involving these atoms unreliable for comparison with other structures. This motion is shown in Fig. 2; a considerable component of it is rocking of the mhp ligands in the equatorial plane, about the P—Ru—P′ axis.
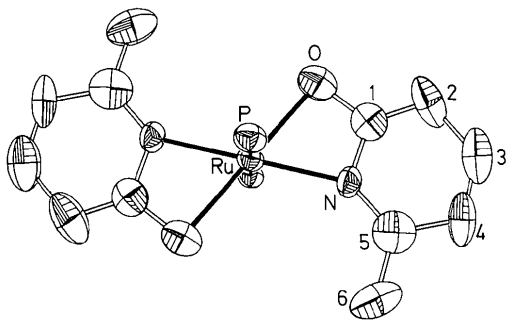

Fig. 2. Thermal motion depicted as 50% probability ellipsoids. Phenyl rings and H atoms are not included.

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Tetrakis[μ-(6-methyl-2-pyridinolato)]-diruthenium (Dichloromethane Solvate)

By WILLIAM CLEGG

Anorganisch-Chemisches Institut der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

Abstract. [Ru$_2$(C$_6$H$_6$NO)$_4$].CH$_2$Cl$_2$, C$_{24}$H$_{24}$N$_4$O$_4$Ru$_2$.·CH$_2$Cl$_2$, M_r = 719·6, monoclinic, $P2_1/n$, a = 12·775 (3), b = 17·155 (4), c = 12·834 (3) Å, β = 103·93 (2)°, U = 2729·9 Å^3, Z = 4, D_x = 1·752 Mg m^{-3}; final R = 0·045 for 3839 reflexions. The molecule, like those of other [M_2(mhp)$_4$] complexes (Hmhp = 6-methyl-2-pyridinol), has approximate $\bar{4}2m$ symmetry. The Ru—Ru length is 2·238 (1) Å.

Introduction. This compound has been prepared in the course of a study of complexes of the 6-methyl-2-pyridinolato (mhp) ligand. A preliminary description of the preparation, spectroscopic properties and crystal structure has already been given (Berry, Garner, Hillier, MacDowell & Clegg, 1980a).

A yellow crystal, 0·3 × 0·3 × 0·2 mm, sealed in a capillary tube, was used for crystallographic measurements performed with a Stoe–Siemens AED diffractometer controlled by a Data General S250 minicomputer (Clegg, 1981). Cell dimensions were obtained from 30 centred reflexions. Intensities were measured for all unique reflexions with 7 < 2θ < 50°

in a θ/ω scan mode, with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Corrections were applied for absorption by an empirical method based on azimuthal-scan measurements (μ = 1·32 mm^{-1}), and for a gradual decay in the intensities of three standard reflexions, amounting to ca 18% by the end of the data collection. The discrepancy index for the 397 azimuthal-scan data was reduced from 0·021 to 0·012 by the absorption correction; transmission factors for the complete data set were 0·456–0·514. 3839 reflexions with $I > 2\sigma(I)$ were used for structure determination.

The structure was solved by conventional Patterson and Fourier techniques, and refined by minimization of $\sum w\Delta^2$ [Δ = |F_o| − |F_c|; $w^{-1} = \sigma^2(F_o)$ + 0·001F_o^2]. Constraints were applied for H atoms [C—H = 0·96 Å, H—C—H = 109·5° in methyl groups, aromatic H on C—C—C external bisector; $U(\text{H}) = gU_{\text{iso}}(\text{C})$, with g = 1·1 for aromatic and 1·2 for methyl H]. H atoms were not included for the CH$_2$Cl$_2$ solvent molecule, which displays high thermal motion. Anisotropic thermal parameters were refined for all other atoms.

Final values for R and R_w [$=(\sum w\Delta^2/\sum wF_o^2)^{1/2}$] are 0·045 and 0·057 respectively. Refined coordinates are given in Table 1, bond lengths and angles in Table 2.*

Discussion. [Ru$_2$(mhp)$_4$].CH$_2$Cl$_2$ is isostructural with the analogous complexes of Cr, Mo and W (Cotton, Fanwick, Niswander & Sekutowski, 1978). The molecules of all these complexes, as well as those of the non-isostructural [Rh$_2$(mhp)$_4$] (Berry, Garner, Hillier, MacDowell & Clegg, 1980b; Clegg, 1980), approximate closely to $\bar{4}2m$ (D_{2d}) symmetry (Fig. 1) in the determined crystal structures. The Ru—Ru length of 2·238 (1) Å is intermediate between those of Mo—Mo [2·065 (1) Å] and Rh—Rh [2·359 (1) Å] in the

* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35612 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[M_2(mhp)$_4$] molecules, consistent with the formulation of the M—M bonds as formally single, double and quadruple for Rh, Ru and Mo respectively.

