

and also as monoanionic dioximates via dissociation of one oxime proton [10,11]. They are also known to act as bridging ligands via coordination through the oxygens [12–15]. While coordination chemistry of the dioxime ligands has been extensively studied with the 3d metal ions [16–20], the dioxime chemistry of ruthenium has not been much explored [21–26]. Herein we report the chemistry of some mono and bis-dioxime complexes of ruthenium(II), where triphenylphosphine (PPh₃) has been used as the coligand. Triphenylphosphine is also a familiar π -acceptor ligand and hence its coordination is expected to result in some interesting effect on the π interaction with the dioxime ligand as well as on the stereochemistry of the complexes. In the present work, the chemistry of dioxime complexes of type [Ru(PPh₃)₂(H₂L)Cl₂] and [Ru(PPh₃)₂(HL)₂] has been studied. The chemistry of the bis-dioximate complexes of transition metal ions has been attracting continuous attention because of their importance with reference to models for vitamin B₁₂ [27–29], dioxygen carriers [30], catalysis in chemical transformations [31–33], intramolecular hydrogen bonding and metal–metal interaction [34–36]. The synthesis, structure, spectroscopic and electron-transfer properties of these complexes have been described in this paper with special emphasis on the π -interaction between dioxime ligands and bivalent ruthenium, and reactivities of the mono-dioxime complexes involving Ru–Cl bond cleavage.

2. Experimental

2.1. Materials

Commercial ruthenium trichloride (Arora Matthey, Calcutta, India) was converted to RuCl₃·3H₂O by repeated evaporation with concentrated hydrochloric acid. Triphenylphosphine (PPh₃) was purchased from Loba Chemie, Mumbai, India. Dimethylglyoxime (H₂dmg) and diphenylglyoxime (H₂dpg) were obtained from s.d. fine-chem, Mumbai, India. [Ru(PPh₃)₃Cl₂] was prepared by following a published procedure [37]. Purification of dichloromethane and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature [38,39]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Preparations

2.2.1. [Ru(PPh₃)₂(H₂dmg)Cl₂]

Dichloromethane (50 cm³) was added to a mixture of [Ru(PPh₃)₃Cl₂] (100 mg, 0.10 mmol) and H₂dmg (18 mg, 0.15 mmol). The resulting red solution was stirred for 1 h. Upon evaporating the solvent, a solid residue

was obtained which was washed thoroughly with ethanol and dried in air. Recrystallization from dichloromethane–hexane solution gave [Ru(PPh₃)₂(H₂dmg)Cl₂] as a crystalline brown solid. The yield was 83 mg (70%). *Anal. Calc.* for C₄₀H₃₈Cl₂N₂O₂P₂Ru: C, 59.11; H, 4.68; N, 3.45. Found: C, 59.14; H, 4.71; N, 3.43%.

2.2.2. [Ru(PPh₃)₂(H₂dpg)Cl₂]

This was synthesized by following the same above procedure and in the same above scale using diphenylglyoxime instead of dimethylglyoxime. [Ru(PPh₃)₂(H₂dpg)Cl₂] was obtained as a microcrystalline brown solid. The yield was 71 mg (73%). *Anal. Calc.* for C₅₀H₄₂Cl₂N₂O₂P₂Ru: C, 64.17; H, 4.49; N, 2.99. Found: C, 64.14; H, 4.46; N, 2.97%.

2.2.3. [Ru(PPh₃)₂(Hdmg)₂]

Method A: [Ru(PPh₃)₃Cl₂] (100 mg 0.10 mmol) was taken in ethanol (50 cm³) and dimethylglyoxime (30 mg, 0.26 mmol) was added to it followed by triethylamine (16 mg, 0.16 mmol). The mixture was refluxed for 1 h. Upon partial evaporation of the solution, [Ru(PPh₃)₂(Hdmg)₂] started to precipitate as a bright orange crystalline solid. It was collected by filtration, washed thoroughly with ethanol and dried in air. Recrystallization from dichloromethane–hexane solution gave [Ru(PPh₃)₂(Hdmg)₂] as a bright orange crystalline solid. The yield was 56 mg (63%). *Anal. Calc.* for C₄₄H₄₄N₄O₄P₂Ru: C, 61.75; H, 5.15; N, 6.55. Found: C, 61.78; H, 5.13; N, 6.57%.

Method B: to a solution of [Ru(PPh₃)₂(H₂dmg)Cl₂] (100 mg, 0.10 mmol) in dichloromethane (30 cm³) was added dimethylglyoxime (18 mg, 0.15 mmol) followed by triethylamine (16 mg, 0.16 mmol). The resulting solution was stirred for 1 h. The color of the solution gradually changed from brown to orange. Upon evaporating the solvent a bright orange crystalline solid was obtained, which was thoroughly washed with water and dried in vacuo over P₄O₁₀. Recrystallization from dichloromethane–hexane solution gave [Ru(PPh₃)₂(Hdmg)₂] as a bright orange crystalline red solid. The yield was 53 mg (60%).

