agreement with the results of crystallographic studies,[11,16] the infrared bands indicating the order Fe(II) > Co(III) > Fe(III) > Cr(III) >> Ni(II) > Cu(II) > Zn(II).

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Registry No. I, 97134-61-7; II, 97134-62-8; $[Ni([9]aneN_3)_2]$, 59034-12-7; $[Cu([9]aneN_3)_2](NO_3)_2$, 59034-09-2; $[Zn([9]aneN_3)_2](NO_3)_2$, 97102-39-1; $[Cr([9]aneN_3)_2]Cl_3$, 97134-63-9; $[Co([9]aneN_3)_2]Cl_3$, 75592-25-5.

Supplementary Material Available: Listings of observed and calculated structure factors, temperature factors, and coordinates for hydrogen atoms (12 pages). Ordering information is given on any current masthead page.

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Nitrogen-15 and Carbon-13 NMR Study of Roussin Salts and Esters and of Pentacyanoferrate Complexes

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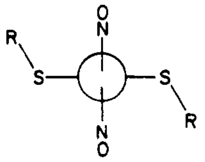
High-frequency ^{15}N NMR spectroscopy, using 99% isotopic enrichment for ^{15}N, shows that the Roussin esters $Fe_2(SR)_2(NO)_4$ (R = Me, *i*-Pr) exist as an equimolar mixture of two conformers having C_{2v} and C_{2h} symmetries respectively. Similar ^{15}N spectroscopy of $[Fe_4X_3(NO)_7]^-$ (X = S, Se) shows that the solid-state structure for X = S persists in aqueous solution and demonstrates that the anion having X = Se is isostructural in solution; this is confirmed by natural-abundance ^{77}Se NMR. The cubane type $Fe_4S_4(NO)_4$ retains its structure in solution, and $Fe_4Se_4(NO)_4$ is isostructural. A combination of ^{13}C and ^{15}N NMR spectra obtained at high frequency with 90% ^{13}C and 99% ^{15}N enrichment reveals two mechanisms for the conversion of $[Fe(CN)_5NO]^{2-}$ to $[Fe(CN)_5NO_2]^{4-}$, one involving nucleophilic attack by hydroxide and the other attack by nitrite. The spectral data allow ready identification of pentacyanoferrate complexes arising from the reactions of nitroprusside with nucleophiles.

The X-ray structural analysis of the ethyl ester of Roussin's red salt, $Fe_2(SEt)_2(NO)_4$, showed[1] the molecule to be centrosymmetric, of approximately C_{2h} ($2/m$) molecular symmetry. In contrast to this solid-state structure, a series of esters $Fe_2(SR)_2(NO)_4$ (R = Me, Et, *n*-Pr, *i*-Pr, CH_2Ph,[2] and Ph[3]) have been shown by ^1H NMR to exist in solution as an equimolar mixture of two components that were presumed to be conformers of C_{2h} and C_{2v} symmetry, **1** and **2**, respectively. Although activation barriers for the equilibration of the two forms were measured[2] for R = Me, Et, *n*-Pr, *i*-Pr, and CH_2Ph, the structures of these two forms in solution have not been rigorously established.



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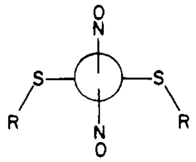

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Roussin's black anion, $[Fe_4S_3(NO)_7]^-$, has been shown to have C_{3v} symmetry in the solid state[4,5] and to react with elemental sulfur[2] to yield the cubane-like complex[6] $Fe_4S_4(NO)_4$. The selenium analogue $[Fe_4Se_3(NO)_7]^-$ has been prepared[2] and characterized by analysis as its tetraphenylarsonium salt. This anion reacted with elemental selenium[7] to yield a complex whose infrared spectrum was very similar to that of $Fe_4S_4(NO)_4$, and the constitution $Fe_4Se_4(NO)_4$ was tentatively assigned. The structures of both $[Fe_4Se_3(NO)_7]^-$ and $Fe_4Se_4(NO)_4$ in solution have not been established directly, but assumed by comparison with their sulfur analogues.

In this paper we present ^{15}N NMR evidence which both establishes the identities of the two forms of $Fe_2(SR)_2(NO)_4$ in solution and provides definite proof of structure for both $[Fe_4Se_3(NO)_7]^-$ and $Fe_4Se_4(NO)_4$ in solution.

