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New rhodium complexes of the tetradentate ligand bis(diacetylmonoxime-imino)propane 1,3 (H_2dopn): synthesis and crystal structure of *trans*-[Rh(Hdopn)Cl]$_2$ and *trans*-[Rh(Hdopn)(I)$_2$] ☆

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Abstract

The reaction between $[Rh(H_2O)_6](ClO_4)_3$ and the monoanion Hdopn$^-$ (H_2dopn = bis(diacetylmonoxime-imino)propane 1,3 = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime) afforded a new dimeric rhodium(II) compound of formula $[Rh(Hdopn)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ (**1**). Treatment of methanolic solution of **1** with NaX (X = Cl$^-$, Br$^-$, I$^-$) results in the replacement of water with halides in **1**, leading to the formation of [Rh(Hdopn)X]$_2$ rhodium(II) dimers. The X-ray crystal structure of $[Rh(Hdopn)Cl]_2 \cdot 0.5H_2O$ (**2**) was determined showing a [Rh(II)–Rh(II)] core. Upon the reaction of **1** with NaI carried out in air, [Rh(Hdopn)(I)$_2$] (**3**) was isolated and characterized by a single-crystal X-ray diffraction analysis.

Keywords: Rhodium complexes; Aqua complexes; Binuclear complexes; Rhodoximes; Oximates; Crystal structure

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1. Introduction

During the past decades the chemistry of transition metal chelates of bidentate or tetradentate tetraaza ligands with delocalized electronic structures has aroused great interest owing to their relevance to the design of biologically active metal centres and development of synthetic catalysts. Studies on rhodium complexes with oximato ligands (rhodoximes) contribute to a better understanding of the mechanistic and kinetic behaviour of cobaloximes, the well-known models of vitamin B_{12} coenzyme [1]. We have recently been exploring the chemistry of Rh(III) and Rh(II) compounds with dioxime and monoxime chelate ligands aiming to gain insight into the origin of the catalytic activity of certain rhodoximes in hydrogenation [2a–2d], hydroformylation [2a], hydrosililation [3], and oxidation [4] reactions.

A good number of six-coordinated rhodoximes have been studied but mainly ones containing the tetradentate bisdimethyldioximate, (Hdmg)$_2$, equatorial ligand [5–16]. It has been demonstrated that a slight modification of the structure of rhodium complexes with dioximes strongly affects the reactivity of these compounds [2,5–12,17].

To date, there have been only a few reports on rhodium complexes containing the monoanion Hdopn$^-$ (H_2dopn = bis(diacetylmonoxime-imino)propane 1,3), also known in the literature as 2,2′2-[1,3-propanediylbis(nitrilo)]bis[3-butanone oximato] = C_1(DO)(DOH)pn as well as 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime) [18] (Fig. 1) and its BF_2-related compounds [19].

Compared to Rh(I) and Rh(III) compounds, there is a small amount of data on Rh(II) rhodoximes containing a [Rh(II)–Rh(II)] core [2d,20]. Since the discovery of the first dinuclear rhodium(II) complex in 1960 [21], such compounds have been the focus of intensive research activity. Areas of interest include metal–metal

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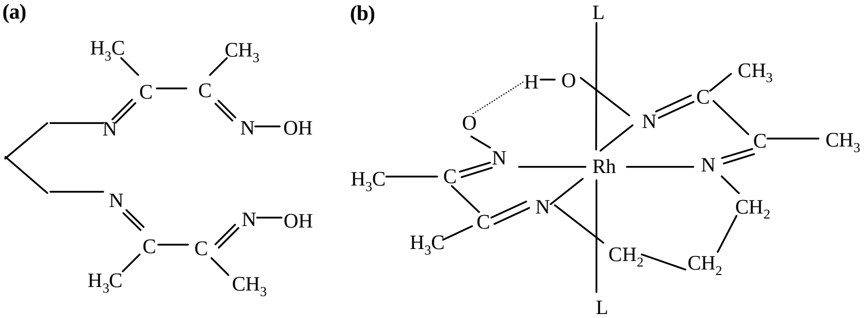

Fig. 1. (a) H_2dopn, (b) [Rh(Hdopn)L_2] complexes.

bonding [22], catalysis [23], antitumour activity [24], and coordination chemistry [22a,22c,23,25].

The chemistry of $RhCl_3 \cdot 3H_2O$ is very rich due to its application in rhodium compound syntheses and as a precatalyst for a variety of organic reactions [26]. In contrast, reports on the chemistry of $[Rh(H_2O)_6](ClO_4)_3$ [27–39] and related polymerised compounds [30,40] are relatively limited.

Despite the scarce data on the application of $[Rh(H_2O)_6](ClO_4)_3$ as a rhodium substrate, we have been able to provide several reports on syntheses of rhodium complexes with different nitrogen donor ligands that are impossible to obtain in reactions using $RhCl_3 \cdot 3H_2O$, e.g. $[Rh(Hdmg)_2L_2]ClO_4$, (Hdmg = monoanion of dimethylglyoxime, L = H_2O, PPh_3) [5], $[Rh(damo)_2(PPh_3)_2](ClO_4)$, (damo = monoanion of diacetyl monoxime) [28b], and different derivatives of tridentate bis(benzimidazole) amine ligands [28a].