2.2.4. [Ru(PPh₃)₂(Hdpg)₂]

This was synthesized by following the same above procedures and in the same above scales. In method A diphenylglyoxime was used instead of dimethylglyoxime and in method B [Ru(PPh₃)₂(H₂dpg)Cl₂] and H₂dpg were used instead of [Ru(PPh₃)₂(H₂dmg)Cl₂] and H₂dmg, respectively. [Ru(PPh₃)₂(Hdpg)₂] was obtained as a bright-orange crystalline solid. The yield was 69 mg (60%). *Anal. Calc.* for C₆₄H₅₂N₄O₄P₂Ru: C, 69.62; H, 4.89; N, 5.08. Found: C, 69.62; H, 4.91; N, 5.06%.

2.2.5. [Ru(PPh₃)₂(Hdpg)(Hdmg)]

Method A: to a solution of [Ru(PPh₃)₂(H₂dpg)Cl₂] (100 mg, 0.10 mmol) in dichloromethane (30 cm³) was added dimethylglyoxime (18 mg, 0.15 mmol) followed by triethylamine (16 mg, 0.16 mmol). The resulting solution was stirred for 1 h. The color of the solution gradually changed from yellowish–orange to red. Upon evaporating the solvent a solid residue was obtained, which was thoroughly washed with water and dried in vacuo over P₄O₁₀. Recrystallization from dichloromethane–hexane solution gave [Ru(PPh₃)₂(Hdpg)(Hdmg)] as a crystalline red solid. The yield was 80 mg (82%). *Anal. Calc.* for C₅₄H₅₀N₄O₄P₂Ru: C, 66.05; H, 5.09; N, 5.70. *Found:* C, 66.07; H, 5.05; N, 5.68%.

Method B: the same above procedure and scale were followed using [Ru(PPh₃)₂(H₂dmg)Cl₂] and diphenylglyoxime instead of [Ru(PPh₃)₂(H₂dpg)Cl₂] and dimethylglyoxime respectively. [Ru(PPh₃)₂(Hdpg)(Hdmg)] was obtained as a crystalline red solid. The yield was 79 mg (78%).

2.2.6. [Ru(PPh₃)₂(H₂dpg)(pic)]ClO₄

An ethanolic solution (30 cm³) of picolinic acid (13 mg, 0.10 mmol) was added to a solution of [Ru(PPh₃)₂(H₂dpg)Cl₂] (100 mg, 0.10 mmol) in dichloromethane (50 cm³). To it triethylamine (16 mg, 0.16 mmol) was added and the resulting solution was initially heated gently to expel dichloromethane as much as possible. The solution was then refluxed for 6 h. The color of the solution changed from yellowish–orange to red. The solution was allowed to cool to room temperature (25°C) and a saturated aqueous solution of sodium perchlorate (0.5 cm³) was added to it. Upon partial evaporation of the solution, a solid

residue was obtained, which was washed thoroughly with cold water and dried in vacuo over P₄O₁₀. Recrystallization from dichloromethane–hexane gave [Ru(PPh₃)₂(H₂dpg)(pic)]ClO₄ as a crystalline red solid. The yield was 87 mg (75%). *Anal. Calc.* for C₅₆H₄₆ClN₃O₈P₂Ru: C, 61.90; H, 4.23; N, 3.87. *Found:* C, 61.93; H, 4.22; N, 3.90%.

2.2.7. [Ru(PPh₃)₂(H₂dpg)(q)]ClO₄

This was synthesized by following the above procedure and scale using 8-hydroxyquinoline (Hq) instead of picolinic acid. [Ru(PPh₃)₂(H₂dpg)(q)]ClO₄ was obtained as a microcrystalline red solid. The yield was 86 mg (73%). *Anal. Calc.* for C₅₉H₄₈ClN₃O₇P₂Ru: C, 63.92; H, 4.33; N, 3.79. *Found:* C, 63.90; H, 4.35; N, 3.78%.

2.2.8. [Ru(PPh₃)₂(H₂dpg)(nn)]ClO₄

This was synthesized by following the same procedure and scale used for the synthesis of [Ru(PPh₃)₂(H₂dpg)(pic)]ClO₄ using 1-nitroso-2-naphthol (Hnn) instead of picolinic acid. [Ru(PPh₃)₂(H₂dpg)(nn)]ClO₄ was obtained as a crystalline red solid. The yield was 92 mg (76%). *Anal. Calc.* for C₆₀H₄₈ClN₃O₈P₂Ru: C, 63.40; H, 4.22; N, 3.70. *Found:* C, 63.41; H, 4.25; N, 3.68%.

