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The Structure and Magnetism of a Trimetallic μ-Oxo Ruthenium(iv) Porphyrin–Iron(iii) Salicylideneamine Complex containing the Fe–O–Ru–O–Fe System[†]

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The redox reaction between *trans*-dioxotetraphenylporphyrinruthenium(vi) and two equivalents of the five-coordinate iron(ii) salicylideneamine complex Fe(salmah) in toluene results in the transfer of two electrons and formation of the novel bis-μ-oxo trimetallic complex $[\mathrm{Ru^{IV}(tpp)\{OFe^{III}(salmah)\}_2}]$ containing first and second row d-block ions which has been characterized by a crystal structure determination and its variable temperature magnetic properties.

The direct synthesis of a series of heterobinuclear μ-oxo complexes has been accomplished using $\mathrm{Cr^{IV}(O)}$ porphyrins as oxidants and a variety of $\mathrm{Fe^{II}}$, $\mathrm{Mn^{II}}$, $\mathrm{Mo^{IV}O}$ and $\mathrm{V^{IV}O}$ compounds as reductants.[1] Similarly several $\mathrm{Fe^{II}}$ and $\mathrm{Mn^{II}}$ complexes have been found capable of reducing $[\mathrm{Mo^{VI}(O)_2(edtc)_2}]$[†] in tetrahydrofuran to form μ-oxo complexes containing MoOFe(Mn) linkages. These mixed metal systems generally have been found to display antiferromagnetic coupling, the prime evidence for the existence of the oxo bridge in the absence of structural data.

We now report that the analogous dioxo-ruthenium(vi) porphyrin[2] $[\mathrm{Ru(tpp)(O)_2}]$ can be reduced by $[\mathrm{Fe^{II}(salmah)}]$[3] to form a heterotrimetallic μ-oxo bridged complex $[\mathrm{Ru^{IV}(tpp)\{OFe^{III}(salmah)\}_2}]$ **1**. Thus when a suspension of $[\mathrm{Ru^{VI}(tpp)(O)_2}]$ in toluene is added to a purple–red solution of $[\mathrm{Fe^{II}(salmah)}]$ immediate dissolution occurs and after stirring for one hour an olive-green solution is obtained [reaction (1)]. The newly formed complex can be isolated from solution as a purple crystalline solid by addition of hexane.

$$[\mathrm{Ru^{VI}(tpp)(O)_2}] + 2\,[\mathrm{Fe^{II}(salmah)}] \rightarrow [\mathrm{Ru^{IV}(tpp)\{OFe^{III}(salmah)\}_2}] \quad (1)$$

1

Compound **1** has been characterised by elemental (C, H, N) and electron microprobe analysis. The distinctive IR band at 819 $\mathrm{cm^{-1}}$ shown by $[\mathrm{Ru(tpp)(O)_2}]$ and associated with the Ru=O stretching frequency is missing in the trimetallic compound which, however, does not display any other frequency which can be identified as arising from the RuOFe system.

A single crystal X-ray structure determination[‡] has been carried out on a crystal having the composition $[\mathrm{Ru(tpp)\{OFe(salmah)\}_2}]\cdot 4\mathrm{CH_2Cl_2}$, obtained from a hexane–$\mathrm{CH_2Cl_2}$ solution. This study shows the compound to be a centrosymmetric species containing the Fe–O–Ru–O–Fe unit (Fig. 1), each FeORu bond system being bent at an angle of 155.2(5)°. The three metal atoms form a linear array.

The ruthenium atom is found in the plane of the four porphyrin nitrogen atoms as required by symmetry while the iron atoms of the salmah complexes lie towards the μ-O atoms, 0.16 Å out of the mean free planes defined by the two imine nitrogens, the tertiary amine nitrogen and one of the phenolic oxygen atoms of each salmah ligand. The remaining phenolic group in each ligand is so positioned that its oxygen lies approximately *trans* (175°) to the μ-oxo oxygen atom.

