Table 2. *Bond distances* (Å) *and angles* (°)

Sn(1)–N(1)	2·085 (8)	O(3)–C(3)	1·23 (1)
Sn(1)–N(2)	2·293 (8)	C(1)–C(2)	1·485 (8)
Sn(1)–O(1)	2·196 (7)	C(3)–C(4)	1·51 (1)
Sn(1)–C(5)	2·18 (1)	C(5)–C(6)	1·54 (2)
Sn(1)–C(9)	2·18 (1)	C(5)–C(7)	1·53 (2)
N(1)–C(2)	1·45 (1)	C(5)–C(8)	1·52 (2)
N(1)–C(3)	1·34 (1)	C(9)–C(10)	1·53 (2)
N(2)–C(4)	1·49 (1)	C(9)–C(11)	1·53 (2)
O(1)–C(1)	1·303 (9)	C(9)–C(12)	1·53 (2)
O(2)–C(1)	1·24 (1)		

C(5)–Sn(1)–C(9)	121·7 (4)	N(1)–C(2)–C(1)	110·3 (5)
O(1)–Sn(1)–C(9)	97·2 (4)	N(1)–C(3)–O(3)	124·4 (9)
O(1)–Sn(1)–C(5)	92·5 (3)	O(3)–C(3)–C(4)	121 (1)
N(2)–Sn(1)–C(9)	100·2 (4)	N(1)–C(3)–C(4)	115·0 (9)
N(2)–Sn(1)–C(5)	99·2 (4)	N(2)–C(4)–C(3)	113·2 (8)
N(2)–Sn(1)–O(1)	149·6 (3)	Sn(1)–C(5)–C(8)	109·7 (7)
N(1)–Sn(1)–C(9)	113·7 (4)	Sn(1)–C(5)–C(7)	107·4 (7)
N(1)–Sn(1)–C(5)	124·3 (4)	Sn(1)–C(5)–C(6)	109·1 (7)
N(1)–Sn(1)–O(1)	75·0 (3)	C(7)–C(5)–C(8)	110·7 (9)
N(1)–Sn(1)–N(2)	75·2 (3)	C(6)–C(5)–C(8)	110·2 (9)
Sn(1)–N(1)–C(3)	123·3 (7)	C(6)–C(5)–C(7)	109·7 (9)
Sn(1)–N(1)–C(2)	119·3 (5)	Sn(1)–C(9)–C(12)	107·7 (8)
C(2)–N(1)–C(3)	116·9 (8)	Sn(1)–C(9)–C(11)	109·2 (7)
Sn(1)–N(2)–C(4)	110·7 (6)	Sn(1)–C(9)–C(10)	109·3 (7)
Sn(1)–O(1)–C(1)	117·1 (5)	C(11)–C(9)–C(12)	111 (1)
O(1)–C(1)–O(2)	121·9 (7)	C(10)–C(9)–C(12)	110·9 (9)
O(2)–C(1)–C(2)	120·2 (6)	C(10)–C(9)–C(11)	109 (1)
O(1)–C(1)–C(2)	117·9 (6)		

N(2)···O(2)(0·5−*x*, *y*−0·5, 0·5−*z*)	2·92 (1)
N(2)···O(4)(*x*−0·5, 0·5−*y*, 0·5+*z*)	2·89 (1)
O(4)···O(2)(*x*, *y*, *z*)	2·77 (1)
O(4)···O(3)(1·5−*x*, −0·5+*y*, 0·5−*z*)	2·76 (1)

e.g. O(1)–Sn(1)–C(9) [97·2 (4)°], is evident. The distortion appears to be caused mainly by the rigidity of the GlyGly ligand, while the two voluminous *tert*-butyl ligands at Sn seem to be of minor influence. The dihedral angles between planes (1) and (2) and the plane through N(1)–C(5)–C(9), from which Sn(1) deviates by only 0·065 (1) Å, are 92·2 (2) and 90·2 (2)°, respectively, and correspond, like the angle C(5)–Sn–C(9) of 121·7 (4)°, to nearly ideal values. This last angle is larger than the appropriate angle in $Ph_2SnGlyGly$ [117·5 (3)° (Huber *et al.*, 1977)], but smaller than in $Cy_2SnGlyGly$ [123·6 (2)° (Vornefeld *et al.*, 1989)].

