

Tetrakis[μ -(6-methyl-2-pyridinolato)]-dirhodium

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Abstract. $[\text{Rh}_2(\text{C}_6\text{H}_6\text{NO})_4]$, $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4\text{Rh}_2$, $M_r = 638.3$, orthorhombic, $Pbca$, $a = 15.643$ (3), $b = 16.083$ (3), $c = 18.666$ (4) Å, $U = 4696.1$ Å³, $Z = 8$, $D_x = 1.805$ Mg m⁻³; final $R = 0.035$ for 5383 reflexions. The molecule has approximate 4_2m symmetry. A Rh–Rh bond of length 2.359 (1) Å is bridged by four 6-methyl-2-pyridinolato (mhp) ligands; there are no axially coordinated ligands.

Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters (Å² $\times 10^4$)Equivalent isotropic U values are calculated from the anisotropic U_{ij} components.

	x	y	z	U
Rh(1)	12234 (1)	16700 (1)	7184 (1)	325 (1)
Rh(2)	12135 (1)	21045 (1)	19254 (1)	360 (1)
O(1)	25037 (11)	21965 (11)	19046 (9)	443 (6)
C(11)	29160 (16)	20971 (15)	13116 (13)	364 (8)
C(12)	38171 (16)	21997 (16)	12980 (16)	425 (9)
C(13)	42433 (18)	20981 (16)	6712 (15)	453 (9)
C(14)	38026 (17)	18970 (19)	452 (17)	484 (10)
C(15)	29427 (16)	18026 (16)	730 (14)	402 (8)
C(16)	24195 (20)	15833 (22)	-5670 (13)	608 (12)
N(1)	25039 (13)	18927 (13)	6982 (10)	358 (6)
O(2)	10063 (12)	28463 (11)	3930 (9)	423 (6)
C(21)	10486 (16)	34511 (17)	8504 (14)	416 (9)
C(22)	10201 (23)	42849 (20)	6012 (17)	662 (13)
C(23)	10731 (24)	49156 (22)	10806 (21)	829 (16)
C(24)	11239 (23)	47556 (22)	18079 (20)	731 (14)
C(25)	11475 (18)	39616 (20)	20293 (16)	529 (10)
C(26)	11944 (23)	37194 (27)	28047 (17)	785 (15)
N(2)	11177 (13)	32986 (14)	15608 (12)	406 (7)
O(3)	-683 (11)	20097 (12)	19601 (9)	450 (6)
C(31)	-4750 (17)	16689 (16)	14363 (14)	405 (8)
C(32)	-13571 (17)	14882 (20)	14951 (17)	531 (10)
C(33)	-17741 (17)	11234 (20)	9384 (17)	571 (11)
C(34)	-13374 (16)	9464 (20)	3064 (17)	532 (11)
C(35)	-4931 (16)	11219 (16)	2618 (13)	402 (8)
C(36)	250 (17)	9509 (18)	-3947 (13)	469 (9)
N(3)	-604 (12)	14651 (13)	8169 (11)	368 (6)
O(4)	14782 (11)	4936 (11)	10244 (10)	443 (6)
C(41)	14387 (17)	2887 (18)	16924 (16)	441 (9)
C(42)	15235 (22)	-5530 (20)	19011 (19)	633 (12)
C(43)	14275 (23)	-7690 (26)	25978 (21)	787 (15)
C(44)	12610 (22)	-1703 (28)	31010 (21)	780 (16)
C(45)	12064 (17)	6489 (23)	29008 (16)	568 (11)
C(46)	10259 (22)	13409 (25)	34030 (16)	772 (14)
N(4)	13016 (12)	8754 (15)	22062 (12)	421 (7)

Introduction. This structure determination is part of an integrated study of metal–metal-bonded systems. The preparation of the compound has been described, with a preliminary account of the UV photoelectron spectra and crystal structure (Berry, Garner, Hillier, MacDowell & Clegg, 1980a).

