The Crystal Structure of Tetra-μ-acetato-diruthenium Chloride

Tadashi TOGANO,† Masao MUKAIDA,†† and Terunosuke NOMURA*

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo 102

(Received October 9, 1979)

Synopsis. The crystal structure of $Ru_2(OCOCH_3)_4Cl$ has been determined from visually estimated Cu $K\alpha$ data. The crystal is composed of the dinuclear, carboxylato-bridged species $Ru_2(OCOCH_3)_4^+$ and the bridging chloride anions. The molecular structure is almost identical with that of the analogous butyrato complex, but the chloride-bridged chains run parallel with the c axis only.

Carboxylato ruthenium complexes of the $Ru_2(OCOR)_4Cl$ type (R=Me, Et, *n*-Pr) were first reported by Stephenson and Wilkinson.[1] The structure determination of the analogous butyrato complex was accomplished by Bennett *et al.*, who revealed that the complex contains a dinuclear carboxylato-bridged species, $Ru_2(OCOC_3H_7)_4^+$, with a very short Ru–Ru distance.[2] It has also been indicated that the Ru atoms of the complex exist in the common nonintegral oxidation state of +2.5.

The present authors prepared the complexes of the $Ru_2(OCOR)_4X$ type (R=H, Me, Ph.; X=Cl, Br, I, SCN, NO_3, CH_3COO) independently[3,4] and presumed that these complexes have structures similar to that of the butyrato complex. The present work was undertaken in order to verify this prediction and to obtain more information about the properties of a series of carboxylato complexes.

Experimental

The crystals of $Ru_2(OCOCH_3)_4Cl$ were prepared as has been described previously;[3] they were recrystallized from a 5 mol dm^{-3} acetic-acid solution by means of slow evaporation at room temperature.

The cell constants were determined using Cu $K\alpha$ radiation by the least-squares refinement of the data from 150 reflections of h 0 l and h k 0 Weissenberg photographs, on which copper-powder lines were superimposed for calibration. The density was measured by flotation in a tetrachloromethane–methyl iodide mixture. The crystal data are as follows: $Ru_2(OCOCH_3)_4Cl$, $F.W.$=437.3, monoclinic, space group C2/c, a=14.869(3), b=7.735(1), c=12.868(3) Å, β=109.56(2)°, V=1393 Å^3, D_m=2.25 g cm^{-3}, D_c=2.26 g cm^{-3} (for Z=4), μ=207.5 cm^{-1} (for Cu $K\alpha$ radiation). The intensity data were collected by multiple-film equi-inclination Weissenberg photographs for the layer lines from 0 to 5 on the b axis and for 0 on the c axis. The two crystals were then re-formed into spheres with average diameters of 0.14 and 0.16 mm respectively. The intensities of 1116 independent reflections were corrected for Lorentz-polarization and absorption effects; 87 of them were, however, too weak to be measured and so were assumed to be zero.

Structure Determination

The positions of the ruthenium and chlorine atoms were determined from a three-dimensional Patterson map. Fourier synthesis, phased with the Ru atoms and Cl atoms, revealed all the carbon and oxygen atoms. The structures was refined by the block-diagonal least-squares method. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[5] The refinement of the positional and thermal parameters, at first isotropic and subsequently anisotropic for all the Ru, Cl, C, and O atoms, but not the H atoms, reduced the discrepancy factor $R=\Sigma(w||F_o|-|F_c||)/\Sigma w|F_o|$ to 0.09, excluding non-observed reflections (R=0.10 for all 1116 reflections). The final atomic coordinates and thermal parameters are listed in Table 1, and the observed and calculated structure factors in Table 2.†††

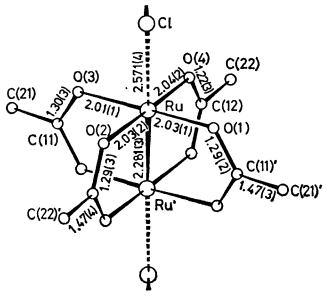

Fig. 1. Molecular structure with the numbering scheme of atoms and bond lengths (/Å) with e.s.d's in parentheses.