In this paper, we describe the preparation and characterization of a binuclear Rh(II) complex formulated as $[Rh(Hdopn)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ (**1**). The water molecules in the axial positions of **1** were shown to easily undergo the substitution reaction with halide anions, forming adducts of the general formula $[Rh(Hdopn)X]_2$, where X = Cl^-, Br^-, J^-. The dimeric structure of $[Rh(Hdopn)Cl]_2$ (**2**) was confirmed by X-ray diffraction. The reaction of **1** with NaI also afforded a Rh(III) product, $[Rh(Hdopn)(I)_2]$ (**3**), the structure of which was determined crystallographically.

As far as we are aware, the complexes presented in this paper are the first examples of rhodium compounds containing the bis(diacetylmonoxime-imino)propane ligand to have been structurally characterized.

2. Experimental

2.1. Measurements and materials

UV–vis room temperature spectra were monitored in the 200–820 nm range by a Hewlett Packard 8452A rapid scan diode array spectrometer. Infrared spectra were recorded on a FT-IR Nicolet Impact 400 spectrometer in the 4000–400 cm^{-1} range as KBr discs or Nujol mulls. The NMR spectra were measured on a Bruker AMX-300 spectrometer (^1H at 300.13, ^{31}P at 121.496 MHz) with TMS as internal standard and 85% H_3PO_4 as external standard for ^1H and $^{31}P\{H\}$, respectively. Elemental analyses were performed at the Elemental Analysis Centre, Wrocław University, on a Perkin–Elmer Elemental Analyser 2400 for CHN and on an ICP ARL 3410 spectrograph for Rh. Mass spectra (ESI) were measured on a Finnigan Mat, TSQ 700.

$RhCl_3 \cdot 3H_2O$ was purchased from Aldrich. Solvents were dried and distilled under nitrogen according to standard methods. The other chemicals were of reagent grade and were used in the commercially available form. All reactions were carried out under a nitrogen or carbon monoxide atmosphere using standard Schlenk techniques unless otherwise noted.

$[Rh(H_2O)_6](ClO_4)_3$ was synthesized according to the method of Ayres and Forrester [39] through the reaction of $RhCl_3 \cdot 3H_2O$ with concentrated perchloric acid. The solid compound was dried under a reduced pressure of 10^{-3} mm Hg at 90 °C. The solutions were standardized spectrophotometrically by the absorption spectrum of $[Rh(H_2O)_6]^{3+}$ with bands at 311 ($\epsilon = 67.4$ $M^{-1}\,cm^{-1}$) and 396 nm ($\epsilon = 62.0$ $M^{-1}\,cm^{-1}$) [38].

H_2dopn was obtained following E. Uhlig and M. Friedrich [41].

2.2. Synthesis and reactions

2.2.1. $[Rh(Hdopn)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ (1)

$[Rh(H_2O)_6](ClO_4)_3$ (276 mg, 0.55 mmol) and 25 cm^3 of absolute dehydrated ethanol were added to a three-neck flask equipped with a magnetic stirring bar and fitted with a reflux condenser attached to a gas flow adapter and oil bubbler. The solution was heated under CO at 65–70 °C until the appearance of traces of a black precipitate, which was filtered off, washed with EtOH, and dried under vacuum. The IR (KBr) spectrum of the black solid: 2076 s, 2029 m, and 1802 s cm^{-1} indicated that it was $Rh_6(CO)_{16}$. Then CO was replaced by N_2 to avoid further formation of $Rh_6(CO)_{16}$, and the deaerated solution of H_2dopn (14 mg, 0.58 mmol in 10 cm^3 of absolute ethanol) was slowly added under N_2 flow. After addition of the ligand, the reaction mixture was heated for 2 h and then cooled at −15 °C for 5 days. The yellow-brownish precipitate was isolated by filtration, washed with deaerated ethanol and diethyl ether, and dried under vacuum. Yield: 0.150 g (58.2%). *Anal.* Calc. for $C_{22}H_{44}N_8O_{15}Cl_2Rh_2$ ($M = 937.32$): C, 28.19; H, 4.73; N, 11.96; Cl, 7.58; Rh, 21.96. Found: C, 28.0; H, 4.5; N, 11.7; Cl, 7.6; Rh, 22.5%. MS (ESI, acetonitrile) m/z 783 $[\{Rh(Hdopn)\}_2(ClO_4)]^+$. Main IR ($cm^{-1}$) (KBr): 635 m, 1127 vs, 1254 m, 1434 m, 1486 m, 1605 s, br; (Nujol mull): 623 s, 1100 vs, 1275 m, 1610 m, 3384 s.

Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared and handled with caution. However, we have not experienced any problems with the complexes described in this work. Carbon monoxide is a toxic gas. Use a well-ventilated fume hood.

