

A Reinvestigation of Dioxobis(ethylenediamine)rhenium(V) Chloride and Dioxotetrakis(pyridine)rhenium(V) Chloride Dihydrate*

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Abstract. $[\text{ReO}_2\text{en}_2]\text{Cl}$ (en = ethylenediamine), monoclinic, $P2_1/c$, $a = 5.588$ (2), $b = 11.060$ (5), $c = 16.359$ (3) Å, $\beta = 100.78$ (2)°, $V = 933.2$ Å³, $Z = 4$, $D_c = 2.50$, $D_o = 2.51$ (2) g cm⁻³. $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ (py = pyridine), monoclinic, Cc , $a = 13.577$ (4), $b = 11.951$ (3), $c = 15.498$ (4) Å, $\beta = 116.3$ (1)°, $V = 2552.0$ Å³, $Z = 4$, $D_c = 1.78$, $D_o = 1.79$ (1) g cm⁻³. The single-crystal structure redetermination gave precise rhenium–oxygen bond lengths: Re–O, 1.765 (7) Å (average) for $[\text{ReO}_2\text{en}_2]\text{Cl}$; Re–O, 1.764 (13) Å (average) for $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Introduction. We have undertaken a study of the correlation between Re–O bond lengths and Re–O vibrational stretching frequencies, and the force constants derived therefrom (Turner, 1976). It has become obvious that, although the X-ray crystal structures of some 20 compounds containing Re–O bonds have been investigated, the errors in the Re–O bond lengths are generally too high for the results to be used in deriving accurate mathematical relationships. To remedy this situation we have examined the crystal structures of a number of Re compounds. We have already reported the crystal structures of KReO_4 (Lock & Turner, 1975), $\text{ReO}(\text{OEt})\text{py}_2\text{Cl}_2$ (Lock & Turner, 1977*a*) and $\text{Re}_2\text{O}_3\text{py}_4\text{Cl}_4$ (Lock & Turner, 1977*b*).

Three compounds containing ions of the type *trans*- ReO_2L_4 have had their crystal structures determined. $\text{K}_3\text{ReO}_2(\text{CN})_4$ has been examined by both neutron diffraction (Fenn, Graham & Johnson, 1971) and X-ray diffraction (Murmah & Schlemper, 1971) giving Re–O bond lengths of 1.773 (8) and 1.781 (3) Å respectively. $[\text{ReO}_2\text{en}_2]\text{Cl}$ has also been the subject of two previous structural determinations by X-ray diffraction, using visually estimated film data (Sergienko, Porai-Koshits & Khodaskova, 1974; Głowiak, Lis & Jeżowska-Trzebiatowska, 1972), giving values of 1.73 (4) and 1.75 (4) Å for the average Re–O bond length. $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ has an average bond length of 1.76 (3) Å (Calvo, Krishnamachari & Lock, 1971).

The ion $[\text{ReO}_2(\text{CN})_4]^{3-}$ has lower Re–O vibrational stretching frequencies than the $[\text{ReO}_2\text{en}_2]^+$ and

$[\text{ReO}_2\text{py}_4]^+$ ions, with a resultant smaller Re–O stretching-force constant. This ‘weaker’ Re–O bond has been explained in terms of the stronger π -acceptor properties of the CN^- ligand, relative to the en and py ligands. Such arguments are incorrect. An increase in the π -acceptor ability of the non-oxygen ligands would tend to increase the strength of the Re–O bond, since the O ligand has π -donor properties. The weaker Re–O bonds in the cyanide complex are more probably a result of the large difference in overall charge between the cyanide and amine complex ions. From our correlations between bond length and stretching-force constant, we would predict that the Re–O bond length in the complexes $[\text{ReO}_2\text{en}_2]\text{Cl}$ and $[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ would be about 0.02 Å shorter than the corresponding bond length in $\text{K}_3\text{ReO}_2(\text{CN})_4$. Such a shortening is probably beyond detection, because of the errors

Table 1. *Data collection and processing*

	$[\text{ReO}_2\text{en}_2]\text{Cl}$	$[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
Data collected	$h, k, \pm l$	$h, k, \pm l$
Maximum 2θ	55°	70°
Total number of reflections	3690	6266
Observed reflections	1952	4330
Unobserved reflections	673	918
Rejected reflections	147	745
Standard deviation of standard reflections	3.5%	1.9%

Table 2. *Additional crystal data*

	$[\text{ReO}_2\text{en}_2]\text{Cl}$	$[\text{ReO}_2\text{py}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
Crystal shape (faces)	{100}, {010}, {001}	(110) (1 $\bar{1}$ 0) (00 $\bar{1}$) (112) (112) (111) (111)
Distances of faces from centre of crystal (mm)	0.095 × 0.08 × 0.075	0.110 × 0.084 × 0.194 × 0.185 × 0.185 × 0.191 × 0.191
Formula weight	373.7	606.1
Absorption coefficient (cm ⁻¹)	131.2	58.6
Direction of crystal alignment	2° from a *	3° from c *

* Studies of the Rhenium–Oxygen Bond. IV.

involved in even the most accurate X-ray structural determinations of third-row transition-metal complexes.