The nitroprusside ion, $[Fe(CN)_5NO]^{2-}$, although stoichiometrically and structurally quite different from Roussin's salts and esters, is in fact readily interconvertible[8,9] with the black Roussin anion, $[Fe_4S_3(NO)_7]^-$. Since we have found[10] that there is very ready isotopic exchange of nitrosyl groups with labeled nitrite in the paramagnetic mononuclear complexes of types $[Fe(NO)_2(SR)_2]^-$ and $Fe(NO)(S_2CNMe_2)_2$, which are readily formed from $Fe_2(SR)_2(NO)_4$ and $[Fe_4S_3(NO)_7]^-$, it was of interest to determine whether the mononuclear nitroprusside ion would also react with isotopically labeled nitrite: we report here ^{13}C and ^{15}N NMR evidence that exchange is rapid and complete in the presence of excess $[^{15}NO_2]^-$.

Nitrogen-15 NMR studies of metal nitrosyls have been few in number,[11-14] but the ^{15}N chemical shift has been established[12-14] as a simple criterion of structure, readily distinguishing between linear and bent M–N–O fragments. Earlier ^{14}N studies have been summarized in a comprehensive review of ^{14}N and ^{15}N NMR spectroscopy.[15]

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Experimental Section

NMR Spectra. The ^{13}C, ^{15}N, and ^{77}Se NMR spectra were recorded in the FT mode on the Bruker WP-200 and WH-360 spectrometers of the Science and Engineering Research Council Regional NMR Service at the University of Edinburgh; all spectra were recorded at 25 °C. ^{13}C spectra were recorded at 90.57 MHz relative to external Me_4Si by using spectral widths between 500 and 20000 Hz and typically using 500 scans, with delays of 0.6 s between pulses of 6 μs. ^{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 4-μs pulses) and 25000 Hz (0.3-s delays between 4-μs pulses). ^{77}Se spectra were recorded at 68.68 MHz, relative to external Me_2Se, with a spectral width of 2000 Hz and 0.24-s delays between 5-μs pulses.

Spectra of $Fe_2(SR)_2(NO)_4$, $Fe_4X_4(NO)_4$, and $(PPN)^+[Fe_4X_3(NO)_7]^-$ were recorded on 2% solutions in CD_2Cl_2, and all spectra of the $[Fe(CN)_5NO]^{2-}$ ion and its derivatives on 2% solutions in D_2O. In no case was it found necessary to use any relaxation agent. Estimated experimental uncertainties in spectral parameters are ±0.1 ppm in chemical shifts and ±0.2 Hz in coupling constants.

$Na[^{13}CN]$ (90% enriched) and $Na[^{15}NO_2]$ (99% enriched) were purchased from MSD Isotopes, Inc., and were used as received. Samples of $(PP^{14}N)^+[Fe_4S_3(^{15}NO)_7]^-$ and $(PP^{14}N)^+[Fe_4Se_3(^{15}NO)_7]^-$ ($PPN^+ \equiv Ph_3PNPPh_3{}^+$) were prepared as described previously:[2] $Fe_4S_4(^{15}NO)_4$ was prepared[2] by reaction of $Na[Fe_4S_3(^{15}NO)_7]$ with elemental sulfur, and $Fe_4Se_4(^{15}NO)_4$ by reaction of $Na[Fe_4Se_3(^{15}NO)_7]$ with elemental selenium.

Bis(μ-methanethiolato)bis[di(^{15}N)nitrosyliron], $Fe_2(SMe)_2(^{15}NO)_4$. $Fe_2(SMe)_2(CO)_6$ (0.50 g, 1.3 mmol) was dissolved in DMF (30 mL), and $Na[^{15}NO_2]$ (0.50 g, 7.1 mmol) was added. The mixture was refluxed under nitrogen for 30 min and then cooled to 100 °C. Toluene (500 mL) was added, causing conversion of green $[Fe(^{15}NO)_2(SMe)_2]^-$ to red $Fe_2(SMe)_2(^{15}NO)_4$. This mixture was filtered and the filtrate evaporated to dryness. The residue was dissolved in CH_2Cl_2 (40 mL) and the solution washed with water (10 × 300 mL). The organic fraction was dried over Na_2SO_4, filtered, and reduced to small volume. The dark red product was precipitated by addition of an equal volume of ice-cold methanol (yield 24%). The compound was identified by ^{1}H and ^{15}N NMR and infrared spectroscopy: $\nu(^{15}NO)$ 1770, 1740 cm^{-1}.

