Reduction of OsO_4 by some Imidazolidine-2-thiones. *X*-Ray Crystal Structure of *trans*-Dichlorotetrakis(*NN'*-diethylimidazolidine-2-thione)-osmium(IV) Diperchlorate †

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Osmium tetroxide is reduced to an Os^{III} complex by reaction with some *N*-monosubstituted imidazolidine-2-thiones in H_2O–EtOH in the presence of $HClO_4$. In order to clarify the mechanism of this reduction, *NN'*-dimethyl- and *NN'*-diethyl-imidazolidine-2-thiones (L), with low reducing power, were employed. Intermediate species of Os^{VI} and Os^{IV} with formulae $[OsO_2L_4][ClO_4]_2$ and $[OsCl_2L_4][ClO_4]_2$ were isolated. The title compound crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 11.845(2)$, $b = 10.451(2)$, $c = 9.376(3)$ Å, $\alpha = 70.659(9)$, $\beta = 86.670(9)$, $\gamma = 86.708(5)$°, and $Z = 1$. The structure was solved by the heavy-atom method and refined by least-squares calculations to a conventional *R* factor of 0.023 for 4 087 counter data. It consists of discrete *trans*-dichlorotetrakis-(*NN'*-dimethylimidazolidine-2-thione)osmium(IV) dications, in which the metal atom is bonded in a nearly idealized octahedral geometry to four S and two *trans* Cl atoms, and of disordered ClO_4^- anions. The i.r.-active $\nu_{asym.}(OsCl_2)$ is assigned at *ca.* 300 cm^{-1} for the $[OsCl_2L_4][ClO_4]_2$ complexes.

Thiourea reacts with OsO_4 in H_2O–EtOH solutions, using $HClO_4$ as acid, to form a complex in which the metal is reduced to +3 and is octahedrally surrounded by six molecules of thiourea, bonded through the sulphur atom. In the same way, variously substituted thioureas, selenourea, *N*-monosubstituted imidazolidine-2-thiones and -2-selones react with OsO_4 to give similar osmium(III) complexes with different kinetic laws.[1-4] In order to clarify the reduction mechanism $Os^{VIII} \longrightarrow Os^{III}$, we have undertaken a new investigation employing *NN'*-dimethyl- and *NN'*-diethyl-imidazolidine-2-thione (L) which have a low reducing power. With these, the reaction yields $[Os^{VI}O_2L_4]^{2+}$ complexes, which when employed as substrates in place of OsO_4 in the above reaction, give the identical specific rate constants and the same final Os^{III} complexes;[5] thus giving evidence in favour of reaction (i) for the *N*-monosubstituted imidazolidines.

$$Os^{VIII} \xrightarrow{\text{fast}} Os^{VI} \xrightarrow{\text{slow}} Os^{III} \qquad \text{(i)}$$

Furthermore, if the osmylic complexes, $[OsO_2L_4][ClO_4]_2$, are not separated from the reaction medium, after some days it is possible to separate violet crystals which we thought were osmium(III) complexes of formula $[OsL_4][ClO_4]_3$ on the basis of the elemental analysis. Since the crystals obtained with *NN'*-diethylimidazolidine-2-thione were suitable, we carried out an *X*-ray crystal-structure determination.

Results and Discussion

Unexpectedly, the *X*-ray structure showed the complex to be *trans*-dichlorotetrakis(*NN'*-diethylimidazolidine-2-thione)-osmium(IV) diperchlorate (see Figure). Contrary to expectations the complexes have general formula $[OsCl_2L_4][ClO_4]_2$ and are octahedrally surrounded by four ligands and two *trans*-chlorides. Since no chloride ion was added in the reaction medium, it must have originated in a reduction of the perchlorate ion.

