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Synthesis and characterization of a novel tetranuclear bimetallic complex containing rhodium(II) and zinc(II) as metal centres

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Abstract

$Rh(Hdmg)_2(PPh_3)Cl$ (Hdmg = monoanion of dimethylglyoxime) undergoes reduction with zinc amalgam to give the tetranuclear bimetallic compound $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, characterized by elemental analysis, electronic, IR and NMR spectroscopy and X-ray crystallography. It crystallizes in the triclinic space group $P\bar{1}$ with: $a = 14.262(4)$, $b = 14.675(4)$, $c = 14.698(4)$ Å, $\alpha = 82.15(4)$, $\beta = 87.57(4)$, $\gamma = 65.89(3)°$, $Z = 2$. The structure was refined up to $R = 0.13$ for 4704 reflections. The molecule consists of two $[Rh(dmg)(Hdmg)(PPh_3)]$ subunits linked by an [Rh(II)–Rh(II)] bond of length equal to 2.852(3) Å and by two Zn ions bridging the oxygens of the equatorial ligands. The binding with zinc relieves the equivalence among the atoms of each subunit.

Keywords: Rhodium complexes; Rhodoxime complexes; Zinc complexes; Bimetallic complexes; Crystal structures

1. Introduction

The versatile behaviours of transition metal chelates of bidentate or tetradentate tetraaza ligands with delocalized electronic structure are a subject of current research in connection with model studies of biologically active metal centres and with the development of synthetic catalysts.

Complexes of rhodium with dioximato ligands are interesting as analogs of cobaloximes, often considered as models of vitamin B_{12} coenzyme [1]. Even if such rhodium compounds have been studied much less extensively than the cobalt ones, recently there has been an upsurge of interest in their chemistry, and indications for a better understanding of their mechanistic and kinetic behaviours are becoming available [2]. Furthermore some rhodoximes have shown very promising catalytic properties [3].

Metal chelates that can incorporate other Lewis acids are encountered more and more often. The oximato group (C=N–O–) can behave as a bridge binding one metal atom through the imino N and another one through the deprotonated O to originate bi- and trinuclear complexes [4]. So in the dioximato compounds the bridging hydrogen of the equatorial O–H...O groups can be substituted by other metal ions. Examples amongst the cobaloximes include species such as $[CH_3Co(Hdmg)(Fedmg)H_2O]^{2+}$ and $[H_2OCo(Hdmg)_2(Fedmg)]^{3+}$ [5]. Copper(II) complexes with ligands derived from oxalates and oxamidates act as chelate agents towards a second metal ion, giving rise to dinuclear, trinuclear and chain metal complexes [6]. Up to now few products resulting from OH hydrogen substitution in rhodoximes are known. Ramasami and Espenson reported the synthesis of $[ClRh(BF_2dmg)_2(PPh_3)]$ [7] and showed that $[CH_3Rh(Hdmg)_2H_2O]$ reacts reversibly with $Fe(H_2O)_6^{3+}$ forming the one to one adduct $[CH_3Rh(Hdmg)(Fedmg)H_2O]^{2+}$ [8].

In this paper we describe the synthesis of the new Rh(II) complex $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, the first tetranuclear bimetallic compound containing both Rh(II) and Zn(II) which has a direct Rh–Rh bond, and is obtained by reducing the $[Rh(Hdmg)_2(PPh_3)Cl]$ rhodoxime with excess of amalgamated zinc in methylene chloride. Furthermore we compare its spectral and structural properties with those of the $[Rh(Hdmg)_2(PPh_3)]_2$ dimer, which is obtained by reducing $[Rh(Hdmg)_2(PPh_3)Cl]$ with $NaBH_4$ [9].

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2. Experimental

2.1. Physical measurements

Room temperature UV–Vis spectra were monitored on either a Perkin-Elmer Lambda 5 or on a Hewlett-Packard 8452 rapid scan diode-array spectrometer in the 230–820 nm range. IR spectra were measured in the range 4000–400 cm^{-1} as KBr disks or Nujol mulls on a Perkin-Elmer 983G spectrometer. NMR spectra were recorded on a Jeol EX-400 spectrometer (^1H at 400 MHz, ^{13}C at 100.46 MHz, ^{31}P at 16.70 MHz) and on a Bruker AMX-300 spectrometer (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.496 MHz). For the ^1H and ^{13}C spectra TMS was used as an internal standard. For the $^{31}P\{^1H\}$ spectra 10% H_3PO_4 was used as an external standard.

