

## The Structure of Tetra- $\mu$ -acetato-bis(acetonitrile)dirhodium(II) (*Rh–Rh*)

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(Received 2 April 1981; accepted 2 June 1981)

**Abstract.**  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CN})_2]$ ,  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_8\text{Rh}_2$ ,  $M_r = 524.10$ , orthorhombic, *Pnma*,  $a = 13.756$  (1),  $b = 13.697$  (2),  $c = 9.908$  (1) Å,  $V = 1866.8$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $d_x = 1.865$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.758$  mm<sup>-1</sup>. The structure was solved using Patterson and Fourier techniques with diffractometer data and refined by least squares to a final *R* (unit-weighted) of 0.039 based on 1457 independent observations each with intensity greater than  $3\sigma$ . The molecule consists of the usual  $\text{Rh}_2(\text{O}_2\text{CR})_4$  arrangement with axially coordinated  $\text{CH}_3\text{CN}$  groups. The Rh–Rh, Rh–N and Rh–N' distances are 2.384 (1), 2.249 (7) and 2.258 (6) Å respectively.

**Introduction.** Since the structure of  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$  was first determined accurately (Cotton, DeBoer, LaPrade, Pipal & Ucko, 1971) following an earlier preliminary structure determination (Porai-Koshits & Antsyshkina, 1962), the structures of more than 30  $[\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2]$  compounds have been determined and Rh–Rh distances ranging from 2.371 (1) Å in  $[\text{Rh}_2(\text{O}_2\text{CCMe}_3)_4(\text{H}_2\text{O})_2]$  (Cotton & Felthouse, 1980) to 2.486 (1) Å in  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{PPh}_3)_2]$  (Cotton, Felthouse & Klein, 1981) have been found. Of these, 15 contain  $\text{O}_2\text{CCH}_3$  groups, but the one with the important axial ligand  $\text{CH}_3\text{CN}$  has not been studied. We report that structure here.

Anhydrous rhodium acetate was prepared from hydrated rhodium trichloride (Engelhard Industries) refluxed in a mixture of glacial acetic acid and ethanol following the literature (Rempel, Legzdins, Smith & Wilkinson, 1971). The acetate (0.100 g) was dissolved in 100 ml of 1:1 acetonitrile/toluene mixture to give a dark-purple solution. Upon slow evaporation of this solution, large red-purple crystals of  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CN})_2]$  were obtained.

A crystal with dimensions 0.30 × 0.50 × 0.70 mm was attached to the end of a glass fiber with epoxy cement and mounted on a Syntex PI diffractometer. All work was done using Mo  $K\alpha$  radiation monochromated by a graphite crystal in the incident beam. Indexing on 15 intense, centered reflections and examination of axial photographs showed a unit cell in the orthorhombic system with dimensions as given in the *Abstract*. Systematic absences of  $0kl$ ,  $k + l \neq 2n$

and  $hk0$ ,  $h \neq 2n$  indicated the space group to be *Pnma* (No. 62) or *Pna2*<sub>1</sub> (No. 33). A Howells–Phillips–Rogers test strongly indicated a centrosymmetric arrangement and refinement was conducted successfully in *Pnma*. Data were collected by  $\theta/2\theta$  scans in the range  $0^\circ < 2\theta < 50^\circ$  giving a total of 1478 data of which 1457 having intensities greater than  $3\sigma$  were used to refine 122 variables. Three reflections were checked periodically and they showed no decay during data collection. An empirical absorption correction ( $\mu = 1.758$  mm<sup>-1</sup>) was made in which a  $\Psi$  scan for each of five reflections near  $\chi = 90^\circ$  was measured. Each reflection was measured at  $10^\circ$  intervals from  $\Psi = 0^\circ$  to  $\Psi = 360^\circ$ . The normalized transmission factors obtained varied from 1.00 to 0.85.