The structure consists of discrete *trans*-tetrakis(*NN'*-diethylimidazolidine-2-thione)osmium(IV) dications and disordered ClO_4^- anions, separated by normal van der Waals distances. The co-ordination geometry around the Os atom, which lies on an inversion centre, is nearly a perfect octahedron, with the largest deviation from 90° in bond angles and in dihedral angles between four-donor co-ordination planes being 1.0°. The Os–Cl and Os–S bond distances are almost similar, and compare well with those previously reported for mono- and poly-nuclear osmium complexes.[6-9]

There are no significant differences between the dimensions of the two crystallographically independent *NN'*-diethylimidazolidine-2-thione ligands, whose internal geometries are consistent with those previously observed in several complexes with analogous heterocyclic penta-atomic ligands.[10-12] However, a significant feature appears, *i.e.* the lengthening of the C–S bond distances [mean value 1.744(3) Å], whose values average 1.69 Å in the above cited metal complexes.[10-12]

Bond distances and angles within the perchlorate ion, which was treated as a disordered model arising from a rotational motion about one Cl–O bond,[13,14] show marked variations and appear acceptable only as mean values.

The shortest interionic contacts in the structure, which range from 3.11 to 3.21 Å, are between the oxygens of the perchlorate group and the ethyl carbon atoms.

The S co-ordination to osmium leaves the structural parameters of the ligand unchanged, except for a lengthening of the C–S bond, which is longer than that reported by Wheatley[15] for imidazolidine-2-thione and found by us in some complexes of similar penta-atomic rings with copper(I) and mercury(II).[10-12]

In the fingerprint region of the i.r. spectra, $[OsCl_2L_4][ClO_4]_2$ showed the typical behaviour of the *S*-bonded complexes. In particular, the upward and downward shifts of *ca.* 60 and 23 cm^{-1} for $\nu(CN)$ and $\nu(CS)$ respectively are observed. Since the complexes show a very low distortion from the local D_{4h} symmetry, only one Os–Cl stretching vibration is expected which was found at *ca.* 300 cm^{-1}. As far as the ClO_4^- ion is concerned, the bond distances Cl–O indicate a lowering of the symmetry from T_d to C_s; this explains the fact that the ν_3 and ν_4 absorptions are multiplets.

Once again, we have found that the disubstituted imidazol-

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† *Supplementary data available* (No. SUP 23576, 32 pp.): structure factors, thermal parameters, least-squares planes, H-atom co-ordinates, H-bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

