

Effect of Ionising Radiation on Potassium Pentacyanonitrosylruthenate(II): an Electron Spin Resonance Study

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O sal pentacianonitrosilrutenato(II) de potássio, em forma amorfa, foi sintetizado e caracterizado por espectroscopias UV, IR, difração de raios X e análise termogravimétrica. Amostras irradiadas por raios X revelam, por espectroscopia de Ressonância Paramagnética Eletrônica, a presença de complexos paramagnéticos de rutênio (I) e de radicais NO₂. Os parâmetros do hamiltoniano de spin medidos para o complexo [Ru(CN)₅NO]³⁻ ($g_{\perp} = 2.0064$, $A_{\perp}(^{14}\text{N}) = 60.7$ MHz, $g_{\parallel} = 1.999$, $A_{\parallel}(^{14}\text{N}) = 77.3$ MHz) indicam uma captura eletrônica em um orbital molecular π^* do grupo nitrosil com a participação de orbitais d_{xz} and d_{yz} do rutênio, como recentemente previsto por cálculos teóricos. Íons de prata, presentes como impurezas oriundas da rota sintética, são reduzidos a Ag(0) durante a irradiação e interagem com quatro nitrogênios equivalentes em um sítio distorcido, originando um espectro de RPE anisotrópico.

Amorphous potassium pentacyanonitrosylruthenate (II) was synthesized and characterized by UV, IR, X-ray diffraction and thermogravimetric analysis. Electron Spin Resonance spectroscopy reveals the presence of paramagnetic ruthenate (I) complexes and NO₂ radicals in the X-irradiated diamagnetic salt. Spin-hamiltonian parameters of the [Ru(CN)₅NO]³⁻ complex ($g_{\perp} = 2.0064$, $A_{\perp}(^{14}\text{N}) = 60.7$ MHz, $g_{\parallel} = 1.999$, $A_{\parallel}(^{14}\text{N}) = 77.3$ MHz) support an electron capture in a π^* molecular orbital of the nitrosyl group mixed with d_{xz} and d_{yz} ruthenium orbitals as recently predicted by theoretical calculations. Silver ions, present as impurities, are reduced to Ag(0) by X-irradiation and coordinate to four magnetically equivalent nitrogens in a distorted site, giving rise to a well resolved anisotropic ESR powder spectrum.

Keywords: pentacyanonitrosylruthenate, ESR, radiation damage

Introduction

Diamagnetic transition metal complexes can render paramagnetic species when submitted to ionising radiation or to electrochemical process. Among the many species that have been characterized by Electron Spin Resonance (ESR), the pentacyanonitrosylferrate(II) complex (nitroprusside salt) is, probably, the most extensively studied. Species like [Fe(CN)₅NOH]²⁻ and [Fe(CN)₅NO]³⁻, generated by electrochemical reduction of a solution of Na₂[Fe(CN)₅NO] in dimethylformamide (DMF), were identified by ESR spectroscopy¹⁻³. Single crystals or powder sodium nitroprusside gamma- or electron-irradiated at different temperatures were

submitted to ESR analysis and in all situations the presence of a [Fe(CN)₅NO]³⁻ species was confirmed^{4,5}. Two d⁷ centers are assigned in the ESR spectra of alkali and alkaline earth pentacyanonitrosylferrate (II) salts, gamma-irradiated at 77 K: [Fe(CN)₄NO]²⁻, with axial symmetry, and [Fe(CN)₅NO]³⁻, with rhombic symmetry⁶. The presence of different cations and/or the presence of hydration water in these species influences the measured g and A values.

On the other hand, the 4d analogous complex, [Ru(CN)₅NO]³⁻ has not been studied in detail. Attempts to produce the paramagnetic complex by electrochemical reduction⁷ lead to a broad unresolved ESR signal. In this work we present a detailed ESR study of potassium pentacyanonitrosyl-ruthenate(II) salt submitted to X-ray irradiation at 298K and 77K.

