Spectroscopic and Reactivity Comparison of Pentacyanonitrosylruthenate(2−) with Pentacyanonitrosylferrate(2−), Nitroprusside

ANTHONY R. BUTLER, ADRIANNE M. CALSY-HARRISON, CHRISTOPHER GLIDEWELL* and IAN L. JOHNSON

Chemistry Department, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, U.K.

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Abstract

Lithium penta(cyano-^{13}C)nitrosylruthenate (2−), $Li_2[Ru(^{13}CN)_5NO]$, in which the anion is the ruthenium analogue of the nitroprusside ion, has been synthesized at 90% isotopic enrichment, and characterized spectroscopically. Despite the very high level of ^{13}C enrichment, no two-bond coupling $^2J(^{13}C_{ax}\text{-}Ru^{13}C_{eq})$ was detected in the high-frequency ^{13}C NMR spectrum of $Li_2[Ru(^{13}CN)_5NO]$, nor was any such coupling observed in $Li_4[Ru(^{13}CN)_5(^{15}NO_2)]$ although both two-bond couplings to ^{15}N, $^2J(^{13}C_{ax}\text{-}Ru^{15}NO_2)$ and $^2J(^{13}C_{eq}Ru^{15}N)$ were observed. $Li_2[Ru(^{13}CN)_5(^{14}NO)]$ reacted with excess of $Li[^{15}NO_2]$ to yield $Li_4[Ru(^{13}CN)_5(^{15}NO_2)]$ only: no $Li_2[Ru(^{13}CN)_5(^{15}NO)]$ was observed. $Li_4[Ru(^{13}CN)_5(^{14}NO_2)]$ however showed no exchange with $Li[^{15}NO_2]$. While $[Ru(CN)_5NO]^{2-}$ reacted with both OH^- and SH^- in reactions similar to those of $[Fe(CN)_5NO]^{2-}$, no reactions were detected between $[Ru(CN)_5NO]^{2-}$ and piperidine, $[CH(CN)_2]^-$, $[CH(COCH_3)_2]^-$, MeS^-, or $[S_2O_4]^{2-}$, all of which are known to react readily with $[Fe(CN)_5NO]^{2-}$.

Introduction

We have recently shown [1–3] that the use of high isotopic enrichment (90% ^{13}C) allows easy identification by ^{13}C NMR of a wide range of cyanoferrate complexes, and moreover allows the course of reactions to be monitored in real time. Thus for example, we were able to distinguish two mechanistic routes for the conversion of $[Fe(CN)_5NO]^{2-}$ to $[Fe(CN)_5NO_2]^{4-}$ [1]: in one, involving direct attack of hydroxide on the nitrosyl ligand, no exchange occurs in the nitrogen attached to iron, whereas in the other, involving nucleophilic attack on the nitrosyl nitrogen atom by nitrite, exchange of nitrogen bound to iron occurs, and is readily observed spectroscopically by use of $[^{15}NO_2]^-$.

In the present paper, we present an NMR study of the analogous ruthenium complex $[Ru(CN)_5NO]^{2-}$, together with some comparison of the reactivity of $[Fe(CN)_5NO]^{2-}$ and $[Ru(CN)_5NO]^{2-}$.

Experimental

$Na[^{13}CN]$ (90% ^{13}C enrichment) and $Na[^{15}NO_2]$ (99% ^{15}N enrichment) were both obtained from MSD Isotopes and ruthenium trihydrate from Alfa: all were used as received. $Na[^{15}NO_2]$ was converted to $Li[^{15}NO_2]$ by precipitation of $Ag[^{15}NO_2]$, using $Ag[^{14}NO_3]$, followed by stirring of $Ag[^{15}NO_2]$ with a stoichiometric quantity of LiCl solution.

$Li_2[Ru(^{13}CN)_5NO]$ was prepared from $RuCl_3\cdot 3H_2O$ via $Na_4[Ru(^{13}CN)_6]$: the preparation was based upon methods described in the literature [4, 5].

