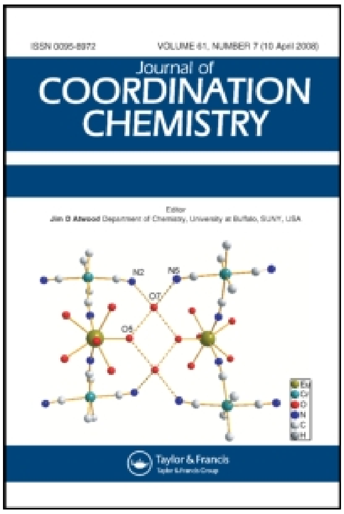

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SYNTHESIS AND CHARACTERIZATION OF A BIS(BENZILDIOXIME)RUTHENIUM(III) COMPLEX AND ITS REDUCTION WITH π-ACIDIC LIGANDS

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The synthesis of a bis(benzildioximato)ruthenium(III) complex of composition K[Ru^{III}(benzildioximato)$_2Cl_2$], **1**, is reported. The interaction of **1** with π-acidic ligands such as CO and PPh_3 results in the reduction of the metal ion and formation of the complex [Ru^{II}(benzildioximato)$_2$Cl(L)]$^{n-}$ where L = CO and PPh_3 (n = 1). The complexes were characterized by elemental analysis, IR, electronic ^{13}C [^1H], ^{31}P [^1H] NMR and EPR spectroscopy, conductance measurements and differential pulse voltammograms. The reduction potentials of the Ru(II)/Ru(I) couples in the complexes **2** and **3** (L = CO, PPh_3, respectively) become more positive with an increase in the π acidity of the ligand coordinated to the metal ion in the order CO > PPh_3.

Keywords: Ruthenium, benzildioxime, synthesis, Lewis bases, electrochemistry

INTRODUCTION

Synthesis and characterization of complexes of ruthenium with chelating nitrogen ligands is the subject of much current research.[1–4] In addition, the coordination chemistry of chelating α-dioxime ligands has been investigated with first row transition metals,[5–8] in view of their roles as analogues of biological systems such as vitamin B_{12},[9,10] dioxygen carriers[11,12] and catalysts in chemical processes.[13–15]

The reaction of $RuCl_2(PPh_3)_3$ with various dioximes such as dimethylglyoxime, 1,2-cyclohexanedione dioxime and diphenylglyoxime yielded complexes which could not be fully characterised due to poor solubility.[16]

In a continued effort to develop new catalysts for oxygenation, carbonylation and hydroformylation, we have found that ruthenium complexes with a ligand possessing σ donor and π acceptor capacities is crucial to maintain catalytic activities.[13–15] With this in mind we have synthesized potassium bis(benzildioximato)ruthenium(III), **1**, and studied its interaction with CO and PPh_3. This resulted in the reduction of the Ru(III) complex to mixed ligand Ru(II) complexes [Ru^{II}(benzildioximato)$_2$Cl(L)]$^{n-}$ (where L = CO and PPh_3, n = 1). The complexes **1**–**3** were

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characterised by elemental analysis, electronic, IR, [^{1}H], ^{13}C [^{1}H] and ^{31}P [^{1}H] spectroscopy, conductance measurements and differential pulse voltammograms.

EXPERIMENTAL

$RuCl_3 \cdot xH_2O$ was purchased from Johnson Mathey, benzildioxime and nitrosoniumtetrafluoroborate from Aldrich and triphenylphosphine from Sisco. $K_2[RuCl_5(H_2O)]$ was prepared according to the literature.[17] Solvents were dried by standard procedures and distilled prior to use. IR spectra of the complexes were recorded in KBr pellets and nujol mulls on a Specord M-80 Carl Zeiss Spectrophotometer. [^{1}H], ^{13}C [^{1}H] and ^{31}P [^{1}H] NMR spectra were obtained on a Jeol FX-100 NMR in DMSO-d_6 and $CDCl_3$ using $[Si(CH_3)_4]$ as internal standard and operating at 99.55, 24.99 and 40.27 MHz, respectively. EPR spectra were recorded on a Bruker Scientific X-band spectrometer (ESP-300) using 100 KHz field modulation and calibrated with DPPH ($g = 2.0036$). The differential pulse voltammograms were recorded with a Princeton Applied Research (PAR) instrument using a glassy carbon electrode *vs* Ag/AgCl and tetrabutylammonium perchlorate as supporting electrolyte in methanol. Microanalyses of the complexes were performed on a Carlo Erba 1106 Analyser.

