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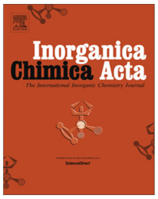

Synthesis and characterization of nitrogen rich ruthenium complexes

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ABSTRACT

Treatment of “ruthenium blue” in ethylene glycol with azide ions produced three ruthenium complexes having different nuclearities and oxidation states. The first, $[Ru(N_3)_6]^{3-}$ (**1**), a mono-nuclear Ru^{III} hexaazide complex has been crystallized by using various counter-cations. The X-ray structure analysis of these salts has revealed a slightly distorted octahedral geometry with a Ru–N bond distance of 2.066(3) Å. The second, $[Ru_2N(N_3)_{10}]^{6-}$ (**2**), is a nitrido-bridged Ru^{III}, Ru^{IV} complex. The Ru–N–Ru bond angle in **2** is 170.8(2)° and the $N_5Ru–N–RuN_5$ system adopts a staggered configuration. The average Ru–N bond distances of the two metal atoms are slightly different. These parameters do not agree with the widely accepted view that most nitrido bridged ruthenium atoms have a Ru=N=Ru allene type structure. Complex **3**, $[(C_2H_4O_2)_2RuN]^-$, a by-product of the reaction, is a Ru^{VI} complex containing a triply-bonded terminal nitride with a Ru≡N bond distance of 1.598(3) Å.

1. Introduction

Recently, there is an increasing interest in metal nitrido and azido complexes due to their electronic properties and their role as nitrogen carriers and suppliers in organic and inorganic reactions [1]. Group eight elements show diverse chemistry with nitrogen species and produce complexes with variant applications [2]. Ruthenium complexes in particular show diverse and rich chemistry that includes redox reactions, nitrogen insertions, nucleophilic additions and oxidation catalysis [3]. So far, most of the compounds that served the above purposes have been heteroleptic ruthenium-azide and ruthenium-nitride complexes containing non-nitrogen ligands in addition to the nitride or azide ligands. Binary azides, which contain large numbers of azide ligands, have been the subject of numerous studies in recent years [4]. The main motivation behind these studies is the potential use of binary azides as high-energy density materials (HEDMs) since each azide group is believed to add about 70 kcal/mol to the energy content of the material [5]. However, due to their explosive nature and temperature and shock sensitivity, the preparation, isolation and storage of these materials have become an experimental challenge. As far as we know, there are no reports in the literature of structurally characterized nitrogen-only ruthenium complexes in which azide and nitride ligands comprise the coordination sphere of the metal atom. Here we report the preparation and single-crystal X-ray structural analysis of several complexes that have originated from the reaction between “ruthenium blue” and azide ions. The first, the mono-nuclear hexaazido Ru^{III} binary complex $[Ru(N_3)_6]^{3-}$ (**1**) was crystallized by using tetramethylammonium and sodium or cobalt hexamine cations that produced $Na(Me_4N)_2\cdot\mathbf{1}$ and $[Co(NH_3)_6]\cdot\mathbf{1}$ respectively. The second, $[Ru_2N(N_3)_{10}]^{6-}$ (**2**), is a di-nuclear complex in which Ru^{III} and Ru^{IV} atoms are bridged by a nitride. We also describe the structure of a by-product in this system that contains the mono-nuclear Ru^{VI} nitrido complex $[(C_2H_4O_2)_2Ru{\equiv}N]^-$ (**3**).

2. Experimental

2.1. General

Caution! Metal azide complexes are potentially explosive. They should be handled on small scale (less than 2 mmol) using appropriate safety precautions.

“$RuCl_3\cdot 3H_2O$” 38.0–42.0% Ru basis (Sigma–Aldrich, Inc.); hexaamminecobalt chloride 99% (Alfa Aesar); tetramethylammonium hydroxide pentahydrate 97% (Sigma–Aldrich, Inc.); sodium azide ⩾99% (Merck Group); ethylene glycol 99.8% (Sigma–Aldrich, Inc.). All reagents and solvents were used without further purification. A 3.0-cm diameter, 8.0-cm length column of DOWEX- 50WX8 100/200 mesh was used for ion-exchange chromatography. FTIR spectra were recorded on a Bruker Tensor 27 FTIR-ATR spectrophotometer. Electronic absorption spectra were recorded on an Ocean-optics USB4000 UV–Vis spectrophotometer. The temperature dependence of the magnetic susceptibility (χ(T)) measurements for compound **2** were performed in a commercial (Quantum

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Design) super-conducting quantum interference device (SQUID) magnetometer, at the Racah Institute of Physics, the Hebrew University Jerusalem. Measurements were made under an applied field H = 10 kOe (0.5 T) in the temperature range of $5 < T < 300$ K.