Preparation of $Na_4[Ru(^{13}CN)_6]$

A 20.0 cm^3 portion of bromine water (0.21 mol dm^{-3}) was pipetted into a three-necked flask containing 0.50 g (1.91 mmol) of $RuCl_3\cdot 3H_2O$. This solution was stirred for 60 s to dissolve the ruthenium chloride, after which 0.891 g (22.3 mmol) of solid NaOH was added in one portion. After a brief period of stirring, the mixture was left to stand for seven minutes, after which time it had become dark brown in colour.

To this solution was added, in one portion, 3.84 g (76.8 mmol) of $Na[^{13}CN]$ and the resulting mixture was stirred for 30 s. The resulting green–brown solution was heated under reflux until it just became colourless: it was then immediately cooled to room temperature, using an ice/salt bath. After addition of dry methanol (30 cm^3), the white precipitate was filtered off, and washed with ice-cold 1:1 methanol–water (150 cm^3) until the filtrate was no longer basic: it was then washed with ice-cold dry methanol (20 cm^3) and dry diethyl ether (20 cm^3). The crude product was dissolved in water (12 cm^3) and an equal volume of methanol was added: this solution was kept in an ice/water bath for 2 h, after which the

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*Author to whom correspondence should be addressed.

crystals of $Na_4[Ru(^{13}CN)_6]$ were filtered off, washed successively with ice-cold 1:1 methanol—water (12 cm^3), dry methanol (5 cm^3) and diethyl ether (5 cm^3). Yield: 0.61 g (1.72 mmol, 90%). IR (nujol); ν (cm^{-1}): 2022, ν(CN); 540, δ(RuCN); 390, ν(RuC): cf. for $K_4[Ru(^{12}CN)_6]$: 2060, 546, 374 [6]. UV (aqueous solution); λ_{max}, 205 nm; ϵ, 3.76 $\times$ 10^4 M^{-1} cm^{-1} (lit. [5]: λ_{max} 205.5 nm; ϵ (3.89 $\pm$ 0.18) $\times$ 10^4 M^{-1} cm^{-1}).

Preparation of Li$_2$[Ru(^{13}CN)$_5$NO]

Concentrated nitric acid (S.G. 1.42) (1 cm^3) was slowly added to a solution of $Na_4[Ru(^{13}CN)_6]$ (0.61 g, 1.72 mmol) in water (0.5 cm^3). The mixture was held at 80 °C, under nitrogen, for 36 h: the volume was maintained by periodic addition of further aliquots of nitric acid. The solution was then cooled, and carefully brought to pH 7 by addition of a saturated solution of Li$_2$CO$_3$. To the neutralized solution was added a 0.1 mol cm^{-3} solution of AgNO$_3$ (100 cm^3) to precipitate Ag$_2$[Ru(^{13}CN)$_5$NO]. The mixture was held at 0 °C for 1 h and the precipitate was then filtered off and thoroughly washed with cold water to remove residual AgNO$_3$. The filtrate was suspended and stirred, in the dark for 48 h, with a solution of LiCl (0.15 g, 3.45 mmol) in water (20 cm^3). The resulting silver chloride was removed by repeated centrifugation. Evaporation of the deep-red solution gave Li$_2$[Ru(^{13}CN)$_5$NO]. Yield: 434 mg (1.55 mmol, 90%), IR (nujol); ν (cm^{-1}): 2139, 2091, 2054, 2024, ν(CN); 1918, ν(NO); 516, δ(RuCN); 420, ν(RuC); cf. Na$_2$[Ru(^{12}CN)$_5$NO]: 2184, 2174, 2166, 2151, 1926, 512, 422 [7]; Li$_2$[Ru(^{12}CN)$_5$-NO]: 2183, 2172, 2164, 2150, 1926, 514, 421. UV (aqueous solution): Li$_2$[Ru(^{13}CN)$_5$NO]; λ_{max}, 430 nm; Li$_2$[Ru(^{12}CN)$_5$NO]; λ_{max}, 435 nm.