2.2.2. *[Rh(Hdopn)Cl]$_2$ · 0.5H$_2$O (**2**)*

An amount of 50 mg (0.053 mmol) of $[Rh(Hdopn)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ was degassed under reduced pressure and the reaction vessel was filled with N_2. The atmosphere was continuously purged using a slow N_2 stream. Subsequently, 20 cm^3 of deaerated methanol containing 10-fold excess of NaCl was added, and the reaction mixture was allowed to stand in a very gentle stream of N_2 until red-orange microcrystal precipitate appeared. Yield: 4.1 mg (10%). *Anal.* Calc. for $C_{22}H_{39}N_8O_{4.5}Cl_2Rh_2$ ($M = 773.29$): C, 34.57; H, 5.14; N, 14.66. Found: C, 34.4; H, 5.3; N; 14.6%. Main IR (cm^{-1}) (KBr): (1121) vs, 1268 w; 1430 m, 1465 m, 1587 m; (Nujol mull): 3350.

2.2.3. *[Rh(Hdopn)(I)$_2$] (**3**)*

This complex was obtained in a manner analogous to that for **2**. After mixing a solution of **1** and NaI, the reaction mixture was left to stand until a red-brownish precipitate appeared. Dark red single crystals were obtained by evaporation in a refrigerator from a CH_2Cl_2/EtOH solution.

The crystals were filtered off, washed carefully with small amount of ethanol and ethyl ether, and dried in vacuo. Yield: 22 mg (70%). *Anal.* Calc. for $C_{11}H_{19}N_4O_2I_2Rh$ ($M = 596.01$): C, 22.52; H, 3.12; N, 9.40. Found: C, 22.3; H, 3.2; N, 9.96%. Main IR (cm^{-1}) (KBr): 1128 s, 1275 m, 1423 s, 1491 s, 1604 m; (Nujol mull) 3380.

2.2.4. *Reactions*

Reactions between **1** and NaX were studied at room temperature as follows: 2.2 mg (0.0023 mmol) of **1** was dissolved in 10 cm^3 of methanol deaerated with N_2. Next, a 10-fold excess of solid NaX was added to the solution of **1** under N_2. The reactions were monitored in sealed quartz cells by observing changes in electronic spectra in the 200–820 nm range.

2.3. *Crystal structure determination*

Crystal data for **2** and **3** are given in Table 1, together with refinement details.

The reactivity of **2** made its crystallization extremely difficult. Unique crystals could only be obtained from the mother solution, but were of poor quality. Structural analyses were performed on three different crystals. The analysis using the best datasets is reported. The quality of the structure did not provide sufficient information about hydrogen atoms in the hydrogen-bonded oxime bridges, and these were not calculated. Data for **2** were collected on a Kuma KM4 κ-axis diffractometer with graphite-monochromated Mo Kα radiation using the ω-2θ scan mode. Three standard reflections showed no variation. For compound **3** the analyses proceeded without problems. All measurements of crystals of **3** were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. Crystals were positioned at 65 mm from the KM4CCD camera. 612 Frames were measured at 0.75° intervals with a counting time of 15–30 s.

The data were corrected for Lorentz and polarization effects. Absorption correction based on least-squares fitted against $|F_c| - |F_0|$ differences was applied for **2** and **3**. Data reduction and analysis were carried out using the Kuma Diffraction (Wrocław) programs [42]. The

Table 1
Crystallographic data for **2** and **3**

	2	**3**
Empirical formula	$C_{22}H_{40}N_8O_5Cl_2Rh_2$	$C_{11}H_{21}N_4O_2I_2Rh$
Formula weight	762.32	596.01
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_{1/n}$
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
a (Å)	32.942(7)	15.022(3)
b (Å)	12.526(3)	14.145(3)
c (Å)	16.167(3)	16.564(3)
α (°)	90	90
β (°)	111.57(3)	94.300(10)
γ (°)	90	90
V (Å)	6204 (2)	3509.8(6)
Z	8	8
D_{calc} (Mg m^{-3})	1.632	2.256
μ (mm^{-1})	1.279	4.498
$F(000)$	3088	2240
Reflections collected	5593	23931
Unique reflections	5499 ($R_{int} = 0.0752$)	8084 ($R_{int} = 0.03481$)
Observed reflections	4171[$I > 2\sigma$(I)]	6285[$I > 2\sigma$(I)]
$R1$, $wR2$ [$I > 2\sigma$(I)]	0.0714, 0.2053	0.0362, 0.0684
$R1$, $wR2$ (all data)	0.0909, 0.2239	0.0558, 0.0754

$R1 = \sum[|F_0| - |F_c|]/|F_0|$; $wR2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$.

structure was solved by the heavy atom method (SHELXS97 program [43]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 programs [44]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from the geometry of molecules and $\Delta\rho$ maps; they were not refined.

All figures and packing diagrams were made using XP [45].

3. Results and discussion

3.1. Synthesis and characterization

The reaction between $RhCl_3{\cdot}3H_2O$ and H_2dopn performed in ethanol, in the presence of air, led to the immediate precipitation of a mixture of different solids of indefinite composition. Application of CO led to the isolation of [Rh(Hdopn)(Cl)$_2$], which has scarcely been described [18].

If $[Rh(H_2O)_6](ClO_4)_3$ is dissolved in ethanol, no reaction takes place at room temperature, whereas rhodium metal is formed rapidly in boiling ethanol.

