Oximato bridged Rh\textsuperscript{III}\textsubscript{2}M\textsuperscript{II} and Rh\textsuperscript{III}M\textsuperscript{I} species (M\textsuperscript{II} = Mn, Co, Ni; M\textsuperscript{I} = Cu, Ag)

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Abstract. The reaction of [RhCl\textsubscript{2}(HPhL)(PhL)] with M\textsuperscript{II}(ClO\textsubscript{4})\textsubscript{2}⋅6H\textsubscript{2}O in presence of alkali has furnished trinuclear [RhCl\textsubscript{2}(PhL)\textsubscript{2}]\textsubscript{2}M(H\textsubscript{2}O)\textsubscript{2}⋅H\textsubscript{2}O (HPhL is phenylazobenzaldoxime; M\textsuperscript{II} = Mn, Co, Ni). A similar reaction with M\textsuperscript{I}(PPh\textsubscript{3})\textsubscript{2}NO\textsubscript{3} yielded binuclear [RhCl\textsubscript{2}(PhL)\textsubscript{2}]M(PPh\textsubscript{3})\textsubscript{2} (M\textsuperscript{I} = Cu, Ag). In these molecules the oximato group acts as a bridge between Rh\textsuperscript{III} (bonded at N) and M\textsuperscript{II} or M\textsuperscript{I} (bonded at O). In structurally characterized [Rh\textsuperscript{III}Cl\textsubscript{2}(PhL)\textsubscript{2}]Mn(H\textsubscript{2}O)\textsubscript{2}.H\textsubscript{2}O the centrosymmetric distorted octahedral MnO\textsubscript{6} coordination sphere is spanned by four oximato oxygen atoms and two water molecules lying in trans position. In the lattice the neighbouring molecules are held together by H\textsubscript{2}O⋅⋅⋅H\textsubscript{2}O hydrogen bonds generating infinite zigzag chains. The manganese atoms lie parallel to the C-axis, the shortest Mn...Mn distance being 7.992 Å. Magnetic exchange interactions if any are small as seen in room temperature magnetic moments. The manganese system displays a strong EPR signal near $g = 2.00$. In the complex [RhCl\textsubscript{2}(PhL)\textsubscript{2}]Cu(PPh\textsubscript{3})\textsubscript{2} the copper atom is coordinated to two oximato oxygen atoms and the two phosphorus atoms in a distorted tetrahedral geometry. The softness of the phosphine ligand is believed to sustain the stable coordination of hard oximato oxygen to soft Cu\textsuperscript{I}. The coordination sphere of the Rh\textsuperscript{III} atom in both the complexes is uniformly trans-Rh\textsubscript{II}Cl\textsubscript{2}.

Keywords. Polynuclear complexes; oximato bridging; rhodium–manganese complexes; rhodium–copper complexes.

1. Introduction

Hetero-diatomic N, O-bridging of transition metal ions by the oximato function as in 1 has been known for long\textsuperscript{1} and interest in the use of this tool as a strategy for designing interesting polynuclear species remains unabated\textsuperscript{2–10}. The majority of this activity has generally concerned metal ions of the first transition series. Heavier ions occur in only a few scattered examples such as Pd\textsubscript{11}, PdCu\textsubscript{12}, Os\textsubscript{2}M\textsubscript{13} and Os\textsubscript{3}\textsuperscript{14} species.

Rhodium(III) arylaoxoimimates of type 2 abbreviated as [RhCl\textsubscript{2}(HArL)(ArL)] have been reported\textsuperscript{15} from this laboratory (HArL is arylazobenzaldoxime). The cis disposition of the two oxime functions makes 2 a potential ligand for binding another metal ion via displacement of the bridge proton. In this work it is demonstrated that this indeed happens leading to novel binuclear and trinuclear species of types Rh\textsuperscript{III}M\textsuperscript{I} (M = Cu, Ag) and Rh\textsuperscript{III}M\textsuperscript{II} (M = Mn, Co, Ni) which have been isolated and characterized. Only the species with Ar = Ph are reported here.