2.2. Materials

$RhCl_3 \cdot nH_2O$ was purchased from Aldrich. Dichloromethane was purified by distillation over P_2O_5 and CaH_2. All other chemicals were of reagent grade and were used as commercially obtained.

2.3. Syntheses of the complexes

[Rh(Hdmg)$_2$PPh$_3$Cl] was prepared according to the procedure of Powell [10]. IR (KBr pellets, cm^{-1}): ν(N–O), 1255vs, 1092vs; ν(N–C), 1530vs; ν(Rh–N), 530s. UV–Vis (EtOH), λ_{max} (ϵ ($l\ mol^{-1}\ cm^{-1}$)): 271 (16 670) nm.

[Rh(Hdmg)$_2$(PPh$_3$)]$_2$ was synthesized according to the literature procedure [9]. IR (KBr pellets, cm^{-1}): ν(N–O), 1240vs, 1070s; ν(N–C), 1520s; ν(Rh–N), 518s. UV–Vis (CH_2Cl_2), λ_{max} (ϵ ($l\ mol^{-1}\ cm^{-1}$)): 456 (48 300), 308sh, 272 (32 350) nm.

[Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$. The reduction was carried out under an Ar/N_2 atmosphere. Zn(Hg) (1%, 20 g) was added to a yellow solution of 0.2 g (0.32 mmol) [Rh(Hdmg)$_2$PPh$_3$Cl] in ~80 ml of dichloromethane. The reaction mixture was stirred for 24 h. The resulting red solution was centrifuged at high speed for 1 h to sediment the finely dispersed solid and then it was filtered through Celite. After addition of ethanol the solution was left to stand in the dark until a dark red precipitate appeared. The product was filtered and dried in vacuo. Yield 40%.

Anal. Found: C, 44.86; H, 4.02; N, 7.99; Cl, 5.13; Zn, 9.24. Calc. for $Rh_2C_{52}H_{56}N_8O_8P_2Cl_2Zn_2$: C.44.92; H, 4.06; N, 8.06; Cl, 5.09; Zn, 9.40%.

IR (KBr pellets, cm^{-1}): ν(N–O), 1230s, 1088vs; ν(N–C), 1526s; ν(Rh–N), 518. UV–Vis (CH_2Cl_2): λ_{max} (ϵ ($l\ mol^{-1}\ cm^{-1}$)): 458 (38 970), 400sh (22 470), 272 (33 061) nm.

The compound is air-stable, insoluble in hexane and moderately soluble in chloroform and dichloromethane to give non-conducting solutions. It is much more light stable than [Rh(Hdmg)$_2$(PPh$_3$)]$_2$.

2.4. X-ray data collection

The low solubility of [Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$ in most of the common solvents made its recrystallization extremely difficult. Crystals could only be obtained from a $CH_2Cl_2/CHCl_3$ solution but were of poor quality and seemed to grow in clusters. The crystals used for data collection and refinement were cleaved from the clusters using a razor blade, but some diffraction maxima appeared still to contain contributions from secondary crystallite fragments. Structure anal-

Table 1
Selected bond lengths in rhodoximes (Å)

Complex	Rh–Rh	Rh–P	N–O	N–C	Rh–N	Ref.
Rh(Hdmg)$_2$(PPh$_3$)Cl		2.327(1)	1.337	1.297	1.992	[23]
[Rh(Hdmg)$_2$(PPh$_3$)]$_2$	2.936(2)	2.438(4)	1.33(2)	1.313(3)	1.99(2)	[8]
[Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$	2.852(3)	2.431(9)	1.34(3)	1.30(4)	2.01(2)	this work
[Rh(Hdmg)(CH$_3$COO)(PPh$_3$)]$_2$	2.618(5)	2.485(9)			1.974(5)	[22]

Table 2
^{13}C and ^{31}P NMR data for rhodoximes, δ (ppm)

Complex	^{13}C [a]	31$^{P\,a}$
[Rh(Hdmg)$_2$(PPh$_3$)]$_2$ [a]	151.35 (C=N), 134.8 (vt, P(*o*-C$_6$H$_5$)$_3$, 131.2 (P(*p*-C$_6$H$_5$)$_3$), 130.7 (vt, P(i-C$_6$H$_5$)$_3$), 129.2 (vt, P(*m*-C$_6$H$_5$)$_3$), 12.6 (CH$_3$)	−2.6 (m, $\|^1J(Rh,P) + {}^2J(Rh,P)\| = 100$ Hz)
[Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$ [b]	156.65 (C=N), 150.0 (C=N), 149.1 (C=N), 148.9 (C=N), 133.8 (vt, P(*o*-C$_6$H$_5$)$_3$), 130.4 (P(*p*-C$_6$H$_5$)$_3$), 128.75 (vt, P (i-C$_6$H$_5$)$_3$), 128.3 (vt, P(*m*-C$_6$H$_5$)$_3$, 13.35 (CH$_3$), 12.8 (CH$_3$), 11.74 (CH$_3$), 11.69 (CH$_3$)	3.6 (m, $\|^1J(Rh,P) + {}^2J(Rh,P)\| = 97$ Hz)