The computations were carried out on HITAC 8800/8700 computer at the Tokyo University Computer Center. The computer program used were UNICS by T. Sakurai *et al.* and HBLS IV by T. Ashida. In HBLS IV, the weighting scheme used was $w=(160.0/F_o)^2$ when $F_o>160.0$ and $w=1$ when $F_o\leqq 160.0$.

Results and Discussion

Bennett *et al.* have revealed that the tetra-*n*-butyrato complex contains dinuclear units consisting of two Ru atoms bridged by four *n*-butyrato groups. These dinuclear units, in crystal form, are linked by bridging chlorine atoms into infinite zigzag chains. The molecular structure of the acetato complex is almost identical with that of the butyrato complex. These dinuclear units have virtual D_{4h} symmetry if the alkyl chains are neglected in the case of the butyrato complex.

The geometry of, and bond distances in, the dinuclear cation and chlorine atoms are shown in Fig. 1. The bond angles and planes are given in Tables 3 and 4 respectively. The six nearest neighbors of a ruthenium atom are four oxygen atoms belonging to four different acetato groups, a ruthenium atom, and a chlorine atom. Six such atoms form distorted octahedral configuration about each of the two ruthenium

† Present address: Toho Girls' High School, 1-41-1 Wakabacho Chofu-shi, Tokyo 182.

†† Present address: Dept. of Chemistry, University of New Brunswick, Fredericton, N. B. Canada E3B 5A3.

††† The complete F_o–F_c data are deposited as document No. 8022 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

Table 1. Atomic parameters ($\times 10^4$) and their estimated standard deviations
The anisotropic thermal factors are of the form: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0018(1)	0698(2)	0787(1)	31(1)	95(4)	28(1)	2(2)	35(1)	9(2)
Cl	0000	2392(10)	2500	40(3)	70(17)	31(3)	0	44(5)	0
O(1)	−1200(9)	1938(21)	−0079(10)	36(6)	157(39)	40(8)	34(24)	33(12)	−11(27)
O(2)	0792(9)	2603(21)	0414(11)	51(8)	136(40)	54(10)	−17(26)	61(14)	−10(29)
O(3)	1240(9)	−0522(21)	1614(10)	41(7)	167(40)	41(9)	38(25)	37(12)	1(27)
O(4)	−0759(9)	−1268(21)	1111(10)	44(7)	153(39)	44(8)	−22(25)	59(13)	−2(27)
C(11)	1602(13)	−1651(31)	1123(14)	37(9)	131(57)	38(11)	−2(33)	35(16)	−17(36)
C(12)	−0979(13)	−2519(29)	0493(15)	44(10)	72(54)	49(12)	−27(33)	54(18)	−11(36)
C(21)	2426(15)	−2711(36)	1764(17)	48(11)	238(73)	54(14)	71(44)	54(21)	13(48)
C(22)	−1505(19)	−3960(35)	0772(20)	85(17)	106(67)	82(19)	−66(50)	105(30)	−21(51)

Table 3. Bond angles and their e.s.d.'s

Atoms	Angle(/°)	Atoms	Angle(/°)
Ru′-Ru-O(1)	89.1(4)	Ru-O(1)-C(11)′	121(1)
Ru′-Ru-O(2)	88.8(5)	Ru-O(2)-C(12)′	120(1)
Ru′-Ru-O(3)	89.7(5)	Ru-O(3)-C(11)	121(1)
Ru′-Ru-O(4)	88.8(4)	Ru-O(4)-C(12)	121(2)
O(1)-Ru-O(2)	90.5(6)	O(1)′-C(11)-O(3)	120(2)
O(2)-Ru-O(3)	88.6(6)	O(2)′-C(12)-O(4)	122(2)
O(3)-Ru-O(4)	91.3(6)	O(1)′-C(11)-C(21)	120(2)
O(4)-Ru-O(1)	89.6(6)	O(2)′-C(12)-C(22)	118(2)
Cl-Ru-O(1)	88.1(4)	O(3)-C(11)-C(21)	118(2)
Cl-Ru-O(2)	90.2(5)	O(4)-C(12)-C(22)	120(2)
Cl-Ru-O(3)	93.1(5)	Ru′-Ru-Cl	177.0(1)
Cl-Ru-O(4)	92.2(5)		

