

A dinuclear manganese carbonyl complex of tetramethylthiourea: X-ray crystal structure of $eq\text{-}[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$

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Abstract

The synthesis and characterization of the novel dimanganese tetramethylthiourea compound $[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ are described. $\text{Mn}_2(\text{CO})_{10}$ undergoes photosubstitution by tetramethylthiourea to yield $eq\text{-}[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ **4** whereas Me_3NO induced substitution at 80°C gives $ax\text{-}[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ **5**. Compound **4** contains an S-coordinated $\text{SC}(\text{NMe}_2)_2$ ligand at an equatorial site while in **5** the ligand is proposed as S-coordinated at an axial site of one of the metal atoms. The crystal structure of **4** has been determined by an X-ray diffraction study. © 1997 Elsevier Science S.A.

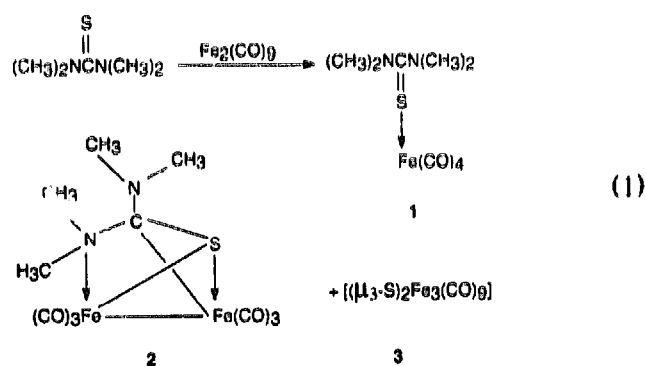
Keywords: Manganese; Carbonyl; Thiourea; X-ray diffraction

1. Introduction

The synthesis and reactivity of mono-, di- and polynuclear transition metal complexes of thiourea and its derivatives have been explored over the past two decades and are a subject of current interest [1–22]. In mononuclear metal complexes the coordination is mainly through the sulfur atom [6–10]. However, a few examples of the coordination of thioureas *via* both the sulfur and nitrogen atoms have been structurally characterized [11–13,20,21]. The cleavages of the carbon–sulfur, carbon–nitrogen, nitrogen–hydrogen and carbon–hydrogen bonds of the ligands have been observed with polynuclear osmium and ruthenium clusters [13–21].

In comparison to the extensive mono- and polynuclear transition metal complexes of the thiourea ligands, so far very little is known about their dinuclear complexes. Alper and co-workers [22] reported that the reaction of $\text{Fe}_2(\text{CO})_9$ with tetramethylthiourea gave a sulfur donor ligand complex **1**, a diiron hexacarbonyl

species containing both nitrogen and sulfur donor atoms **2** and $[\mu_3\text{-S}]_2\text{Fe}_3(\text{CO})_9$ **3** (Eq. (1)).



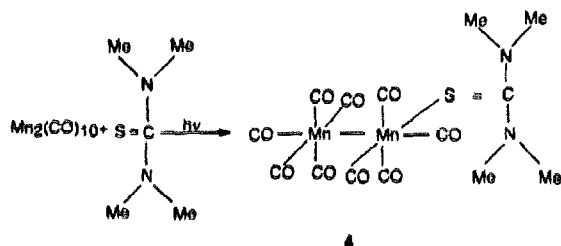
In continuation of our previous studies on the reactivity of thioureas with triosmium clusters [21], we have investigated the reactions of $\text{Mn}_2(\text{CO})_{10}$ with tetramethylthiourea by both photochemical and thermal methods which led to the synthesis of $[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ in two isomeric forms. The results of these studies are described herein. One of these species, claimed to be the axial isomer, was previously reported briefly by Carriedo et al. [7]. During the progress of this

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work Adams et al. reported some di- and tri-nuclear rhenium compounds of *N,N*-diethyl-*p*-tolylthiourea [23].

2. Results and discussion

The photochemical reaction between $\text{Mn}_2(\text{CO})_{10}$ and tetramethylthiourea proceeds without the cleavage of Mn–Mn bond and leads to the formation of an orange coloured complex **4** in 25% yield, shown by elemental analysis, IR, ^1H NMR and a single-crystal X-ray diffraction study to be $eq\text{-}[\text{Mn}_2(\text{CO})_9(\eta^1\text{-SC}(\text{NMe}_2)_2)]$. The IR spectrum of **4** exhibits the terminal CO groups stretching vibration bands at 2083m, 2010s, 1985vs, 1982sh, 1949s and 1912s cm^{-1} . As expected the νCN band for **4** (1552 cm^{-1}) occurs at higher frequency than in the free ligand (1510 cm^{-1}).



