CHEMISTRY LETTERS, pp. 997-1000, 1979. Published by the Chemical Society of Japan

MOLECULAR STRUCTURE OF AQUAETHYLENEDIAMINETETRAACETATOOSMIUM(IV) MONOHYDRATE: [Os(edta)(H_2O)]·H_2O

Masami SAITO, Takashi UEHIRO, Fujio EBINA, Toschitake IWAMOTO,
Akira OUCHI, and Yukichi YOSHINO
Department of Chemistry, College of General Education,
The University of Tokyo, Komaba, Meguro, Tokyo 153

The title complex, obtained as the first characterized solid Os(IV)-edta complex, crystallizes in the monoclinic space group $P2_1/a$ with a=14.956(7), b=8.181(3), c=14.600(7) Å, β=126.64(3)°, and Z=4. In the complex molecule [Os(edta)(H_2O)], the seven-coordinate Os(IV) sits in a monocapped trigonal prism formed with two N and four O atoms of sexidentate edta and with an O atom of H_2O.

In conjunction with the development in this laboratory of coordination chemistry of the ethylenediaminetetraacetato (edta) complexes of platinum group metals, especially those of osmium, we have succeeded in isolating an osmium(IV) complex of the composition Os(edta)$(H_2O)_2$ as the first solid edta complex of osmium(IV) by the aerial oxidation of H[$OsCl_2$(H_2edta)]·$2.5H_2O$$^{1)}$ in the aqueous solution. The complex had once been supposed to have a dimer structure because of its diamagnetism$^{2)}$. In fact, a μ-oxo bridged dimer $(NH_4)_4[Cl_5Os\text{-}O\text{-}OsCl_5]$ was reported to be diamganetic$^{3)}$, whereas the monomeric hexahaloosmate(IV) complexes are paramagnetic with the effective magnetic moments of the Os(IV) 1.2-1.8 B.M.$^{4)}$ For the present complex, however, any spectroscopic evidence to support the supposed dimer structure has never been obtained in the infrared and Raman spectra. Therefore, we undertook to analyze its crystal and molecular structure by single crystal X-ray diffraction method.

The title complex was prepared by aeration of the aqueous solution of H[$OsCl_2$(H_2edta)]·$2.5H_2O$ (3×10^{-3} mols in 20 cm^3 H_2O) for 6 hr at 20°C as brilliant black crystals. They were recrystallized from an acidic (0.5 M H_2SO_4) solution by leaving it in a refrigerator for a week. Among the single crystals thus obtained, those with the dimensions of ca. 0.5×0.5×0.5 mm were shaped into spheres of ca. 0.25 mm diameter by air-blowing method. Anal. Found: C, 23.29; H, 3.14; N, 5.54; Os, 36.29%. Calcd for $C_{10}H_{16}N_2O_{10}Os$: C, 23.35; H, 3.14; N, 5.45; Os, 36.98%. The oxidation state of osmium was determined as +IV by iodometry. After preliminary Weissenberg photographs were taken, a 0.25 mmϕ crystal was mounted on a Rigaku automated four-circle diffractometer[5)] to refine the unit cell parameters and to collect intensity data using MoKα radiation ($\lambda = 0.71073$ Å). The crystal data are: $C_{10}H_{16}N_2O_{10}Os$, F.W. = 514.4; monoclinic, space group $P2_1/a$, $a = 14.956 \pm 0.007$, $b = 8.181 \pm 0.003$, and $c = 14.600 \pm 0.007$ Å, $\beta = 126.64 \pm 0.03°$, $U = 1433.4 \pm 0.9$ Å^3; $D_x = 2.38$ and $D_m = 2.40$ g cm^{-3}; $Z = 4$; systematic absences, h0l for h = odd, and 0k0 for k = odd.

Of independent 4485 reflections collected by ω-2θ scan technique up to $2\theta = 60°$, 3294 ones with intensities $F_o > 3\sigma(F_o)$ were used for the structure refinement after the correction for absorption (μ(MoKα) = 92.9 cm^{-1}) had been applied. All the calculations were carried out on a HITAC 8800/8700 computer at the Computer Center of this University using the programs in UNICS[6)] and their local versions. The atomic scattering factors used were those listed in the International Tables[7)]. The structure was solved by the heavy atom method. The position of the Os atom was located on the three-dimensional Patterson map. The remaining nonhydrogen atoms were found by successive structure factor and electron density map calculations. The positional parameters for all nonhydrogen atoms and their anisotropic thermal parameters were refined by a block-diagonal least-squares procedure to a conventional R = 0.039 with the shifts of those parameters less than 30% of their esd's. A perspective view of the complex molecule is shown in Fig. 1 along with the numbering scheme of the atoms. One of the two water molecules in a formula unit is the water of crystallization placed among the complex molecules. In the complex molecule, the two N and four O atoms of the sexidentate edta ligand locate at the six corners of a distorted trigonal prism enveloping the Os atom, and the O(1) atom of a water molecule coordinates to the Os through the square face of the prism formed by the four O atoms of edta. Thus, the Os atom has the seven-coordinate structure of a distorted monocapped trigonal prism type as shown in Fig. 2. This is the first example of a seven coordination of osmium(IV) so far has been surveyed in literature.

