Complexation of a Tetradentate Tetra-anionic Ligand to Osmium(IV): a Step Towards the Development of Multianionic Chelating Ligands for Use in Stabilizing Oxidizing Inorganic Complexes

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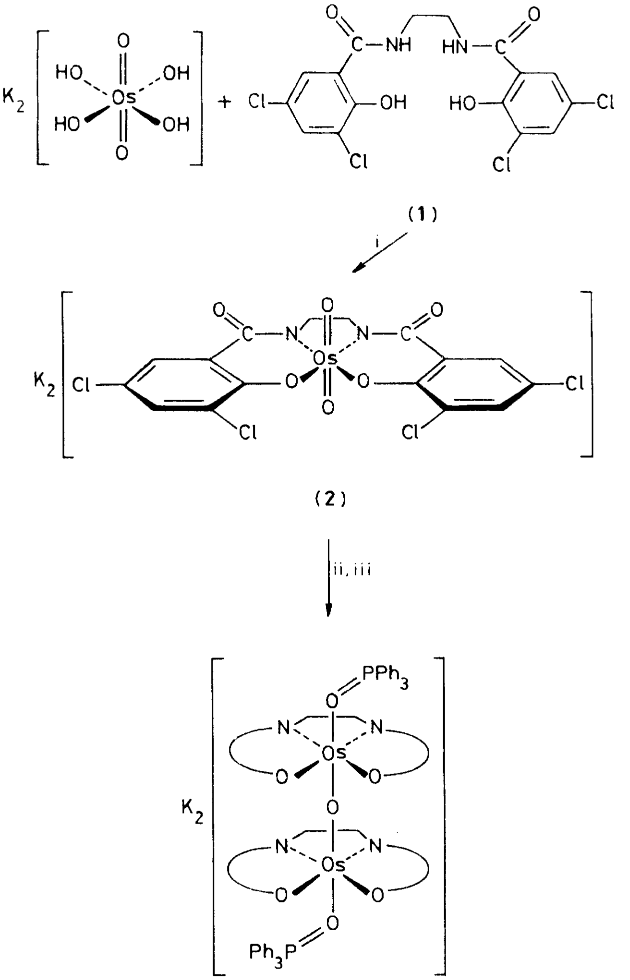
The compound 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [H_4(chba-Et)] (**1**) readily co-ordinates to osmium(VI) as a tetradentate tetra-anion; the *X*-ray crystal structure of the reduced complex, $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{–}O]$ (**3**), demonstrates that this ligand can bind as a tetradentate tetra-anion to the equatorial sites of a single octahedral metal centre and the potassium ion is found in two unusual co-ordination environments in complex (**3**).

The variety of useful inorganic oxidizing agents presently available is limited by the lack of suitable ligands which can form stable highly oxidizing metal complexes. We are interested in exploring new reactivity in oxidation chemistry and our approach has been to design multianionic chelating ligands to generate new highly oxidizing inorganic complexes. The co-ordination chemistry of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane [H_4(chba-Et)], (**1**) (see Scheme 1), has been investigated as a test case in our work. The ligand (**1**) has been designed to be reasonably resistant to oxidation, to form five- and six-membered chelate rings upon co-ordination, to be easily synthesized and derivatized, and to contain the organic amide functional group which is known to stabilize high oxidation states when *N*-co-ordinated.[1]

We have recently shown[2] that it is possible to co-ordinate (**1**) as a bridging ligand between two chromium(III) centres in which both types of monodentate organic amide co-ordination were found. In this paper we report that it is also possible to co-ordinate (**1**) as a tetradentate tetra-anion to a single metal centre, an important preliminary objective.

