

a plane; the main distortion from ideal octahedral geometry is the bending of the Co-S bonds away from the perpendicular to this plane by an average of 7.3°, due to the meridional spanning by the central portion of the ligand. In the cation containing Co1, the trans pyridine planes form a dihedral angle of 13.8° with each other and dihedral angles of 89.4 and 97.7° with the central pyridine plane. Analogous values in the cation containing Co2 are 23.5, 72.7, and 94.0°, respectively.

A linear pentadentate ligand, 1,9-bis(2-pyridyl)-2,5,8-triazanone, which is similar to ligand **4b**, also forms an octahedral cobalt(III) complex where the sixth coordination site is taken by a chloro ligand.<sup>27</sup>

The [CoCl<sub>4</sub>]<sup>2-</sup> anion exhibits only small deviations from ideal tetrahedral geometry.<sup>28</sup> The average Co-Cl distance is 2.271 Å, and the average angle is 109.48°. These are significantly different as compared to the orthorhombic form of K<sub>2</sub>[CoCl<sub>4</sub>] and agree very well with the monoclinic form where the mean Co-Cl distance is 2.274 Å and the average angle is 109.45°.<sup>28</sup>

**3. Magnetic and Spectral Properties.** The magnetic and spectral data for various complexes are listed in Table III. The visible spectra of all the cobalt(II) complexes were dominated by a very intense band around 18 200–19 200 cm<sup>-1</sup>, which is typical of the highest energy transition, <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P), for octahedral cobalt(II) complexes.<sup>29</sup> An additional strong transition, [<sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(P)], at 14 700 cm<sup>-1</sup> was observed in the [Co(**4b**)Cl]<sub>2</sub>[CoCl<sub>4</sub>] complex due to the presence of the tetrahedral species [CoCl<sub>4</sub>]<sup>2-</sup>.

The PBP complexes [Co(**1a**)H<sub>2</sub>O]<sup>2+</sup> and [Co(**4a**)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> showed only one very strong band at 18 700 and 18 200 cm<sup>-1</sup>, respectively, while in the similar PBP complexes of Co(II), e.g., [Co(DAPSC)(Cl)H<sub>2</sub>O]<sup>+</sup> and [Co(DAPSC)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> Gerloch et al.<sup>30</sup> reported a single band at ca. 15 800 cm<sup>-1</sup> and

a split band at ca. 18 000 cm<sup>-1</sup>, all assigned as involving transitions to components of <sup>4</sup>P. However, they recorded the electronic spectra of single crystals. The magnetic moments of the Co(II) complexes range from 4.74 to 5.24 μ<sub>B</sub>. For the two PBP complexes these values lie at the upper end of this range given for six-coordinate Co(II) complexes in a pseudooctahedral field.<sup>29</sup> Similar values have been reported for the [Co(H<sub>2</sub>dapp)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> complex.<sup>31</sup>

In all the nickel(II) complexes three bands were observed, which can be assigned to the three spin-allowed transitions, ν<sub>1</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>], ν<sub>2</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F)], and ν<sub>3</sub> [<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P)], which is a characteristic feature of the spectra of octahedral Ni(II) species, and the pattern resembles the spectra of dichlorotetraaza macrocyclic nickel(II) complexes.<sup>32</sup> The magnetic moments of the Ni(II) complexes reported herein range from 2.98 to 3.20 μ<sub>B</sub>, which corresponds to two unpaired electrons along with some orbital contribution.

### Conclusion

The hexa- and the penta-dentate ligands are a potential source of pentagonal-bipyramidal transition-metal complexes when CH<sub>2</sub>-O-CH<sub>2</sub> is the connecting bridge between the 2,2'-bipyridine and/or pyridine units (e.g., **1a** and **4a**, respectively). Octahedral species are formed when a sulfur atom is substituted in the bridge instead of an oxygen atom (e.g., **1b** and **4b**). Attempts to obtain single crystals and thereby know precisely the geometry of the complexes with CH<sub>2</sub>-NH-CH<sub>2</sub> bridged ligands are in progress.

**Acknowledgment.** We wish to thank the National Science Foundation for partial support of this work.

**Supplementary Material Available:** Tables of bond distances, bond angles, coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes for the complexes [Ni(C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>S<sub>2</sub>)]Cl<sub>2</sub>·EtOH·2H<sub>2</sub>O (Tables S1-S5), [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> (Tables S6-S10), and [Co(C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>S<sub>2</sub>)Cl]<sub>2</sub>[CoCl<sub>4</sub>]·2H<sub>2</sub>O·2MeOH (Tables S11-S14), respectively (67 pages). Ordering information is given on any current masthead page.

