

LETTERS TO THE EDITOR

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

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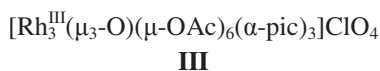
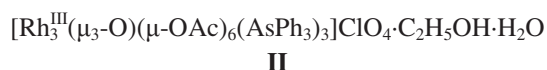
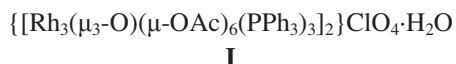
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Earlier [1] we have found that the complexes $[\text{Rh}_3(\mu_3\text{-O})(\mu\text{-OAc})_6(\text{L})_3]\text{ClO}_4$ (L = pyridine, β -picoline, and triphenylphosphine) are weak paramagnetics. In the present work we synthesized three new rhodium μ_3 -oxoacetates **I–III** and characterized them by X-ray diffraction analysis.



The X-ray diffraction analysis showed that the main fragment of the crystal structures of all the isolated compounds is the complex cation $[\text{Rh}_3(\mu_3\text{-O})(\mu\text{-OAc})_6(\text{L})_3]^+$, 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 $P1$; 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 $\text{Rh}(\text{II}, \text{III}, \text{III})$ and $\text{Rh}(\text{III}, \text{III}, \text{III})$ 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 $P1$; 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 $\text{Rh}_3(\mu_3\text{-O})$ frame.

The initial compound for the synthesis of complexes **I–III** was the complex $[\text{Rh}_3(\mu_3\text{-O})(\mu\text{-OAc})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \cdot 3.5\text{H}_2\text{O}$ (**IV**) [2].

(μ_3 -Oxo)hexakis(μ -acetato)tristriphenylphosphinotrirrhodium(II, III)(μ_3 -oxo)hexakis(μ -acetato)tristriphenylphosphinotrirrhodium(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. $\text{C}_{132}\text{H}_{128}\text{ClO}_{31} \cdot \text{P}_6\text{Rh}_6$. 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. $\text{C}_{68}\text{H}_{71}\text{As}_3\text{ClO}_{19}\text{Rh}_3$. 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.

ACKNOWLEDGMENTS

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