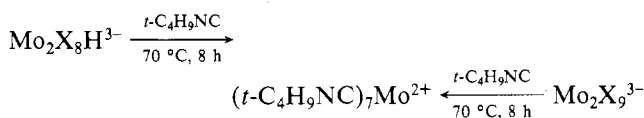


$W_2Cl_9^{3-}$  produced high (~80%) yields of the heptakis(*tert*-butyl isocyanide)molybdenum(II) cation, isolated as its  $PF_6^-$  salt.<sup>13</sup>



### Conclusions

The reaction of tripotassium enneachloroditungstate with *tert*-butyl isocyanide, when carried out in the presence of a small amount of water, produces heptakis(*tert*-butyl iso-

- (13) Established by a comparison of the single-crystal X-ray crystallographic parameters of this material with those reported for  $[(t-C_4H_9NC)_7Mo][PF_6]_2$ .  
 (14) Muettterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* 1974, 96, 1748.

cyanide)tungsten(II) hexatungstate,  $[(t-C_4H_9NC)_7W][W_6O_{19}]$ . The cation exhibits distorted capped trigonal-prismatic geometry, similar to that observed for several other heptaleptic complexes. The ready synthesis of this ion provides a unique opportunity to examine the chemical and dynamic properties of cationic tungsten(II) and, in particular, to explore its utility as a precursor to complexes of mononuclear tungsten(III). Such studies are currently underway.

**Acknowledgment.** The technical assistance of Mr. Ralph Nuzzo during the early course of this investigation is gratefully acknowledged. We also are indebted to our colleague Professor Joseph Potenza for helpful discussions.

**Registry No.**  $[(t-C_4H_9NC)_7W][W_6O_{19}]$ , 72016-74-1;  $K_3W_2Cl_9$ , 23403-17-0.

**Supplementary Material Available:** Thermal parameters and observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,  
Texas A&M University, College Station, Texas 77843

## Structural Characterization of Two Tetrakis( $\mu$ -carbonato) Complexes of Dirhodium(II)

F. ALBERT COTTON\* and TIMOTHY R. FELTHOUSE

Received July 24, 1979

The presence of the dinuclear  $Rh_2(CO_3)_4^{4-}$  unit has been confirmed by using X-ray crystallography for the following two complexes of rhodium(II):  $Cs_4[Rh_2(CO_3)_4(H_2O)_2] \cdot 6H_2O$  (**1**) and  $Cs_4Na_2[Rh_2(CO_3)_4Cl_2] \cdot 8H_2O$  (**2**). Both compounds crystallize in the space group  $P2_1/c$  with two formula weights in unit cells having the dimensions  $a = 7.867$  (1) Å,  $b = 7.963$  (1) Å,  $c = 18.211$  (2) Å,  $\beta = 91.83$  (1)°, and  $V = 1140.2$  (3) Å<sup>3</sup> and  $a = 9.798$  (2) Å,  $b = 10.753$  (2) Å,  $c = 12.906$  (3) Å,  $\beta = 107.98$  (2)°, and  $V = 1293.2$  (4) Å<sup>3</sup> for **1** and **2**, respectively. The structure of **1** was refined by using 1833 reflections with  $I > 3\sigma(I)$  to final discrepancy indices of  $R_1 = 0.051$  and  $R_2 = 0.070$ , while the structure of **2** converged with  $R_1 = 0.037$  and  $R_2 = 0.050$  for 1266 reflections with  $I > 3\sigma(I)$ . The  $Rh_2(CO_3)_4^{4-}$  unit in **1** is located on a crystallographic center of inversion with a Rh-Rh distance of 2.378 (1) Å. Two water molecules occupy the axial positions with a Rh-O distance of 2.344 (5) Å. Compound **2** also has the  $Rh_2(CO_3)_4^{4-}$  unit located on a crystallographic center of inversion with a Rh-Rh bond distance of 2.380 (2) Å. The axial positions are occupied by  $Cl^-$  ions with a Rh-Cl distance of 2.601 (3) Å. The  $Cl^-$  ions are associated in an ionic fashion with the  $Na^+$  ions in the lattice.