NMR Spectra

The ^{13}C and ^{15}N NMR spectra were recorded in the FT mode using the Bruker WH-360 spectrometer of the Science and Engineering Research Council Regional NMR Service at the University of Edinburgh; all spectra were recorded at 25 °C. The ^{13}C spectra were recorded at 90.57 MHz relative to external TMS, using spectral widths between 500 and 20 000 Hz, and typically 500 scans, with delays of 0.6 s between pulses of 6 μs. The ^{15}N spectra were recorded at 36.51 MHz relative to external CH$_3$^{15}NO$_2$, with spectral widths between 400 Hz (2.5 s delays between pulses of 4 μs) and 25 000 Hz (0.3 s delays between pulses of 4 μs). All spectra were recorded using 4% solutions in D$_2$O.

EHMO Calculations

Molecular orbital calculations were made with the extended Hückel method [8, 9]. The molecular geometry of [Ru(CN)$_5$NO]$^{2-}$ was averaged from the experimental geometry [7] to exact C_{4v} symmetry. The atomic parameters were as published [10—13].

Results and Discussion

NMR Spectra

The ^{13}C NMR spectrum of the [Fe(^{13}CN)$_5$NO]$^{2-}$ ion, which has [14, 15] C_{4v} molecular symmetry, is of AX$_4$ type, characterized in aqueous solution by δ_A, +132.4; δ_X, +134.4; J_{AX} [=$^2J(^{13}C_{ax}Fe^{13}C_{eq})$], 17.7 Hz. The corresponding spectrum of the isostructural [7] ion [Ru(^{13}CN)$_5$NO]$^{2-}$ is however markedly different it exhibits two resonances, δ +130.0 and +130.1, assigned on the grounds of their relative intensities to the axial and equatorial ligands respectively. However, despite the high abundance of ^{13}C, no coupling $^2J(^{13}C_{ax}Ru^{13}C_{eq})$ was detected, and with a linewidth measured at 4 Hz, we estimate that 1 Hz represents an upper limit to J above which it would be readily recognized.

When [Ru(^{13}CN)$_5$(^{14}NO)]$^{2-}$, as the lithium salt, was held during 24 h with Li[^{15}NO$_2$], such that the molar ratio ^{14}N:^{15}N in the oxo-species was 1:10, the ^{13}C NMR spectrum of [Ru(^{13}CN)$_5$(^{14}NO)]$^{2-}$ was completely replaced by that of [Ru(^{13}CN)$_5$-(^{15}NO$_2$)]$^{4-}$, characterized by $\delta(^{13}C_{ax})$, +163.9; $\delta(^{13}C_{eq})$, +163.4: $^2J(^{13}C_{ax}Ru^{15}N)$, 6.3 Hz; $^2J(^{13}C_{eq}$-Ru^{15}N), 4.8 Hz: again no ^{13}C—^{13}C coupling $^2J(^{13}C_{ax}$-Ru$^{13}C_{eq})$ was detected. Nor was any [Ru(^{13}CN)$_5$-(^{15}NO)]$^{2-}$ detected. This observation should be contrasted with the reaction between excess [^{15}NO$_2$]$^-$ and the analogous iron nitrosyl, [Fe-(^{13}CN)$_5$(^{14}NO)]$^{2-}$, where the major product was [1] [Fe(^{13}CN)$_5$(^{15}NO)]$^{2-}$, with [Fe(^{13}CN)$_5$(^{15}NO$_2$)]$^{4-}$ as a minor product. Despite the essentially complete incorporation of ^{15}N into the nitrito ligand in [Ru(^{13}CN)$_5$(^{15}NO$_2$)]$^{4-}$, as shown by the doublet structure of the ^{13}C resonances, we were unable to detect any ^{15}N resonance from this complex: the sole resonance detected was that of excess [^{15}NO$_2$]$^-$.