- (27) Bombieri, G.; Forsellini, E.; Pra, A. D.; Tobe, M. L. *Inorg. Chim. Acta* **1981**, *51*, 177.  
 (28) Vermin, W. J.; Verschoor, G. C.; Ijdo, D. J. W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 3325.  
 (29) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 771.  
 (30) Gerloch, M.; Morgenstern-Badarau, I.; Audiere, J.-P. *Inorg. Chem.* **1979**, *18*, 3220.

(31) Wester, D.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 755.

(32) Sugimoto, M.; Nonoyama, M.; Ito, T.; Fujita, J. *Inorg. Chem.* **1983**, *22*, 950.

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

## Structure and Bonding in Dirhodium(II) Tetrasalicylate

DANIEL P. BANCROFT, F. ALBERT COTTON,\* and SCOTT HAN

Received September 15, 1983

The tetrakis(salicylato)dirhodium(II) molecule has been obtained in crystalline form as the ethanol-aquo adduct, [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)], and the structure has been determined by X-ray crystallography. The molecular structure, though interesting, does not contain any unconventional or "unique" features. The Rh-Rh distance is 2.385 (2) Å, and the eight equatorial ligand sites are occupied by the carboxyl oxygen atoms in the usual way, with an average Rh-O distance of 2.040 [4] Å. One axial site has an ethanol molecule, Rh-O = 2.30 (1) Å, and the other a water molecule, Rh-O = 2.30 (1) Å. Within each salicylate moiety the *o*-OH group is hydrogen bonded to a carboxyl oxygen atom, with O...O distances in the range 2.49 (2)-2.60 (2) Å. Each phenyl ring is within an average of 7.7° of being coplanar with its own carboxyl group. The *o*-OH oxygen atoms are not involved in any intermolecular interactions. The infrared spectrum exhibits a broad band at ca. 3250 cm<sup>-1</sup> characteristic of these intramolecularly hydrogen-bonded OH groups. The visible spectrum is quite typical of Rh<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>L<sub>2</sub> compounds with L ligands such as alcohols or water. The crystalline compound used for the X-ray work had a total composition [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)]·C<sub>2</sub>H<sub>5</sub>OH·H<sub>2</sub>O and formed monoclinic crystals in space group *P2<sub>1</sub>/n* with unit cell dimensions of *a* = 14.830 (4) Å, *b* = 15.953 (4) Å, *c* = 15.130 (2) Å, β = 90.90 (2)°, and *V* = 3579 (2) Å<sup>3</sup>, with *Z* = 4.

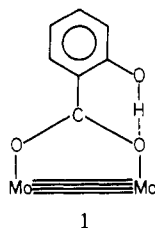
### Introduction

In a recent paper from this laboratory<sup>1</sup> the structures of two compounds containing the dimolybdenum tetrasalicylate,

Mo<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>, unit (in which the OH group is ortho to the carboxyl group) were reported. The most interesting feature of these structures was the fact that in every carboxylato ligand there is an internal hydrogen bond that constrains the phenyl ring to be approximately coplanar with its carboxyl

(1) Cotton, F. A.; Mott, G. N. *Inorg. Chim. Acta* **1983**, *70*, 159.

group (1). In one of the molybdenum compounds, in which



no additional donor molecules were present to occupy axial positions, some of the OH groups also used their in-plane lone pairs to form bonds to the axial positions of molybdenum atoms in neighboring molecules.

In view of these results, we found some of the conclusions drawn in a study<sup>2</sup> of several salicylato compounds of the dirhodium(II) unit somewhat surprising. It was proposed that "the oxygen atom of the phenol group is not joined to the proton, and hence forms a bond with the metal atom." The authors several times commented on "the unique state of the protons in the Rh<sub>2</sub><sup>4+</sup> salicylates" and emphasized the alleged mystery concerning these hydrogen atoms by writing the formulas of the compounds as "Rh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>OCOO)<sub>4</sub>(H)<sub>4</sub>X<sub>2</sub>, where X = H<sub>2</sub>O, NH<sub>3</sub>, etc."

