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Synthesis and Crystal Structure of Dinuclear Rh(II) Complexes with 1,10-Phenanthroline and its 4,7- and 3,4,7,8-Methyl Derivatives

M. CALLIGARIS, L. CAMPANA, G. MESTRONI, M. TORNATORE and E. ALESSIO

Dipartimento di Scienze Chimiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

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Abstract

The synthesis of complexes $[Rh_2(OAc)_2Cl_2(chel)_2]$ (chel = 1,10-phenanthroline, 4,7-Me_2-phen, 3,4,7,8-Me_4-phen) is reported. The complexes easily exchange the chlorine atoms with both neutral and anionic ligands.

The crystal structure of the cationic derivatives $[Rh_2(OAc)_2(phen)_2(NMid)_2](ClO_4)_2$ (**1**), $[Rh_2(OAc)_2(4,7\text{-}Me_2\text{-phen})_2(NMid)_2](ClO_4)_2$ (**2**) and $[Rh_2(OAc)_2(3,4,7,8\text{-}Me_4\text{-phen})_2(NMid)_2](ClO_4)_2$ (**3**) (NMid = N-methyl imidazole) have been determined by three dimensional X-ray analyses. Crystal data are: $a = 10.737(5)$, $b = 14.265(3)$, $c = 15.211(3)$ Å, $\alpha = 71.66(2)°$; $\beta = 69.99(3)°$, $\tau = 74.15(3)°$, triclinic, space group $P1$, $Z = 2$ (**1**); $a = 16.081(5)$, $b = 14.040(2)$, $c = 20.390(4)$ Å, $\beta = 98.91(3)°$, monoclinic, space group $P2_1/c$, $Z = 4$ (**2**); $a = 11.9274$, $b = 24.931(7)$, $c = 16.495(13)$ Å, $\beta = 92.58(5)°$, monoclinic, space group $P2_1/c$, $Z = 4$ (**3**). Least-squares refinement based on 9067 (**1**), 7050 (**2**) and 4300 (**3**) converged to $R = 0.046$ for *1* and 0.074 for **2** and **3**. All the phenanthroline derivatives are dinuclear with Rh–Rh distances of 2.5557(4), 2.565(1) and 2.564(1) Å in **1**, **2** and **3**, respectively. Structural features seem to emphasize the importance of the bridging ligands and van der Waals interactions in determining the Rh–Rh bond length.

Introduction

Transition metal complexes with 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy) and substituted derivatives act as catalysts in several reactions [1]. Regular trends of the activity as a function of the chelating system (chel) nature are generally observed, in particular with the unhindered methyl-substituted phenanthrolines [1].

Among the various reactions the transfer hydrogenations from alcohols, usually propan-2-ol, to ketones promoted by Rh and Ir derivatives are of particular interest [2, 3]. Ir(I) derivatives of the type [Ir(chel)(HD)X] (HD = 1,5-hexadiene, X = Cl, Br, I), for example, promote the reduction of the 4-tertbutyl-cyclohexanone (4-TBCE) to the corresponding equatorial alcohol with high activity and selectivity (97% selectivity with chel = 3,4,7,8-Me_4-phen) [3]; on the other hand rhodium derivatives of the type $[Rh_2(OAc)_2Cl_2(chel)_2]$ or $[Rh(HD)Cl]_2$ + chel promote the reduction of the same substrate to the corresponding axial alcohol (82% selectivity with chel = 4,7-Me_2-phen) [2, 4].

The activity and the selectivity, as a function of the nature of chel, observed in the case of the reduction of 4-TBCE with propan-2-ol, show a regular trend with the iridium complexes, and a mononuclear Ir(I) derivative has been suggested as active species [3]. Using the rhodium complexes, surprisingly, a dramatic change of both activity and selectivity has been observed on going from the 4,7-Me_2-phen to the 3,4,7,8-Me_4-phen derivative, as can be clearly seen from the data reported in Table I.

The differences experimentally observed with the two chelates cannot be easily explained in terms

TABLE I. Reduction of 4-TBCE by Propan-2-ol. Catalyst Precursor: $[Rh(1,5\text{-hexadiene})Cl]_2$ + chel

chel	pK_a	ν(CO)^a	Conv. (%)	OH ax. (%)
phen	4.86	2016.7	17	77
5,6-Me_2-phen	5.60		26	77
4,7-Ph_2-phen	4.84	2015.5	67	76.5
4,7-Me_2-phen	5.94	2015.4	93	82
3,4,7,8-Me_4-phen	6.31	2015	8	30

Reaction conditions: $[Rh] = 2 \times 10^{-4}$ M; [4-TBCE]/[Rh] = 650; [chel]/[Rh] = 2; [KOH]/[Rh] = 18; $[H_2O] = 0.1\%$; $T = 83$ °C; propan-2-ol = 50 ml. $^a A_1$ symmetry ν(CO) in $[Mo(chel)(CO)_4]$, see ref. 1.

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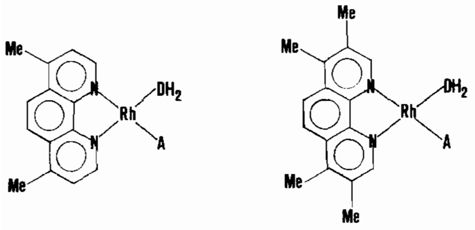
of electronic and/or steric properties of the active site assuming mononuclear Rh(I) complexes as catalysts (see Scheme 1).



Scheme 1. DH$_2$ = Hydrogen donor; A = Hydrogen acceptor.

A possible explanation of the observed trend can be given assuming dinuclear clusters as active species, structurally related to the [$Rh_2(phen)_2(HCOO)_2Cl_2$] [5], with the phen molecules faced to each other and the propan-2-ol and ketone moieties coordinated to rhodium via their oxygen atoms.

Going from the 4,7-Me_2-phen to the 3,4,7,8-Me_4-phen derivative the active species would decompose due to the excessive steric hindrance of the two faced 3,4,7,8-Me_4-phen molecules; such a decomposition would favour the formation of a Rh(I) mononuclear species responsible for the equatorial alcohol synthesis. In agreement with this hypothesis, using the [$Rh_2(OAc)_2$(4,7-Me_2-phen)$_2Cl_2$] complex as catalyst precursor instead of the Rh(I) system formed '*in situ*', a higher catalytic activity is obtained [4]. In contrast to rhodium, iridium does not appear to form dimeric carboxylate compounds [6].

Another possible explanation is based on the hypothesis of a nucleophilic attack of an isopropoxo ion (favoured by the alkaline medium) at position 2 (or 9) of the N-chelate ligand, coordinated to rhodium, with formation of a monoanionic chelate. Such an attack would be sterically unfavoured in the case of 2,9 and 3,8 substituted phenanthrolines (e.g. 2,9-Me_2-phen and 3,4,7,8-Me_4-phen) (see Scheme 1), but possible for the other phenanthrolines.

The hypothesis of nucleophilic attacks to coordinated bipy or phen ligands has been frequently proposed by Gillard [7] and other authors [8], in order to rationalize several anomalous kinetic and spectroscopic data observed for transition metal complexes containing such ligands. The increased steric hindrance of this catalyst could explain the preferred formation of the axial isomer, with respect to the equatorial one, in the reduction of 4-TBCE.