K[Ru(benzildioximato)$_2$Cl$_2$] 1

A methanolic solution of benzildioxime (0.02 mol) was refluxed with $K_2[RuCl_5(H_2O)]$ (0.01 mol) for 10 to 12 hrs with constant stirring in an argon atmosphere. The resulting solution was filtered to remove KCl and was concentrated to 10 cm^3. The complex was precipitated by addition of diethylether, dissolved in the minimum quantity of methanol and passed through a silica column, eluting with methanol and benzene. The compound was obtained from the second fraction. It was dried *in vacuo*. Yield: 50%.

K[Ru(benzildioximato)(CO)Cl] 2

Some (0.01 mol) of the complex **1** in ethanol was bubbled with carbon monoxide for 8 to 10 hrs with constant stirring. The resulting solution was filtered and the filtrate concentrated to 10 cm^3 using a rotary evaporator. The complex was precipitated by diethylether and ethylacetate, filtered and dried *in vacuo*. Yield: 40%.

K[Ru(benzildioximato)(PPh$_3$)(Cl)]3

A solution of **1** (0.01 mol) in ethanol was refluxed with a slight excess of PPh_3 (0.016 mol) for 1 hr. The resulting solution was filtered, concentrated and precipitated by diethylether and ethyl acetate. The complex was filtered, washed with methanol, then diethylether and dried *in vacuo*. Yield: 42%.

RESULTS AND DISCUSSION

The stoichiometric compositions of the complexes are consistent with the elemental analyses given in Table I. Millimolar solutions of complexes **1–3** in DMF indicate

TABLE I
Analytical and Molar Conductance Data for the Ru(III) and Ru(II) Benzildioxime Complexes

Complex	Found (calc.) %C	%H	%N	Molar conductance (nM) $Ohm^{-1} cm^2 mol^{-1}$
K[Ru(benzildioxime)$_2$Cl$_2$]	49.6 (50.5)	2.9 (3.1)	7.1 (7.6)	64
K[Ru(benzildioxime)$_2$(CO)Cl]	52.0 (52.7)	2.9 (3.1)	7.2 (7.9)	70
K[Ru(benzildioxime)$_2$(PPh$_3$)Cl]	61.0 (61.3)	3.2 (3.9)	5.5 (5.9)	71

that they are 1:1 electrolyte. The magnetic moment, μ_{eff}, of 1.98BM confirms **1** as being paramagnetic, while complexes **2** and **3** are diamagnetic.

IR spectra of the complexes **1–3** show two bands at 1870 and 1660 cm^{-1} characteristic of δ(-O-H···O-) and δ(O-H), respectively, for deprotonated (benzildioxime) ligand in a *trans* disposition.[18] A medium intensity band at 1560–1550 cm^{-1} is assigned to ν(C=N) of the same moiety while ν(N-O) lies near 1310 and 1110 cm^{-1} in all complexes. In the far IR region ν(Ru-Cl) lies near 330 cm^{-1}.

Electronic spectra of all complexes show bands at 270–366 nm assigned to (benzildioxime) $\pi \rightarrow \pi^*$ transitions. In addition, the absorbance at longer wavelength is assigned to charge transfer bands associated with the central ruthenium atom and the chelate rings of the coordinated dioxime (Table II). Similar types of spectra are also reported for other related transition metal complexes.[19,20]

The EPR spectrum of a powder sample of **1** gives three g values, $g_x = 2.42$, $g_y = 2.33$ and $g_z = 2.27$, characteristic of a distorted octahedral complex. A differential pulse voltammogram of complex **1** shows a $E_{1/2}$ value for the Ru(III)/Ru(II) couple at −0.1 volts which is also consistent with other similar complexes containing nitrogen donors.[21,22]

