A Novel Mixed Valence Rhodium Dimer, $[Rh_2(OAc)_4]^+$

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Summary Oxidation of $[Rh_2(OAc)_4]$ gives novel mixed valence species, $[Rh_2(OAc)_5]$ and $[Rh_2(OAc)_4Cl]$ in which the acetate-bridged structure of the Rh^{II} complex is retained.

The complex $[Rh_2(OAc)_4]$ is well known,[1] and a number of related rhodium(II) species with metal–metal bonds have recently been described.[2] We report the characterisation of a new mixed-valence species, $[Rh_2(OAc)_4]^+$.

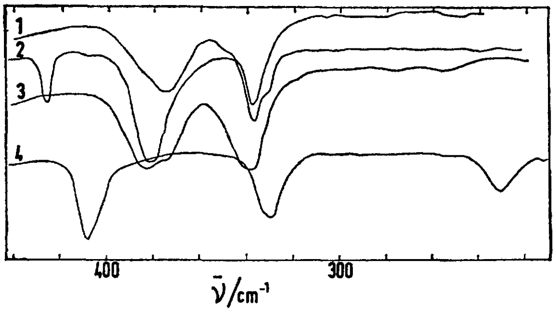

Figure 1. I.r. spectra of (1) $[Rh_2(OAc)_4(NH_3)_2]$, (2) $[Rh_2(OAc)_4(py)_2]$, (3) $[Rh_2(OAc)_4]$, and (4) $[Rh_2(OAc)_4Cl]$.

This complex is obtained by electrolytic oxidation of $[Rh_2(OAc)_4]$ at a bright platinum anode, in acid solution. It is absorbed by Dowex 50W-X8 cation exchange resin, but eluted by 1·0 M $HClO_4$. Potentiometric titrations using a bright platinum electrode indicate that reactions (1) proceed rapidly and quantitatively in aqueous $HClO_4$. The

$$[Rh_2(OAc)_4] \underset{Fe^{2+}}{\overset{Ce^{4+}}{\rightleftarrows}} [Rh_2(OAc)_4]^+ \tag{1}$$

number of electrons transferred per rhodium dimer molecule is 0·99 ± 0·01 (average of four experiments) and the standard redox potential for the $[Rh_2(OAc)_4]^+/[Rh_2(OAc)_4]$ couple is 1·25 ± 0·01 V at 25 °C in 1·0 M $HClO_4$.

Solid compounds $[Rh_2(OAc)_5]$ and $[Rh_2(OAc)_4Cl]$ have been isolated. The latter is somewhat variable in chlorine content and on standing in open air reverts to $[Rh_2(OAc)_4]$. The low-frequency i.r. spectra of a freshly prepared sample, and of three rhodium(II) complexes, are shown in Figure 1.

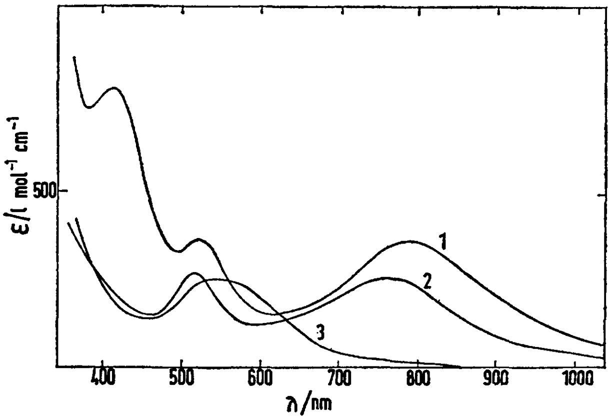

Figure 2. Absorption spectra of $[Rh_2(OAc)_4]^+$ complexes in: (1) 0·02 M Cl^- in 1 M $HClO_4$, (2) 1 M $HClO_4$, and (3) 3·5 M NH_3.

The band at 426 cm^{-1} in $[Rh_2(OAc)_4(py)_2]$ (py = pyridine) is assigned to Rh–py ligand stretching and the band at 231 cm^{-1} in $[Rh_2(OAc)_4Cl]$ is assigned to Rh–Cl stretching (*cf.* 194 and 223 cm^{-1} for Re–Cl stretching[3] in $[Re_2(OAc)_4Cl]$); the other two bands in the low-frequency spectra are assigned to ligand modes consisting mainly of metal–oxygen stretching and deformation. The fact that the same number of such bands occurs in the mixed valence compound as in the rhodium(II) compounds implies that on the i.r. time-scale the valencies are equivalent and not localised as $Rh^{II}Rh^{III}$.†

† The e.s.r. spectra of both $[Rh_2(OAc)_5]$ and $[Rh_2(OAc)_4Cl]$ have been obtained and are consistent with the presence of one unpaired electron in each case.

Besides the brown chloro-complex a violet ammine is formed in solution. Visible and near i.r. spectra of the three mixed valence species which we have characterised are shown in Figure 2. The low energy bands are shifted according to the spectrochemical series. As expected from the redox potential, the mixed valence complex is reduced to rhodium(II) by NCS^-, NCO^-, NO_2^-, N_3^-, SO_3^{2-}, I^-, and thiourea. With Br^- also there is rapid reduction at room temperature but when solutions of $[Rh_2(OAc)_4]^+$ and Br^- are mixed at 5 °C a blood-red complex is formed which fades in *ca.* 10 s to the apple-green bromide adduct of $[Rh_2(OAc)_4]$.

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