Synthesis, thermal properties and photoisomerization of trans-[Ru(NO)Py₂Cl₂(H₂O)]H₂PO₄·H₂O

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MS received 7 December 2016; revised 1 March 2017; accepted 5 March 2017

Abstract. The reaction of trans-[Ru(NO)Py₂Cl₂(OH)] with concentrated o-phosphoric acid, after washing the mixture with diethyl ether, gave trans-[Ru(NO)Py₂Cl₂(H₂O)]H₂PO₄·2H₃PO₄·H₂O (I) in nearly quantitative yield. The structure of this compound was determined by X-ray diffraction analysis: space group P-1. Washing of I with ethanol afforded the dihydrophosphate salt trans-[Ru(NO)Py₂Cl₂(H₂O)]H₂PO₄·H₂O (II) (yield 97%). The thermal decomposition of I and II in a helium atmosphere resulted in the formation of ruthenium phosphide RuP as a predominant component along with Ru₂P or Ru₃P. Preliminary photoisomerization experiments for trans-[Ru(NO)Py₂Cl₂(OH)] and trans-[Ru(NO)Py₂Cl₂(H₂O)]H₂PO₄·H₂O suggested the presence of metastable states. DSC experiments have been carried out for both compounds. The measured kinetic parameters for the metastable decay for trans-[Ru(NO)Py₂Cl₂(H₂O)]H₂PO₄·H₂O were $E_a = 90.7 \pm 2.4$ kJ/mol, $\log_{10}(k_0/\text{sec}^{-1}) = 18.9 \pm 0.6$, and $T_d = 217$ K.

Keywords. Ruthenium nitrosyl complexes; pyridine; X-ray crystallography-thermal analysis; photoinduced linkage isomer; ruthenium phosphide; DSC.

1. Introduction

Ruthenium phosphides RuP and Ru₃P are known as stable catalysts for electrochemical oxygen reduction, seem to be good candidates as substrate in fuel cell electrodes and more active catalysts than Ru for the hydrodesulfurization of dibenzothiophene and hydrodenitrogenation of quinoline. Phosphorus-rich phosphides, for example, – RuP₂ and RuP₃, are n-type semiconductors with band gaps of 0.8 eV and 1.67 eV, respectively. The convenient method for synthesis is heating of a mixture of elements at 1200°C (RuP₂) and 1000°C (RuP₃). Catalytically active phosphides RuP₂ and RuP can be prepared by mixing of RuCl₃ and hypophosphite solutions and heating of the resulting precipitate in inert atmosphere at ~550°C. And the other process of preparation of RuP consists of high temperature reduction of pyrophosphate salt, RuP₂O₇·H₂O by hydrogen at 800–1000°C. This work shows the new method for synthesis of nanosized particles of RuP by thermolysis of hydrophosphate complex salt of nitrosyl ruthenium.

In the stable state, the NO group is coordinated to the transition metal through the N atom. Exposure of the starting nitrosyl complex to laser radiation produces isomers in which NO is coordinated through either the O atom (MS1 state) or simultaneously the O and N atoms (MS2). Reversible photoisomerization offers scope for the synthesis of hybrid materials combining lattice photochromism, conductance, magnetism, special optical properties, etc in the same crystal. Trans-[Ru(NO)(Py)₃Cl](PF₆)₂·0.5H₂O and trans-[Ru(NO)Py₂(NO₂)₂(OH)]Cl₃ exhibit highest known populations of the metastable states among ruthenium nitrosyl complexes and the metastable state (MS1) of trans-[Ru(NO)(NH₃)₄(H₂O)]Cl₃ has the highest decomposition temperature, $T_d = 293$ K. Thus, we have the interesting combination of pyridine and water molecules in coordination sphere of nitrosyl complex, and hence a high value of $T_d$ may be observed. The purpose of this work is to report the preparation of novel complex salt of dipyridine nitrosylruthenium, its structural investigation, thermal decomposition and preliminary photoisomerization studies.
2. Experimental

2.1 Materials and methods

Trans-[Ru(NO)Py2Cl2(OH)] was prepared from K2[Ru(NO)Cl5].12 The latter compound was obtained with an yield of ∼97% from commercially available ruthenium trichloride hydrate as described in the literature.13 Other reagents and solvents were used as purchased and were reagent grade or better.

Elemental analyses were performed on a EURO EA3000 (Euro Vector). Inductively coupled plasma mass spectrometry (ICP-MS) was performed on “Thermo Scientific”, iCAP-6500. Thermal analyses were carried out on thermobalance TG 209 F1 Iris® by NETZSCH (heating rate 10°C/min, He-flow 30 mL/min, Al2O3-crucible, sample mass ∼10 mg).