The molecules are linked by a three-dimensional network of hydrogen bonds, involving both H atoms of the water molecule and the NH_2 group, O(2) of the carboxylate group and O(3) of the peptide link. Considering that in the title compound the C(1)–O(1) and C(1)–O(2) bonds are longer and that the C(1)–C(2) bond is shorter than the appropriate bonds in the $R_2SnGlyGly$ compounds which contain no water [R = Ph/Cy/*tert*-Bu: C(1)–O(1) 1·293 (14)/1·287 (6)/1·303 (9); C(1)–O(2) 1·200 (13)/1·216 (6)/1·24 (1); C(1)–C(2) 1·549 (18)/1·522 (7)/1·485 (8) Å], it is inferred that these changes in bond lengths are a consequence of the formation of the extended hydrogen-bond system.

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Structures of Tetrakis(μ-acetato)bis(2-amino-4,6-dimethylpyrimidine)dirhodium(II) and its Monohydrate

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Abstract. $[Rh_2(C_2H_3O_2)_4(C_6H_9N_3)_2]$, $M_r = 688·30$, triclinic, $P\bar{1}$, $a = 11·342$ (2), $b = 7·996$ (2), $c = 8·032$ (1) Å, $\alpha = 89·74$ (2), $\beta = 106·55$ (1), $\gamma = 102·96$ (2)°, $V = 679·1$ (2) Å^3, $Z = 1$, $D_x = 1·683$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 12·46$ cm^{-1}, $F(000) = 346$, $T = 296$ K, $R = 0·023$ for

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2836 observed reflections. $[Rh_2(C_2H_3O_2)_4(C_6H_9N_3)_2]\cdot H_2O$, $M_r = 706{\cdot}32$, monoclinic, $C2/c$, $a = 22{\cdot}683$ (6), $b = 8{\cdot}776$ (1), $c = 14{\cdot}883$ (3) Å, $\beta = 116{\cdot}18$ (1)°, $V = 2659$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}764$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 12{\cdot}78$ cm^{-1}, $F(000) = 1424$, $T = 296$ K, $R = 0{\cdot}037$ for 2484 observed reflections. In each complex, which has a crystallographic centre of symmetry at the midpoint of the Rh—Rh bond, the dirhodium-tetraacetate nucleus is occupied at the two axial positions by the ring nitrogens of the pyrimidine ligands. Interligand N—H···O and C—H···O hydrogen bonds stabilize the structure.

Introduction. In a report on interactions between tetrakis(μ-acetato)dirhodium(II), an antitumor agent, and 4-amino-5-(aminomethyl)-2-methylpyrimidine (aamp), a nucleobase derivative or a degradation product of thiamine (vitamin B_1), we suggested that the absence of the metal bonding to the ring nitrogen which is flanked by the methyl and the amino substituents may be due to the steric interference of the octahedral environment about the rhodium atom (Aoki & Yamazaki, 1984). However, against this argument, we obtained complexes formed between $[Rh_2(AcO)_4]$ and 2-amino-4,6-dimethylpyrimidine (admp), $[Rh_2(AcO)_4(admp)_2]$ (1) and $[Rh_2(AcO)_4(admp)_2].H_2O$ (2), which involve the Rh-ring nitrogen bonding (Aoki & Yamazaki, 1985). We report here their detailed crystal structures.

