxide ligand, for which a value of 0.8 has been reported (Beyers, Chou, Lever & Parish, 1969).

The four shortest hydrogen bonds are shown in Fig. 2. The aqua ligand H₂O(81) (Fig. 1) makes hydrogen bonds to both of the crystal water molecules; O(81)···O(83): 2.698 (5), O(81)···O(84): 2.667 (5) Å. The carbonyl oxygen O(13) is acceptor for hydrogen bonds from the aqua ligand H₂O(82) and the crystal water H₂O(83); O(13)···O(82): 2.790 (4), O(13)···O(83): 2.784 (4) Å.

The authors are grateful to Dr Heiner Winkler who recorded the Mössbauer spectrum. Financial support from the Danish Natural Science Research Council and Thomas B. Thriges Foundation for the purchase of the X-ray diffraction equipment is gratefully acknowledged.

Acta Cryst. (1988). C44, 1533–1535

Structure of [DyCl₃(triethylene glycol)].18-crown-6*

BY ROBIN D. ROGERS† AND RUSSELL D. ETZENHOUSER

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA

(Received 22 March 1988; accepted 25 April 1988)

Abstract. Trichloro(triethylene glycol)dysprosium–1,4,7,10,13,16-hexaoxacyclooctadecane (1/1), [DyCl₃(C₆H₁₄O₄)]·C₁₂H₂₄O₆, *M_r* = 683.4, monoclinic, *C*2/*c*, *a* = 18.666 (9), *b* = 9.769 (5), *c* = 14.931 (6) Å, β = 108.67 (5)°, *V* = 2579 Å³, *Z* = 4, *D_x* = 1.76 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 30.9 cm⁻¹, *F*(000) = 1372, *T* = 123 K, final *R* = 0.035 for 2108 observed [*F_o* ≥ 5σ(*F_o*)] reflections. The Dy ion is seven-coordinate in a distorted pentagonal bipyramidal geometry. The Dy atom and equatorial Cl [Dy–Cl = 2.621 (2) Å] reside on a crystallographic twofold axis. The axial chlorines [Dy–Cl = 2.607 (1) Å] are bent away from the equatorial Cl position [Cl_{ax}–Dy–Cl_{ax} = 162.65 (7)°]. The alcoholic O atoms [Dy–O = 2.316 (4) Å] donate hydrogen bonds to a crown ether molecule (which resides around a center of inversion) forming polymeric hydrogen-bonded chains. The unique etheric Dy–O separation is 2.455 (4) Å.

* *f*-Element/Crown Ether Complexes. 25. Part 24: Rogers & Etzenhouser (1988).

† To whom correspondence should be addressed.

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