[ReO₂en₂]Cl was prepared by the conventional method (Johnson, Lock & Wilkinson, 1964) and was recrystallized from 50% aqueous methanol at 5°C. [ReO₂py₄]Cl·2H₂O was prepared (Calvo *et al.*, 1971) and recrystallized from reagent-grade pyridine. For both compounds, small single crystals were chosen for X-ray measurements. Unit-cell parameters were obtained by least-squares refinement of 15 accurately centred reflections in the range 20° < 2θ < 30° on a Syntex P1 diffractometer. Intensity measurements were made at 22°C (graphite-monochromatized Mo Kα, λ = 0.71069 Å, ω-2θ scan). Scan rates were varied automatically from 2 to 24° min⁻¹, depending on the intensity of the reflection. A reflection was considered observed with $I > 3\sigma(I)$, unobserved, but used in subsequent calculations, with $3\sigma(I) > I > \sigma(I)$, and was rejected when $I \leq \sigma(I)$. Details of data collection and processing are shown in Table 1. For both compounds absorption corrections were applied, and secondary-extinction corrections (Larson, 1967) were used. The treatment of intensities, errors, and the application of the Lorentz-polarization correction have been discussed previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977).

Crystal data for both compounds are shown in the *Abstract* and Table 2. The structures of the compounds were refined* using the known atomic coordinates (Głowiak *et al.*, 1972; Calvo *et al.*, 1971) as initial parameters. Scattering curves for all elements were taken from *International Tables for X-ray Crystallog-*

raphy (1974) with anomalous-scattering corrections for Re and Cl taken from the same source.

Weighting schemes were introduced so that $w(|F_o| - |F_c|)^2$ was locally independent of F_o and $\sin \theta/\lambda$. Details of the refinements are shown in Table 3. Final atomic coordinates are listed in Table 4. Selected interatomic distances and angles for [ReO₂en₂]Cl are shown in Table 5, and for [ReO₂py₄]Cl·2H₂O in Table 6.*

* Lists of observed and calculated structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33119 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Atomic coordinates

[ReO ₂ en ₂]Cl			
	x	y	z
Re	0.24479 (6)	0.11021 (3)	0.23937 (2)
Cl	0.1539 (5)	0.7813 (3)	0.0530 (2)
O(1)	0.486 (1)	0.0044 (6)	0.2593 (5)
O(2)	0.002 (1)	0.2141 (6)	0.2192 (4)
N(1)	0.191 (1)	0.0635 (8)	0.1094 (5)
N(2)	0.485 (1)	0.2384 (8)	0.1978 (5)
N(3)	0.305 (1)	0.1555 (8)	0.3695 (5)
N(4)	0.008 (1)	0.9779 (7)	0.2846 (5)
C(1)	0.406 (2)	0.108 (1)	0.0740 (6)
C(2)	0.461 (2)	0.237 (1)	0.1050 (6)
C(3)	0.264 (2)	0.042 (1)	0.4186 (6)
C(4)	0.018 (2)	0.990 (1)	0.3747 (7)