The anion [Ru(CN)$_5$NO]$^{2-}$ reacts readily with hydroxide to form [Ru(CN)$_5$NO$_2$]$^{4-}$ [7, 16]. When the reaction of [Ru(^{13}CN)$_5$(^{14}NO)]$^{2-}$ with hydroxide was conducted in the presence of a ten-fold molar excess of [^{15}NO$_2$]$^-$, the resulting ^{13}NMR spectrum was that of [Ru(^{13}CN)(^{14}NO$_2$)]$^{4-}$ rather than that of [Ru(^{13}CN)$_5$(^{15}NO$_2$)]$^{4-}$. This shows that the reaction of [Ru(CN)$_5$NO]$^{2-}$ with hydroxide is much faster than its reaction with nitrite, and that any subsequent reaction of [Ru(CN)$_5$(NO$_2$)]$^{4-}$ with nitrite is very slow. Although [Ru(^{13}CN)$_5$(^{14}NO)]$^{2-}$ reacts readily with [^{15}NO$_2$]$^-$ to yield [Ru(^{13}CN)$_5$(^{15}NO$_2$)]$^{4-}$, [Ru(^{13}CN)$_5$(^{14}NO$_2$)]$^{4-}$ showed no such reaction.

Solutions containing both [Ru(^{13}CN)$_5$NO)]$^{2-}$ and hydroxide showed the development, over a period of days, of a singlet in the ^{13}C spectrum at δ +172.8: the same singlet appeared, over a period of many months, in the spectrum of a solution of Li$_2$[Ru(^{13}CN)$_5$NO)] alone. This singlet we tentatively assign to the aqua complex [Ru(^{13}CN)$_5$(H$_2$O)]$^{3-}$, in which the axial and equatorial carbons are

fortuitously isochronous. In either case the aqua complex was probably formed via the nitrito complex $[Ru(^{13}CN)_5(NO_2)]^{4-}$. On the other hand solutions of the sodium salt $Na_2[Ru(^{13}CN)_5NO]$ showed no sign whatever, even after many months at room temperature, of the δ 172.8 signal. In $Li_4[Ru(^{13}CN)_6]$, the ^{13}C chemical shift is +161.5.

Although we have readily observed ^{13}C resonances in cyanoruthenates, we have never been able to detect any ^{15}N resonances, even at 99% ^{15}N enrichment, for either nitrosyl or nitrito ligands bound to ruthenium: this contrast is surprising as both ^{15}N and ^{13}C in these examples are directly bound to the ruthenium centre. It is difficult to see why no ^{15}N resonance could be detected: some 70% of ruthenium atoms, at natural composition, are isotopes having $I = 0$, and hence no quadrupole moment, even though the remaining isotopes ^{99}Ru and ^{101}Ru are both quadrupolar.

Electronic Structures

The frontier orbitals of $[Ru(CN)_5NO]^{2-}$, as revealed by EHMO calculations, are very similar to those found [17] for the isostructural and isoelectronic $[Fe(CN)_5NO]^{2-}$. In Table I, we present the energies of the frontier orbitals for $[Ru(CN)_5NO]^{2-}$, and those close in energy, together with their symmetry types in C_{4v} and approximate descriptions. In addition, similar data for $[Fe(CN)_5NO]^{2-}$ are also provided [17].

In $[Ru(CN)_5NO]^{2-}$, the LUMO is of π type, localised in the π^* orbitals of the nitrosyl ligand, with coefficients much higher for nitrogen than for oxygen. Of all the ligand atoms, the nitrogen atom of the nitrosyl ligand bears the highest charge, so that for both orbital-controlled and charge-controlled reactions with nucleophiles (essentially involving soft and hard nucleophiles respectively) the site of

attack is expected always to be the nitrogen atom in the nitrosyl ligand. The highest occupied orbitals are lone pair orbitals delocalized amongst the equatorial cyanide ligands; indeed all of the highest occupied ligand orbitals are of this type: the nitrogen atom of the axial cyanide ligand bears the same charge (−0.933 e) as those of the equatorial cyanide ligands. Hence although electrophiles will always attack the nitrogen atoms of the cyanide ligands, as opposed to the oxygen of the nitrosyl ligand (charge, −0.189 e), there appears to be no preference between the two types of cyanide ligand. In $[Fe(CN)_5NO]^{2-}$, however, there is a slight preference for the axial cyanide ligand as the site for reactions with electrophiles [2, 17].