With the aim to verify the first above reported hypothesis about the nature of the active species, we report in this paper the synthesis and the structures of three dirhodium(II) compounds of the type [$Rh_2(OAc)_2(chel)_2(NMid)_2$]($ClO_4$)$_2$ (chel = phen, 4,7-Me_2-phen, 3,4,7,8-Me_4-phen; NMid = N-methylimidazole). The structural determination of such a series of complexes would allow the study of the Rh–Rh distance as a function of the steric hindrance between the faced chel ligands.

Experimental

Materials

Rh(II) acetate was purchased from Fluka AG. 1,10-Phenanthroline, 4,7-Me_2-phen and 3,4,7,8-Me_4-phen were purchased from Merck, ICN pharmaceuticals and Janssen, respectively. All reagents were used as received.

Synthesis of Complexes

[$Rh_2(OAc)_2Cl_2(chel)_2$] (chel = phen, 4,7-Me_2-phen, 3,4,7,8-Me_4-phen)

To a methanolic solution of chel (1 mmol), 0.257 g of [Rh_2-$(OAc)_2$]·$4H_2O$ (1/2 mmol) and 1 mmol of HCl were added. The resulting solution was heated to reflux for 45 min and then cooled in ice. The brown solid formed was filtered off, washed with acetone and vacuum dried.

[$Rh_2(OAc)_2(phen)_2(H_2O)_2]^{2+}(PF_6^-)_2$

The complex was obtained by addition of NH_4PF_6 to an aqueous solution of the chloro-derivative; on standing violet needles precipitated.

[$Rh_2(OAc)_2(I)_2(phen)_2$]

The complex was obtained as a microcrystalline red solid by addition of a stoichiometric amount of NaI to an aqueous solution of the chloro-derivative.

[$Rh_2(OAc)_2(chel)_2(NMid)_2]^{2+}(ClO_4^-)_2$ (chel = phen, 4,7-Me_2-phen, 3,4,7,8-Me_4-phen)

The chloro-derivatives were dissolved in CH_3OH–H_2O (50%:50%) and treated with an excess of NMid; after addition of $NaClO_4$ orange microcrystalline solids precipitated from the solution. The elemental analyses (%) of all the synthesized compounds (C, H, N) were in good agreement with the calculated values.

Crystal Data

Crystals were grown by slow evaporation of an acetone–methanol–water solution. Space group and cell parameters were obtained by using Weissenberg and precession photographs. Unit cell parameters of all three compounds were refined and their intensity data collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Crystallographic data and other per-

TABLE II. Crystallographic Data for **1**–**3**

	1	**2**	**3**
Formula	$C_{36}H_{34}N_8O_{12}Cl_2Rh_2$	$C_{40}H_{42}N_8O_{12}Cl_2Rh_2$	$C_{44}H_{50}N_8O_{12}Cl_2Rh_2$
Molecular weight	1047.4	1103.5	1159.6
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P1$	$P2_1/c$	$P2_1/c$
a (Å)	10.737(5)	16.081(5)	11.927(4)
b (Å)	14.265(3)	14.040(2)	24.931(7)
c (Å)	15.211(3)	20.390(4)	16.495(13)
α (°)	71.66(2)	90	90
β (°)	69.99(3)	98.91(3)	92.58(5)
γ (°)	74.15(3)	90	90
V (Å^3)	2042(1)	4548(2)	4900(4)
Z	2	4	4
D_{calc} (g cm^{-3})	1.70	1.61	1.57
λ (Å)	0.71069 (graphite-monochromated Mo Kα)		
μ(Mo Kα) (cm^{-1})	10.0	9.0	8.4
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
θ range (°)	2.5–30	2.5–28	3–25
Intensity monitors[a]	3	3	3
Unique data with $I > 3\sigma(I)$	9067	7050	4300
R[b]	0.046	0.074	0.074
R_w[c]	0.072	0.085	0.111
p[d]	0.02	–[e]	0.07

[a] Measured after each hour. [b] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [d] $w = [1 + \sigma^2(F_o) + pF_o^2]^{-1}$. [e] $w = 1$.

tinent information are summarized in Table II. Intensities were corrected for Lorentz-polarization factors and anomalous dispersion. An empirical absorption correction was also applied by using the scan data from close to axial reflections.

Structure Determination and Refinement

The structures of **1**, **2** and **3** were solved by the heavy-atom method; the positions of the Rh atoms were determined from the Patterson map and were then used to phase Fourier maps which revealed all other non-hydrogen atoms. Hydrogen atoms of **1** and non-methyl hydrogen atoms of **2** were included at calculated positions and held fixed ($B = 5.0$ Å^2) during the final full-matrix least-squares refinement which converged to $R = 0.046$ for **1** and 0.074 for **2** and **3**.

The electron density maps of **2** revealed that the oxygen atoms of the two crystallographically independent perchlorate ions were disordered or affected by a high thermal motion. Furthermore the N7–NMid group was found to be essentially oriented in two coplanar positions related by a rotation of 180° around the Rh2–N7 bond. Thus N8, C34 and C33, C35 can be exchanged assuming half occupancy factors. Consequently C36 will statistically occupy two positions, C36 and C36′. Different disorder models for the perchlorate O atoms and the N7–NMid atoms did not refine satisfactorily. Eventually, these atoms were located in an average position and refined isotropically, allowing them to assume high thermal factors. Only C36 was located in two positions (C36 and C36′) with half occupancy. The other structural parameters were not affected by the different disorder models.

No disorder was found in the other two compounds, but, because of the small number of observed intensities in **3**, anisotropic thermal factors were assigned only to Rh, Cl and O, N coordination atoms. All non-hydrogen atoms of **1** were refined with anisotropic thermal parameters.

Atomic scattering factors and anomalous dispersion terms were taken from the literature [9]. All calculations were done by using computer programs from the Enraf-Nonius SDP package [10]. The final positional parameters for non-hydrogen atoms of **1**, **2** and **3** are listed in Tables III, IV and V respectively. Selected bond lengths and angles are given in Tables VI and VII. Least-squares planes of interest are reported in Table VIII. See also 'Supplementary Material'. Figure 1 reports the numbering system used to define atoms in all three compounds.

