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SOME ASPECTS OF RHODIUM(II) CHEMISTRY: THE HEXACHLOROBIS-(NN-DIMETHYLACETAMIDE)DIRHODATE(II) AND NONACHLORODIRHODATE(III) ANIONS

BRIAN R. JAMES* and GEORGE ROSENBERG

Department of Chemistry, The University of British Columbia, Vancouver, V6T 1W5 (Canada)

Over the past few years some studies from this laboratory have been concerned with the activation of gas molecules (especially H_2, CO, and O_2) by solutions of rhodium(I) complexes both in aqueous and non-aqueous media [1—5]. Studies involving catalytic hydrogenation of activated olefins using various rhodium complexes have shown that yellow solutions containing Rh^{I}(olefin) species are formed in both aqueous and *NN*-dimethylacetamide (DMA) solutions [1,4]. In attempts to investigate potential oxygenation catalysts for olefins, such rhodium(I) solutions have been subjected to oxygen atmospheres at mild conditions (1 atm, 80°C). Aqueous acid chloride solutions containing Rh^{I}(maleic acid) species [prepared by treating chlororhodate(III) solutions with H_2 in the presence of maleic acid [1]] are simply oxidized stoichiometrically ($O_2 : Rh = 1 : 2$) to orange solutions containing chlororhodate(III) species such as $RhCl_5(H_2O)^{2-}$. The same net stoichiometric oxidation to rhodium(III) chlorides is observed [1] in DMA solutions containing LiCl, although an intermediate green colouration (λ_{max} 675 nm) is apparent at oxygen uptakes corresponding to a one equivalent oxidation:

$$\begin{array}{lll} Rh^{I}(MA) \xrightarrow{\frac{1}{4}O_2} & Rh^{II}? \xrightarrow{\frac{1}{4}O_2} & Rh^{III}Cl_n \\ \text{yellow} & \text{green} & \text{orange} \end{array} \qquad (1)$$

The green solutions showed a room temperature E.S.R. signal ($g = 4.63$), and could contain some paramagnetic rhodium(II) species; however, no pure complexes could be isolated. It is worth noting that the diamagnetic rhodium(II) acetate $Rh_2(CH_3CO_2)_4$ with bridging acetates and metal—metal bonding [6], the solvated diamagnetic ion [7] Rh_2^{4+}, and the ion [8] $Rh_2(H_2O)_{10}^{4+}$ which is slightly dissociated into the paramagnetic monomeric form, all give rise to green solutions and the origin of the band in the 600 nm region, which is sensitive to the nature of terminal ligands (including solvents), has been discussed in terms of an MO scheme implying a Rh—Rh single bond [9].

Solutions of the cyclooctene complex $[RhCl(C_8H_{14})_2]_2$ in DMA containing

LiCl, lose cyclooctene and adsorb O_2 to form in situ a 1 : 1 molecular oxygen complex [5], Rh^IO_2; the solutions give an E.S.R. signal which was attributed to a $Rh^{II}—O_2^-$ species, and catalyse oxidations by O_2 through free-radical peroxide processes [5]. The catalytic activity of these initially orange solutions decreases with time, and is accompanied by the appearance of a greenish tinge ($\lambda_{max} \sim 670$ nm) and a new E.S.R. signal with components $g_1 = 2.11$, $g_2 = 2.04$, $g_3 = 1.97$ at 77K [5,10]. We have now isolated a rhodium(II) complex giving rise to this paramagnetism, following some related studies on the interaction of O_2 with solutions of the dicarbonyl anion [2] $Rh(CO)_2Cl_2^-$.

The reaction of oxygen with the dicarbonyldichlororhodate(I) complex in aqueous HCl solution yields [11,12] only Rh(III) products, initially $Rh(CO)Cl_5^{2-}$ and then $RhCl_5(H_2O)^{2-}$. The corresponding reaction in the DMA—LiCl media [12], however, produces initially a rhodium(II) species (again via the Rh^IO_2 complex mentioned above) which has been isolated as a green tetraphenylarsonium salt $[Ph_4As]_2[Rh_2Cl_6(DMA)_2]$, (1). In DMA, (1) is slowly oxidized by O_2 to give the known [13] nonachlorodirhodate(III) anion, $Rh_2Cl_9^{3-}$ (2), which can also be readily isolated as the tetraphenylarsonium salt from DMA solutions of commercially available $RhCl_3 \cdot 3H_2O$. Details for the synthesis of (1) and (2) are given in the Syntheses section.