Reaction of $[Rh(H_2O)_6](ClO_4)_3$ with H_2dopn carried out under an N_2 atmosphere leads to a mixture of rhodium compounds, whose identification has failed so far. It was established that substitution at the Rh(III) centres was catalysed by two-electron reducing agents. The latter include, among others, ethanol and carbon monoxide [18,46].

The interaction of ethanolic solution of $[Rh(H_2O)_6](ClO_4)_3$ with CO, in the absence of H_2dopn, gives $Rh_6(CO)_{16}$. Its identification was confirmed by microanalysis and the IR frequencies registered at 2076, 2029, and 1802 cm^{-1}, which are characteristic for the isolated rhodium carbonyl [47]. When the filtrate separated from the first "drops" of $Rh_6(CO)_{16}$ is allowed to react with H_2dopn under a nitrogen atmosphere and next left to stand in a refrigerator for a few days, a rhodium(II) species formulated as [Rh(Hdopn)(H$_2$O)]$_2$(ClO$_4$)$_2 \cdot H_2O$ (**1**), based on elemental analysis and mass spectra measurements, was found as a solid product. The formula was confirmed by its behaviour. The compound is stable in air as a solid. It is soluble in water, acetone, methanol, ethanol, and acetonitrile. The solutions are unstable and spontaneously decompose over time, even in the absence of air. This finding is in accord with results reported in the literature, describing the reactivity and instability of [Rh(Hdopn)(Cl)$_2$] [19].

Addition of a 10-fold excess of the X anion to the solution of **1** changes its colour from pale yellow to dark yellow, red-orange, red, and dark red for Cl$^-$, Br$^-$, SCN$^-$, and I$^-$, respectively. The substitution reactions proceed immediately under conditions described in Section 2. The patterns of all the electronic spectra are similar and the observed shifts correspond to the positions of ligands in a spectrochemical series (Fig. 2, Table 2).

Rapid substitution of X$^-$ in **1** confirms the Rh(II) oxidation state in this dimer. It is well known that substitutions in Rh(III) compounds are generally slow [48], whereas they take place easily in different Rh(II) dimers [22c,23d].

The highest energy band is assigned to an intraligand $\pi \rightarrow \pi^*$ transition of the C=N group, by analogy to the results reported for rhodium [49], ruthenium [50], cobalt [51], and other related α-dioximato compounds [52].

On the basis of the high extinction coefficients, the peaks and shoulders between 300 and 500 nm are ascribed to 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 [50]. The red shift of bands in the 300–500 nm range registered for the complexes presented in this paper, in line with the position of ligands in the spectrochemical series, resembles

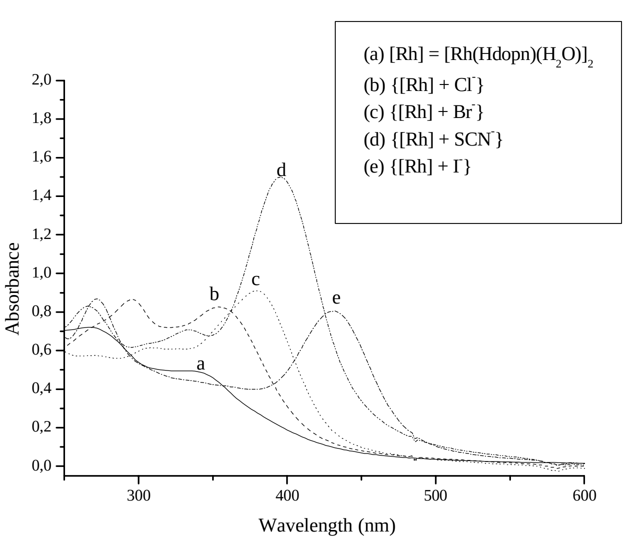

Fig. 2. UV–vis spectra for reactions of **1** with X$^-$ in CH_3OH solution, (X$^-$ = Cl, Br, SCN, I).

Table 2
Electronic absorption spectra for **1**, [Rh(Hdopn)X]$_2$ and **3**

Complex	X[a]	λ_{max}, nm (ε, L mol^{-1} cm^{-1} × 10^{-2})
[Rh(Hdopn)(H$_2$O)]$_2$(ClO$_4$)$_2$[a]		266 (157), 334 (105)
[Rh(Hdopn)(X)]$_2$[a]	Cl$^-$	275 sh, 296 (170), 354 (163)
	Br$^-$	236 sh, 310 sh, 378 (182)
	SCN$^-$	266 (166), 335 sh, 396 (240)
	I$^-$	272 (172), 432 (162)
[Rh(dopn)(I)$_2$][b]		274 (362), 352 (111)

[a] In methanol at ambient temperature, in an N_2 atmosphere.
[b] In CH_2Cl_2.

a similar effect observed for dinuclear rhodium(II) carboxylates and indicates the involvement of [Rh(II)–Rh(II)] core orbitals in the bonding of axial ligands.

Measurements of the UV–vis spectra over time revealed that both **1** and its substitution products are unstable even under an N_2 atmosphere (Fig. 3).