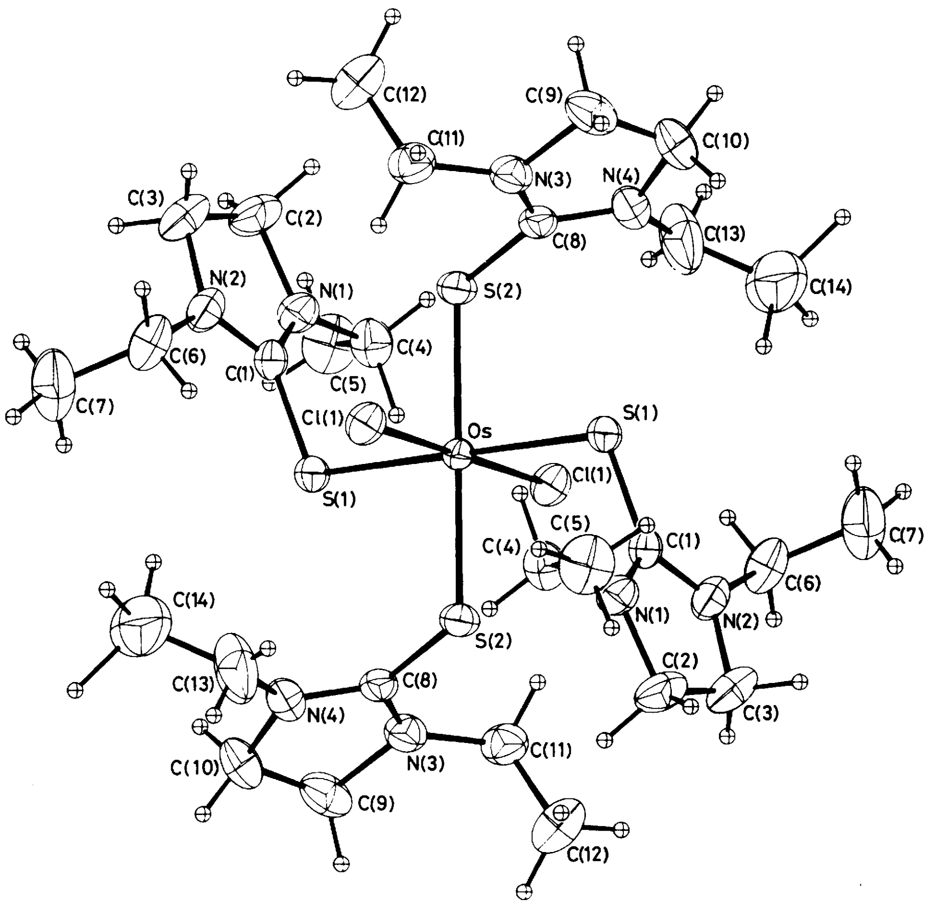

Figure. ORTEP view of the *trans*-dichlorotetrakis(*NN'*-diethylimidazolidine-2-thione)osmium(IV) dication, showing the labelling scheme and thermal motion ellipsoids at the 40% probability level. The hydrogen atoms are represented as spheres of arbitrary radius

idine-2-thiones differ from the monosubstituted derivatives, as previously found for their complexes with copper(I) and mercury(II), which showed different stoicheiometries.[13,16] In the osmium complexes, we recognise strong differences between the *N*-mono- and *NN'*-di-substituted imidazolidines both in their kinetic behaviour and in the fact that they stabilize different oxidation states. In fact, in the case of the *N*-monosubstituted imidazolidines the reduction of Os^{VIII} proceeds quickly to $[OsL_6]^{3+}$, whereas, for the *NN'*-disubstituted ligands we may obtain both the Os^{VI} and Os^{IV} complexes, as $[OsO_2L_4]^{2+}$ and $[OsCl_2L_4]^{2+}$.

Experimental

Preparation of the Complexes.—By reacting OsO_4 (0.05 mol) with *NN'*-dimethyl- or *NN'*-diethyl-imidazolidine-2-thione (0.6 mol) in EtOH and $HClO_4$ (2 mol dm^{-3}) at room temperature, light brown complexes of formula $[OsO_2L_4][ClO_4]_2$ are precipitated with diethyl ether after 30 min. If the osmylic complexes are not separated by precipitation, a further reduction occurs and after two days violet crystals are obtained. Elemental analysis for the *NN'*-dimethylimidazolidine-2-thione complex: Found: C, 24.0; H, 4.2; N, 11.1; S, 13.0. Calc. for $C_{20}H_{40}Cl_4N_8O_8OsS_4$: C, 24.5; H, 4.1; N, 11.4; S, 13.1%; and for the *NN'*-diethylimidazolidine-2-thione complex: Found: C, 30.4; H, 5.2; N, 10.2; S, 11.4. Calc. for $C_{28}H_{56}Cl_4N_8O_8OsS_4$: C, 30.8; H, 5.2; N, 10.3; S, 11.7%.

Infrared Measurements.—The i.r. spectra were recorded on a Perkin-Elmer 325 instrument in the range 4 000—200 cm^{-1} using KBr discs (4 000—400 cm^{-1}) and Nujol mulls between CsI discs (450—200 cm^{-1}).

Crystal Data.—$C_{28}H_{56}Cl_4N_8O_8OsS_4$, M = 1 093.16, Triclinic, a = 11.845(2), b = 10.451(2), c = 9.376(3) Å, α = 70.659(9), β = 86.670(9), γ = 86.708(5)°, U = 1 092.4 Å^3, space group $P\bar{1}$, D_m = 1.65 g cm^{-3}, Z = 1, D_c = 1.66 g cm^{-3}, $F(000)$ = 551.9, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 32.4 cm^{-1}, crystal dimensions 0.38 × 0.24 × 0.14 mm.