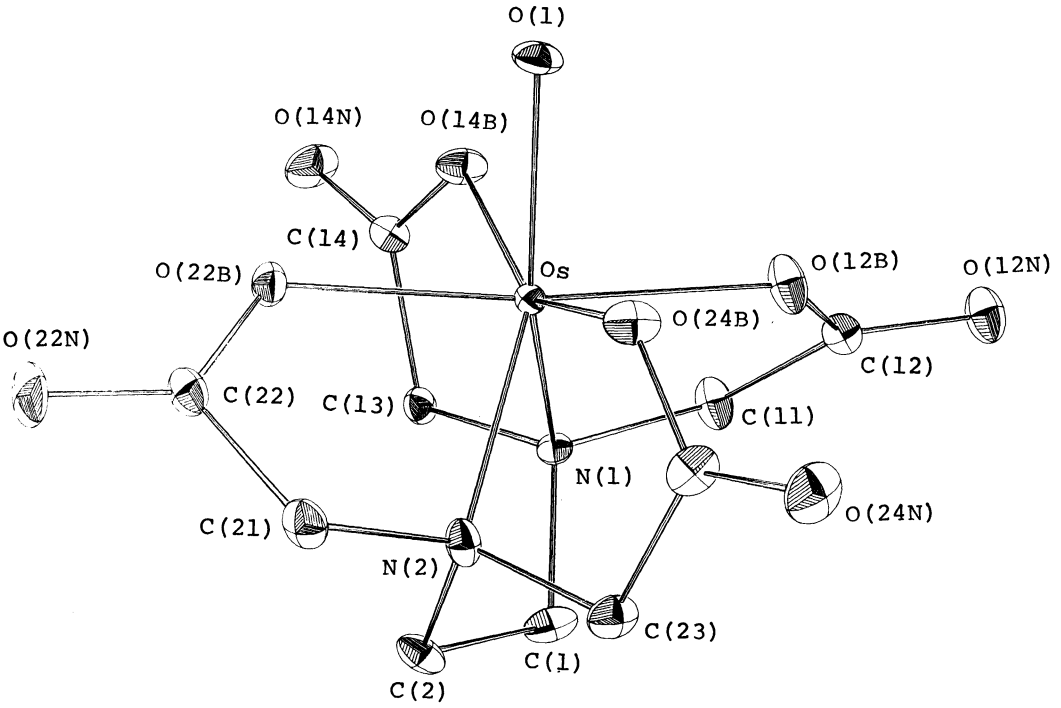

Figure 1. Molecular structure of [Os(edta)(H_2O)]

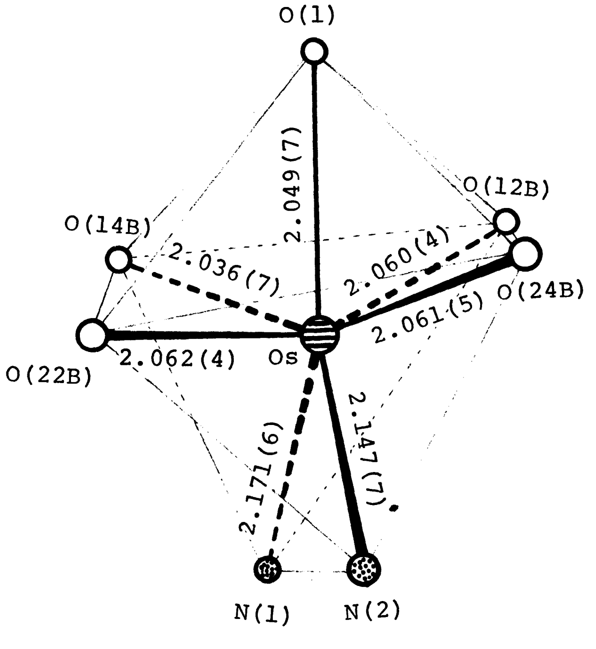

Figure 2. Monocapped trigonal prism structure around the Os(IV)

As Fig. 2 shows, the Os-N bonds are longer by 0.08-0.1 Å than any Os-O bonds in the coordination sphere. The same tendency has been observed for the seven-coordinate [M(edta)(H_2O)] type complex either with a distorted trigonal prism structure (e.g., [Mg(edta)(H_2O)]$^{2-}$)[8] or with a pentagonal biprism structure (e.g., [Fe(edta)(H_2O)]$^{-}$)[9] in which the edta behaves as a sexidentate ligand. In the considerably distorted monocapped trigonal prism, the Os atom is placed 0.029 Å beneath the distorted square face formed with the four O atoms of edta, among which an exceptionally short Os-O(14B) distance 2.036 Å has been observed. The Os-O(1) bond, 2.049 Å, is shorter than the other three Os-O bonds with the average 2.060 Å length.

The diamagnetism of this complex can be interpreted in terms of the non-degenerate 4d orbitals in the ligand field of seven coordination. Furthermore, it should be noted that the 18 electron rule is fulfilled for the Os(IV) by the seven electron pairs from the ligating atoms and the four 4d electrons from the Os(IV).

References and Notes

1) M. Saito, T. Uehiro, and Y. Yoshino, Chem. Lett., 1977, 809.

2) M. Saito, T. Uehiro, and Y. Yoshino, Abstracts of the 27th Conference on Coordination Chemistry, the Chemical Society of Japan, Matsumoto (1977), p. 273.

3) R. R. Miano and C. S. Garner, Inorg. Chem., 4, 337 (1965).

4) A. F. Trotman, ed., "Comprehensive Inorganic Chemistry," Vol. 3, Pergamon Press Ltd., Oxformd (1973), p. 1211.

5) The intensity data were collected by the courtesy of Professor Yasuzo Uchida at the Department of Industrial Chemistry, Faculty of Engineering of this University.

6) The Universal Crystallographic Computation Program System (UNICS), ed. by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

7) International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).

8) J. J. Stezowski, R. Countryman, and J. L. Hoard, Inorg. Chem., 12, 1749 (1973).

9) M. D. Lind, M. J. Hamor, and J. L. Hoard, Inorg. Chem., 3, 34 (1964).

(Received June 11, 1979)