Syntheses and Reactivity of Cofacial, Dimeric Metal–Metal Bonded Ruthenium(II) Mixed Valence Ruthenium(II/III), and Ruthenium(III) Complexes of $[C_{22}H_{22}N_4]^{2-}$, a Dibenzo-tetra-aza[14]annulene Ligand

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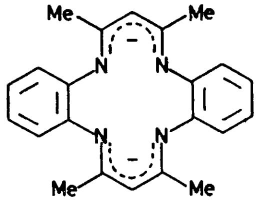
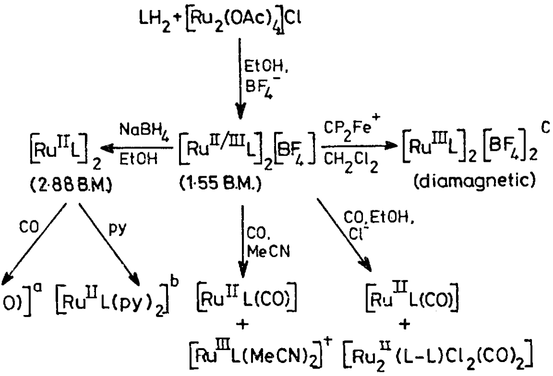
Summary A novel series of metal–metal bonded Ru^{II}, mixed valence $Ru^{II/III}$, and Ru^{III} complexes $[Ru(C_{22}H_{22}N_4)]_2{}^{n+}$, of a dibenzotetra-aza[14]annulene ligand have been isolated and characterized which possess ground spin-triplet, spin-doublet, and singlet states, respectively.

RUTHENIUM complexes, particularly of porphyrinato ligands, are of current interest as potential thermal and/or photochemical redox catalysts and as models for biological oxygen transport systems.[1,2] The tetra-aza[14] annulene ligand, $[C_{22}H_{22}N_4]^{2-}$, L^{2-}, although superficially resembling porphyrins, has important differences: the 14-membered inner ring of the dianion is a 16π-antiaromatic system, the delocalization is restricted to the pentane-2,4-di-iminato rings, the 'core size' is approximately 0·1 Å shorter than that for porphyrins, and steric interactions of the methyl groups with the benzenoid rings lead to a saddle shape that produces a displacement of the co-ordinated metal from the N_4 plane.[3]



We report the synthesis and reactions of a novel series of dimeric Ru–Ru bonded systems, varying only in the oxidation state of the metal, of the $[C_{22}H_{22}N_4]^{2-}$ macrocyclic ligand. These metal–metal bonded systems are formed without bridging ligands such as carboxylates and must overcome the nonbonding repulsions of the macrocyclic ligands. The reaction of mixed valence ruthenium(II/III) acetate chloride, $Ru_2(OAc)_4Cl$,[4] with the protonated ligand LH_2 in ethanol affords a dark green, air-sensitive paramagnetic salt with the formulation $[RuL]_2Cl{\cdot}(EtOH)_n$



SCHEME. Spectroscopic data: ^{a} [Ru^{II}L(CO)], δ (C$_6$D$_6$) 2·10 (s, 12H, Me), 4·68 (s, 2H, γ-CH), and 6·71 (m, 8H, ArH); ν(CO) 1903 cm^{-1}; *m/e* 472 (M^+); ^{b} [Ru^{II}L(py)$_2$], δ (C$_6$D$_6$) 9·58 (m, 2H, 2H, α-py-H), *ca.* 6·67 (m, *ca.* 5H, ArH or py-H), 6·25 (m, 2H, py-H), 4·00 (s, 1H, γ-CH), and 1·89 (s, 6H, Me); ^{c} [Ru^{III}L]$_2$ [BF$_4$]$_2$, δ CD$_3$CN) 3·32 (s, 12H, Me), 5·41 (s, 2H, γ-CH), and 7·42 and 7·75 (m, 8H, ArH). All n.m.r. spectra were run at 270 MHz.

(n = 1 or 2) in *ca.* 65% yield (see Scheme). The compound has a solid-state magnetic moment of 1·55 B.M., corresponding to one unpaired electron for the dimer system, whereas the precursor acetate has a quartet ground state.[4] Support for this mixed valence metal–metal bonded Ru$^{II/III}$ formulation comes from the electrochemical properties and derivative chemistry of the complex. In acetonitrile solution, two reversible one-electron redox couples are observed by cyclic voltammetry: an oxidation wave at −0·20 V (*vs.* 0·1M Ag–AgClO$_4$ in MeCN) and a reduction wave at −1·03 V. Both electrochemical transformations were also carried out chemically.

Reduction of [RuL]$_2^+$ with NaBH$_4$ in ethanol generates a very air-sensitive brown crystalline material, [RuL]$_2$, which exhibits a dimer parent peak at *m/e* 888 in its mass spectrum.† Unlike its apparently diamagnetic octaethylporphyrin analogue,[2a] [RuL]$_2$ is paramagnetic with two unpaired electrons, μ_{eff} = 2·88. B.M.

