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Tetravalent Ruthenium Porphyrin. II. The Molecular and Crystal Structure of μ-Oxo-bis[(octaethylporphinato)ruthenium(IV) chloride] Benzene Solvate

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The crystal structure of μ-oxo-bis[(octaethylporphinato)ruthenium(IV) chloride] benzene solvate, [Ru(IV)(oep)Cl]$_2$O–C$_6$H$_6$, was determined by the X-ray method. The complex crystallizes in the tetragonal space group P4/nnc, a=13.912(2) Å, c=17.821(4) Å, and Z=2. The structure was solved by the heavy-atom method and refined to R=0.084 for 958 reflections. The [Ru(IV)(oep)Cl]$_2$O complex has the crystallographic D$_4$-422 symmetry and contains the binuclear (Cl)N$_4$Ru–O–RuN$_4$(Cl) coordination group with the Ru–O(μ) distance of 1.793(2) Å, the Ru–Cl distance of 2.320(6) Å, and the Ru–N distance of 2.038(9) Å. The Ru–O–Ru bond is explicitly linear, and the two porphinato cores rotate around the Ru–O–Ru bond by 21.0° from the eclipsed form. The porphinato core is planar within 0.04 Å, and the Ru atom is displaced only by 0.07 Å out of the plane defined by the four porphinato nitrogen atoms toward the bridging O atom. These results are compared with those of the previously reported [Ru(IV)(oep)(OH)$_2$]O–CH$_3$OH crystal.

The stereochemistry of ruthenium-porphyrins has been intensively investigated, primarily by regarding them as a model of heme protein systems,[1,2] since the Ru ion has been established to serve as a suitable substitute for the Fe ion. We have previously reported the crystal structure of μ-oxo-bis[(octaethylporphinato)ruthenium(IV) hydroxide] methanol solvate, [Ru(IV)(oep)(OH)]$_2$O–CH$_3$OH, as a model of the iron(IV) porphyrin observed in oxidative reaction of the native Fe(III) hemoprotein of peroxidase.[2] The title crystal, [Ru(IV)(oep)Cl]$_2$O–C$_6$H$_6$, is isomorphic with the [Ru(IV)(oep)(OH)]$_2$O–CH$_3$OH crystal.[2] In this paper, we report the structure of the [Ru(IV)(oep)Cl]$_2$O–C$_6$H$_6$ crystal, and discuss the geometry of these isomorphous crystals.

Experimental

[Ru(IV)(oep)Cl]$_2$O was prepared by treatment with dilute hydrochloric acid of a dichloromethane solution of [Ru(IV)(oep)(OH)]$_2$O.[3] Purple-red, plate-like crystals were obtained by recrystallization from a 1 : 1 mixture of benzene and dichloromethane. A prelimenary X-ray photographic examination indicated a centrosymmetric space group P4/nnc with Laue symmetry 4/mmm and systematic absences of $hk0$ for $h+k$ odd, $0kl$ for $k+l$ odd, and hhl for l odd. A crystal with dimensions of 0.2×0.2×0.1 mm^3 was mounted on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\bar{\lambda}$=0.71073 Å). The unit cell dimensions refined by a least-squares treatment of the setting angles of 47 reflections are a=13.912(2) Å, c=17.821(4) Å, D_x=1.304 g/cm^3 (for two [Ru(IV)(oep)Cl]$_2$O and two benzene molecules per unit cell), and D_m=1.300 g/cm^3 (by flotation in an aqueous calcium chloride solution).

Intensity data of 1826 reflections in the range $2\theta < 50°$ were collected in the ω-2θ scan mode with a scan rate of 5° min^{-1} in ω. Three reflections were monitored every 60 reflections. The intensity data were converted to the $|F_o|$ data in the usual manner, and a total of 958 independent reflections with $|F_o| > 3.0\sigma(F_o)$ were retained as observed, where the standard deviations $\sigma(F_o)$ were estimated from counting statistics. No absorption correction was applied (μ=5.53 cm^{-1} for Mo $K\alpha$).