[ReO ₂ py ₄]Cl·2H ₂ O			
	x	y	z
Re	0.0	0.0	0.0
Cl	-0.0666 (3)	0.3741 (2)	0.1262 (2)
O(1)	0.1035 (9)	-0.0795 (9)	-0.0137 (8)
O(2)	-0.0910 (8)	0.0844 (9)	0.0225 (7)
O(3)	0.2221 (6)	0.2854 (7)	0.4811 (6)
O(4)	0.0240 (9)	0.385 (1)	0.3551 (8)
N(1)	-0.046 (1)	-0.146 (1)	0.057 (1)
N(2)	-0.114 (1)	-0.029 (1)	-0.146 (1)
N(3)	0.061 (1)	0.145 (1)	-0.042 (1)
N(4)	0.122 (1)	0.039 (1)	0.142 (1)
C(11)	-0.100 (1)	-0.135 (1)	0.109 (1)
C(12)	-0.135 (2)	-0.225 (2)	0.147 (2)
C(13)	-0.105 (1)	-0.333 (1)	0.129 (1)
C(14)	-0.045 (1)	-0.340 (1)	0.082 (1)
C(15)	-0.015 (1)	-0.247 (1)	0.043 (1)
C(21)	-0.096 (2)	-0.111 (2)	-0.194 (1)
C(22)	-0.180 (2)	-0.137 (2)	-0.287 (1)
C(23)	-0.268 (1)	-0.066 (1)	-0.333 (1)
C(24)	-0.284 (1)	0.019 (1)	-0.277 (1)
C(25)	-0.203 (1)	0.039 (1)	-0.186 (1)
C(31)	0.123 (1)	0.133 (2)	-0.091 (1)
C(32)	0.157 (2)	0.124 (2)	-0.125 (1)
C(33)	0.131 (2)	0.333 (2)	-0.104 (1)
C(34)	0.072 (1)	0.347 (1)	0.051 (1)
C(35)	0.040 (1)	0.251 (1)	-0.020 (1)
C(41)	0.108 (1)	0.122 (1)	0.105 (1)
C(42)	0.173 (1)	0.143 (1)	0.290 (1)
C(43)	0.272 (1)	0.088 (1)	0.336 (1)
C(44)	0.292 (2)	0.002 (2)	0.289 (2)
C(45)	0.216 (1)	-0.020 (1)	0.188 (1)

Table 3. Refinement of the structures

	[ReO ₂ en ₂]Cl	[ReO ₂ py ₄]Cl·2H ₂ O
Number of variables	69	128
R ₁ *	0.0590	0.0498
R ₂ *	0.0483	0.0420
1/w	18.45 - 0.242 F _o + 0.00159 F _o ²	18.60 - 0.231 F _o + 0.00106 F _o ²
g†	9.8 × 10 ⁻⁷	2.48 × 10 ⁻⁸
Maximum shift in last cycle	0.02σ	0.2σ
Average shift in last cycle	0.003σ	0.05σ
Maximum peak in final difference synthesis	0.61 e Å ⁻³ , at 0.17, 0.11, 0.15	0.63 e Å ⁻³ , at 0.08, 0.07, 0.10
Minimum valley in final difference synthesis	-0.54 e Å ⁻³ at 0.27, 0.12, 0.18	-0.72 e Å ⁻³ at -0.11, -0.09, 0.02 (0.7 Å from Re)

*R₁ = Σ||F_o| - |F_c||/Σ|F_o|; R₂ = [Σ w(|F_o| - |F_c|)²/Σ w|F_o|²]^{1/2}.

† g is the secondary-extinction parameter (Larson, 1967).

Table 5. Selected interatomic distances (Å) and angles (°) for [ReO₂en₂]Cl

Re—O(1)	1.769 (7)	Re—N(3)	2.152 (8)	N(3)—C(3)	1.53 (1)
Re—O(2)	1.761 (7)	Re—N(4)	2.191 (8)	N(4)—C(4)	1.47 (1)
Re—N(1)	2.154 (8)	N(1)—C(1)	1.51 (2)	C(1)—C(2)	1.53 (2)
Re—N(2)	2.150 (9)	N(2)—C(2)	1.50 (1)	C(3)—C(4)	1.54 (2)
O(1)—Re—O(2)	179.3 (3)	O(2)—Re—N(4)	90.4 (3)	Re—N(2)—C(2)	111.8 (6)
O(1)—Re—N(1)	89.1 (3)	N(1)—Re—N(2)	80.0 (3)	Re—N(3)—C(3)	108.5 (6)
O(1)—Re—N(2)	89.7 (3)	N(3)—Re—N(4)	79.3 (3)	Re—N(4)—C(4)	111.4 (6)
O(1)—Re—N(3)	90.0 (3)	N(1)—Re—N(4)	101.0 (3)	N(1)—C(1)—C(2)	107.5 (9)
O(1)—Re—N(4)	89.0 (3)	N(2)—Re—N(3)	99.7 (3)	N(2)—C(2)—C(1)	108.5 (9)
O(2)—Re—N(1)	90.7 (3)	N(1)—Re—N(3)	179.0 (3)	N(3)—C(3)—C(4)	105.6 (8)
O(2)—Re—N(2)	90.9 (3)	N(2)—Re—N(4)	178.4 (3)	N(4)—C(4)—C(3)	111.3 (9)
O(2)—Re—N(3)	90.3 (3)	Re—N(1)—C(1)	109.1 (6)		
Possible hydrogen-bonding distances					
Cl—N(1)	3.25 (1)	Cl—N(1)'	3.41 (1)	O(2)—N(2)'	2.86 (1)
Cl—N(3)	3.37 (1)	O(1)—N(4)	2.88 (1)	O(2)—N(4)'	2.92 (1)
Cl—N(3)'	3.36 (1)	O(1)—N(2)	3.02 (1)		