Scanning electron microscopy was performed on JEOL JSM 6700F. Energy of the incident beam was 15 keV, working distance – 8 mm. For obtaining picture was used as secondary electron detector, as backscattered electron detector in mode “compo”.

2.1a IR spectra: IR spectra of the samples were measured in KBr pellets on a Scimitar FTS 2000 FT-IR spectrometer within the wavenumber range 4000–375 cm⁻¹. To detect the formation of photoinduced isomer, the pellets of substance in KBr was irradiated with a diode laser (450 nm, 100 mW) for 30 min while cooling with liquid nitrogen and then the IR spectrum was recorded immediately.

2.1b X-ray diffraction: Powder X-ray diffraction examination of ground crystals was performed on Shimadzu XRD-7000 diffractometer (CuK-α radiation, Ni – filter, 2θ range: 5–60°). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder, and a smooth thin layer was formed after drying. Indexing of the diffraction patterns was carried out using data for compounds reported in the PDF database (RuP - PDF 010-74-6496, Ru2P and RuP2 - PDF 010-89-3031).14 The range of coherent scattering values for individual peaks was calculated by Scherrer equation with external etalon (Si) band width considering.

2.1c Single-crystal structure analysis: Unit cell parameters and intensity data were measured on an automated four-circle X8 APEX Bruker diffractometer (MoKα radiation, graphite monochromator, CCD area detector). The structures were solved by the heavy atom method and refined in the anisotropic approximation; hydrogen atoms were put in idealized positions and refined isotropically. All calculations were performed using SHELXTL.15 Crystal data and selected refinement details for I are given in Table 1. CCDC No.1476880 contains the supplementary crystallographic data for this paper. The copy of CIF-file in text-format is shown in Supplementary Information of this paper.

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2.1d Differential scanning calorimetry: A NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter was used to study the kinetics and thermal effects of the reversible photoinduced transition. To study MS1 the sample was placed in liquid nitrogen vapor and irradiated with a diode laser (100 mW, 450 nm) for 30 min. The sample was then quickly transferred to a device for DSC. The calorimetric measurements of powdered samples (1–3 mg) were performed in open aluminium crucibles by the heat-flow measurement method at different heating rates of 5.9, 6.0 and 8.9 K/min in a 25 mL/min Ar flow. To increase the accuracy, the measurements were performed without a supply of gas or liquid nitrogen in the measurement cell during the experiment. The sensitivity calibration of the sample carrier sensors and temperature scale were performed by heating and observing crystal-to-crystal transition measurements of standard samples (C₆H₁₂, Hg, KNO₃, In). The processing of the experimental data was performed with the Netzsch Proteus Analysis software.

2.2 Synthesis of the complexes

2.2a Synthesis of trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂PO₄·2H₃PO₄·H₂O (I): 0.3 g (7.9·10⁻⁴ mol) of trans-[Ru(NO)Py₂Cl₂(OH)] was moistened by 0.5 mL of concentrated o-phosphoric acid on porous glass filter; then, the resulting wine-reddish mixture was washed thrice with 5–10 mL diethyl ether and dried in air flow. Yield is 0.51 g (~96%). Red crystals suitable for a single-crystal X-ray analysis were obtained by the slow evaporation of solution in dilute phosphoric acid. All reactions were conducted at room temperature. Found, %: C–18.2; H–3.3; N–8.4. Anal. calc. for C₁₀H₁₆N₃O₇PCl₂Ru, %: C–24.4; H–2.9; N–8.4.

2.2b Synthesis of trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂PO₄·H₂O (II): 0.3 g (4.5·10⁻⁴ mol) of trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂PO₄·2H₃PO₄·H₂O was washed on porous glass filter with 3 mL of ethanol, diethyl ether and dried. Yield is 0.21 g (~97%). Found, %: C–24.4; H–2.9; N–8.4. Anal. calc. for C₁₀H₁₆N₃O₇PCl₂Ru, %: C–24.4; H–3.3; N–8.5.