TABLE III. Atomic Parameters[a] of $[Rh_2(OAc)_2(phen)_2(N\text{-}Mid)_2](ClO_4)_2$ (1) with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B (Å^2)
Rh1	0.88181(3)	0.59151(2)	0.77412(2)	2.107(6)
Rh2	0.84835(3)	0.77565(2)	0.77497(2)	2.211(6)
Cl1	0.5582(1)	0.6294(1)	0.2861(1)	5.02(4)
Cl2	0.7187(1)	1.1018(1)	1.1650(1)	4.11(3)
O1	1.0262(3)	0.5699(2)	0.8409(2)	2.88(7)
O2	0.9509(3)	0.7186(3)	0.8780(2)	3.19(7)
O3	0.7325(3)	0.5825(2)	0.9021(2)	3.02(7)
O4	0.6704(3)	0.7487(3)	0.8770(2)	3.24(8)
O5	0.5505(6)	0.5721(6)	0.3802(4)	8.3(2)
O6	0.4428(5)	0.6458(6)	0.2583(4)	8.0(2)
O7	0.6329(7)	0.7032(6)	0.2464(7)	11.6(3)
O8	0.6547(9)	0.5573(7)	0.2268(6)	12.0(3)
O9	0.6618(6)	1.1969(5)	1.1873(5)	8.6(2)
O10	0.8356(6)	1.1060(6)	1.0847(5)	10.1(2)
O11	0.6239(5)	1.0649(5)	1.1485(5)	10.0(2)
O12	0.756(1)	1.0375(7)	1.2442(5)	13.0(3)
N1	1.0133(3)	0.6007(3)	0.6425(2)	2.29(7)
N2	0.7503(3)	0.6107(3)	0.6997(3)	2.39(7)
N3	0.9116(4)	0.4276(3)	0.8070(3)	2.71(8)
N4	1.0029(5)	0.2704(4)	0.8540(4)	4.4(1)
N5	1.0175(3)	0.8067(3)	0.6703(3)	2.52(7)
N6	0.7699(4)	0.8330(3)	0.6635(3)	2.48(7)
N7	0.7964(4)	0.9200(3)	0.8156(3)	3.14(9)
N8	0.6596(6)	1.0395(3)	0.8818(4)	4.7(1)
C1	1.0264(5)	0.6332(4)	0.8823(3)	2.84(9)
C2	1.1280(6)	0.6055(5)	0.9388(4)	4.4(1)
C3	0.6544(5)	0.6605(4)	0.9232(3)	3.0(1)
C4	0.5299(7)	0.6473(5)	1.0078(5)	5.1(2)
C5	1.1480(4)	0.5877(4)	0.6180(3)	2.9(1)
C6	1.2256(5)	0.5977(4)	0.5216(4)	3.5(1)
C7	1.1651(6)	0.6200(4)	0.4503(4)	3.5(1)
C8	1.0244(5)	0.6309(3)	0.4740(3)	2.9(1)
C9	0.9492(6)	0.6509(4)	0.4073(3)	3.9(1)
C10	0.8158(6)	0.6547(4)	0.4347(3)	4.0(1)
C11	0.7411(5)	0.6398(3)	0.5351(3)	3.2(1)
C12	0.6009(5)	0.6373(4)	0.5721(4)	3.9(1)
C13	0.5420(5)	0.6223(4)	0.6683(4)	4.0(1)
C14	0.6187(5)	0.6093(4)	0.7318(4)	3.3(1)
C15	0.8109(4)	0.6246(3)	0.6023(3)	2.40(8)
C16	0.9535(4)	0.6190(3)	0.5717(3)	2.35(8)
C17	0.8181(6)	0.3682(4)	0.8312(4)	4.1(1)
C18	0.8732(7)	0.2720(5)	0.8576(6)	5.6(2)
C19	1.0220(5)	0.3652(4)	0.8234(4)	3.3(1)
C20	1.0991(9)	0.1815(6)	0.8829(7)	7.6(3)
C21	1.1400(5)	0.7985(4)	0.6781(4)	3.3(1)
C22	1.2476(5)	0.8221(4)	0.5966(5)	4.2(1)
C23	1.2322(6)	0.8544(4)	0.5061(5)	4.2(1)
C24	1.1016(5)	0.8670(4)	0.4959(4)	3.3(1)
C25	1.0703(7)	0.9014(4)	0.4055(4)	4.4(1)
C26	0.9429(7)	0.9140(4)	0.4015(4)	4.4(1)
C27	0.8334(5)	0.8938(3)	0.4883(3)	3.2(1)
C28	0.6972(6)	0.9084(4)	0.4904(4)	4.0(1)
C29	0.6034(5)	0.8885(4)	0.5772(4)	4.1(1)
C30	0.6396(4)	0.8506(4)	0.6643(4)	3.1(1)
C31	0.8643(4)	0.8567(3)	0.5764(3)	2.52(9)
C32	0.9990(4)	0.8423(3)	0.5796(3)	2.53(9)
C33	0.8609(6)	0.9470(4)	0.8641(4)	4.6(1)
C34	0.7791(7)	1.0200(5)	0.9051(5)	5.5(2)
C35	0.6755(6)	0.9773(4)	0.8271(4)	3.7(1)
C36	0.540(1)	1.1129(6)	0.9115(6)	7.8(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos \text{gamma})B(1,2) + ac(\cos \text{beta})B(1,3) + bc(\cos \text{alpha})B(2,3)]$.

TABLE IV. Atomic Parameters[a] of $[Rh_2(OAc)_2(4,7\text{-}Me_2\text{-}phen)_2(N\text{-}Mid)_2](ClO_4)_2$ (2) with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B (Å^2)
Rh1	0.30543(4)	0.21665(5)	0.38343(4)	2.67(1)
Rh2	0.17693(5)	0.26782(5)	0.43521(4)	3.11(1)
Cl1	0.6060(3)	0.4568(3)	0.3953(2)	7.9(1)*
Cl2	−0.1421(3)	0.1863(4)	0.2486(3)	8.7(1)*
O1	0.2236(4)	0.2215(5)	0.2956(3)	3.9(1)
O2	0.1258(4)	0.3023(5)	0.3394(4)	4.2(2)
O3	0.3254(4)	0.3602(4)	0.3765(3)	3.6(1)
O4	0.2340(5)	0.3995(5)	0.4443(4)	4.2(2)
O5	0.685(2)	0.474(2)	0.393(1)	21.1(9)*
O6	0.575(1)	0.439(1)	0.3279(8)	13.0(5)*
O7	0.578(1)	0.538(2)	0.425(1)	17.2(7)*
O8	0.6050(9)	0.374(1)	0.4358(7)	10.4(4)*
O9	−0.090(2)	0.108(2)	0.261(1)	20.3(8)*
O10	−0.112(2)	0.245(2)	0.205(1)	21.0(9)*
O11	−0.219(1)	0.162(2)	0.217(1)	19.7(8)*
O12	−0.150(1)	0.226(2)	0.310(1)	18.1(7)*
N1	0.2937(5)	0.0758(5)	0.3979(4)	2.7(1)
N2	0.3861(5)	0.2043(5)	0.4694(4)	2.9(1)
N3	0.4094(5)	0.1892(5)	0.3256(4)	3.1(2)
N4	0.5352(6)	0.1868(6)	0.2970(5)	4.2(2)
N5	0.1226(5)	0.1386(6)	0.4310(4)	3.1(2)
N6	0.2220(5)	0.2224(5)	0.5266(4)	3.2(2)
N7	0.0626(6)	0.3303(7)	0.4688(5)	5.0(2)
N8	−0.0283(8)	0.391(1)	0.5268(6)	7.2(3)*
C1	0.1568(6)	0.2676(8)	0.2909(5)	3.9(2)
C2	0.1054(8)	0.285(1)	0.2215(6)	6.5(3)
C3	0.2905(6)	0.4199(7)	0.4102(5)	3.6(2)
C4	0.3176(8)	0.5237(7)	0.4084(7)	5.4(3)
C5	0.2483(6)	0.0126(7)	0.3592(5)	3.3(2)
C6	0.2453(7)	−0.0840(7)	0.3770(5)	3.7(2)
C7	0.2892(6)	−0.1185(7)	0.4360(5)	3.6(2)
C8	0.3392(6)	−0.0514(6)	0.4769(5)	2.9(2)
C9	0.3914(7)	−0.0763(7)	0.5386(5)	3.6(2)
C10	0.4400(6)	−0.0097(7)	0.5761(5)	3.5(2)
C11	0.4410(6)	0.0884(7)	0.5542(5)	3.1(2)
C12	0.4898(6)	0.1605(8)	0.5908(5)	3.6(2)
C13	0.4873(6)	0.2507(8)	0.5624(5)	3.9(2)
C14	0.4348(6)	0.2708(7)	0.5011(5)	3.7(2)
C15	0.3908(5)	0.1134(6)	0.4944(4)	2.7(2)
C16	0.3401(6)	0.0435(6)	0.4560(4)	2.6(2)
C17	0.4097(7)	0.1212(7)	0.2753(5)	4.0(2)
C18	0.4883(8)	0.1190(8)	0.2570(6)	4.4(2)