The O—Ru—Ru—N torsion angles for the four ligands are 3·9 (2), 3·5 (2), 3·8 (2) and 2·6 (2)° (mean

Table 1. Atomic coordinates (×10⁴) and equivalent isotropic thermal parameters (Å² ×10⁴)

$U = \frac{1}{3}$ of the trace of the orthogonalized U_{ij} matrix.

	x	y	z	U
Ru(1)	1795·4 (3)	1711·5 (2)	2747·9 (3)	302 (2)
Ru(2)	2442·7 (3)	529·7 (2)	3297·3 (3)	292 (2)
O(1)	2829 (3)	869 (2)	4880 (3)	357 (13)
C(11)	2698 (4)	1591 (3)	5125 (4)	356 (19)
C(12)	2998 (5)	1839 (4)	6203 (4)	454 (22)
C(13)	2863 (6)	2596 (4)	6435 (5)	611 (27)
C(14)	2436 (6)	3119 (4)	5626 (6)	658 (29)
C(15)	2149 (5)	2871 (3)	4587 (5)	487 (24)
C(16)	1662 (7)	3380 (3)	3645 (6)	666 (32)
N(1)	2277 (3)	2105 (2)	4336 (3)	347 (16)
O(2)	313 (3)	1442 (2)	2975 (3)	403 (14)
C(21)	106 (4)	738 (3)	3255 (4)	344 (19)
C(22)	−920 (5)	531 (4)	3347 (5)	511 (25)
C(23)	−1111 (5)	−210 (4)	3659 (5)	517 (25)
C(24)	−267 (5)	−741 (3)	3843 (5)	445 (23)
C(25)	706 (4)	−533 (3)	3747 (4)	366 (20)
C(26)	1647 (5)	−1084 (3)	3927 (6)	548 (27)
N(2)	915 (3)	196 (2)	3448 (3)	326 (16)
O(3)	2104 (3)	98 (2)	1779 (3)	449 (15)
C(31)	1576 (5)	519 (3)	997 (4)	440 (22)
C(32)	1263 (6)	218 (4)	−53 (5)	631 (29)
C(33)	696 (7)	653 (4)	−853 (6)	781 (35)
C(34)	429 (7)	1425 (5)	−648 (6)	729 (33)
C(35)	763 (5)	1729 (4)	356 (5)	521 (25)
C(36)	566 (7)	2555 (4)	641 (5)	634 (30)
N(3)	1330 (4)	1275 (3)	1181 (3)	390 (17)
O(4)	3242 (3)	2069 (2)	2488 (3)	446 (16)
C(41)	4060 (5)	1604 (3)	2709 (5)	404 (21)
C(42)	5069 (5)	1835 (4)	2572 (5)	520 (25)
C(43)	5935 (5)	1335 (4)	2850 (6)	664 (31)
C(44)	5803 (5)	608 (4)	3268 (6)	593 (28)
C(45)	4807 (4)	392 (3)	3362 (4)	400 (20)
C(46)	4571 (5)	−404 (3)	3733 (5)	534 (24)
N(4)	3949 (3)	883 (2)	3117 (3)	328 (15)
C(50)	3742 (14)	1240 (11)	9836 (10)	2510 (94)
Cl(1)	4110 (3)	2165 (2)	9418 (3)	1464 (18)
Cl(2)	3853 (3)	515 (2)	8927 (3)	1501 (19)