3. Results and Discussion

3.1 Synthesis and characterization

Room-temperature reaction of hydroxo complex trans-[Ru(NO)(Py)₂Cl₂(OH)] with concentrated HCl or H₂SO₄ results in protonation of the coordinated hydroxide ion, yielding the corresponding salts of aqua complexes trans-[Ru(NO)(Py)₂Cl₂(H₂O)]Cl·2H₂O and trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂SO₄. Reaction with o-H₃PO₄ yields the same aqua complex trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂PO₄·2H₃PO₄·H₂O (I) containing two molecules of ortho-phosphoric acid. Washing with ethanol results in removing of acid molecules and formation of trans-[Ru(NO)(Py)₂Cl₂(H₂O)]H₂PO₄·H₂O (II). Synthesized product contains water molecule indicated by elemental analysis and IR studies. The stretching vibration bands of ν(NO) were observed at 1901 cm⁻¹ (I) and 1902 cm⁻¹ (II), and these values fall within a range characteristic of most nitrosyl complexes of ruthenium that combine the diamagnetic metal center Ru(II) and the linearly coordinated species NO⁺. The ν(NO) frequency depends on the ligand that is trans- to the nitrosyl group and is shifted to the shorter wavelengths when moving from the neutral hydroxo complex trans-[Ru(NO)Py₂Cl₂(OH)] (1817 cm⁻¹) to the cationic aqua complex trans-[Ru(NO)(Py)₂Cl₂(H₂O)]⁺ (1897–1904 cm⁻¹).

IR-spectra of I (ν, cm⁻¹): 3550 m ν(OH₃PO₄), 3350 m ν(H₂O), 3150–3030 weak ν(CH); 2800 wide s ν(H₂Ocoord.); 2340 wide s ν(OH...O); 1904 vs ν(NO); 1636 wide m δ(H₂O); 1608 m, 1489 weak, 1453 m, 1362 weak ν(C=C), ν(C=N); 1220, 1170 wide s, 988 wide vs ν(H₂PO₄, H₃PO₄); 1221, 1111 weak, 1072 m, 1038, 1016 weak δ(CHplane); 903, 872 weak sh δ(RuOH); 761, 691 s, 651 m δ(CHout-off-plane); 615, 596 weak ν(Ru–N(NO)), δ(RuNO); 551 ν(Ru–O); 505 s, 495 s sh, 409 m δ(H₂PO₄, H₃PO₄); 453 m ν(Ru–NPy).

In the IR-spectra of II, the H₂PO₄-bands at 3550, 1170 and 988 cm⁻¹ are more intensive compared to I.

3.2 Crystal structure

The crystal structure of I is made up of complex cations trans-[Ru(NO)(Py)₂Cl₂(H₂O)]⁺, outersphere H₂PO₄⁻ anions and molecules of phosphoric acid and water. The structure of the complex with atomic numbering and thermal displacement ellipsoids is shown in Figure 1. Selected bond lengths and bond angles are listed in Table 2.

The pyridine molecules are trans to each other; the square environment in the equatorial plane is completed with two chloride ions. The Ru–N(Py) bond lengths are ~2.1 Å. The RuCl bond lengths are ~2.35 Å. The axial positions in complex I are occupied by the nitrosyl group and water molecule. The Ru–O(1) bond length is ~2.05 Å. The geometrical parameters of the fragment {RuNO}₃⁺ also agree well with the literature data. The NO and Ru–N(NO) bond lengths are nearly 1.15 and 1.72 Å, respectively; the O–N–Ru angle approximates to 180°. In the complex, the central Ru atom deviates from the equatorial plane by ~0.1 Å toward the nitrosyl-group.

In the coordinated pyridine molecules, the average N–C and C–C bond lengths have standard values (~1.35 and 1.38 Å, respectively). The planes of the
The structure of trans-[Ru(NO)Py2Cl2(H2O)]+ with outer-sphere environment in compound I. The coordination polyhedron of the Ru atom is a slightly distorted octahedron (RuN3Cl2O). The bond angles at the Ru atoms deviate from 90° by at most 5.8°.

Table 2. Selected bond lengths and bond angles in trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·2H3PO4·H2O (I).

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pyridine rings make with each other angles of ~90°, the angles between their planes and the equatorial plane are 45–55°.

In the dihydrophosphate-ion the P–OH bond length is 1.56–1.57 Å; the other three P–O bonds are close in length to each other (on average, ~1.50–1.51 Å). The anions are united through the hydrogen bonds O–H···O (2.6 Å). The bond distances in H2PO4- molecules are about 0.01–0.02 Å shorter.

The general view of the packing pattern in the crystal of complex I is shown in Figure 2. The complex cations are linked to the dihydrophosphate ions by hydrogen bonds involving the coordinated water molecule and the O atoms of the H2PO4− (O(w)···O 2.5–2.9 Å). The shortest Ru...Ru distance is 6.0 Å. Half of pyridine-molecule is linked by π-stacking interaction with evaluated distance of C...C ~3.7 Å.

3.3 TGA studies

Compounds I and II were studied by thermal analysis (Figure 3). There are no clear-cut steps in thermal curves apart from the first step of thermolysis of I at ~90°C, when the compound loses one outer-sphere water molecule (calc. –2.7%, found on TG-curve –2.4%).