Table 1. Positional and thermal parameters for the atoms of [Ru$^{\text{IV}}$(oep)Cl]$_2$O·C$_6$H$_6$

Estimated standard deviations in the least significant figure(s) are given in parentheses. B_{eq} is the equivalent isotropic temperature factor defined by Hamilton.[8]

Atom	x	y	z	B_{eq}/Å^2
Ru	1/4	1/4	0.1494(1)	2.43
Cl	1/4	1/4	0.0192(3)	4.24
O(μ)	1/4	1/4	1/4	2.54
N	0.3707(6)	0.3329(7)	0.1457(6)	2.82
C(1)	0.3774(7)	0.4293(8)	0.1476(8)	2.79
C(2)	0.4779(10)	0.4601(10)	0.1476(8)	3.98
C(3)	0.5289(10)	0.3785(10)	0.1493(10)	4.55
C(4)	0.4630(9)	0.2987(12)	0.1471(10)	3.70
C(5)	0.2954(13)	0.4915(10)	0.1465(12)	3.78
C(6)	0.5100(12)	0.5626(10)	0.1492(11)	4.95
C(7)	0.5269(17)	0.6012(17)	0.0727(17)	8.71
C(8)	0.6413(15)	0.3707(16)	0.1607(14)	9.05
C(9)	0.6813(15)	0.3597(20)	0.0866(17)	13.00
C(10)	0.2422(59)	0.2025(64)	−0.1838(18)	7.45
C(11)	1/4	0.1461(43)	−1/4	8.23
H(C4)	0.310 (10)	0.560 (10)	0.152 (9)	
H(C6A)	0.571 (12)	0.546 (11)	0.188 (7)	
H(C6B)	0.471 (12)	0.597 (11)	0.193 (8)	
H(C7A)	0.544 (11)	0.678 (12)	0.078 (8)	
H(C7B)	0.462 (11)	0.622 (12)	0.045 (9)	
H(C7C)	0.598 (11)	0.572 (11)	0.050 (9)	
H(C8A)	0.665 (12)	0.281 (10)	0.069 (9)	
H(C8B)	0.650 (11)	0.454 (12)	0.193 (8)	
H(C9A)	0.670 (11)	0.301 (10)	0.194 (8)	
H(C9B)	0.751 (12)	0.355 (9)	0.104 (7)	
H(C9C)	0.654 (12)	0.395 (11)	0.053 (9)	
H(C10)	0.265 (28)	0.142 (21)	−0.163 (17)	
H(C11)	0.274 (0)	0.055 (28)	−0.250 (0)	

The structure was solved by the heavy-atom method and refine by full-matrix least-squares. The Ru atom was located from sharpened Patterson maps, and the C, N, O, and Cl atoms of the [Ru(IV)(oep)Cl]$_2$O complex were picked up from successively synthesized Fourier maps. Subsequent leastaquares refinement and difference Fourier synthesis revealed a disordered solvent benznene molecule. All hydrogen atoms were located geometrically (C–H=1.00 Å) and included in the structure factor calculations of the least-squares refinement by assuming their isotropic thermal parameters as 8.0 Å^2. A further refinement with the weighting scheme of $w=1/(\sigma(F_o)^2$ was carried out to convergence. The final R value was 0.084. Atomic scattering factors[4a] and anomalous terms[4b] were taken from the International Tables for X-Ray Crystallography. All computations were performed on a FACOM M-200 computer at the Data Processing Center, Kyoto University by using the program system KPAX.

Results

The atomic parameters are listed in Table 1. Tables of anisotropic thermal parameters and of observed and calculated structure factors are kept as a Document No. 8254 at the Chemical Society of Japan. Figure 1 displays a single [Ru(oep)Cl]$_2$O complex and two disordered benzene molecules. The [Ru(oep)Cl]$_2$O binuclear complex exists at a crystallographic D$_4$-422 symmetry position. The required fourfold axis passes through the Cl–Ru–O–Ru–Cl bond, and the two twofold axes perpendicular to the fourfold axis pass through the central oxygen atom. One-fourth of the porphinato moiety is an asymmetric unit. The numbering scheme for the independent atoms is given in Figs. 1 and 2. The benzene molecules exist at another 422 symmetry position, and they are disordered in two different orientations about the fourfold axis.