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Experimental

Reagents $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich), KCN (Vetec), KOH, MeOH, Et_2O , Br_2 , AgNO_3 , K_2CO_3 and KCl (Grupo Química) were used without further purification. Water was distilled and further deionized.

Ultraviolet-visible spectra were obtained using a HP 8452A diode array spectrophotometer. Infrared spectra were obtained using a dispersive 467 Perkin-Elmer spectrophotometer for the 4000 to 500 cm^{-1} region and a 2000 FTIR Perkin-Elmer spectrophotometer for the 600 to 30 cm^{-1} region. The TGA analysis used a Shimadzu TGA-50H detector.

Powdered samples of $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ were irradiated with X-rays produced by a tungsten tube operating at 80 kV, 5 mA current. Irradiation times were 30 and 60 min, at room and liquid nitrogen temperature. ESR spectra were recorded, in continuous wave, on a Bruker ESP-380e CW/FT spectrometer at X-band frequency and on a Bruker ER-420 spectrometer at Q-band frequency. Attempts to detect pulsed ESR were unsuccessful: no FID and no spin echo were detected, at temperatures down to liquid helium.

Synthesis and characterization

The starting compound, $\text{K}_4[\text{Ru}(\text{CN})_6]$, was obtained using Krause and Violette procedure⁸. In this process, the amount of KCN was increased by 20% to compensate for the fast decomposition observed for this reagent.

The synthesis of the potassium pentacyanonitrosylruthenate (II) salt was carried out following the procedure described by Butler *et al.*⁹. The pH was adjusted carefully to 6.0 with a 2% K_2CO_3 solution. The K_2CO_3 solution was added in small amounts under magnetic stirring to avoid the formation of local basic regions inside the solution, which would result in the formation of an unwanted dark precipitate. This unknown dark precipitate is probably formed from the reaction of $[\text{Ru}(\text{CN})_5\text{NO}]^{2-}$ with OH^- in the same way as the yellow $[\text{Ru}(\text{CN})_5\text{NO}_2]^{4-}$ is formed together with a pink-red unknown product when the former is placed in the presence of OH^- or SH^- .⁹

The infrared spectra of $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ in KBr and polyethylene are in agreement with those obtained by Olabe *et al.*¹⁰ for the $\text{Na}_2[\text{Ru}(\text{CN})_5\text{NO}]$ complex in mineral oil. The ultraviolet-visible spectrum, obtained in aqueous solution, presents one band with $\lambda_{\text{max}} = 440$ nm, in agreement with the value related by Guenzburger *et al.*¹¹ of 444.4 nm. X-ray diffraction analysis reveals the amorphous nature of the complex and the presence of KCl and AgCl crystals in the synthesized sample. Thermogravi-

metric measurements clearly indicate the presence of one crystallization water. The synthesized sample is therefore to amorphous $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$.

Results and Discussion

Room temperature irradiation of synthesized sample produces several paramagnetic species. When measured at room temperature, ESR spectra exhibit a 12.7 MHz linewidth intense triplet at $g \cong 2.0064$, a single line 22.4 MHz wide at $g = 2.0005$ and other weaker lines. This central spectrum is flanked by multiplets distant of about 300 Gauss from its centre.

The $[\text{Ru}(\text{CN})_5\text{NO}]^{3-}$ species

The intense triplet (Figure 1b) is attributed to the interaction of the unpaired electron with a nitrogen nucleus of a nitrosyl group in a $[\text{Ru}(\text{CN})_5\text{NO}]^{3-}$ species. Measurements at Q-band made it possible to identify the perpendicular and parallel components of this species (Table 1). The g -tensor for the $[\text{Ru}(\text{CN})_5\text{NO}]^{3-}$ species presents axial symmetry with $g_{\perp} > g_{\parallel} \approx g_e$. From the NO ^{14}N hyperfine tensor we calculate $A_{\text{iso}} = 66.2$ MHz and $A_{\text{aniso}} = 5.5$ MHz. Ratio between these values and those calculated considering one unpaired electron in a 2s or in a 2p nitrogen orbital leads to unpaired electron densities¹² of 4.3% and 11.8% respectively. Recent calculations¹³ using Density Functional theory indicate that in this complex, as well as in the Fe analogous complex, the unpaired electron molecular orbital is primarily π^* (NO) mixed with metal d_{xz} and d_{yz} orbitals. Measured g -values for both complexes qualitatively agree with this result as shown in Table 1. Unpaired electron spin densities on the NO nitrogen are also shown in Table 1. Higher spin-density values and lower g -values for the ruthenium species follow the larger 4d wave-function delocalization.