The ^1H NMR spectrum contains a singlet at δ 3.23 ppm indicating that the methyl groups of the tetramethylthiourea ligand are equivalent. The exact coordination geometry of the compound was confirmed by a single crystal X-ray crystallographic study. The structure of a single molecule of **4** is depicted in Fig. 1 and selected bond distances and angles are presented in Table 1. The molecule contains two mutually bonded manganese atoms with the Mn–Mn distance of 2.928(2) Å which is somewhat longer than that found in $\text{Mn}_2(\text{CO})_{10}$ (2.9030(6) Å) [24]. The overall structure of **4** is similar to that of $\text{Mn}_2(\text{CO})_{10}$, in which two square-pyramidal

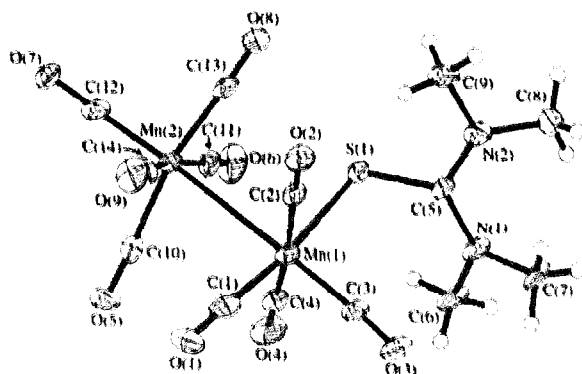


Fig. 1. X-ray structure of $eq\text{-}[\text{Mn}_2(\text{CO})_9(\eta^1\text{-SC}(\text{NMe}_2)_2)]$ **4** showing the atom labelling scheme used. The thermal ellipsoids are drawn at 50% probability.

Table 1

Bond lengths (Å) and angles ($^\circ$) involving the non-hydrogen atoms for $[\text{Mn}_2(\text{CO})_9(\text{C}_5\text{H}_{12}\text{N}_2\text{S})]$ **4**