2.2. X-ray crystallography

Intensity data were collected on a Bruker SMART APEX CCD X-ray diffractometer system controlled by a Pentium-based PC running the SMART software package [6]. Mo Kα radiation ($\lambda = 0.71073$ Å) with a graphite-monochromator in the incident beam, and a three-circle goniometer with χ fixed at $+54.76^{O}$ were used. Intensity data were corrected for absorption using the face-indexed absorption correction program incorporated into Bruker-XPREP. The structures were solved and refined by the SHELXTL software package [7]. All structures were refined to convergence using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in fixed positions using the riding model.

2.3. Synthesis

2.3.1. Preparation of "ruthenium blue"

"$RuCl_3·3H_2O$" (0.42 g, 1.58 mmol) was placed in a 50 mL round-bottom flask. Ethylene glycol (20 mL) was added and the solution was stirred for 2 h at 130 °C under nitrogen atmosphere. The solution color turned from dark brown to deep blue. The solution was cooled down to room temperature and kept under nitrogen for further manipulations.

2.3.2. Preparation of $Na_3[Co(NH_3)_6](N_3)_6$

$[Co(NH_3)_6]^{3+}$ ions were loaded into a cation-exchange column by passing a solution of $[Co(NH_3)_6]Cl_3$ (0.2 M, 100 mL) through it. The saturated column was washed with water and a solution of NaN_3 (5 M) was used for the elution of $[Co(NH_3)_6]^{3+}$. Slow evaporation of the orange eluate yielded orange crystals of $Na_3[Co(NH_3)_6](N_3)_6$, suitable for X-ray analysis. The exact formula of the title compound has been confirmed by X-ray crystallography.[1] Yield 56%. FTIR: 3364(w), 3231 (m, br), 2028(vs br), 1612–1532 (m, br), 1335(s), 846(s), 634(s).

2.3.3. Preparation of $(Me_4N)N_3$

An aqueous solution of NaN_3 (0.78 M, 100 mL) was passed through a cation-exchange column. The resulting acidic HN_3 solution was neutralized with $(Me_4N)(OH)$ and evaporated to dryness to yield a colorless solid of $(Me_4N)(N_3)$. Yield 22%. FTIR: 3291(w), 3022(w), 1989(vs br), 1488(vs), 1406(m), 944(vs), 630(m), 458(m).

2.3.4. Preparation of $Na(Me_4N)_2[Ru(N_3)_6]$ ($Na(Me_4N)_2·$**1**)

An aqueous solution of NaN_3 (5 M, 5 mL) was added to a "ruthenium blue" solution (2 mL, 0.16 mmol). Significant gas liberation and a rapid change of color from blue to brownish-red were observed. $(Me_4N)N_3$ (0.066 g, 0.57 mmol) was added to the solution. The solution was kept overnight at 4 °C yielding red crystals of $Na(Me_4N)_2·$**1**, suitable for X-ray analysis. Yield 16%. UV–Vis: λ_{max} (nm) (ε, M^{-1} Cm^{-1})(CH_2Cl_2): 437 (2246.1). FTIR: 2029 (vs br), 1479(s), 1446(m), 1415(w), 1341(w), 1292(s), 1170(vw), 947(s), 665(m), 592(m).

2.3.5. Preparation of $[Co(NH_3)_6][Ru(N_3)_6]$ ($[Co(NH_3)_6]·$**1**)

An aqueous solution of NaN_3 (5 M, 5 mL) was added to a "ruthenium blue" solution (1 mL, 0.08 mmol). Significant gas liberation and a rapid change of color from blue to brownish-red were observed. Once the reaction was completed a solution of $[Co(NH_3)_6]Cl_3$ (0.2 M, 2 mL) was added to the ruthenium-azide solution forming an orange precipitant of $[Co(NH_3)_6]·$**1**. Yield 60%. Orange crystals suitable for X-ray analysis[2] were obtained by the addition of $[Co(NH_3)_6]Cl_3$ (0.1 M, 2 mL) to the ruthenium-azide solution. The solution was left standing in a closed vessel for 24 h. FTIR: 3170 (w, br), 3254 (w, br) 2023 (vs), 1605 (m), 1327 (m), 1287 (s), 1033 (w), 843 (m), 669 (w, br), 588 (w, br).