(continued)

TABLE IV. *(continued)*

Atom	*x*	*y*	*z*	*B* (Å^2)
C19	0.4856(6)	0.2267(7)	0.3380(5)	3.6(2)
C20	0.6271(7)	0.208(1)	0.2990(7)	5.7(3)
C21	0.0681(6)	0.1016(7)	0.3812(5)	3.7(2)
C22	0.0374(6)	0.0083(8)	0.3852(5)	4.0(2)
C23	0.0634(6)	−0.0487(7)	0.4392(5)	3.3(2)
C24	0.1186(6)	−0.0096(7)	0.4935(5)	3.1(2)
C25	0.1473(6)	−0.0583(7)	0.5548(5)	3.5(2)
C26	0.1997(6)	−0.0147(7)	0.6055(5)	3.7(2)
C27	0.2277(6)	0.0820(7)	0.5991(5)	3.1(2)
C28	0.2802(6)	0.1312(8)	0.6503(5)	3.6(2)
C29	0.2997(7)	0.2263(8)	0.6378(5)	4.1(2)
C30	0.2701(6)	0.2695(7)	0.5760(5)	3.8(2)
C31	0.2008(6)	0.1306(6)	0.5393(4)	2.7(2)
C32	0.1458(6)	0.0844(6)	0.4864(5)	2.9(2)
C33	−0.0159(8)	0.332(1)	0.4298(7)	5.7(3)*
C34	−0.0670(9)	0.373(1)	0.4719(7)	6.0(3)*
C35	0.0574(8)	0.366(1)	0.5293(7)	5.7(3)*
C36	−0.062(2)	0.430(2)	0.584(1)	6.2(6)*
C36′	−0.151(3)	0.395(3)	0.450(2)	11(1)*
C37	0.2829(8)	−0.2222(8)	0.4554(7)	5.1(3)
C38	0.5415(8)	0.140(1)	0.6580(6)	5.1(3)
C39	0.0339(8)	−0.1522(8)	0.4396(6)	4.9(3)
C40	0.3148(8)	0.0846(9)	0.7150(5)	4.9(3)

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as in footnote Table III.

TABLE V. Atomic Parameters[a] of [Rh$_2$(OAc)$_2$(3,4,7,8-Me$_4$phen)$_2$(N-Mid)$_2$](ClO$_4$)$_2$ (3) with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	*B* (Å^2)
Rh1	0.32305(9)	0.09282(4)	0.18462(6)	2.73(2)
Rh2	0.23659(9)	0.08631(4)	0.32380(6)	2.71(2)
Cl1	0.1282(4)	0.4501(2)	0.3165(3)	6.3(1)
Cl2	−0.2221(6)	0.1619(3)	0.4399(4)	9.5(2)
O1	0.4714(7)	0.0740(4)	0.2482(6)	3.3(2)
O2	0.3850(8)	0.0490(4)	0.3588(6)	3.6(2)
O3	0.2888(7)	0.0117(3)	0.1783(5)	3.1(2)
O4	0.1837(8)	0.0126(3)	0.2860(6)	3.5(2)
O5	0.085(2)	0.405(1)	0.270(2)	16.0(8)*
O6	0.044(1)	0.4880(7)	0.320(1)	8.7(4)*
O7	0.167(2)	0.4343(8)	0.394(1)	10.3(5)*
O8	0.211(3)	0.465(1)	0.270(2)	18(1)*
O9	−0.288(2)	0.185(1)	0.380(1)	14.3(7)*
O10	−0.194(2)	0.109(1)	0.412(2)	14.7(7)*
O11	−0.103(2)	0.179(1)	0.434(2)	15.1(8)*
O12	−0.253(3)	0.162(1)	0.514(2)	20(1)*
N1	0.3474(9)	0.1726(4)	0.1863(6)	2.9(2)
N2	0.1823(9)	0.1142(5)	0.1184(6)	2.9(2)
N3	0.421(1)	0.0823(5)	0.0739(6)	3.5(2)
N4	0.472(1)	0.0601(5)	−0.0468(8)	4.1(2)*
N5	0.2861(8)	0.1588(4)	0.3631(6)	2.8(2)
N6	0.0993(9)	0.1270(4)	0.2899(6)	2.9(2)
N7	0.173(1)	0.0697(5)	0.4433(7)	3.5(2)
N8	0.064(1)	0.0608(5)	0.5448(8)	4.9(3)*

(continued)

TABLE V. *(continued)*

Atom	*x*	*y*	*z*	*B* (Å^2)
C1	0.470(1)	0.0523(5)	0.3158(8)	3.3(3)*
C2	0.579(1)	0.0290(7)	0.348(1)	5.0(3)*
C3	0.229(1)	−0.0105(5)	0.2289(8)	3.0(2)*
C4	0.213(1)	−0.0704(7)	0.222(1)	5.3(4)*
C5	0.436(1)	0.1997(6)	0.2170(9)	3.7(3)*
C6	0.441(1)	0.2563(6)	0.2135(9)	3.6(3)*
C7	0.354(1)	0.2849(6)	0.1706(9)	3.7(3)*
C8	0.267(1)	0.2566(5)	0.1349(8)	3.3(2)*
C9	0.172(1)	0.2791(7)	0.089(1)	5.2(4)*
C10	0.091(1)	0.2505(6)	0.054(1)	4.6(3)*
C11	0.089(1)	0.1933(5)	0.0634(8)	3.1(2)*
C12	0.006(1)	0.1597(6)	0.028(1)	4.5(3)*
C13	0.012(1)	0.1053(6)	0.0401(9)	3.7(3)*
C14	0.103(1)	0.0833(6)	0.0858(9)	3.7(3)*
C15	0.172(1)	0.1692(6)	0.1074(9)	3.5(3)*
C16	0.267(1)	0.2016(5)	0.1444(8)	3.1(2)*
C17	0.535(1)	0.0959(6)	0.067(1)	4.6(3)*
C18	0.565(2)	0.0823(7)	−0.007(1)	5.4(4)*
C19	0.391(1)	0.0597(5)	0.0050(8)	3.2(3)*
C20	0.466(2)	0.0418(8)	−0.134(1)	6.7(5)*
C21	0.376(1)	0.1712(6)	0.4083(9)	3.6(3)*
C22	0.400(1)	0.2245(6)	0.4330(9)	4.0(3)*
C23	0.329(1)	0.2644(6)	0.409(1)	4.6(3)*
C24	0.233(1)	0.2519(5)	0.3619(8)	3.4(3)*
C25	0.149(1)	0.2901(7)	0.335(1)	5.1(4)*
C26	0.055(1)	0.2744(6)	0.2937(9)	3.7(3)*
C27	0.029(1)	0.2196(6)	0.2760(9)	3.6(3)*
C28	−0.073(1)	0.1994(6)	0.238(1)	4.2(3)*
C29	−0.087(1)	0.1449(6)	0.2319(9)	3.9(3)*
C30	−0.000(1)	0.1101(6)	0.2581(9)	3.8(3)*
C31	0.110(1)	0.1811(5)	0.3014(8)	3.2(2)*
C32	0.215(1)	0.1981(5)	0.3445(8)	3.2(2)*
C33	0.235(2)	0.0436(8)	0.506(1)	6.1(4)*
C34	0.166(2)	0.0390(8)	0.570(1)	5.8(4)*
C35	0.075(1)	0.0803(6)	0.468(1)	4.2(3)*
C36	−0.036(2)	0.0663(8)	0.594(1)	6.5(4)*
C37	0.365(2)	0.3465(8)	0.167(1)	6.3(4)*
C38	−0.094(1)	0.1849(7)	−0.022(1)	5.1(4)*
C39	0.352(2)	0.3233(7)	0.431(1)	5.6(4)*
C40	−0.162(2)	0.2383(9)	0.208(1)	6.8(5)*
C41	0.545(1)	0.2821(7)	0.255(1)	4.7(3)*
C42	−0.076(1)	0.0647(7)	0.005(1)	4.9(3)*
C43	0.503(2)	0.2315(7)	0.488(1)	5.5(4)*
C44	−0.198(2)	0.1182(8)	0.199(1)	5.9(4)*