The substitution reaction of $[Rh(Hdopn)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ (**1**) with NaCl afforded a Rh(II) dimer, $[Rh(Hdopn)Cl]_2 \cdot 0.5H_2O$ (**2**). The isolation of this chloride adduct confirms the binuclear composition of **1**. The limited stability of the solutions of **1** and its halide derivatives demonstrates a high reactivity of the Rh(II) compounds studied and can account for the low yields of **1** and **2**.

The complex $[Rh(Hdopn)(I)_2]$ (**3**) was isolated as the final product of the reaction of **1** with NaI. Contrary to **1** and **2**, compound **3** is stable both as a solid and in solutions. It is only sparingly soluble in MeOH and EtOH, but dissolves in $CHCl_3$ and CH_2Cl_2.

The perchlorate salt (**1**) shows a strong band between 1087 and 1122 cm^{-1} (antisymmetric stretch) and a sharp band of medium intensity at 631 cm^{-1} (antisymmetric bend) indicative of uncoordinated perchlorate anions. Based on earlier reports [52,53], the N–O absorptions in the 1100–1128 and 1258–1268 cm^{-1} ranges are assignable to the ν(NO) stretching vibration. The first N–O infrared absorption could not be observed for **1** because of the occasional superposition of the bands originating from the perchlorate anions. For complexes **2** and **3**, the first N–O stretch was registered at 1121 and 1128 cm^{-1}, respectively. The bands in the wavenumber regions 1420–1491 and 1587–1605 $cm^{-}1$ are assigned to the ν(CN) vibrations for the oxime and imine groups, respectively [52]. Chaudhuri and co-workers [52] revealed that the ν(CN) vibration of the oxime group for complexes with $Hdopn^-$ ligand, containing divalent metal, was situated at a frequency significantly lower that that for the compounds containing the corresponding trivalent metal ions. Moreover, it has been shown that C=N vibrations are not pure CN stretches and can be due to the weakening of the back donation from the metal towards the equatorial ligand, to the effect of the intermolecular hydrogen bonds on the equatorial oxygen's electron density [51,52] as well as to the influence of axial ligands [5]. These findings indicate that the interpretation of such data requires great care.

The band around 3325 cm^{-1}, in Nujol mulls, indicates the presence of O–H bands attributed to the O–H···O hydrogen bonds in the frame of the Hdopn monoanion as well as to coordinated water molecules.

The two couples of equivalent methyls of the $Hdopn^-$ ligand resonate at different frequencies (Table 3). The

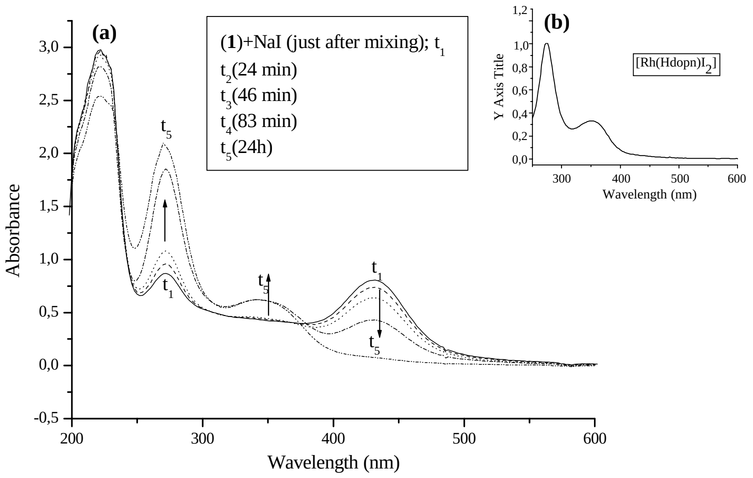

Fig. 3. Superimposed UV–vis spectra of (a) conversion of $[Rh(Hdopn)I]_2$ over time (MeOH, N_2) and (inset b) complex **3** (CH_2Cl_2, air); $[Rh_2] = 2.5 \times 10^{-4}$ M.

Table 3
^1H NMR spectral data for **1** and **2**, interaction of **1** with Br^- and I^-, and complex **3**

	O–N=C–CH_3	C–N=C–CH_3	N–CH_2–C–CH_2–N	N–C–CH_2–C–N
1[b]	2.31	2.41	3.44, 4.08	[a]
2[b]	2.29	2.40	3.53, 4.09	[a]
1 + Br^{-b}	2.26	2.37	3.48, 4.05	[a]
1 + I^{-b}	2.24	2.36	3.42, 4.08	[a]
3[c]	2.37	2.35	4.08	2.69

[a] ^1H NMR signals from the N–C–CH_2–C–N protons were obscured by the stronger O–N=C–CH_3 and C–N=C–CH_3 signals.
[b] D_2O.
[c] CD_2Cl_2.

singlets in the regions 2.24–2.37 and 2.35–2.41 ppm are assigned to methyls of the CH_3–C=N–O and CH_3–C=N–C fragments, respectively. The CH_3 protons are shown to be shifted upfield in the order: $H_2O < Cl < Br < I$. An analogous trend has been demonstrated for dimethylglioximates of cobalt [54]. The propylene bridge protons give complex multiplets. The broad resonance at 2.69 ppm for **3** is due to the central methylenes. The multiplets between 4.02 and 4.08 ppm can be ascribed to the N–CH_2 protons. Similar signals in ^{1}H NMR spectra have been found for related compounds of rhodium [18,19d] and cobalt [55]. Hydrogen-bonded proton resonances could not be observed owing to the fast exchange with the water of the solvents.

