Notes

Paramagnetic Dioxygen Complexes of Rhodium

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Electron spin resonance spectra of *cis*- and *trans*-$[Rh(O_2)(en)_2Cl]^+$, $[\{Rh(en)_2Cl\}_2(\mu\text{-}O_2)]^{3+}$, and $[\{Rh(4Me\text{-}py)_4Cl\}_2(\mu\text{-}O_2)]^{3+}$ (en = ethylenediamine, 4Me-py = 4-methylpyridine) ions in solution show that the unpaired electron is largely localized on the dioxygen and that the complexes may nominally be described as having the $Rh^{III}\text{–}O_2^-$ unit. A molecular-orbital picture of the bonding in the complexes is presented.

PARAMAGNETIC dioxygen complexes of cobalt are numerous and well established. In particular, electron spin resonance (e.s.r.) spectroscopy has proved useful in elucidating aspects of their structure and bonding.[1] Corresponding complexes of rhodium are, however, much rarer.[2-5] We have found that, in reducing conditions, complexes of rhodium(III) with pyridine (py) and halide (X^-) combine with oxygen to give a red-orange species and isolable blue dimers.[1,5] Also, in the presence of dioxygen, aqueous solutions of salts of the colourless *cis*- and *trans*-$[Rh(en)_2(NO_2)_2]^+$ (en = ethylenediamine) become red in daylight and *cis*- and *trans*-$[Rh(en)_2(NO_2)(O_2)]^+$ are formed. In the presence of aquarhodium(III) species, the red monomers readily form blue or purple dimers of the type $[X(en)_2Rh(O_2)Rh(en)_2X]^{3+}$.

We have studied the e.s.r. spectra of *cis*- and *trans*-$[Rh(en)_2Cl(O_2)]Cl$ and $[(RhYCl)_2(\mu\text{-}O_2)]Cl_3$, Y = $(en)_2$ or $(4Me\text{-}py)_4$ where 4Me-py = 4-methylpyridine. The spectra are interpreted in terms of a molecular-orbital energy-level diagram which describes well the bonding between the Rh and the O_2 moieties.

EXPERIMENTAL

Complexes were prepared as previously described.[1,5] Spectra were recorded on a Varian E3 spectrometer at room temperature and at 77 K and were calibrated using diphenylpicrylhydrazyl (dpph) as a marker.

RESULTS AND DISCUSSION

The e.s.r. spectra of solutions of all the complexes were very similar (Table). At room temperature, a single line of half-width *ca.* 10 G † centred at *ca.* $g = 2.03—2.04$ was observed. Frozen solutions at 77 K yielded spectra showing three g features, two >2 and one <2 with line-widths *ca.* 14 G. In all cases there was no evidence of hyperfine coupling to rhodium or any other nuclei. A typical spectrum is shown in Figure 1.

E.s.r. parameters for various dioxygen–rhodium complexes

Species	g_1	g_2	g_3	g_{av}	g_{iso}
trans-$[Rh(en)_2Cl(O_2)]^+$	2.0768	2.0229	1.9996	2.0331	2.0330
cis-$[Rh(en)_2Cl(O_2)]^+$	2.0861	2.0229	1.9919	2.0336	2.0330
$[\{Rh(en)_2Cl\}_2(\mu\text{-}O_2)]^{3+}$	2.0972	2.0301	1.9889	2.0397	2.0378
$[\{Rh(4Me\text{-}py)_4Cl\}(\mu\text{-}O_2)]^{3+}$	2.0917	2.0268	1.9898	2.0361	

Analysis of the e.s.r. spectra was aided by reference to the extended-Hückel calculations of Hoffmann *et al.*[6] for the generalized $L_5M(X_2)$ molecule, where X_2 is a diatomic molecule like O_2. LCAO–MO–SCF,[7] INDO–UHF,[8] and Fenske–Hall parameter-free molecular-orbital calculations [9] have also been carried out with roughly similar conclusions, at least as far as the orbital containing the unpaired electron is concerned. Hoffmann *et al.* have shown that $\{MO_2\}^9$ complexes such as $[Rh(en)_2Cl(O_2)]^+$ should have a bent MO_2 unit, whereas $\{MO_2\}^{10}$ complexes ‡ should have sideways-bound O_2 as in $[RhCl(O_2)(PPr^i_3)_2]$.[3]

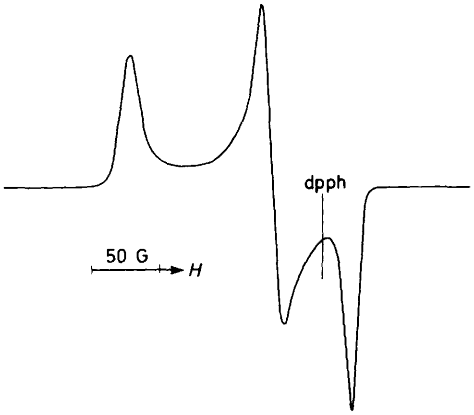

FIGURE 1 E.s.r. spectra of a frozen solution of $[\{Rh(4Me\text{-}py)_4Cl\}_2(\mu\text{-}O_2)]^{3+}$ in dimethylformamide at 77 K

The g *Tensor.*—The observation of three g features strongly supports a bent Rh–O–O configuration. The very close similarity of our g^- tensors to those of HOO· [10] and ROO· [10,11] suggests that the unpaired electron is in a π^* orbital on O_2 having only a small amount of d_{yz} contribution. Had there been much rhodium character to the unpaired electron's orbital, then much larger deviations from $g = 2$ would be observed and also some hyperfine coupling to the rhodium. If the xz plane is defined as the Rh–O–O molecular plane, with the z axis

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† Throughout this paper: 1 G = 10^{-4} T.