Treatment of a colourless acetone solution of (**1**) with a blue solution of $K_2[OsO_2(OH)_4]$ dissolved in methanol results in a colour change to orange. Removal of solvents *in vacuo* followed by recrystallization of the residue from ethanol–diethyl ether affords a quantitative yield of the orange microcrystalline salt $K_2[OsO_2(\eta^4\text{-chba-Et})]$ (**2**).† This octahedral *trans*-dioxo osmium(VI) complex is diamagnetic as expected.[3] Reduction of this compound with triphenylphosphine (2.5 mol per mol of osmium) in tetrahydrofuran followed by addition of CH_2Cl_2 resulted on one occasion in the deposition of dark crystals of the μ-oxo bridged osmium(IV) dinuclear species, $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{–}O]$ (**3**), which has been characterized by an *X*-ray crystal structure determination.

Crystal data for (**3**): $C_{68}H_{46}Cl_8K_2N_4O_{12}Os_2P_2\cdot\frac{3}{2}C_3H_6O\cdot H_2O$, $M = 2004.45$, monoclinic, space group $P2_1/c$, $a = 18.72(1)$, $b = 15.290(9)$, $c = 28.24(2)$ Å, $\beta = 107.49(5)°$, $U = 7709(9)$ Å^3, $Z = 4$, $D_c = 1.727(2)$ g cm^{-3}, $\mu = 3.98$ mm^{-1}; data ($+h$, $+k$, $\pm l$) were collected on a locally modified Syntex $P2_1$ diffractometer with Mo-K_α radiation ($\lambda = 0.7107$ Å) up to $2\theta = 36°$; a total of 6065 intensity measurements were made with 6° min^{-1} θ–2θ scans. The three standard reflections, remeasured after each block of 97 reflections, indicated a 16% linear decay. The data were corrected for decomposition, but not for absorption; averaging gave 5331 reflections, 4900 with $I > 0$ and 3411 with $I > 3\sigma(I)$.



Scheme 1. i, Acetone–MeOH; ii, Ph_3P, heat; iii, acetone–tetrahydrofuran–O_2.

The positions of the osmium atoms were derived from a Patterson map, and the subsequent Fourier and difference Fourier maps indicated the locations of the remaining non-hydrogen atoms; the hydrogen atoms were placed at calculated positions and were not refined. The Gaussian amplitudes of the μ-oxo and H-atom co-ordinates ($U = 0.035$ and 0.063 Å^2) and the population of the unco-ordinated acetone molecule (set to 0.5) were not refined either. The final cycle of refinement gave a goodness-of-fit of 2.03 and

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† Satisfactory elemental analyses were obtained. I.r. (ν, cm^{-1}) 820s ($Os^{16}O_2$), 788s ($Os^{18}O_2$). ^{1}H N.m.r. (CD_3COCD_3) δ 8.21 [d, 2 H, ^4J(H–H) 3 Hz] and 7.27 [d, 2 H, ^4J(H–H) 3 Hz] (aromatic C–H), 3.88 (s, 4 H) (N-CH_2CH_2-N).