[a] CD_3OD.
[b] $CDCl_3$.

Table 3
^{1}H NMR spectral data for rhodoximes

Complex	^{1}H (δ, ppm)
$[Rh(Hdmg)_2(PPh_3)]_2$	[a] 7.45–7.15 (m, 30H, $P(C_6H_5)_3$ 1.76 (vt, 24H, CH_3, split = 1.5 Hz)
$[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$	[b] 13.3 (s, 2H, OH), 7.6–7.2 (m, 30H, $P(C_6H_5)_3$), 1.72 (vt, 6H, CH_3, split = 1.7), 1.65 (vt, 6H, CH_3, split = 2.2), 1.40 (vt, 6H, CH_3, split = 1.7), 1.20 (vt, 6H, CH_3, split = 2.2 Hz)
	[c] 13.24 (s, 2H, OH), 7.5–7.2 (m, 30H, $P(C_6H_5)_3$), 1.75 (vt, 6H, CH_3, split = 1.7), 1.61 (vt, 6H, CH_3, split = 2.2), 1.43 (vt, 6H, CH_3, split = 1.7), 1.32 (vt, 6H, CH_3, split = 2.2 Hz)
	[d] 13.3 (s, 2H, OH), 7.5–7.2 (m, 30H, $P(C_6H_5)_3$), 1.71 (vt, 6H, CH_3), 1.61 (vt, 6H, CH_3), 1.42 (vt, 6H, CH_3), 1.32 (vt, 6H, CH_3)

[a] CD_3OD.
[b] $CDCl_3$.
[c] CD_2Cl_2.
[d] CD_2Cl_2, −70 °C.

yses were performed on three different crystals, all showing broad, ill-shaped peaks. This could account for the poor agreement factors. The analysis using the best data sets is reported. Data were collected on a Kuma KM4 κ-axis diffractometer with graphite-monochromated Mo Kα radiation using the ω–2θ scan mode. Of the 6316 independent reflections measured 4704 were observed ($F > 4\sigma(F)$). Three standard reflections showed no variation. Data were corrected for Lorentz, polarization and absorption effects (DIFABS program [11]). Correction coefficients were in the range 0.834–1.220. The structure was solved and refined using SHELXS-86 [12] and SHELXL-93 [13] programs. Full-matrix least-squares refinement of non-hydrogen atoms (H atom parameters were fixed) converged at $R = 0.13$. Scattering factors were those incorporated in the programs and from the literature [14]. For crystal data, see Table 4 and Section 5.

3. Results and discussion

3.1. Infrared spectra

Burger et al. demonstrated that in the dioximato complexes of transition metals, the d orbitals of the central atom can overlap efficiently the unoccupied π orbitals of the ligand. The M→N=C interaction can be monitored in the IR spectrum through the frequency of the CN vibrations [15]. In line with this the highest value for ν(CN) (1530 cm^{-1}) is observed in $[Rh(Hdmg)_2PPh_3Cl]$ which has the shortest C–N bond (1.297 Å) (Table 1) and the lowest frequency (1520 cm^{-1}) is observed in $[Rh(Hdmg)_2(PPh_3)]_2$, where the C–N distance (1.313 Å) is the longest one. The ν(CN) stretching frequency appears at 1526 cm^{-1} in the polynuclear $[Rh(Hdmg)(ClZndmg)PPh_3]_2$ for which the C–N bond length is 1.30(4) Å.

