Structure of Tetra-μ-formatodiruthenium Bromide

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Synopsis. X-Ray structural determination of $Ru_2(HCOO)_4Br$ showed that the unit cell contains two crystallographically independent formato bridged dinuclear units, $Ru_2(HCOO)_4^+$, each of which is centrosymmetric. Two adjacent units are bridged by bromide ion to make infinite zigzag chains.

Since the $Ru_2(RCOO)_4X$ type of complexes were prepared by Stephenson *et al.* and one of the present authors independently,[1,2] extensive studies of the complexes have been reported.[3-12] These studies showed that the complexes can be classified into three types with different crystal structures; an infinite zigzag chain structure bridged by halide ions,[5,7] an infinite linear chain structure bridged by halide ions,[12] and a structure comprizing discrete dinuclear unit.[6] The basic structural parameters for the dinuclear unit in each type are essentially identical.

Here we wish to report the crystal structure analysis of $[Ru_2(HCOO)_4Br]$. This work was carried out to clarify whether the bonding mode of formate ion in the title complex is similar to that of the analogous monocarboxylate or not.

There existed twinned crystals. By taking oscillation and Weissenberg photographs, a single crystal (*ca.* $0.08\times0.07\times0.18$ mm^3) was chosen and mounted on a RIGAKU four-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Unit cell parameters were refined by least-squares for 19 strong reflections in the 2θ range of 12—15°. Crystal data: $Ru_2(HCOO)_4Br$, F.W.=462.12, monoclinic, space group $P2_1/c$ (systematic absences: $h0l$, l=odd and $0k0$, k=odd), a=9.944(1), b=7.728(1), c=12.679(1) Å, β=93.52(1)°, V=972.46(19) Å^3, D_m=3.175 g cm^{-3} (by flotation in CCl_4/CH_2I_2 mixture), D_c=3.158 g cm^{-1} for Z=4, μ(Mo $K\alpha$)=74.06 cm^{-1}.

TABLE 1. ATOMIC PARAMETERS ($\times10^4$)

Atom	x	y	z	B_{eq}/Å^2
Ru(1)	779(1)	689(1)	555(0)	1.7(0.0)
Ru(2)	4357(1)	4169(1)	522(0)	1.6(0.0)
Br	2733(1)	2325(1)	1771(1)	2.4(0.0)
O(11)	172(5)	2975(6)	−90(4)	2.4(0.1)
O(12)	2140(5)	350(6)	−551(4)	2.5(0.1)
O(13)	1309(5)	−1632(6)	1204(4)	2.5(0.1)
O(14)	−611(5)	971(6)	1645(4)	2.6(0.1)
O(21)	3949(5)	6306(6)	1374(4)	2.3(0.1)
O(22)	2739(5)	4665(6)	−477(4)	2.3(0.1)
O(23)	4812(5)	2060(6)	−332(4)	2.4(0.1)
O(24)	6010(5)	3707(6)	1499(4)	2.5(0.1)
C(11)	−735(7)	2986(8)	−838(5)	2.3(0.1)
C(12)	1797(8)	−387(9)	−1413(6)	2.6(0.1)
C(21)	4442(7)	7737(10)	1108(6)	2.6(0.1)
C(22)	2885(7)	5603(9)	−1289(5)	2.2(0.1)

Intensity data were collected within the range of $2\theta\leqq70°$ using the ω-scan mode up to $2\theta=30°$, and 2θ-ω mode above $2\theta=30°$ at a scan speed of 4° min^{-1}. Three strong standard reflections were measured every 100 reflections; no significant change in intensity was noted during the data collection. The observed intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied; 2654 unique reflections with $|F_o|\geqq3\sigma(|F_o|)$ were obtained. The structure was solved by the heavy atom method and refined by block-diagonal least-squares to R=0.036, anisotropic temperature factors being used. The final difference Fourier map showed no significant peak. Atomic scattering factors from tables[13] with correction for anomalous dispersion were used; the unit weight was given to all reflections. Calculations were performed on the FACOM 230-75 Computer using the UNICS III program system.[14]†† Atomic parameters are given in Table 1.

The crystal consists of two independent formato-bridged dinuclear units, $Ru_2(HCOO)_4^+$, and a bridging

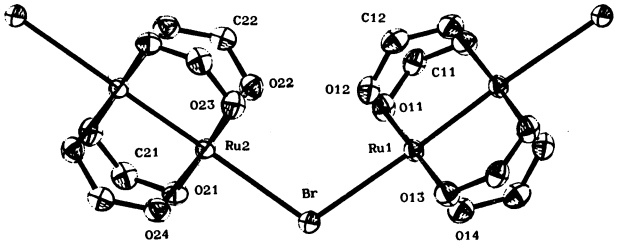

Fig. 1. Structure of $Ru_2(HCOO)_4Br$. Unlabeled atoms are related to labeled ones by a center of inversion at midpoint of Ru–Ru bond.