In this report we demonstrate that there is nothing abnormal or "unique" about the salicylato ligand in these compounds. As in the molybdenum compounds, it adopts an internally hydrogen-bonded structure and functions simply as a bidentate, bridging carboxylato ligand.

## Experimental Section

**Preparation.** A mixture of 0.50 g (1.9 mmol) of RhCl<sub>3</sub>·3H<sub>2</sub>O and 0.52 g (3.8 mmol) of salicylic acid in 20 mL of 50% aqueous ethanol was heated at 70–80 °C for 1 h. The color of the reaction mixture changed from red to a deep blue-green. The ethanol was evaporated under vacuum, and a blue-green precipitate formed. This solid was then recrystallized from 20 mL of absolute ethanol. The yield was about 0.34 g, ca. 41%. Crystals suitable for X-ray diffraction study were grown by slow evaporation in air of a 95% ethanol solution. The compound may be dried by heating at 100 °C under vacuum for 2 h.

**X-ray Crystallography.** Diffraction data were collected on a Syntex P1 four-circle diffractometer using graphite-monochromated Mo Kα (λ<sub>K</sub> = 0.71073 Å) radiation. Lorentz and polarization corrections were applied. The structure was determined by using standard Patterson, least-squares, and Fourier techniques.<sup>3</sup> Of 2730 data collected, those 2120 with  $I \geq 2.5\sigma(I)$  were used to refine 416 parameters to final residuals of  $R = 0.049$  and  $R_w = 0.061$ . Pertinent crystallographic data as well as expressions for  $R$ ,  $R_w$ , and  $w$  are given in Table I.

All non-hydrogen atoms were refined anisotropically except for atoms C(3), C(22), and C(28) in the molecule and atoms belonging to the solvent molecules in the lattice. Attempts to refine the three carbon atoms anisotropically produced imaginary amplitudes of vibration even though their isotropic thermal parameters were satisfactory. The only peak in the final difference Fourier map over 1.0 e/Å<sup>3</sup> (1.304) indicated a possible slight disorder in the OH group corresponding to the phenyl ring containing O(14). However, the peak was only 1.03 Å from the phenyl carbon atom and attempts to refine a disordered model were unsatisfactory.

**Spectroscopic Measurements.** Infrared spectra (4000–200 cm<sup>-1</sup>, Nujol mull) were recorded on a Perkin-Elmer 783 spectrophotometer. A Cary 17D spectrophotometer was used to obtain the UV-vis

Table I. Crystallographic Parameters

formula	[Rh <sub>2</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> OH) <sub>4</sub> (HOCH <sub>2</sub> CH <sub>3</sub> )(H <sub>2</sub> O)]·CH <sub>3</sub> CH <sub>2</sub> OH·H <sub>2</sub> O
fw	882.44
space group	P2 <sub>1</sub> /n
a, Å	14.830 (3)
b, Å	15.953 (4)
c, Å	15.130 (2)
α, deg	90.0
β, deg	90.90 (2)
γ, deg	90.0
V, Å <sup>3</sup>	3579 (2)
Z	4
d <sub>calc</sub> , g/cm <sup>3</sup>	1.638
cryst size, mm	0.4 × 0.25 × 0.1
μ(Mo Kα), cm <sup>-1</sup>	9.754
data colln	Syntex P1
instrument	
radiation	Mo Kα
scan method	θ-2θ
data colln range (2θ), deg	5.0–50.0
no. of unique data	2730
F <sub>o</sub> <sup>2</sup> ≥ 2.5σ(F <sub>o</sub> <sup>2</sup> )	2120
no. of parameters	416
refined	
R <sup>a</sup>	0.049
R <sub>w</sub> <sup>b</sup>	0.061
quality-of-fit indicator <sup>c</sup>	1.256
largest shift/esd, final cycle	0.10

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/\sigma(|F_o|^2)$ . <sup>c</sup> Quality of fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$ .

