Crystal Structure and U.V. Photoelectron Spectra of Tetrakis-(6-methyl-2-oxopyridinato)dirhodium

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Summary $Rh_2(mhp)_4$ (where Hmhp = 6-methyl-2-hydroxypyridine) has been prepared and characterised by *X*-ray crystallography and shown to involve a metal–metal separation of 2·359(1) Å; the He I and He II photoelectron spectra of $Rh_2(mhp)_4$ provide evidence for the presence of a metal–metal single bond.

THE electronic structure of the complexes $M_2(mhp)_4$ (where M = Cr, Mo, and/or W and Hmhp = 6-methyl-2-hydroxypyridine) have been well documented by photoelectron (p.e.) spectral studies,[1–3] although there are some differences in the assignments proposed by ourselves[1,2] and Cotton *et al.*[3] Herein we describe the preparation and characterisation of $Rh_2(mhp)_4$, together with the first p.e. spectral data for an Rh_2^{4+} complex. These data help clarify the controversy concerning the formulation of the Rh^{II}–Rh^{II} interaction as a triple[4] or single[5,6] bond.

Reactions between Na(mhp) and $Rh_2(O_2CMe)_2(MeOH)_2$ or $RhCl_3.3H_2O$ in methanol have afforded one yellow-brown and two green products. Analytical data and mass spectrometry showed the yellow-brown material to be composed of $Rh_2(mhp)_4$ molecules, as confirmed by *X*-ray crystallography.

Crystal data: $C_{24}H_{24}N_4O_4Rh_2$, orthorhombic, space group *Pbca*, $a = 15{\cdot}643(3)$, $b = 16{\cdot}083(3)$, $c = 18{\cdot}666(4)$ Å, $Z = 8$. The structure was solved and refined from 5383 independent reflections with $2\theta \leqslant 60°$ and $I > 2\sigma(I)$, which had been measured with Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) and a Stoe–Siemens four-circle diffractometer and corrected for absorption ($\mu = 14{\cdot}2\ cm^{-1}$). Hydrogen atoms were included in the refinement with constraints on bond lengths, angles, and thermal parameters. All other atoms were refined anisotropically. The final *R* index is 0·0354 (0·0375 weighted).†

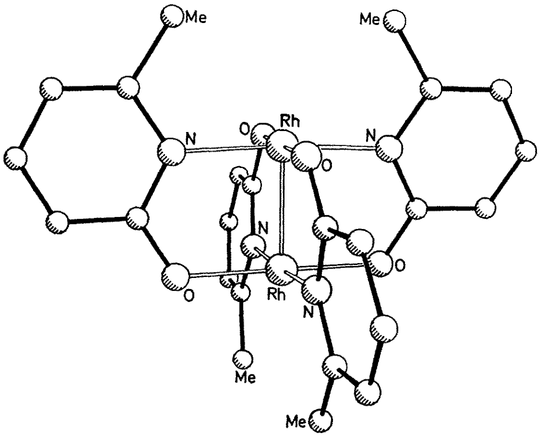

FIGURE 1. Molecular structure of $Rh_2(mhp)_4$.

The molecular structure of $Rh_2(mhp)_4$ (Figure 1) closely corresponds to D_{2d} symmetry, as found for the $M_2(mhp)_4$ (where M = Cr,[7] Mo,[7] W,[7] or Ru[8]) molecules. The average lengths of Rh–O and Rh–N bonds, 2·017(4) and 2·043(5) Å, respectively, are shorter than the corresponding[7] values for $Mo_2(mhp)_4$ of 2·086(8) and 2·167(14) Å, representing a reduction in atomic radius across the 4d transition metal series. This variation in metallic radius must be included in any consideration of the relative lengths of the Mo–Mo and Rh–Rh bonds with respect to their bond orders. The length of the Rh–Rh bond in $Rh_2(mhp)_4$ of 2·359(1) Å is the shortest approach of these metal atoms so far reported. This is not unexpected, given the structural data available[7,9] for Cr_2^{4+} and Mo_2^{4+} centres. Thus a set of four mhp ligands bridging over two metal atoms leads to the latter having a relatively low net positive charge so the direct metal–metal interactions are enhanced; also the location of the methyl groups discourages the binding of ligands along the metal–metal axis which could weaken[10] the metal–metal bond. However, the Rh–Rh bond in $Rh_2(mhp)_4$ is only some 0·027 Å shorter than in $Rh_2(O_2CMe)_4(H_2O)_2$.[4] Thus, as established[11] for Mo_2^{4+} systems, axial binding *per se* need not cause a marked increase in the length of an Rh^{II}–Rh^{II} bond.[6,12]