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as in footnote Table III.

Results

The synthesis of the complexes easily occurs according to the Scheme 2. On the basis of the crystal structure determinations reported below all the synthesized complexes can be assumed to be dinuclear species with the same geometry. The

TABLE VI. Selected Bond Distances (Å) for 1, 2 and 3

Atoms	Compounds		
	1	2	3
(a) Rh coordination			
Rh1–Rh2	2.5557(4)	2.565(1)	2.564(1)
Rh1–O1	2.048(2)	2.052(3)	2.032(8)
Rh1–O3	2.036(2)	2.049(3)	2.058(9)
Rh1–N1	2.010(3)	2.013(3)	1.99(1)
Rh1–N2	2.005(2)	2.019(3)	2.00(1)
Rh1–N3	2.188(3)	2.223(4)	2.18(1)
Rh2–O2	2.050(2)	2.056(3)	2.066(8)
Rh2–O4	2.054(2)	2.059(3)	2.070(9)
Rh2–N5	1.995(3)	2.010(3)	2.03(1)
Rh2–N6	2.012(3)	1.996(4)	2.01(1)
Rh2–N7	2.207(3)	2.238(5)	2.23(1)
(b) OAc groups			
O1–C1	1.256(4)	1.245(6)	1.25(1)
O2–C1	1.259(4)	1.271(6)	1.25(1)
O3–C3	1.254(4)	1.270(6)	1.27(2)
O4–C3	1.262(4)	1.260(6)	1.24(2)
(c) phen ligands[a]			
N1–C5	1.337(9)	1.334(10)	1.328(15)
N1–C16	1.369(8)	1.370(4)	1.361(25)
C5–C6	1.405(6)	1.413(9)	1.408(7)
C6–C7	1.359(3)	1.388(14)	1.378(28)
C7–C8	1.414(8)	1.419(2)	1.399(25)
C8–C9	1.434(11)	1.440(8)	1.434(5)
C8–C16	1.394(4)	1.403(3)	1.384(28)
C9–C10	1.344(8)	1.373(1)	1.334(23)
C15–C16	1.424(6)	1.434(6)	1.482(18)
C7–C37		1.534(19)	1.515(12)
C6–C41			1.538(25)
(d) NMid ligands[a]			
N3–C17	1.364(7)	1.401(6)[b]	1.401(1)
N3–C19	1.320(2)	1.321(5)	1.294(22)
N4–C18	1.374(7)	1.396(7)	1.376(1)
N4–C19	1.336(4)	1.363(6)	1.348(37)
N4–C20	1.455(1)	1.500(6)	1.490(23)
C17–C18	1.331(3)	1.374(7)	1.355(31)
(e) ClO_4 anions[a]			
Cl–O	1.41(5)	1.38(4)	1.39(7)

[a] Average values. The standard deviation of the mean is calculated by the 'scatter formula': $[\Sigma_1^{N}i(d_i - \bar{d})^2/(N - 1)]^{1/2}$. The sum is extended to all chemically equivalent parameters. [b] Only values for the N3–NMid molecule are reported because of the disorder in the other molecule.

TABLE VII. Selected Bond Angles (°) for 1, 2 and 3

Atoms	Compounds		
	1	2	3
(a) Rh coordination			
O1–Rh1–Rh2	84.38(7)	84.35(9)	84.3(2)
O1–Rh1–O3	92.0(1)	89.6(1)	88.0(3)
O1–Rh1–N1	94.0(1)	95.7(1)	95.6(4)
O3–Rh1–Rh2	84.65(7)	84.16(9)	84.1(2)
O3–Rh1–N2	92.1(1)	93.3(1)	94.2(4)
O3–Rh1–N3	86.7(1)	89.7(1)	87.4(4)
N1–Rh1–Rh2	96.60(7)	96.6(1)	96.6(3)
N1–Rh1–N2	82.0(1)	81.4(1)	82.1(4)
N1–Rh1–N3	93.0(1)	90.2(1)	92.7(4)
N2–Rh1–Rh2	97.04(7)	96.7(1)	98.2(3)
N2–Rh1–N3	92.9(1)	90.6(1)	92.5(4)
O2–Rh2–Rh1	84.09(7)	84.5(1)	84.5(3)
O2–Rh2–O4	91.0(1)	88.9(1)	85.9(4)
O2–Rh2–N5	91.8(1)	93.7(1)	94.6(4)
O2–Rh2–N7	87.3(1)	88.4(2)	89.5(4)
O4–Rh2–Rh1	83.93(7)	85.0(1)	85.1(2)
O4–Rh2–N6	95.8(1)	96.4(1)	97.8(4)
O4–Rh2–N7	84.3(1)	89.8(2)	89.4(4)
N5–Rh2–Rh1	97.15(8)	95.9(1)	96.2(3)
N5–Rh2–N6	81.5(1)	81.0(1)	81.8(4)
N5–Rh2–N7	95.0(1)	89.7(2)	89.3(4)
N6–Rh2–Rh1	96.22(8)	95.5(1)	94.3(3)
N6–Rh2–N7	93.7(1)	92.1(2)	92.0(4)
(b) OAc groups[a]			
Rh–O–C	120.5(6)	120.8(7)	120.8(3)
O–C–O	124.7(2)	124.8(5)	125.3(3)
O–C–CH_3	117.7(5)	118(1)	117(1)
(c) phen ligands[a]			
Rh1–N1–C5	128.8(5)	128.3(5)	129(1)
Rh1–N1–C16	113.1(5)	113.8(5)	113.9(9)
C5–N1–C16	118.1(2)	117.9(8)	117.0(8)
N1–C16–C15	116.0(4)	115.7(7)	115.0(2)

[a] See footnote a of Table VI.

chloro-derivatives dissociate in water at room temperature to give solutions of the dicationic aquo-derivatives with two axial water molecules; only the axial positions are labile and the coordinated water easily exchanges with monodentate ligands to give the corresponding derivatives. All the complexes air stable both in solution and in the solid state; however, the chloro-derivatives slowly react with an excess of chel, in alcoholic medium, to give deep green solutions very sensitive to dioxygen, probably of mononuclear Rh(II) complexes.