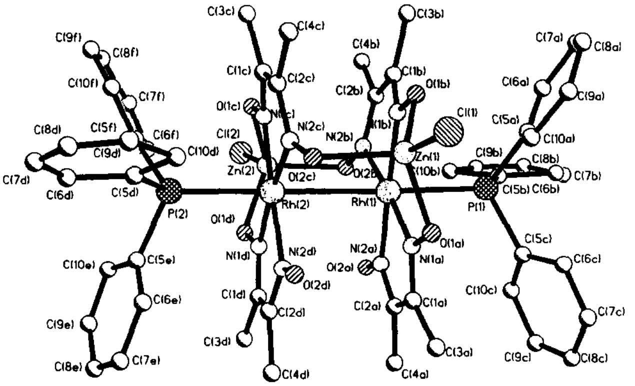

Fig. 1. Molecular structure with labelling scheme for non-hydrogen atoms of $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$.

All the rhodium complexes exhibit two strong bands in the 1255–1230 and 1092–1070 cm^{-1} ranges. They are assigned to NO stretching on the basis of earlier reports [4c,15,16]. The decrease of the former NO stretching frequency (Table 1) and the increase of the average N–O distance implies a decrease of the average N–O bond strength after the formation of the O–Zn bonds. The latter NO frequency parallels the trend observed for ν(CN) vibrations. This suggests that this absorption has some CN stretching character.

All complexes reported here display a strong sharp absorption in the region 518–530 cm^{-1} which has been assigned to a rhodium–nitrogen vibration [16c].

3.2. Electronic spectra

The highest energy band is assigned to an intraligand (α-dioxime) $\pi \rightarrow \pi^*$ transition, by analogy to the results reported for cobalt [15,16a], ruthenium [17] and rhodium [18] α-dioximato compounds. On the basis of the high extinction coefficients, the peaks and shoulders between 300 and 500 nm are ascribed to the charge transfer bands involving the central rhodium atom and the equatorial macrocycle. Such metal to ligand charge transfer (MLCT) absorptions can occur in complexes where unsaturated ligands like dimethylglyoxime, containing empty antibonding π-orbitals, are bonded to oxidizable metals [4].

3.3. NMR spectroscopy

The $[Rh(Hdmg)_2(PPh_3)]_2$ dimer, built up of two $[Rh(Hdmg)_2(PPh_3)]$ subunits linked only by an Rh–Rh bond [9], reacts in chloroform, therefore the NMR measurements were run in methanol. Instead the spectra of $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ were run both in $CDCl_3$ and CD_2Cl_2.

In line with the solid state structures the ^{31}P spectra of these complexes are the AA′ parts of AA′XX′ spin systems [19]. The $|^1J(Rh,P) + ^2J(Rh,P)|$ values can be read directly from the ^{31}P spectra resulting in about 100 and 97 Hz for the former and the latter, respectively (Table 2). The ^{31}P spectral patterns are similar to those of the well known $[Rh(CH_3COO)_2(PPh_3)]_2$ and $[Rh(CH_3COO)_2(P(OCH_3)_3)]_2$ dimers [20], where the two Rh(II) ions are connected by a direct metal–metal bond and by four carboxylate bridges, resulting in a lantern structure, and the $|^1J(Rh,P) + ^2J(Rh,P)|$ values are about 136 and 95 Hz, respectively. In all these compounds the axial P–Rh–Rh–P sequence gives rise to a particularly interesting spin system, the four $I = 1/2$ nuclei being in a linear arrangement. $^3J(P,P)$ is expected to be very large, by analogy to what was found for AMRX spin systems of the lantern compounds bearing two different phosphorus ligands [20]. Unluckily this parameter cauld not be obtained by spectral analysis for $[Rh(Hdmg)_2(PPh_3)]_2$ and $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ as the central resonances overlap and the intensity of the relevant external ones is below the detection limit. The phosphine carbons correspond to the M parts of AA′MXX′ spin systems. Their spectra indicate that complexation with rhodium has very similar effects on the triphenylphosphine in the two compounds.

Substantial differences are found in the spectra of the equatorial ligands. For $[Rh(Hdmg)_2(PPh_3)]_2$ all the methyl protons are isochronous, their resonance being split by the coupling with phosphorus. The methyl carbons resonate at δ 12.6 ppm and the quaternary carbons at δ 151.35 ppm, i.e. close to those of the monomeric triphenylphosphine Rh(III) rhodoxime [21].

