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Solid-phase room-temperature decomposition of a complex salt *trans*-$[Rh(\gamma\text{-Pic})_4Cl_2]MnO_4$

Anatoliy B. Venediktov *, Danila B. Vasilchenko, Irina V. Yushina, Tatyana I. Nedoseykina, Evgeniy Yu. Filatov, Sergey V. Korenev

Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia

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ABSTRACT

Permanganate salt of the complex cation *trans*-$[Rh(\gamma\text{-Pic})_4Cl_2]^+$ (γ-Pic = γ-picoline) was synthesized. The unusual decomposition reaction of the salt was studied at room temperature. This process has been found to conserve the γ-picoline ligands in cation untouched. A number of transformations in anionic part of salt have been observed. Metallic products of the salt thermal decomposition have been studied.

1. Introduction

Complexes of rhodium(III) with pyridine and its substituted derivatives are of large interest in different branches of chemical science due to their unusual and useful properties. Such complexes are precursors of active catalysts for water–gas shift, hydrogenation, hydroformylation, carbonylation of methanol and other related reactions [1]. Unprecedented antibacterial and antitumor activity was found for the complexes of rhodium(III) with methylpyridines [2]. *Trans*-$[RhL_4Cl_2]^+$ cations (L = Py or γ-picoline) appeared useful for isolation of unusual anionic species in the form of stable adducts [3]. In our recent work [4] the cation *trans*-$[Rh(\gamma\text{-Pic})_4Cl_2]^+$ was used for examination of methyl group oxidation in coordinated γ-picoline without destruction of the $[RhN_4Cl_2]$ coordination core. This oxidation was carried out with $KMnO_4$ as the oxidant, and a poorly soluble salt *trans*-$[Rh(\gamma\text{-Pic})_4Cl_2]MnO_4$ is initially formed, which rapidly decomposes in boiling solution. The decomposition of the salt was observed under darkroom conditions at room temperature as well. Several ways for decomposition of MnO_4^- are known for solid salts involving both complex and simple inorganic cations, but they require either thermal- [5] or photoactivation [6] to achieve high reaction rate. Therefore, the above-mentioned rapid decomposition of *trans*-$[Rh(\gamma\text{-Pic})_4Cl_2]MnO_4$ requires deeper study to understand the nature of such instability.

In the present work, we have studied an uncommon solid-state room-temperature decomposition reaction of aforesaid permanganate salt. In addition, final products of thermal decomposition of the salt have been studied.

2. Experimental

The salt $[Rh(\gamma\text{-Pic})_4Cl_2]Cl\cdot 2.5H_2O$ was prepared by the method described previously [4] from commercial 'rhodium chloride' of composition $RhCl_3\cdot 3H_2O$. All employed solvents and reagents were of analytical grade and were used without further purification. Elemental CHN-analyses were performed with Euro EA 3000 analyzer.

Solid state IR spectra were measured with a Scimitar FTS 2000 (4000–400 cm^{-1}, KBr pellets) spectrometer and Vertex 80 IR-FT spectrometer (400–100 cm^{-1}, PE pellets).

UV–Vis spectra were recorded with a Shimadzu UV-3101 PC spectrometer. Diffuse reflectance spectroscopy was carried out with Shimadzu UV–Vis–NIR spectrometer UV-3101 PC using $BaSO_4$ as a reference. The reflectance spectra were recorded in 240–800 nm range.

A Bruker AVANCE 500 (AV500) spectrometer was used in order to obtain ^{13}C nuclear resonance spectra with d_6-acetone as a reference.

Differential thermal analysis of the synthesized compound was carried out with a TG 209 F1 Iris® (NETZSCH) in He stream (70 ml/min) at heating rate 10 K/min.

X-ray diffraction study of polycrystalline samples was carried out on DRON-SEIFERT-RM4 diffractometer (Cu Kα – radiation

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* Corresponding author. Tel.: +7 383 3165633; fax: +7 383 3309489.
E-mail address: venedik@niic.nsc.ru (A.B. Venediktov).