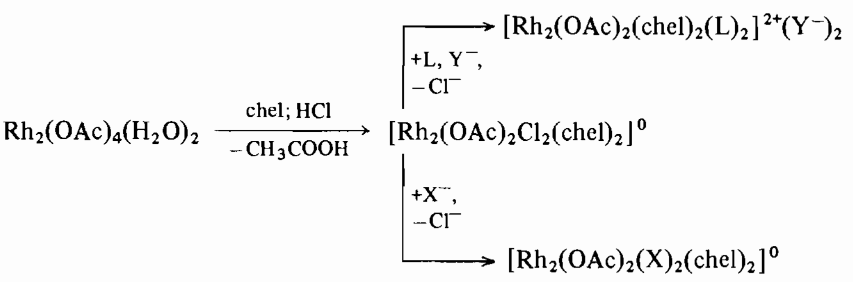
Molecular Structures

The crystal structures consist of perchlorate anions and dirhodium cations in which the metal–metal bond is supported by two bridging acetate groups. The nitrogen atoms of the phenanthroline molecules coordinate to the rhodium atoms in *trans* positions with respect to the acetate oxygen atoms, so that they roughly face each other (Fig. 1).

The NMid ligands complete the metal distorted octahedral geometry occupying axial positions, *trans* to rhodium atoms. The Rh–N (NMid) distances

TABLE VIII. Deviations (Å) from Selected Least-squares Planes for 1, 2 and 3

Plane	Atoms and displacements
Compound **1**	
O1, O3, N1, N2	O1 −0.003; O3 0.003; N1 0.004; N2 −0.004; Rh1 0.015
O2, O4, N5, N6	O2 0.011; O4 −0.010; N5 −0.012; N6 0.011; Rh2 0.003
O1, O2, C1, C2	O1 0.004; O2 0.004; C1 −0.010; C2 0.003; Rh1 −0.206; Rh2 0.493
O3, O4, C3, C4	O3 0.004; O4 0.004; C3 −0.012; C4 0.003; Rh1 0.367; Rh2 −0.301
N1, N2, C5–C16	N1 0.057; N2 0.068; C5 −0.046; C6 −0.087; C7 −0.038; C8 0.026; C9 0.040; C10 0.023; C11 0.010; C12 −0.075; C13 −0.083; C14 −0.007; C15 0.059; C16 0.053; Rh1 0.148
N5, N6, C21–C32	N5 0.064; N6 0.050; C21 −0.019; C22 −0.073; C23 −0.044; C24 0.001; C25 0.021; C26 0.029; C27 0.011; C28 −0.028; C29 −0.072; C30 −0.033; C31 0.041; C32 0.052; Rh2 0.183
Compound **2**	
O1, O3, N1, N2	O1 0.005; O3 −0.005; N1 −0.005; N2 0.005; Rh1 −0.009
O2, O4, N5, N6	O2 0.009; O4 −0.009; N5 −0.010; N6 0.010; Rh2 0.001
O1, O2, C1, C2	O1 −0.001; O2 −0.001; C1 0.002; C2 0.000; Rh1 0.348; Rh2 −0.289
O3, O4, C3, C4	O3 0.002; O4 0.002; C3 −0.006; C4 0.002; Rh1 −0.236; Rh2 0.367
N1, N2, C5–C16	N1 −0.032; N2 −0.042; C5 0.017; C6 0.042; C7 0.010; C8 −0.016; C9 0.002; C10 0.000; C11 −0.004; C12 −0.008; C13 0.044; C14 0.031; C15 −0.019; C16 −0.026; Rh1 −0.109; C37 −0.011; C38 −0.078
N5, N6, C21–C32	N5 0.041; N6 0.041; C21 −0.027; C22 −0.065; C23 −0.005; C24 0.019; C25 0.002; C26 0.003; C27 0.012; C28 −0.018; C29 −0.054; C30 −0.023; C31 0.037; C32 0.037; Rh2 0.156; C39 0.060; C40 0.004
Compound **3**	
O1, O3, N1, N2	O1 0.018; O3 −0.018; N1 −0.019; N2 0.019; Rh1 −0.022
O2, O4, N5, N6	O2 0.024; O4 −0.024; N5 −0.026; N6 0.025; Rh2 −0.002
O1, O2, C1, C2	O1 −0.001; O2 −0.001; C1 0.003; C2 −0.001; Rh1 0.419; Rh2 −0.183
O3, O4, C3, C4	O3 −0.004; O4 −0.004; C3 0.010; C4 −0.003; Rh1 −0.082; Rh2 −0.576
N1, N2, C5–C16	N1 −0.029; N2 −0.012; C5 0.053; C6 0.012; C7 −0.003; C8 −0.005; C9 −0.015; C10 0.015; C11 −0.010; C12 0.037; C13 0.015; C14 0.000; C15 −0.039; C16 −0.019; Rh1 0.007; C37 −0.016; C38 0.034; C41 0.050; C42 0.032
N5, N6, C21–C32	N5 0.121; N6 0.062; C21 −0.005; C22 −0.122; C23 −0.095; C24 0.020; C25 0.016; C26 0.045; C27 0.047; C28 −0.025; C29 −0.117; C30 −0.076; C31 0.063; C32 0.065; Rh2 0.271; C39 −0.173; C40 −0.014; C43 −0.321; C44 −0.325



Scheme 2. L = H_2O, NMid; $Y^- = ClO_4^-, PF_6^-$; $X^- = I^-$.

do not show any trend in going from **1** to **3** (average value, 2.21(2) Å).