### Introduction

The dirhodium(II) tetracarboxylates have recently attracted much interest,<sup>1-4</sup> largely due to the variety of axial ligands which form stable adducts. The effect of axial ligation invariably has been an overall weakening of the Rh-Rh bond<sup>1,2</sup> which has been formulated<sup>4</sup> as primarily a single bond. Our recent work<sup>5</sup> on the  $Rh_2^{4+}$  system has shown that a small but significant shortening of the Rh-Rh bond occurs when non-carboxylate bridging ligands such as 2-oxo-6-methylpyridine (mhp) are employed which eliminate axial interactions.

Another factor which can influence the metal-metal bond length in tetracarboxylate systems is the nature of the R group substituent of the carboxylate bridge. An extensive investigation of  $Cr_2(O_2CR)_4L_2$ -type compounds<sup>6</sup> has shown that the Cr-Cr distance decreases as the parent carboxylic acid becomes weaker and, thus, a better donor ligand. In this series of dichromium(II) carboxylates, the Cr-Cr bond length in the  $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$  anion was found to be significantly shorter than that in any carboxylate complex. Accordingly,

it was of interest to prepare the analogous rhodium(II) complex and observe the effect of the carbonate ligand on the Rh-Rh bond length.

Several years ago, Wilson and Taube reported<sup>7</sup> the preparation and characterization via elemental analysis, infrared and electronic spectra, magnetic susceptibility, and electrochemistry of several carbonate complexes of rhodium(II). They concluded that the complexes most probably resembled the  $Rh_2(OAc)_4(H_2O)_2$  complex<sup>8</sup> with bridging bidentate carbonate ligands. The work reported here confirms their expectations with the presentation in detail of the structures of two compounds containing the  $Rh_2(CO_3)_4^{4-}$  unit.

### Experimental Section

**Compound Preparation.** Rhodium(II) acetate was prepared by using an established procedure.<sup>9</sup> A sample of  $Cs_4[Rh_2(CO_3)_4(H_2O)_2] \cdot 6H_2O$  (**1**) was prepared by using a procedure given by Wilson and Taube.<sup>7</sup> A 0.1-g sample of  $Rh_2(O_2CCH_3)_4$  was suspended in 2-3 mL of an aqueous 2 M  $Cs_2CO_3$  solution. The solution was heated to 100 °C for about 15 min. A microcrystalline dark blue solid formed. Suitable crystals were obtained by slow evaporation of the reaction mixture.

$Cs_4Na_2[Rh_2(CO_3)_4Cl_2] \cdot 8H_2O$  (**2**) was isolated from a solution containing  $Na_4[Rh_2(CO_3)_4] \cdot xH_2O$  (prepared as per the Cs analogue)

- (1) Christoph, G. G.; Koh, Y.-B. *J. Am. Chem. Soc.* 1979, 101, 1422 and references therein.  
 (2) Koh, Y. B.; Christoph, G. G. *Inorg. Chem.* 1979, 18, 1122.  
 (3) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* 1979, 101, 2897.  
 (4) Norman, J. G., Jr.; Kolari, H. *J. Am. Chem. Soc.* 1978, 100, 791.  
 (5) Cotton, F. A.; Felthouse, T. R., to be submitted for publication.  
 (6) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* 1978, 17, 2004.

- (7) Wilson, C. R.; Taube, H. *Inorg. Chem.* 1975, 14, 405.  
 (8) Cotton, F. A.; De Boer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B* 1971, 27, 1664.  
 (9) Rempel, G. A.; Legzdins, P.; Smith, P.; Wilkinson, G. *Inorg. Synth.* 1971, 13, 90.

Table I. Crystallographic Data

parameter	1	2
space group	$P2_1/c$	$P2_1/c$
$a$ , Å	7.867 (1)	9.798 (2)
$b$ , Å	7.963 (1)	10.753 (2)
$c$ , Å	18.211 (2)	12.906 (3)
$\beta$ , deg	91.83 (1)	107.98 (2)
$V$ , Å <sup>3</sup>	1140.2 (3)	1293.2 (4)
$d_{\text{calcd}}$ , g/cm <sup>3</sup>	3.27	3.18
$Z$	2	2
fw	1121.59	1238.48
cryst size, mm	0.2 × 0.3 × 0.4	0.1 × 0.2 × 0.2
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	78.857	71.975
range $2\theta$ , deg	4–50	4–45
no. unique data	1991	1409
no. data, $F_o^2 > 3\sigma(F_o^2)$	1833	1266
no. variables	136	134
$R_1$	0.051	0.037
$R_2$	0.070	0.050
esd	1.774	1.091

and an excess of CsCl. Slow evaporation of the aqueous mixture gave green crystals of 2.

