Multiple Rhodium(II)–Rhodium(III) Bond in the Dimer $[Rh_2(O_2CMe)_4(H_2O)_2]$-$[ClO_4]\cdot H_2O$; *X*-Ray Crystal Structure

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Summary The crystal and molecular structure of tetra-μ-acetatorhodium(II)–rhodium(III) perchlorate has been determined; the complex contains the bimolecular species $[Rh_2(O_2CMe)_4(H_2O)_2]^+$ with a very short Rh^{II}–Rh^{III} distance of 2·3165(20) Å.

Binuclear carboxylato-bridged complexes of the type $M_2(O_2CR)_4$ are among the most suitable complexes for investigating different types of metal–metal interactions and for studying the relationship between the electronic configuration of metal ions and the multiplicity of metal–metal bonding.[1] The structure of these complexes has therefore been the subject of great interest to workers in this field. The $[Rh_2(O_2CMe)_4(H_2O)_2]^+$ ion described recently[2–4] is, together with the ion $[Ru_2(O_2CC_3H_7)_4]^+$,[5] a good example of this type of complexes having the metal in different oxidation states. Crystals of the complex $[Rh_2(O_2CMe)_4(H_2O)_2][ClO_4]\cdot H_2O$ were prepared by a method described earlier.[4]

Crystal data: $C_8H_{16}ClO_{14}Rh_2$, M 595·5, triclinic, space group $P\bar{1}$, $a = 8{\cdot}187(2)$, $b = 8{\cdot}114(2)$. $c = 16{\cdot}120(3)$ Å, $\alpha = 91{\cdot}85(3)$, $\beta = 101{\cdot}84(3)$, $\gamma = 115{\cdot}17(3)°$, $D_m = 2{\cdot}09$, $D_c = 2{\cdot}10$ g cm^{-3}, $Z = 2$. Intensities were collected on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated Cu-K_α radiation. The structure was solved by heavy atom methods. Full-matrix least-squares refinement based on 1783 reflections with $F > 3{\cdot}92\sigma(F)$ yielded final R_1 and R_2 values of 0·054 and 0·073, respectively; consideration of all of 1937 reflections gave the values 0·06 and 0·073, respectively. A perspective view of the molecular structure of the complex is shown in the Figure.†

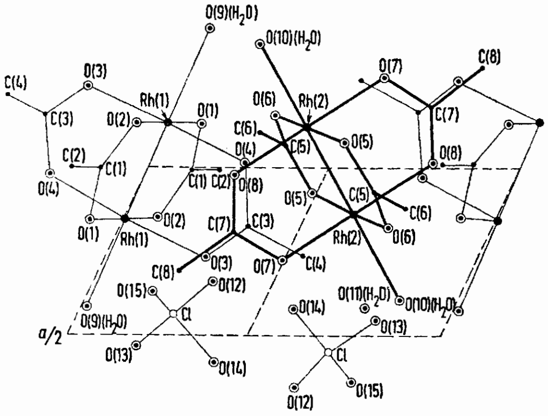

FIGURE. The structure of $[Rh(O_2CMe)_4(H_2O)_2][ClO_4]\cdot H_2O$. Bond lengths are: Rh(1)–Rh(1), 3·315(2); Rh(1)–O(1), 2·014(13); Rh(1)–O(2), 2·012(12); Rh(1)–O(3), 2·013(11); Rh(1)–O(4), 2·012(11); Rh(1)–0(9), 2·228(15); Rh(2)–Rh(2), 2·318(2); Rh(2)–O(5), 2·022(12); Rh(2)–O(6), 2·015(12); Rh(2)–O(7), 2·021(14); Rh(2)–O(8), 2·006(15); and Rh(2)–O(10), 2·216(13) Å.

The complex contains binuclear carboxylato-bridged species $[Rh_2(O_2CMe)_2(H_2O)_2]^+$ with a mean Rh–Rh distance of 2·3165(20) Å. The mean Rh–O(acetate) bond length is 2·014 Å, and the Rh–O(H_2O) distance is 2·222 Å. This complex has the shortest Rh–Rh distance known so far, except the Rh–Rh distance of 2·3855(5) Å in the diamagnetic complex $[Rh_2(O_2CMe)_4(H_2O)_2]$ which involves multiple bonding, probably of the order 3.[6] This suggests that the Rh–Rh bond order in the paramagnetic species $[Rh_2(O_2CMe)_4(H_2O)_2]^+$ is higher than 3.

There are at least three different experimental and theoretical approaches to the problem of Rh–Rh bonding in the binuclear carboxylato-bridged complexes. According to Dubicki and Martin[7] it is a single (σ) bond which can be described by the pattern of orbitals: $e_u{}^4(\pi)$, $a_{1g}{}^2(\sigma)$, $b_{2g}{}^2(\delta)$, $b_{1u}{}^2(\delta^*)$. $e_g{}^4(\pi^*)$. Norman and Kolari[8] proposed a different M–M bonding set of orbitals on the basis of an SCF-SW-X_α calculation for the $MoCl_8{}^{2-}$ ion. Earlier Bennet *et al.*[5] had suggested that the complex contains a triple Rh–Rh bond arising from the configuration: $a_{1g}{}^2(\sigma)$, $e_u{}^4(\pi)$, $b_{2g}{}^2(\delta)$, $a_{1g}{}^2(\sigma_n)$, $a_{2u}{}^2(\sigma_n')$, $b_{1u}{}^2(\delta^*)$.

Although all three interpretations are consistent with the closed shell configuration required by the observed diamagnetism of $[Rh_2(O_2CMe)_4]$, only the last was supported by experiments showing a very short Rh–Rh bond in the diamagnetic complex $[Rh_2(O_2CMe)_4]$; this receives further support from our X-ray data for the paramagnetic complex $[Rh_2(O_2CMe)_4(H_2O)_2][ClO_4]\cdot H_2O$. Therefore the order of the Rh^{II}–Rh^{III} bond in $[Rh_2(O_2CMe)_4(H_2O)_2]^+$ species is most probably more than 3 and can be described by the following orbitals: $a_{1g}{}^2(\sigma)$, $e_u{}^4(\pi)$ $b_{2g}{}^2(\delta)$ $a_{1g}{}^2(\sigma_n)$, $a_{2u}{}^2(\sigma_n')$, $b_{1u}{}^1(\delta^*)$. Assuming, after Cotton,[1,5] that $a_{1g}(\sigma_n)$ and $a_{2u}(\sigma_n')$ orbitals are essentially non-bonding, and the half-filled antibonding b_{1u} (δ^*) orbital partially nullifies the bonding effect of the $b_{2g}(\delta)$ orbital, the Rh^{II}–Rh^{III} bonding set of orbital is given by: $a_{1g}{}^2(\sigma)$, $e_u{}^4(\pi)$, $b_{2g}{}^2(\delta)$, $b_{1u}{}^1(\delta^*)$, leading to the bond order of 3·5(σ, 2π, 0·5δ).

(*Received*, 17*th Jaunary* 1977; *Com.* 041.)

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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.

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