Table 4. Best planes

Equations of planes[a)]
1. Ru, Ru′, O(1), O(3)′, C(11)′;
$6.42x+7.36y-4.18z-0.015=0$
2. Ru, Ru′, O(2), O(4)′, C(12)′;
$-7.23x+4.73y-2.32z-0.027=0$
3. Ru, O(1), O(2), O(3), O(4);
$-2.81x+4.78y+8.78z+11.15=0$

Dihedral angles
planes (1) and (2) 90.5°
planes (1) and (3) 90.4°
planes (2) and (3) 89.4°

a) The monoclinic-coordinate system (x, y, z) corresponds to the crystal (a, b, c) axes.

atoms. The mean values of the four different Ru–O bond lengths, all four O–Ru–O angles, the O–O′ distances (2.22 Å) in the carboxylato groups, and the Ru–Cl distance were not significantly different from those of the butyrato complex. The very short Ru–Ru distance (2.281 Å), which was identical with that of the butyrato complex, implies that the interaction between the two metal ions is strong. The oxidation state of the Ru atoms in these complexes is thought to be +2.5, since the two metal atoms of a dinuclear cation are structurally equivalent. The abnormally high magnetic moments (2.90 BM (293 K) for the acetato complex[4)] and 3.37 BM (294 K) for the butyrato complex[1)]) and the electronic spectrum of the $Ru_2(OCOR)_4Cl$ species have been interpreted on the basis of a partial molecular orbital diagram of the M_2X_8 species.[2)]

The only difference between the acetato and butyrato complexes was found in their crystal structures. In both complexes, chloride ions bridged adjacent dinuclear cations to form infinite zigzag chains. In the butyrato complex (tetragonal, space group I42d), there are alternating chains parallel to the a axis and the b axis. However as is shown in Fig. 2, the chains of the acetato complex (monoclinic, space group C2/c) lie along the c axis only. This finding is thought to reflect a substitution effect of R groups in the complexes.

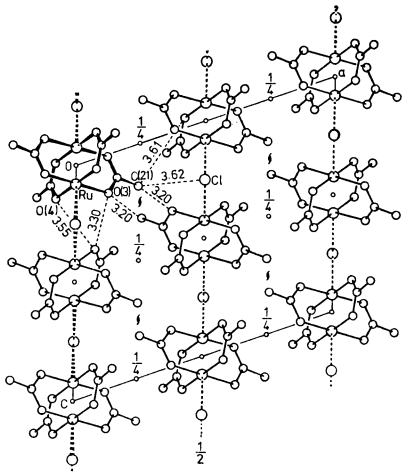

Fig. 2. Projection of the $Ru_2(OCOCH_3)_4Cl$ onto the (0 1 0) plane.

While this manuscript was being prepared, structural studies of similar dinuclear carboxylato complexes of ruthenium were reported by Bino *et al.*[6)] However, there are some differences between the two acetato complexes, $Ru_2(O_2CCH_3)_4Cl\cdot 2H_2O$, in their article and the $Ru_2(O_2CCH_3)_4Cl$ in our article. In the former complex, the Cl bridges are perfectly linear, but in the latter complex the Cl bridges form zigzag chains, with an angle of 127.6° at the Cl atom.

The authors wish to thank Dr. Teruo Nomura of St. Paul's (Rikkyo) University for his help and advice.

References

1) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).
2) M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, **8**, 1 (1969).
3) M. Mukaida, T. Nomura, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **40**, 2462 (1967).
4) M. Mukaida, T. Nomura, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **45**, 2143 (1972).
5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1968), Vol. III, p. 201.
6) A. Bino, F. A. Cotton, and T. R. Felthouse, *Inorg. Chem.*, **18**, 2599 (1979).