3.2. Description of the crystal structures

Molecular structures of compounds **2** and **3** are depicted in Figs. 4 and 5, respectively. Selected bond lengths and angles are listed in Tables 4 and 5, respectively.

Complex **2** consists of two equivalent [Rh(Hdopn)Cl] halves linked by an Rh–Rh bond. The Rh(II) ions are coordinated by a disordered octahedral array of a tet-

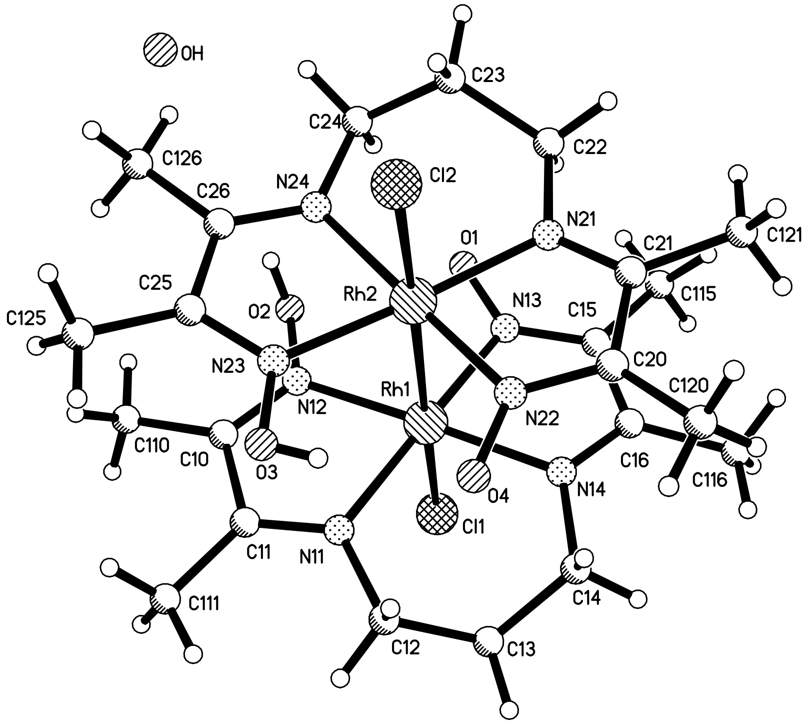

Fig. 4. Molecular structure scheme of $[Rh(Hdopn)Cl]_2$ (**2**).

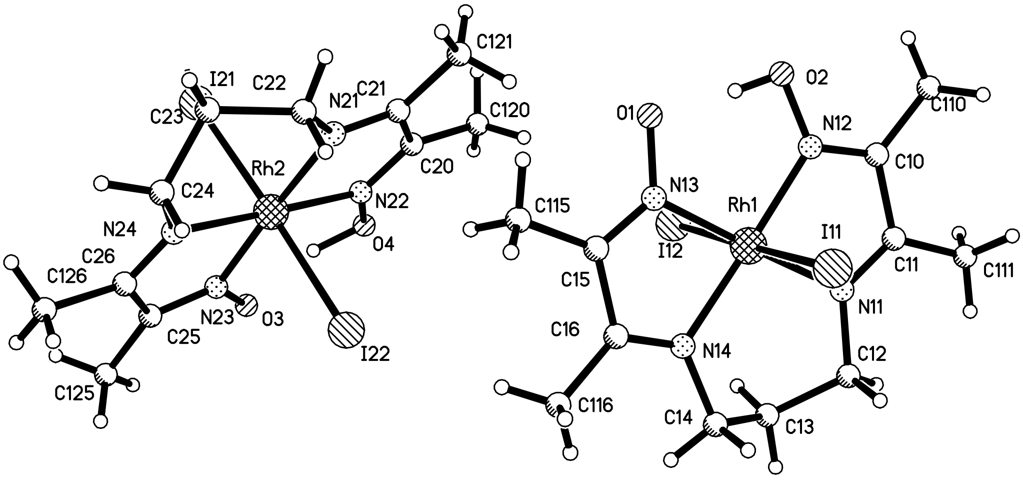

Fig. 5. Molecular structure of $[Rh\ (Hdopn)(I)_2]$ (**3**), with labelling scheme.