Observation of $I = 5/2$ ^{99}Ru (12.7% natural abundance) and ^{101}Ru (17% natural abundance) hyperfine interactions proved to be rather difficult. Besides the amorphous nature of samples, which broadens the ESR spectrum, lines corresponding to ruthenium isotopes are already broadened by a partial superposition due to a small difference in their magnetic moments¹⁴.

The NO_2 species

ESR measurements as function of temperature allows the progressive observation of another set of triplets. Figure 1a shows the results at 5K. Hyperfine interaction is anisotropic, with 173.7MHz and 126.8 MHz

for perpendicular and parallel components, respectively. These values suggest the presence of a NO_2 species, in agreement with the values reported in reference 15 for this radical. This species relaxes fast and can only be observed below 150K. For samples irradiated at 77K, only a small amount of NO_2 is formed and $[\text{Ru}(\text{CN})_5\text{NO}]^{3-}$ is the prevailing species. The single line at $g = 2.0005$, less intense on samples irradiated at 77K, remains not identified.

Table 1. g -values, NO ^{14}N -hyperfine coupling constants and unpaired electron densities on nitrogen 2s and 2p orbitals

Species	g^{\wedge}	g_j	$A^{\wedge a}$	A_j^a	f_s (%)	f_p (%)
$[\text{Ru}(\text{CN})_5\text{NO}]^{3-}$	2.0064	1.9990	60.7	77.3	4.3	11.8
$[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ ^b	2.0355	2.0062	40.2	47.7	2.8	5.2

^a hyperfine interactions in MHz units; ^b from ref. [5].

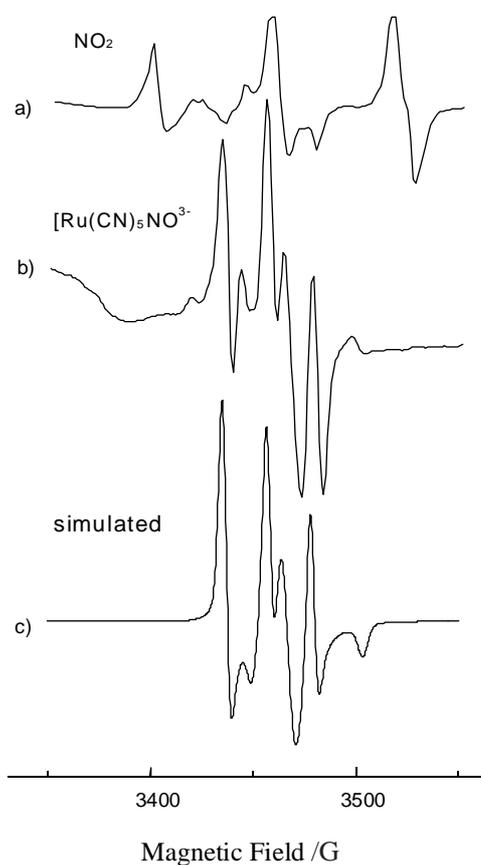


Figure 1. First derivative X-band ESR spectrum of $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ irradiated at room temperature for one h: (a) spectrum measured at 5K; (b) room temperature spectrum; (c) simulated room temperature spectrum.

