A Dimeric Macrocyclic Rhodium(I) Complex with a Weak Metal–Metal Bond

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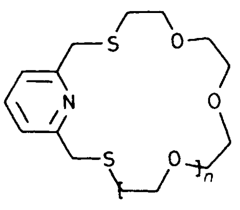
A series of cationic rhodium carbonyl complexes of macrocyclic ligands show weak metal–metal interactions; the crystal structure of one exhibits a long Rh–Rh bond.

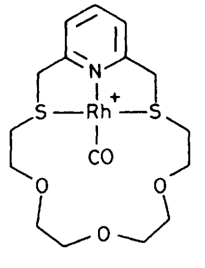
The description of the electronic structures of systems with weak metal–metal bonds between square-planar systems has received attention;[1] dinuclear rhodium isocyanide complexes in particular have been studied because of the rich photochemical and photophysical properties of their low-lying excited states.[2] During studies directed toward the synthesis of heterodinuclear complexes of noble metals and cations of Groups 1A and 2A,[3,4] we have prepared a set of cationic rhodium carbonyl macrocyclic complexes which also show weak metal–metal interactions.

Reaction of the macrocycle (**1**)[5] with $[Rh_2Cl_2(CO)_4]$ in methanol was accompanied by brisk evolution of CO, and upon addition of an excess of ammonium hexafluorophosphate, diamond-shaped, ruby-red crystals of the complex (**2**) were formed. The i.r. carbonyl stretch band occurred at 2010 cm^{-1}, consistent with a terminal rhodium carbonyl,[3,4] and the ^{1}H n.m.r. spectrum (298 K; CD_2Cl_2) revealed that the benzylic methylene protons were diastereotopic (δ 4.79 and 5.07), consistent with stereogenic sulphur centres with a stable configuration. The crystal structure of (**2**) revealed that the complex† was dimeric, with a weak rhodium–rhodium interaction [Rh–Rh 3.3320(6) Å]. Similarly weak rhodium–rhodium bonds have been observed in other dicationic systems.[6] The co-ordination about each rhodium may be regarded as a distorted square pyramid in which the principle distortion arises from the S(8)–Rh–S(20) bond angle of 169.8°, due to the intrinsically small 'bite' angles of the two adjacent five-membered ring chelates (Figure 1). In solution dissociation occurs readily [particularly in co-ordinating solvents (*e.g.* MeCN and Me_2CO)] to give yellow solutions. The crystal structure also reveals that the Rh–CO vector is directed away from the polyether chain, which itself folds back over the

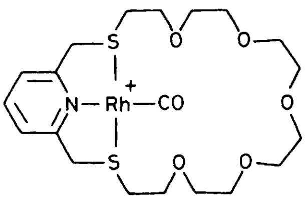


(**1**) n = 1

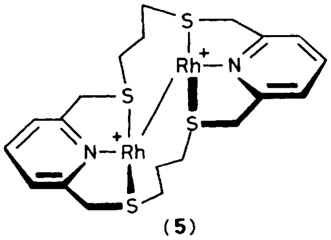
(**3**) n = 3



(**2**)



(**4**)



(**5**)

