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The Diazirine Complex $[(NH_3)_5Ru(N_2C_6H_{10})]^{2+}$: Synthesis, Structure and Conversion into the Dinitrogen Complex $[(NH_3)_5RuN_2]^{2+}$

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A remarkable feature of the $[(NH_3)_5RuN_2]^{2+}$ ion is the amazing variety of its ways of formation. Besides direct synthesis of $[(NH_3)_5RuN_2]^{2+}$ from N_2 and $[(NH_3)_5RuH_2O]^{2+}$ [1], a large number of indirect routes to this compound have been described in which, as the source of dinitrogen ligand, use was made of hydrazine [2] and its organic derivatives [3], ammonia [4], sodium azide [2, 5], nitrous oxide [6], diazo compounds [7], *etc.* [8–10].

Recently we have reported the new reaction leading to the formation of $[(NH_3)_5RuN_2]^{2+}$ [11]. On reacting a neutral aqueous solution of $[(NH_3)_5RuH_2O]^{2+}$ with an equimolar quantity of 3,3-pentamethylenediazirine under Ar, a dark red solution is formed containing two complexes (I) and (II) characterized by absorption at 370 and 478 nm, respectively. If the solution is acidified with sulfuric acid, and then exposed to air (or treated with hydrogen peroxide), both absorption bands rapidly disappear, and cyclohexanone, $[(NH_3)_5RuN_2]^{2+}$, and a complex of unknown structure with $\lambda_{max} \sim 430$ nm are produced. Under the same conditions, acidification alone has no effect on the I and II bands at 370 and 478 nm.

Here we wish to report the isolation, some properties and structure of complex I, the source of the $[(NH_3)_5RuN_2]^{2+}$ ion in the oxidation reaction.

Results and Discussion

When an 8–10 fold excess of diazirine with respect to $[(NH_3)_5RuH_2O]^{2+}$ is used, complex I is the sole product of the reaction. In aqueous methanol (~ 1:1) at 20 °C the reaction is completed in 20–30 min ([Ru] ~ 0.03–0.04 *M*). If, on the other hand, a 4–8:1 excess of $[(NH_3)_5RuH_2O]^{2+}$ with respect to diazirine is taken, complex II is predominantly formed.

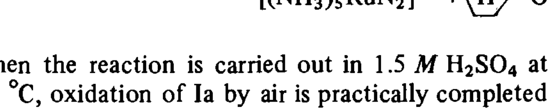
Both complexes were isolated from solution as hexafluorophosphates (Ia) and (IIa), but only Ia could be obtained in the analytically pure state.

Complex Ia is a brick red diamagnetic substance ($\lambda_{max} \sim 370$ nm, $\epsilon_{370} = 9.3 \times 10^3$; $H_2O–C_2H_5OH$/95:5) soluble in CH_3OH, C_2H_5OH and acetone, less readily in water and THF, and insoluble in aliphatic and aromatic hydrocarbons. In the solid state, the complex is moderately stable in air at 20 °C, but is rapidly oxidized in solution, especially in acidic medium (see below). According to elemental analysis the complex can be formulated as $[(NH_3)_5Ru(N_2C_6H_{10})](PF_6)_2$.

The IR spectrum of Ia, besides absorption bands due to the ammonia ligands, the cyclohexane ring and PF_6^-, displays a medium-weak band at 1492 cm^{-1}, which can be assigned to the stretching vibrations of the coordinated N=N bond of the diazirine ligand. In accordance with this assignment, the band is shifted by 32 cm^{-1} to the longer wave region on transition to the labelled complex $[(NH_3)_5Ru(^{15}N_2C_6H_{10})](PF_6)_2$. The IR and Raman spectra of free 3,3-pentamethylenediazirine show two bands at 1569 (s) and 1592(m) cm^{-1} in the N=N stretching region, probably due to Fermi resonance (*cf.* [12]). Hence, the coordination of diazirine to ruthenium causes a decrease in $\nu_{N=N}$ of 89 cm^{-1}.

A study of the chemical behaviour of Ia showed that it readily transforms into II on reacting with excess $[(NH_3)_5RuH_2O]^{2+}$. The reverse transformation II → I occurs on treating II with an aqueous solution of NH_3, or with excess diazirine.

A remarkable property of Ia is its ability to undergo rapid oxidation by air or H_2O_2 in acidic medium (H_2SO_4, HCl, CF_3COOH) with the formation of the dinitrogen complex $[(NH_3)_5RuN_2]^{2+}$ and cyclohexanone.



When the reaction is carried out in 1.5 *M* H_2SO_4 at 20 °C, oxidation of Ia by air is practically completed in 10 min ([Ia] ~ 0.01 *M*), the yield of $[(NH_3)_5RuN_2]^{2+}$ reaching 90–100%, and the yield of cyclohexanone ~ 72%. The reaction of Ia with hydrogen peroxide is even more rapid. In neutral solution the rate of the process is considerably diminished.