Bis(μ-propane-2-thiolato)bis[di(^{15}N)nitrosyliron], $Fe_2(S\text{-}i Pr)_2(^{15}NO)_4$, was prepared from $Fe_2(S\text{-}i Pr)_2(CO)_6$ and identified in similar fashion (yield 25%): $\nu(^{15}NO)$ 1712 cm^{-1}.

Sodium Hexa(^{13}C)cyanoferrate(II), $Na_4[Fe(^{13}CN)_6]$. $Na[^{13}CN]$ (4.0 g, 80 mmol) and sodium hydroxide (1.1 g, 28 mmol) were dissolved in water (15 mL). Ammonium ferrous sulfate hexahydrate (5.1 g, 13 mmol) was added in portions with continuous stirring. The resulting brown solution was boiled for 5 min and filtered hot. The filtrate was set aside in the dark, whereupon crystallization occurred. The product was filtered off, washed with a little cold water, and dried in air. Infrared: $\nu(^{13}CN)$ 2020, 2000, 1980 cm^{-1}; $\nu(^{12}CN)$ 2060, 2045, 2020 cm^{-1}.

The combined filtrate and washings were then treated successively with an excess of ferrous ammonium sulfate and ferric chloride to precipitate Prussian blue. This precipitate was filtered off, washed well with water, and then stirred for 1 h with a solution of 3 g of NaOH in 100 mL of water. The resulting mixture was filtered twice through Hyflosupercel to remove iron(III) oxide. The filtrate was then concentrated on the rotary evaporator and the concentrate allowed to crystallize, yielding further $Na_4[Fe(^{13}CN)_6]$, while the final filtrate was reserved for further recycling. By the use of this recycling process via Prussian blue, overall conversion of $Na[^{13}CN]$ to $Na_4[Fe(^{13}CN)_6]$ in excess of 90% was achieved.

Sodium Penta(^{13}C)cyanonitrosylferrate(2−) Dihydrate, $Na_2[Fe(^{13}CN)_5NO]\cdot 2H_2O$. A mixture of nitric acid (sp gr 1.42; 2.25 mL) and water (1.0 mL) was cooled in an ice/water bath. To the cold acid was added with stirring $Na_4[Fe(^{13}CN)_6]$ (2.50 g, 8.0 mmol); a further 1.55 g (5.0 mmol) was added in portions during 4 h. After being stirred for an additional period of 1 h at room temperature, the mixture was heated to 60 °C, and Na_2CO_3 (0.22 g, 2.1 mmol) was added in small portions during 30 min. The temperature was raised to 75 °C and a further 0.18 g (1.7 mmol) Na_2CO_3 added, again in portions. The mixture was stirred for another 1 h at 65 °C. After addition of water (3 mL) and methanol (10 mL), the solution was kept at 50 °C under N_2 for 2 days. The mixture was then filtered through Hyflosupercel, and the Hyflo was washed with methanol until the washings were colorless. The combined filtrate and washings were concentrated on the rotary evaporator until crystals just began to form, and the mixture was set aside in the dark to crystallize. The dark red crystals were filtered off, and the filtrate was further concentrated to yield a further crop, with overall yield of ~60%. The product was recrystallized from water until the infrared spectrum showed it to be free of nitrate.

Anal. Calcd for $C_5H_4FeN_6Na_2O_3$ (90% enriched in ^{13}C): C, 21.3; H, 1.3; N, 27.8. Found: C, 20.9; H, 1.3; N, 27.2. Infrared: $\nu(^{13}CN)$ 2122, 2110, 2105, 2093 cm^{-1}; $\nu(^{12}CN)$ 2171, 2155, 2143 cm^{-1}. (Cf. $Na_2[Fe(^{12}CN)_5NO]\cdot 2H_2O$: $\nu(^{12}CN)$ 2172, 2159, 2154, 2141 cm^{-1}.)

