Structure of the Fe(salen)ONO₂ Dimer, a Ferric Complex with a Unidentate Nitrate Ligand

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Abstract. Nitrato[N,N'-ethylenebis(salicylidene-iminato)]iron(III) dimer, [Fe$_2$(C$_{16}$H$_{14}$N$_2$O$_2$)$_2$(NO$_3$)$_2$], $M_r = 768\cdot4$, monoclinic, $P2_1/n$ [alternative setting of $P2_1/c$–C_{2h}^5 (No. 14)], $a = 14\cdot603$ (4), $b = 6\cdot933$ (2), $c = 15\cdot532$ (4) Å, $\beta = 98\cdot46$ (2)°, $V = 1555\cdot3$ Å³, $Z = 2$, $D_x = 1\cdot64$ Mg m⁻³, λ(Mo $K\alpha$, graphite monochromated) = 0·71073 Å, $\mu = 1\cdot03$ mm⁻¹, $F(000) = 788$, $T = 293$ K, $R = 0\cdot059$, $wR = 0\cdot032$ for 1744 independent reflections. The study appears to be the first in which unidentate bonding of nitrate to iron(III) has been crystallographically verified. As in [Fe(salen)-Cl]₂, the sixth coordination site of each iron was occupied by an oxygen atom belonging to the salen ligand in the other half of the dimer.

Introduction. We have reported previously that treatment of μ-oxo-bis[N,N'-ethylenebis(salicylidene-iminato)iron(III)], [Fe(salen)]₂O, with nitric oxide followed by dioxygen produces a black powder whose purple solutions are capable of converting added secondary amines to carcinogenic nitrosamines (Croisy, Fanning, Keefer, Slavin & Uhm, 1980). The structural chemistry of this interesting N-nitrosating agent has thus far defied elucidation, in part because most of our attempts to grow crystals of the material suitable for X-ray crystallographic studies have led only to recovery of a fine powder. Occasionally, however, some crystals have been isolated after allowing saturated dichloromethane:hexane solutions to stand in the cold for several weeks.

Though the samples we obtained of the crystalline compound were invariably less than ideal for crystallographic purposes despite repeated attempts at improvement, the structure of the compound has now been determined as (I). Independent synthesis of this nitrato complex has shown that it is not the species responsible for the N-nitrosating activity (Fanning,

Resce, Lickfield & Kotun, 1985). Nevertheless the crystallographic investigation is itself interesting as apparently the first in which unidentate attachment of a nitrato ligand to ferric iron has been confirmed by X-ray diffraction.

(I)
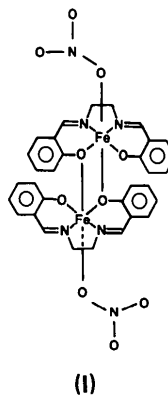
Experimental. One gram of [Fe(salen)]₂O (Lewis, Mabbs & Richards, 1967) was dissolved in 75 cm³ of dichloromethane, and argon was bubbled through the solution for several minutes. The mixture was saturated with nitric oxide, then dioxygen was slowly passed into the reaction vessel for about 15 min. An intense violet color immediately formed when dioxygen came into contact with the solution. The reaction mixture was evaporated under reduced pressure, leaving a black powder which was purified by dissolving it in dichloromethane, filtering and precipitating the product from the filtrate by adding hexane. The yield of purified powder was 800 mg (68%). (C$_{16}$H$_{14}$FeN$_3$O$_5$)$_2$; C, H, N, Fe calculated: 50·02, 3·67, 10·94, 14·54%; found (Galbraith Laboratories, Knoxville, TN): 49·96, 3·72, 10·79, 14·29%. Some small crystals were obtained by

filtering a saturated dichloromethane solution of the black powder, adding a small amount of hexane to the filtrate and allowing the mixture to stand in the refrigerator for several weeks.