2.3. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin–Elmer 783 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV 240 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 Vibrating sample magnetometer. ¹H NMR spectra were recorded on a Bruker AC-200 NMR spectrometer using TMS as the internal standard. Solution electrical conductivities were measured using a Phillips PR 9500 bridge with a solute concentration of 10^{−3} M. Electrochemical measurements were made using a PAR model 273 potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. A RE 0089 X–Y recorder was used to trace the voltammograms.

2.4. Crystallography

[Ru(PPh₃)₂(H₂dpg)Cl₂]. Single crystals of [Ru(PPh₃)₂(H₂dpg)Cl₂] were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data were collected on an Enraf–

Table 1
Crystallographic data

	[Ru(PPh ₃) ₂ (H ₂ dpg)Cl ₂]	[Ru(PPh ₃) ₂ (Hdmg) ₂]
Empirical formula	C ₅₀ H ₄₄ N ₂ O ₃ P ₂ Cl ₂ Ru	C ₄₄ H ₄₄ N ₄ O ₄ P ₂ Ru
Formula weight	954.82	855.87
Space group	orthorhombic, P2 ₁ 2 ₁ 2 ₁	monoclinic, P2 ₁ /c
<i>a</i> (Å)	12.026(3)	8.6568(21)
<i>b</i> (Å)	17.5853(22)	16.024(3)
<i>c</i> (Å)	21.194(3)	13.8305(22)
<i>V</i> (Å ³)	4482.0(13)	1884.2(6)
<i>Z</i>	4	2
<i>λ</i> (Å)	0.71073	0.7107
Crystal size (mm)	0.50 × 0.13 × 0.05	0.10 × 0.15 × 0.38
<i>T</i> (°C)	25	25
<i>μ</i> (cm ^{−1})	5.727	5.394
<i>R</i> _F	0.039 ^a	0.036 ^a
<i>R</i> _w	0.036 ^b	0.037 ^b
Goodness-of-fit	1.21 ^c	1.36 ^c

^a $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

^c Goodness-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (M - N)]^{1/2}$, where *M* is the number of reflections and *N* is the number of parameters refined.

Nonius CAD-4 diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Three standard reflections measured every 3600 s of X-ray exposure showed no significant intensity variation over the course of data collection. X-ray data reduction, structure solution and refinement were done using the NRCVAX package [40].

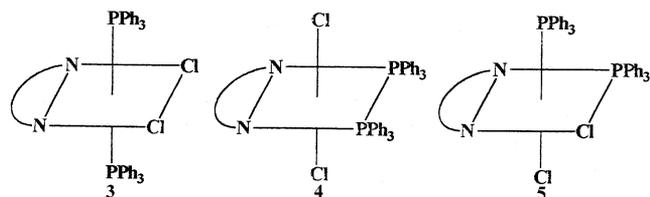
[Ru(PPh₃)₂(Hdmg)₂]. Single crystals of [Ru(PPh₃)₂(Hdmg)₂] were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data collection and structure solution and refinement were done as described above.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. [Ru(PPh₃)₂(H₂L)Cl₂] complexes

Reaction of the dioxime ligands (H₂L) with [Ru(PPh₃)₃Cl₂] affords, under different experimental conditions, different products. Simple reaction of the dioxime ligands with [Ru(PPh₃)₃Cl₂] in 1:1 mole ratio in dichloromethane solution at ambient temperature yields complexes of type [Ru(PPh₃)₂(H₂L)Cl₂]. It is interesting to note that the dioxime ligands do not undergo any proton loss during complexation. Elemental (C, H, N) analytical data agree well with the proposed composition of the complexes. These complexes are diamagnetic which corresponds to the bivalent state of ruthenium (low-spin d⁶, $S = 0$) in these complexes. As the dioxime ligands are symmetric in nature, the [Ru(PPh₃)₂(H₂L)Cl₂] complexes may exist in three geometrical isomeric forms (3–5). To find out the stereochemistry, structure of [Ru(PPh₃)₂(H₂dpg)Cl₂] has been determined by X-ray crystallography.



The structure is shown in Fig. 1 and selected bond parameters are listed in Table 2. The diphenylglyoxime ligand is coordinated to ruthenium as a neutral bidentate *N,N*-donor ligand forming five-membered chelate ring with a bite angle of 76.7(2)°. The two PPh₃ ligands are mutually trans and the two chlorides are mutually *cis* and therefore Ru(PPh₃)₂(H₂dpg)Cl₂ has structure 3. Ruthenium is sitting in a N₂P₂Cl₂ coordination sphere which is distorted significantly from ideal octahedral geometry as reflected in the bond parameters around ruthenium. While the Ru–P and Ru–Cl bond distances are quite normal [41–44], the Ru–N lengths are notice-