The bond lengths and angles for the porphyrin skeleton (Fig. 2) are similar to those of the [Ru(oep)(OH)]$_2$O crystal[2] and they are normal in comparison with those reported for the planar porphyrins.[5] Deviations from the least-squares plane of the 24 ring atoms of the porphinato core are given on the left-hand side in Fig. 2. The porphinato core is planar within 0.04 Å, and the ruthenium ion is displaced only by 0.07 Å out of the plane defined by the four porphinato nitrogen atoms toward the bridging O(μ) atom. Figure 3 presents a perspective diagram of the environment of one ruthenium ion. The Ru(IV)–N distance, 2.038(9) Å, is slightly shorter than the Ru(IV)–N distance (2.067(14) Å) observed in [Ru(oep)(OH)]$_2$O[2] and than the Ru(II)–N distances (2.041—2.052 Å) reported in ruthenium(II) porphyrin complexes.[1] The Ru(IV)–O(μ) distance, 1.793(2) Å, is shorter than that reported for Ru(IV)–O(μ), 1.847(13) Å, in [Ru(IV)(oep)(OH)]$_2$O[2] and is comparable with that reported for Ru(IV)–O(μ), 1.80 Å, in (Cl$_5$Ru(IV)ORu(IV)Cl$_5$)$^{4-}$.[6] The Ru(IV)–Cl distance, 2.320(6) Å, is similar to that reported for Ru(IV)–Cl, 2.34 Å, in (Cl$_5$Ru(IV)ORu(IV)Cl$_5$)$^{4-}$ [6] and is in good agreement with the sum of single-bond radii, 2.32 Å.

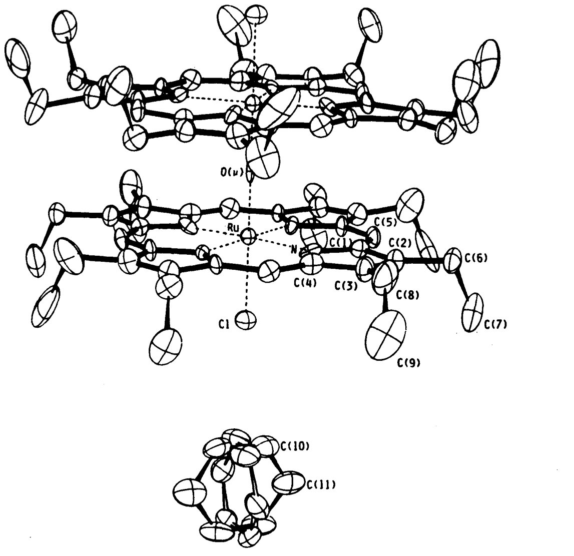

Fig. 1. Computer-drawn model in perspective of the [Ru(oep)Cl]$_2$O molecule and the disordered benzene molecules. The vibrational ellipsoids are drawn at the 30% probability level. The labeling scheme used for the atoms in the molecules is also shown.

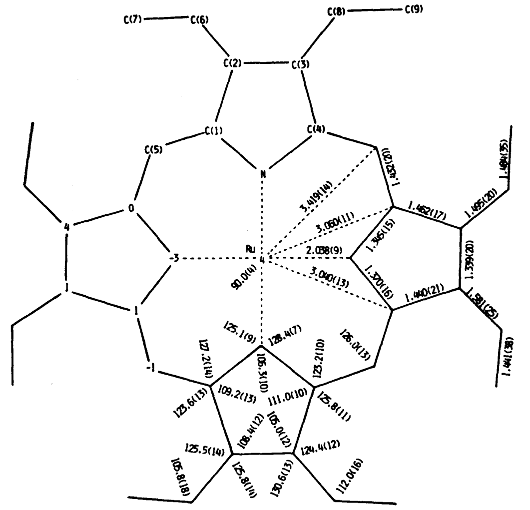

Fig. 2. Formal diagram of the porphinato skeleton in [Ru(oep)Cl]$_2$O. On the top of the diagram, the numbering scheme for the atoms is displayed. On the left-hand side of the diagram, the numbered symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. On the right-hand side and the bottom of the diagram are the structurally independent bond distances and angles. The numbers in parentheses are the standard deviations.