The crystal selected for study was a nearly rectangular parallelepiped $0.25 \times 0.30 \times 0.48$ mm. Lattice parameters were determined from 15 reflections $(2\theta > 25°)$. Intensity measurements were made for 2854 independent reflections having $2\theta \leq 50.7°$, $h\ 0\to17$, $k\ 0\to8$, $l\ -18\to18$, with graphite-monochromated Mo $K\alpha$ radiation using $1.0°$-wide ω scans on a computer-controlled four-circle Nicolet $P\bar{1}$ Autodiffractometer. The intensity data were corrected empirically for absorption effects (transmission factors $0.520-1.000$) using ψ scans for four reflections having 2θ between 9.3 and $21.9°$ and were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements $= 0.603$ Å^{-1}. Six check reflections showed no significant fluctuation in intensity. The structure was solved using the heavy-atom technique and the resulting structural parameters were refined to convergence $[R(F) = 0.059$, $wR(F) = 0.032$ with $w = 1/\sigma^2(F)$ for 1744 independent reflections having $2\theta \leq 50.7°$ and $I > 3\sigma(I)$, $S = 1.29]$ using empirically weighted full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for H atoms, maximum shift of any parameter (including those of H atoms) in the final cycle $= 0.34\sigma$, number of parameters refined $= 282$. Positions for the 14 independent H atoms were calculated using idealized sp^3 or sp^2 hybridized geometry for the C atoms and a C—H bond length of 0.96 Å, and were allowed to vary as independent isotropic atoms in subsequent least-squares refinement cycles. Atomic scattering factors and f', f'' values were from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction was necessary. There were no peaks (more than 1.1 Å away from the Fe atom) in the final difference Fourier synthesis above the background level (0.39 e Å^{-3}), and there were no intermolecular contacts which were significantly less than the van der Waals values (Pauling, 1960). Calculations were performed with versions of the Nicolet *E-XTL* (Syntex, 1978) and *SHELXTL* (Sheldrick, 1983) interactive crystallographic software packages as modified at Crystalytics Company.*

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* The full Crystalytics Co. crystal structure analysis report including sources of scattering factors, anisotropic thermal parameters, fractional coordinates for H atoms, least-squares planes and deviations therefrom, tables of h, k, l, F_o and F_c, and bond lengths and angles not given in Table 2 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44198 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters (with e.s.d.'s in parentheses) and equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Fe	0.45774 (6)	−0.01198 (15)	0.09095 (6)	3.5
O(1)	0.5668 (3)	0.0971 (6)	0.0437 (3)	3.4
O(2)	0.3610 (3)	0.1696 (7)	0.0703 (3)	3.9
O(3)	0.5164 (4)	0.0838 (10)	0.2141 (5)	5.4
O(4)	0.3932 (6)	0.1103 (16)	0.2642 (5)	10.3
O(5)	0.5196 (5)	0.1307 (21)	0.3400 (6)	13.0
N(1)	0.5397 (4)	−0.2628 (8)	0.1140 (4)	3.7
N(2)	0.3659 (4)	−0.2085 (8)	0.1333 (4)	3.9
N(3)	0.4859 (6)	0.1053 (11)	0.2632 (6)	5.8
C(1)	0.6549 (4)	0.0796 (10)	0.0869 (4)	3.5
C(2)	0.7143 (5)	0.2361 (13)	0.0870 (5)	4.4
C(3)	0.8076 (6)	0.2162 (18)	0.1258 (6)	5.8
C(4)	0.8392 (6)	0.0484 (17)	0.1624 (6)	5.9
C(5)	0.7814 (5)	−0.1070 (16)	0.1639 (5)	5.2
C(6)	0.6862 (4)	−0.0930 (11)	0.1277 (4)	3.8
C(7)	0.6302 (5)	−0.2605 (11)	0.1329 (4)	4.1
C(8)	0.4879 (6)	−0.4388 (11)	0.1222 (6)	4.5
C(9)	0.4091 (6)	−0.3839 (12)	0.1724 (5)	4.7
C(10)	0.2779 (5)	−0.1779 (12)	0.1333 (5)	4.4
C(11)	0.2288 (4)	−0.0069 (13)	0.1023 (4)	4.2
C(12)	0.1300 (5)	0.0012 (17)	0.1007 (6)	5.6
C(13)	0.0791 (5)	0.1547 (17)	0.0740 (6)	6.1
C(14)	0.1209 (6)	0.3199 (17)	0.0476 (6)	6.0
C(15)	0.2164 (5)	0.3223 (13)	0.0480 (5)	4.8
C(16)	0.2700 (4)	0.1600 (11)	0.0738 (4)	3.7