**X-ray Crystallography. Collection of Data.** Data for both compounds were collected on a Syntex PI automated four-circle diffractometer using Mo ( $\lambda = 0.71073$  Å) radiation with a graphite crystal monochromator in the incident beam. The quality of each crystal was judged satisfactory from the relatively narrow widths at half height for  $\omega$  scans of several reflections. The unit cell constants were obtained from a least-squares fit of 15 strong reflections in the range  $29^\circ \leq 2\sigma \leq 32^\circ$  1 and  $23^\circ \leq 2\sigma \leq 31^\circ$  for 2. Data were collected at  $22 \pm 3$  °C by using the  $\theta$ - $2\theta$  scan technique with a variable scan rate from 4.0 to 24.0°/min. Other general procedures for data collection have been given elsewhere.<sup>10</sup> Crystallographic data and other information have been collected in Table I. For each crystal, Lorentz and polarization corrections were applied in addition to an absorption correction. Absorption corrections were made by using an empirical method based on  $\psi$  scans ( $\psi = 0$ – $360^\circ$  every  $10^\circ$ ) for  $\chi$  values near  $90^\circ$ . For 1, five sets of  $\psi$  scans were used with maximum, minimum, and average relative transmission values of 1.00, 0.57, and 0.82, respectively. Compound 2 used four sets of  $\psi$  scans with transmission values ranging from 1.00 to 0.58 with an average value of 0.87.

**Solution and Refinement of the Structures.**<sup>11</sup> The Cs and Rh atom positions in both structures were obtained via direct methods using the MULTAN program. Each structure was successfully refined in the space group  $P2_1/c$  with anisotropic thermal parameters for all nonhydrogen atoms in 1 and anisotropic thermal parameters for all nonhydrogen atoms excluding lattice oxygen (water) atoms which were left with isotropic thermal parameters. Both structures were refined to convergence with final discrepancy indices given by

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_2 = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

and listed in Table I. A table of observed and calculated structure factors for each compound is available as supplementary material.

## Results

The positional and thermal parameters are recorded in Tables II and III and 1 and 2, respectively. Tables IV and V present the bond distances and angles for these compounds.

The structure of  $\text{Cs}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (1) consists of discrete cesium cations and  $[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]^{4-}$  anions which participate in hydrogen-bonded contacts with the six lattice water molecules. The two independent cesium ions in the asymmetric unit reside about crystallographic inversion

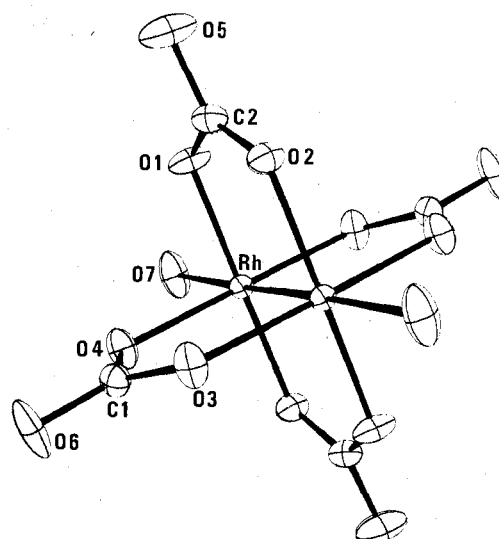


Figure 1. An ORTEP plotting of the  $[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]^{4-}$  anion in  $\text{Cs}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (1) with thermal ellipsoids at the 50% probability level. The anion is located about a center of inversion.

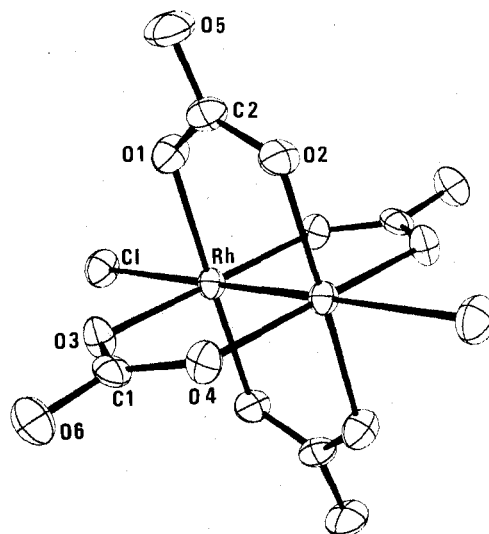


Figure 2. The  $[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]^{6-}$  anion in  $\text{Cs}_4\text{Na}_2[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2] \cdot 8\text{H}_2\text{O}$  (2) drawn with 50% probability vibrational ellipsoids. The anion is located about an inversion center.