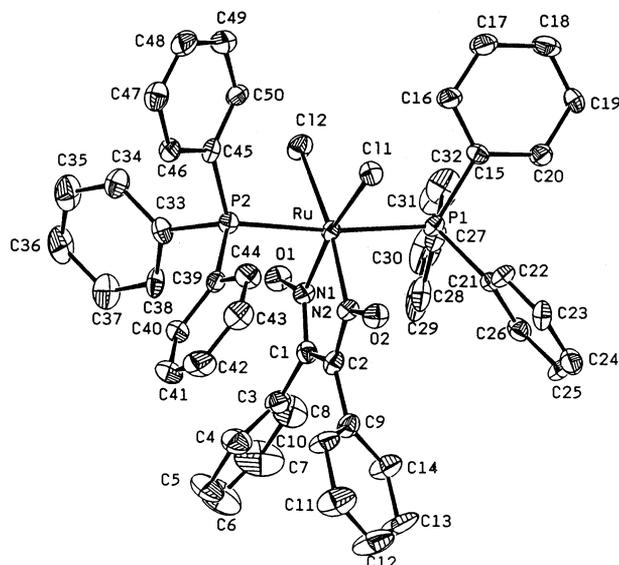


Fig. 1. View of the [Ru(PPh₃)₂(H₂dpg)Cl₂] molecule.

ably shorter than the known Ru(II)–N lengths where the N-donor ligand is not involved in π -interaction with the metal [45–49]. The C–N lengths within the coordinated dioxime ligands are also significantly longer than localized C=N bond [50]. The decrease in Ru–N distance and increase in C–N distance within the ruthenium–dioxime chelate clearly indicate strong π -interaction between ruthenium and the diimine fragment of the dioxime ligands. In complexes of ruthenium(II) containing the Ru(PPh₃)₂ moiety, the PPh₃ ligands usually take up mutually *cis* positions because of favorable π -interaction [51–53]. In [Ru(PPh₃)₂(H₂dpg)Cl₂], the H₂dpg ligand appears to function as a better π -acid by virtue of having the diimine fragment (as also observed in the structural characterization of [Ru(PPh₃)₂(H₂dpg)Cl₂]) and hence forces the bulky PPh₃ ligands to mutually trans positions for less steric hindrance. As properties of the two [Ru(PPh₃)₂(H₂L)Cl₂] complexes are similar (vide infra), the [Ru(PPh₃)₂(H₂dmg)Cl₂] complex is assumed to have a similar structure (3) like [Ru(PPh₃)₂(H₂dpg)Cl₂].

Infrared spectra of the [Ru(PPh₃)₂(H₂L)Cl₂] complexes show strong vibrations due to the Ru(PPh₃)₂ fragment near 520, 695 and 740 cm⁻¹ [54,55]. A sharp band observed near 1030 cm⁻¹ in both the complexes is assigned to the ν (N–O) vibration. The ν (O–H) stretches appear near 3400 cm⁻¹ and the ν (Ru–Cl) vibrations are observed at 310–335 cm⁻¹. The [Ru(PPh₃)₂(H₂L)Cl₂] complexes are moderately soluble in common organic solvents like dichloromethane, chloroform, acetone, etc. producing red solutions. ¹H NMR spectra of these complexes have been recorded in CDCl₃ solution. An isolated signal, observed near 10.5 ppm in both the complexes, is assigned to the oxime

Table 2

Selected bond lengths (Å) and bond angles (°) for [Ru(PPh₃)₂(H₂dpg)Cl₂] and [Ru(PPh₃)₂(Hdmg)₂]

[Ru(PPh ₃) ₂ (H ₂ dpg)Cl ₂]			[Ru(PPh ₃) ₂ (Hdmg) ₂]				
Ru–Cl(1)	2.442(2)	O(1)–N(1)	1.376(8)	Ru–P	2.417(1)	O(1)–Ha	1.68(5)
Ru–Cl(2)	2.461(2)	O(2)–N(2)	1.379(8)	Ru–N(1)	2.030(3)	N(1)–C(2)	1.317(6)
Ru–P(1)	2.387(2)	N(1)–C(1)	1.321(10)	Ru–N(2)	2.002(3)	N(2)–C(3)	1.290(6)
Ru–P(2)	2.410(2)	N(2)–C(2)	1.322(10)	O(1)–N(1)	1.329(5)	C(2)–C(3)	1.466(7)
Ru–N(1)	1.973(5)	C(1)–C(2)	1.45(1)	O(2)–N(2)	1.387(5)	C(1)–C(2)	1.484(7)
Ru–N(2)	1.962(6)	C(1)–C(3)	1.47(1)	O(2)–H	1.15(5)	C(3)–C(4)	1.488(7)
C(2)–C(9)	1.48(1)						
P(1)–Ru–P(2)	173.1(8)	N(1)–Ru–N(2)	76.7(2)	P–Ru–Pa	179.9	N(2)–Ru–N(2a)	180.0
Cl(1)–Ru–N(1)	167.3(2)	Cl(1)–Ru–Cl(2)	102.79(8)	N(1)–Ru–N(1a)	180.0	N(1)–Ru–N(2)	77.1(1)
Cl(2)–Ru–N(2)	166.6(2)						