Experimental. The complexes (1) and (2) were prepared by mixing $[Rh_2(AcO)_4].2MeOH$ (51 mg, 0·1 mmol) dissolved in 20 mL of hot water and admp (24 mg, 0·2 mmol) dissolved in 5 mL of water and allowing the solution to stand at room temperature. Crystals appeared after one day in two crystalline forms, one being columns (1) and the other plates (2), in the same batch.

Cell parameters were determined on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0{\cdot}71073$ Å) from 20 high-order reflections [$24 < 2\theta < 34°$ for (1) and $20 < 2\theta < 29°$ for (2)]. Details of the data collection together with structure refinement are summarized in Table 1. Throughout the data collection the intensities of the three standard reflections were monitored every 100 measurements; variations in intensity were within 2% for both of the complexes. Intensities were corrected for Lp effects but not for absorption.

The structures were solved by heavy-atom methods and refined with block-diagonal least squares, minimizing the function $\sum w(F_o - |F_c|)^2$. All H atoms were located from difference Fourier maps, except for one attached to a water molecule which rides on a dyad axis in (2). All non-hydrogen atoms were refined anisotropically and H atoms isotropically. Final atomic coordinates with their e.s.d.'s are listed in Tables 2 and 3.* Neutral atomic scattering factors and anomalous-dispersion corrections for Rh were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the *UNICS*III program system (Sakurai & Kobayashi, 1979) on a FACOM 780 computer.

Table 1. *Experimental details*

Compound	(1)	(2)
Crystal size (mm)	0·13 × 0·23 × 0·31	0·08 × 0·35 × 0·49
Crystal colour	Deep violet	Violet–red
2θ range measured (°)	3·0–55·0	3·0–55·0
Scan mode	ω scan for $2\theta \le 30°$ ω–2θ scan for $2\theta > 30°$	ω scan for $2\theta \le 30°$ ω–2θ scan for $2\theta > 30°$
Scan range (°)	1·2 + 0·5tanθ	1·2 + 0·5tanθ
Unique data measured	3133	3063
Unique data used $[F_o > 3\sigma(F_o)]$	2836	2484
Scan speed (2θ)(°min^{-1})	4	4
Background counting(s)	5	5
Transmission factors*	0·95–1·06	0·93–1·26
Final number of variables	223	228
Weighting scheme w	$w = 1{\cdot}0$	$w = \sigma(F_o)^{-2}$
R	0·023	0·037
wR	0·026	0·031
S	0·66	1·97
$(\Delta/\sigma)_{min}$	0·23 [H1(C4α)]	0·37 [H1(C12)]
$(\Delta\rho)_{max}$(e Å^{-3})	0·41 [1·1 Å from the Rh atom]	0·99 [1·2 Å from the Rh atom]

* ψ-scan method; normalized to an average of unity.

Discussion. Interatomic distances and angles are listed in Table 4. Molecular structures of (1) and (2) are shown in Figs. 1(*a*) and (*b*), respectively, and their crystal packings are in Figs. 2(*a*) and (*b*).

The structural feature of the $[Rh_2(AcO)_4(admp)_2]$ unit is fundamentally equivalent for both of the complexes; a crystallographic inversion centre exists at the midpoint of the Rh—Rh bond. The dimensions of the dirhodium-tetraacetate core have normal values (Aoki & Yamazaki, 1985). The admp ligand coordinates to the two axial positions of the dirhodium-tetraacetate cage through the ring nitrogen N(1). The base ring bisects the two dirhodium-diacetate planes. This geometry appears to be doubly advantageous, that is, to avoid unfavourable steric interactions and, more importantly, to form two types of interligand hydrogen bonds between the amino substituent and the acetate oxygen(s) and between the methyl substituent and the acetate oxygens. The structural rigidity of the RhO_4 core is of particular benefit for the formation of