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(λ = 1.5418 Å), graphite monochromator on the diffracted beam, scintillation detector with amplitude discrimination) in 2θ range 5–60°. The samples were prepared by deposition of a suspension in hexane on the polished side of a quartz sample holder. Similarly prepared polycrystalline quartz sample (a = 5.4309 Å) was used as an external standard. Indexing of the diffraction patterns for the products of thermolysis was carried out using the data for pure metals and compounds reported in the PDF database [7], 2θ range 5–120° was used. Unit cell parameters were refined by the full-profile technique within the whole diffraction range with the POWDERCELL 2.4 program [8].

Mn K-edge XAFS spectrum of MnO_2 was measured in transmission mode at Kurchatov centre of synchrotron radiation (Moscow, Russia). IFFEFIT program suite [9,10] was used for treatment of the XAFS data. Fitting was done in R-space in the range from 1.0 to 3.0 Å. EXAFS fit was performed simultaneously in k-weightings of one, two and three to avoid errors in coordination numbers and Debye–Waller factors.

Surface morphologies of the materials were studied using a transmission electron microscope JEOL JEM-100CX and scanning electron microscope JSM 6700F with EDS EX-23000 BU.

2.1. [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$

Aqueous saturated solution of $KMnO_4$ was added dropwise to ~0.01 M solution of [Rh(γ-Pic)$_4$Cl$_2$]Cl·2.5H$_2$O at room temperature. The dark-pink precipitate appeared immediately. Addition of $KMnO_4$ was stopped when the mother liquor turned to pale-pink. The precipitate was collected by filtration, washed with H_2O and Et_2O and dried in air stream (15 min). The yield of the reaction was ca. 98%. Dry salt was kept in darkness at 0 °C. The compound is slightly soluble in water, readily soluble in ethanol and acetone, but substantially reacts with them. IR (KBr): 3083(ν_{C-H}), 3047(ν_{C-H}), 2956(ν_{C-H}), 2922(ν_{C-H}), 1621($\nu_{C=N}$), 1503($\nu_{C=C}$), 1444($\nu_{C=C}$), 1433($\nu_{C=C}$), 1370($\nu_{C=C}$), 1336($\nu_{C=C}$), 1237(δ_{C-H}), 1212(δ_{C-H}), 1115(δ_{C-H}), 1064(δ_{C-H}), 1041(δ_{C-H}), 902(ν_3(MnO$_4^-$)), 813(γ_{C-H}), 719(γ_{C-H}), 559(δ_{ring}), 508(δ_{ring}).

Due to the decomposition reaction during the crystallization our attempts to grow a single crystal of the salt were unsuccessful therefore all synthesized and studied samples of [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$ are powders of plate crystals with size of ca. 5–10 μm (SEM, Fig. 1).

2.2. [Rh(γ-Pic)$_4$Cl$_2$]HCO$_3$

To water solution of [Rh(γ-Pic)$_4$Cl$_2$]Cl·2.5H$_2$O (~0.01 M) was added quintuple excess of sodium hydrocarbonate. Pale yellow precipitate was filtered out, recrystallized from acetone, washed with Et_2O. Air-dry salt was kept in dessicator (with conc. H_2SO_4) 48 h to obtain anhydrous product. Yield: 90%. IR (KBr): 3080(ν_{C-H}), 3051(ν_{C-H}), 2953(ν_{C-H}), 2919(ν_{C-H}), 1621($\nu_{C=N}$), 1608 ($\nu_{C=O}$), 1509($\nu_{C=C}$), 1439($\nu_{C=C}$), 1433($\nu_{C=C}$), 1371($\nu_{C=C}$), 1360(HCO$_3^-$), 1333($\nu_{C=C}$), 1232(δ_{C-H}), 1214(δ_{C-H}), 1117(δ_{C-H}), 1061(δ_{C-H}), 1037(δ_{C-H}), 810(γ_{C-H}), 722(γ_{C-H}), 703(HCO$_3^-$), 565(δ_{ring}), 512(δ_{ring}). *Anal.* Calc. for $C_{25}H_{29}Cl_2N_4O_3Rh$: C, 49.44; H, 4.81; N, 9.22. Found: C, 49.32; H, 8.9; N, 9.1%.