Crystals are yellow-brown, air-stable pyramids. Intensities were collected from a crystal of maximum dimension 0.5 mm by a profile-fitting procedure (Clegg, 1980) with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a Stoe–Siemens four-

Table 2. Bond lengths (Å) and angles (°)

Rh(1)–Rh(2)	2.359 (1)			
Rh(1)–N(1)	2.035 (2)	Rh(2)–O(1)	2.024 (2)	
Rh(2)–N(2)	2.043 (2)	Rh(1)–O(2)	2.016 (2)	
Rh(1)–N(3)	2.043 (2)	Rh(2)–O(3)	2.012 (2)	
Rh(2)–N(4)	2.050 (2)	Rh(1)–O(4)	2.016 (2)	
Rh(2)–Rh(1)–N(1)	88.4 (1)	Rh(1)–Rh(2)–O(1)	89.8 (1)	
Rh(1)–Rh(2)–N(2)	87.8 (1)	Rh(2)–Rh(1)–O(2)	90.5 (1)	
Rh(2)–Rh(1)–N(3)	87.4 (1)	Rh(1)–Rh(2)–O(3)	90.9 (1)	
Rh(1)–Rh(2)–N(4)	87.6 (1)	Rh(2)–Rh(1)–O(4)	90.5 (1)	
N(1)–Rh(1)–N(3)	175.8 (1)	O(1)–Rh(2)–O(3)	179.2 (1)	
N(2)–Rh(2)–N(4)	175.3 (1)	O(2)–Rh(1)–O(4)	178.0 (1)	
N(1)–Rh(1)–O(2)	89.7 (1)	O(1)–Rh(2)–N(2)	89.9 (1)	
N(1)–Rh(1)–O(4)	88.6 (1)	O(1)–Rh(2)–N(4)	90.5 (1)	
N(3)–Rh(1)–O(2)	90.7 (1)	O(3)–Rh(2)–N(2)	90.5 (1)	
N(3)–Rh(1)–O(4)	91.0 (1)	O(3)–Rh(2)–N(4)	89.2 (1)	
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
O(n)–C(n1)	1.291 (3)	1.296 (3)	1.289 (3)	1.291 (3)
C(n1)–C(n2)	1.419 (4)	1.420 (4)	1.414 (4)	1.415 (4)
C(n2)–C(n3)	1.356 (4)	1.355 (5)	1.360 (4)	1.354 (5)
C(n3)–C(n4)	1.395 (4)	1.384 (5)	1.393 (4)	1.370 (6)
C(n4)–C(n5)	1.355 (4)	1.343 (5)	1.353 (4)	1.372 (6)
C(n5)–N(n)	1.362 (3)	1.380 (4)	1.355 (3)	1.355 (4)
N(n)–C(n1)	1.354 (3)	1.353 (3)	1.366 (3)	1.362 (4)
C(n5)–C(n6)	1.490 (4)	1.501 (4)	1.495 (4)	1.482 (5)
Rh(m)–O(n)–C(n1)	120.4 (2)	119.8 (2)	120.0 (2)	120.2 (2)
O(n)–C(n1)–C(n2)	119.8 (2)	119.4 (2)	120.7 (2)	120.4 (3)
O(n)–C(n1)–N(n)	121.1 (2)	120.9 (2)	120.7 (2)	120.7 (2)
C(n2)–C(n1)–N(n)	119.1 (2)	119.7 (3)	118.7 (2)	118.9 (3)
C(n1)–C(n2)–C(n3)	119.3 (3)	119.3 (3)	119.8 (3)	120.0 (3)
C(n2)–C(n3)–C(n4)	120.5 (3)	120.8 (3)	120.0 (3)	119.9 (4)
C(n3)–C(n4)–C(n5)	119.0 (3)	118.7 (3)	119.2 (3)	120.0 (4)
C(n4)–C(n5)–C(n6)	122.8 (3)	123.0 (3)	122.8 (2)	124.1 (3)
C(n4)–C(n5)–N(n)	121.4 (2)	122.6 (3)	121.7 (2)	120.8 (3)
C(n6)–C(n5)–N(n)	115.8 (2)	114.4 (3)	115.5 (2)	115.1 (3)
Rh(m)–N(n)–C(n1)	119.7 (2)	120.2 (2)	120.3 (2)	119.9 (2)
Rh(m)–N(n)–C(n5)	119.6 (2)	120.8 (2)	119.2 (2)	119.8 (2)
C(n1)–N(n)–C(n5)	120.7 (2)	118.9 (2)	120.5 (2)	120.3 (3)

Rh(m) is Rh(1) or Rh(2) as appropriate.

circle diffractometer. 5383 unique reflexions with $7 \leq 2\theta \leq 60^\circ$ and $I > 2\sigma(I)$ were measured in the ω/θ scan mode. Cell dimensions were obtained by least squares from 30 centred reflexions.