Table I. ^{15}N NMR Data for Iron–Chalcogen–Nitrosyl Cluster Compounds

compd	$\delta(^{15}N)^a$
$Fe_2(SMe)_2(NO)_4$ (C_{2h})	+30.5 (s)
$Fe_2(SMe)_2(NO)_4$ (C_{2v})	+23.1 (d) and +36.2 (d) (J = 2.8 Hz)
$Fe_2(SPr\text{-}i)_2(NO)_4$ (C_{2h})	+30.2 (s)
$Fe_2(SPr\text{-}i)_2(NO)_4$ (C_{2v})	+26.7 (d) and +35.7 (d) (J = 2.6 Hz)
$(PPN)^+[Fe_4S_3(NO)_7]^{-\,b}$	+7.7 (s), +36.0 (d, J = 4.3 Hz), +76.1 (d, J = 4.3 Hz)
$(PPN)^+[Fe_4Se_3(NO)_7]^{-\,b,c}$	+7.8 (s), +29.5 (d, J = 4.1 Hz), +74.9 (d, J = 4.1 Hz)
$Fe_4S_4(NO)_4$	+12.8 (s)
$Fe_4Se_4(NO)_4{}^c$	+20.5 (s)

[a] Chemical shifts from $CH_3{}^{15}NO_2$ as external reference; spectra recorded on samples enriched to 99% ^{15}N in CD_2Cl_2 solution at 298 K. All observed couplings are $^2J(^{15}NFe^{15}N)$. [b] Natural-abundance nitrogen in PPN$^+$ cation. [c] No coupling of ^{15}N to ^{77}Se was detected.

Sodium Penta(^{13}C)cyano(^{15}N)nitrosylferrate(2−), $Na_2[Fe(^{13}CN)_5(^{15}NO)]$. $Na_2[Fe(^{13}CN)_5(^{14}NO)]\cdot 2H_2O$ (50 mg, 0.17 mmol) was dissolved in D_2O (3 mL) under nitrogen in the absence of light. $Na[^{15}NO_2]$ (120 mg, 1.7 mmol) was added, and the ^{13}C and ^{15}N NMR spectra of the whole sample were recorded.

Results and Discussion

Roussin Esters $Fe_2(SR)_2(NO)_4$. The ^{15}N NMR spectra of both $Fe_2(SMe)_2(NO)_4$ and $Fe_2(S\text{-}i Pr)_2(NO)_4$ show the presence of an intense singlet and a pair of doublets (Table I): we assign the singlet to conformer **1** and the pair of doublets, an AX system, to conformer **2**. In conformer **1**, all the nitrosyl ligands are equivalent in C_{2h} symmetry; in conformer **2**, although the two irons are equivalent and the two R groups are equivalent, the two nitrosyl ligands in each $Fe(NO)_2$ fragment are nonequivalent, and the coupling $^2J(^{15}NFe^{15}N)$ between the ^{15}N nuclei yields the observed AX spectra: no long-range coupling $^4J(^{15}NFeSFe^{15}N)$ was detected. The integrated intensities are consistent, for both R = Me and R = *i*-Pr, with the presence of an equimolar mixture of the two forms, as deduced[2] earlier from the ^{1}H spectra. The chemical shifts lie in the region characteristic[12-14] of linear M–N–O groups, consistent with the structure[1] of $Fe_2(SEt)_2(NO)_4$ in the solid state.

The ^{15}N NMR spectra of the esters $Fe_2(SR)_2(NO)_4$ thus provide far more structural information than the ^{1}H spectra, which indicate simply the presence of two forms, in each of which the two R groups are equivalent. The establishment of the C_{2h} structure, especially in $Fe_2(SMe)_2(NO)_4$, is significant as we have observed[16] that both conformers of this ester are subject to aromatic-solvent-induced shifts (ASIS) of comparable magnitudes. One of the more recent theoretical treatments[17] of the ASIS phenomenon, based upon dipole–quadrupole interactions, requires that all solutes subject to ASIS have permanent electric dipole moments. In C_{2h} symmetry, there is no such dipole moment, so this model cannot be applicable, at least to the present system.

Attempts to record the ^{15}N NMR spectrum of the red Roussin anion $[Fe_2S_2(^{15}NO)_4]^{2-}$ as its PPN$^+$ salt have proven unsuccessful: all samples to date have been rapidly and cleanly converted into $[Fe_4S_3(^{15}NO)_7]^-$ (see below) as the only species detectable by ^{15}N NMR spectroscopy.