The ^1H spectrum of $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$ shows four well separated multiplets (Table 3). As above the splitting is due to coupling with ^{31}P nuclei; in the $\{^{31}P\}^1H$ spectra they appear as four singlets. Long-range coupling of J values 0.5–3 Hz was also observed in $[Rh(Hdmg)_2PPh_3X]$ (X = alkyl, Cl, PPh_3) [2f,21] and in $[Co(Hdmg)_2LX]$ (L = PPh_3, PBu_3) [22]. The two OH protons, one per bis-dimethylglyoximato unit, originate a singlet at 13.3 ppm. Its position and linewidth are not appreciably influenced by the temperature, down to −70 °C. The carbon spectrum consists

Table 4
Crystal data and structure refinement

Chemical formula	$C_{52}H_{54}N_8O_8P_2Cl_2Zn_2Rh_2$
Formula weight	1144.04
Crystal size (mm)	0.08 × 0.08 × 0.15
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	14.262(3)
b (Å)	14.675(3)
c (Å)	14.698(3)
α (°)	82.15(3)
β (°)	87.57(3)
γ (°)	65.89(3)
Volume (Å^3)	2781.2(10)
Z	2
Density (calc.) (Mg m^{-3})	1.658
Density (meas.) (Mg m^{-3})	1.67
Absorption coefficient (mm^{-1})	1.66
F(000)	1400
θ Range for data collection (°)	2.08–22.99
Ranges of h, k, l	0–14, −14–15, −16–16
Measured reflections	6316
Independent reflections	6316 (R(int) = 0.0000)
Data/restraints/parameters	6316/0/686
Goodness-of-fit on F^2	1.277
R	0.1339
wR	0.3637
Extinction coefficient	0.0000(2)
Largest difference peak and hole (e Å^{-3})	4.234 and −2.216

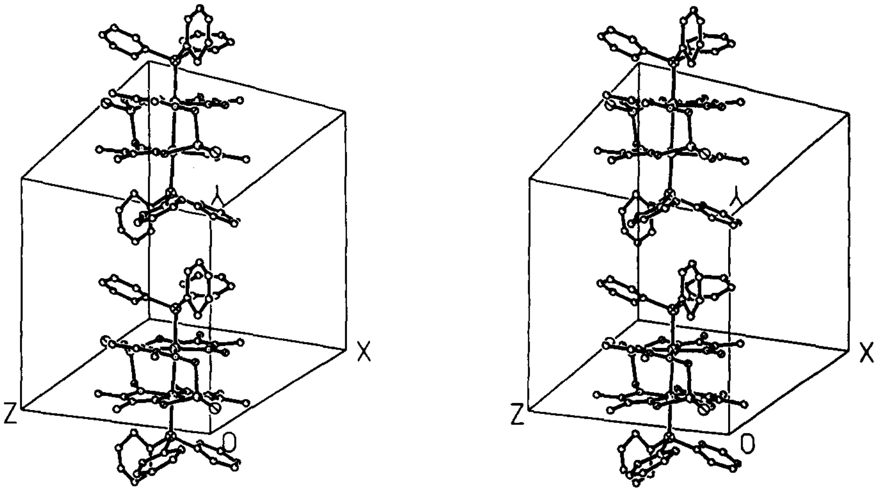

Fig. 2. Stereographic packing diagram of $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$.