2.3.6. Preparation of $[Co(NH_3)_6]_2[Ru_2N(N_3)_{10}]$ ($[Co(NH_3)_6]_2·$**2**)

An aqueous solution of NaN_3 (5 M, 5 mL) was added to a solution prepared by mixing 1 mL ethylene glycol and 1 mL "ruthenium blue". Significant gas liberation and a rapid change of color from blue to brownish-red were observed. The mixture was left standing at r.t. in a closed vessel. After three days a solution of $[Co(NH_3)_6]Cl_3$ (0.1 M, 3 mL) was added to the ruthenium-azide solution at 30 °C forming a deep brown precipitant of $[Co(NH_3)_6]_2·$**2**. Yield 9%. Purple-brown needles suitable for X-ray analysis were obtained by layering a solution of $[Co(NH_3)_6]Cl_3$ (0.1 M, 2 mL) on top of the ruthenium-azide solution (2 mL). FTIR: 3152 (s, br), 2012 (multiple, vs), 1604(s, br), 1341(s), 1283(s), 1018(m), 846(m), 674(w), 663(w), 552(w).

2.3.7. Preparation of $[Co(NH_3)_6][RuN(C_2H_4O_2)_2]_3$, ($[Co(NH_3)_6]·($**3**$)_3$)

A saturated solution of $Na_3[Co(NH_3)_6](N_3)_6$ in ethylene glycol (2 mL) was added to a "ruthenium blue" solution (2 mL, 0.16 mmol) at 30 °C. Gas liberation was observed and an unidentified brown precipitant was formed immediately. After 2 min at 30 °C a small number of brown-orange cubic crystals of $[Co(NH_3)_6]·($**3**$)_3$, suitable for X-ray analysis were formed. FTIR: 3233–3145, 3049(m), 2897(m), 2836(m), 2048(m, br), 1613(w), 1460(w), 1363–1330, 1214(w), 1067(s), 1038(vs), 904(s), 885(s), 660(vs), 620(m), 575(s), 523(s).

3. Results and discussion

3.1. Synthesis

Since commercial "$RuCl_3·3H_2O$" is an ill-defined starting material, we used ethylene glycol as a reducing agent and a solvent. The reaction between "$RuCl_3·3H_2O$" and ethylene glycol at 130 °C produced a deep blue solution of "ruthenium blue", a species believed to be a poly-nuclear ruthenium chloride complex with an average oxidation state between two and three [8]. Related blue species of other platinum-group metals are also known in the literature [9]. The reaction between the blue ruthenium species and azide ions produced large amounts of gaseous nitrogen and $[Ru(N_3)_6]^{3-}$ (**1**). Since both N_3^- and "ruthenium blue" are strong reducing agents, one must assume that ethylene glycol and/or water are involved in the reaction through an elaborate mechanism. Schmidtke and Garthoff reported in 1966 the synthesis of the tetra-*n*-butylammonium salt of complex **1** [10]. The complex was obtained by reacting $K_2[RuCl_6]$ with a large excess of N_3^- ions that reduce the Ru^{IV} atom to Ru^{III} and substitute the chloride ligands. The structure of the red crystals was not elucidated in this study. Here we describe a different route that utilizes a less expensive starting material, namely, "$RuCl_3·3H_2O$", and cobalt hexamine or tetramethylammonium as counter-ions.

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[1] Crystal data for $Na_3[Co(NH_3)_6](N_3)_6$: empirical formula, $CoH_{18}N_{24}Na_3$; formula weight = 482.28; crystal system, rhombohedral; space group, $R\bar{3}c$; $a = 9.7230(4)$ Å, $b = 9.7230(4)$ Å, $c = 33.636(3)$ Å; $\alpha = 90°$ $\beta = 90°$ $\gamma = 120°$.

[2] Crystal data for $[Co(NH_3)_6]·$**1**: empirical formula, $CoH_{18}N_{24}Ru$; formula weight = 514.38; crystal system, hexagonal; space group, $R\bar{3}$; $a = 12.166(2)$ Å, $b = 12.166(2)$ Å, $c = 10.066(3)$ Å; $\alpha = 90°$ $\beta = 90°$ $\gamma = 120°$ $V = 1290.4(5)$ Å^3; $Z = 3$; $\rho_{calcd} = 1.986$ Mg/m^3; $\mu = 1.891$ mm^{-1}; range of $2\theta = 4.37$ to 24.99°; total refl. = 2861; indep. refl. (R_{int}) = 450 ($R_{int} = 0.2167$); data with $I > 2\sigma(I) = 450$; parameters = 42; $R_1 = 0.0763$, wR_2 (I) = 0.1609.