Tetrairon Complexes. The C_{3v} structure of the Roussin black anion $[Fe_4S_3(NO)_7]^-$ found[4,5] by X-ray analysis (**3**) has three distinct nitrosyl environments in the ratio 1:3:3. In addition to the unique apical nitrosyl ligand, there are two sets of nitrosyls on the basal irons that may be described as "axial" and "equatorial". The axial Fe–N–O fragments are approximately parallel to the symmetry axis, and all the Fe–N–O are essentially linear.[4,5] Consistent with this, the ^{15}N NMR spectrum (Table

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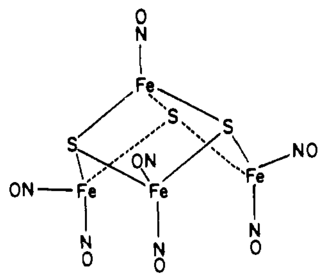

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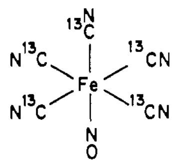
I) consists of a singlet and a pair of doublets. The relative intensities lead to the assignment of the singlet to the apical nitrosyl and the two doublets as an AX system exhibiting the coupling $^2J(^{15}NFe^{15}N)$: as in the spectra of the esters $Fe_2(SR)_2(NO)_4$, no long-range couplings were resolved.

The ^{15}N NMR spectrum of the selenium analogue of the black Roussin anion, $[Fe_4Se_3(NO)_7]^-$, is very similar (Table I) to that of $[Fe_4S_3(NO)_7]^-$: the structure of the selenium anion has been inferred[2] from the known[4,5] structure of $[Fe_4S_3(NO)_7]^-$, but the ^{15}N NMR spectrum provides proof of the structural similarity of these two ions. Likewise, the similarity of the ^{15}N NMR spectra of $Fe_4S_4(NO)_4$ and $Fe_4Se_4(NO)_4$, each prepared by reaction of $[Fe_4X_3(NO)_7]^-$ with elemental X, demonstrates their structural similarity in solution.

In neither $[Fe_4Se_3(NO)_7]^-$ nor $Fe_4Se_4(NO)_4$ were any satellites observed in the ^{15}N spectrum due to coupling of ^{15}N to ^{77}Se. The ^{77}Se spectrum of $[Fe_4Se_3(NO)_7]^-$ consisted of a single, rather broad absorption having $\delta(^{77}Se) = +1468.0$ relative to external Me_2Se, with $\nu_{1/2} = 26$ Hz. No coupling was detected, nor was more than one chemical shift resolvable, consistent with the C_{3v} symmetry of $[Fe_4Se_3(NO)_7]^-$.

The Nitroprusside Ion and Its Derivatives. These have been shown by X-ray analysis to have C_{4v} symmetry[18] in which there are four equivalent equatorial cyanide ligands and a unique axial cyanide. When nitroprusside is prepared from 90% enriched $Na[^{13}CN]$, it follows, assuming the ^{12}C and ^{13}C isotopes are distributed statistically between the two sites, that 59.0% of the ions are $[Fe(^{13}CN)_5NO]^{2-}$ (**4**), 26.2% are $[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3NO]^{2-}$ (**5**), and 6.6% are $[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4NO]^{2-}$ (**6**): no other isotopic species represents more than 2.9% of the ions, and the NMR spectra can be interpreted simply in terms of the three predominant species **4**–**6** (cf. Table II). In **4** there are two ^{13}C environments, in **5** there are three (although no discrimination between the two equatorial ^{13}CN sites is observed), and in **6** there is a single ^{13}C environment. Species **6** is observed in the ^{13}C NMR spectrum solely because its ^{13}C nuclei all have identical environments. The spectral interpretation was eased by a comparison of the spectra of $[Fe(^*CN)_5(^{14}NO)]^{2-}$ and $[Fe(^*CN)_5(^{15}NO)]^{2-}$. The nitroprusside ion is found to undergo ready nitrogen exchange with labeled nitrite: the predominant mode of reaction of the nitrosyl group is nucleophilic attack at nitrogen, and a W-intermediate (**7**) seems the most plausible. With a sufficient excess of $[^{15}NO_2]^-$, all the nitroprusside is converted to the ^{15}NO form.