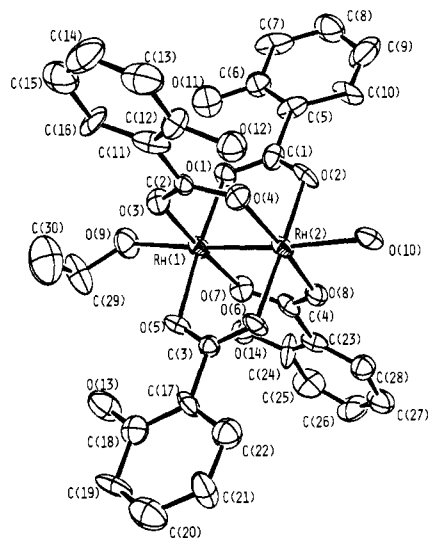


Figure 1. The [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(HOCH<sub>2</sub>CH<sub>3</sub>)(H<sub>2</sub>O)] molecule. Thermal ellipsoid representations of the numbered atoms are at the 40% probability level.

spectrum (ethanol solution) at room temperature.

## Results

All atomic coordinates are listed in Table II. An ORTEP drawing of the [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH)<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)] unit, without hydrogen atoms, is presented in Figure 1. This drawing defines the labeling scheme for all the atoms of this unit. In addition the unit cell contains O(15), C(31), and C(32), which make up the noncoordinated ethanol molecule, and O(16), which belongs to the noncoordinated water molecule. Selected bond distances and angles for the dirhodium unit are listed in Tables III and IV, respectively. Complete tables of distances and angles are available as supplementary

(2) Shchelokov, R. N.; Maiorova, A. G.; Kuznetsova, G. N.; Golovanova, I. F.; Evstaf'eva, O. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1049.

(3) Calculations were performed on a VAX 11/780 computer equipped with the Enraf-Nonius Structure Determination Package at the Department of Chemistry, Texas A&M University, College Station, TX.

Table II. Final Atomic Coordinates<sup>a</sup>

atom	x	y	z	atom	x	y	z
Rh(1)	0.22253 (7)	0.15358 (8)	0.07847 (7)	C(8)	0.419 (1)	0.124 (1)	0.502 (1)
Rh(2)	0.25858 (7)	0.29690 (7)	0.10611 (7)	C(9)	0.405 (1)	0.208 (1)	0.478 (1)
O(1)	0.2901 (6)	0.1253 (6)	0.1934 (6)	C(10)	0.375 (1)	0.231 (1)	0.3928 (9)
O(2)	0.3145 (6)	0.2611 (7)	0.2242 (6)	C(11)	0.4837 (9)	0.191 (1)	-0.0319 (9)
O(3)	0.3407 (6)	0.1440 (6)	0.0138 (6)	C(12)	0.541 (1)	0.256 (1)	-0.048 (1)
O(4)	0.3777 (6)	0.2763 (6)	0.0417 (6)	C(13)	0.627 (1)	0.246 (1)	-0.087 (1)
O(5)	0.1566 (6)	0.1929 (6)	-0.0345 (6)	C(14)	0.650 (1)	0.163 (1)	-0.104 (1)
O(6)	0.1972 (6)	0.3272 (6)	-0.0118 (6)	C(15)	0.592 (1)	0.095 (1)	-0.092 (1)
O(7)	0.1077 (6)	0.1713 (6)	0.1469 (6)	C(16)	0.506 (1)	0.107 (1)	-0.0561 (9)
O(8)	0.1371 (6)	0.3074 (6)	0.1648 (6)	C(17)	0.1179 (9)	0.295 (1)	-0.1418 (9)
O(9)	0.1895 (7)	0.0137 (6)	0.0626 (7)	C(18)	0.0793 (9)	0.234 (1)	-0.200 (1)
O(10)	0.3026 (6)	0.4314 (6)	0.1402 (6)	C(19)	0.042 (1)	0.258 (1)	-0.282 (1)
O(11)	0.3461 (8)	0.0155 (7)	0.2972 (7)	C(20)	0.047 (1)	0.341 (1)	-0.303 (1)
O(12)	0.5199 (8)	0.3380 (8)	-0.0307 (8)	C(21)	0.083 (1)	0.403 (1)	-0.247 (1)
O(13)	0.0729 (7)	0.1536 (7)	-0.1762 (7)	C(22)	0.119 (1)	0.383 (1)	-0.164 (1)
O(14)	-0.042 (1)	0.112 (1)	0.208 (1)	C(23)	-0.0048 (9)	0.2608 (9)	0.2094 (9)
O(15)	0.613 (1)	0.495 (1)	-0.007 (1)	C(24)	-0.062 (1)	0.192 (1)	0.224 (1)
O(16)	0.4071 (8)	0.4514 (8)	0.3022 (8)	C(25)	-0.149 (1)	0.205 (1)	0.255 (1)
C(1)	0.3162 (9)	0.1858 (9)	0.244 (1)	C(26)	-0.179 (1)	0.284 (1)	0.269 (1)
C(2)	0.3928 (9)	0.2037 (9)	0.0097 (8)	C(27)	-0.122 (1)	0.352 (1)	0.255 (1)
C(3)	0.1600 (9)	0.2702 (8)	-0.0547 (9)	C(28)	-0.034 (1)	0.343 (1)	0.225 (1)
C(4)	0.0876 (9)	0.2448 (9)	0.1714 (8)	C(29)	0.158 (1)	-0.027 (1)	-0.016 (1)
C(5)	0.3565 (9)	0.161 (1)	0.3350 (9)	C(30)	0.228 (2)	-0.020 (2)	-0.085 (1)
C(6)	0.368 (1)	0.079 (1)	0.356 (1)	C(31)	0.634 (2)	0.514 (2)	0.092 (2)
C(7)	0.400 (1)	0.054 (1)	0.440 (1)	C(32)	0.675 (2)	0.447 (2)	0.121 (2)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Selected Bond Distances (Å)<sup>a</sup>