Reactivity

The red−brown anion $[Ru(CN)_5NO]^{2-}$ reacts readily with OH^- and SH^- to yield respectively pale yellow $[Ru(CN)_5NO_2]^{4-}$ and a pink−red product of unknown constitution. However the literature on these products is full of confusion, and many conflicting values for the absorption maxima have been published. Thus for $[Ru(CN)_5NO]^{4-}$, the reported values of λ_{max} include 325 [7] and 365 [16] nm; for the product formed by SH^-, the values include 430 [7] and 485 [18] nm. The nitrito complex $[Ru(CN)_5NO_2]^{4-}$ undergoes a slow reaction with water to yield $[Ru(CN)_5H_2O]^{3-}$, for which λ_{max} values of 285 [7] and 310 [19, 20] nm have been recorded, while the absorption at 285 nm has been ascribed to both $[Ru(CN)_5H_2O]^{3-}$ [7] and $[Ru(CN)_5NH_3]^{3-}$ [20]. There are even major differences between the various reported absorption spectra for $[Ru(CN)_5NO]^{2-}$ itself [4, 7, 18].

Our own measurements showed clearly that for $[Ru(CN)_5NO_2]^{4-}$ there are no absorption maxima at all in the visible region, merely the tail of the UV

TABLE I. Frontier Orbitals for $[M(CN)_5NO]^{2-}$ (M = Fe or Ru): Energies, Symmetries, and Approximate Bonding Descriptions

M = Ru			M = Fe[a]		
Energy (eV)	Symmetry	Approximate description	Energy (eV)	Symmetry	Approximate description
−5.20	a_1	d_{z^2}	−4.68	a_1	d_{z^2}
−5.93	b_1	$d_{x^2-y^2}$	−5.54	b_1	$d_{x^2-y^2}$
−8.05	e	$\pi^*(CN)_{ax}$	−8.45	e	$\pi^*(CN)_{ax}$
−10.38(LUMO)	e	$\pi^*(NO)$	−10.01(LUMO)	e	$\pi^*(NO)$
−13.18(HOMO)	e	lone pairs; $(CN)_{eq}$	−12.79(HOMO)	b_2	d_{xy}
−13.62	a_1	lone pair; $(CN)_{ax}$	−12.95	e	lone pairs; $(CN)_{eq}$
−14.16	b_2	d_{xy}	−13.12	e	d_{yz}, d_{zx}
−14.23	a_1	lone pairs; $(CN)_{eq}$	−13.33	a_1	lone pair; $(CN)_{ax}$
−14.30	e	d_{yz}, d_{zx}	−13.76	b_1	lone pairs; $(CN)_{eq}$
−14.60	b_1	lone pairs; $(CN)_{eq}$	−13.95	a_1	lone pairs; $(CN)_{eq}$
−14.62	a_2	$\pi(CN)_{eq}$	−14.49	e	$\pi(CN)_{ax}$
−14.64	e	$\pi(CN)_{ax}$	−14.56	a_2	$\pi(CN)_{eq}$

[a]Ref. 17.