THE $[Ph_4As]_3[Rh_2Cl_9]$ COMPLEX (2)

Previous preparative methods of (2) have involved either extraction of the anionic complex from aqueous media by organic solutions containing a quarternary ammonium halide salt [13], or direct addition of such a salt to an aqueous solution of chlororhodate(III) species followed by solvent evaporation [13,14]. Visible spectral data in a number of solvents are given in Table 1; the extinction coefficients reported by Work and Good [13] are low and their product could contain some monomeric chlororhodate(III) species which have similar absorption maxima but much smaller extinction coefficients [15]. Displacement of the absorption maxima and increased band intensities for $Rh_2Cl_9^{3-}$ relative to $RhCl_6^{3-}$ may be due [16] to a charge transfer contribution to the *d*—*d* transitions resulting from distortion of octahedral coordination around the metal (see below).

Work and Good [13] reported the X-ray diffraction powder photograph of $[(C_2H_5)_4N]_3[Rh_2Cl_9]$ together with that of the corresponding nonachlorodichromate(III) compound, and concluded that the two compounds were isomorphous. The crystal structure of $[Ph_4As]_3[Rh_2Cl_9]$ has now been determined in this department using Patterson and Fourier techniques [17]. Preliminary refinement of the structure to $R \sim 0.08$ based on about 3500 reflections (Mo-K_α) has located the positions of the rhodium and chlorine atoms. Analogous to the $Cr_2Cl_9^{3-}$ ion [18], the ion contains two pyramidally distorted $RhCl_6$ octahedra sharing a face (Fig. 1). The compound crystallised in the monoclinic system, space group $P2_1/c$, with lattice parameters $a = 13.23$, $b = 20.95$, $c = 26.23$ Å, and $\beta = 103.63°$; there are four formula units in the

TABLE 1

Visible and IR spectral data of $Rh_2Cl_9^{3-}$ and $Rh_2Cl_6(DMA)_2^{2-}$

$Rh_2Cl_9^{3-}$			
λ_{max} nm (ε)	in DMA[a]	446 (410),	554 (145)
	CH_2Cl_2[a]	444 (400),	546 (155)
	C_6H_6[b]	435 (310),	540 (100)
	CH_3CN[c]	440 (440),	544 (130)
	$C_6H_5NO_2$[d]	442 (—),	546 (—)
	solid[a]	450 (—),	555 (—)
ν(Rh—Cl)	[a]330(s), 319(s),	274(m) cm^{-1}	
	[b]331(s), 319(s),	277(m)	
$Rh_2Cl_6(DMA)_2^{2-}$			
λ_{max} nm (ε)	in DMA	670 (100)	
ν(Rh—Cl)	330(s), 318(s)	272(w) cm^{-1}	

[a] This work. [b] Ref. 13. [c] Ref. 14. [d] S.N. Ivanova et al., Russ. J. Inorg. Chem., 12 (1967) 861.

unit cell. The rhodiums are displaced from the octahedra centres, so that the Rh—Cl distance is shorter when the Cl atom belongs to one octahedron [2.32(1) Å], than when shared between two [2.36(2) Å]; the Rh ... Rh distance is 3.11 Å. The pyramidal distortion results in a Cl_b—Rh—Cl_b angle of 81(2)° as compared to the Cl_t—Rh—Cl_t angle of 91(1)°; the Cl_b—Rh—Cl_t(*cis*) is 94(2)°, and the Cl_b—Rh—Cl_t(*trans*) angle is 173(3)°. A similar distortion (~4°) from colinearity of the *trans* Cl_t—metal—Cl_b system was found [18] for $Cs_3Cr_2Cl_9$. The Rh—Cl—Rh angle is 82(1)°.

Only three ν(Rh—Cl) stretching modes are observed in the far IR (Table 1) instead of the expected four for an ion of D_{3h} symmetry (2 terminal, 2 bridging); as suggested before [13], one band is thought to be obscured.

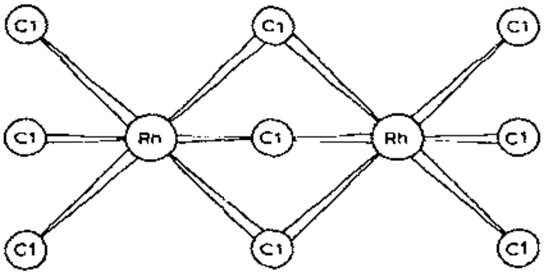

Fig. 1. Structure of the $Rh_2Cl_9^{3-}$ anion. In text, Cl_b and Cl_t indicate bridging and terminal chlorines, respectively; number in parentheses for bond distances and angles is the r.m.s.d. in the last figure quoted.