The Ag(0) centre

Attempts to attribute the multiplets that flank the central spectrum, as described above, to a pair interaction, as reported in reduced sodium nitroprusside⁵, were not

possible. On the other hand, X-rays analysis reveals the presence of AgCl crystals on the synthesized sample, suggesting that silver ions may be also present in the sample as an impurity. $\text{Ag}(0)$ paramagnetic centres are reported in the literature¹⁶; g -values are close to the free electron value and hyperfine interaction with the $I=1/2$ silver isotopes is about 600 Gauss and isotropic. Attempts to fit this part of the spectrum considering isotropic couplings to one $\text{Ag}(0)$ and to four equivalent nitrogens improved the situation but still were not satisfactory. The best fit is obtained assuming a small rhombicity in the g -tensor and in silver hyperfine coupling, as shown in Table 2 and Figure 2. Fittings were performed in third order perturbation theory with the aid of Simfonia software, kindly supplied by Bruker-Physik. The amorphous nature of the sample precludes a better looking fitting, although line positions are very well reproduced; the reason for this is that line shapes for amorphous samples are not the same as for powdered samples, assumed by the software.

Table 2. Spin-hamiltonian parameters for the $\text{Ag}(0)$ centre in various irradiated matrices

Matrix	$A_x^{a,b}$	A_y	A_z	g_x^a	g_y	g_z
H_2O (4.2 K) ^c	-630			2.001		
$\text{MeCN}/\text{AgNO}_3$ ^d	-631			1.997		
$\text{MeCN}/\text{AgClO}_4$ ^e	-538 ± 2			1.997		
KCl ^f	-640			2.000		
$\text{Ru}(\text{CN})_5\text{NO}/\text{AgCl}$	-638 ± 2^g	-576 ± 5	-756 ± 2	2.000^g	1.998	1.980^a

If only the x -component is quoted, the tensor is reported to be isotropic; ^b ^{109}Ag hyperfine interaction in Gauss ($1\text{G}=10^4\text{ T}=2.8\text{ MHz}$ if $g=2.0023$); ^cRef. [17]; ^dRef. [18]; ^eRef. [16], $A(^{14}\text{N})=6.5 \pm 0.5\text{ G}$; ^fRef. [19]; ^gThis work; $A_{\text{iso}} = -657 \pm 3$, $g_{\text{iso}} = 1.993$, $A(^{14}\text{N}) = 13.0 \pm 0.2\text{ G}$.

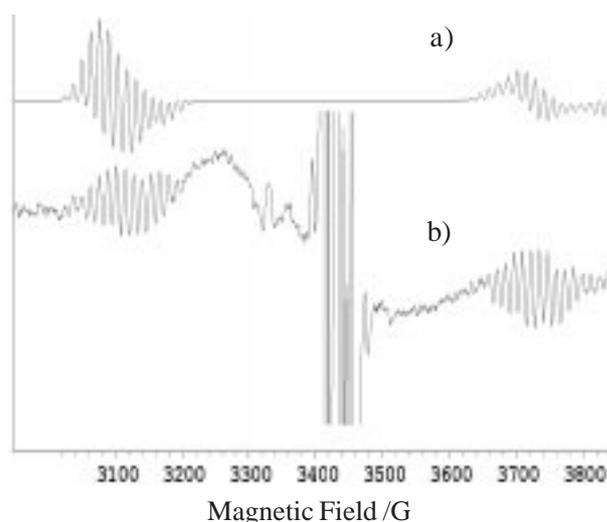


Figure 2. Comparison between room temperature first derivative X-band ESR spectrum of the silver center (b) and powder spectrum simulation (a) taking into account silver isotopic composition, hyperfine interactions with four equivalent nitrogens and rhombicity as described in the text. The amorphous nature of samples is revealed in the experimental line shapes but not in the simulated powder spectrum.

Table 2 also displays a review of Ag(0) data found in the literature. To our knowledge this is the first report on anisotropic Ag(0) ESR spectrum. Anisotropy may result from a mixture between silver 6s orbital and 5d orbitals, allowed by a low local symmetry. The four nitrogens appear to interact identically with the unpaired electron. The measured hyperfine interaction is assumed to be isotropic; its value is 13 Gauss, twice as large as found in reference 16, where coordination is postulated to be tetrahedral. This reinforces a non-tetrahedral coordination; participation of Ag(0) 5d orbitals in the molecular orbital would increase unpaired electron density on the ligands.

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