Structure Analysis.—Intensity data were collected at room temperature on an automated Philips PW 1100 four-circle diffractometer with the ω–2θ scan technique up to $\theta \leqslant 26°$. The intensities of two standard reflections, monitored at 120-reflection intervals, showed no significant changes. All data were corrected for Lorentz and polarization effects and an absorption correction was applied (calculated transmission coefficients range from 0.47 to 0.63). A total of 4 236 independent reflections were measured, of which 4 087 reflections with $I > 3\sigma(I)$ were denoted observed and used in the structure determination.

The structure was solved by conventional Patterson and Fourier methods; full-matrix least-squares refinement of positional and anisotropic thermal parameters for all the non-hydrogen atoms, and of positional parameters for the hydrogen

Table 1. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os	0.5	0.5	0.5	C(9)	0.892 3(5)	0.772 2(5)	0.364 4(7)
Cl(1)	0.477 0(1)	0.416 6(1)	0.299 8(1)	C(10)	0.862 2(6)	0.771 8(6)	0.211 0(7)
S(1)	0.480 5(1)	0.275 5(1)	0.675 7(1)	N(4)	0.792 2(4)	0.652 3(4)	0.245 3(4)
C(1)	0.616 4(4)	0.205 1(4)	0.721 1(5)	C(11)	0.828 6(4)	0.628 0(6)	0.631 9(6)
N(1)	0.678 0(3)	0.139 7(4)	0.643 6(5)	C(12)	0.927 0(6)	0.528 8(7)	0.689 2(8)
C(2)	0.791 0(5)	0.102 2(7)	0.706 4(7)	C(13)	0.763 7(8)	0.593 6(8)	0.131 5(7)
C(3)	0.780 5(5)	0.136 1(7)	0.848 8(7)	C(14)	0.714 7(8)	0.690 5(12)	−0.001 8(9)
N(2)	0.669 4(4)	0.209 6(4)	0.840 3(4)	Cl(2)	0.942 6(1)	0.170 8(1)	0.194 7(2)
C(4)	0.650 7(5)	0.118 2(5)	0.503 7(6)	O(1)	0.936 3(8)	0.292 6(8)	0.078 5(7)
C(5)	0.656 1(6)	−0.029 9(6)	0.520 5(8)	O(2A) *	0.832 6(9)	0.128 3(15)	0.214 5(16)
C(6)	0.623 3(6)	0.258 4(6)	0.960 7(6)	O(3A)	0.997 5(9)	0.063 5(11)	0.131 7(12)
C(7)	0.573 2(8)	0.148 6(8)	1.093 2(7)	O(4A)	0.984 1(14)	0.140 9(13)	0.333 6(13)
S(2)	0.698 3(1)	0.453 8(1)	0.482 3(1)	O(2B)	1.058 6(12)	0.183 4(19)	0.183 8(21)
C(8)	0.771 5(4)	0.601 1(4)	0.393 6(5)	O(3B)	0.912 4(18)	0.229 5(22)	0.324 0(20)
N(3)	0.820 5(3)	0.667 8(4)	0.468 5(4)	O(4B)	0.880 4(32)	0.081 4(19)	0.185 8(25)

* The refined occupancy factors of the A- and B-labelled oxygen atoms are 0.62 and 0.38, respectively.

Table 2. Bond distances (Å) and angles (°) involving non-hydrogen atoms with estimated standard deviations in parentheses