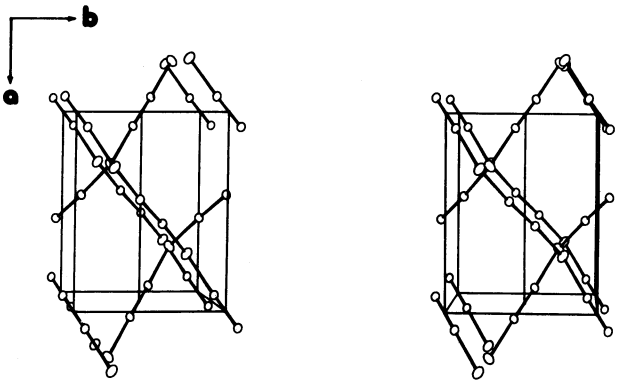

Fig. 2. Crystal packing of the –Ru–Ru–Br– skeletal chains viewed along the c axis. Carbon and oxygen atoms were omitted for clarity.

†† Complete F_o-F_c data and tables of anisotropic thermal parameters, least-squares planes and dihedral angles[15] are kept at the Chemical Society of Japan, Document No. 8260.

Table 2. Interatomic distances and angles

Distance	l/Å	Distance	l/Å
Ru(1)–Ru(1′)	2.2897(7)	Ru(2)–Ru(2′)	2.2901(7)
Br	2.7170(8)	Br	2.7313(9)
O(11)	2.023 (5)	O(21)	2.027 (5)
O(12)	2.024 (5)	O(22)	2.023 (4)
O(13)	2.030 (5)	O(23)	2.024 (5)
O(14)	2.025 (5)	O(24)	2.028 (5)
C(11)–O(11)	1.268 (8)	C(21)–O(21)	1.264 (9)
O(13′)	1.266 (8)	O(23′)	1.277 (9)
C(12)–O(12)	1.260 (8)	C(22)–O(22)	1.274 (8)
O(14′)	1.281 (9)	O(24′)	1.264 (8)
Angle	**φ/°**	**Angle**	**φ/°**
Br –Ru(1)–O(11)	90.46(14)	Br –Ru(2)–O(21)	88.36(14)
–O(12)	88.15(14)	–O(22)	89.18(14)
–O(13)	91.26(14)	–O(23)	92.83(14)
–O(14)	93.24(14)	–O(24)	92.31(14)
–Ru(1′)	176.43(3)	–Ru(2′)	177.07(3)
O(11)–Ru(1)–O(12)	91.65(20)	O(21)–Ru(2)–O(22)	90.11(19)
–O(13)	177.69(20)	–O(23)	178.57(19)
–O(14)	89.00(20)	–O(24)	89.98(19)
–Ru(1′)	89.08(4)	–Ru(2′)	89.36(14)
O(12)–Ru(1)–O(13)	89.94(20)	O(22)–Ru(2)–O(23)	90.71(19)
–O(14)	178.45(20)	–O(24)	178.52(20)
–Ru(1′)	88.32(14)	–Ru(2′)	88.99(14)
O(13)–Ru(1)–O(14)	89.37(20)	O(23)–Ru(2)–O(24)	89.17(19)
–Ru(1′)	89.29(14)	–Ru(2′)	89.48(14)
O(14)–Ru(1)–Ru(1′)	90.28(14)	O(24)–Ru(2)–Ru(2′)	89.53(14)
Ru(1)–O(11)–C(11)	119.3 (4)	Ru(2)–O(21)–C(21)	118.4 (4)
–O(12)–C(12)	120.1 (5)	–O(22)–C(22)	119.2 (4)
–O(13)–C(11′)	118.8 (4)	–O(23)–C(21′)	118.2 (4)
–O(14)–C(12′)	117.5 (4)	–O(24)–C(22′)	118.6 (4)
O(11)–C(11)–O(13′)	123.5 (6)	O(21)–C(21)–O(23′)	124.5 (7)
O(12)–C(12)–O(14′)	123.7 (7)	O(22)–C(22)–O(24′)	123.7 (6)
Ru(1)–Br–Ru(2)	109.99(3)		

bromide ion as is shown in Fig. 1. Each of the units is composed of two rutheniums and four formate ions and has a crystallographic center of inversion on the middle of the Ru–Ru bond. Bromide ion bridges adjacent dinuclear units to form infinite zigzag chains, with Ru(1)–Br–Ru(2) angle of 109.99(3)°. These chains are on planes parallel to {1 1 0} as shown in Fig. 2. One chain extends along ⟨1 1 0⟩ on $z=0$, and the other on $z=1/2$. The two crystallographically independent dinuclear units show no significant differences in geometrical parameters except the Ru–Br bond (Table 2). The average Ru–Ru and Ru–O bond lengths are 2.290 and 2.026 Å, respectively. The Ru–Ru–Br angles slightly deviate from 180°. Such anglar bend appears in the zigzag chains as well as in the discrete complex ions.[6] Dihedral angles of the planes defined by Ru_2O_2C group are nearly 90°, as expected. Two oxygens in every group deviate from the plane by 0.01—0.03 Å to twist the plane. The Ru deviates more than 0.02 Å from the plane formed by the four equatorial O atoms, in the direction to elongate the Ru–Ru distance. In agreement with a previous prediction,[2] the present result shows that the $[Ru_2(RCOO)_4X]$ type of complexes reported so far have the same bonding mode in reference to the monocarboxylato ligand.

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