The thermal decomposition of II also starts by losing crystallization water molecule, but the corresponding process is not fixed apart at the TG curve, because there are two other processes of removal of water – decomposition of H2PO4− and aqua-complex. According to the previous studies of thermal properties of nitrosyl ruthenium pyridine complexes,16 the heating of I and II at ~200°C must result in the loss of pyridine molecules. Further decomposition of I and II (above 300–350°C) occurs in several poorly resolved stages which are attributed to mixed processes of coordinated pyridine molecule decomposition, removal of NO and HCl.16,19 The final products, as indicated by powder X-ray diffraction, contain nano-powder ruthenium phosphides RuP, Ru2P and RuP2.

The products of thermolysis of I (up to 780°C) are RuP (82±5% mass., OCD ~20 nm), Ru2P (7±5% mass., OCD ~80 nm) and RuP2 (11±5% mass.) (see Figure S1 and Table S1 in Supplementary Information). The average molar mass of the products of thermolysis...
of I is 336.8 a.m.u., which indicates that the sample contains other amorphous phase, as indicated by IR spectra – it is polyphosphate complexes of ruthenium (ν, cm⁻¹: 1100 sh s wide; 980 vs wide ν₆(PO₄); 492 s ν₄(PO₄); 401 sh m ν(Ru-O)). The products of thermolysis of II (up to 780°C) are RuP (∼90±5% mass., OCD ∼30 nm) and Ru₂P (10±5% mass., OCD ∼80 nm) (see Figure S2 and Table S2 in Supplementary Information). The average molar mass of the products of II is 135,1 a.m.u., which indicates that the sample contains a small amount (∼3 a.m.u.) of amorphous CHN-phase. The nitric acid solution of thermolysis product analysed by ICPMS method, found that the product contains 19.8% of phosphorous (calculated 20.7%); the ruthenium content was much lower than the calculated value (Found 11.3% of ruthenium, calculated 79.3%), probably due to bad resolution of Ru for this analytical method.

The investigation by scanning electron microscopy confirms the dimensions of nanoparticles. Microphotograph of thermolysis products of I, obtained by detector of backscattered electrons, shows three phases: light, medium and hard (Figure S3a). The microphotographs obtained by both detectors – secondary and backscattered electrons show that harder particles of thermolysis
product II are covered by lighter substance, which is practically invisible in backscattered electron image (Figure S3b, c).

3.4 Photoisomerization studies

The photochemical transformations that occurred under the illumination of the polycrystalline samples of compounds, trans-[Ru(NO)Py2Cl2(OH)] and trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·H2O (II) were studied by IR spectroscopy. An additional band at 1673 cm\(^{-1}\) (for trans-[Ru(NO)Py2Cl2(OH)]) and 1745 cm\(^{-1}\) (for II), which can be interpreted as \(\nu(\text{NO})\) for the MS1 state,\(^{10,11}\) appears in the IR spectrum of the irradiated sample (Figure 4). The difference between \(\nu(\text{NO})\) signals for ground state (GS) and metastable state (MS1) is about 150 cm\(^{-1}\) (for trans-[Ru(NO)Py2Cl2(OH)]) and 160 cm\(^{-1}\) (for aqua complex II) which are slightly higher that corresponding difference for other nitro-syl pyridine complexes of ruthenium: \(\sim 130\) cm\(^{-1}\) (for cis-[Ru(NO)Py2(NO2)2(OH)]\(^{11}\)), \(\sim 140\) cm\(^{-1}\) (for cis-[Ru(NO)Py2Cl2(OH)]\(^{20}\) and fac-[Ru(NO)Py2Cl3]\(^{21}\)).

The DSC method was used to study the kinetics of the backward isomerization of the MS1 state. The measurements were carried out for three different weighed samples at different heating rates. The resulted dependence of the heat flow on temperature (Figure 5) is well approximated by the first-order kinetics\(^{20}\):

\[
\dot{H} = H_{\text{tot}} \cdot k_0 \cdot \exp \left( -\frac{E_a}{k_B \cdot T} - \frac{k_0}{q} \int_{T_0}^{T} e^{-\frac{E_a}{k_B \cdot T'}} \cdot dT' \right),
\]

Where, \(\dot{H}\) is the heat flow, \(H_{\text{tot}}\) – the overall effect, \(k_0\) – the pre-exponential factor, \(E_a\) – activation energy, \(q\) – ramp rate, \(k_B\) – the Boltzmann constant, \(T_0\) – the starting temperature.