The Ru–O–Ru* bond is explicitly linear, and the two porphinato cores, related to each other by the twofold symmetry, rotate about the straight Ru–O–Ru* bond by 21.0° from the eclipsed form. (The atom with or without an asterisk superscribed is associated with the upper or lower core of the binuclear porphyrin complex, respectively.) The interplanar separation between the mean planes of the porphinato cores is 3.66 Å; the interatomic distances are 3.59 Å for Ru–Ru*, 3.79 Å for N–N*, 3.79 Å for C$_a$–C$_a$*, 3.67 Å for C$_b$–C$_b$*, and 3.70 Å for C$_m$–C$_a$*. (C$_a$, C$_b$, and C$_m$ are used for the three chemically and structurally distinctive types of carbon atoms, pyrrole-α, pyrrole-β, and methine carbons, respectively.) The rotation angle and interplanar distance between the two porphinato cores are slightly less than the corresponding angle and distance in the [Ru(IV)(oep)(OH)]$_2$O crystal.[2] However, in the same way as described in the report on [Ru(IV)-(oep)(OH)]$_2$O,[2] the binuclear porphyrin structure of the present complex is stabilized by the intramolecular π-π interactions between the face-to-face contact porphyrins and by the dπ-pπ-dπ interaction in the Ru(IV)–O–Ru(IV) bond, and diamagnetism of the present complex is also well interpreted in terms of the π-π interactions in the Ru(IV)–O–Ru(IV) bond system with the low-spin Ru(IV) atom.

The average C–C bond length and the average C–C–C bond angle of benzene molecule are 1.39(5) Å and 119(5)°, respectively. The disordered benzene molecules are surrounded by the six $[Ru(oep)Cl]_2O$ complexes. The molecular plane of each benzene molecule is perpendicular to the porphinato planes, and the shortest interatomic distance is 3.62(4) Å between the Cl and C(10) atoms along the c axis. The [Ru(IV)-(oep)Cl]$_2$O complexes and solvate benzene molecules are packed with van der Waals contacts.

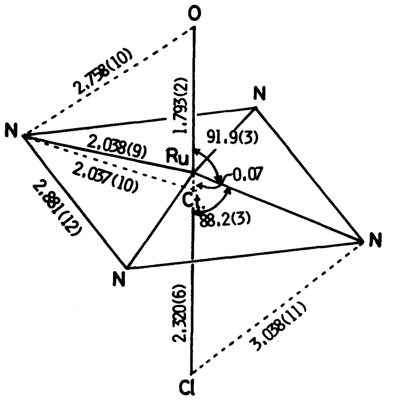

Fig. 3. Perspective diagram of the six-coordination group around the ruthenium(IV) atom in the $[Ru(oep)Cl]_2O$ molecule. C_t represents the center of the porphinato skeleton.

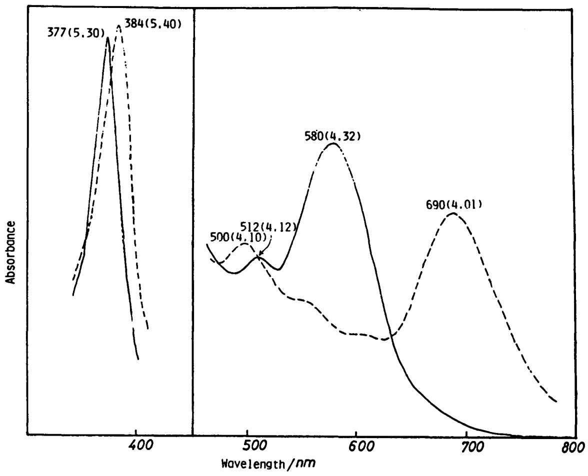

Fig. 4. Absorption spectra for $[Ru(oep)Cl]_2O$ (----) and $[Ru(oep)(OH)]_2O$ (——) in CH_2Cl_2. Extinction coefficients (log ε_{max}) are given in parentheses following λ_{max} (nm).