2. Experimental

2.1 Materials and methods

The starting complexes Cu\textsuperscript{I}(PPh\textsubscript{3})\textsubscript{2}NO\textsubscript{3}\textsuperscript{16}, Ag\textsuperscript{I}(PPh\textsubscript{3})\textsubscript{2} NO\textsubscript{3}\textsuperscript{17} and trans-[Rh\textsuperscript{III}Cl\textsubscript{2}(HPhL)(PhL)]\textsuperscript{15} were synthesized as reported. Hydrated transition metal perchlorates were prepared by treating the corresponding metal carbonates with 70% aqueous perchloric acid, followed by re-crystallization. All other chemicals and solvents were of reagent grade and were used as received.Electronic and IR spectra were recorded.
with a Shimadzu UV-1601 PC and Nicolet Magna IR series II/Perkin Elmer 783 spectrometers. Room temperature magnetic susceptibility was measured with a Model 155 PAR vibrating sample magnetometer fitted with a Walker Scientific L75FBA magnet. Microanalysis (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer.

2.2 Synthesis of the complexes

2.2a \([\text{Rh}^{II}Cl_2(\text{PhL})_2]M^II(H_2O)_2H_2O\): These complexes were synthesized in good yields (70–80%) by reacting \([\text{Rh}^{II}Cl_2(\text{HPhL})(\text{PhL})]\) and \(M^II(\text{ClO}_4)_2\) in 2:1 molar ratio in the presence of alkali. Details of a representative case (\(M = \text{Mn}\)) are given below. The other compounds (\(M = \text{Co}, \text{Ni}\)) were prepared analogously.

2.2b \([\text{RhCl}_2(\text{PhL})_2]Mn(H_2O)_2H_2O\): To a suspension of \(0.2 \text{ g, 0.34 mmol}\) in 15 ml of absolute ethanol was added NaOH (0.014 g, 0.35 mmol) and the contents were stirred till dissolution. To the green solution thus obtained an ethanolic solution of Mn(II)ClO_4-6H_2O (0.062 g, 0.17 mmol) was added drop-wise. The colour changed to deep red and the contents were allowed to stir for 2 h. The dark red crystalline precipitate that separated was filtered, washed with ethanol and dried in vacuo over fused CaCl_2. Yield: 0.339 g, 75%. Anal. Calc. for \(\text{C}_{52}\text{H}_{36}\text{N}_6\text{O}_6\text{Cl}_2\text{Mn}: C, 46.14; H, 3.42; N, 12.42%\). Found: C, 46.4; H, 3.37; N, 12.48%. IR (KBr, cm\(^{-1}\)): 3400 (H\(_2\)O stretch), 360 (Rh–Cl stretch). UV-Vis (CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon, M^{-1} cm^{-1}\))): 575 (6850), 550 (5900), 460 (12000), 410 (16370), 360 (18030) \(\mu_{\text{eff}} = 5.94\) \(\mu\)B. EPR g values (polycrystalline): 2.014 (major); 1.542, 2.716, 4.628, 5.975 (minor).

2.2c \([\text{RhCl}_2(\text{PhL})_2]Co(H_2O)_2H_2O\): Trans-\([\text{RhCl}_2(\text{HPhL})(\text{PhL})]\) (0.2 g, 0.34 mmol) and \(\text{Co}(\text{ClO}_4)_2\cdot6\text{H}_2\text{O}\) (0.063 g, 0.17 mmol) were used. Yield: 0.348 g, 77%. Anal. Calc. for \(\text{C}_{52}\text{H}_{36}\text{N}_6\text{O}_6\text{Cl}_2\text{Co}: C, 46.00; H, 3.41; N, 12.38%\). Found: C, 46.08; H, 3.37; N, 12.37%. IR (KBr, \(cm^{-1}\)): 3400 (H\(_2\)O stretch), 360 (Co–Cl stretch). UV-Vis (CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon, M^{-1} cm^{-1}\))): 595 (7920), 585 (7600), 410 (19700), 360 (21500) \(\mu_{\text{eff}} = 5.13\) \(\mu\)B. EPR g values after doping with 1% \([\text{RhCl}_2(\text{PhL})_2]\cdot\text{Mn(H}_2\text{O})_2\cdot\text{H}_2\text{O}\) (polycrystalline): 2.001 (major); 1.538, 2.650, 4.596, 5.868 (minor).