Table 6. Selected interatomic distances (Å) and angles (°) in [ReO₂py₄]Cl·2H₂O

Re—O(1)	1.782 (13)	Re—N(1)	2.166 (14)	Re—N(3)	2.143 (12)
Re—O(2)	1.745 (12)	Re—N(2)	2.143 (12)	Re—N(4)	2.139 (9)
Non-bonded distances					
Cl—O(3)	3.346 (8)	Cl—O(4)	3.20 (1)	O(1)—O(3)	2.96 (2)
O(2)—O(3)	2.79 (1)	O(3)—O(4)	2.79 (1)		
Pyridine rings					
	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 4	
N(<i>i</i>)—C(<i>i</i> 1)	1.32 (2)	1.31 (3)	1.37 (3)	1.36 (2)	
C(<i>i</i> 1)—C(<i>i</i> 2)	1.41 (3)	1.42 (2)	1.37 (3)	1.37 (2)	
C(<i>i</i> 2)—C(<i>i</i> 3)	1.41 (3)	1.39 (2)	1.42 (3)	1.38 (2)	
C(<i>i</i> 3)—C(<i>i</i> 4)	1.33 (3)	1.41 (2)	1.40 (3)	1.36 (3)	
C(<i>i</i> 4)—C(<i>i</i> 5)	1.40 (3)	1.37 (2)	1.38 (2)	1.47 (3)	
C(<i>i</i> 5)—N(<i>i</i>)	1.33 (2)	1.34 (2)	1.38 (2)	1.35 (3)	
O(1)—Re—O(2)	174.5 (4)	O(2)—Re—N(1)	91.7 (6)	N(1)—Re—N(3)	173.9 (4)
O(1)—Re—N(1)	90.0 (6)	O(2)—Re—N(2)	93.3 (5)	N(1)—Re—N(4)	89.0 (4)
O(1)—Re—N(2)	91.6 (5)	O(2)—Re—N(3)	89.9 (5)	N(2)—Re—N(3)	90.2 (5)
O(1)—Re—N(3)	87.9 (5)	O(2)—Re—N(4)	87.9 (5)	N(2)—Re—N(4)	175.2 (6)
O(1)—Re—N(4)	87.0 (5)	N(1)—Re—N(2)	95.6 (5)	N(3)—Re—N(5)	85.2 (4)
Re—N(1)—C(11)	121 (1)	Re—N(2)—C(21)	119 (1)	Re—N(3)—C(31)	120 (1)
Re—N(1)—C(15)	121 (1)	Re—N(2)—C(25)	118 (1)	Re—N(3)—C(35)	121 (1)
Re—N(4)—C(14)	122 (1)	Re—N(4)—C(45)	123 (1)		
Pyridine rings					
	<i>i</i> = 1	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 4	
C(<i>i</i> 1)—N(<i>i</i>)—C(<i>i</i> 5)	119 (1)	123 (1)	119 (1)	115 (1)	
N(<i>i</i>)—C(<i>i</i> 1)—C(<i>i</i> 2)	124 (1)	118 (1)	121 (2)	126 (1)	
C(<i>i</i> 1)—C(<i>i</i> 2)—C(<i>i</i> 3)	116 (1)	120 (2)	119 (2)	119 (2)	
C(<i>i</i> 2)—C(<i>i</i> 3)—C(<i>i</i> 4)	118 (1)	117 (1)	120 (2)	118 (2)	
C(<i>i</i> 3)—C(<i>i</i> 4)—C(<i>i</i> 5)	123 (1)	119 (1)	118 (1)	120 (2)	
C(<i>i</i> 4)—C(<i>i</i> 5)—N(<i>i</i>)	119 (1)	120 (2)	123 (2)	121 (1)	