* Lists of structure factors, anisotropic thermal parameters, H-atom positions, bond distances and angles involving H atoms, least-squares planes, and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51584 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates and B_{eq} values* (Å²) *for* $[Rh_2(AcO)_4(admp)_2]$ (1) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Rh	0·10245 (2)	0·02003 (3)	−0·02400 (3)	2·2
O(11)	0·0761 (2)	0·2444 (2)	−0·1333 (3)	3·0
O(12)	−0·1151 (2)	0·2065 (3)	−0·0901 (3)	3·2
O(13)	0·1791 (2)	0·1395 (3)	0·2200 (3)	3·2
O(14)	−0·0113 (2)	0·0991 (3)	0·2662 (2)	2·9
C(11)	−0·0277 (3)	0·2841 (3)	−0·1488 (4)	2·8
C(12)	−0·0497 (3)	0·4397 (4)	−0·2489 (5)	4·2
C(13)	0·1070 (3)	0·1488 (3)	0·3135 (3)	2·7
C(14)	0·1700 (3)	0·2249 (5)	0·4966 (4)	3·9
N(1)	0·3013 (2)	0·0683 (3)	−0·0792 (3)	2·9
C(2)	0·3777 (3)	0·2295 (4)	−0·0506 (4)	2·9
N(3)	0·4693 (2)	0·2901 (3)	−0·1265 (3)	3·4
C(4)	0·4949 (3)	0·1770 (5)	−0·2253 (4)	3·8
C(5)	0·4315 (3)	0·0069 (5)	−0·2454 (4)	3·8
C(6)	0·3336 (3)	−0·0449 (4)	−0·1739 (4)	3·1
N(2α)	0·3642 (3)	0·3395 (3)	0·0639 (4)	4·3
C(4α)	0·5950 (4)	0·2458 (6)	−0·3122 (6)	6·0
C(6α)	0·2581 (3)	−0·2270 (4)	−0·2021 (5)	4·1

Table 3. *Final atomic coordinates and B_{eq} values* (Å²) *for* $[Rh_2(AcO)_4(admp)_2].H_2O$ (2) *with e.s.d's in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Rh	0·20316 (2)	0·22855 (4)	0·01664 (3)	2·2
O(11)	0·2193 (1)	0·4412 (3)	0·0808 (2)	3·0
O(12)	0·3066 (1)	0·4792 (3)	0·0499 (2)	3·2
O(13)	0·1464 (1)	0·3206 (3)	−0·1211 (2)	3·1
O(14)	0·2339 (1)	0·3584 (3)	−0·1517 (2)	3·0
C(11)	0·2665 (2)	0·5177 (5)	0·0835 (3)	2·7
C(12)	0·2788 (3)	0·6707 (5)	0·1349 (4)	4·3
C(13)	0·1740 (2)	0·3710 (5)	−0·1732 (3)	2·7
C(14)	0·1303 (2)	0·4499 (6)	−0·2704 (4)	4·0
N(1)	0·1113 (2)	0·1918 (4)	0·0511 (3)	2·7
C(2)	0·0646 (2)	0·3016 (5)	0·0259 (3)	2·9
N(3)	0·0130 (2)	0·3021 (5)	0·0484 (3)	3·5
C(4)	0·0062 (2)	0·1828 (6)	0·0978 (3)	3·6
C(5)	0·0503 (2)	0·0653 (6)	0·1251 (4)	3·8
C(6)	0·1029 (2)	0·0716 (5)	0·1008 (3)	3·1
N(2α)	0·0683 (2)	0·4237 (5)	−0·0256 (3)	4·4
C(4α)	−0·0525 (3)	0·1851 (7)	0·1205 (4)	5·5
C(6α)	0·1508 (3)	−0·0573 (6)	0·1296 (4)	4·2
O(W)	0*	0·2068 (8)	−¼*	8·9

* Fixed by symmetry.