Table 2. *Selected interatomic distances (Å) and bond angles (°)*

Fe—O(1)	1.997 (4)	Fe—N(1)	2.112 (6)
Fe—O(2)	1.883 (4)	Fe—N(2)	2.085 (6)
Fe—O(3)	2.086 (7)		
Fe—O(1)′	2.152 (4)	Fe···Fe′	3.250 (1)
O(1)···O(2)	3.133 (6)	N(1)···N(2)	2.627 (8)
O(1)···O(1)′	2.585 (6)	O(2)···O(1)′	2.867 (6)
O(1)···O(3)	2.850 (8)	O(2)···O(3)	2.999 (8)
O(1)···N(1)	2.775 (7)	O(2)···N(2)	2.795 (7)
O(3)···N(1)	2.910 (9)	O(1)′···N(1)	2.935 (7)
O(3)···N(2)	3.115 (9)	O(1)′···N(2)	3.149 (7)
O(3)—N(3)	0.95 (1)	N(1)—C(7)	1.310 (9)
O(4)—N(3)	1.36 (1)	N(2)—C(10)	1.303 (9)
O(5)—N(3)	1.23 (1)		
O(1)—C(1)	1.366 (7)	N(1)—C(8)	1.451 (10)
O(2)—C(16)	1.341 (8)	N(2)—C(9)	1.460 (10)
O(1)—Fe—O(2)	107.6 (2)	Fe—O(3)—N(3)	127.4 (8)
O(1)—Fe—N(1)	84.9 (2)	Fe—O(1)—C(1)	122.0 (4)
O(1)—Fe—O(1)′	77.0 (2)	Fe—O(1)—Fe′	103.0 (2)
O(1)—Fe—O(3)	88.5 (2)	Fe′—O(1)—C(1)	117.6 (4)
O(1)—Fe—N(2)	161.4 (2)	Fe—O(2)—C(16)	133.1 (4)
O(2)—Fe—N(2)	89.4 (2)	Fe—N(1)—C(7)	123.7 (5)
O(2)—Fe—O(1)′	90.3 (2)	Fe—N(1)—C(8)	114.6 (5)
O(2)—Fe—O(3)	98.0 (2)	Fe—N(2)—C(9)	114.7 (5)
O(2)—Fe—N(1)	166.2 (2)	Fe—N(2)—C(10)	125.0 (5)
O(3)—Fe—O(1)′	164.9 (2)	N(1)—Fe—N(2)	77.5 (2)
O(3)—Fe—N(1)	87.8 (2)	N(1)—Fe—O(1)′	87.0 (2)
O(3)—Fe—N(2)	96.6 (2)	N(2)—Fe—O(1)′	96.0 (2)
O(1)—C(1)—C(2)	118.3 (6)	N(1)—C(8)—C(9)	106.1 (6)
O(1)—C(1)—C(6)	121.3 (6)	N(2)—C(9)—C(8)	107.9 (6)
O(3)—N(3)—O(4)	126.9 (10)	N(2)—C(10)—C(11)	125.5 (7)
O(3)—N(3)—O(5)	129.1 (10)	C(6)—C(7)—N(1)	124.3 (7)
O(4)—N(3)—O(5)	104.0 (9)	C(7)—N(1)—C(8)	120.8 (6)
O(2)—C(16)—C(11)	121.8 (6)	C(9)—N(2)—C(10)	120.1 (6)
O(2)—C(16)—C(15)	117.8 (6)		

Primed (′) atoms are related to non-primed atoms by the crystallographic inversion center at $\tfrac{1}{2}, 0, 0$.

Discussion. Final atomic coordinates with estimated standard deviations are given in Table 1, and Table 2 lists the values of selected bond distances, polyhedral edge lengths, and bond angles. An *ORTEP* (Johnson, 1965) diagram specifying the atom-labeling convention used in this paper and showing a perspective drawing of the centrosymmetric Fe(salen)ONO$_2$ dimer is provided in Fig. 1.