The approximate positions of the two Rh atoms were obtained from a three-dimensional Patterson map. Refinement of these positions gave discrepancy indices of  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.30$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.38$ . The remaining N, O, and C atoms were found in subsequent difference Fourier maps, alternated with cycles of least-squares refinement. Final refinement on the positional and anisotropic thermal parameters for all 16 atoms gave discrepancy indices of  $R_1 = 0.039$  and  $R_2$

Table 1. Positional and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = \frac{1}{3} \text{trace } \bar{B}$			
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
Rh(1)	0.18290 (4)	0.2500	0.15428 (5)	2.37 (1)
Rh(2)	0.10402 (4)	0.2500	-0.05994 (5)	2.58 (1)
O(1)	0.0872 (2)	0.3536 (3)	0.2138 (4)	3.15 (7)
O(2)	0.0111 (3)	0.3521 (3)	0.0130 (4)	3.62 (8)
O(3)	0.2736 (3)	0.3550 (3)	0.0820 (4)	4.05 (8)
O(4)	0.1996 (3)	0.3563 (3)	-0.1189 (4)	3.75 (8)
N(1)	0.2550 (5)	0.2500	0.3590 (6)	3.9 (1)
N(2)	0.0358 (5)	0.2500	-0.2663 (7)	5.0 (2)
C(1)	0.0200 (4)	0.3821 (4)	0.1346 (5)	3.0 (1)
C(2)	-0.0535 (4)	0.4535 (5)	0.1871 (7)	4.5 (1)
C(3)	0.2622 (4)	0.3871 (5)	-0.0385 (6)	3.8 (1)
C(4)	0.3269 (6)	0.4681 (6)	-0.0862 (10)	7.0 (2)
C(5)	0.2774 (5)	0.2500	0.4666 (8)	4.2 (2)
C(6)	0.3072 (7)	0.2500	0.6052 (11)	9.6 (5)
C(7)	0.0193 (5)	0.2500	-0.3788 (8)	3.5 (2)
C(8)	0.0014 (7)	0.2500	-0.5245 (9)	5.6 (3)

Table 2. *Bond distances for*  
 $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CN})_2]$  (Å)

Rh(1)–Rh(2)	2.384 (1)	C(3)–O(3)	1.282 (6)
–O(1)	2.024 (3)	–O(4)	1.246 (6)
–O(3)	2.034 (3)	–C(4)	1.499 (7)
–N(1)	2.258 (6)	N(1)–C(5)	1.110 (8)
Rh(2)–O(2)	2.028 (3)	C(5)–C(6)	1.43 (1)
–O(4)	2.047 (3)	N(2)–C(7)	1.138 (9)
–N(2)	2.249 (7)	C(7)–C(8)	1.46 (1)
C(1)–O(1)	1.273 (5)		
–O(2)	1.278 (6)		
–C(2)	1.500 (6)		

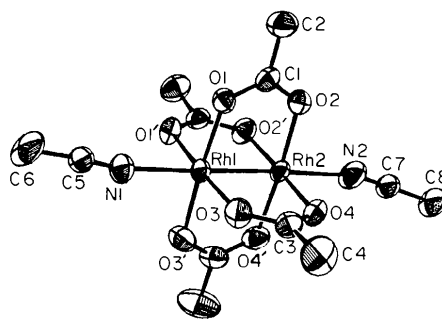


Fig. 1. A computer-drawn representation of the molecule, showing the atom-labelling scheme. Thermal ellipsoids enclose 40% of the electron density.

= 0.060, and the e.s.d. of an observation of unit weight was 1.53. The largest peak in the final difference Fourier map was  $0.99 \text{ e \AA}^{-3}$ . This and several other peaks appeared to be associated with H atoms on the methyl C atoms, but we did not consider it worthwhile to continue refinement including them.

The positional parameters are listed in Table 1 and the bond distances are given in Table 2. The bond angles are all close to 90, 180 or 120°, as suggested by Fig. 1 which shows the molecule and the numbering scheme used.\*

**Discussion.**  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{CN})_2]$  has the expected structure, qualitatively. The two Rh atoms and the NCC chains of the acetonitrile molecules lie in a mirror plane. This mirror contains no acetate groups, so that there are two crystallographically independent ligands. The NCC chains are linear within the uncertainties but deviate slightly, 1.0 (2) and 2.4 (2)°, from collinearity with the Rh–Rh bond. The Rh–N distances, 2.258 (6) and 2.249 (7) Å, are equal within the uncertainties.

\* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36211 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

They are about 0.10 Å longer than the only previously observed Rh–N axial bond in a dirhodium(II,II) compound, namely  $[\text{Rh}_2(\text{mhp})_4(\text{CH}_3\text{CN})]$ , where Hmhp is 2-hydroxy-6-methylpyridine (Cotton & Felthouse, 1981). The Rh–N distances are quite similar to those in the pyridine adduct,  $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{C}_5\text{H}_5\text{N})_2]$ , 2.227 (3) Å (Koh & Christoph, 1978). The Rh–Rh bond length is about equal to the shortest previously known.

We thank the National Science Foundation for support.

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