The lower energy regions of the He I and He II photoelectron spectra of $Rh_2(mhp)_4$ are shown in Figure 2 and the ionization energies (I.E.'s) are listed in the Table, together with suggested assignments. The latter have been deduced with particular reference to the p.e. spectral details obtained[1,2] for $Mo_2(mhp)_4$ and noting the change in the metals 4d electronic configuration from 8 (Mo_2^{4+}) to 14 (Rh_2^{4+}), assuming that (i) the metal–metal bonding orbitals are at a higher binding energy than the metal–metal antibonding orbitals and (ii) the relative peak areas corresponding to

TABLE. Ionization energies for $Rh_2(mhp)_4$.

Peak	Ionization energy/eV	Assignment	Orbital character[a]
A	6·49(2)	Rh–Rh δ^*	a_2
B	7·25(2)	Rh–Rh π^*	e
C	7·64(2)	mhp π	b_1,e
D	8·00(2)	Rh–Rh δ	b_1
E	8·37(2)	mhp π	a_2
F	8·53(3)	Rh–Rh π (σ)	e(a_1)

[a] In D_{2d} symmetry.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

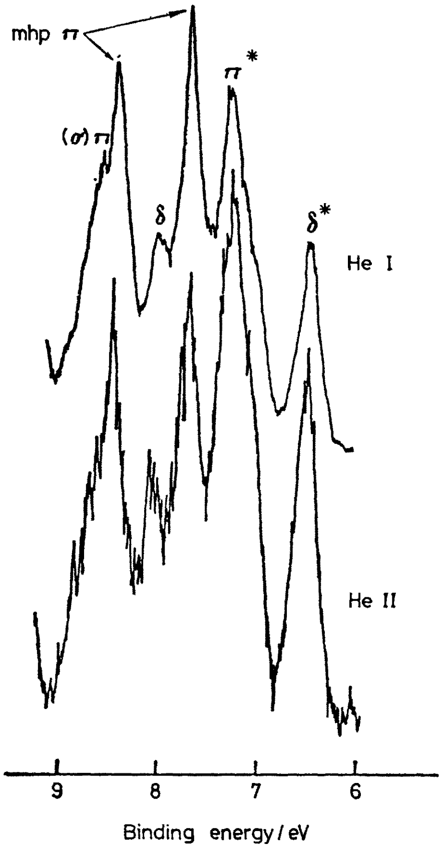

FIGURE 2. Lower energy regions of the He I and He II photoelectron spectra of $Rh_2(mhp)_4$.

ionizations from the metal orbitals approximately correlate with the level's electron population. The sharp feature at 7·64 eV is attributed to ionization from the highest filled (π) orbital of the mhp ligands, this orbital has significant N and O p_π character and is antibonding between these atoms. This feature is analogous to the I.E. of $Mo_2(mhp)_4$ at 7·59 eV.[1,2] The two lowest energy features, at 6·49 and 7·25 eV, are attributed to ionizations from the Rh–Rh δ^* and π^* orbitals, respectively. This reversal of the normally expected order is attributed to the strong interaction between the Rh–Rh δ^* orbital and the a_2 combination of the highest filled ligand orbitals. This interaction should stabilise the ligand a_2 combination and ionization from this is considered to give rise to the other sharp feature of the spectrum at 8·37 eV. The remaining features of the spectrum, at 8·00 and 8·53 eV, are attributed to ionizations from the Rh–Rh δ and π orbitals, respectively. No clear evidence has been obtained in these studies for the ionizations from the Rh–Rh σ orbital and, by analogy with the assignments proposed[1,2] for $Mo_2(mhp)_4$ and related compounds, we tentatively suggest that this may be contained within the same band envelope as the π ionization.

Therefore, these p.e. spectral data are consistent with this Rh–Rh bond having the $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$ configuration, corresponding to a metal–metal single bond, as suggested by SCF-Xα calculations[6] for $Rh_2(O_2CH)_4$. The alternative interpretation[4] of the metal–metal triple bond would require the filling of two metal p_z combinations leading to a configuration such as[11] $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(p_{z_1})^2(p_{z_2})^2$. This is inconsistent with the p.e. spectral data reported here, in particular the profile and relative intensities of the two lowest energy spectral features.

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