‡ $\{MO_2\}^9$ and $\{MO_2\}^{10}$ are used to denote the number of $d + \pi$ electrons, following the convention of Hoffmann *et al.*[6]

along the Rh–O bond, then the unpaired electron is largely in the π_y^* orbital.

The *g* tensors are similar to those found in the numerous related superoxo-cobalt complexes and the few other rhodium complexes.[2,3] However, values for the rhodium complexes (certainly including those studied here) deviate from the free-electron value more than those of cobalt. This is because the larger spin–orbit coupling constant of rhodium influences the unpaired electron *via* the d_{yz} contribution to the molecular orbital of that unpaired electron. The *g* tensors of the cobalt complexes tend to have axial symmetry and this probably arises because of a fortuitous spacing of other orbital energy levels with which the ground state may mix.

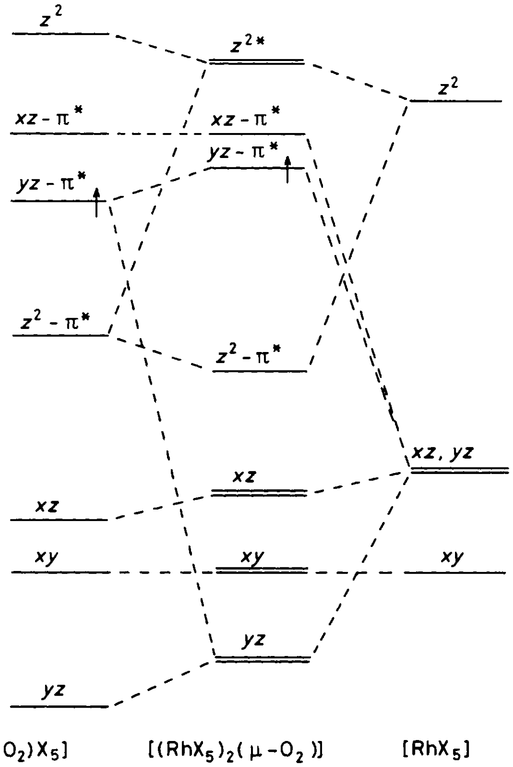

FIGURE 2 A qualitative molecular-orbital energy-level diagram showing the interaction of $[Rh(O_2)X_5]$ with another $[RhX_5]$ species to form $[(RhX_5)_2(\mu-O_2)]$ for the case of a bent Rh–O–O moiety. The arrow denotes the orbital containing the unpaired electron

Hyperfine Coupling.—The absence of detectable hyperfine coupling to ^{103}Rh suggests values $<$ *ca.* 5 G. Such small values would be expected since the nuclear magnetic moment of ^{103}Rh is about 2% that of ^{59}Co. From the already small hyperfine couplings to ^{59}Co (typically $<$20 G) in the related cobalt complexes we would predict hyperfine couplings to ^{103}Rh of $<$1 G even if there were more direct delocalization of the unpaired electron into the d_{yz} orbital. As described in detail for the superoxo-cobalt complexes,[1] the isotropic hyperfine coupling to rhodium arises by a spin-polarization mechanism involving the Rh–O σ bond, the small anisotropic coupling coming from a few per cent of direct delocalization of the electron into the cobalt d_{yz} orbital. Several workers have subsequently reaffirmed this mechanism.[12]

The problem still remains as to what is the oxidation state of the rhodium and what is the charge on the dioxygen? The conclusion that the e.s.r. results resemble those of the O_2^- ion does not mean that there is a single negative charge on the dioxygen. The e.s.r. results tell us that the unpaired electron is in a π^* orbital largely on the O_2, as in O_2^-, but the amount of actual charge transfer is difficult to assess. Nevertheless, for electron-accounting purposes it is convenient to represent the oxidation states formally as $Rh^{III}-O_2^-$. The tendency to form dimers supports the localization of a substantial negative charge on the terminal oxygen atom.

The *g* tensors for the dimeric species deviate from 2 to a greater extent than do those of the monomeric species. This implies greater mixing of the orbital containing the unpaired electron with orbitals which are now closer than in the monomeric case. This is as expected by reference to a simplified molecular-orbital energy-level diagram (Figure 2) relating the energies of the $[RhX_5]$, $[Rh(O_2)X_5]$, and $[(RhX_5)_2(\mu-O_2)]$ species corresponding to a specific angle of bending of the Rh–O–O moiety. The optical transitions give further support to this since the strong band at 485 nm for monomeric *trans*-$[Rh(en)_2Cl(O_2)]^+$ is at higher energy than the band at 545 nm for $[\{Rh(en)_2Cl\}_2(\mu-O_2)]^{3+}$.[5]

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