O–H proton. The aromatic protons are observed within 6.1–7.6 ppm. The methyl signal of the coordinated dimethylglyoxime ligand in [Ru(PPh₃)₂(H₂dmg)Cl₂] is observed as a sharp resonance at 1.92 ppm. Electronic spectra of the [Ru(PPh₃)₂(H₂L)Cl₂] complexes have been recorded in dichloromethane solution. Spectral data are presented in Table 3. Each complex shows several intense absorptions in the visible and ultraviolet region. The absorptions in the ultraviolet region are assignable to transitions involving ligand orbitals. Three absorptions are displayed by both the [Ru(PPh₃)₂(H₂L)Cl₂] complexes in the visible region, of which the lowest energy one is much weaker in intensity¹ and is assigned to the d–d (¹A₁ → ¹T₁) transition. The other probable d–d (¹A₁ → ¹T₂) transition could not be identified due to intense absorptions at higher energies. The other two intense absorptions in the visible region are probably due to allowed metal-to-ligand charge-transfer transitions. Multiple charge-transfer transitions in such mixed-ligand complexes may result from lower symmetry splitting of the metal level, the presence of different acceptor orbitals and from the mixing of singlet and triplet configurations in the excited state through spin–orbit coupling [56–59]. To have an insight into the nature of the observed charge-transfer transitions, qualitative EHMO calculations have been performed [60,61] on a model of the [Ru(PPh₃)₂(H₂L)Cl₂] complexes replacing the methyl/phenyl groups of the dioxime ligands and the phenyl groups of triphenylphosphines by hydrogen. Partial MO diagram is shown in Fig. 2. The highest occupied molecular orbital (HOMO) and the next two occupied orbitals (HOMO-1 and HOMO-2) have major contributions from the metal t₂ orbitals. Hence these three filled orbitals may be attributed to the metal t₂ orbitals. The lowest unoccupied molecular orbital (LUMO) and the next unoccupied orbital (LUMO + 1) are relatively closely spaced and these are localized almost completely

on the diimine part of the dioxime ligand. Hence these two vacant orbitals may be assumed to be imine π*-orbital of the dioxime ligands. The two charge-transfer transitions observed in the [Ru(PPh₃)₂(H₂L)Cl₂] complexes may therefore be assigned to transitions occurring from the filled metal t₂ levels to the π*-(imine)orbitals of the dioxime ligands.

Table 3

Electronic spectral and cyclic voltammetric data

Compounds	Electronic spectral data ^a λ _{max} (nm) (ε, M ⁻¹ cm ⁻¹)	Cyclic voltammetric data ^{a,b} E _{1/2} (V) (ΔE _p , mV)
[Ru(PPh ₃) ₂ (H ₂ dmg)Cl ₂]	222 (44 900), 247 (44 200), 300 °(9100), 360(9200), 440 °(1500)	0.84(80), 1.31(140)
[Ru(PPh ₃) ₂ (H ₂ dpg)Cl ₂]	232 (40 100), 278 (39 600), 312 °(6900), 406(10 200), 467 °(1100)	0.98(80), 1.38(110)
[Ru(PPh ₃) ₂ (Hdmg) ₂]	235(34 800), 260(37 400), 300 °(5700), 375(7400), 440 °(1000)	0.36(80), 0.94(120)
[Ru(PPh ₃) ₂ (Hdpg) ₂]	240(44 400), 270 °(35 400), 315 °(11 800), 406(7300), 438 °(5000)	0.52(70), 1.03(120)
[Ru(PPh ₃) ₂ (Hdmg)- (Hdpg)]	240(40 200), 254(37 600), 324 °(9400), 390(9400), 440 °(2600)	0.46(70), 1.00(100)
[Ru(PPh ₃) ₂ (H ₂ dpg)- (pic)]ClO ₄	224(82 800), 256(81 400), 328 °(18 100), 392(18 100)	0.66(70), 1.60(250)
[Ru(PPh ₃) ₂ (H ₂ dpg)- (q)]ClO ₄	224(56 600), 252 °(44 900), 292(34 200), 364(11 500)	0.60(70), 1.50(240)
[Ru(PPh ₃) ₂ (H ₂ dpg)- (nn)]ClO ₄	224(84 100), 252(71 000), 308 °(22 700), 400(5500), 490(22 200)	0.68(80), 1.42(320)

^a In dichloromethane solution.^b Supporting electrolyte, TBAP; reference electrode, SCE; E_{1/2} = 0.5(E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; ΔE_p = E_{pa} – E_{pc}; scan rate, 50 mV s⁻¹.^c Shoulder.¹ After deducting the contribution of the next intense absorption.