Each iron atom of the dimer proved to lie in a distorted octahedral environment consisting of four O and two N atoms. The four coordination sites of the quasi-square girdle are occupied by the O and N atoms of a single tetradentate salen ligand whose chelating atoms [N(1), O(1), O(2) and N(2)] are coplanar to within 0·02 Å, with the Fe being displaced out of the plane toward the nitrate ligand by 0·10 Å.

One of the axial positions of each Fe is occupied by a nitrato ligand. The relative positions of the atoms in the Fe and nitrate groupings are shown in two different perspectives in Figs. 1 and 2. An extremely short [O(3)—N(3)] bond length and unusual anisotropic thermal parameters [for O(4) and O(5)] (see deposited

Fig. 1. Structure and atom-numbering scheme. Primed (') atoms are related to non-primed atoms by the center of inversion at ½, 0, 0. Non-hydrogen atoms are represented by (boundary) thermal-vibration ellipsoids drawn to encompass 50% of the electron density. H atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Fig. 2. Coordination about a single iron atom in the Fe(salen)ONO$_2$ dimer (top view). Non-hydrogen atoms are represented by thermal-vibration ellipsoids drawn to encompass 50% of the electron density. H atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

material for latter) were observed in the nitrate ligand. Presumably these effects are artifacts of the diffraction data which resulted from using a crystal of marginal quality; these anomalies could presumably be eliminated if a better crystal were ever obtained. The crystal used for data collection was the best of more than two dozen examined from different preparations and recrystallizations. An example of a similar phenomenon was reported in Day, George & Iske (1975) and Day, Day, George & Tavanaiepour (1980), where, in the period between the original and later reports, higher quality crystals and (consequently) diffraction data were obtained for the compound being studied and the anomalous structural features were eliminated.

The sixth coordination site of each Fe atom is occupied by an oxygen atom belonging to the other salen ligand of the dimer, forming a four-membered

cyclic $\begin{array}{c} \text{Fe}\!-\!-\!-\text{O} \\ | \qquad | \\ \text{O}\!-\!-\!-\text{Fe} \end{array}$ structure. Each of the salen ligands

in the dimer assumes a stepped conformation, with the nitrate N positioned over the step containing the N(2) and O(2) atoms; this arrangement is also shown in Fig. 2, which views the molecule from above the salen plane.

Complexes in which a nitrate group is covalently bound to a single metal atom have been categorized by Addison, Logan, Wallwork & Garner (1971) according to the difference in distance between the metal center and the two nitrate O atoms nearest it. The difference is of course zero in symmetrically bidentate complexes, small but real (*i.e.* 0·2–0·7 Å) in unsymmetrically bidentate attachment, and very large (0·8–1·1 Å, too great to involve significant bonding of the more distant oxygen) in unidentate complexes (Addison, Logan, Wallwork & Garner, 1971).

Most metals display an apparent preference for bidentate rather than unidentate coordination by nitrate (Addison, Logan, Wallwork & Garner, 1971; Cotton & Wilkinson, 1980). Ferric complexes appear to be no exception; for example, all four nitrates in the tetra-kisnitratoferrate(III) ion have been shown to be essentially symmetrically bidentate, with an average distance between the iron and the two nearest oxygens being 2·135 (31) Å (King, Logan, Morris & Wallwork, 1971; Addison, Blackwell, Harrison, Jones, Logan, Nunn & Wallwork, 1973; Blackwell, Nunn & Wallwork, 1975). The axial ligand of (nitrato)iron(III)-tetraphenylporphyrin [Fe(tpp)O$_2$NO] was found to be unsymmetrically bidentate, the relevant Fe—O distances being 2·323 and 2·019 Å, a difference of 0·3 Å (Phillippi, Baenziger & Goff, 1981).

