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LETTERS TO THE EDITOR

Trinuclear Rhodium μ_3-Oxoacetate Complexes with Triphenylphosphine, Triphenylarsine, and α-Picoline

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Earlier [1] we have found that the complexes $[Rh_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(L)_3]ClO_4$ (L = pyridine, β-picoline, and triphenylphosphine) are weak paramagnetics. In the present work we synthesized three new rhodium μ_3-oxoacetates **I–III** and characterized them by X-ray diffraction analysis.

$$\{[Rh_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(PPh_3)_3]_2\}ClO_4\cdot H_2O$$
I

$$[Rh_3^{III}(\mu_3\text{-}O)(\mu\text{-}OAc)_6(AsPh_3)_3]ClO_4\cdot C_2H_5OH\cdot H_2O$$
II

$$[Rh_3^{III}(\mu_3\text{-}O)(\mu\text{-}OAc)_6(\alpha\text{-}pic)_3]ClO_4$$
III

The X-ray diffraction analysis showed that the main fragment of the crystal structures of all the isolated compounds is the complex cation $[Rh_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(L)_3]^+_n$, where L = PPh_3 (**I**), $AsPh_3$ (**II**), and α-picoline (**III**); n = 1 (**II, III**) or 2 (**I**).

Compound **I** crystallizes in a triclinic system, space group $P\bar{1}$; a 11.749, b 22.693, c 26.223 Å; α 91.570, β 90.048, γ 100.630°; Z 2, R 14.0%. Based on the X-ray analysis, elemental analysis, and magnetic susceptibility we concluded that compound **I** represents a superposition of Rh(II, III, III) and Rh(III, III, III) complexes. The existence of such a mixed-valence compound can explain the paramagnetic properties of rhodium oxoacetates described earlier in [1].

Complex **II** crystallizes in a triclinic system, space group $P\bar{1}$; a 16.448, b 17.490, c 28.166 Å; α 81.92, β 74.12, γ 72.27°; Z 4, R 3.78%. Complex **III** crystallizes in a monoclinic system, space group $P2_1$; a 18.360, b 8.162, c 27.754 Å; β 96.86°, Z 2, R 7.49%.

The X-ray diffraction analysis of complexes **II** and **III** showed that there is one perchlorate anion per each trinuclear unit. This result explains the formal oxidation state +3 for all rhodium atoms constituting the $Rh_3(\mu_3\text{-}O)$ frame.

The initial compound for the synthesis of complexes **I–III** was the complex $[Rh_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6\cdot(H_2O)_3]ClO_4\cdot 3.5H_2O$ (**IV**) [2].

(μ_3-Oxo)hexakis(μ-acetato)tristriphenylphosphinotrirhodium(II, III)(μ_3-oxo)hexakis(μ-acetato)tristriphenylphosphinotrirhodium(III) perchlorate hydrate (I). A 0.2 g sample of complex **IV** was dissolved in 30 ml of methanol. To the solution, 0.2 g of PPh_3 and 0.05 g of $NaClO_4$ were added. The reaction mixture was heated a water bath for 2–3 h until its color changed from brown to red. The solution was reduced at room temperature to 10 ml and filtered. Red crystals formed in 1 day. The product was recrystallized from 96% ethanol. Complex I is readily soluble in dichloromethane, chloroform, and ethanol. Found, %: C 51.2; H 4.3; Cl 1.4; Rh 20.5. $C_{132}H_{128}ClO_{31}P_6Rh_6$. Calculated, %: C 52.0; H 4.2; Cl 1.2; Rh 20.3.

(μ_3-Oxo)hexakis(μ-acetato)tristriphenylarsinorhodium(III)ethanol hydrate (II) was synthesized by an analogous procedure, using $AsPh_3$ instead of PPh_3. Dark red crystals of compound **II** are readily soluble in dichloromethane, chloroform, and ethanol. Found, %: C 46.6; H 4.1; Cl 2.4; Rh 17.7. $C_{68}H_{71}As_3ClO_{19}Rh_3$. Calculated, %: C 46.4; H 4.1; Cl 2.0; Rh 17.5.

(μ_3-Oxo)hexakis(μ-acetato)tri(α-picolino)rhodium(III)dimethanol dihydrate (III) was synthesized by an analogous procedure, using α-picoline instead of PPh_3, without recrystallization in ethanol. Dark red

crystals of compound **III** are readily soluble in dichloromethane and chloroform and worse in ethanol and methanol. Found, %: C 33.0; H 4.5; Cl 3.1; Rh 26.2. $C_{32}H_{53}ClN_3O_{22}Rh_3$. Calculated, %: C 32.7; H 4.5; Cl 3.0; Rh 26.3.

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