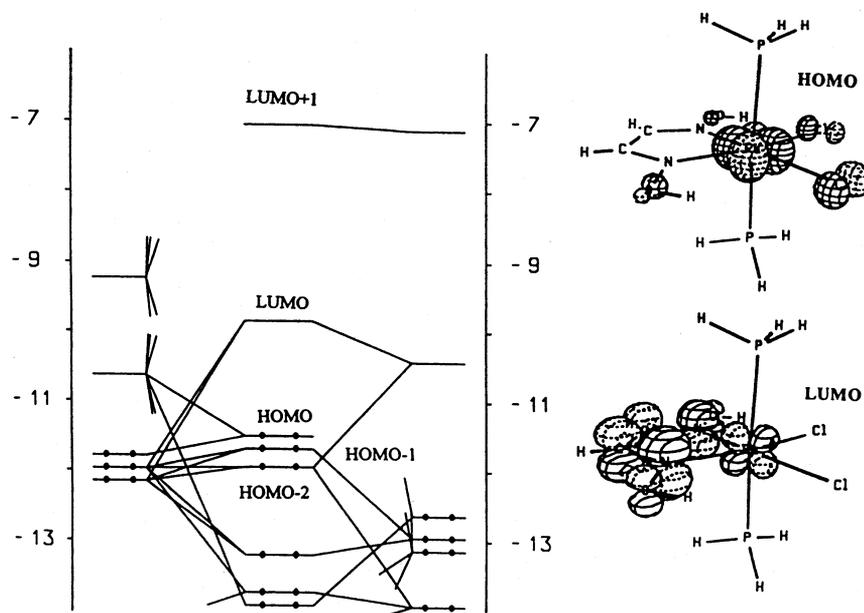


Fig. 2. Partial MO diagram of $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$.

3.1.2. $[\text{Ru}(\text{PPh}_3)_2(\text{HL})_2]$ complexes

Reaction of two moles of the dioxime ligands with one mole of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ proceeds smoothly in refluxing ethanol in the presence of a base to afford bis-dioximato complexes of type $[\text{Ru}(\text{PPh}_3)_2(\text{HL})_2]$ in decent yields. The bis-dioximato complexes can also be synthesized from $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ by reacting them with the respective dioxime ligand in presence of a base. A mixed-bis-dioximato complex, viz. $[\text{Ru}(\text{PPh}_3)_2(\text{Hdpq})(\text{Hdmg})]$, has been prepared by reacting either $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpq})\text{Cl}_2]$ or $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dmg})\text{Cl}_2]$ with H_2dmg or H_2dpq respectively in the presence of a base. Composition of the bis-dioximato complexes has been verified by their microanalytical data. All the three bis-dioximato complexes are diamagnetic, which corresponds to the +2 state of ruthenium in these complexes. The structure of $[\text{Ru}(\text{PPh}_3)_2(\text{Hdmg})_2]$ has been determined by X-ray crystallography. The structure is shown in Fig. 3 and relevant bond distances and angles are presented in Table 2. The dioxime ligands are coordinated to ruthenium, via loss of one oxime proton, as monoanionic bidentate *N,N*-donor ligands forming five-membered chelate ring with a bite angle of $77.1(1)^\circ$. The two Hdmg ligands which share the equatorial plane, are hydrogen bonded in the usual intramolecular fashion. The two PPh_3 ligands occupy mutually trans positions, the two oxime-nitrogens and the two oximate-nitrogens are also mutually trans. From the bond parameters around ruthenium, the RuN_4P_2 core appears to be much less distorted from ideal octahedral geometry relative to the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes. While the $\text{Ru}-\text{P}$ distance is normal, bond distances within the $\text{Ru}(\text{Hdmg})$

fragment are quite interesting. The two sets of $\text{Ru}-\text{N}$, $\text{C}-\text{N}$ and $\text{N}-\text{O}$ distances within the $\text{Ru}(\text{Hdmg})$ chelate are all very different. All these features indicate that deprotonation of one oxime function has made the Hdmg ligand unsymmetrical and the diimine character of it is also reduced to a great extent. The other two bis-dioximato complexes are assumed to have similar structure as $[\text{Ru}(\text{PPh}_3)_2(\text{Hdmg})_2]$ as all three bis-dioximato complexes display similar spectroscopic and electron-transfer properties (vide infra).