The Ru–(μ)O bond length is 1.866(6) Å, very similar to the $\mathrm{Ru^{IV}}$–(μ)O distance [1.850(4) Å] found for the one other trinuclear di-(μ)oxo bridged $\mathrm{Ru^{IV}}$ compound that has been structurally characterised, the mixed valence, 'Ruthenium red' analogue $[\mathrm{(NH_3)_5Ru^{III}ORu^{IV}(en)_2ORu^{III}(NH_3)_5}]\mathrm{Cl_6}$.[4] This compound has the same formal oxidation state distribu-

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[†] *Abbreviations used*: tpp = the dianion of 5,10,15,20-tetraphenylporphyrin; tmp = the dianion of 5,10,15,20-tetrakis-*p*-methoxyphenylporphyrin; oep = the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; edtc = the monoanion of diethyl dithiocarbamate; en = ethylenediamine; salmah = the dianion of *N,N'*-4-methyl-4-azaheptane-1,7-diylbis(salicylideneamine); salah = the dianion of *N,N'*-4-azaheptane-1,7-diylbis(salicylideneamine); 14-tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; 16-tmc = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane; L = the pentaanion of 1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid; tmtaa = the dianion of 5,7,12,14-tetramethyldibenzo[*b,j*][1,4,8,11]tetraazacyclotetradecine; py = pyridine; pip = piperidine.

[‡] *Crystal data* for **1**, $\mathrm{C_{90}H_{86}Cl_8Fe_2N_{10}O_6Ru}$: $M = 1900$, triclinic, space group $P\bar{1}$, $a = 12.494(7)$, $b = 13.517(7)$, $c = 13.592(6)$ Å; $\alpha = 71.47(4)$, $\beta = 89.70(4)$, $\gamma = 80.47(4)°$; $U = 2144(2)$ $\mathrm{Å^3}$; $D_c = 1.47$ $\mathrm{g\,cm^{-3}}$, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 8.14$ $\mathrm{cm^{-1}}$, $F(000) = 976$, $T = 176$ K. Siemens/Nicolet R3m/v diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å); 4015 unique data collected ($3.5 < 2\theta < 40.0°$), 2686 with $F > 6.0\sigma(F)$. Three standard reflections monitored every 197 reflections showed no drop in intensity over the data collection period. A numerical absorption correction was applied (transmission factors; maximum 0.8640, minimum 0.7555). Anomalous dispersion corrections were applied to atomic scattering factors for neutral atoms. The structure was solved by Patterson methods. Full-matrix least-squares refinement (Siemens SHELXTL Plus) employing anisotropic thermal parameters for Ru, Fe and Cl and isotropic thermal parameters for all other atoms (single fixed parameter for hydrogen positioned in geometrically idealized positions: C–H 0.96 Å) converged at $R = 0.060$ and $R_w = 0.073$. Largest peak in the difference Fourier synthesis was 0.82 e $\mathrm{Å^{-3}}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