Figure 4. Infrared spectra of trans-[Ru(NO)Py2Cl2(OH)] (left) and II (right) in the spectral region of the \(\nu(\text{NO})\) stretching vibration in the ground state (GS) and after illumination.

Figure 5. Calculated (lines) and experimental (dots) DSC curves for trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·H2O (II) (green – 3 K/min, red – 6K/min and blue – 9 K/min).
All the curves were calculated in a range of 209–241 K giving \( E_a \) and \( \log_{10}(k_0/\text{sec}^{-1}) \) as 90.7±2.4 kJ/mol and 18.9±0.6, respectively. It was suggested earlier\(^2\) that the decomposition temperature \( (T_d) \) of MS1 can be accepted as the value corresponding to the decay rate of \( 10^{-3}\text{ s}^{-1} \). For the studied compound, \( T_d = 217 K \).

The DSC experiment for trans-[Ru(NO)Py2Cl2(OH)] was uninformative, because the yield of MS1-isomer was so small and hence the thermal effect is almost invisible (see Figure S4 in Supplementary Information).

4. Conclusions

We have prepared trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·2H3PO4·H2O (I) and trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·H2O (II) in high yields. Compound I has been structurally characterized by XRD, and the calculated diffractogram corresponds to powder diffraction data. Both compounds have been characterized by thermal analysis. Heating of salts up to \( \sim 780^\circ C \) affords a mixture of ruthenium phosphides. Thus, RuP (~80% mass) with admixtures of Ru2P and RuP2 in amorphous polyphosphate ruthenium phase from I and RuP (~90% mass) with impurity of Ru2P from II, were inferred by powder X-ray diffraction, ICP-MS analysis and electronic microphotography. Preliminary photoisomerization experiments on trans-[Ru(NO)Py2Cl2(OH)] and trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·H2O (II) were performed, and metastable states were indicated by IR spectroscopy with stretching bands (NO) at 1673 cm\(^{-1}\) (trans-[Ru(NO)Py2Cl2(OH)]) and 1745 cm\(^{-1}\) (II). DSC experiments have been carried out for both the compounds. The measured kinetic parameters of MS1 decay for trans-[Ru(NO)Py2Cl2(H2O)]H2PO4·H2O are \( E_a \) = 90.7±2.4 kJ/mol, \( \log_{10}(k_0/\text{sec}^{-1}) \) = 18.9±0.6, and \( T_d = 217 K \).

Supplementary Information (SI)

CCDC No. 1476880 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). DSC curve for trans-[Ru(NO)Py2Cl2(OH)], powder diffraction data and microphotographs for thermolysis products of I and II are available in Supplementary Information at www.ias.ac.in/chemsci.

Acknowledgements

Authors thank Dr. Gennady A. Kostin and Artem A. Mikhailov for laser experiments; Dr. Anna P. Zubareva, Dr. Olga S. Kosheeva and Dr. Alphiya R. Tsygankova for the elemental analysis; Dr. Dmitry P. Pischur for recording the DSC curves; and Natalya P. Korotkevich for powder X-ray diffraction study.

References

4. Honle W, Kremer R and Schnering H G 1987 Ruthenium(III)triphosphide RuP3: Preparation, crystal structure and properties Z. Kristallogr. 179 443


16. Makhinya A N, Il’in M A, Baidina I A, Plyusnin P E and Gallyamov M R 2014 Structure and properties of tripyridine nitrosocomplexes of ruthenium: Mer-[Ru(NO)Py3Cl(OH)]Cl1.5H2O and mer-[Ru(NO)Py3Cl(H2O)]Cl2·2H2O·0.5HCl J. Struct. Chem. 55 682


18. Emel’yanov V A, Baidina I A, Il’in M A and Gromilov S A 2006 Synthesis and crystal structure of nitrosoruthenium aquadiammine complex, [Ru(NO)\(\text{NH}_3\))\_2\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}·\text{H}_2\text{O} J. Struct. Chem. 47 380

19. Makhinya A N, Il’in M A, Baidina I A, Plyusnin P E, Alferova N I and Pishchur D P 2014 Structure, synthesis, and thermal properties of trans-[Ru(NO)(\text{NH}_3))_4(SO_4)]\text{NO}_3·\text{H}_2\text{O} J. Struct. Chem. 55 311

20. Makhinya A N, Il’in M A, Yamaletdinov R D, Korolkov I V and Baidina I A 2016 Synthesis and crystal structure of nitrosoruthenium complexes cis-[Ru(NO)Py2Cl2(OH)] and cis-[Ru(NO)Py2Cl2(H2O)]Cl. Photoinduced transformations of cis-[Ru(NO)Py2Cl2(OH)] New J. Chem. 40 10267