Discussion. The structure of [ReO₂en₂]Cl has been discussed previously (Głowiak *et al.*, 1972; Sergienko *et al.*, 1974) and our atomic coordinates do not differ significantly from the previous refinements, though our e.s.d.'s are considerably lower. On the basis of these

more accurate data we can say that the average Re—O bond length is 1.765 (7) Å. The two independent Re—O bond lengths [1.769 (7) and 1.761 (7) Å] do not differ significantly, and there is no need to invoke hydrogen bonding to explain the difference in Re—O bond

lengths (*contra* Sergienko *et al.*, 1974). Bond lengths and angles within the ethylenediamine ligands are normal [C—C bond lengths 1.53 (2), 1.54 (2) Å, C—N bond lengths 1.47 (1)–1.53 (1) Å, bond angles in the range 107 (1)–111 (1)°]. The chloride ion is weakly hydrogen bonded to four N atoms [3.25 (1)–3.41 (1) Å]. The packing in the structure has previously been discussed in some detail (Sergienko *et al.*, 1974).

The structure of [ReO₂py₄]Cl·2H₂O has also been discussed previously (Calvo *et al.*, 1971) and our parameters do not differ significantly from the previous parameters, although our e.s.d.'s are considerably lower. The two independent Re—O bonds [1.782 (13) and 1.745 (12) Å] do not differ at the 3σ confidence level, although they do at the 2σ level. The Re—N distances obtained for both the pyridine and ethylenediamine complexes are in good agreement with previous values obtained for Re—N single bonds (Lock & Turner, 1977*a,b*). Although the atoms within the pyridine rings were allowed to vary independently, the bond lengths and angles obtained are in excellent agreement with the expected values (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). The 'edge on' configuration of the pyridine rings, and the slight tilt (~10°) of these rings from idealized *D*_{4h} symmetry are discussed in some detail elsewhere (Calvo *et al.*, 1971). The important steric requirement of pyridine rings, particularly the effects of the α-hydrogen, has also been discussed (Lock & Turner, 1977*b*). The two water molecules are necessary in the formation of the structure. The anhydrous compound can be prepared only with difficulty, and no evidence was ever found of a monohydrate (*contra* Beard, Calhoun, Casey &

Murmann, 1968) although an oxidation product, [ReO₂py₄](ReO₄), (orthorhombic orange prisms) was obtained from aqueous solutions of [ReO₂py₄]Cl·2H₂O. The structure is held together by weak hydrogen bonds between the chloride ions, water molecules and pyridine rings (see Table 6 for distances).

The values obtained for the Re—O bond lengths in these compounds, 1.765 (7) Å (average) for [ReO₂en₂]Cl and 1.764 (13) Å (average) for [ReO₂py₄]Cl·2H₂O, are very close to the value predicted from correlations between bond length and force constant (1.762 Å) (Turner, 1976). The bond length obtained for the ethylenediamine complex is shorter than the Re—O bond in K₃ReO₂(CN)₄ [1.781 (3) Å] at the 95% confidence level. According to the model of π-bonding from filled oxygen *p* orbitals to empty orbitals (*d*_{zz} and *d*_{yz}) on the Re atom (Johnson *et al.*, 1964) the complexes [ReO₂en₂]Cl and [ReO₂py₄]Cl·2H₂O contain genuine Re—O double bonds. Using a value of 2.04 Å for a Re—O single bond [derived from the sum of covalent radii (Cotton & Lippard, 1965)] it is now possible to derive Pauling bond orders for Re—O bonds.

Selected values of bond orders for Re—O compounds are shown in Table 7.

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Table 7. Bond lengths and bond orders

Compound	Re—O bond length (Å)	Bond order*	Reference
Sum of Re ^v —O covalent radii	2.04	1.00*	<i>a</i>
[ReO ₂ en ₂]Cl	1.765 (7)	2.00*	<i>b</i>
KReO ₄	1.723 (4)	2.23	<i>c</i>
K ₃ ReO ₂ (CN) ₄	1.781 (3)	1.92	<i>d</i>
ReO(OEt)Cl ₂ py ₂	1.684 (7)	2.45	<i>e</i>
	1.896 (6)	1.44	
[Pt(NH ₃) ₄] ₂ [Re ₂ O ₃ (CN) ₈]	1.698 (7)	2.37	<i>f</i>
	1.915 (1)	1.37	
ReOCl ₄ (H ₂ O)	1.63 (2)	2.81	<i>g</i>
	2.27 (2)	0.56	
[ReO(OH)en ₂][ClO ₄] ₂	1.72 (1)	2.24	<i>h</i>
	1.832 (8)	1.69	

References: (*a*) Cotton & Lippard (1965); (*b*) this work; (*c*) Lock & Turner (1975); (*d*) Murmann & Schlemper (1971); (*e*) Lock & Turner (1977*a*); (*f*) Shandles, Schlemper & Murmann (1971); (*g*) Fraiss & Lock (1972); (*h*) Betzner, Brown, Lock, Park & Turner (1977).