centers. The anionic dirhodium unit is located on an inversion center and a view of this unit is given in Figure 1. The carbonate groups are disposed about the two rhodium atoms in a regular fashion, imparting close to  $D_{4h}$  symmetry to the anionic unit. The Rh–Rh distance is 2.378 (1) Å and the axial position is occupied by a water oxygen atom, O(7), at a distance of 2.344 (5) Å from Rh. The two independent  $\text{CO}_3^{2-}$  groups have C–O distances which average to 1.29 [2] Å.<sup>12</sup> There is no significant difference between the C–O distances to coordinated oxygen atoms and the outer, uncoordinated ones at the level of precision (roughly  $\pm 0.01$  Å) obtained for these distances. The O–C–O angles involving the ligating oxygen atoms average to  $123 [1]^\circ$ ,<sup>12</sup> while the other O–C–O angles have a mean value of  $119 [1]^\circ$ .<sup>12</sup> The four independent water molecules participate in eight hydrogen-bonded contacts (2.7–2.9 Å) involving the terminal carbonate oxygen atoms O(5) and O(6), the bridging carbonate oxygen atom O(1), and the other water oxygen atoms. The cesium atoms have no

(10) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *Organomet. Chem.* 1973, 50, 227. Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* 1979, 18, 1143.

(11) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package with local modifications.

(12) The standard deviations for average values are given in brackets and were calculated according to the formula  $[\sum(d_i - \bar{d})^2 / (N - 1)]^{1/2}$ , where  $d_i$  is the  $i$ th distance and  $\bar{d}$  is the average of  $N$  distances.

**Table II.** Positional and Thermal Parameters and Their Estimated Standard Deviations for  $\text{Cs}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  (1)<sup>a</sup>

atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cs(1)	0.50540 (8)	0.48187 (9)	0.13809 (4)	1.83 (2)	5.08 (3)	2.99 (3)	-0.08 (2)	0.03 (2)	0.68 (2)
Cs(2)	0.11619 (8)	0.52118 (7)	0.63548 (3)	3.46 (2)	2.21 (2)	2.24 (2)	0.20 (2)	0.69 (2)	0.25 (2)
Rh	0.10893 (7)	0.60326 (6)	-0.00199 (3)	0.74 (2)	0.94 (2)	1.14 (2)	-0.22 (2)	0.17 (2)	0.06 (2)
O(1)	0.0756 (8)	0.6093 (7)	-0.1133 (3)	2.0 (2)	2.9 (2)	1.0 (2)	-0.7 (2)	0.2 (2)	0.2 (2)
O(2)	0.1273 (7)	0.5898 (6)	0.1096 (3)	1.9 (2)	1.6 (2)	1.4 (2)	-0.6 (2)	-0.0 (2)	-0.1 (2)
O(3)	0.2800 (7)	0.4145 (7)	-0.0107 (3)	0.8 (2)	1.4 (2)	3.4 (3)	-0.1 (2)	0.2 (2)	0.2 (2)
O(4)	-0.0726 (7)	0.7833 (7)	0.0078 (3)	1.0 (2)	1.5 (2)	3.0 (2)	0.2 (2)	-0.1 (2)	-0.2 (2)
O(5)	-0.0583 (9)	0.5246 (9)	-0.2152 (3)	3.2 (3)	4.5 (3)	1.3 (2)	-1.1 (2)	-0.1 (2)	0.0 (2)
O(6)	0.3391 (8)	0.1435 (7)	-0.0237 (4)	1.6 (2)	1.5 (2)	6.3 (4)	0.7 (2)	0.6 (2)	-0.5 (3)
O(7)	0.3242 (8)	0.8058 (7)	-0.0082 (4)	2.0 (2)	1.2 (2)	5.3 (3)	-0.4 (2)	0.2 (2)	-0.0 (2)
O(8)	0.2567 (8)	0.7891 (10)	0.7817 (4)	2.4 (3)	4.2 (3)	4.3 (3)	-0.1 (3)	0.2 (2)	1.1 (3)
O(9)	0.5220 (13)	0.5288 (13)	0.6539 (5)	5.0 (4)	8.1 (5)	3.3 (4)	1.6 (4)	0.5 (3)	-0.3 (4)
O(10)	0.2882 (16)	0.2341 (15)	0.2601 (6)	9.8 (7)	5.5 (5)	8.0 (6)	2.6 (5)	-2.4 (5)	-0.9 (5)
C(1)	0.2295 (9)	0.2580 (9)	-0.0145 (4)	1.1 (2)	1.5 (3)	1.8 (3)	0.2 (2)	0.1 (2)	0.1 (2)
C(2)	-0.0358 (11)	0.5111 (10)	-0.1446 (5)	1.6 (3)	1.9 (3)	1.4 (3)	0.0 (2)	0.2 (3)	-0.1 (2)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