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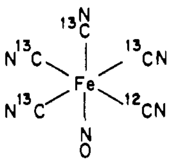

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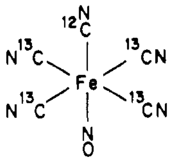

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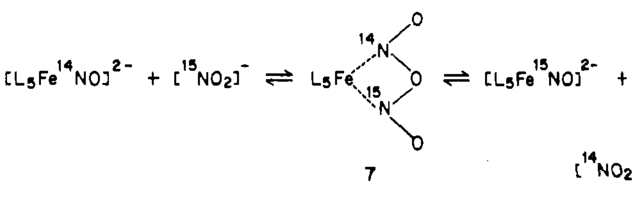

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Table II. ^{13}C and ^{15}N NMR Data[a] for Three Isotopic Forms of $[Fe(CN)_5NO]^{2-}$

	$[Fe(^{13}CN)_5(^{15}NO)]^{2-}$ (**4**)		
$\delta(^{13}C_{ax})$	+132.4 (p × d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	17.7
$\delta(^{13}C_{eq})$	+134.4 (d × d)	$^2J(^{13}C_{ax}Fe^{15}N)$	13.1
$\delta(^{15}N)$	−9.9 (d × p)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.6
	$[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3(^{15}NO)]^{2-}$ (**5**)		
$\delta(^{13}C_{ax})$	+132.4 (q × d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	17.6
$\delta(^{13}C_{eq})$	*b*	$^2J(^{13}C_{ax}Fe^{15}N)$	13.1
$\delta(^{15}N)$	−9.9 (d × q)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.5
	$[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4(^{15}NO)]^{2-}$ (**6**)		
$\delta(^{13}C_{eq})$	+134.4 (d)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.6
$\delta(^{15}N)$	*b*		

[a] Chemical shifts (measured in aqueous solutions) from external $Me_4Si(^{13}C)$ or $CH_3{}^{15}NO_2(^{15}N)$; coupling constants in Hz, ±0.2 Hz: d = doublet, q = quartet, p = quintet. [b] Not observed; see text.

The ^{13}C and ^{15}N NMR spectra, measured at 90.6 and 36.5 MHz, respectively, are both first order and can readily be analyzed to yield the parameters given in Table II.

In the equatorial ^{13}CN region, at +134.4 ppm, **4** yields a double doublet due to coupling both to $^{13}CN_{ax}$ and ^{15}NO, whereas **6** exhibits only the doublet coupling to ^{15}NO. The equatorial region of the spectrum of **5** is expected to be virtually identical with the equatorial region of **4**: no absorption due to **5** was observed in this region, and we assume that it is overlaid by that of the more abundant form **4**. In the axial ^{13}CN region at +132.2 ppm, **6** is necessarily absent: the axial region of **4** is a quintet of doublets and that of **5** is a quartet of doublets. Thus, the equatorial region appears as a combination of the spectra of **4** and **6** and the axial region as a combination of the spectra of **4** and **5**: with the exception of δ ($^{13}C_{eq}$) in **5**, all the lines of each multiplet are clearly resolved. In the ^{13}C spectrum of $[Fe(CN)_5(^{14}NO)]^{2-}$, likewise enriched to 90% in ^{13}C, the spectral parameters are identical except that no coupling to nitrogen is observed: this spectrum serves as a check on the overall spectral assignment. Comparison of the two spectra shows that no residual ^{14}N species can be detected after exchange with $[^{15}NO_2]^-$.

The ^{15}N spectra of **4** and **5** consist of a doublet of quintets and a doublet of quartets, respectively: the ^{15}N spectrum of **6**, expected to be a single quintet having $J = 3.6$ Hz, was not detected, probably because of the low abundance of **6**. The ^{15}N chemical shifts measured for **4** and **5** are identical, -9.9 ppm, and may be compared with a value of −13.5 ppm measured[12] on nitroprusside of natural isotopic composition in all elements. We emphasize that the extent of $^{14}NO/[^{15}NO_2]^-$ exchange can only be determined accurately from the ^{13}C spectrum and not from the ^{15}N spectrum.

The reaction of $[Fe(CN)_5(^{14}NO)]^{2-}$ with $[^{15}NO_2]^-$ yields not only $[Fe(CN)_5(^{15}NO)]^{2-}$ but also a small quantity of $[Fe(CN)_5(^{15}NO_2]^{4-}$. The ^{13}C and ^{15}N spectra of this anion can be interpreted in terms of the three isotopic forms **8**–**10** whose ^{13}C distributions are identical with those of **4**–**6**, respectively. The spectra of **8**–**10** are first order and can readily be analyzed as before to yield the spectral parameters given in Table III: in the ^{15}N spectrum only the resonances due to **8** could be clearly resolved.