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

Ru(1)–Ru(2)	2·238 (1)		
Ru(1)–N(1)	2·094 (4)	Ru(2)–O(1)	2·055 (3)
Ru(2)–N(2)	2·087 (5)	Ru(1)–O(2)	2·038 (4)
Ru(1)–N(3)	2·093 (4)	Ru(2)–O(3)	2·031 (4)
Ru(2)–N(4)	2·083 (5)	Ru(1)–O(4)	2·050 (4)
Ru(2)–Ru(1)–N(1)	89·2 (1)	Ru(1)–Ru(2)–O(1)	92·2 (1)
Ru(1)–Ru(2)–N(2)	89·7 (1)	Ru(2)–Ru(1)–O(2)	92·0 (1)
Ru(2)–Ru(1)–N(3)	88·7 (1)	Ru(1)–Ru(2)–O(3)	92·9 (1)
Ru(1)–Ru(2)–N(4)	89·0 (1)	Ru(2)–Ru(1)–O(4)	92·5 (1)
N(1)–Ru(1)–N(3)	177·8 (2)	O(1)–Ru(2)–O(2)	174·9 (1)
N(2)–Ru(2)–N(4)	178·6 (2)	O(2)–Ru(1)–O(4)	175·5 (2)
N(1)–Ru(1)–O(2)	90·0 (2)	O(1)–Ru(2)–N(2)	89·6 (2)
N(1)–Ru(1)–O(4)	89·8 (2)	O(1)–Ru(2)–N(4)	91·1 (2)
N(3)–Ru(1)–O(2)	89·9 (2)	O(3)–Ru(2)–N(2)	90·1 (2)
N(3)–Ru(1)–O(4)	90·6 (2)	O(3)–Ru(2)–N(4)	89·3 (2)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
O(n)–C(n1)	1·300 (6)	1·306 (7)	1·288 (6)	1·290 (7)
C(n1)–C(n2)	1·409 (8)	1·390 (9)	1·408 (8)	1·400 (9)
C(n1)–N(n)	1·353 (7)	1·368 (7)	1·368 (8)	1·364 (7)
C(n2)–C(n3)	1·353 (9)	1·372 (9)	1·333 (10)	1·377 (9)
C(n3)–C(n4)	1·381 (9)	1·389 (9)	1·408 (11)	1·384 (10)
C(n4)–C(n5)	1·363 (9)	1·327 (9)	1·360 (9)	1·359 (9)
C(n5)–C(n6)	1·500 (9)	1·504 (8)	1·500 (9)	1·500 (8)
C(n5)–N(n)	1·371 (7)	1·353 (7)	1·372 (7)	1·358 (7)
Ru(m)–O(n)–C(n1)	119·7 (3)	120·4 (3)	119·6 (4)	119·5 (4)
O(n)–C(n1)–C(n2)	120·4 (5)	121·1 (5)	121·0 (5)	121·3 (5)
O(n)–C(n1)–N(n)	119·4 (5)	119·0 (5)	119·7 (5)	119·5 (5)
C(n2)–C(n1)–N(n)	120·2 (5)	119·9 (5)	119·3 (5)	119·2 (5)
C(n1)–C(n2)–C(n3)	119·2 (5)	119·9 (6)	120·6 (7)	119·9 (6)
C(n2)–C(n3)–C(n4)	120·4 (6)	118·2 (6)	119·5 (7)	119·8 (7)
C(n3)–C(n4)–C(n5)	119·8 (6)	120·9 (6)	120·2 (7)	118·9 (6)
C(n4)–C(n5)–C(n6)	124·6 (6)	123·2 (5)	124·1 (6)	122·7 (6)
C(n4)–C(n5)–N(n)	120·7 (5)	121·9 (5)	120·0 (6)	122·1 (5)
C(n6)–C(n5)–N(n)	114·7 (5)	114·8 (5)	115·9 (5)	115·2 (5)
Ru(m)–N(n)–C(n1)	119·3 (3)	118·7 (3)	118·8 (3)	119·4 (4)
Ru(m)–N(n)–C(n5)	120·9 (4)	122·2 (4)	120·9 (4)	120·6 (4)
C(n1)–N(n)–C(n5)	119·8 (5)	119·1 (5)	120·3 (5)	119·9 (5)

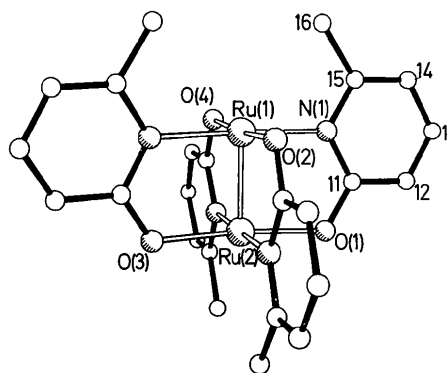|			
C(50)–Cl(1)	1·775 (19)	C(50)–Cl(2)	1·735 (17)
Cl(1)–C(50)–Cl(2)	111·6 (8)		

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

Fig. 1. The [Ru$_2$(mhp)$_4$] molecule. The numbering scheme follows the same pattern for all four ligands.