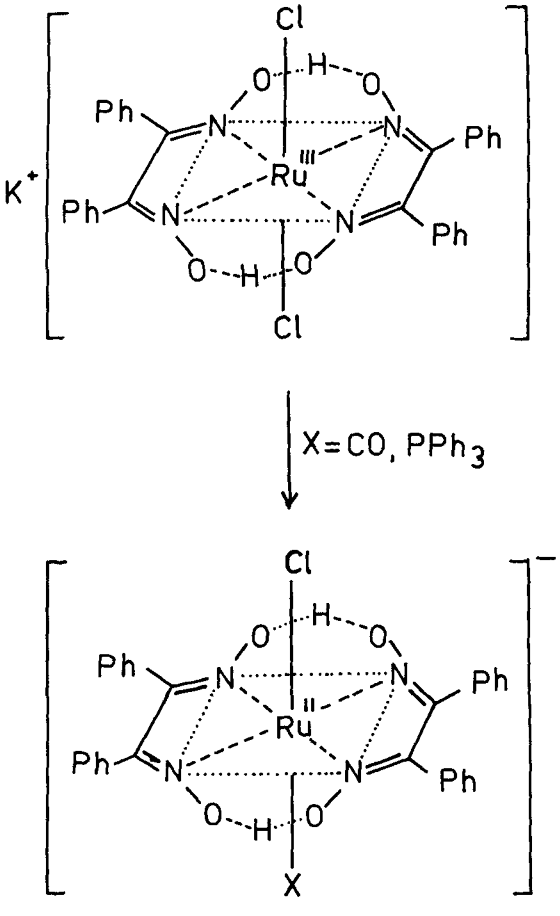
Interaction of **1** with the π-acidic ligands CO and PPh$_3$ (Scheme 1) causes a reduction of Ru(III) to Ru(II). Similar behaviour was noted for [Ru^{II}(EDTA-H)(CO)]$^{-}$[23] and [Ru^{II}Cl$_2$(PPh$_3$)$_3$].[24]

Complexes **2** and **3** are diamagnetic. The [^{1}H] NMR spectra show a singlet associated with intramolecular hydrogen bonding at 10.5–13.5 ppm and a signal at δ 7.4 ppm due to phenyl groups. These results are consistent with those reported by others for dioxime ligands.[25,26] The proton decoupled ^{13}C NMR spectra of **2** and **3** shows four closely spaced singlets in the range 127.3–130.5 ppm. A singlet at 157.2 ppm is assigned to the imine carbon atom which as reported for other dioxime complexes.[25,26]

CO gas was bubbled through a solution of **1** in methanol to give the complex [Ru(benzildioximato)$_2$(CO)Cl]$^{-}$, **2**. The complex is a 1:1 electrolyte in DMF. The electronic spectrum of the complex in DMF shows a charge transfer band at 364 (ε = 16150 M cm^{-1}). The intraligand band occurs at 346 (ε = 25010) along with a shoulder at 471 nm respectively. IR spectra of **2** show a band at 1995 cm^{-1} assigned to ν(Ru-C≡O).

TABLE II
IR Stretching Frequencies and Electronic Spectroscopic Data for the Ru(III) and Ru(II) Benzildioxime Complexes

Complex	$\delta(\text{-O-H} \cdots \text{O-})$	$\nu(\text{C=N})$	$\delta(\text{O-H})$	$\nu(\text{Ru-Cl})$	λ_{max}	$(\varepsilon\, M^{-1}\, cm^{-1})$
$K[Ru(\text{benzildioxime})_2Cl_2]$	1870	1560	1660	330	366 439 530^{sh}	$(\varepsilon = 20090)$ $(\varepsilon = 20260)$ $(\varepsilon = 12910)$
$K[Ru(\text{benzildioxime})_2(CO)Cl]$	1865	1565	1655	325	346 364 471	$(\varepsilon = 25010)$ $(\varepsilon = 16150)$ $(\varepsilon = 13260)$
$K[Ru(\text{benzildioxime})_2(PPh_3)(Cl)$	1870	1555	1660	325	289 362 434^{sh}	$(\varepsilon = 25010)$ $(\varepsilon = 11610)$ $(\varepsilon = 9550)$



SCHEME - I

Complex 1 reacts with PPh_3 in methanol to give $[Ru(benzildioximato)(PPh_3)Cl]^-$, 3. The stoichiometric composition of the complex matches with elemental analysis and conductance measurements which shows that the complex is 1:1 electrolyte in DMF. The electronic spectrum of the complex show only one high intensity charge transfer band at 362 ($\varepsilon = 11610$) along with a shoulder at 434 mm while the intraligand band lies at 289 ($\varepsilon = 25010$) nm. IR spectra gives ν(Ru–P) at 510 cm^{-1}. The ^{31}P [^1H] NMR spectra of the complex shows a multiplet at δ 51 ppm. This downfield shift is due to the presence of a *trans* chloride in the complex. ^{13}C [^1H] NMR spectrum also shows a multiplet at 135.3 ppm due to aromatic rings.[26]

The π-acidic ligands CO and PPh_3 have a marked effect on the reduction potential. A shift of the redox potential to more positive values is due to a decrease in electron density on Ru(II) upon coordination of a strong π-acidic ligand.[29] Hence the reduction potential of the Ru(II)/Ru(I) couples lie in the range -0.32 to -0.41 volts for 2 and 3. This shift is in accord with the decreasing π-acidity of the ligands, CO > PPh_3.

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