The NMid molecules are differently oriented in the three compounds as well as in the same cation. This is clearly shown by the torsion angles around the Rh1–N3 and Rh2–N7 bonds, such as N1–Rh1–N3–C19 and N5–Rh2–N7–C35: 70.7°, 132.0° (**1**); −125.0°, 111.4° (**2**); −124.7°, 88.3° (**3**). Furthermore they are tilted from perpendicularity to the relative coordination O_2N_2 planes as shown by the following dihedral angles: 78.2°, 76.5° for N3– and N7–NMid molecules respectively, in **1**; 84.8°, 87.5° in **2**; 88.1°, 85.7° in **3**. The Rh1–Rh2–N7 and Rh2–Rh1–N3 bond angles are 165.30(8)° and 167.02(7)° respectively, the Rh–N bonds being bent slightly away from the phen ligands. This indicates that the orientation of the axial ligands is essentially controlled by intermolecular contacts,

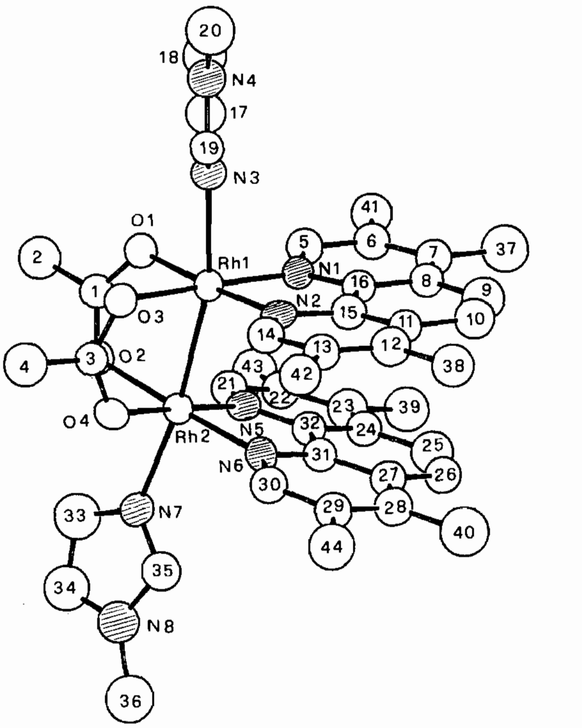


Fig. 1. ORTEP drawing of $[Rh_2(OAc)_2(3,4,7,8\text{-}Me_4\text{-}phen)_2\text{-}(NMid)_2]^{2+}$ (**3**) showing atom numbering system (thermal ellipsoids at 50% probability). Carbon atoms are identified by their sequence number.

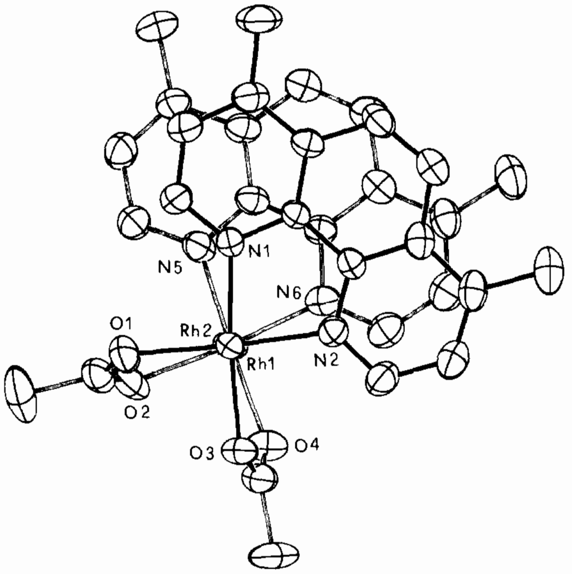


Fig. 2. ORTEP drawing of $[Rh_2(OAc)_2(4,7\text{-}Me_2\text{-}phen)_2\text{-}(NMid)_2]^{2+}$ (**2**) (thermal ellipsoids at 50% probability) showing the staggering of the 4,7-Me_2-phen ligands. For sake of clarity NMid molecules have been omitted. For the complete atom numbering see Fig. 1.

just as found by Cotton and Felthouse for $[Rh(OAc)_2(4\text{-}CNpy)]_2$, suggesting that also in this case the Rh–N bonding is purely of the σ type [11].

A comparison of some average dimensions in the $Rh_2(OAc)_2$ moieties shows that these are practically identical in all three compounds: Rh–O 2.047(8), 2.054(4), 2.06(2) Å; C–O 1.258(4), 1.26(1), 1.25(1) Å; Rh–Rh–O 84.3(3), 84.5(3), 84.5(3)°; Rh–O–C 120.5(6), 120.8(7), 120.8(3)°; O–C–O 124.7(2), 124.8(6), 125.5(7)° in **1**, **2** and **3**, respectively. These values are very similar to those found in $Rh_2(OAc)_4$ complexes [6, 11], with the exception of the average Rh–Rh–O bond angle which is nearly 4° narrower in the present complexes owing to the longer Rh–Rh distances (*vide infra*).

Bond lengths and angles of the phenanthroline molecules are comparable, within experimental error, in all three compounds and conform with previously found values, both of the free [12, 13] and coordinated molecules [12, 14, 15].

The acetate groups are planar, but the Rh atoms are significantly out of these planes, on opposite sides (Table VIII). In **1**, **2** and **3** they are inclined at each other by 87.5°, 83.8° and 72.5° respectively.

In **1** the phen ligands are rotated about the Rh–Rh axis by *ca.* 20° from the eclipsed configuration (torsion angles: N1–Rh1–Rh2–N5, −19.6°; N2–Rh1–Rh2–N6, −20.1°) in order to alleviate repulsive interactions between the two ligands (see Fig. 2). The dihedral angle between the least-squares planes defined by each of the phen ligands is 9.4°, with the phen ligands approaching on the side of the nitrogen atoms (planes 2 and 4 of Fig. 3). On the other hand, the coordination planes defined by N1, N2, O1, O3 and N5, N6, O2, O4 are inclined at 16.9° in order to draw closer the oxygen atoms and favour the bonding of the acetate bridges (planes 1 and 3 in Fig. 3).

In **2** and **3** the substituted phen ligands are twisted around the Rh–Rh axis by 17.8° and 16.0°, respectively. Torsion angles N1–Rh1–Rh2–N5 and N2–Rh1–Rh2–N6 are −17.5°, −18.0° in **2** (Fig. 2) and −15.6°, −16.3° in **3**. The coordination O_2N_2 planes are inclined at 15.7° and 15.8° in **2** and **3** towards the OAc ligands, while the 4,7-Me_2- and 3,4,7,8-Me_4-phen ligands form dihedral angles of 9.0° and 10.4°, respectively.

This shows that the overall arrangement of the phen ligands is determined by the constraints imposed by the bridging OAc groups and van der Waals interactions, in which the attractive terms play an important role too. In fact the closest intramolecular contacts are scarcely greater than the sum of the van der Waals radii of the non-bonded atoms.

This kind of ligand arrangement is similar to that found in $[Rh_2(OAc)_2(dmg)_2(PPh_3)_2]$, where the dimethylglyoximato (dmg) ligands are rotated around the Rh–Rh bond by 20° from an eclipsed configuration and form a dihedral angle of *ca.* 15° [16]. The Rh–Rh distance of 2.5557(4) Å found in [Rh_2-