The ruthenium(II) dimer, [RuL]$_2$, dissociates in the presence of the strong field ligands CO or pyridine (py) yielding diamagnetic monomeric orange-brown [RuL(CO)] or blood-red [RuL(py)$_2$], respectively. In acetonitrile solution, both derivatives exhibit two reversible one-electron couples: For the [RuL(CO)]^n system, $0 \rightleftharpoons +1$ occurs at −0·19 and $+1 \rightleftharpoons +2$ at +0·34 V; for [RuLpy$_2$]^n, $0 \rightleftharpoons +1$ occurs at −0·73 and $+1 \rightleftharpoons +2$ at +0·09 V.

The Ru$^{II/III}$ complex, [RuL]$_2^+$ disproportionates upon reaction with CO to yield [RuL(CO)] and [RuL(MeCN)$_2$]$^+$ which were identified by their characteristic one-electron redox couple pairs. In acetone or ethanol, however, [RuL]$_2$Cl reacts with an excess of CO to form [RuL(CO)] and a dark green species analysing as RuLCl(CO). This latter sparingly soluble compound is diamagnetic in the solid state, exhibits a ν(CO) at 1897 cm^{-1}, and has a dimer peak in its mass spectrum corresponding to [Ru$_2$L$_2$]$^+$. These features are most consistent with a Ru^{II} formulation of a dimeric, but not metal–metal bonded complex, [Ru$_2$(L–L)(CO)$_2$Cl$_2$], resulting from coupling of radical ligands at the γ-carbon atom of one of the pentane-2,4-di-iminato rings. Precedent for the requisite ligand-based radical of the type [RuL(CO)]$^+$ occurs in ruthenium porphyrin chemistry,[1] and dimerization of [NiL]$^+$ *via* coupling at the γ-carbon atom has been observed to accompany both electrochemical and chemical oxidation of NiL.[5] A short-lived ligand-based π-radical has been detected in the e.s.r. spectra of CH$_2$Cl$_2$ solutions which have been quickly frozen following oxidation of [RuL(CO)] with [cp$_2$Fe]$^+$[BF$_4$]$^-$ (cp = cyclopentadienyl).

Oxidation of [RuL]$_2$[BF$_4$] with [Cp$_2$Fe]$^+$ in CHCl$_2$ solution yields the diamagnetic and air-sensitive Ru^{III} dimer, [RuL]$_2$[BF$_4$]$_2$. Cyclic voltammetry measurements of this complex indicate that it is identical to that generated by electrochemical oxidation of [RuL]$_2^+$.

The magnetic characteristics of the formal Ru^{II}, Ru$^{II/III}$, and Ru^{III} dimeric complexes, *i.e.*, spin-triplet, spin-doublet, and spin-singlet states, respectively, are consistent with the following bonding scheme involving the $d\pi(xz,yz)$ and $d\sigma(z^2)$ orbitals. An orbital ordering of $\pi^4\sigma^2\pi^{*2}\sigma^*$ for the Ru^{II} dimer corresponds to a net bond order of two. Oxidation to [RuL]$_2^+$ and [RuL]$_2^{2+}$ removes antibonding electrons and increases the formal bond orders to 2·5 and 3, respectively. Strong axial ligands capable of raising the σ level above π^* level lead to full occupancy of the π^* orbitals and reduction of the bond order to zero for the [RuL]$_2$ complex, consistent with the dissociation observed in the presence of CO and py. The apparently diamagnetic Ru^{II} porphyrin dimer [2a] may be rationalized by assuming modest shifts of the $d\pi$ and $d\sigma$ orbitals relative to one another.

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† The [RuL]$_2$ dimer is isomorphous with the rhodium compound, [RhL]$_2$ which has a Rh–Rh distance of 2·625 Å; the two macrocyclic ligands are rotated 90° relative to one another to minimize nonbonding repulsions: V. Goedken, P. DeHaven, and L. Warren, unpublished results.

[1] G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1973, **95**, 5939; G. M. Brown, F. R. Hopf, T. J. Meyer, and D. G. Whitten, *ibid.*, 1975, **97**, 5385.
[2] (a) F. R. Hopf, T. P. O'Brien, W. R. Scheidt, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1975, **97**, 277; G. W. Sovocool, F. R. Hopf, and D. G. Whitten, *ibid.*, 1972, **94**, 4350; (b) F. R. Hopf and D. G. Whitten, *ibid.*, 1976, **98**, 7422.
[3] M. C. Weiss, B. Bursten, S. M. Peng, and V. L. Goedken, *J. Amer. Chem. Soc.*, 1976, **98**, 8021; V. L. Goedken, J. J. Pluth, S. M. Peng, and B. Bursten, *ibid.*, p. 8014.
[4] F. A. Cotton and E. Pedersen, *Inorg. Chem.*, 1975, **14**, 388 and refs. therein.
[5] F. C. McElroy and J. D. Dabrowiak, *J. Amer. Chem. Soc.*, 1976, **98**, 7112.