Mn(1)–Mn(2)	2.928(2)	Mn(1)–S(1)	2.428(2)
Mn(1)–C(1)	1.815(7)	Mn(1)–C(2)	1.853(6)
Mn(1)–C(3)	1.805(7)	Mn(1)–C(4)	1.852(7)
Mn(2)–C(10)	1.853(7)	Mn(2)–C(11)	1.853(6)
Mn(2)–C(12)	1.800(7)	Mn(2)–C(13)	1.847(7)
Mn(2)–C(14)	1.849(6)	S(1)–C(5)	1.737(6)
O(1)–C(1)	1.149(7)	O(2)–C(2)	1.147(7)
O(3)–C(3)	1.156(7)	O(4)–C(4)	1.169(7)
O(5)–C(10)	1.149(7)	O(6)–C(11)	1.146(6)
O(7)–C(12)	1.165(7)	O(8)–C(13)	1.149(7)
O(9)–C(14)	1.146(6)	N(1)–C(5)	1.328(7)
N(1)–C(6)	1.469(7)	N(1)–C(7)	1.494(7)
N(2)–C(5)	1.378(7)	N(2)–C(9)	1.469(7)
N(2)–C(8)	1.471(7)		
C(3)–Mn(1)–C(1)	90.6(3)	C(3)–Mn(1)–C(2)	92.7(3)
C(1)–Mn(1)–C(2)	91.0(3)	C(3)–Mn(1)–C(4)	95.2(3)
C(1)–Mn(1)–C(4)	93.5(3)	C(2)–Mn(1)–C(4)	170.8(3)
C(3)–Mn(1)–S(1)	95.7(2)	C(1)–Mn(1)–S(1)	173.3(2)
C(2)–Mn(1)–S(1)	86.5(2)	C(4)–Mn(1)–S(1)	88.1(2)
C(3)–Mn(1)–Mn(2)	176.1(2)	C(1)–Mn(1)–Mn(2)	86.5(2)
C(2)–Mn(1)–Mn(2)	84.7(2)	C(4)–Mn(1)–Mn(2)	87.6(2)
S(1)–Mn(1)–Mn(2)	87.0(1)	C(12)–Mn(2)–C(13)	95.8(3)
C(12)–Mn(2)–C(14)	95.4(3)	C(13)–Mn(2)–C(14)	88.9(3)
C(12)–Mn(2)–C(10)	95.7(3)	C(13)–Mn(2)–C(10)	168.5(3)
C(14)–Mn(2)–C(10)	91.0(3)	C(12)–Mn(2)–C(11)	96.1(3)
C(13)–Mn(2)–C(11)	89.5(3)	C(14)–Mn(2)–C(11)	168.5(3)
C(10)–Mn(2)–C(11)	88.3(3)	C(12)–Mn(2)–Mn(1)	177.0(2)
C(13)–Mn(2)–Mn(1)	87.0(2)	C(14)–Mn(2)–Mn(1)	83.5(2)
C(10)–Mn(2)–Mn(1)	81.6(2)	C(11)–Mn(2)–Mn(1)	85.0(2)
C(5)–S(1)–Mn(1)	110.3(2)	C(5)–N(1)–C(6)	122.0(5)
C(5)–N(1)–C(7)	124.4(5)	C(6)–N(1)–O(7)	113.5(5)
C(5)–N(2)–C(9)	122.4(5)	C(5)–N(2)–C(8)	122.4(5)
C(9)–N(2)–C(8)	114.3(5)	O(1)–C(1)–Mn(1)	177.5(6)
O(2)–C(2)–Mn(1)	178.2(6)	O(3)–C(3)–Mn(1)	175.7(5)
O(4)–C(4)–Mn(1)	179.2(6)	N(1)–C(5)–N(2)	119.1(5)
N(1)–C(5)–S(1)	123.8(5)	N(2)–C(5)–S(1)	117.1(5)
O(5)–C(10)–Mn(2)	177.0(6)	O(6)–C(11)–Mn(2)	177.6(5)
O(7)–C(12)–Mn(2)	178.8(5)	O(8)–C(13)–Mn(2)	176.8(5)
O(9)–C(14)–Mn(2)	178.5(6)		

MnL_5 groups are joined by a Mn–Mn single bond with the equatorial ligands adopting a staggered arrangement on the two metal atoms. Tetramethylthiourea ligand is coordinated through the sulfur atom and occupies one of the equatorial coordination sites. Similar examples where a sulfur atom occupies an equatorial position include the compounds $[\text{Re}_2(\text{CO})_9(\eta^1\text{-SC}(\text{NEt}_2)\text{N}(\text{H})(p\text{-tolyl}))]$ [23], $[\text{Re}_2(\text{CO})_9(\eta^1\text{-SCH}_2\text{CMe}_2\text{CH}_2)]$ [25], and $[\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)]$ [26]. In other compounds, the sulfur donor ligands have been found to form bridges between a pair of metal atoms; examples are $[\text{Re}_2(\text{CO})_9(\mu^1\text{-SC}(\text{NEt}_2)\text{N}(\text{H})(p\text{-tolyl}))]$ [23] and $[\text{Re}_2(\text{CO})_{10}(\mu_2\text{-H})_3(\mu_2\text{-SC}(\text{NEt}_2)\text{N}(\text{H})(p\text{-tolyl}))]$ [23].

The Mn–S bond length in **4** (2.428(2) Å) is only slightly longer than the value (2.41 Å) expected on the basis of the covalent radii sum of Mn and S (1.39 and 1.02 Å) [27]. This value is also comparable with that