With a difference of slightly greater than 1 Å [Fe—O separations of 2·086 (7), 3·098 (8) and 3·966 (10) Å], the Fe(salen)ONO$_2$ dimer thus complements the other covalent ferric nitrate complexes which have been investigated by crystallographic procedures, in that it is
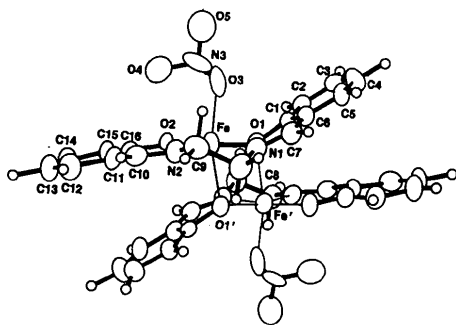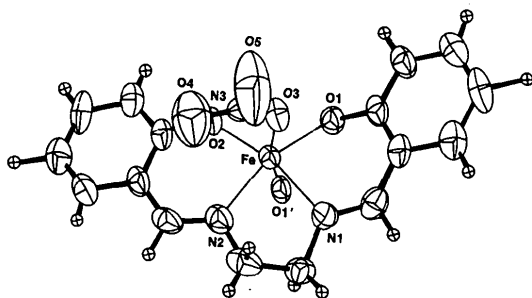
neither symmetrically nor unsymmetrically bidentate, but rather unidentate. In this respect, [Fe(salen)-ONO$_2$]$_2$ is reminiscent of the interesting iron(II) nitrato complex, π-cyclopentadienyliron(II)dicarbonyl nitrate, which has recently been shown to exhibit Fe—O separations of 1·974 (1), 3·043 (1) and 4·018 (1) Å and is thus also unidentate (Struchkov, Aleksandrov, Kaganovich & Rybinskaya, 1981).

A computer survey of substructures in the CAS ONLINE file retrieved literature citations for approximately 100 substances reported to contain at least one covalent iron–nitrate bond, but we were able to locate crystal structure solutions only for the three complexes reviewed above (King, Logan, Morris & Wallwork, 1971; Addison, Blackwell, Harrison, Jones, Logan, Nunn & Wallwork, 1973; Blackwell, Nunn & Wallwork, 1975; Phillippi, Baenziger & Goff, 1981; Struchkov, Aleksandrov, Kaganovich & Rybinskaya, 1981) and one other unsymmetrically bidentate ferric nitrate (Nishida, Shimo, Takahashi & Kida, 1984). We conclude that the present study represents the first crystal structure determination of a unidentate iron(III) nitrato complex.

The search also revealed some apparent confusion in the literature regarding the assignment of bidentate vs unidentate coordination modes. For example, 11 of the 14 registry numbers retrieved for the tetrakisnitrato-ferrate(III) ion and its salts are associated with unidentate structures in the CAS ONLINE file, even though available evidence solidly supports the bidentate interpretation (King, Logan, Morris & Wallwork, 1971; Addison, Blackwell, Harrison, Jones, Logan, Nunn & Wallwork, 1973; Blackwell, Nunn & Wallwork, 1975). In addition, two different registry numbers have been assigned to Fe(tpp)O$_2$NO, one for the bidentate structure known to be correct (Phillippi, Baenziger & Goff, 1981) and one for a unidentate nitrato alternative. At least part of this confusion may result from the difficulty [stressed repeatedly in the literature (Cotton & Wilkinson, 1980; Nakamoto, 1978; James & Kimber, 1969; Logan & Simpson, 1965; Reiff, Baker & Erickson, 1968; Rakowski, Rycheck & Busch, 1975)] of distinguishing bidentate from unidentate coordination of nitrate using non-diffractometric methods, underscoring the published conclusion that X-ray crystallography is required for unambiguous differentiation of unidentate from bidentate bonding in metal nitrates (Rosenthal, 1973).

Also of interest is the dimeric nature of [Fe-(salen)ONO$_2$]$_2$, a feature which has previously been observed in the similar chloro compound, [Fe(salen)-Cl]$_2$ (Gerloch & Mabbs, 1967). The tendency for the salen complexes to form dimeric structures has been attributed to the coordinating donor ability of the salen oxygen groups and to the flexibility of the Schiff base ligand with regard to coordination geometry and conformation (Lauffer, Heistand & Que, 1983). It is noteworthy that the Fe—O(1) bond is longer by >0·1 Å than the Fe—O(2) linkage, presumably because O(1) is bonded to both Fe atoms while O(2) is attached to only one; a similar inequality of Fe—O distances is found in the dimeric chloro complex (Gerloch & Mabbs, 1967).