**Table III.** Positional and Thermal Parameters and Their Estimated Standard Deviations for  $\text{Cs}_4\text{Na}_2[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]\cdot 8\text{H}_2\text{O}$  (2)<sup>a</sup>

atom	x	y	z	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cs(1)	0.45259 (9)	0.38078 (7)	0.33599 (6)	3.92 (4)	1.75 (3)	2.46 (3)	0.12 (3)	1.20 (3)	0.29 (3)
Cs(2)	0.11358 (10)	0.25729 (9)	0.01233 (8)	2.76 (3)	4.54 (4)	3.68 (4)	-0.67 (3)	1.00 (3)	0.02 (3)
Rh	0.51638 (9)	0.59829 (8)	0.96319 (7)	1.44 (3)	1.20 (3)	1.77 (3)	-0.03 (3)	0.54 (3)	0.13 (3)
Cl	0.5411 (3)	0.8151 (3)	0.8815 (3)	2.6 (1)	1.8 (1)	3.0 (1)	-0.1 (1)	0.6 (1)	0.5 (1)
Na	0.2511 (6)	0.7714 (5)	0.8205 (5)	4.0 (2)	2.3 (2)	3.8 (2)	-0.4 (2)	0.2 (2)	0.3 (2)
O(1)	0.3511 (8)	0.5573 (7)	0.8254 (6)	2.0 (3)	1.8 (3)	2.6 (3)	-0.3 (3)	0.3 (3)	0.4 (3)
O(2)	0.3220 (9)	0.3691 (7)	0.8960 (6)	2.4 (3)	1.4 (3)	2.1 (3)	-0.6 (3)	0.4 (3)	-0.0 (3)
O(3)	0.3662 (8)	0.6715 (7)	1.0254 (6)	2.5 (3)	1.5 (3)	2.8 (3)	0.4 (3)	1.4 (2)	0.2 (3)
O(4)	0.3389 (7)	0.4843 (7)	1.1000 (6)	1.2 (3)	2.3 (3)	2.4 (3)	0.1 (3)	0.9 (2)	0.2 (3)
O(5)	0.1686 (10)	0.4332 (8)	0.7418 (7)	2.4 (4)	3.2 (4)	2.5 (4)	-0.5 (3)	-0.6 (3)	-0.3 (3)
O(6)	0.2261 (8)	0.6522 (8)	1.1306 (6)	2.4 (3)	2.2 (3)	3.2 (3)	-0.2 (3)	1.7 (2)	-0.3 (3)
O(7)	0.170 (1)	0.5969 (9)	0.5771 (8)	4.2 (2)					
O(8)	0.002 (1)	0.7358 (10)	0.7566 (9)	4.5 (2)					
O(9)	-0.029 (1)	0.5194 (12)	0.8550 (10)	5.8 (3)					
O(10)	0.193 (1)	0.9707 (13)	0.8873 (10)	6.4 (3)					
C(1)	0.310 (1)	0.603 (1)	1.0835 (9)	1.6 (4)	1.8 (4)	1.9 (4)	-0.3 (4)	0.3 (4)	-0.8 (4)
C(2)	0.281 (1)	0.452 (1)	0.8207 (9)	2.1 (4)	2.5 (5)	1.4 (4)	-0.1 (4)	0.6 (3)	0.2 (4)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

**Table IV.** Bond Distances (Å) and Angles (Deg) for  $\text{Cs}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  (1)