bifunctional C⟨H···O / H···O⟩Rh hydrogen bonds since, otherwise, the C—H···O hydrogen bonding may be weak. There is a minor difference in the amino···acetate hydrogen-bonding system between the two complexes, that is, a single hydrogen bond for (1) and a bifurcated one for (2); in (1), though the N(2α) still makes a close contact with the acetate O(11) [3·117 (3) Å], the H1(N2α)···O(11) distance [2·69 (3) Å] corresponds to a van der Waals contact [sum of van der Waals radii for H···O = 2·70 Å (Taylor & Kennard, 1982)]. The

Table 4. *Interatomic distances* (Å) *and angles* (°) *of* $[Rh_2(AcO)_4(admp)_2]$ (1) *and* $[Rh_2(AcO)_4(admp)_2].H_2O$ (2) *with e.s.d's in parentheses*

	(1)	(2)
(*a*) Coordination sphere		
Rh–N(1)	2·368 (3)	2·376 (5)
Rh–O(11)	2·039 (2)	2·055 (3)
Rh–O(12^i)	2·041 (2)	2·040 (3)
Rh–O(13)	2·046 (2)	2·045 (3)
Rh–O(14^i)	2·047 (2)	2·032 (3)
Rh–Rh^i	2·4141 (3)	2·4148 (6)
N(1)–Rh–O(11)	89·44 (9)	90·9 (1)
N(1)–Rh–O(12^i)	95·28 (9)	93·8 (1)
N(1)–Rh–O(13)	92·90 (8)	92·7 (1)
N(1)–Rh–O(14^i)	91·76 (8)	92·1 (1)
O(11)–Rh–O(12^i)	175·27 (9)	175·3 (2)
O(11)–Rh–O(13)	92·15 (8)	90·7 (1)
O(11)–Rh–O(14^i)	86·92 (8)	88·7 (1)
O(12^i)–Rh–O(13)	87·32 (8)	88·9 (1)
O(12^i)–Rh–O(14^i)	93·22 (8)	91·3 (1)
O(13)–Rh–O(14^i)	175·24 (9)	175·3 (1)
Rh–N(1)–C(2)	119·4 (2)	119·8 (3)
Rh–N(1)–C(6)	123·5 (2)	125·1 (3)
Rh–O(11)–C(11)	118·3 (2)	118·5 (3)
Rh–O(12^i)–C(11^i)	119·6 (2)	119·3 (3)
Rh–O(13)–C(13)	119·2 (2)	119·2 (2)
Rh–O(14^i)–C(13^i)	119·8 (2)	119·6 (3)
N(1)–Rh–Rh^i	177·60 (6)	178·71 (8)
O(11)–Rh–Rh^i	88·23 (6)	87·8 (1)
O(12^i)–Rh–Rh^i	87·05 (7)	87·5 (1)
O(13)–Rh–Rh^i	87·79 (6)	87·4 (1)
O(14^i)–Rh–Rh^i	87·52 (6)	87·9 (1)
(*b*) 2-Amino-4,6-dimethylpyrimidine ligand		
N(1)–C(2)	1·362 (3)	1·358 (6)
C(2)–N(3)	1·348 (4)	1·351 (7)
N(3)–C(4)	1·337 (5)	1·328 (7)
C(4)–C(5)	1·375 (5)	1·367 (7)
C(5)–C(6)	1·375 (5)	1·393 (9)
C(6)–N(1)	1·359 (4)	1·350 (7)
C(2)–N(2α)	1·338 (5)	1·342 (7)
C(4)–C(4α)	1·499 (6)	1·513 (9)
C(6)–C(6α)	1·496 (4)	1·496 (7)
N(1)–C(2)–N(3)	125·6 (3)	126·2 (4)
C(2)–N(3)–C(4)	116·8 (3)	117·4 (4)
N(3)–C(4)–C(5)	121·0 (3)	120·8 (5)
C(4)–C(5)–C(6)	119·4 (4)	119·3 (5)
C(5)–C(6)–N(1)	121·0 (3)	121·3 (4)
C(6)–N(1)–C(2)	115·5 (3)	115·0 (5)
N(1)–C(2)–N(2α)	118·7 (3)	119·1 (5)
N(3)–C(2)–N(2α)	115·7 (3)	114·8 (4)
N(3)–C(4)–C(4α)	116·5 (3)	116·2 (4)
C(5)–C(4)–C(4α)	122·4 (4)	123·0 (5)
C(5)–C(6)–C(6α)	120·6 (3)	119·6 (5)
N(1)–C(6)–C(6α)	118·4 (3)	119·1 (5)
(*c*) Acetate ligands		
C(11)–O(11)	1·260 (4)	1·251 (6)
C(11)–O(12)	1·256 (4)	1·261 (7)
C(11)–C(12)	1·507 (5)	1·509 (7)
C(13)–O(13)	1·271 (4)	1·272 (7)
C(13)–O(14)	1·255 (3)	1·255 (6)
C(13)–C(14)	1·503 (4)	1·513 (6)
O(11)–C(11)–O(12)	126·5 (3)	126·9 (4)
O(11)–C(11)–C(12)	116·8 (3)	117·3 (5)
O(12)–C(11)–C(12)	116·7 (3)	115·8 (5)
O(13)–C(13)–O(14)	125·6 (2)	125·6 (4)
O(13)–C(13)–C(14)	116·6 (3)	116·8 (4)
O(14)–C(13)–C(14)	117·7 (3)	117·6 (5)