2.2d \([\text{RhCl}_2(\text{PhL})_2]Ni(H_2O)_2H_2O\): Trans-\([\text{RhCl}_2(\text{HPhL})(\text{PhL})]\) (0.2 g, 0.32 mmol), NaOH (0.013 g, 0.33 mmol) and Ni(ClO\(_4\))\(_2\)-6H\(_2\)O (0.059 g, 0.16 mmol) were employed. Yield: 0.329 g, (73%). Anal. Calc. for \(\text{C}_{52}\text{H}_{36}\text{N}_6\text{O}_6\text{Cl}_2\text{Ni}: C, 46.01; H, 3.42; N, 12.38%\). Found: C, 46.09; H, 3.48; N, 12.34%. IR (KBr, \(cm^{-1}\)): 3400 (H\(_2\)O stretch), 355 (Co–Cl stretch). UV-Vis (CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon, M^{-1} cm^{-1}\))): 580 (7560), 560 (6740), 460 (10230), 415 (15330), 360 (15970) \(\mu_{\text{eff}} = 5.20\) \(\mu\)B.

EPR g values after doping with 1% \([\text{RhCl}_2(\text{PhL})_2]\cdot\text{Mn(H}_2\text{O})_2\cdot\text{H}_2\text{O}\) (polycrystalline): 1.983 (major); 1.660, 2.416, 3.043, 3.774, 4.668, 6.262 (minor)

2.2e \([\text{Rh}^{III}Cl_2(\text{PhL})_2]M^III(\text{PPh}_3)_2\) (\(M = \text{Cu, Ag}\)): The \([\text{Rh}^{III}Cl_2(\text{PhL})_2]\cdot\text{M(PPh}_3)_2\) complexes were synthesized in good yields by reacting trans-\([\text{Rh}^{III}Cl_2(\text{HPhL})(\text{PhL})]\) in ethanol with equimolar amount of \(\text{M'(PPh}_3)_2\text{NO}_3\) in presence of base. Details of a representative case (\(M = \text{Mn}\)) are given below.

2.2f \([\text{RhCl}_2(\text{PhL})_2]Cu(\text{PPh}_3)_2\): To a suspension of \(0.2 \text{ g, 0.34 mmol}\) in 15 ml of absolute ethanol was added NaOH (0.014 g, 0.35 mmol) and the contents were stirred till dissolution. An ethanolic solution of Cu(PPh\(_3\))NO\(_3\) (0.22 g, 0.34 mmol) was then added and the mixture was stirred for 5 h affording a blue-green crystalline precipitate which was collected by filtration and washed with 50% aqueous ethanol followed by drying in vacuo. Yield: 0.324 g, (79%). Anal. Calc. for \(\text{C}_{52}\text{H}_{36}\text{N}_6\text{O}_6\text{Cl}_2\text{P}_2\text{Cu}: C, 61.52; H, 4.16; N, 6.94%\). Found: C, 61.46; H, 4.14; N, 6.99%. IR (KBr, \(cm^{-1}\)): 360 (R–HCl–stretch). UV-Vis (CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon, M^{-1} cm^{-1}\))): 610 (2870), 450 (4330), 400 (5330).

2.2g \([\text{RhCl}_2(\text{PhL})_2]Ag(\text{PPh}_3)_2\): Trans-\([\text{RhCl}_2(\text{HPhL})(\text{PhL})]\) (0.2 g, 0.34 mmol), NaOH (0.014 g, 0.35 mmol) and Ag(PPh\(_3\))NO\(_3\) (0.236 g, 0.34 mmol) were employed. Yield: 0.311 g, (73%). Anal. Calc. for \(\text{C}_{52}\text{H}_{36}\text{N}_6\text{O}_6\text{Cl}_2\text{P}_2\text{AgRh}: C, 59.35; H, 4.02; N, 6.70%\). Found: C, 59.42; H, 4.05; N, 6.62%. IR (KBr, \(cm^{-1}\)): 365 (R–HCl–stretch). UV-Vis (CH\(_2\)Cl\(_2\), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon, M^{-1} cm^{-1}\))): 590 (2550), 460 (4300), 415 (7660).

2.3 X-ray crystallography

Single crystals of \([\text{RhCl}_2(\text{PhL})_2]\cdot\text{Mn(H}_2\text{O})_2\cdot\text{H}_2\text{O}\) were grown by slow diffusion of hexane into dichloromethane solution at room temperature. Cell parameters were de-