Empirical absorption corrections, derived from measurements of sets of reflexions at different azimuthal angles, were applied ($\mu = 1.42 \text{ mm}^{-1}$) with the usual Lp corrections. The structure was solved by Patterson and Fourier methods, and $\sum w\Delta^2$ was minimized in the refinement [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$]. Anisotropic thermal parameters were refined for all non-H atoms. H atoms were included in the refinement, with constraints on geometry (C—H = 0.96 Å, CH₃ groups as rigid groups with H—C—H = 109.5°, aromatic H on external bisector of C—C—C angle) and with isotropic thermal parameters fixed at 1.1 (aromatic H) or 1.2 (methyl H) times the equivalent isotropic value for the corresponding C atom.

The final R is 0.035, with $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.038$. Refined coordinates are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The molecule (Fig. 1) has no crystallographically imposed symmetry, but the geometry is close to $42m$ (D_{2d}), Table 2. Other [$M_2(\text{mhp})_4$] molecules (mhp represents the anion of 6-methyl-2-pyridinol, Hmhp) possess the same molecular symmetry; the complexes of Cr, Mo and W (Cotton, Fanwick, Niswander & Sekutowski, 1978) and of Ru (Berry, Garner, Hillier, MacDowell & Clegg, 1980b) are all isostructural, crystallizing with one un-

coordinated molecule of CH_2Cl_2 per [$M_2(\text{mhp})_4$] molecule in space group $P2_1/n$.

Several complexes of Rh^{II} with a Rh—Rh bond bridged by four ligands have already been characterized, but all have additional axial ligands attached to the Rh atoms. Christoph & Koh (1979) studied a series of [$\text{Rh}_2(\text{OAc})_4X_2$] complexes with a variety of X ligands, and found the Rh—Rh lengths to vary between 2.3963 (2) and 2.4555 (3) Å. Rh—Rh in [$\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$] is 2.3855 (5) Å (Cotton, DeBoer, LaPrade, Pipal & Ucko, 1971). In the carbonato-bridged complexes $\text{Cs}_4[\text{Rh}_2(\text{CO}_3)_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ and $\text{Cs}_4\text{Na}_2[\text{Rh}_2(\text{CO}_3)_4\text{Cl}_2] \cdot 8\text{H}_2\text{O}$ the Rh—Rh bonds are shorter, 2.378 (1) and 2.380 (2) Å respectively (Cotton & Felthouse, 1980); the shortening relative to [$\text{Rh}_2(\text{OAc})_4$]. $2\text{H}_2\text{O}$ is not great, but is probably real. Thus, the Rh—Rh length is dependent on the nature of the bridging ligand, as well as on the presence and nature of axial ligands.

In [$\text{Rh}_2(\text{mhp})_4$] the Rh—Rh length is 2.359 (1) Å, which is the shortest found so far for Rh. Similar shortenings of M — M bonds in [$M_2(\text{mhp})_4$] and similar complexes compared with carboxylato-bridged species have already been noted for Cr, Mo and W (Cotton, Koch & Millar, 1977; Cotton, Fanwick, Niswander & Sekutowski, 1978, and references therein), and can be attributed to the electronic structure of the four mhp ligands, which reduce the net positive charge on the metal atoms, encouraging M — M bonding, while simultaneously sterically blocking the axial positions for possible ligands.

When the molecule is viewed along the Rh(2)—Rh(1) bond, the Rh—N and Rh—O bonds for each ligand do not quite eclipse each other. The torsion angles about Rh(2)—Rh(1) for each ligand, in the order 1 to 4, are 5.7 (2), 5.5 (2), 5.7 (2) and 7.6 (2)° (mean 6.1°). [According to the sign convention of Klyne & Prelog (1960), these and all other torsion angles in the following discussion are negative.] Corresponding values for the [$M_2(\text{mhp})_4$] structures already published (Cotton, Fanwick, Niswander & Sekutowski, 1978) are: Cr 1.7, 2.2, 1.8, 2.0 (mean 1.9°); Mo 1.3, 1.4, 1.5, 1.1 (mean 1.3°); W 1.2, 0.3, 1.8, 2.1 (mean 1.4°) (e.s.d.'s for these torsion angles are not available, but are probably greater than for the Rh complex by factors of approximately 1–2, 2–3 and 4–5 for $M = \text{Cr}$, Mo and W respectively, in view of the relative e.s.d.'s for bond lengths and angles). The greater twist in the Rh case can be attributed to steric interaction of the methyl groups. Table 3 compares mean values of relevant bond lengths, torsion angles and $\text{C}(\text{Me}) \cdots \text{C}(\text{Me})$ distances in the four complexes. Although the mean Rh—O lies between Cr—O and W—O and is considerably longer than Cr—O, the mean Rh—N is the shortest M —N for these complexes, and the difference between mean M —N and M —O is much smaller for $M = \text{Rh}$ than for $M = \text{Cr}$, Mo, W. The