[2.405(3) Å] observed in the mononuclear cationic complex $cis\text{-}[\text{Mn}(\text{CO})_4\{\text{SC}(\text{NMe}_2)_2\}_2]^+$ [7] and suggests that the thiourea ligand in the present compound is strongly bonded to manganese. The C–S double bond distance $\text{S}(1)\text{-C}(5) = 1.737(6)$ Å is similar to those observed for other $\eta^1\text{-S}$ -coordinated thiourea ligands, e.g., $cis\text{-}[\text{Mn}(\text{CO})_4\{\text{SC}(\text{NMe}_2)_2\}_2]^+$ {1.752(8)} [7], $[\text{Os}_3(\text{CO})_{11}\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ {1.74(2) Å} [21], $[\text{Os}_3(\text{CO})_9(\mu\text{-OH})(\mu\text{-MeOC=O})\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ {1.739(13) Å} [21] and $[\text{Re}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NEt}_2)\text{N}(\text{H})(p\text{-tolyl})\}]$ {1.75(1) Å} [23]. Other parameters related to thiourea are as expected, although the C(5)–N(2) bond [1.378(7) Å] appears to be marginally longer than the chemically equivalent C(5)–N(1) bond [1.328(7) Å]. Similar asymmetry was also observed in the two corresponding C–N bonds in $cis\text{-}[\text{Mn}(\text{CO})_4\{\text{SC}(\text{NMe}_2)_2\}_2]^+$ {1.328(11), 1.306(10) Å} [7]. The C(5), N(1) and N(2) atoms have all planar configurations, the S(1)–C(5)–N(1) angle becomes wider compared with S(1)–C(5)–N(2) [123.8(5) vs. 117.1(5)°] due to steric interactions of O(3) with both the methyl groups on N(1) [O(3)...C(6) = 3.399(9), O(3)...C(7) = 3.345(8) Å]. As expected, the Mn(1)–S(1)–C(5) angle {110.3(2)°} is close to tetrahedral and only slightly smaller than the corresponding value {112.6(3)°} in $cis\text{-}[\text{Mn}(\text{CO})_4\{\text{SC}(\text{NMe}_2)_2\}_2]^+$ [7].

The Mn–C(CO) bonds vary from 1.800(7) to 1.853(7), average 1.836 Å, with the three shortest bonds lying either *trans* to S(1) [Mn(1)–C(1) = 1.815(7) Å], or *along* the Mn–Mn axis [Mn(1)–C(3) = 1.805(7) Å and Mn(2)–C(12) = 1.800(7) Å]. The Mn–Mn–CO(equatorial) angles are all acute [81.6(2)–87.6(2)°] and the OC(axial)–Mn–CO(equatorial) angles are all obtuse [90.6(3) to 96.1(3)°]. All Mn–C–O systems are close to linear [175.7(5)–179.2(6), average 177.7°] with the C–O distances lying in the narrow range 1.146(6)–1.169(7), average 1.153 Å. These features are similar to those observed for $\text{Mn}_2(\text{CO})_{10}$ [24] and other related metal carbonyl species. The shortest intermolecular non-hydrogen contact is 3.190(10) Å involving the O(7) and C(6) (at 1 + x, y, z). This value suggests fairly tight packing of molecules in the unit cell.

Trimethylamine-*N*-oxide induced reaction of $\text{Mn}_2(\text{CO})_{10}$ with tetramethylthiourea at 80°C results in the isolation of an orange coloured complex **5** in 40% yield. The infrared spectrum of **5**, in the carbonyl stretching region, is virtually identical to that of **4** indicating that they have very similar structures. The ^1H NMR spectrum of **5** displays a singlet at δ 3.07 ppm (3.23 ppm for **4**). This difference is small but remains unchanged when a mixed sample of **4** and **5** shows two distinct methyl singlets in the ^1H NMR spectrum. This leads us to believe that compound **5** is an isomer of **4**, in which the tetramethylthiourea ligand is coordinated to a manganese centre *via* the sulfur atom and adopts an axial position in the coordination polyhedron. We were unable to obtain X-ray quality crystals of **5** and so could

not confirm the structure unequivocally by diffraction methods. It may be noted in this context that Carriedo et al. obtained, by photolysis, an orange coloured isomer of $[\text{Mn}_2(\text{CO})_9\{\text{SC}(\text{NMe}_2)_2\}]$ which they claimed to be the *axial* isomer [7]. The colour (orange) and ^1H NMR spectrum (a sharp singlet at δ 3.26 ppm) of this compound are virtually identical with our compound **4**, suggesting that the compound was most probably the *equatorial* isomer. It may be further noted that although the IR spectra for the two isomers **4** and **5** are expected to be different, this is not always the case; in many $\text{M}_2(\text{CO})_9\text{L}$ and $\text{M}_2(\text{CO})_8\text{L}_2$ (M = Mn, Re) type complexes the carbonyl absorption bands observed for different isomeric forms are hardly any different [3,28]. An interesting aspect of the present study is the dramatic dichotomy between photochemical and thermal reactions of $\text{Mn}_2(\text{CO})_{10}$ with tetramethylthiourea.