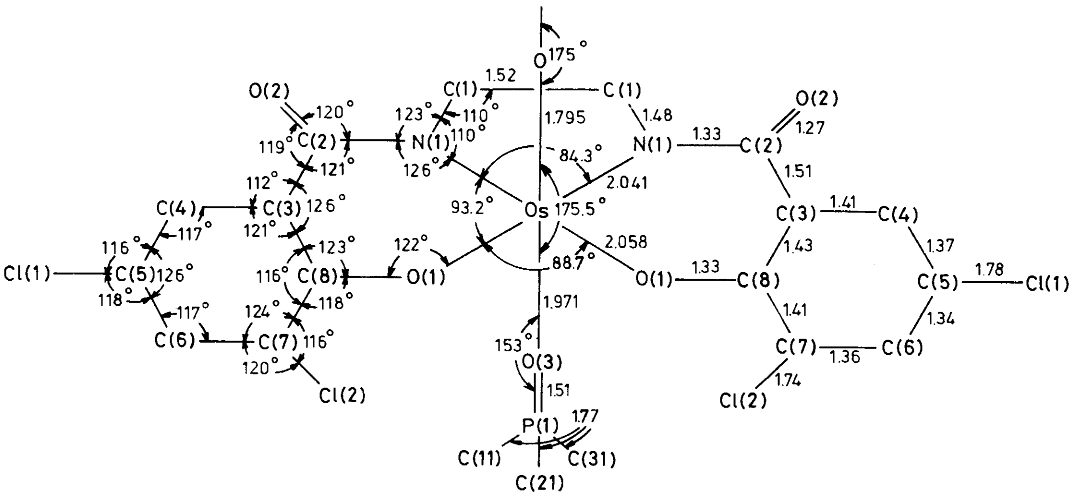

Figure 1. Schematic representation of $K_2[\{Os(\eta^4\text{-chba-Et})(OPPh_3)\}_2\text{-}O]$ (**3**), giving bond lengths (Å) and angles (°). O(3)–P(1)–C(av.) 110°, C–P(1)–C(av.) 108°.

$R = 0.111$ ($R_{3\sigma} = 0.076$);‡ the number of parameters was 503. Figure 1 gives the average (over the four sets of chemically equivalent) bond lengths and angles for the dianion of the molecule.

This structure exhibits the first examples of bonds between Os^{IV} and an *N*-co-ordinated organic amido ligand, a phenoxide ligand, and a phosphine oxide ligand; related structural studies have been performed.[4] This study also reveals unusual co-ordination environments for the potassium ions. One potassium ion, centred in a square pyramid, is well within bonding distance for the four phenolic oxygen atoms [K^+–O(phenol) av. = 2.87 Å] and one acetone solvate molecule [K^+–O(acetone) = 2.80 Å]; this potassium ion is further co-ordinated to the μ-oxo ligand [K^+–O(oxo) = 3.16 Å]. The second potassium ion is apparently four co-ordinate, situated at the centre of a distorted tetrahedron, linking adjacent anions by bonding with two pairs of eclipsed organic amido oxygen atoms, one pair from each dinuclear unit [K^+–O(amide) av. = 2.66 Å]. Low co-ordination numbers for potassium ions are rare.[5] The close interligand contacts of the bis-hydroxybenzamido ligands in this eclipsed conformation are predominantly Cl···Cl contacts, ranging from 3.6 to 3.9 Å, close to the sum of van der Waals' radii for Cl (*ca.* 3.6 Å). Presumably the co-ordination of the potassium ions plays a significant role, and results in the observed eclipsed conformation of the two planar ligands. The dinuclear octahedral Os^{IV} oxo-bridged structure has been observed previously in the complex $Cs_4[\{OsCl_5\}_2\text{-}\mu\text{-}O]$[6] and a bent oxo-bridged dinuclear Os^{IV} complex, $Os_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4(PPh_3)_2$, has also been structurally characterized.[7] The general strategy of producing highly oxidizing inorganic complexes using specially designed multianionic chelating ligands has been successful in our work and will soon be reported.

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, the National Science Foundation, and the Atlantic Richfield Corporation of America for support of this work and Engelhard for a generous loan of precious metal compounds. B. D. S. acknowledges support from the California Institute of Technology as a Myron A. Bantrell Fellow in Chemistry, 1981—1983. T. E. K. is the Union Carbide Fellow in Chemical Catalysis.

Received, 19th October 1983; Com. 1377

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‡ The CRYM computing system was used (D. J. Duchamp, California Institute of Technology). Least-squares refinement minimizes $\Sigma\omega\Delta^2$ with weights $\omega^{-1} = \{[\sigma(I)]^2 + (0.02 \times \text{scan counts})^2\}(k^2/Lp)^2$ and $\Delta = F_O^2 - (F_c/k)^2$. The goodness-of-fit is $\surd[\Sigma\omega\Delta^2/(n - p)]$, $R = \Sigma|F_O - |(F_c/k)||/\Sigma F_O$ (for reflections with $I > 0$), $R_{3\sigma} = R$ [for reflections with $I > 3\sigma(I)$]. The atomic co-ordinates from this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.