Distances within $[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]^{4-}$			
Rh-Rh'	2.378 (1)	O(1)-C(2)	1.293 (8)
Rh-O(1)	2.036 (4)	O(2)-C(2)	1.265 (8)
Rh-O(2')	2.035 (4)	O(3)-C(1)	1.309 (7)
Rh-O(3')	2.027 (4)	O(4)-C(1)	1.287 (7)
Rh-O(4')	2.035 (4)	O(5)-C(2)	1.296 (8)
Rh-O(7)	2.344 (5)	O(6)-C(1)	1.270 (7)
Angles within $[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2]^{4-}$			
Rh'-Rh-O(1)	88.7 (1)	O(3')-Rh-O(7)	91.4 (2)
Rh'-Rh-O(2')	87.8 (1)	O(4)-Rh-O(7)	91.7 (2)
Rh'-Rh-O(3')	88.3 (1)	Rh-O(1)-C(2)	119.3 (4)
Rh'-Rh-O(4)	88.6 (1)	Rh'-O(2)-C(2)	120.9 (4)
Rh'-Rh-O(7)	178.9 (1)	Rh'-O(3)-C(1)	120.6 (4)
O(1)-Rh-O(2')	176.3 (2)	Rh-O(4)-C(1)	120.4 (4)
O(1)-Rh-O(3')	90.2 (2)	O(3)-C(1)-O(4)	121.9 (5)
O(1)-Rh-O(4)	90.1 (2)	O(3)-C(1)-O(6)	119.0 (5)
O(1)-Rh-O(7)	90.3 (2)	O(4)-C(1)-O(6)	119.1 (5)
O(2')-Rh-O(3')	90.8 (2)	O(1)-C(2)-O(2)	123.4 (6)
O(2')-Rh-O(4)	88.7 (2)	O(1)-C(2)-O(5)	117.2 (6)
O(2')-Rh-O(7)	93.2 (2)	O(2)-C(2)-O(5)	119.4 (6)
O(3')-Rh-O(4)	176.9 (2)		

**Table V.** Bond Distances (Å) and Angles (Deg) for  $\text{Cs}_4\text{Na}_2[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]\cdot 8\text{H}_2\text{O}$  (2)

Distances within $[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]^{6-}$			
Rh-Rh'	2.380 (2)	O(1)-C(2)	1.32 (1)
Rh-Cl	2.601 (3)	O(2)-C(2)	1.28 (1)
Rh-O(1)	2.050 (8)	O(3)-C(1)	1.29 (1)
Rh-O(2')	2.039 (8)	O(4)-C(1)	1.31 (1)
Rh-O(3)	2.040 (8)	O(5)-C(2)	1.27 (2)
Rh-O(4')	2.044 (7)	O(6)-C(1)	1.28 (1)
Angles within $[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]^{6-}$			
Rh'-Rh-Cl	177.64 (9)	Rh-O(1)-C(2)	119.0 (7)
Rh'-Rh-O(1)	89.3 (2)	Rh'-O(2)-C(2)	122.0 (7)
Rh'-Rh-O(2')	87.7 (2)	Rh-O(3)-C(1)	119.9 (7)
Rh'-Rh-O(3)	89.0 (2)	Rh'-O(4)-C(1)	120.0 (7)
Rh'-Rh-O(4')	88.2 (2)	O(3)-C(1)-O(4)	123 (1)
O(1)-Rh-O(2')	177.0 (3)	O(3)-C(1)-O(6)	120 (1)
O(1)-Rh-O(3)	87.2 (3)	O(4)-C(1)-O(6)	118 (1)
O(1)-Rh-O(4')	91.2 (3)	O(1)-C(2)-O(2)	122 (1)
O(2)-Rh-O(3)	92.2 (3)	O(1)-C(2)-O(5)	119 (1)
O(2')-Rh-O(4')	89.2 (3)	O(2)-C(2)-O(5)	119 (1)
O(3)-Rh-O(4')	176.8 (3)		

interatomic contacts closer than 3.0 Å.