Table 4 (*cont.*)

(*d*) Hydrogen bonds

D	*A*	*D*···*A*	H···*A*	*D*···*A*	H···*A*
N(2α)	O(11)			3·077 (5)	2·38 (4)
N(2α)	O(13)	2·918 (4)	2·09 (4)	2·863 (7)	2·10 (6)
N(2α)	N(3^{ii})	3·091 (4)	2·21 (4)	2·959 (6)	2·10 (5)
C(6α)	O(12^{i})	3·234 (5)	2·43 (5)	3·288 (8)	2·59 (5)
C(6α)	O(14^{i})	3·099 (5)	2·53 (5)	3·038 (7)	2·33 (5)
O(*W*)*	O(13)			3·176 (3)	
O(*W*)*	O(13^{iii})			3·176 (3)	

Symmetry code: (none) x, y, z; (i) $-x, -y, -z$ for (1) or $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-y, -z$ for (2); (ii) $1-x, 1-y, -z$ for (1) or $-x, 1-y, -z$ for (2); (iii) $-x, y, -\frac{1}{2}-z$ for (2).

* Hydrogen atom was not located.

presence of the substituent(s) adjacent to the coordinating ring N apparently affects the Rh–N bond length in the $[Rh_2(carboxylato)_4(L)_n]$ framework (L = nitrogen-donor aromatic ligand): 2·227 (6) Å for non-substituted pyridine (Koh & Christoph, 1978), 2·284 (8) and 2·293 (7) Å for one-neighbour-substituted (by methyl group) pyrimidine bases, *i.e.* thiamine monophosphate (Aoki & Yamazaki, 1985) and aamp (Aoki & Yamazaki, 1984), respectively, and 2·362 (4) and 2·413 (3) Å for both-neighbours-substituted (by phenyl fragments) tricyclic ligands, phenazine (Cotton & Felthouse, 1981) and acridine (Cotton & Felthouse, 1981), and 2·368 (3) and 2·376 (5) Å for both-neighbours-substituted (by amino and methyl groups) pyrimidine bases of the present complexes (1) and (2), respectively. Although unfortunately no methyl hydrogen atoms were located in the thiamine monophosphate and the aamp complexes, the interligand methyl···acetate C···O distances [3·28 (1) and 3·29 (1) Å for the former and 3·21 (1) and 3·24 (1) Å for the latter complexes] suggest hydrogen-bonding interactions between them.

