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Diruthenium(II) Tetrakis-6-methyl-2-oxypyridine, $[Ru_2(mph)_4]$, and Comparisons of the Metal–Metal Bonding in $[M_2(mhp)_4]$ (M = Mo, Ru or Rh) Complexes

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The nature of the metal–metal interaction(s) in dimetal entities is currently undergoing much investigation [1–8]. Recently, photoelectron (p.e.) spectral data have been reported for the molecules $[M_2(mhp)_4]$ (where M = Cr, Mo, or W); H{mhp} = 6-methyl-2-hydroxypyridine) [1, 4, 5] and $[Rh_2(mhp)_4]$ [6]; these studies provided good, direct evidence for a $(\sigma)^2(\pi)^4(\delta)^2$ metal–metal quadruple bond in the former molecules and a $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$ metal–metal single bond in the latter. The clear interpretations of the electronic structure of these M_2^{4+} centres obtained from these studies has prompted further such investigations. Herein, we report the preparation, crystal structure, and p.e. spectrum of $[Ru_2(mhp)_4]$, together with a comparison of the characteristics of the metal–metal interactions across the series $[Mo_2(mhp)_4]$, $[Ru_2(mhp)_4]$, and $[Rh_2(mhp)_4]$.

$[Ru_2(mhp)_4]$ was isolated in *ca.* 8% yield, following reaction between $[Ru_2(OAc)_4Cl]$ and Na(mhp) in MeOH, at room temperature under an atmosphere of purified dinitrogen; the mass spectrum of the compound contained, as the highest m/e feature, a multiplet, centred at 634 and having the profile expected for a diruthenium moiety, consistent with the sublimation and subsequent ionization of the molecular species. The magnetic susceptibility of the compound in CD_2Cl_2 solution was determined on a Bruker 80 MHz NMR spectrometer, using the method of Evans [9]; at 308 K, μ_{eff} for the dimer was found to be 2.9 μ_B. Crystals of the CH_2Cl_2 solvate suitable for diffraction studies were obtained by recrystallisation from CH_2Cl_2/pentane solution.

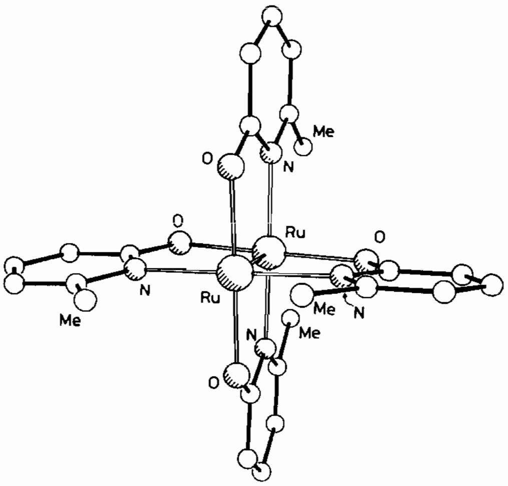

Fig. 1. Structure of the $[Ru_2(mhp)_4]$ molecule.

Crystal data

$C_{24}H_{24}N_4O_4Ru_2 \cdot CH_2Cl_2$, monoclinic, $P2_1/n$ (alternative setting of $P2_1/c$), a = 12.775(3), b = 17.155(3), c = 12.834(3) Å, β = 103.93(2)°, Z = 4. The structure was solved and refined from 3839 independent reflections with $2\theta \leqslant 50°$ and $I > 2\sigma(I)$, which had been measured with MoK_α radiation (λ = 0.71069 Å) and a Stoe-Siemens four-circle diffractometer and corrected for absorption (μ = 13.20 cm^{-1}). Hydrogen atoms were included in the refinement with constraints on bond lengths, angles and thermal parameters. All other atoms were refined anisotropically. The atoms of the CH_2Cl_2 molecule appear to have a large thermal motion and thus the position of this molecule could be somewhat disordered. The final R index is 0.0451 (0.0572 weighted).

The $[Ru_2(mhp)_4]$ molecule (Fig. 1) is isostructural with the other $[M_2(mhp)_4]$ (M = Cr, Mo, W [10], or Rh [6]) molecules reported thus far and closely corresponds to D_{2d} point symmetry. The length of the metal–metal bond and the average length of the metal–nitrogen and metal–oxygen bonds are compared, for those molecules containing the 4d elements in the Table. The lengths of these M–N and M–O bonds vary with M as Mo > Ru > Rh, corresponding to the general reduction in atomic radius across the 4d transition metal series. This variation in metallic radius, together with the varying occupancy of the orbitals involved in the metal–metal interaction, is presumed to determine the relative lengths of the metal–metal bonds within this closely related group of molecules. The length of the Ru–Ru bond in $[Ru_2(mhp)_4]$ is the shortest approach of these two atoms reported so far and, as discussed earlier [6], this is undoubtedly attributable

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TABLE I. Comparisons of Structural and Spectroscopic Properties for the Molecules [$M_2(mhp)_4$] (M = Mo, Ru, or Rh).