Table 5
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{eq}
Rh(1)	0.2265(2)	−0.0013(2)	0.27918(15)	0.0253(7)
Rh(2)	0.2536(2)	0.1799(2)	0.28504(14)	0.0236(7)
Zn(1)	0.4847(3)	−0.0845(3)	0.2271(2)	0.0317(10)
Zn(2)	−0.0071(3)	0.2840(3)	0.2311(2)	0.0322(10)
P(2)	0.2718(7)	0.3364(6)	0.2897(5)	0.037(2)
P(1)	0.2098(7)	−0.1586(6)	0.2697(7)	0.039(2)
Cl(1)	0.6439(6)	−0.1834(7)	0.2038(6)	0.052(2)
Cl(2)	−0.1665(7)	0.3903(8)	0.2028(7)	0.059(3)
O(1A)	0.4434(15)	−0.1332(18)	0.3470(16)	0.047(6)
O(1B)	0.3842(16)	−0.0628(15)	0.1309(14)	0.034(6)
O(1C)	0.0935(15)	0.2911(16)	0.1366(12)	0.035(5)
O(1D)	0.0388(16)	0.2887(15)	0.3539(12)	0.033(5)
O(2A)	0.0562(16)	0.0627(17)	0.4104(16)	0.044(6)
O(2B)	0.0136(16)	0.1373(14)	0.2336(14)	0.032(5)
O(2C)	0.4674(16)	0.0559(14)	0.2385(15)	0.033(5)
O(2D)	0.4285(14)	0.0675(14)	0.4154(13)	0.028(5)
N(1A)	0.3445(18)	−0.0827(17)	0.3682(13)	0.024(6)
N(1B)	0.2868(19)	−0.0121(25)	0.1511(15)	0.036(9)
N(1C)	0.1888(17)	0.2359(18)	0.1588(16)	0.029(6)
N(1D)	0.1373(18)	0.2288(20)	0.3762(17)	0.033(7)
N(2A)	0.1603(18)	0.0113(17)	0.4015(19)	0.031(7)
N(2B)	0.1052(16)	0.0858(19)	0.1991(16)	0.037(6)
N(2C)	0.3727(17)	0.1245(16)	0.2080(15)	0.024(6)
N(2D)	0.3230(20)	0.1202(16)	0.4090(16)	0.027(6)
C(1A)	0.3179(24)	−0.0917(23)	0.4563(21)	0.029(8)
C(2A)	0.2146(27)	−0.0378(24)	0.4717(18)	0.032(9)
C(3A)	0.3996(27)	−0.1579(26)	0.5263(19)	0.048(10)
C(4A)	0.1700(28)	−0.0409(24)	0.5690(21)	0.041(9)
C(1B)	0.2215(25)	0.0233(23)	0.0861(21)	0.029(8)
C(2B)	0.1153(23)	0.0764(25)	0.1116(22)	0.042(8)
C(3B)	0.2540(25)	0.0060(25)	−0.0125(19)	0.041(8)
C(4B)	0.0253(27)	0.1336(31)	0.0461(28)	0.056(11)
C(1C)	0.2574(23)	0.2223(21)	0.0921(18)	0.024(7)
C(2C)	0.3611(23)	0.1606(27)	0.1183(18)	0.037(8)
C(3C)	0.2233(27)	0.2758(23)	−0.0041(18)	0.034(9)
C(4C)	0.4489(24)	0.1281(28)	0.0499(18)	0.038(9)
C(1D)	0.1632(22)	0.2049(23)	0.4631(22)	0.033(8)
C(4D)	0.3195(29)	0.1109(30)	0.5749(23)	0.053(10)
C(3D)	0.0865(26)	0.2446(27)	0.5373(21)	0.043(9)
C(2D)	0.2712(24)	0.1476(23)	0.4799(20)	0.033(8)
C(5A)	0.2956(35)	−0.2305(21)	0.1774(25)	0.047(12)
C(6A)	0.2493(35)	−0.2374(28)	0.1033(22)	0.059(12)
C(7A)	0.3084(47)	−0.2900(36)	0.0324(40)	0.087(17)
C(8A)	0.4149(58)	−0.3208(42)	0.0448(31)	0.102(23)
C(9A)	0.4646(41)	−0.3167(32)	0.1275(35)	0.099(19)
C(10A)	0.4002(25)	−0.2590(24)	0.1917(27)	0.049(11)
C(5B)	0.0876(27)	−0.1537(20)	0.2437(17)	0.047(9)
C(6B)	0.0663(33)	−0.2503(26)	0.2342(23)	0.059(12)
C(7B)	−0.0178(42)	−0.2465(40)	0.2334(24)	0.076(15)
C(8B)	−0.1030(26)	−0.1581(29)	0.2162(18)	0.048(12)
C(9B)	−0.0969(34)	−0.0706(31)	0.2215(26)	0.056(12)
C(10B)	−0.0026(40)	−0.0432(67)	0.2323(25)	0.155(55)
C(5C)	0.2436(26)	−0.2441(27)	0.3787(22)	0.044(9)
C(6C)	0.3353(35)	−0.3305(28)	0.3962(30)	0.069(12)
C(7C)	0.3482(36)	−0.3853(35)	0.4799(37)	0.075(15)
C(8C)	0.2776(38)	−0.3596(29)	0.5501(21)	0.059(12)
C(9C)	0.1840(31)	−0.2791(34)	0.5323(33)	0.066(13)
C(10C)	0.1714(28)	−0.2241(28)	0.4453(24)	0.046(9)
C(5D)	0.3937(32)	0.3434(23)	0.2695(17)	0.048(11)
C(6D)	0.4001(39)	0.4404(30)	0.2769(26)	0.077(13)
C(7D)	0.4938(52)	0.4425(47)	0.2562(31)	0.102(20)
C(8D)	0.5751(32)	0.3661(28)	0.2366(19)	0.042(10)
C(9D)	0.5714(29)	0.2843(38)	0.2267(21)	0.067(14)
C(10D)	0.4790(27)	0.2545(44)	0.2426(20)	0.084(24)
C(5E)	0.2421(23)	0.3825(25)	0.4030(20)	0.043(10)
C(6E)	0.3164(27)	0.3317(26)	0.4685(21)	0.041(9)
C(7E)	0.2987(35)	0.3603(29)	0.5603(23)	0.057(11)
C(8E)	0.2097(38)	0.4372(31)	0.5811(25)	0.067(13)
C(9E)	0.1357(35)	0.4871(35)	0.5110(34)	0.072(14)
C(10E)	0.1529(33)	0.4634(24)	0.4216(25)	0.049(11)
C(5F)	0.1925(37)	0.4370(22)	0.2015(25)	0.059(15)
C(6F)	0.0811(19)	0.4623(19)	0.2134(18)	0.025(6)
C(7F)	0.0226(34)	0.5293(25)	0.1324(28)	0.057(13)
C(8F)	0.0655(37)	0.5661(27)	0.0587(22)	0.061(11)
C(9F)	0.1679(36)	0.5386(33)	0.0547(29)	0.073(12)
C(10F)	0.2282(36)	0.4720(26)	0.1251(19)	0.067(14)