Rh(1)-Rh(2)	2.385 (2)	O(5)-C(3)	1.27 (2)
-O(1)	2.043 (9)	O(6)-C(3)	1.24 (2)
-O(3)	2.026 (8)	O(7)-C(4)	1.27 (2)
-O(5)	2.052 (9)	O(8)-C(4)	1.25 (2)
-O(7)	2.027 (9)	O(9)-C(29)	1.43 (2)
-O(9)	2.30 (1)	O(11)-C(6)	1.39 (2)
Rh(2)-O(2)	2.04 (1)	O(12)-C(12)	1.37 (2)
-O(4)	2.057 (8)	O(13)-C(18)	1.34 (2)
-O(6)	2.046 (9)	O(14)-C(24)	1.33 (2)
-O(8)	2.027 (8)	C(1)-C(5)	1.55 (2)
-O(10)	2.30 (1)	C(2)-C(11)	1.51 (2)
O(1)-C(1)	1.29 (2)	C(3)-C(17)	1.50 (2)
O(2)-C(1)	1.24 (2)	C(4)-C(23)	1.52 (2)
O(3)-C(2)	1.23 (2)	C(29)-C(30)	1.48 (3)
O(4)-C(2)	1.28 (2)		

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Angles (deg)<sup>a</sup>

Rh(2)-Rh(1)-O(1)	87.4 (3)	Rh(1)-O(5)-C(3)	118 (1)
-O(3)	87.9 (3)	Rh(2)-O(6)-C(3)	118 (1)
-O(5)	87.6 (3)	Rh(1)-O(7)-C(4)	118.8 (9)
-O(7)	88.0 (3)	Rh(2)-O(8)-C(4)	119.9 (9)
-O(9)	175.8 (3)	Rh(1)-O(9)-C(29)	126 (1)
Rh(1)-Rh(2)-O(2)	88.5 (3)	O(1)-C(1)-O(2)	126 (2)
-O(4)	87.5 (3)	O(3)-C(2)-O(4)	125 (1)
-O(6)	88.6 (3)	O(5)-C(3)-O(6)	127 (2)
-O(8)	87.6 (3)	O(7)-C(4)-O(8)	125 (1)
-O(10)	175.4 (2)	O(11)-C(6)-C(5)	122 (2)
Rh(1)-O(1)-C(1)	119 (1)	O(12)-C(12)-C(11)	122 (2)
Rh(2)-O(2)-C(1)	119 (1)	O(13)-C(18)-C(17)	122 (2)
Rh(1)-O(3)-C(2)	121.0 (9)	O(14)-C(24)-C(23)	126 (2)
Rh(2)-O(4)-C(2)	118.8 (9)	O(9)-C(29)-C(30)	110 (2)

material. All atoms in this structure reside on general positions, and no crystallographic symmetry is imposed on any part of the structure. Table V gives O...O distances for hydrogen bonds, and Table VI gives the angles between the planes of the phenyl ring and the carboxyl group in each salicylate ligand.