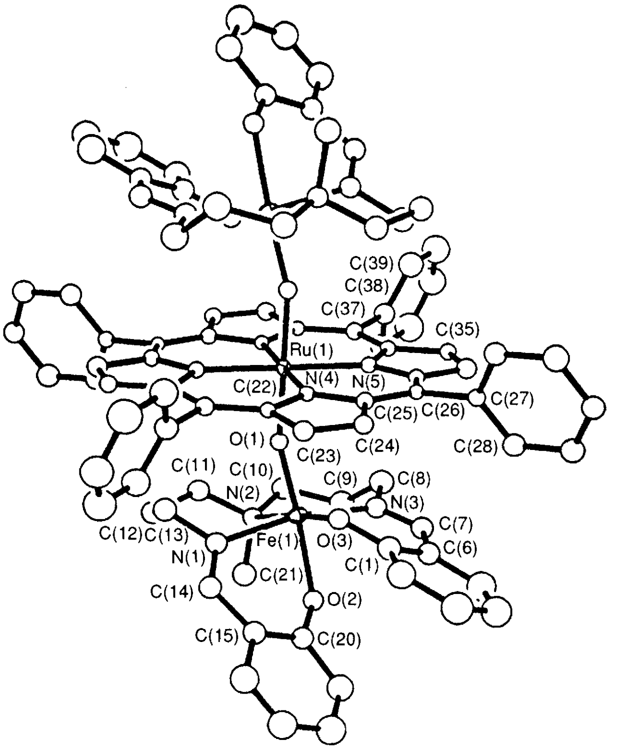


Fig. 1 Molecular structure of [Ru(tpp){OFe(salmah)}$_2$]·4CH$_2$Cl$_2$ **1** (the hydrogen atoms have been omitted for clarity). Selected interatomic distances (Å) and angles (°): Ru(1)–O(1), 1.866(6); Ru(1)–N(4), 2.051(9); Ru(1)–N(5), 2.060(8); Fe(1)–O(1), 1.848(6); Fe(1)–O(2) 2.072(6); Fe(1)–O(3) 1.955(9); Fe(1)–N(1) 2.129(9); Fe(1)–N(2) 2.315(11); Fe(1)–N(3), 2.102(9); Ru(1)–O(1)–Fe(1), 155.2(5); O(1)–Ru(1)–N(4), 89.7(3); O(1)–Ru(1)–N(5), 89.2(3); O(1)–Fe(1)–O(2), 175.2(3); O(1)–Fe(1)–O(3), 97.1(3); O(1)–Fe(1)–N(1), 95.9(3); O(1)–Fe(1)–N(2), 86.9(3); O(1)–Fe(1)–N(3), 97.0(3).

tion as the Ru(OFe)$_2$. It shows essentially a linear [RuORu 177.2(4)°] RuORuORu bond system.

The distance is also comparable to similar distances in the homobinuclear Ru^{IV}–O–Ru^{IV} porphyrin complexes [{Ru^{IV}(OC$_6$H$_4$Me-*p*)(tpp)}$_2$O][5] [1.789(11) Å], [{Ru^{IV}(HO)(oep)}$_2$O][6] [1.847(13) Å] and [{Ru^{IV}(oep)}$_2$O][7] [1.793(2) Å]. The distance is greater than for a Ru^{IV}=O bond as observed in [Ru^{IV}O(MeCN)(14-tmc)](PF$_6$)$_2$[8]† [1.765(5) Å] and even greater than for a Ru^{VI}=O distance as in [Ru^{VI}(O)$_2$(16-tmc)](ClO$_4$)$_2$[9]† [1.705(7) Å]. These comparisons support the Ru^{IV}–O–Fe^{III} nature of the complex. The Fe–(μ)O distance of 1.848(6) Å is however notably larger than has been reported for any other bimetallic μ-oxo bridged Fe^{III} compound.[10] It is indeed similar to the Ru–(μ)O distance. Fe–(μ)O distances have generally been found to be in the range 1.75–1.79 Å.[9] One compound having comparable Fe–(μ)O distances is the tetrametallic species [Fe$_4$O$_2$(CO$_3$)$_2$L$_2$]$^{6-}$† where values of 1.828(4) and 1.830(4) Å have been observed.[11] A recent accurate crystallographic study of the mixed metal complex [(tpp)Cr^{III}OFe^{III}(tmtaa)][12]† **2** has given a value of 1.759(11) Å for the Fe–O distance with *d*(Cr–O) = 1.776(11) Å. The Fe–O distance in the N$_3$O plane of the salmah ligand is nevertheless quite comparable, at 1.955(9) Å, with Fe–O distances to ligand oxygen atoms in other bidentate[13] and tetradentate[14] salicylideneamine Fe^{III} μ-oxo complexes which are also close to 1.95 Å. The remaining Fe–O bond length to the phenolic O, *trans* to the bridging oxygen is somewhat longer at 2.072(6) Å which may result from a '*trans*' effect phenomenon. The (μ)O–Fe–O angle is almost linear [175.2(3)°]. A similar conformation of the pentadentate ligand has been observed in a V^{III} complex[15] and in a peroxo bridged dinuclear Co^{III} species[16] containing the analogous salah† ligand but the difference between the M–O distances appears to be minimal in these compounds. In the [Co(salah)(1-methylimidazole)]$^+$ cation the ligand is arranged such that the oxygen and nitrogen atoms of the salicylidene rings occupy *trans* positions in the equatorial plane, the amine nitrogen and 1-methylimidazole being in axial positions.[17]