Table 4
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Rh(1)–N(13)	1.976(7)	Rh(2)–N(22)	1.961(7)
Rh(1)–N(12)	1.978(7)	Rh(2)–N(21)	1.981(7)
Rh(1)–N(14)	2.000(6)	Rh(2)–N(23)	1.984(7)
Rh(1)–N(11)	2.014(7)	Rh(2)–N(24)	2.006(7)
Rh(1)–Cl(1)	2.487(2)	Rh(2)–Cl(2)	2.479(2)
Rh(1)–Rh(2)	2.7599(9)		
O(1)–N(13)	1.336(10)	O(4)–N(22)	1.324(9)
O(2)–N(12)	1.345(10)	O(3)–N(23)	1.341(9)
N(14)–C(16)	1.305(11)	N(24)–C(26)	1.290(12)
N(14)–C(14)	1.461(11)	N(24)–C(24)	1.482(12)
N(13)–C(15)	1.293(12)	N(23)–C(25)	1.308(12)
N(12)–C(10)	1.277(12)	N(22)–C(20)	1.300(11)
N(11)–C(11)	1.304(11)	N(21)–C(21)	1.298(12)
N(11)–C(12)	1.460(12)	N(21)–C(22)	1.457(12)
Bond angles			
N(13)–Rh(1)–N(12)	99.9(3)	N(22)–Rh(2)–N(21)	79.4(3)
N(13)–Rh(1)–N(14)	79.5(3)	N(22)–Rh(2)–N(23)	100.1(3)
N(12)–Rh(1)–N(14)	175.6(3)	N(21)–Rh(2)–N(23)	174.8(3)
N(13)–Rh(1)–N(11)	175.2(3)	N(22)–Rh(2)–N(24)	175.3(3)
N(12)–Rh(1)–N(11)	78.9(3)	N(21)–Rh(2)–N(24)	101.7(3)
N(14)–Rh(1)–N(11)	101.3(3)	N(23)–Rh(2)–N(24)	78.3(3)
N(13)–Rh(1)–Cl(1)	85.1(2)	N(22)–Rh(2)–Cl(2)	86.01(19)
N(12)–Rh(1)–Cl(1)	87.94(19)	N(21)–Rh(2)–Cl(2)	89.8(2)
N(14)–Rh(1)–Cl(1)	87.66(18)	N(23)–Rh(2)–Cl(2)	85.02(19)
N(11)–Rh(1)–Cl(1)	90.2(2)	N(24)–Rh(2)–Cl(2)	89.4(2)
N(13)–Rh(1)–Rh(2)	92.9(2)	N(22)–Rh(2)–Rh(1)	92.33(19)
N(12)–Rh(1)–Rh(2)	91.62(19)	N(21)–Rh(2)–Rh(1)	92.55(19)
N(14)–Rh(1)–Rh(2)	92.77(17)	N(23)–Rh(2)–Rh(1)	92.67(19)
N(11)–Rh(1)–Rh(2)	91.7(2)	N(24)–Rh(2)–Rh(1)	92.2(2)
Cl(1)–Rh(1)–Rh(2)	177.89(6)	Cl(2)–Rh(2)–Rh(1)	176.86(6)

radentate Hdopn$^-$ anion, one chloride, and a bond to another rhodium. The metal centres are displaced inwards toward each other from the planes of nitrogen atoms of the Hdopn$^-$ ligands. This displacement serves to minimize steric repulsions between the macrocylic ligands and causes a shortening of the Rh–Rh bond length. The Rh–Rh distance of 2.7599(9) Å in **2** is shorter than that found for $[Rh(Hdmg)_2(PPh_3)]_2$, 2.936(2) Å [20b] and $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, 2.852(3) Å [20a] but longer than the value of 2.625(2) Å in $[Rh(C_{22}H_{22}N_4)]_2$ [23d]. The Rh–Cl axial bond length with a mean value of 2.484(2) Å is shorter than that estimated for $Li_2[Rh(CH_3COO)_2Cl]_2$, 2.601(1) Å [56]. A comparison of the structural parameters obtained for **2** with those presented in Table 6 indicates the intense trans effect of the Rh–Rh bond. Simultaneously, the cis effect of equatorial ligands on the Rh–Rh separations is also demonstrated. This is in agreement with data described for binuclear rhodium(II) carboxylates [23d,57]. The mean Rh–N distance of 1.987(7) Å is in the range found for $[Rh(Hdmg)_2(PPh_3)]_2$, 1.990(2) [20b]; $[Rh(Hdmg)(CH_3COO)(PPh_3)]_2$, 1.947(5) [20c], and $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, 2.01(2) Å [20a]. The distances O1···O2 and O3···O4, 2.577(10) and 2.613(9) Å, respectively, correspond to O atoms in O–H···O bridges.

Complex **3** crystallizes as discrete molecules in which the Rh atom has a disordered octahedral environment, with two oxime and two imine nitrogens from the tetradentate ligand in a square-plane arrangement and two iodo anions in *trans* positions (Fig. 5). Two independent molecules of **3** are located in an asymmetric unit. Selected distances and angles are given in Table 5. The displacements of Rh out of the planes N11N12N13N14 and N21N22N23N24 are 0.012 (2) and 0.001(2) Å, respectively. The six-membered rings Rh1N14C14C13C12N11, Rh2N24C24C23C22N21 are puckered with C13 and C23 positioned at 0.686(6) and 0.668(6) Å out of the ring mean planes, respectively. This produces an overall "chair" conformation of the ligand. The average Rh–N length of 1.993(4) Å for **3** is 0.1 Å longer than the corresponding Rh–N distance in $[Rh\{C_2(DO)(DOBF_2)\}CH_3PPh_3]$ (where $C_2(DO)(DOBF_2)$ – monoanion of difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate) [19a] and similar to those found for $[Rh(Hdmg)_2(PPh_3)]_2$, 1.990(2) Å [20b], and $[Rh(Hdmg)(PPh_3)Cl]$, 1.992 (4) Å [15]. The Rh–I axial separation of 2.6513(6) Å (av) for **3** follows the trend of covalent radii, Cl < I, and are in line with those found for $[Rh(Hdmg)_2(PPh_3)Cl]$, 2.381(1) Å [15], and $[Rh(Hdmg)_2(PPh_3)I)]$, 2.6879(5) Å [58], as well as for $[Rh(Hdmg)_2pyCl]$ and $[Rh(Hdmg)_2pyI]$, 2.3290(4)