(continued)

Table 5 (continued)

of four different resonances for the eight quaternary carbons and another four for the eight methyls. This is in line with the retention in solution of the solid state structure; here each zinc is chelated by two oxygen atoms of one of the bisdimethylglyoximato subunits and bridges them to one of the oxygens of the other subunit, so that there is only one oxygen atom not involved in coordination with zinc in each subunit, vide infra. This implies a complete chemical inequivalance within the atoms of each bisdimethylglyoximato moiety and leaves only a one to one equivalence between the atoms of the two equatorial ligands.

3.4. Crystal structure of [Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$

The molecular structure of the complex is depicted in Figs. 1 and 2. Crystal data are reported in Table 4. Atomic positions, interatomic distances and angles are given in Tables 5 and 6.

The molecule has no crystallographic symmetry and because of the PPh$_3$ groups, it also lacks any virtual symmetry. The tetranuclear molecule consists of two equivalent [Rh(Hdmg)(ClZndmg)(PPh$_3$)] halves linked by an Rh–Rh bond and by two Zn ions. The Rh–Rh bond length of 2.852(3) Å is shorter than that found for [Rh(Hdmg)$_2$(PPh$_3$)]$_2$, 2.936(2) Å [9], but longer than that observed in [Rh(Hdmg)(CH$_3$COO)(PPh$_3$)]$_2$, 2.618(5) Å [23]. The mean Rh–N distance of 2.01(2) Å is similar to those found for [Rh(Hdmg)$_2$(PPh$_3$)]$_2$, 1.990(2) [9], [Rh(Hdmg)(CH$_3$COO)(PPh$_3$)]$_2$, 1.947(5) Å [23], [Rh(Hdmg)$_2$PPh$_3$Cl], 1.992 Å [24], and in alkylpyridinerhodoximes, 1.986 Å [2b]. The Rh–P bond length with a mean value of 2.431(9) Å is close to those of [Rh(Hdmg)$_2$(PPh$_3$)]$_2$ and [Rh(Hdmg)(CH$_3$COO)(PPh$_3$)]$_2$, 2.438(4) [9] and 2.485(9) [23] Å, respectively. It is worth noting that the value for [Rh(Hdmg)$_2$PPh$_3$Cl] is 2.327 Å [24]. The O···O contacts between the dimethylglyoxime rings range from 2.67 to 2.69 Å for O(2A)–O(2B)

Table 6
Selected bond lengths (Å), bond angles (°) and torsion angles (°)

Bond lengths (Å)

Rh(1)	N(2A)	1.99(3)
Rh(1)	N(2B)	1.99(2)
Rh(1)	N(1B)	2.04(2)
Rh(1)	N(1A)	2.02(2)
Rh(1)	P(1)	2.438(9)
Rh(1)	Rh(2)	2.852(3)
Rh(2)	N(2C)	1.95(2)
Rh(2)	N(1C)	2.02(2)
Rh(2)	N(2D)	2.02(2)
Rh(2)	N(1D)	2.04(2)
Rh(2)	P(2)	2.424(9)
Zn(1)	O(1B)	1.96(2)
Zn(1)	O(1A)	1.97(2)
Zn(1)	O(2C)	2.00(2)
Zn(1)	Cl(1)	2.181(9)
Zn(2)	O(1D)	1.96(2)
Zn(2)	O(1C)	1.98(2)
Zn(2)	O(2B)	2.05(2)
Zn(2)	Cl(2)	2.187(9)