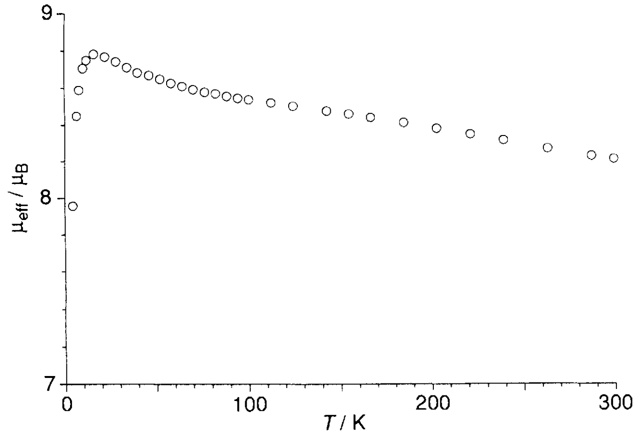
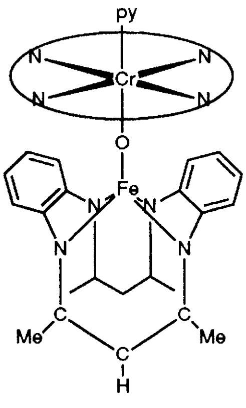


Fig. 2 Plot of μ_{eff} (per mol) *vs.* temperature for **1**. A 1 Tesla applied field was used on the Squid magnetometer (Quantum Design, San Diego, USA).

The bent nature of the RuOFe bond systems in the present complex contrasts with the linearity of the one other homotrimetallic Ru^{III}ORu^{IV}ORu^{III} complex characterised[4] and of other homobimetallic Ru^{IV} oxo bridged compounds[1] but is the normal mode found for Fe$^{III}{}_2$O[10] species and is known for Ru$_2{}^{III}$O compounds.[18] The Cr^{III}OFe^{III} complex[12] **2** recently studied also shows an essentially linear arrangement for the bond system [176.6(9)°] confirming the earlier incomplete study[19] of the porphyrin species [(py)(tpp)CrOFe(tmp)]† which also showed a linear CrOFe bond system. Molecular orbital concepts of bonding in homobinuclear M–O–M compounds which stressed the contributions of π bonding in such systems have been successful[20–22] in predicting that linear bonds will result when eight or fewer metal electrons have to be accommodated along with four oxygen electrons in the set of orbitals associated with the σ–π MOM bonding scheme. More than eight electrons will result in filling antibonding levels with a resultant bending of the M–O–M group of atoms unless steric constraints due to interactions between ligands prevent this.[22] In the present case, with a Ru^{IV}–Fe^{III} system providing nine electrons, a bent bonded system would be predicted, as observed. The Cr^{III}OFe^{III} compound with an eight electron count for the two metals would be expected to be linear also as observed.[12] The linearity of the Ru^{III}ORu^{IV}ORu^{III} system with nine electrons in each Ru^{III}Ru^{IV} segment is not predicted by this correlation which may indicate the greater strength of π bonding in the linear mode between second row d-block metals which stabilises this configuration.