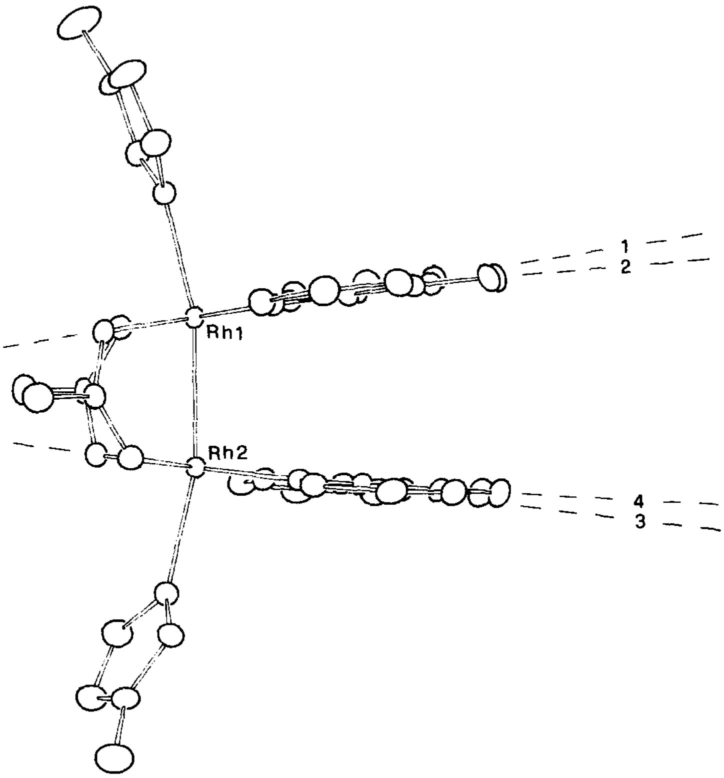


Fig. 3. ORTEP drawing of $[Rh_2(OAc)_2(phen)_2(NMid)_2]^{2+}$ (1) (thermal ellipsoids at 20% probability) emphasizing the tilting of various atom planes. 1 and 3 are the traces of the equatorial coordination planes through Rh1 and Rh2, respectively; 2 and 4 are the traces of the mean planes through the two phen ligands.

$(OAc)_2(phen)_2(NMid)_2]^{2+}$ (1) is only slighter shorter than that of 2.561 Å found in the neutral complex $[Rh_2(OAc_2(phen)_2Cl_2]$ [17]. This could indicate that the Rh–Rh bonding is scarcely affected by the substitution of the Cl^- ligands with neutral NMid molecules. Similar distances have been also reported for the Rh_2 formato complex: $[Rh_2(O_2CH)_2(phen)_2Cl_2]$ (2.577 Å) [5].

Some information about the influence of the chel nature on the Rh–Rh distance can be obtained from the comparison of the structural parameters of **1** with those of the strictly related 4,7-Me_2-phen **2** and 3,4,7,8-Me_4-phen (**3**) derivatives. In **2** the Rh–Rh distance is increased from 2.5557(4) Å of **1** to 2.565(1) Å. This can be explained in terms of the increased bulkiness of the methyl substituted phenanthroline and the increased negative charge density on the rhodium atoms [1]. On the contrary, no lengthening is observed on passing from **2** (2.565(1) Å) to **3** (2.564(1) Å), in spite of the increased bulkiness and basicity of the latter ligand. This suggests that the Rh–Rh bond distance is finally controlled by the 'bite' of the bridging acetate ligands which prevents further lengthening of the metal–metal distance. This hypothesis is supported by the deflections of the equatorial planes and the marked deviations from planarity of the N1,N2 3,4,7,8-Me_4-phen ligand (Table VII) forced to 'face' the other 3,4,7,8-Me_4-phen molecule by the constraints of the acetate ligands.

As a matter of fact, the Rh–Rh distance increases on passing from $[Rh(OAc)_2]_2$ (range: 2.385(5)–2.4555(3) Å) [6, 9] or $[Rh_2(OAc)_2(oxypyridine)_2]$ compounds (range: 2.365(1)–2.388(1) Å) [18] to $[Rh_2(OAc)_2(phen)_2]$ derivatives (mean: 2.558(3) Å) and $[Rh_2(OAc)_2(dmg)_2(PPh_3)_2]$ (2.618(5) Å) [16], up to 2.936(2) Å in $[Rh_2(dmg)_4(PPh_3)_2]$ [19]. It seems likely that this trend is essentially due to the steric hindrance of the chelate ligands and to the number of the bridging acetate groups.

Conclusions

From a general point of view it can be said that the stability of the Rh–Rh bond in these complexes is mainly due to the presence of the bridging acetate groups. The introduction of one bidentate chelating system (e.g. dmg or phen) in the coordination sphere of each Rh atom, discplaces two bridging acetate groups and weakens the Rh–Rh bond. As a consequence the metal–metal bond length increases, but such a lengthening is controlled by the 'bite' of the two remaining bridging ligands.

The introduction of a second molecule of chel displaces the two remaining acetate groups to give a planar arrangement of the two chelates around the rhodium atom in the case of dmg ligand and the Rh–Rh bond length reaches the maximum observed value. On the other hand, the introduction of a second molecule of phen, or of substituted derivatives, probably causes the cleavage of the Rh–Rh bond to give mononuclear paramagnetic Rh(II) derivatives. In fact, with these chelates the planar arrangement of two chel units is unstable, due to the strong steric interactions between the hydrogens in 2 and 9 positions.

The structural data reported in this paper, and in particular the essential role played by the acetate 'bite' in stabilizing the Rh–Rh bond, allow us to rule out the hypothesis of dinuclear species, structurally related to those here reported, as catalysts in hydrogen transfer reactions from alcohols to ketones. Work is in progress concerning the hypothesis of a nucleophilic attack to the coordinated chelate ligand.

Supplementary Material

Anisotropic thermal parameters, hydrogen atom coordinates and tables of observed and calculated structure factors are available on request.

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References

1 G. Clauti, G. Zassinovich and G. Mestroni, *Inorg. Chim. Acta, 112*, 103 (1986).
2 G. Zassinovich, G. Mestroni and A. Camus, *J. Organomet. Chem., 168*, C37 (1979).
3 F. Vinzi, G. Zassinovich and G. Mestroni, *J. Mol. Catal., 18*, 359 (1983).
4 G. Mestroni, unpublished results.
5 H. Pasternak and F. Pruchnik, *Inorg. Nucl. Chem. Lett., 12*, 591 (1976).
6 E. B. Boyar and S. D. Robinson, *Coord. Chem. Rev., 50*, 109 (1983).
7 R. D. Gillard, *Coord. Chem. Rev., 50*, 303 (1983).
8 E. C. Constable, *Polyhedron, 2*, 551 (1983).
9 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
10 'Enraf-Nonius SDP Package', B. A. Frenz & Associates, Inc., College Station, Tex. 77840; Enraf-Nonius, Delft, Holland.
11 F. A. Cotton and T. R. Felthouse, *Acta Crystallogr., Sect. C, 40*, 42 (1984).
12 R. L. Stanfield, S. R. Ernst, M. L. Hackert, V. Vijaywargia, K. Venkatasubramanian and N. S. Poonia, *Acta Crystallogr., Sect. C, 40*, 1681 (1984).
13 S. Nishigaki, H. Yoshioka and K. Nakatan, *Acta Crystallogr., Sect. B, 34*, 875 (1978).
14 C. L. Jones, G. H. Milburn, L. Sawyer and D. L. Hughes, *Acta Crystallogr., Sect. B, 37*, 1548 (1981).
15 A. Hazell and A. Mukhopadhyay, *Acta Crystallogr., Sect. B, 36*, 1647 (1980).
16 J. Halpern, E. Kimura, J. Molin-Case and C. S. Wong, *Chem. Commun.*, 1207 (1971).
17 F. Pruchnik, private communication.
18 F. A. Cotton and T. R. Felthouse, *Inorg. Chem., 20*, 584 (1981).
19 K. G. Caulton and F. A. Cotton, *J. Am. Chem. Soc., 93*, 1914 (1971).