Previous studies showed that for simple substitution products of the type $[\text{Mn}_2(\text{CO})_9\text{L}]$, the substituent ligand L can occupy either an axial or an equatorial site. It seems that steric factors play an important role since axial isomers are obtained when L = PPh₃, PMePh₂, PBu₃, or P(OPh)₃ [3,29,30] while the equatorial isomers are formed when L = PMe₂Ph, Py, α -Pic, acetonitrile, EtCN, PhCN, or PH₃ [3,29,31]. To our knowledge, compounds **4** and **5** appear to be the first example of the isolation of a dimanganese compound of the type $[\text{Mn}_2(\text{CO})_9\text{L}]$ in two isomeric forms.

3. Experimental

All reactions were performed under an atmosphere of dry, oxygen-free, nitrogen. Solvents were freshly distilled under nitrogen from usual drying agents immediately before use. Photochemical reactions were performed by irradiation with a 125 watt medium pressure mercury lamp. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer. Elemental analyses were performed at the microanalytical Laboratory, Institut für Anorganische und Analytische Chemie, Universität Freiburg, Germany.

3.1. Synthesis of $eq\text{-}[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ **4**

$\text{Mn}_2(\text{CO})_{10}$ (0.199 g, 0.51 mmol) and tetramethylthiourea (0.067 g, 0.51 mmol) were dissolved in benzene (50 cm³) and taken in a Carius tube. After degassing the tube was sealed and irradiated for 5 h. The colour changed from yellow to orange. The tube was then opened and the solvent removed under reduced pressure. The residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (3:1, v/v) gave one major band which yielded $eq\text{-}[\text{Mn}_2(\text{CO})_9\{\eta^1\text{-SC}(\text{NMe}_2)_2\}]$ **4** as brown orange crystals (0.063 g, 25%)

from hexane/CH₂Cl₂ at –20°C. (Found: C, 34.25; H, 2.62; N, 5.75. C₁₄H₁₂Mn₂SN₂O₉ requires: C, 34.02; H, 2.45; N, 5.67%). IR(ν CO, CH₂Cl₂): 2083m, 2010s, 1985vs, 1982sh, 1949s, 1912s cm⁻¹; ν CN(KBr): 1552 cm⁻¹. ¹H NMR (CDCl₃): 3.23(s) ppm.

3.2. Synthesis of *ax*-[Mn₂(CO)₉{ η ¹-SC(NMe₂)₂}] 5

A methanolic solution (10 cm³) of Me₃NO · 2H₂O (0.62 g, 0.56 mmol) was added dropwise to a benzene solution (50 cm³) of Mn₂(CO)₁₂ (0.205 g, 0.53 mmol) and tetramethylthiourea (0.069 g, 0.52 mmol) over 30 min. The reaction mixture was heated to reflux for 4 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (3:1, v/v) gave three bands. The faster moving band gave unreacted Mn₂(CO)₁₀ (~0.005 g). The second band gave a trace amount of an uncharacterized product while the slower moving band yielded *ax*-[Mn₂(CO)₉{ η ¹-SC(NMe₂)₂}] 5 as yellow crystals (0.104 g, 40%). Found: C, 34.38; H, 2.70; N, 5.65. C₁₄H₁₂Mn₂SN₂O₉ requires: C, 34.02; H, 2.45; N, 5.67%; IR(ν CO, CH₂Cl₂): 2083m, 2010s, 1986vs, 1982sh, 1946s, 1911s cm⁻¹; ν CN(KBr): 1556 cm⁻¹. ¹H NMR (CDCl₃): 3.07(s) ppm.

3.3. X-ray crystallography for [Mn₂(CO)₉{ η ¹-SC(NMe₂)₂}] 4

Brown orange crystals of 4 suitable for X-ray work were grown from a hexane/dichloromethane solution at –40°C. A single crystal of dimensions 0.25 × 0.10 × 0.03 mm³ and mounted on the goniostat using silicone oil as adhesive.

Crystal Data: [Mn₂(CO)₉(C₅H₁₂N₂S)]. *M* = 494.195, Triclinic, *a* = 9.941(3), *b* = 10.422(6), *c* = 11.361(2) Å, α = 73.91(3), β = 63.38(5)°, γ = 72.67(2)°, *U* = 990.2(7) Å³ (by least squares refinement of diffractometer angles for 250 reflections within θ = 2.0–24.8°, λ = 0.71069 Å), space group *P* $\bar{1}$ (No. 2), *Z* = 2, *D*_c = 1.658 g cm⁻³, *F*(000) = 496, μ = 14.28 cm⁻¹, *T* = 140 K.