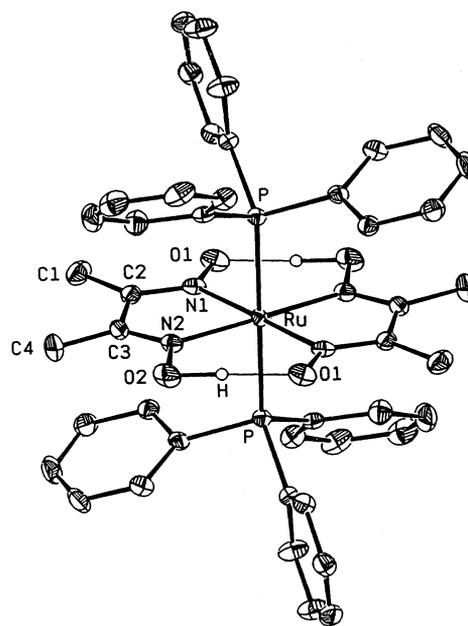


Fig. 3. View of the $[\text{Ru}(\text{PPh}_3)_2(\text{Hdmg})_2]$ molecule.

Infrared spectra of the bis-dioximato complexes show strong absorptions due to the $\text{Ru}(\text{PPh}_3)_2$ fragment near 520, 700 and 750 cm^{-1} as before. A strong band displayed near 1225 cm^{-1} by all these complexes is assigned to the $\nu(\text{N}-\text{O})$ stretch. The bis dioximato complexes are soluble in common organic solvents like dichloromethane, chloroform, etc., producing orange solutions. ^1H NMR spectra, recorded in CDCl_3 solution, show the aromatic proton signals within 7.0–8.0 ppm. An isolated resonance observed near 10.0 ppm is assigned to the oxime O–H signal. The methyl signal of the dimethylglyoximate ligand in $[\text{Ru}(\text{PPh}_3)_2(\text{Hdmg})_2]$ is observed at 2.19 ppm. Electronic spectra of these complexes have been recorded in dichloromethane solution. Spectral data are listed in Table 3. Intense absorptions are observed in both visible and ultraviolet regions. The absorptions in the ultraviolet region are believed to be occurring within the ligand orbitals. Qualitative EHMO calculations on the bis-dioximato complexes show similar results as obtained in the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes. The top three filled orbitals having predominantly ruthenium t_2 character and the first two vacant orbitals having ligand (HL) π^* -character. Hence the absorptions in the visible region are assigned to metal (t_2)-to-ligand (π^* of HL) charge-transfer transitions.

3.1.3. The $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})(\text{L}')]\text{ClO}_4$ complexes

Complexes of ruthenium(II) having a *cis*- RuCl_2 fragment have always been of particular interest with reference to their possible reactivities arising from the dissociation of the Ru–Cl bonds. The coordinated chlorides are found to be displaceable by chelating bidentate ligands under relatively mild condition. Such reactivities have already been utilized in the preparation of the bis-dioximate complexes (vide supra). Though both of the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes display similar reactivities with regard to displacement of the chlorides by bidentate chelating ligands, only the reactions of $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})\text{Cl}_2]$ are reported here. A group of three acidic ligands, viz., picolinic acid(Hpic), quinolin-8-ol(Hq) and 1-nitroso-2-naphthol(Hnn), (abbreviated in general as HL', where H stands for the acidic hydrogen) have been used for these reactions. All these ligands are known to coordinate ruthenium, via loss of the acidic proton, as bidentate N,O-donors forming five-membered chelate rings [9,62,63]. Reaction of these ligands with $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ proceeds smoothly in stirring dichloromethane in the presence of a base to afford complexes of type $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ which have been isolated as perchlorate salts in the solid state. Elemental (C, H, N) analytical data of these complexes agree well with their compositions. The $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes are diamagnetic, which indicates that ruthenium is in its +2 oxidation state in these complexes. The $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes are assumed to have a geometry similar to that

of the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})\text{Cl}_2]$ complex with the two PPh_3 ligands in mutually trans positions and the two chlorides replaced by L'.

Infrared spectra of the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes are mostly similar to the spectrum of $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})\text{Cl}_2]$, which is obviously due to presence of the common $\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})$ fragment. Some new vibrations are of course observed in the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes, of which the two vibrations uniformly displayed by all the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes near 1100 and 620 cm^{-1} , are due to the presence of perchlorate ion. The $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes are soluble in polar organic solvents like acetonitrile, dichloromethane, etc. Conductivity studies in acetonitrile solution show that these complexes behave as 1:1 electrolytes ($\Lambda_M = 1140\text{--}155\text{ }\Omega^{-1}\text{ cm}^2\text{ M}^{-1}$). ^1H NMR spectra of the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes recorded in CDCl_3 solution, show the oxime OH resonance near 10.4 ppm. The aromatic protons are observed within 6.0–8.0 ppm as overlapping signals. However, intensity measurements correspond nicely to the total number of aromatic protons in the respective complexes. Electronic spectra of the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')]\text{ClO}_4$ complexes has been recorded in dichloromethane solution (Table 3). Each complex shows intense absorptions in the visible region probably due to the allowed metal-to-ligand charge-transfer transitions. Intense absorptions are also observed in the ultraviolet region as before.