The molar conductivity of (2) in DMA at 23° C was 147 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$. This is considerably lower than that expected for 3:1 electrolytes (200—250 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$) [19] but this is attributed to the bulky nature and low mobility of both cation and anion. A molecular weight determination in dimethylformamide, DMF (M.Wt.380) shows that (2) is completely dissociated in polar aprotic solvents. A 1 : 1 electrolyte containing a binuclear rhodium anion, H[Rh_2(*N*-phenylanthranilate)Cl] has a molar conductance in DMF of about half that expected, and this was also attributed to the bulky anion [20].

THE $[\text{Ph}_4\text{As}]_2[\text{Rh}_2\text{Cl}_6(\text{DMA})_2]$ COMPLEX (1)

The elemental analysis of the compound, and a broad IR band between 1620—1540 cm^{-1} shows the presence of coordinated DMA; the broad band is probably due to the lowered ν(C—O) and ν(C—N) for coordinated DMA [19,21], overlapping with ν(C—C) of the Ph_4As^+ cation. Similar ν(C—C) vibrations were observed in the 1620 cm^{-1} region for (2).

Various data summarised below indicate a dimeric structure for the anion, and a plausible structure is shown in Fig. 2 with square planar RhCl_4 units sharing equatorial sites with one DMA ligand at *trans* axial positions.

Group theory for the C_{2h} structure shown predicts three IR active ν(Rh—Cl) bands. The far IR bands at 330 and 318 cm^{-1} (Table 1) can be assigned to terminal stretching modes, and the weak band at 272 cm^{-1} to bridged chlorine

The molar susceptibility of (1) determined by the Gouy method was 380×10^{-6} c.g.s.u./Rh at 22° C, which corresponds to a magnetic moment of 0.95 BM, although this is subject to some uncertainty owing to a large diamagnetic correction (400×10^{-6} c.g.s.u./Rh). Nevertheless, the value is lower than the spin only value of 1.73 BM for a single unpaired electron.

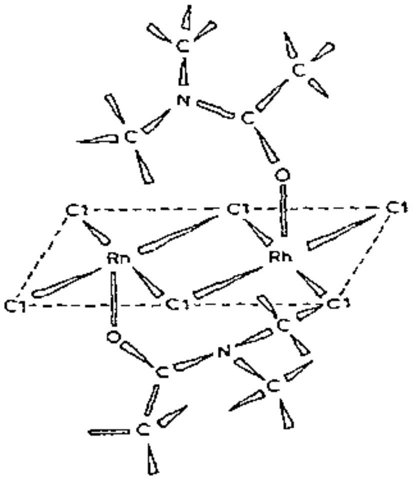

Fig. 2. Plausible structure of the $\text{Rh}_2\text{Cl}_6(\text{DMA})_2^{2-}$ anion.

Unusually low magnetic moments for some monomeric rhodium(II) phosphine (L) square planar complexes of the type *trans*-$RhCl_2L_2$ have been attributed to intermolecular metal—metal interactions in the solid state [22—24], and a similar type of interaction may exist in the rhodium(II) tetraphenylporphyrin complex Rh(TPP) ($\mu \sim 1.2$ BM) [25]. If the unpaired electron on each rhodium of $Rh_2Cl_6(DMA)_2^{2-}$ were present in a d_{xy} orbital situated in the plane between the equatorial chlorides, a weak interaction may be possible between the half-occupied orbitals on the metal atoms, and this could also lead to a reduction in the magnetic moment. The E.S.R. spectrum of (1) in DMA (Table 2) is very similar to that of the species formed during oxygenation of $[RhCl(C_8H_{14})_2]_2$ in LiCl/DMA (see above), and analysis of the spectrum of the latter [10] indicated a structure with the odd electron occupying the d_{xy} orbital.

The molar conductivity of (1) (115 ohm^{-1} cm^2 mole^{-1} in DMA at 23°C) is consistent with the presence of a 2 : 1 electrolyte and the dimeric anion formulation. The range of conductivities for 2 : 1 complexes is reported [19] as 130—180 ohm^{-1} cm^2 mole^{-1}, but considering the data for the 3 : 1 nonachlorodirhodate(III) system, a somewhat lower conductivity is expected.

An observed molecular weight of 1050 in $CHCl_3$ is consistent with partial dissociation of (1) (M.Wt. 1359) into ions, and rules out a formulation involving a monomeric anion.