Table 5
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Rh(1)–N(13)	1.978(4)	Rh(2)–N(23)	1.982(4)
Rh(1)–N(12)	1.979(4)	Rh(2)–N(22)	1.987(4)
Rh(1)–N(11)	1.997(4)	Rh(2)–N(24)	1.992(4)
Rh(1)–N(14)	2.008(4)	Rh(2)–N(21)	2.013(4)
Rh(1)–I(12)	2.6484(6)	Rh(2)–I(22)	2.6567(6)
Rh(1)–I(11)	2.6573(6)	Rh(2)–I(22)	2.6567(6)
N(11)–C(11)	1.301(6)	N(22)–C(20)	1.291(5)
N(11)–C(12)	1.473(5)	N(22)–O(4)	1.355(4)
N(21)–C(21)	1.280(6)	N(13)–C(15)	1.305(6)
N(21)–C(22)	1.474(5)	N(13)–O(1)	1.337(5)
N(23)–C(25)	1.311(6)	N(24)–C(26)	1.302(5)
N(23)–O(3)	1.320(4)	N(24)–C(24)	1.466(6)
N(14)–C(16)	1.278(5)	N(12)–C(10)	1.296(5)
N(14)–C(14)	1.471(5)	N(12)–O(2)	1.340(4)
Bond angles			
N(13)–Rh(1)–N(12)	99.78(15)	N(23)–Rh(2)–N(22)	99.90(15)
N(13)–Rh(1)–N(11)	178.37(15)	N(23)–Rh(2)–N(24)	79.66(15)
N(12)–Rh(1)–N(11)	78.97(15)	N(22)–Rh(2)–N(24)	178.67(15)
N(13)–Rh(1)–N(14)	78.58(15)	N(23)–Rh(2)–N(21)	177.83(15)
N(12)–Rh(1)–N(14)	178.31(15)	N(22)–Rh(2)–N(21)	78.29(15)
N(11)–Rh(1)–N(14)	102.67(15)	N(24)–Rh(2)–N(21)	102.17(15)
N(13)–Rh(1)–I(12)	89.68(11)	N(23)–Rh(2)–I(21)	88.62(11)
N(12)–Rh(1)–I(12)	88.44(11)	N(22)–Rh(2)–I(21)	89.07(10)
N(11)–Rh(1)–I(12)	91.31(10)	N(24)–Rh(2)–I(21)	89.67(11)
N(14)–Rh(1)–I(12)	91.92(10)	N(21)–Rh(2)–I(21)	92.53(10)
N(13)–Rh(1)–I(11)	89.37(11)	N(23)–Rh(2)–I(22)	90.40(11)
N(12)–Rh(1)–I(11)	91.25(11)	N(22)–Rh(2)–I(22)	92.29(10)
N(11)–Rh(1)–I(11)	89.62(10)	N(24)–Rh(2)–I(22)	88.97(11)
N(14)–Rh(1)–I(11)	88.37(10)	N(21)–Rh(2)–I(22)	88.49(10)
I(12)–Rh(1)–I(11)	178.934(18)	I(21)–Rh(2)–I(22)	178.443(18)

Table 6
Selected bond lengths in binuclear rhodium(II) complexes (Å)

Compound	Rh–Rh	Rh–L	Ref.
$Li_2[Rh(CH_3COO)_2Cl]_2$	2.397(1)	2.601(1)	[56]
$[Rh(Hdmg)(CH_3COO)(PPh_3)]_2$	2.618(5)	2.485(9)	[20c]
$[Rh(C_{22}H_{22}N_4)]_2$[a]	2.625(2)	–	[23d]
$[Rh(Hdopn)Cl]_2$	2.7599(9)	2.484(2)	this work
$[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$	2.852(3)	2.431(9)	[20a]
$[Rh(Hdmg)_2(PPh_3)]_2$	2.936(2)	2.438(4)	[20b]

[a] $C_{22}H_{24}N_4$, tetraaza[14]annulene ligand.

and 2.6423(4) Å, respectively [59]. The I–Rh–I fragments are characterized by angles of 178.93(2)° and 178.44(2)°.

The O···O contacts in O–H···O bridges are 2.543 (5) and 2.582(5) Å for O1···O2 and O3···O4. These values are significantly shorter than the mean value of 2.615 Å in rhodoximes with the $(Hdmg)_2$ equatorial ligand [5,21] but longer than that of 2.446 (av) Å reported for related Co complexes [55a,55c,55d].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. CCDC-209371 for **2** and CCDC-209372 for **3**.

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