### Discussion

As shown in Figure 1, the basic structural unit in this compound is a typical Rh<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>L<sub>2</sub> molecule. The Rh-Rh distance, 2.385 (2) Å, is well within the range for such com-

Table V. Hydrogen Bonding Distances (Å)<sup>a</sup>

O(1)-O(9)	3.04 (2)	O(9)-O(16) <sup>c</sup>	2.70 (2)
O(1)-O(11)	2.49 (2)	O(10)-O(11)	2.76 (1)
O(2)-O(10)	3.00 (2)	O(10)-O(15) <sup>b</sup>	2.67 (2)
O(4)-O(12)	2.59 (1)	O(10)-O(16) <sup>c</sup>	2.90 (2)
O(5)-O(13)	2.54 (1)	O(12)-O(15) <sup>b</sup>	2.88 (2)
O(7)-O(14)	2.60 (2)	O(13)-O(16) <sup>c</sup>	2.99 (2)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup> Oxygen atom of solvent CH<sub>3</sub>CH<sub>2</sub>OH in the lattice. <sup>c</sup> Oxygen atom of solvent H<sub>2</sub>O in the lattice.

Table VI. Dihedral Angles (deg) between Phenyl Rings and the Corresponding CO<sub>2</sub> Group

phenyl plane	CO <sub>2</sub> plane	angle
C(5)-C(6)-C(7)-C(8)-C(9)-C(10)	O(1)-C(1)-O(2)	7.3
C(11)-C(12)-C(13)-C(14)-C(15)-C(16)	O(3)-C(2)-O(4)	9.7
C(17)-C(18)-C(19)-C(20)-C(21)-C(22)	O(5)-C(3)-O(6)	5.4
C(23)-C(24)-C(25)-C(26)-C(27)-C(28)	O(7)-C(4)-O(8)	8.4
	av	7.7

pounds.<sup>4-6</sup> It is almost identical with that<sup>7</sup> in Rh<sub>2</sub>(O<sub>2</sub>CC-H<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>, 2.3855 (5) Å, and the axial Rh-O distance in the acetate, 2.310 (3) Å, is effectively equal to the axial Rh-OH<sub>2</sub> and Rh-O(H)C<sub>2</sub>H<sub>5</sub> distances here, each of which is 2.30 (1) Å.

This appears to be the first arenecarboxylato compound of Rh<sub>2</sub><sup>4+</sup> to have been characterized structurally, although various axial adducts of the benzoate, Rh<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>L<sub>2</sub>, have been prepared.

As previously observed in the two molybdenum salicylate compounds, in each salicylate ligand, the ortho hydroxyl group forms an internal hydrogen bond to one of the carboxyl oxygen atoms. This causes each phenyl ring to be nearly coplanar with

(4) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(5) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73.

(6) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109.

(7) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. R. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1664.

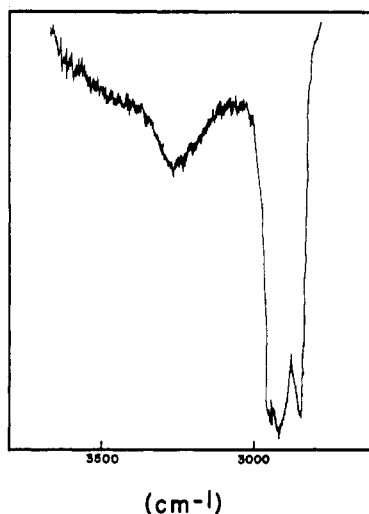


Figure 2. Infrared spectrum of  $\text{Rh}_2(\text{OOCC}_6\text{H}_4\text{OH})_4$  in a Nujol mull.

its carboxyl group. As shown in Table VI the dihedral angles range from  $5.4^\circ$  to  $9.7^\circ$ , with an average value of  $7.7^\circ$ . The internal hydrogen bonds are moderately strong, with  $\text{O}\cdots\text{O}$  distances ranging from 2.49 (2) to 2.60 (2) Å. The existence of these hydrogen bonds does not significantly lower the symmetry of the carboxyl groups as they coordinate to the  $\text{Rh}_2^{4+}$  unit, however. The four  $\text{Rh}-\text{O}$  bonds to carboxyl oxygen atoms that participate in hydrogen bonding have an average value of 2.045 [6] Å while the average of the other four is 2.035 [5] Å.<sup>8</sup> The difference is, obviously, not significant. The grand average value of all eight  $\text{Rh}-\text{O}$  distances is 2.040 [4] Å. Also, the  $\text{Rh}-\text{Rh}-\text{O}$  angles show no dependence on whether the oxygen atom concerned is hydrogen bonded or not, and the average value of all eight is  $87.9 [1]^\circ$ .