3·5°). This slight, but significant, twist about the Ru—Ru bond fits in well with the pattern already described for [M_2(mhp)$_4$] complexes (Clegg, 1980). The mean torsion angle, mean Ru—N [2·089 (5) Å], mean Ru—O [2·044 (10) Å] and the difference between these two mean bond lengths [0·045 (12) Å] are all intermediate between the corresponding values for the Mo and Rh complexes; C(Me)···C(Me) distances [3·98 (1) and 4·03 (1) Å] are similar to those in the Rh complex, supporting the explanation of the twist in terms of steric interactions between methyl groups.

The Ru—Ru length appears to be the shortest yet determined between two Ru atoms. In complexes containing the [Ru$_2$(O$_2$CR)$_4$]$^+$ structural unit, Ru—Ru varies between 2·248 (1) and 2·292 (7) Å, depending on the nature of R and of additional axial ligands (Bino, Cotton & Felthouse, 1979; Bennett, Caulton & Cotton, 1969). The Ru—Ru bond in these complexes has a formal bond order of 2·5 (Bennett, Caulton & Cotton, 1969; Norman & Kolari, 1978), compared with the value of 2 in [Ru$_2$(mhp)$_4$] (Berry, Garner, Hillier, MacDowell & Clegg, 1980a). This tendency of mhp and a variety of similar ligands to support very short M—M bonds is now well established for many transition metals, and has both electronic and steric causes.

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Structure of Bis[(isopropylthio)acetato]copper(II) Dihydrate

BY T. OGAWA, M. SHIMOI AND A. OUCHI

Department of Chemistry, College of General Education, The University of Tokyo, Komaba 3-8-1, Meguro, Tokyo 153, Japan

Abstract. [Cu(C$_5$H$_9$O$_2$S)$_2$].2H$_2$O, $a = 14\cdot318$ (2), $b = 10\cdot968$ (2), $c = 4\cdot949$ (1) Å, $\beta = 93\cdot74$ (2)°, $Z = 2$, $D_m = 1\cdot57$, $D_x = 1\cdot56$ Mg m^{-3}; $R = 0\cdot043$ for 1802 independent reflexions. The space group is $P2_1$; however, the symmetry of the molecular arrangement is very close to $P2_1/a$, which was used to determine the average structure in this work. The (isopropylthio)acetato acts as a terdentate ligand, coordinating *via* one S, and one carboxylato O to a Cu atom, and *via* the other O to another Cu atom. The Cu atom has a deformed octahedral coordination, and the complexes are aligned to form a polymer chain parallel to **c**. The crystalline waters are in interstitial positions, forming hydrogen bonds with one O atom of a carboxyl group and with two other water molecules.

Introduction. (Alkylthio)acetic acid is an interesting ligand, as it is able to coordinate to metals using its S atom, as well as both O atoms of its carboxyl group. For alkoxyacetato complexes of metals, a number of interesting modes of coordination have been found (Forrest, Prout & Rossotti, 1966; Prout, Carruthers & Rossotti, 1971; Carruthers, Prout & Rossotti, 1975). Accordingly, various structures for alkylthioacetato complexes of metals are expected; for example, bis[(propylthio)acetato]cobalt(II) consists of hexameric units (Shimoi, Ebina, Ouchi, Yoshino & Takeuchi, 1979). In the case of bis[(isopropylthio)-acetato]copper(II) dihydrate, two kinds of crystals were obtained: a pale-blue complex, which has spectral properties similar to those of other Cu^{II} (alkylthio)-acetates, and a black-violet isomer. The latter seems to be more stable than the former, but as yet. black-violet isomers have not been obtained for other (alkylthio)-acetate complexes. The surface reflectance spectra of a crystalline powder of the black-violet isomer shows