maxima at *ca.* 200 nm: we observed no maxima at either 325 [7] or 365 [16] nm. In the reaction of $[Ru(CN)_5NO]^{2-}$ with SH^-, we observed a clear maximum at 530 nm, close to the maxima (520–525 nm) observed in reactions of $[Fe(CN)_5NO]^{2-}$ with RS^- and assigned to intermediates of type $[Fe(CN)_5N(O)SR]^{3-}$ [21]. It is therefore tempting to assign the band at 530 nm to the intermediate $[Ru(CN)_5N(O)SH]^{3-}$, whose subsequent decay to $[Rh(CN)_5H_2O]^{3-}$ involves loss, and presumably decomposition, of HNSO. We observed no absorption maxima at either 430 [7] or 485 [18] nm in the SH^- reaction. Our spectrum of $[Ru(CN)_5NO]^{2-}$ was consistent with that of Garnier [4] but not with those of Olabe [7] or Müller [18], in that we observed a band at 430 nm but one at 345 [7] or 490 [18] nm. We have used lithium salts, as did Garnier [4], whereas others have generally used the much less soluble sodium or potassium salts. It is therefore possible that the observed spectral differences could in part be ascribed to the effect of ion-pairing and other interionic phenomena. To test this we recorded the effect of increasing concentrations of KCl on the spectrum of $Li_2[Ru(CN)_5NO]$. When KCl was absent, λ_{max} was at 430 nm: increasing concentration of KCl caused λ_{max} to shift, but even when the sample was saturated in KCl, λ_{max} had only shifted to 423 nm, still remote from some of the values cited in the literature [7, 18].

While $[Ru(CN)_5NO]^{2-}$ reacts readily [22] with hydrazine in alkaline solution to yield $[Ru(CN)_5H_2O]^{3-}$, we found that, unlike the analogous $[Fe(CN)_5NO]^{2-}$ [23], there was no perceptible reaction between $[Ru(CN)_5NO]^{2-}$ and piperidine. Likewise, the carbanions of $CH_2(CN)_2$ and $CH_2(COCH_3)_2$ reacted with $[Ru(CN)_5NO]^{2-}$ very much more slowly than hydroxide, as the sole product was $[Ru(CN)_5NO_2]^{4-}$: in contrast these carbanions react rapidly with $[Fe(CN)_5NO]^{2-}$ to form red adducts such as $[Fe(CN)_5N(O)C(CN)_2]^{4-}$ [24]. Similarly, whereas $[Fe(CN)_5NO]^{2-}$ reacts rapidly [25] with MeS^-, no reaction was observed between MeS^- and $[Ru(CN)_5NO]^{2-}$.

The nitroprusside ion $[Fe(CN)_5NO]^{2-}$ undergoes a redox reaction with both $S_2O_4^{2-}$ and RS^- to yield the paramagnetic iron(I) complex $[Fe(CN)_4NO]^{2-}$, readily detected by ESR spectroscopy. With $[Ru(CN)_5NO]^{2-}$ neither $S_2O_4^{2-}$ nor RS^- anions gave any paramagnetic product. This failure to undergo reduction is a reflection of the immense stability of low-spin d^6 ruthenium(II). This is further exemplified by the extreme reluctance, compared with $[Fe(CN)_5NO]^{2-}$, of $[Ru(CN)_5NO]^{2-}$ to undergo photolytic redox reactions. Whereas $[Fe(CN)_5NO]^{2-}$ is rapidly photolyzed in aqueous solution to give the iron(III) complex $[Fe(CN)_5H_2O]^{2-}$ [26], or in the presence of excess thiocyanate the blue complex $[Fe(CN)_5(SCN)]^{3-}$ [27, 28] (which allows easy visualization

of the course of the photolysis, with the iron(III) complex visible after exposure to diffuse daylight for only a few minutes), the ruthenium complex $[Ru(CN)_5NO]^{2-}$ shows signs of such photolysis only after many days exposure to sunlight. The difficulty of effecting oxidation of low spin ruthenium(II), compared with low spin iron(II) is illustrated by the standard e.m.f.s reported for the couples $[M(CN)_6]^{4-}/[M(CN)_6]^{3-}$: for M = Fe, $e^{\ominus}$ is 0.361 V [29], while for M = Ru, $e^{\ominus}$ is 0.86 V [30]. There is however some doubt about the ruthenium e.m.f. since bromine oxidation of $[Ru(CN)_6]^{4-}$ causes oxidation not of Ru(II) to Ru(III), but of one of the cyanide ligands yielding cyanogen bromide and the ruthenium(II) complex $[Ru(CN)_5H_2O]^{3-}$.

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