Bond angles (°)

N(2A)	Rh(1)	N(2B)	99.8(10)
N(2A)	Rh(1)	N(1B)	177.0(10)
N(2B)	Rh(1)	N(1B)	77.5(10)
N(2A)	Rh(1)	N(1A)	76.4(9)
N(2B)	Rh(1)	N(1A)	175.5(9)
N(1B)	Rh(1)	N(1A)	106.4(9)
N(2A)	Rh(1)	P(1)	91.9(7)
P(1)	Rh(1)	Rh(2)	177.5(3)
N(2C)	Rh(2)	P(2)	94.5(7)
P(2)	Rh(2)	Rh(1)	178.5(2)
O(1B)	Zn(1)	O(1A)	111.2(9)
O(1B)	Zn(1)	O(2C)	102.5(9)
O(1A)	Zn(1)	O(2C)	104.7(10)
O(1B)	Zn(1)	Cl(1)	117.0(6)
O(1A)	Zn(1)	Cl(1)	108.4(7)
O(2C)	Zn(1)	Cl(1)	112.3(7)
O(1D)	Zn(2)	O(1C)	111.3(8)
O(1D)	Zn(2)	O(2B)	103.8(8)
O(1C)	Zn(2)	O(2B)	100.1(8)
O(1D)	Zn(2)	Cl(2)	111.6(7)
O(1C)	Zn(2)	Cl(2)	116.0(6)
O(2B)	Zn(2)	Cl(2)	112.8(7)
C(5B)	P(1)	Rh(1)	118.7(9)
C(5C)	P(1)	Rh(1)	112.6(12)
C(5A)	P(1)	Rh(1)	111.9(9)
C(5D)	P(2)	Rh(2)	120.7(11)
C(5F)	P(2)	Rh(2)	112.3(9)
C(5E)	P(2)	Rh(2)	113.4(12)

Torsion angles (°)

N(1B)	Rh(1)	Rh(2)	N(2C)	−31(1)
N(2B)	Rh(1)	Rh(2)	N(1C)	−29(1)
N(1A)	Rh(1)	Rh(2)	N(2D)	−24(1)
N(2A)	Rh(1)	Rh(2)	N(1D)	−23(1)
P(1)	Rh(1)	Rh(2)	P(2)	139(9)

and O(2C)–O(2D) and from 3.24 to 3.26 Å for O(1A)–O(1B) and O(1C)–O(1D), respectively. The former mean of 2.68 Å is very similar to that found in Rh(Hdmg)$_2$PPh$_3$Cl, 2.663 Å, and in [Rh(Hdmg)(PPh$_3$)]$_2$, 2.623 Å, and is normal for H-bonded Hdmg rings [24,9]. The latter values correspond to the distances of the oxygen atoms chelating the zinc. The presence of only two H bonds in the studied compound is in complete agreement with the NMR data, vide supra.

4. Conclusions

In [Rh(Hdmg)(ZnCldmg)PPh$_3$]$_2$ the zinc plays two roles: it both substitutes one hydrogen bridge between the facing dmgs of the same equatorial moiety and connects the two Rh(II) subunits so that they are linked by two OZnO bridges and by the Rh–Rh bond. Other examples of O...H–O bridge substitution in rhodoximes have been reported for monomeric Rh(III) derivatives [25]. There are other Rh(II) dinuclear complexes bearing further linkages in addition to the Rh–Rh bond [20,26,27], but this is the first example of multiple bridges between two rhodoxime subunits. In the [Rh(Hdmg)$_2$L]$_2$ dimers reported so far the two subunits are joined only by an Rh–Rh bond.

One of the principal questions raised in the past concerns the degree to which various factors contribute to the differences in the Rh–Rh bond length in dinuclear rhodium(II) compounds [28,29]. Interestingly for the title complex this length is shorter than for the [Rh(Hdmg)$_2$(PPh$_3$)]$_2$ dimer, but much longer than for the lantern compounds. Even if strong differences in the coordination sphere must be taken into account, the presence of bridges plays a major role.

Furthermore the binding to zinc lowers the symmetry of the equatorial coordination making it in this sense closer to the corrins.

It has also been demonstrated that rhodium compounds with dioximato ligands can serve as suitable candidates for designing new heteronuclear complexes. Further reactions with other metal ions are underway in current studies.

5. Supplementary material

Additional material comprising H atom coordinates, thermal parameters, and remaining bond lengths and angles is available from the Cambridge Crystallographic Data Centre.

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