The salicylate ligands are oriented so that three of them have their OH groups directed toward the ethanol axial ligand while only one points the other way. This arrangement seems to be correlated with the orientation of the ethyl group, which is directed away from the *o*-OH groups of the first three salicylate ligands but toward the region of the ortho position of the one whose hydroxyl group points the other way. In view of the apparently negligible electronic effect of the OH groups upon the carboxyl oxygen atoms it is not at all unreasonable to suppose that the 3:1 arrangement of the salicylate ligands is sterically determined. This could imply that in a diaquo (or other symmetrical)  $\text{Rh}_2(\text{O}_2\text{CC}_6\text{H}_4\text{OH})_4\text{L}_2$  molecule a 2:2 arrangement would be preferred.

(8) A number in ( ) indicates an esd for a given individual value while a number in [ ] is equal to  $[\sum \Delta_i^2/n(n-1)]^{1/2}$ , where  $\Delta_i$  is the deviation of the *i*th value in a set of *n* such values from the arithmetic mean of *n* values.

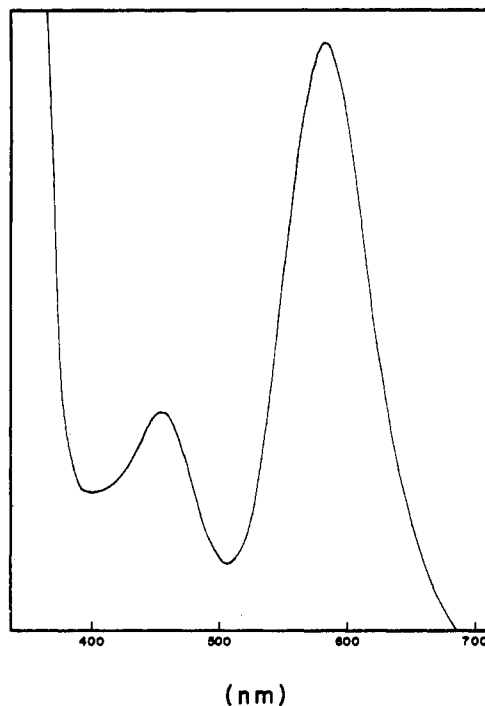


Figure 3. Portion of the visible spectrum of  $\text{Rh}_2(\text{OOCC}_6\text{H}_4\text{OH})_4$  in ethanol solution at  $25^\circ\text{C}$ .

The spectroscopic results are in good agreement with the crystallographic data. The infrared spectrum (Figure 2) of the dried compound gives a broad band at  $3255\text{ cm}^{-1}$ , which corresponds well with hydrogen-bonded hydroxyl stretching frequencies in salicylic acids.<sup>9</sup> The visible spectrum shown in Figure 3 has the characteristic absorptions of  $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$  complexes. The first peak at 585 nm ( $17090\text{ cm}^{-1}$ ,  $\epsilon = 244$ ) has been assigned to the  $\text{Rh}-\text{Rh } \pi^* \rightarrow \text{Rh}-\text{O } \sigma^*$  transition and the second band at 455 nm ( $21980\text{ cm}^{-1}$ ,  $\epsilon = 108$ ) to the  $\text{Rh}-\text{O } \pi \rightarrow \text{Rh}-\text{O } \sigma^*$  transition.<sup>10</sup> It is interesting to note that even though aryl groups are present in this case and aligned so as to facilitate conjugation with the  $\pi$  system of the carboxyl group, the electronic spectrum is not significantly different from that of the acetate.<sup>10</sup>

**Acknowledgment.** We thank the National Science Foundation for support of this research.

**Supplementary Material Available:** Complete tables of bond distances and angles, a table of rms amplitudes of thermal vibrations, a table of general temperature factor expressions ( $B$ 's), and a table of observed and final calculated structure factors (20 pages). Ordering information is given on any current masthead page.

(9) Brooks, C. J. W.; Eglinton, G.; Morman, J. F. *J. Chem. Soc.* **1961**, 661.  
 (10) Miskowski, V. M.; Schaefer, W. P.; Sadeghi, B.; Santarsiero, B. D.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 1154.