3.2. Cyclic voltammetric studies

Electrochemical properties of all the complexes have been studied by cyclic voltammetry in dichloromethane solution (0.1 M TBAP). Voltammetric data are presented in Table 3 and selected voltammograms are shown in Fig. 4. Each complex shows two one-electron oxidative responses on the positive side of SCE. The first response is assigned to ruthenium(II)–ruthenium(III) oxidation and the second to ruthenium(III)–ruthenium(IV) oxidation. One-electron nature of both the responses has been established by comparing current height of each response with that of ferrocene–ferrocenium couple under identical experimental conditions. The ruthenium(II)–ruthenium(III) oxidation is reversible, characterized by a peak-to-peak separation of 70–80 mV and the anodic-peak-current (i_{pa}) is almost equal to the cathodic-peak-current (i_{pc}). The ruthenium(III)–ruthenium(IV) oxidation is quasi-reversible. It is interesting to note here that the ruthenium(III)–ruthenium(IV) oxidation potential is rather close to the ruthenium(II)–ruthenium(III) oxidation potential than is usually observed. This closeness indicates that this second electron-transfer reaction is probably associated with proton-transfer from the ox-

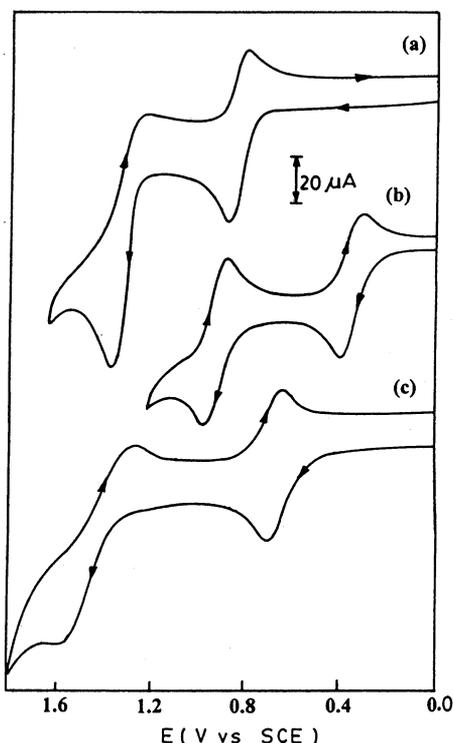
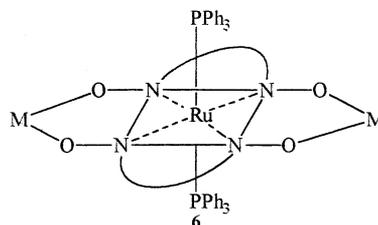


Fig. 4. Cyclic voltammograms of (a) $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dmg})\text{Cl}_2]$; (b) $[\text{Ru}(\text{PPh}_3)_2(\text{Hdmg})_2]$; and (c) $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{nn})]\text{ClO}_4$ in dichloromethane solution (0.1 M TBAP) at a scan rate of 50 mV s^{-1} .

ime function. Potential of both the oxidation is found to be quite sensitive to the composition of the complexes. In the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes, the dioxime ligands behave as efficient diimine ligands with strong π -acid character and therefore stabilizes the bivalent state of ruthenium to a great extent. This is reflected in the relatively high magnitude of ruthenium(II)–ruthenium(III) oxidation potential in these complexes. In the bis dioximato complexes the diimine character of the dioxime ligand is reduced because of deprotonation of one oxime function which results in the destabilization of the bivalent state of ruthenium, and this is reflected in the negative shift of the ruthenium(II)–ruthenium(III) oxidation potential in these complexes by more than 400 mV relative to that in the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes. The ruthenium(II)–ruthenium(III) oxidation potential in $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{dpg})(\text{L}')^+]$ complexes is observed to be lower than that in $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$. This shows that replacement of the chloride ligands by these N,O-donor ligands has stabilized the trivalent state of ruthenium and this may be primarily attributed to coordination of ruthenium by the hard oxygen (phenolate or carboxylate) center of the N–O ligands. The ruthenium(III)–ruthenium(IV) oxidation potential follows a similar trend as the ruthenium(II)–ruthenium(III) oxidation potential.

4. Conclusions

The present study shows that reaction of dioxime ligands with $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ affords stable complexes of ruthenium(II) where the dioxime ligands bind to ruthenium(II) either in the neutral dioxime form or in the monoanionic dioximate form. While the $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})\text{Cl}_2]$ complexes have been found to be useful starting material for the synthesis of complexes of type $[\text{Ru}(\text{PPh}_3)_2(\text{H}_2\text{L})(\text{L}')^+]$, the bis-dioximato complexes appear to be suitable as ‘bridging ligand’ (via dissociation of the remaining two oxime protons), in the synthesis of trinuclear complexes of type **6**.



Such possibilities are currently under exploration.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148069 and CCDC no. 148070. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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