It should be mentioned that the free 3,3-pentamethylenediazirine is unaffected by air or hydrogen peroxide at room temperature (50% aq. MeOH, $[H_2SO_4] \sim 1.5$ *M*, 2–3 days). Hence, complexation to ruthenium activates the diazirine CN bonds to oxidative cleavage.

In order to elucidate the mode of the diazirine to metal coordination in complex Ia, its X-ray structural analysis was carried out.* Crystals of the complex are monoclinic, $a = 12.654(9)$, $b = 13.791(9)$, $c = 22.723(15)$ Å, $\beta = 97.98(7)^\circ$, $d_{meas.} = 1.88$, $d_{calc.} = 1.89$ g/cm^3, $Z = 8$, space group $P2_1/c$. The asymmetric unit contains two independent complex cations $[(NH_3)_5Ru(N_2C_6H_{10})]^{2+}$ of close structure and, correspondingly, four PF_6^- ions. The geometry of the complex cation is shown in Fig. 1.

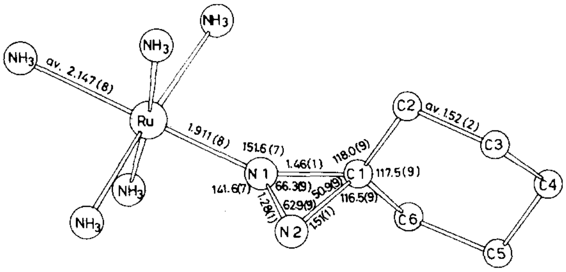


Fig. 1. Molecular structure of $[(NH_3)_5Ru(N_2C_6H_{10})]^{2+}$ with bond lengths and angles averaged over two independent cations in the asymmetric unit.

Complex Ia has a distorted octahedral coordination with five ammonia ligands and the nitrogen atom of 3,3-pentamethylenediazirine as the sixth ligand, *i.e.* the diazirine molecule in Ia is bound to ruthenium only *via* a single N atom.

Among structural parameters of the complex the following significant details are to be noted:

1. The Ru–N(1) bond in Ia (1.906 and 1.916(8) Å; av. 1.911 Å) is by ~ 0.24 Å shorter than its Ru–NH_3 bonds, the length of which varies from 2.126 to 2.164(8) Å (av. 2.147 Å). As the Ru–NH_3 bonds are typically single, the observed shortening of the Ru–N(1) distance means that the diazirine–metal bond in Ia is intermediate between a single and a double bond.

2. The average N(1)–N(2) distance in Ia is 1.28Å (individual values are 1.29 and 1.26(1) Å). This exceeds by 0.04–0.05 Å the length of the N=N double bond in the non-coordinated diazirines CH_2N_2 (1.228 Å) [13] and $(CH_3)_2CN_2$ (1.235 Å) [14]. Thus, complexation with ruthenium leads to lengthening of the N=N bond in the three-membered cycle in conformity with the aforementioned decrease in ν_{NN} on passing from the free to the complexed diazirine.

3. The C–N bonds in the diazirine ring are non-equivalent, C(1)–N(2) (1.50 and 1.51(1) Å; av. 1.51 Å) being by 0.05 Å longer than C(1)–N(1) (1.46 and 1.46(1) Å; av. 1.46 Å).

The other structural parameters of the complex are nonexceptional. The N(1) atom has a planar-trigonal configuration (the sum of the valence angles at N(1) is 359.4°), whereas the C(1) atom has a distorted tetrahedral configuration. The diazirine ring deviates from the pseudoequatorial plane of the Ru octahedron, the dihedral angle between these two planes being 8.7° and 35.7° for two independent complex cations, respectively. The cyclohexane ring is in the chair conformation with an average C–C bond length of 1.52(2) Å and an average bond angle of 109(1)°.

The data obtained bear evidence of a significant contribution of back-donation $d_\pi(Ru) \rightarrow p_\pi^*(N{=}N)$ into the diazirine–metal interaction in the complex Ia. As a result of this effect the electron density on the ruthenium atom should decrease, correspondingly increasing on the coordinated diazirine molecule. It is this which is apparently the reason why in the reaction of Ia with dioxygen or with hydrogen peroxide the oxidant selectivity attacks the diazirine ligand without affecting Ru(II).

The structure of complex IIa is not so evident. The aforementioned data on the transformation of I into II under the action of $[(NH_3)_5RuH_2O]^{2+}$ and the reverse transition II → I in the treatment of II with excess diazirine or with aqueous NH_3, lead to the supposition that IIa might be the binuclear complex $[(NH_3)_5Ru(N_2C_6H_{10})Ru(NH_3)_5](PF_6)_4$ in which the diazirine ligand bridges two ruthenium atoms. However, further study is required for a final conclusion on the structure of this compound.

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* X-ray data were obtained with a Syntex $P2_1$ diffractometer (λMoK_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 45^\circ$, 4316 reflections with $F^2 \geqslant 2\sigma$). The structure was solved by the heavy atom method and refined by the full-matrix anisotropic least squares procedure; $R = 0.061$.

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