The structure  $\text{Cs}_4\text{Na}_2[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]\cdot 8\text{H}_2\text{O}$  (2) is comprised of  $\text{Cs}^+$  and  $\text{Na}^+$  cations,  $[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2]^{6-}$  anions, and water molecules in the lattice. The anionic fragment, depicted in Figure 2, is located on an inversion center and has a very regular structure possessing close to  $D_{4h}$  symmetry as was found in **1**. The Rh-Rh distance of 2.380 (2) Å is statistically indistinguishable from the value found in **1**. The Cl<sup>-</sup> ion

occupies the axial position, with a very long Rh-Cl distance of 2.601 (3) Å and has a slightly bent Rh'-Rh-Cl angle of 177.64 (9)°. The carbonate C-O distances which are all equivalent within the errors have an average value of 129 [1]°. The O-C-O angles are nearly identical with those in **1** and average to 122.5 [7]° for the bridging O-C-O groups and 119 [1]° for the others. Seven hydrogen-bonded interactions (2.63-2.92 Å) can be identified involving the four independent water molecules. Whereas the cesium ions show no coordinated contacts shorter than 3.0 Å as in **1**, the sodium

ion has a distorted octahedral coordination geometry involving Cl, O(1), O(3), O(6), O(8), and O(10) with distances of 2.744 (7), 2.495 (9), 2.75 (1), 2.52 (1), 2.35 (1), and 2.44 (1) Å, respectively.

### Discussion

An examination of the bond distances and angles in Tables IV and V for compounds **1** and **2** reveals that the  $\text{Rh}_2(\text{CO}_3)_4^{4+}$  units are essentially identical. The only structural parameter which differs significantly between the two compounds is the Rh-axial ligand distance, as might be expected. The Rh-O(7) distance in **1** of 2.344 (5) Å is to be compared with a value of 2.310 (3) Å found in  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ .<sup>8</sup> The slightly weaker (0.034 Å) Rh-O axial bond in the carbonate complex is matched with a slightly stronger Rh-Rh bond (by  $\sim 0.008$  Å), and once again, the persistent inverse relationship between metal-metal and metal-axial ligand bond lengths<sup>13-15</sup> is observed. In complex **2** the axial position is occupied by a  $\text{Cl}^-$  ion which is associated with the Rh atom at a distance of 2.601 (3) Å. Such a long distance precludes any but the weakest type of bonding interaction. The high negative charge already on the complex undoubtedly contributes to a lengthening of the Rh-Cl bond. In contrast, the Rh-Cl bond length in  $[\text{C}(\text{NH}_2)_3][\text{Rh}_2(\text{OAc})_4\text{Cl}_2]$ , where  $[\text{C}(\text{NH}_2)_3]^+$  is the guanidinium ion, is significantly shorter with a value of 2.49 Å,<sup>16</sup> but

here there is no negative charge on the  $\text{Rh}_2(\text{OAc})_4$  unit tending to repel the incoming  $\text{Cl}^-$  ion as in the carbonate complex **2**.

A recent survey<sup>2</sup> of some 48 metal tetracarboxylate structures including 6 rhodium(II) acetate adducts reveals that the M-O-C and O-C-O angles are the most responsive to changes in M-M bond length. The average Rh-O-C and O-C-O angles in the two carbonate complexes are nearly identical with values of 120.3 (4) and 122.6 (6)° for **1** and 120.3 (4)° and 122.5 (1.0)° for **2**. The Rh-O-C angles are slightly greater than in  $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ <sup>8</sup> for which the angle is 119.5 (3)°, while the O-C-O angles in the carbonates are slightly less than the angle in the acetate complex (124.8 (3)°). Both of these angular variations are in accord with the shorter Rh-Rh distances observed in the two carbonate structures presented here.

The  $[\text{Rh}_2(\text{CO}_3)_4]^{4+}$  ion is one of only two such carbonate-bridged dimetal units to be prepared, the other being the  $[\text{Cr}_2(\text{CO}_3)_4]^{4+}$  ion.<sup>6</sup> Since the bridging carbonate ion appears to be completely compatible with the retention of the usual metal-metal bond lengths in these two cases, it seems likely that carbonate-bridged species should be stable for other dimetal ions such as  $\text{Mo}_2^{4+}$  and  $\text{Re}_2^{6+}$ , but it appears that no effort has been made yet to isolate them.

**Acknowledgment.** We thank the National Science Foundation for support and Dr. A. Bino for his assistance in this work. We are grateful to Engelhard Industries for a loan of rhodium trichloride.