All crystallographic measurements were made at 140 K on a Delft Instruments FAST TV area detector diffractometer equipped with a rotating anode FR591 generator (50 kV, 40 mA), bufferboard and DEP image intensifier with Mo-K α radiation (λ = 0.71069 Å), and an Oxford Cryostream low temperature cooling system, controlled by a microVax 3200 and driven by MADNES software, by following previously described procedures [32]. 2557 reflections were measured (2.0 ≤ θ ≤ 24.8°; index ranges –11 ≤ *h* ≤ 11; –10 ≤ *k* ≤ 11; –12 ≤ *l* ≤ 12), which after due processing gave 2149 unique data [merging *R* = 0.052 after absorption correction [33] (max. and min. absorption correction factors = 0.683, 0.879)].

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$ Å²) for [Mn₂(CO)₉(O₅H₁₂N₂S)] 4. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*i*} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Mn(1)	3617.2(11)	2668.2(9)	6522.1(9)	21(1)
Mn(2)	256.0(11)	3245.6(9)	7789.1(9)	21(1)
S(1)	3558(2)	817(2)	8385(2)	24(1)
O(1)	3352(5)	4905(4)	4315(4)	37(1)
O(2)	3266(5)	699(4)	5240(4)	31(1)
O(3)	6986(5)	2151(4)	4994(4)	36(1)
O(4)	3573(5)	4530(5)	8164(5)	40(1)
O(5)	674(5)	6137(4)	7089(4)	30(1)
O(6)	631(5)	3005(5)	10322(4)	43(1)
O(7)	–3148(5)	3967(4)	8973(4)	33(1)
O(8)	395(5)	239(5)	8313(5)	39(1)
O(9)	490(5)	3320(4)	5050(4)	41(1)
N(1)	6621(6)	140(5)	7776(5)	26(1)
N(2)	5436(6)	–1607(5)	8046(5)	26(1)
O(1)	3425(7)	4053(7)	5190(6)	30(2)
O(2)	3376(7)	1453(6)	5745(6)	22(2)
O(3)	5679(8)	2327(6)	5635(6)	26(2)
O(4)	3580(7)	3813(6)	7531(6)	26(2)
O(5)	5353(7)	–259(6)	8032(5)	21(2)
O(6)	6571(7)	1346(6)	8234(6)	31(2)
O(7)	8209(6)	–528(6)	6954(6)	30(2)
O(8)	6498(8)	–2728(6)	8501(7)	36(2)
O(9)	4285(7)	–2051(6)	7858(6)	31(2)
O(10)	556(7)	5018(7)	7341(6)	23(2)
O(11)	521(7)	3085(6)	9341(6)	26(2)
O(12)	–1810(8)	3690(6)	8518(6)	25(2)
O(13)	381(7)	1385(7)	8115(6)	25(2)
O(14)	418(7)	3300(6)	6091(7)	27(2)

The structure was solved via direct methods using the program SHELXS86 [34] and refined by full-matrix least squares on *F*² using all 2149 unique data using SHELXL93 [35] with anisotropic displacement coefficients for the non-hydrogen atoms and individual isotropic temperature factors for the hydrogen atoms (riding model). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0333 \times P)^2]$, where $P = [(F_o^2) + 2(F_c^2)]/3$; this gave satisfactory agreement analyses. Final $wR_2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$ and $R_1 = \sum(F_o - F_c)/\sum(F_o)$ values were 0.092 and 0.053, respectively, for 268 parameters and 2149 data (ρ_{min} , $\rho_{\text{max}} = -0.34, 0.35$ eÅ⁻³; (Δ/σ)_{max} 0.01). The corresponding wR_2 and R_1 values for the 1643 data with $F_o > 4\sigma(F_o)$ were 0.087 and 0.039 respectively. Diagrams were drawn with SNOOPI [36]. All calculations were performed on a Pentium P5-90 personal computer. Sources of scattering factor data are given in ref. [35]. The bond lengths and angles, and fractional coordinates of the nonhydrogen atoms are given in Tables 1 and 2, respectively. The anisotropic displacement parameters of the non-hydrogen atoms, hydrogen atom parameters, and tables of structure factors have been deposited as supplementary material.

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