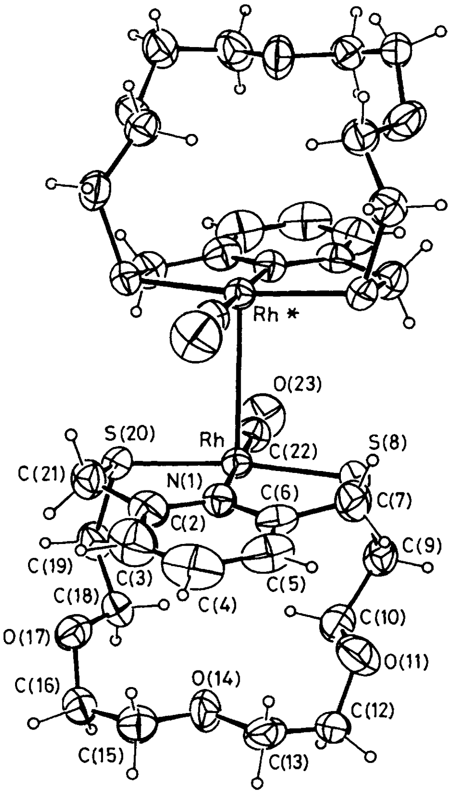


Figure 1. Perspective (ORTEP) drawing of the dication; selected bond lengths and angles: Rh–S(8) 2.295(2), Rh–S(20) 2.298(2), Rh–N(1) 2.060(4), Rh–C(22) 1.833(6). Rh–Rh 3.3320(6) Å; N(1)–Rh–S(8) 85.1, N(1)–Rh–S(20) 85.7, N(1)–Rh–C(22) 179.2, S(8)–Rh–S(20) 169.8, S(8)–Rh–C(22) 94.2°.

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† *Crystal data for* (**2**): $[C_{16}H_{23}NO_4RhS_2]_2[PF_6]_2$, M_r = 1210.72, tetragonal, space group $P4_12_12$, a = 11.800(2), c = 31.822(8) Å, U = 4430.9 Å^3, Z = 4, D_x = 1.81 g cm^{-3}, μ(Mo-K_α) = 10.8 cm^{-1}, F(000) = 2432; 2844 unique reflections were observed of which 1737 were used in refinement to give R = 0.027, R_w = 0.033. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

electron-poor pyridinium ring. Similarly stabilising interactions between macrocyclic polyethers and pyridinium cations have been defined recently.[7]

From the more flexible 24-membered ring ligand (**3**)‡ an analogous complex (**4**) was prepared. The complex gave an exchange-broadened ^{1}H n.m.r. spectrum at 298 K in CD_2Cl_2: on cooling to 260 K the spectrum sharpened and revealed a simple AB pattern for the benzylic protons. The inversion at sulphur ($\Delta G^\ddagger$ = 64 kJ mol^{-1}) may be attributed to a ring 'skip' of the polyether chain over the Rh–CO vector. The i.r. carbonyl stretching frequencies of (**2**) and (**4**) were not perturbed by addition of metal salts (Li^+, Na^+, or K^+) to solutions of the complexes in CH_2Cl_2 or acetone. Despite the fact that the oxygen lone-pair of a metal-bound carbonyl ligand may interact with a proximate Lewis acidic centre,[8] in these and other[4] recently reported macrocyclic ligands incorporating a 2,6-bis(mercaptomethyl)pyridine sub-unit, such an alignment is disfavoured.§ The tendency of the rhodium centres to interact, and the weakly stabilising effect of the pyridinium ring intramolecularly associating with the polyether chain, negates such an orientation. Interestingly, the analogous cationic rhodium carbonyl complexes with shorter $[CH_2]_5$ or $CH_2CH_2OCH_2CH_2$ chains between the sulphur atoms form violet and indigo crystalline complexes, respectively, suggestive of a stronger dimeric Rh–Rh interaction.[2] Such a weak bond may also occur in the deep red dirhodium complex (**5**)[3] in which the rhodium atoms are constrained to interact by the ring topology. This complex is soluble only in polar solvents (Me_2SO and MeCN), to give red solutions. The photochemical properties of these systems are being examined accordingly.

We thank the S.E.R.C. and N.S.E.R.C. for support.

Received, 18th May 1987; Com. 658

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‡ The macrocycle (**3**) is prepared by reaction of 2,6-bis(mercaptomethyl)pyridine with hexaethylene glycol ditosylate in refluxing butanol. It forms well defined monocationic complexes with other noble metals, for example $[(\mathbf{3})PtCl]^+Cl^-$ and $[(\mathbf{3})PdCl]^+Cl^-$. All new compounds and complexes gave satisfactory microanalytical and spectroscopic data (^{1}H and ^{13}C n.m.r., i.r., and fast-atom bombardment mass spectrometry) in accord with the proposed structures.

§ Similar arguments explain the lack of magnetic coupling observed between a copper(II) cation bound to a pyridine[NS_2] ligand and a proximate iron porphyrin, as the copper $d_{x^2-y^2}$ orbital will be oriented *away* from the iron d_{z^2} orbital.[9]

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