**Registry No.** **1**, 72207-19-3; **2**, 72207-20-6;  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ , 15956-28-2;  $\text{Na}_4[\text{Rh}_2(\text{CO}_3)_4]$ , 53078-66-3.

**Supplementary Material Available:** Tables of observed and calculated structure factors for the two compounds (14 pages). Ordering information is given on any current masthead page.

- (13) Cotton, F. A.; Extine, M.; Gage, L. D. *Inorg. Chem.* **1978**, *17*, 172.  
 (14) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.  
 (15) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1977**, *16*, 1867.  
 (16) Nefedov, V. I.; Salyn, Ya. V.; Sadovskiy, A. P. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 299. The correct literature citation for this structure has yet to appear. This reference merely cites the bond distance; see ref 52 in ref 1.

Contribution from the Department of Chemistry,  
 Texas A&M University, College Station, Texas 77843

## Structural Studies of Three Tetrakis(carboxylato)dirhodium(II) Adducts in Which Carboxylate Groups and Axial Ligands Are Varied

F. ALBERT COTTON\* and TIMOTHY R. FELTHOUSE

Received August 2, 1979

Three dirhodium(II) compounds, namely,  $\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4(\text{H}_2\text{O})_2$  (**1**),  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{THT})_2$  (**2**), and  $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{Me}_2\text{SO})_2$  (**3**) (THT = tetrahydrothiophene,  $\text{Me}_2\text{SO}$  = dimethyl sulfoxide), have been prepared and their structures determined by X-ray crystallography. These structures were refined to final  $R_1$  values of 0.036, 0.032, and 0.036 for **1**, **2**, and **3**, respectively. Compound **1** crystallizes in the space group  $P\bar{1}$  with  $a = 9.408$  (1) Å,  $b = 11.799$  (2) Å,  $c = 6.984$  (1) Å,  $\alpha = 105.98$  (1)°,  $\beta = 94.24$  (1)°,  $\gamma = 99.48$  (1)°, and  $Z = 1$ . The centrosymmetric structure has a relatively short Rh-Rh bond length of 2.371 (1) Å with axially coordinated water molecules at a distance of 2.295 (2) Å. Compound **2** crystallizes in the space group  $Pbcn$  with four formula weights in a unit cell having the dimensions  $a = 9.801$  (2) Å,  $b = 16.087$  (3) Å, and  $c = 14.592$  (3) Å. The complex is located on a crystallographic center of inversion with a Rh-Rh bond length of 2.413 (1) Å and an axial Rh-S(THT) distance of 2.517 (1) Å. Crystals of **3** are orthorhombic, space group  $Pbca$ , with four formula units located on inversion centers in a unit cell having the dimensions  $a = 8.377$  (2) Å,  $b = 16.726$  (2) Å, and  $c = 14.840$  (2) Å. The  $\text{Me}_2\text{SO}$  molecules coordinate through the sulfur atoms with a Rh-S distance of 2.451 (1) Å. The Rh-Rh bond length in **3** of 2.406 (1) Å is very slightly shorter than the value found for the THT adduct.

### Introduction

Transition-metal tetracarboxylates of the form  $\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2$  have played a key role in unraveling the effects of bridging ligands, as controlled by the R group substituents, and axial donor ligands on the metal-metal bond length. Structural studies of dichromium(II) tetracarboxylates reveal that a wide ( $\sim 0.3$  Å) range of Cr-Cr distances is possible from 2.214 (1) Å<sup>1</sup> (R = O<sup>-</sup>, L = H<sub>2</sub>O) to 2.541 (1) Å<sup>2</sup> (R = CF<sub>3</sub>,

L = OEt<sub>2</sub>). A considerably narrower range of metal-metal bond lengths has been found for the second-row transition metals. The dimolybdenum(II) tetracarboxylates, for example, display only about a 0.04 Å variation in Mo-Mo bond length from 2.088 (1) Å in  $\text{Mo}_2(\text{piv})_4$ <sup>3</sup> (piv =  $\text{O}_2\text{CCMe}_3$  and L is an oxygen atom from a bridging pivalate group of a neighboring molecule) to 2.129 (2) Å in  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$ .<sup>4</sup> Generally

(1) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 2004.

(2) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.

(3) Cotton, F. A.; Extine, M.; Gage, L. D. *Inorg. Chem.* **1978**, *17*, 172.

(4) Cotton, F. A.; Norman, J. G., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5697.