For both compounds, the crystal packings are dominated by van der Waals contacts, a pair of base–base hydrogen bonds, which are related by a centre of symmetry, between the amino substituent N(2α) and the ring nitrogen N(3), and by base–base stacking interactions with average spacings of 3·47 Å for (1) and 3·55 Å for (2). The ring–ring overlappings are considerable in (1) while scarce in (2). In (2), a water molecule of crystallization, which lies on a dyad axis along **b**, is an additional factor stabilizing the crystal structure by forming hydrogen bonds with the self-related (by a dyad axis) acetate oxygens [O(13)].

In summary, an octahedral MO_4 nucleus does not exclude axial coordination by a ring nitrogen-donor with either side substituted, at least for the present system in which substituents are the amino and methyl groups, in addition to the acridine (or phenazine) systems. We also emphasize the significance of the methyl group as a hydrogen-bonding donor, at least for

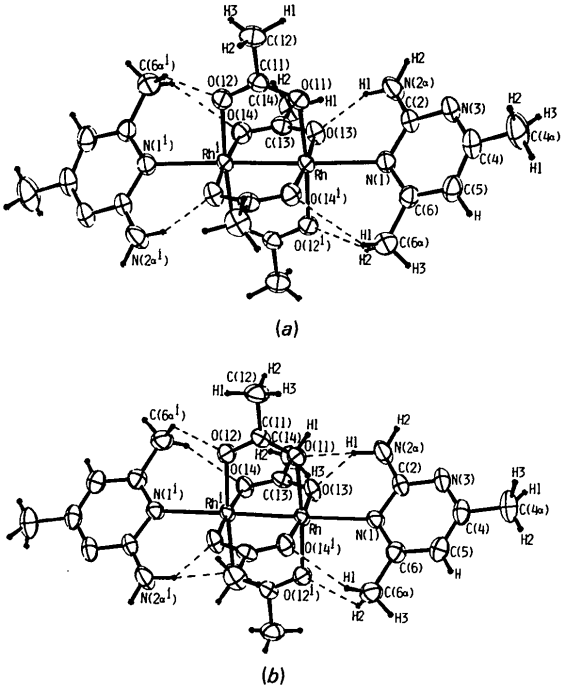

Fig. 1. Molecular structures of (*a*) (1) and (*b*) (2), where broken lines denote hydrogen bonds. Non-hydrogen atoms are shown as 50% probability ellipsoids, and H atoms as spheres of arbitrary size. A water molecule in (2) is omitted. Atoms with superscript i are related to the corresponding atoms without superscript by a centre of symmetry at the midpoint of the Rh–Rh bond.

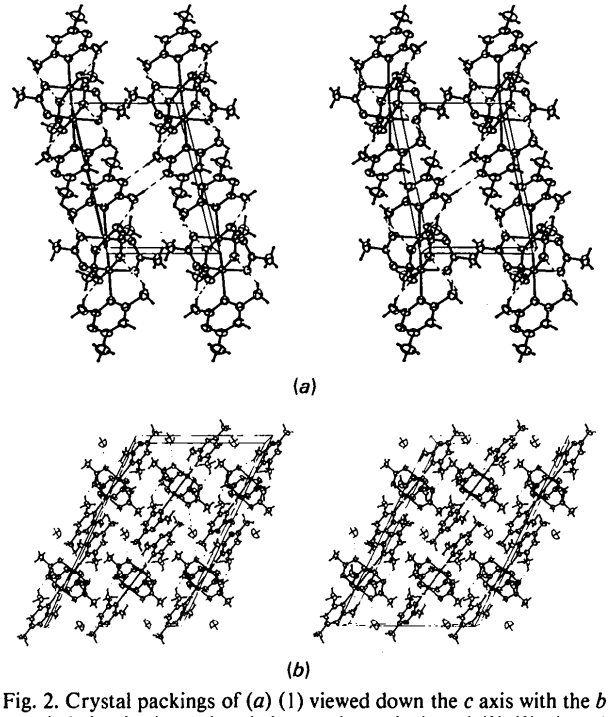

Fig. 2. Crystal packings of (*a*) (1) viewed down the *c* axis with the *b* axis being horizontal and the *a* axis vertical, and (*b*) (2) viewed down the *b* axis with the *c* axis horizontal and the *a* axis vertical. Broken lines denote hydrogen bonds.

that attached to the π-ring system and especially when it meets stereochemically desirable environments, such as the present octahedral MO_4 rigid core.