Comparison of the chemical shifts in $[Fe(CN)_5NO]^{2-}$ and $[Fe(CN)_5(NO_2)]^{4-}$ shows that the equatorial carbon resonance is slightly to low field of the axial carbon in both but that in the tetranegative anion the carbon shifts are both some 40 ppm to low field of those in $[Fe(CN)_5NO]^{2-}$. Similarly, the ^{15}N resonance in $[Fe(CN)_5(NO_2)]^{4-}$ is shifted some 185 ppm downfield from that in $[Fe(CN)_5NO]^{2-}$. We note that the ^{15}N resonance of the nitrito-*N* ligand in a series of rhodium(I) complexes occurs[13] at ca. 45 ppm from $CH_3{}^{15}NO_2$, considerably shifted from the nitro resonance observed here.

Addition of aqueous sodium hydroxide to the solution containing $[Fe(CN)_5NO]^{2-}$ and $[^{15}NO_2]^-$ caused the ^{13}C spectrum of [Fe-

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Table III. ^{13}C and ^{15}N NMR Data[a] for Three Isotopic Forms of $[Fe(CN)_5NO_2]^{4-}$

	$[Fe(^{13}CN)_5(^{15}NO_2)]^{4-}$ (**8**)		
$\delta(^{13}C_{ax})$	+174.0 (p × d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	9.1
$\delta(^{13}C_{eq})$	+176.7 (d × d)	$^2J(^{13}C_{ax}Fe^{15}N)$	5.4
$\delta(^{15}N)$	+174.4 (d × p)	$^2J(^{13}C_{eq}Fe^{15}N)$	1.9
	$[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3(^{15}NO_2)]^{4-}$ (**9**)		
$\delta(^{13}C_{ax})$	+174.2 (q × d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	9.1
$\delta(^{13}C_{eq})$	*b*	$^2J(^{13}C_{ax}Fe^{15}N)$	5.4
$\delta(^{15}N)$	*b*	$^2J(^{13}C_{eq}Fe^{15}N)$	*b*
	$[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4(^{15}NO_2)]^{4-}$ (**10**)		
$\delta(^{13}C_{eq})$	+176.7 (d)	$^2J(^{13}C_{eq}Fe^{15}N)$	1.9
$\delta(^{15}N)$	*b*		

[a] See footnote *a*, Table II. [b] Not observed; see text.

$(CN)_5(^{15}NO_2)]^{4-}$ to grow in intensity at the expense of the spectrum of $[Fe(CN)_5(^{15}NO)]^{2-}$. It has previously been demonstrated[19,20] that the nitroprusside ion reacts with hydroxide to yield $[Fe(CN)_5NO_2]^{4-}$. Hence, we have detected, by the combined use of ^{13}C and ^{15}N NMR spectroscopy, two routes for the conversion of $[Fe(CN)_5(NO)]^{2-}$ into $[Fe(CN)_5(NO_2)]^{4-}$, both by addition of hydroxide and by direct exchange with nitrite via **7**. The essential difference between these routes is that addition of hydroxide causes no exchange of the nitrogen bound to iron, whereas attack by nitrite via **7** can cause isotopic exchange of nitrogen. An attempt to observe the reverse of the hydroxide reaction, by addition of acid, was inconclusive, as any change was accompanied by extensive decomposition. When aqueous sodium hydroxide was added to $[Fe(CN)_5(^{14}NO)]^{2-}$ in the absence of added nitrite, the ^{13}C spectrum of nitroprusside was very rapidly replaced by that of $[Fe(CN)_5(^{14}NO_2)]^{4-}$ accompanied by the weak spectrum of a second pentacyanoiron(II) complex characterized by δ ($^{13}C_{ax}$) 177.2, δ ($^{13}C_{eq}$) 172.8, and $^2J(^{13}C_{ax}Fe^{13}C_{eq})$ = 9 Hz. This second species was not identified, but it may have been $[Fe(CN)_5(H_2O)]^{3-}$.

In all samples of $[Fe(CN)_5NO]^{2-}$, no matter how carefully handled, we detected the slow emergence of a minor resonance, a singlet at +177.9 ppm. This may have been due to the primary photoproduct[21,22] $[Fe(CN)_5H_2O]^{2-}$, in which the kinetic lability of the aqua ligand in the d^5 complex allows scrambling, possibly via a pseudorotation process, of the axial and equatorial ligands in the intermediate $[Fe(CN)_5]^{2-}$. Alternatively this singlet could be due to $[Fe(CN)_6]^{4-}$, whose reported[23] chemical shift is +177.2 ppm, since free cyanide, as from the photoproduct $[Fe(CN)_5H_2O]^{2-}$, is known[24] to react with nitroprusside, yielding $[Fe(CN)_6]^{4-}$.