* Bond order defined by Pauling equation, bond length = *A* + *B* ln(bond order). *A*, *B* are defined by fixing Re—O single and double bonds.

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Sodium 5,6-Dihydro-2-thiouracil-6-sulfonate Monohydrate

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Abstract. C₄H₇N₂O₅S₂Na, monoclinic, $P2_1/c$, $Z = 4$, $a = 13.101$ (4), $b = 7.043$ (3), $c = 9.654$ (5) Å, $\beta = 101.98$ (4)°, $D_m = 1.90$ (1), $D_c = 1.90$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $R = 0.033$ for 2045 observed reflections. This is the product of a bisulfite addition reaction of 2-thiouracil at pH 8. The sulfonate group is found attached axially at the 6-position of the thiouracil.

Introduction. The title compound was prepared by addition of bisulfite ion to 2-thiouracil. Preliminary precession photographs of the crystals obtained from aqueous solution showed monoclinic symmetry and extinction patterns ($0k0$ reflections absent when k odd, $h0l$ reflections absent when l odd) consistent with the space group $P2_1/c$. The calculated density for $Z = 4$ agreed with the experimental density obtained by flotation in a monobromoethane–chloroform mixture. A small crystal (0.4 × 0.2 × 0.2 mm) was then mounted on a Syntex $P2_1$ diffractometer. Accurate cell dimensions were determined from a least-squares fit of 2θ , ω , φ and χ for 15 reflections with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Data were collected with a θ – 2θ scan technique, the details of which have been reported (Seccombe, Lee & Henry, 1975). 2642 reflections were measured with $2\theta \leq 60^\circ$ of which 2045 had $I \geq 3\sigma(I)$ and were used for data analysis. The data were then corrected for the 1.8% decay that was observed, and reduced to the structure factor amplitudes by the application of the Lorentz–polarization correction. Because of the small linear absorption coefficient, 3.39 cm⁻¹, and the small size of the crystal, no absorption or extinction correction was made.

The positions of the S and Na atoms were found from a Patterson map. All other atoms, including H, were found in subsequent electron density and difference electron density maps. For the refinement, all non-hydrogen atoms were treated with anisotropic thermal parameters and all H atoms with fixed isotropic thermal parameters. The final discrepancy indices were $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.033$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.042$.

The positional and isotropic thermal parameters are given in Table 1 with their estimated standard

Table 1. Positional ($\times 10^5$; for H $\times 10^3$) and isotropic thermal (\AA^2) parameters with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
S(1)	15760 (4)	73961 (8)	11856 (6)	1.24 (6)
S(2)	35651 (4)	23543 (7)	-4964 (5)	1.93 (5)
Na	49649 (7)	1112 (11)	25919 (9)	1.94 (9)
O(1)	36431 (12)	5781 (22)	-12501 (16)	1.72 (17)
O(2)	43941 (11)	25652 (21)	7689 (14)	2.13 (15)
O(3)	34528 (12)	39906 (23)	-14219 (16)	2.35 (17)
O(4)	4164 (12)	32891 (25)	-29360 (15)	2.24 (18)
O(w)	40357 (13)	76443 (25)	12326 (17)	1.50 (18)
N(1)	22447 (13)	39237 (26)	9063 (17)	1.84 (18)
N(3)	10175 (14)	50569 (27)	-9873 (18)	1.34 (19)
C(2)	16249 (15)	53378 (29)	3377 (21)	1.47 (20)
C(4)	9205 (15)	33624 (31)	-17239 (20)	1.57 (21)
C(5)	14085 (16)	16806 (30)	-9085 (22)	1.58 (21)
C(6)	23815 (16)	21612 (29)	1978 (20)	2.08 (19)
H($w,1$)	341 (3)	763 (5)	115 (4)	3.29
H($w,2$)	408 (3)	774 (5)	48 (4)	3.29
H(1)	258 (3)	414 (5)	163 (3)	2.12
H(2)	63 (3)	609 (5)	-136 (3)	2.85
H(5,1)	87 (3)	137 (5)	-43 (3)	2.34
H(5,2)	154 (3)	72 (4)	-154 (3)	2.34
H(6)	251 (2)	112 (5)	89 (3)	2.06

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