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Structure of the Rhodium Complex of a Reactant in Directed Hydrogenation

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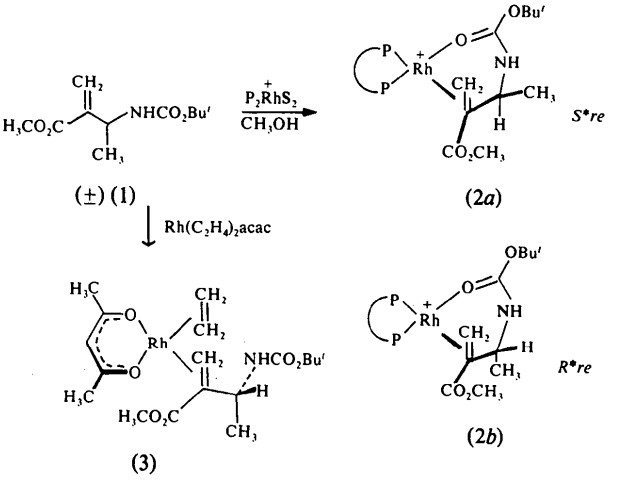
Abstract. {η^2-[2*R**(*re*),3*R**]-3-(*tert*-Butoxycarbonylamino)-2-methoxycarbonylbut-1-ene]}(η^2-ethene)(2,4-pentanedionato)rhodium, $[Rh(C_5H_7O_2)(C_2H_4)(C_{11}H_{19}NO_4)]$, $M_r = 459{\cdot}35$, monoclinic, $P2_1/n$, $a = 12{\cdot}547\ (3)$, $b = 9{\cdot}021\ (2)$, $c = 18{\cdot}869\ (5)$ Å, $\beta = 105{\cdot}68\ (2)°$, $V = 2056{\cdot}2\ (9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}48$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8{\cdot}42$ cm^{-1}, $F(000) = 952$, $T = 290$ K, $R = 0{\cdot}046$ for 2384 unique observed $[I/\sigma(I) \geq 2{\cdot}0]$ reflections. The potentially chelating ligand is only bound to Rh through its olefin group, in *R re* conformation (and its *S si* enantiomer). Rh—C is 2·13 (1) Å, Rh—O is 2·036 (3) Å and C—C(olefin) 1·38 (1) Å.

Introduction. The directed hydrogenation of α′-substituted acrylate esters can lead to high stereoselectivity (Brown, 1987) and, with an optically active ligand coordinated to the catalytic metal centre, kinetic resolution of racemic starting material can occur. This leads to catalytic asymmetric synthesis of a range of saturated and unsaturated esters (Brown & Cutting, 1985; Brown & James, 1987; Brown, James & Prior, 1987). Selectivity arises through the coordination of both olefin and directing group to rhodium during key stages of the catalytic cycle. There is a lack of appropriate structural information on the chelate binding of reactants such as (1). The chiral centre adjacent to the olefin requires that two configurational isomers of coordinated catalytic intermediates exist; these are schematized as (2*a*) and (2*b*). Catalytic hydrogenation studies suggest that complexes of type (2*a*) are favoured in the stereochemically determining step of the catalytic cycle.



Several attempts have been made to clarify these stereochemical requirements, but difficulty has been found in preparing crystalline samples suitable for X-ray characterization. In the course of this work the unsaturated amide (1) (Brown & James, 1987) was reacted with bis(ethylene)rhodium acetylacetonate, with the displacement of one molecule of ethylene. The complex (3) produced provides an analogue of (2*a*–*b*),

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