The room temperature (300 K) magnetic moment of the trimetallic complex, μ_{eff}, is 8.25 μ_B which is slightly lower than the spin-only values calculated for a Fe^{III}Ru^{IV}Fe^{III} d^{5}d^{4}d^5 system of 8.83 μ_B assuming an S = 5/2–1–5/2 system and 8.37 μ_B assuming an S = 5/2–0–5/2 system. The magnetic properties of linear trimers such as **1** are of particular interest, not only because this compound provides a rare combination of first and second row d-block ions,[23] but also because fragments of this type provide useful building blocks for understanding molecular magnetic materials.[24] The 77 K Mössbauer spectrum of **1** shows a single asymmetric quadrupole doublet with values of the isomer shift (δ 0.56 mm s^{-1}) and quadrupole splitting (ΔE_Q 1.24 mm s^{-1}) typical of those expected for



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six-coordinate high-spin ($S = 5/2$) Fe^{III} Schiff-base species.[25] The spin state of the central Ru^{IV} d^4 ion is likely to be $S = 1$ by analogy with other recently reported $X_2Ru^{IV}(tpp)$[26] and $O{=}Ru^{IV}$ (porphyrin)[27] species.

Variable temperature magnetic moment data for **1** give clear evidence, albeit in a rather unusual fashion, for exchange-coupling within the Fe^{III}–O–Ru^{IV}–O–Fe^{III} unit. It can be seen in Fig. 2 that the observed μ_{eff} value (per mol) actually increases in a 'ferromagnetic-like'[24] way from 8.25 μ_B at 300 K towards a maximum of 8.8 μ_B at *ca.* 20 K before decreasing rapidly as the temperature is decreased to 4.2 K, the latter feature being due to ground-state zero field splitting effects. The 20–300 K data originate from the exchange-coupled 5/2–1–5/2 'irregular spin-state' combination[24] in a manner similar to that recently observed in related linear trimers, including an $Fe^{III}Ni^{II}Fe^{III}$ compound which contains multiatomic dimethylglyoximato bridging groups.[28] This latter compound has the same spin-state combination as in **1** and shows a maximum value of μ_{eff} at low temperatures of similar magnitude to that observed for the Ru(μ-OF)$_2$ compound owing to population of an $S' = 4$ ground state ($\mu_{calc.} = 8.94$ μ_B), which results from antiferromagnetic coupling between the adjacent and terminal metals. The characteristic dip in μ_{eff} noted at intermediate temperatures in the $Fe^{III}Ni^{II}Fe^{III}$[28] and related systems[24] is not present in **1** on account of it having a more negative $J_{Fe\text{-}Ru}$ value. Fitting of the magnetic data to theoretical calculations is presently being pursued; a value of $J_{Fe\text{-}Ru}$ of at least *ca.* -60 cm^{-1} is emerging which seems to be reasonable in relation to the strongly antiferromagnetically coupled $Fe^{III}OFe^{III}$ and $Ru^{IV}ORu^{IV}$ systems[5,10] (*N.B.* The separation between the ground $S' = 4$ and the next higher $S' = 3$ level is $2J$.) The magnetic orbitals on the central Ru^{IV} involved in overlap with the μ-oxo p_x and p_y orbitals are likely to be d_{xz} and d_{yz}, where z is the Ru–(μ)O direction. The terminal Fe^{III} groups can utilize any suitably oriented orbitals to complete the superexchange pathway, the precise mechanism of which should become apparent from a comparative study with other M–O–Ru–O–M compounds (M = Cr, Mn).

Other compounds similar to the tpp derivatives have been prepared by the reaction of $[Ru^{VI}(oep)(O)_2]$ and $[Ru^{VI}(tmp)(O)_2]$ with $[Fe^{II}(salmah)]$. These compounds all appear indefinitely stable in the solid state, and are soluble in organic solvents such as CH_2Cl_2. The complexes show evidence for decomposition however when their solutions are exposed to the air. Products such as $[\{Ru^{IV}(HO)(tpp)\}_2O]$ and $[\{Fe(salmah)\}_2O]$ are most probably formed. Similar redox reactions have been observed to occur between $[Ru^{VI}(\mathbf{P})(O)_2]$ and $[Fe^{II}(tpp)(pip)_2]$ (**P**[†] = oep, tpp, tmp) and other low-valent metal porphyrins such as $[Mn^{II}(tpp)]$ and $[Cr^{II}(tpp)]$. The magnetic and structural properties of these trimetallic compounds are currently being investigated.[29]

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