These spectroscopic observations on nitroprusside and certain of its derivatives show that, by use of double labeling with ^{13}C and ^{15}N, it is possible to obtain a ready distinction between the several species in solution, on the basis of their characteristic chemical shifts and coupling constants. This will prove of value for the identification, in solution, of the inorganic products resulting from the reactions of the nitroprusside ion with nucleophiles[25,26] and in studies of the physiological action of nitroprusside.[27]

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Registry No. $Fe_4S_3(NO)_7^-$, 97210-39-4; $Fe_4Se_3(NO)_7^-$, 97210-40-7; $Fe_2(SMe)_2(NO)_4$, 79408-10-9; $Fe_2(S\text{-}i\text{-}Pr)_2(NO)_4$, 96613-18-2; $Fe(CN)_5(NO)^{2-}$, 15078-28-1; $Fe(CN)_5(NO_2)^{4-}$, 15003-01-7; $Fe_4S_4(NO)_4$, 53276-80-5; $Fe_4Se_4(NO)_4$, 81366-92-9; $Fe_2(SMe)_2(^{15}NO)_4$, 97234-18-9; $Fe_2(S\text{-}i\text{-}Pr)_2(^{15}NO)_4$, 97234-19-0; $Na_4[Fe(^{13}CN)_6]$, 97210-41-8; $Na_2[Fe(^{13}CN)_5NO]$, 94792-79-7; $Na_2[Fe(^{13}CN)_5(^{15}NO)]$, 97210-42-9.

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Photochemistry of Metal–Metal-Bonded Complexes. 1. MLCT Photolysis of $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M′ = Mn, Re) in 2-MeTHF between 133 and 230 K

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The photolysis in 2-MeTHF is reported for several complexes $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M′ = Mn, Re) at temperatures varying from 133 to 230 K. Above 200 K homolysis of the metal–metal bond occurs for the complexes with M = Mn and M′ = Mn, Re. At temperatures below 200 K the main reaction products are $[M(CO)_5]^-$ and $[M'(CO)_3(\alpha\text{-diimine})(2\text{-MeTHF})]^+$ if M = Mn, Re and M′ = Mn. Although these 2-MeTHF-coordinated cations reacted back with $[M(CO)_5]^-$ to the parent compound upon raising the temperature, several $P(n\text{-}Bu)_3$-substituted complexes $[M(CO)_5]^-[M'(CO)_3(\alpha\text{-diimine})(P(n\text{-}Bu)_3)]^+$ could be isolated. It appeared that the ions were not formed by direct heterolysis of the metal–metal bond but instead by thermal disproportionation of a photosubstituted product $(CO)_5MM'(CO)_2(\alpha\text{-diimine})(2\text{-Me-THF})$. Several $P(n\text{-}Bu)_3$-substituted complexes $(CO)_5MM'(CO)_2(\alpha\text{-diimine})(P(n\text{-}Bu)_3)$ could be identified for M = Re, M′ = Mn. Contrary to the complexes with M = Mn, Re and M′ = Mn, the corresponding $(CO)_5MnRe(CO)_3(\alpha\text{-diimine})$ ones did not show photosubstitution of CO but instead breaking of a metal–nitrogen bond upon photolysis at 133 K. It is proposed that this bond breaking is the primary photoprocess at lower temperatures and that it is followed by release of CO in the case of M′ = Mn. An energy vs. distortion diagram is presented according to which the homolytic splitting of the metal–metal bond and the breaking of the metal–nitrogen bond occur from two different close-lying excited states, $^3\sigma_b\pi^*$ and $^3d_\pi\pi^*$, respectively.

Introduction

In this paper we report the photolysis in 2-MeTHF between 133 and 230 K of the metal–metal-bonded complexes $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ [M, M′ = Mn,Re except M = M′ = Re; α-diimine = 1,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (bpy′), pyridine-2-carbaldehyde *p*-tolylimine (*p*-Tol-PyCa) or 1,4-diaza-1,3-butadiene (R-DAB, RN=CH—CH=NR).[1] The complexes, having the structure shown in Figure