Property	[$Mo_2(mhp)_4$]	[$Ru_2(mhp)_4$]	[$Rh_2(mhp)_4$]
M–N bond length/A	2.167(16)	2.089(5)	2.043(5)
M–O bond length/A	2.086(8)	2.044(10)	2.017(4)
M–M bond length/A	2.065(1)	2.238(1)	2.359(1)
ν(M–M)/cm^{-1}	432	281	184
Electronic configuration	$(\sigma)^2(\pi)^4(\delta)^2$	$(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^3$	$(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$
δ–π splitting/eV	2.2	1.4	0.5
M–M bond order	4	2	1

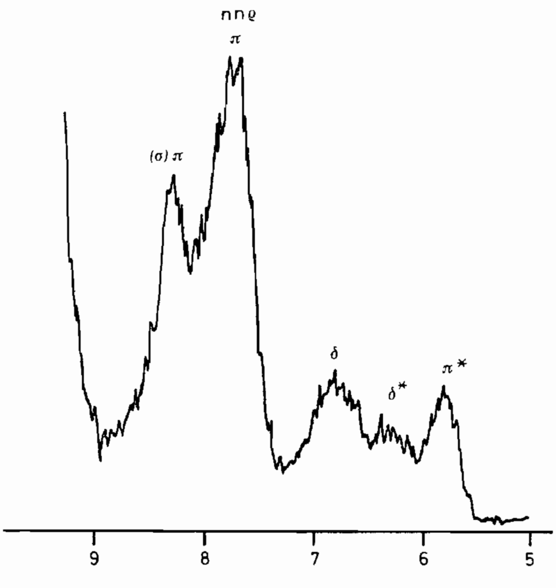

Fig. 2. He(I) photoelectron spectrum of [$Ru_2(mhp)_4$].

to electronic and steric effects of the mhp ligands encouraging metal–metal bond formation; in fact, this Ru–Ru bond is 0.01–0.05 Å *shorter* than that typical [11] of $Ru_2(O_2CR)_4^+$ centres which contain one *less* electron in a metal–metal *antibonding* orbital.

The He(I) p.e. spectrum of [$Ru_2(mhp)_4$] is presented in Fig. 2 and, by comparison with the p.e. spectral assignments we have presented for [Mo_2-$(mhp)_4$] [1, 4] and [$Rh_2(mhp)_4$] [6] and with reference to the 12 valence electrons of the Ru_2^{4+} centre, may be interpreted as follows:

(i) The broad band centred at 7.7 eX is correlated with ionization from the four molecular orbitals (m.o.s.) which correlate with the highest filled π m.o. of the ligand [4]. The breadth of this band is approximately the same as observed for the corresponding feature in the He(I) p.e. spectrum of [Mo_2-$(mhp)_4$], which occurs at 7.6 eV; however, for [$Rh_2(mhp)_4$] these ligand ionizations are split into two components at 8.4 and 7.6 eV due to a strong (Rh–Rh δ^*) – (ligand π) interaction [6]. Therefore, we take the breadth of the band at 7.6 eV in Fig. 2 to indicate that this metal–metal interaction is significantly less than that in [$Rh_2(mhp)_4$] and approximately the same as that in [$Mo_2(mhp)_4$].

(ii) The band at 8.2 eV is assigned to the ionizations from the Ru–Ru π (and possibly σ) orbital; this ionization energy is between the corresponding values measured for [$Mo_2(mhp)_4$] and [Rh_2-$(mhp)_4$] of 8.0 and 8.5 eV, respectively [1, 4, 6].

(iii) The principal component of the broad band centred at 6.8 eV is assigned to the ionizations from the Ru–Ru δ orbital; this ionization energy is between the corresponding values of 8.0 and 5.8 eV, respectively, for [$Rh_2(mhp)_4$] and [$Mo_2(mhp)_4$] [1, 4, 6].

(iv) The lowest energy region of the p.e. spectrum is correlated with ionizations from the Ru–Ru δ^* and π^* m.o.s. which collectively contain four electrons. The implication of two unpaired electrons from the μ_{eff} value and the intensity profile suggest a $(\delta^*)^1$-$(\pi^*)^3$ electronic configuration, with the bands centred at *ca.* 6.3 and 5.8 eV being due to δ^* and π^* ionizations, respectively. Such a simple explanation does not take account of spin multiplet effects which are expected to be particularly important for these ionizations and lead to a significant broadening of the band envelopes. The proposed assignment places the δ^* and π^* orbitals at a similar energy but, unlike the situation for [$Rh_2(mhp)_4$] [6], the metal–ligand interaction is apparently insufficient to raise the δ^* m.o. above the π^* m.o., as also implied by the lack of any splitting (i) in the band at 7.7 eV.

Therefore, we propose that this Ru_2^{4+} centre has a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1(\pi^*)^3$ electronic configuration, as suggested by an SCF-X_α-SW calculation for [Ru_2-$(O_2CH)_4$] [8]. The decrease in the net metal–metal interaction from [$Mo_2(mhp)_4$] to [$Ru_2(mhp)_4$] to [$Rh_2(mhp)_4$] is clearly seen from the structural and spectral comparisons presented in Table I. Thus, concomitant with the formal bond order of the metal–metal interaction decreasing from 4 to 2 to 1 as the population of the δ^* and π^* orbitals increases from 0 to 4 to 6, the length of the metal–metal bond increases, the separation between the δ and π orbitals decrease, and the ν(M–M) stretching frequency decreases. These variations are consistent with a simple m.o. description of the metal–metal interactions within these [M_2(mhp)$_4$] complexes.

Acknowledgements

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