Discussion

The $[Ru(IV)(oep)Cl]_2O–C_6H_6$ crystal is isomorphic with $[Ru(IV)(oep)(OH)]_2O–CH_3OH$.[2] Table 2 summarizes the unit cell dimensions and the geometric parameters of the coordination groups for the two μ-oxo ruthenium porphyrin derivatives. As shown in Fig. 4, the absorption spectra of the Cl-derivative ($[Ru(IV)(oep)Cl]_2O$) exhibit a large bathochromic shift as compared with those of the OH-derivative ([Ru(IV)-(oep)(OH)]$_2$O). These spectroscopic shifts suggest that the Cl^- and OH^- ligands on the Ru(IV) atom obey the general order of the spectrochemical series, $OH^- > Cl^-$. Thus the Cl^- ion is considered to be a weaker ligand for the Ru(IV) atom than the OH^- ion. The difference of the ligand strengths reflects the geometric parameters of the two coordination groups. As shown in Table 2, the deviation of the Ru atom out of the porphinato mean plane for the Cl-derivative is larger than that for the OH-derivative. This large Ru deviation toward the O^{2-} atom in the Cl-derivative is reasonable, since the O^{2-} atom is a stronger ligand for the Ru(IV) atom than the Cl^- and OH^- atoms, and the degree of Ru(IV) displacement toward the strong ligand depends on the ligand strengths at the opposite side. The Ru(IV)–O(μ) bond of the Cl-derivative is significantly shorter than the corresponding bond of the OH-derivative, and the Ru–N bond of the Cl-derivative is also slightly shorter than that of the OH-derivative. These shortening effects of the Ru–O(μ) and Ru–N bonds of the Cl-derivative will be explained in terms of "the structural trans and cis effects." That is, when a ligand of the six coordinated metal complex is replaced by a weaker ligand, the other trans and cis ligand-metal bonds will be strengthened because of the neutralization of the electric charge around the central metal ion. In the present case, replacement of the axial OH^- ligand by a weaker Cl^- ligand strengthens the trans Ru–O(μ) and cis Ru–N bonds, and consequently results in the shortening of these bonds. As to the shortening values of these bonds, the Ru–O(μ) bond is more shortened than the Ru–N bond. Thus the trans effect seems to be more effective than the cis effect. This inference is correct in view of the fact that the Ru–O(μ) distance of the Cl-derivative is very close to that in the case of the $Cl_5Ru–O–RuCl_5$ system in which the strong equatorial nitrogen ligands of the porphyrin complex is replaced by the weak Cl^- ligands;[6] the Ru–O(μ) bond distance depends largely on the trans Cl^- ligand and depends less on the cis ligand. Other examples of such dominant trans effect have been found in the Ru(II)(tpp)(CO)X (X=Py and EtOH) complexes[1b,1c] and in the Fe(II)(tpp)(NO)X (X=1-MeIm, 4-MePip, and none) complexes.[7] It may, therefore, be pointed out that the dominant trans effect is a general tendency in the six coordinated metalloporphyrin complexes.

Another noticeable point in Table 2 is that the unit cell volume of the Cl-derivative is significantly smaller than that of the OH-derivative. This volume change is due mainly to the lattice deviation along the c axis, in which direction the substitution of Cl^- for OH^- or of C_6H_6 for CH_3OH is allowed to take place. The Cl^- and C_6H_6 groups in the Cl-derivative have normal van der

Table 2. Comparison of the unit cell dimensions and coordination geometries for $[Ru(IV)(oep)Cl]_2O$ and $[Ru(IV)(oep)(OH)]_2O$

Molecule		$[Ru(IV)(oep)Cl]_2O$	$[Ru(IV)(oep)(OH)]_2O$
Crystal data	a/Å	13.912(2)	13.98(1)
	c/Å	17.821(4)	18.03(12)
	V/Å^3	3449(1)	3522(20)
Coordination geometry	Ru–N(Å)	2.038(9)	2.067(14)
	Ru–C_t(Å)	0.07$^{a)}$	0.03$^{a)}$
		0.04$^{b)}$	0.01$^{b)}$
	Ru–O(μ)(Å)	1.793(2)	1.847(13)
	Ru–L(Å)	2.320(6); L=Cl	2.195(26); L=OH
	P–P$^{c)}$(Å)	3.66	3.71
	N–Ru–Ru*–N*(°)	21.0(3)	22.7(4)

a) Deviation out of the plane defined by the four porphinato nitrogen atoms. b) Deviation from the 24-atom porphinato mean plane. c) P–P means the interplanar distance between the mean planes of the porphinato cores.

Waals contacts along the c axis, while the disordered CH_3OH molecule in the OH-derivative occupy an excessively large space.$^{2)}$ This space difference of solvent occupation may be a main factor for the large lattice deviation along the c axis. Deformation of the six-coordinate Ru(IV) group, of course, has a contribution to the anisotropic lattice deviation. The large trans effect and the small cis effect mentioned above are consistent with the large lattice deviation along the c axis.

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