3. Results and discussion

3.1. The room-temperature decomposition process

Addition of $KMnO_4$ to solution of the [Rh(γ-Pic)$_4$Cl$_2$]Cl·2.5H$_2$O results in precipitation of low-soluble salt [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$. Due to the decomposition reaction during the crystallization our attempts to grow a single crystal of the salt were unsuccessful therefore all synthesized and studied samples of [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$ are powders of plate crystals (Fig. 1) with size of ca. 5–10 μm. Powder diffraction pattern of the salt was indexed using earlier published single crystal data for isostructural [Rh(γ-Pic)$_4$Cl$_2$]ReO$_4$ [4]. Unit cell parameters were refined by the full-profile technique using all diffraction data with Rietveld-Toraya (plate, according to SEM) preferred orientation model for (0 1 1) plane (Fig. 2). Cell parameters for permanganate salt (space group $P2_1/c$, a = 11.804(4) Å, b = 11.260(4) Å, c = 21.762(8) Å, β = 103.88(3)°, V = 2800.9(4) Å^3) are less that parameters of [Rh(γ-Pic)$_4$Cl$_2$]ReO$_4$ salt (a = 11.866, b = 11.296, c = 22.049, β = 104.10°, V = 2866.4 Å^3) due to smaller ion radius of manganese versus rhenium.

Permanganate salt at room temperature gradually decomposes with formation of a brown substance. Decomposition occurs both in daylight and in darkness. The process is accompanied by notable spectral changes. The evolution of electronic spectrum for a sample of the salt during 24 h (T = 20 ± 1 °C) is shown in Fig. 3.

The bands of MnO_4^- ion in the region 480–600 nm disappear and a broad band at 320–390 nm with a shoulder around 500 nm is formed. Analogous broad band with shoulder around 500 nm

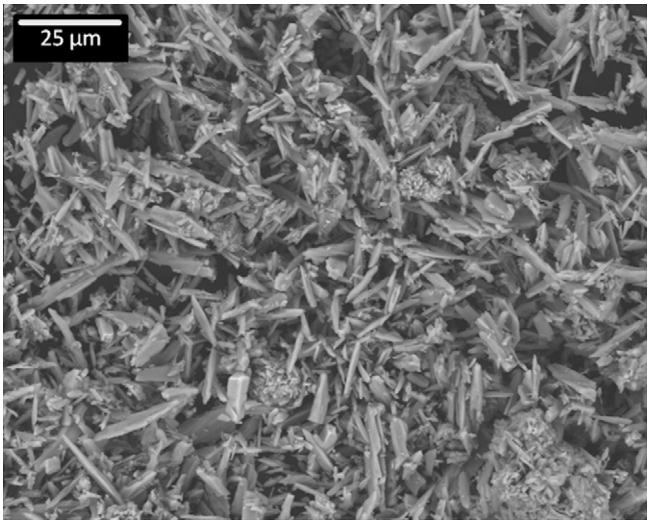

Fig. 1. The SEM image of [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$ salt powder.

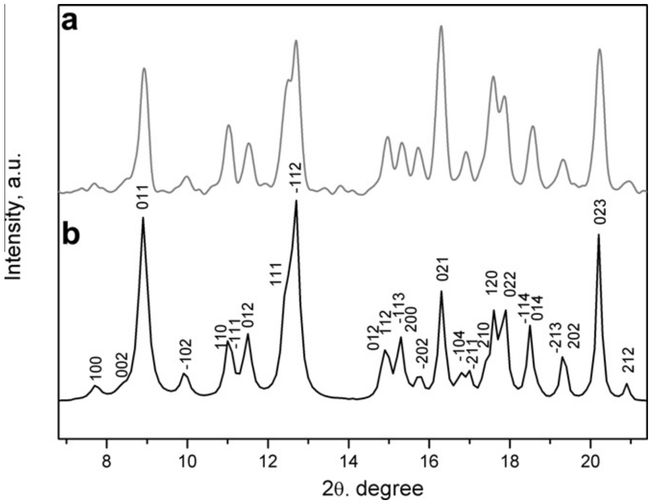

Fig. 2. Diffraction patterns of [Rh(γ-Pic)$_4$Cl$_2$]MnO$_4$ with indexing according to [Rh(γ-Pic)$_4$Cl$_2$]ReO$_4$ crystal structure.