As also occurs in [Fe(salen)Cl]$_2$ (Gerloch & Mabbs, 1967), the two salicylidene rings of each monomer unit are not coplanar. The dihedral angle between the two planes is 22° for the nitrate and 19° for the chloride (Gerloch & Mabbs, 1967). The aryl ring over which the nitrate is positioned [i.e. that containing C(10)—C(16)] is bent down from the NOON plane by 10° while the other group is bent up from this plane by 31°.

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(+)-3,5-*O*-(*R*)-Benzylidene-6-deoxy-6-iodo-1,2-*O*-isopropylidene-α-D-glucofuranose

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Abstract. 2,2-Dimethyl-5-iodomethyl-7-phenyl-[1′,3′]-dioxolo[4′,5′:4,5]furo[3,2-*d*][1,3]dioxane, $C_{16}H_{19}IO_5$, $M_r = 418 \cdot 23$, monoclinic, $P2_1$, $a = 6 \cdot 0913$ (6), $b = 9 \cdot 1636$ (7), $c = 14 \cdot 7957$ (9) Å, $\beta = 94 \cdot 172$ (6)°, $V = 823 \cdot 7$ (2) Å^3, $Z = 2$, $D_x = 1 \cdot 686$ g cm^{-3}, $\lambda = 0 \cdot 71073$ Å, Mo $K\alpha$, $\mu = 19 \cdot 398$ cm^{-1}, $F(000) = 416$, $T = 298$ K, $R = 0 \cdot 016$ for 1890 independent reflections with $F^2 > 3\sigma(F^2)$. The dioxane ring is in the chair conformation, where the iodomethyl is axial and *trans* to the phenyl group.

Introduction. In connection with a program directed towards the synthesis of a series of 6-substituted glucose analogs, a reliable source of the protected glucose derivatives 3,5-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose was required.

TBDMS- = t-BuMe₂Si-

The traditional zinc-halide-catalyzed acetalization of the D-glucose acetonide (1) has been presumed to give thermodynamically the more stable product (3*a*) [Brigl & Grüner (1932) and references cited therein]. How-ever, pyridinium-tosylate-catalyzed acetal exchange between benzaldehyde dimethyl acetal and 6-*O*-(*tert*-butyldiphenylsilyl)-1,2-*O*-isopropylidene-α-D-gluco-furanose (2) gave an isomeric compound (3*b*) (Åker-feldt & Bartlett, 1986). The hydroxy compound (3*a*) was converted to the corresponding iodide (4). It was of interest to determine the configuration of the phenyl group of the benzylidene acetal relative to that of the iodomethyl side chain in compound (3*a*) as compared to isomer (3*b*).

The configuration of the benzylic carbon was assigned unambiguously by two-dimensional NOESY ¹H NMR spectroscopy. For iodide (4), nuclear Over-hauser interaction is seen between the benzylic methine H(C7) and the methylene hydrogens H′(C6) and H″(C6) (Åkerfeldt & Bartlett, 1986). Thus in compound (4), and hence in (3*a*), the phenyl group and C(6) are *trans* with respect to the 1,3-dioxane ring, *S*-benzal configuration (Åkerfeldt & Bartlett, 1986).

Experimental. Clear colorless crystals obtained from ethanol/hexane were kindly provided by Karin S. Åkerfeldt and Professor Paul A. Bartlett. Density was not measured. Crystal $0 \cdot 36 \times 0 \cdot 38 \times 0 \cdot 12$ mm. Precession photographs, monoclinic space group $P2_1$, 0*k*0, $k = 2n$. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 24 reflections, $26 < 2\theta < 31°$, graphite-monochromatized Mo $K\alpha$, θ–2θ scans. 2361 intensities collected during 30 h in hemisphere *h*, ±*k*, ±*l* ($h = 0$ to 5, $k = -9$ to 9, $l = -15$ to 15), $3 < 2\theta < 45°$, scan speed $0 \cdot 91$ to $6 \cdot 67°$ min^{-1}. Average of $3 \cdot 4\%$ decrease in intensity in three intensity standards equally distributed over reciprocal space during 24 h of X-ray exposure time; linear correction applied. No crystal reorientation required in data collection. Data correction for background, scan speed,