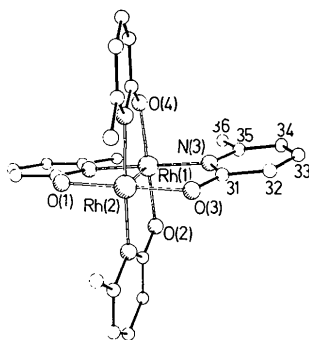


Fig. 1. View of the [$\text{Rh}_2(\text{mhp})_4$] molecule, showing the atom numbering. Only ligand 3 is labelled in full; the other ligands follow the same scheme. C atoms are labelled by number only; H atoms are omitted.

* Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35395 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

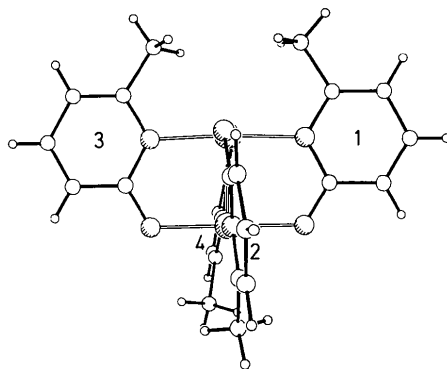


Fig. 2. View on to the mean plane of O(1), N(1), O(3) and N(3). The ligands are numbered. H atoms are included.

Table 3. Some geometrical features of $[M_2(\text{mhp})_4]$ molecules

E.s.d.'s are estimated from published e.s.d.'s and the spread of averaged values.

	$M = \text{Rh}$	$M = \text{Cr}$	$M = \text{Mo}$	$M = \text{W}$
$M-M$ (Å)	2.359 (1)	1.889 (1)	2.065 (1)	2.161 (1)
Mean $M-O$ (Å)	2.017 (4)	1.969 (9)	2.086 (7)	2.037 (7)
Mean $M-N$ (Å)	2.043 (5)	2.067 (4)	2.167 (14)	2.11 (3)
(Mean $M-N$) (mean $M-O$) (Å)	0.026 (5)	0.098 (10)	0.081 (16)	0.07 (3)
$C(\text{Me})\cdots C(\text{Me})$ (Å)	3.90 (1)	3.98 (2)	4.20 (2)	4.19 (5)
Mean $O-M-M-N$ torsion (°)	-6.1 (9)	-1.9 (3)	-1.3 (4)	-1.4 (8)

effect is to pull the methyl groups of mutually *trans* ligands closer in $[\text{Rh}_2(\text{mhp})_4]$. The twist about the

Rh-Rh bond counteracts this, reducing $\text{Me}\cdots\text{Me}$ steric interactions. The effect of the twist can be seen in Fig. 2.

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References

- BERRY, M., GARNER, C. D., HILLIER, I. H., MACDOWELL, A. A. & CLEGG, W. (1980a). *J. Chem. Soc. Chem. Commun.* pp. 494-495.
- BERRY, M., GARNER, C. D., HILLIER, I. H., MACDOWELL, A. A. & CLEGG, W. (1980b). Submitted for publication.
- CHRISTOPH, G. G. & KOH, Y.-B. (1979). *J. Am. Chem. Soc.* **101**, 1422-1434.
- CLEGG, W. (1980). *Acta Cryst.* **A36**. In the press.
- COTTON, F. A., DEBOER, B. G., LAPRADE, M. D., PIPAL, J. R. & UCKO, D. A. (1971). *Acta Cryst.* **B27**, 1664-1671.
- COTTON, F. A., FANWICK, P. E., NISWANDER, R. H. & SEKUTOWSKI, J. C. (1978). *J. Am. Chem. Soc.* **100**, 4725-4732.
- COTTON, F. A. & FELTHOUSE, T. R. (1980). *Inorg. Chem.* **19**, 320-323.
- COTTON, F. A., KOCH, S. & MILLAR, M. (1977). *J. Am. Chem. Soc.* **99**, 7372-7374.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521-523.