The rhodium(II) anion shows a characteristic absorption maximum at 670 nm (ϵ = 100) in DMA which imparts a greenish tinge to the solution. The origin of this band is uncertain.

Figure 2 is based on molecular models which show that pseudo-octahedral symmetry around each Rh can be achieved. *Trans* coordination of the DMA at the axial positions above and below the planar Rh_2Cl_6 skeleton results in blocking the vacant coordination site of the neighbouring Rh by the *N*-methyl group of DMA; this arrangement provides the closest possible contact with the Rh and *N*-methyl group. The apparent stability of (1), as for the *trans*-

TABLE 2

E.S.R. spectra of $Rh_2Cl_6(DMA)_2^{2-}$

g_1	g_2	g_3	g_{av}	g (isotropic)[a]	
2.103	2.031	1.971	2.035	2.036	This work[b]
2.103	2.031	1.972	2.035	—	This work[c]
2.114	2.048	1.969	2.042	—	Ref. 10[d]
2.115	2.036	1.972	2.042	2.048	Ref. 4[d]

[a] g (isotropic) determined at 25°C.
[b] g_1, g_2, g_3 determined at 77K in glass state in DMA or CH_2Cl_2.
[c] Solid state at 25°C.
[d] From oxygenation of $[Rh(C_8H_{14})_2Cl]_2$ in DMA/LiCl at 77K.

$RhCl_2L_2$ complexes, is thus attributed to a kinetic effect, i.e. blocking the vacant sites and thereby hindering approach of reagents. The $RhCl_2L_2$ complexes are formed only with bulky tertiary phosphines, where *t*-butyl or methyl groups block axial sites [22—24].

Oxidation of (1) by O_2 in DMA to (2) is accompanied by loss of the E.S.R. signals and the greenish colour. DMA solutions of (1) or (2) are reduced by H_2 eventually to the metal possibly by disproportionation of Rh(I), since in the presence of activated olefins the Rh(I) is stabilised as an olefin complex and catalytic hydrogenation of the olefin occurs [1,26].

Preliminary experiments indicate that complex (1) may be a useful precursor for the synthesis of other rhodium(II) complexes. Treatment with acetic acid/acetate readily yields the well-known rhodium(II) acetate; and addition of nitrogen bases (pyridine, dipyridyl, phenanthroline) to CH_2Cl_2 solutions of (1) gives new species, as indicated by the detection of three component E.S.R. spectra, significantly different to those obtained for (1), although pure complexes have not yet been isolated.

SYNTHESES

$RhCl_3 \cdot 3H_2O$ was obtained from Johnson Matthey Ltd. $[Rh(CO)_2Cl]_2$ was synthesised according to the literature [27]; the carbonyl dimer dissolves in DMA containing LiCl to give the $Rh(CO)_2Cl_2^-$ anion [2].

$[Ph_4As]_2[Rh_2Cl_6(DMA)_2]$, (1).

0.4 g $[Rh(CO)_2Cl]_2$ and 1.0 g LiCl were dissolved in 35 ml distilled DMA. The initially yellow solution was heated under O_2 at 75°C for 10 h; the final brown solution was cooled to 20°C, filtered (to remove Li_2CO_3), and treated with a methanolic solution (<5 ml) of 2.6 g Ph_4AsCl. Treatment of the solution at 0°C with ether yields a brown oil, which gives a fine green powder on addition of cold H_2O. Filtering, washing with H_2O and ether, and drying in vacuo gives 0.7 g (50%) of (1). Calcd. for (1): C, 49.45; H, 4.27; N, 2.06; Cl, 15.67; Rh, 15.16%. Found: C, 49.23; H, 4.32; N, 1.74; Cl, 15.79; Rh, 15.39%.

$[Ph_4As]_3[Rh_2Cl_9]$, (2).

50 ml DMA containing 2.2 g $RhCl_3 \cdot 3H_2O$ and 2.6 g LiCl was stirred in air at 80°C for 1 h, and then cooled to 20°C. 10 g Ph_4AsCl dissolved in 5 ml CH_3OH were then added. Treatment of the orange-brown solution with 150 ml H_2O gave a brown precipitate which was filtered, washed with cold H_2O and ether, and dried in vacuo (yield 5.4 g, 77%). Calcd. for (2): C, 51.60; H, 3.58; Cl, 19.08; Rh, 12.30% Found. C, 50.23; H, 3.66; Cl, 18.91; Rh, 12.18%.

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