Os–Cl(1)	2.351(1)	C(3)–N(2)	1.477(5)	Os–S(2)	2.378(1)	C(10)–N(4)	1.475(5)
Os–S(1)	2.394(1)	N(2)–C(6)	1.453(5)	S(2)–C(8)	1.742(3)	N(4)–C(13)	1.459(6)
S(1)–C(1)	1.747(3)	C(4)–C(5)	1.502(6)	C(8)–N(3)	1.317(4)	C(11)–C(12)	1.512(6)
C(1)–N(1)	1.318(4)	C(6)–C(7)	1.504(8)	C(8)–N(4)	1.327(4)	C(13)–C(14)	1.450(10)
C(1)–N(2)	1.328(4)	Cl(2)–O(1)	1.376(6)	N(3)–C(9)	1.473(5)	Cl(2)–O(2B)	1.38(1)
N(1)–C(2)	1.473(5)	Cl(2)–O(2A)	1.38(1)	N(3)–C(11)	1.456(5)	Cl(2)–O(3B)	1.54(2)
N(1)–C(4)	1.459(5)	Cl(2)–O(3A)	1.53(1)	C(9)–C(10)	1.503(7)	Cl(2)–O(4B)	1.25(2)
C(2)–C(3)	1.487(7)	Cl(2)–O(4A)	1.35(1)				

S(1)–Os–S(2)	89.00(5)	N(2)–C(6)–C(7)	113.3(4)	C(9)–C(10)–N(4)	103.6(3)
Cl(1)–Os–S(1)	89.53(5)	O(1)–Cl(2)–O(2A)	103(1)	C(10)–N(4)–C(8)	109.6(3)
Os–S(1)–C(1)	107.6(1)	O(1)–Cl(2)–O(3A)	108(1)	C(8)–N(3)–C(11)	126.6(3)
S(1)–C(1)–N(1)	124.5(3)	O(1)–Cl(2)–O(4A)	130(1)	C(9)–N(3)–C(11)	121.6(3)
S(1)–C(1)–N(2)	123.6(3)	O(2A)–Cl(2)–O(3A)	99(1)	N(3)–C(11)–C(12)	112.4(4)
N(1)–C(1)–N(2)	111.9(3)	O(2A)–Cl(2)–O(4A)	107(1)	C(8)–N(4)–C(13)	126.8(4)
C(1)–N(1)–C(2)	110.4(3)	O(3A)–Cl(2)–O(4A)	105(1)	C(10)–N(4)–C(13)	123.2(4)
N(1)–C(2)–C(3)	103.3(4)	Cl(1)–Os–S(2)	89.21(5)	N(4)–C(13)–C(14)	114.2(7)
C(2)–C(3)–N(2)	103.9(3)	Os–S(2)–C(8)	111.8(1)	O(1)–Cl(2)–O(2B)	87(1)
C(3)–N(2)–C(1)	109.7(3)	S(2)–C(8)–N(3)	123.1(3)	O(1)–Cl(2)–O(3B)	96(1)
C(1)–N(1)–C(4)	127.9(3)	S(2)–C(8)–N(4)	124.3(3)	O(1)–Cl(2)–O(4B)	116(1)
C(2)–N(1)–C(4)	121.3(3)	N(3)–C(8)–N(4)	112.4(3)	O(2B)–Cl(2)–O(3B)	100(1)
N(1)–C(4)–C(5)	111.4(4)	C(8)–N(3)–C(9)	110.2(3)	O(2B)–Cl(2)–O(4B)	133(2)
C(1)–N(2)–C(6)	127.4(3)	N(3)–C(9)–C(10)	103.2(3)	O(3B)–Cl(2)–O(4B)	116(2)
C(3)–N(2)–C(6)	122.3(3)				

atoms (previously located in difference maps) led to convergence at $R = 0.032$ and $R' = 0.036$. At this stage a difference synthesis showed evidence of disorder among the perchlorate oxygen atoms. Further least-squares refinement, in which the perchlorate group was treated as a disordered model, led to final convergence at $R = 0.023$ and $R' = 0.025$. Unit weights were used at all stages; no trend of $\Sigma w(|F_o|-|F_c|)^2$ *vs.* $|F_o|$, sin θ, or Miller indices was observed. Correction for secondary extinction was not deemed necessary.

Complex neutral-atom scattering factors[17] were employed throughout; major calculations were carried out on a CDC Cyber 7600 computer using the SHELX 76 program package[18] and the ORTEP plotting program.[19]

Final fractional co-ordinates of the non-hydrogen atoms are given in Table 1, and bond distances and angles in Table 2.

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