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A multinuclear (^{1}H, ^{13}C, ^{15}N) NMR study of *cis*-halonitrosylbis(dithiocarbamato)iron(II) complexes: effect of replacement of S by Se

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Abstract

The ^{1}H and proton-decoupled ^{13}C NMR spectra of several *cis*-Fe(NO)(E_2CNR_2)$_2$X complexes (where R is an organic substituent, E = S and/or Se, and X = Cl$^-$, Br$^-$ or I$^-$) have been measured at room temperature in $CDCl_3$, as well as the ^{15}N NMR spectrum (natural abundance) of *cis*-Fe(NO)($S_2CN(C_2H_5)_2$)$_2$I. The two *C*E$_2$ signals observed between 190 and 206 ppm in the {^{1}H}^{13}C NMR spectra of these *cis*-Fe(NO)(E_2CNR_2)$_2$X complexes provide an indication of the structural rigidity of these compounds in solution. The multiple ^{13}C NMR peaks observed for the four $E_2CN(\mathit{C}H_2R)_2$ α-carbons further support this rigidity. The ^{13}C NMR signal of the α-C atoms of the ligand is dependent on the proximate chalcogen, the second chalcogen of the ligand and the ligand atoms to which each of these is *trans*. The ^{13}C NMR spectra of the *cis*-Fe(NO)(E_2CNR_2)$_2$X complexes are comparable to the spectra of the structurally similar *cis*-Fe(S_2CNRR')$_2$(CO)$_2$ complexes and give insight into the interpretation of the ^{13}C NMR spectra of the Co(SSeCNR$_2$)$_3$ series. The {^{1}H}^{13}C NMR spectrum of *cis*-Fe(SSeCN(C_2H_5)$_2$)$_2$(CO)$_2$ is included for comparison. The ^{1}H NMR spectra are complex; the diethyl derivative exhibits a complex multiplet which is interpreted as four overlapping ABX_3 systems for the $NC\mathit{H}_2(C\mathit{H}_3)$ protons. The ^{15}N NMR spectrum of *cis*-Fe(NO)($S_2CN(C_2H_5)_2$)$_2$I exhibits three peaks: 210.92, 209.09 and 29.28 ppm. This is interpreted as each dithiocarbamate ligand experiencing a different magnetic environment and the NO ligand. The ^{15}N NMR spectrum is compared to tetraethylthiuram disulfide, Co($S_2CN(C_2H_5)_2$)$_3$ and *cis*-Fe($S_2CN(C_2H_5)_2$)$_2$(CO)$_2$ and is interpreted as indicating similar S_2C-NRR$'$ rotational barriers.

Keywords: Iron; Dithiocarbamate; Diselenocarbamate; Thioselenocarbamate; Nitrosyl; ^{13}C NMR; ^{15}N NMR

1. Introduction

Iron complexes of the dithio- (dtc), thioseleno- (tsc) and diselenocarbamate (dsc) ligands have a rich tradition in the literature. These studies cover a range of topics from the physical properties of iron dithiocarbamates and the spin-crossover magnetic behavior of Fe(dtc)$_3$ complexes [1–3], to the more recent bioanalytical application of iron dithiocarbamates as radical traps for NO [4–9]. Our research into iron dithiocarbamate complexes, and their related chalcogenide derivatives, has employed a range of physical techniques to explore the properties of varying series of iron complexes of the general formulae Fe(L)$_3$ [10–16], Fe(L)$_2$NO [17–20] and Fe(L)$_2$(CO)$_2$ [16,21], among others. Recently we have been probing the solution properties of iron and other transition metal systems with dithio-, thioseleno- and diselenocarbamate ligands by multinuclear NMR spectroscopy [22,23]. As part of these ongoing studies, we now report results for a series of *cis*-Fe(NO)(E_2CNR_2)$_2$X complexes, where R is an organic substituent, E = S and/or Se, and X = Cl$^-$, Br$^-$ or I$^-$.

In 1988 Duffy and Appleton [22] reported proton-decoupled ^{13}C and ^{15}N NMR data from a series of

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cis-$Fe(S_2CNRR')_2(CO)_2$ complexes (where R and R′ are organic substituents) in $CDCl_3$. Their study indicated the utilization of $\{^1H\}^{13}C$ NMR in detecting evidence for hindered rotation about the C–N bond in the dithiocarbamate ligand. Correlation between the ^{13}CO, ν_{CO} and the pK_a of the ligand's parent amine were noted. They also reported the first ^{15}N (natural abundance) NMR spectra for Fe dithiocarbamates. These ^{15}N chemical shifts were also consistent with partial C–N double bond character. No correlation between ^{15}N chemical shifts and ^{13}CO chemical shifts, CO force constants or the pK_a values of the ligand's parent amine was detected.

In 1991, Dietzsch et al. [23] reported the multinuclear (^1H, $\{^1H\}^{13}C$, ^{59}Co, ^{77}Se) NMR spectra of a series of Co(III) and In(III) tris thioseleno- and diselenocarbamates in $CDCl_3$. For the $In(SSeCNR_2)_3$ complexes, evidence was presented for hindered rotation about the C–N bond. For the corresponding $Co(SSeCNR_2)_3$ compounds, evidence was presented for both hindered rotation about the C–N bond and the existence of *fac* and *mer* isomers of the complex in solution. In a rare NMR study of hindered C–N bond rotation preceding the Dietzsch et al. study, temperature-dependent, ^1H NMR studies of diamagnetic $Co(S_2CNRR')_3$ complexes in $CDCl_3$ had revealed barriers to rotation of approximately 60–85 kJ/mol [24].

The limited, prior studies to our multinuclear NMR studies had been focused primarily on organometallic dithiocarbamates with second, third or late first row transition elements [25,26]. Few studies of ^{13}C NMR spectra with Fe or Co dithiocarbamates were reported [27]. One key observation from those collected data is that E_2CNRR signals typically are observed in the range of 185–220 ppm [25].

In continuing our multinuclear NMR studies, the *cis*-$Fe(NO)(S_2CNR_2)_2I$ series provided an attractive system which was a variation of *cis*-$Fe(S_2CNRR')_2(CO)_2$. Büttner and Feltham [28] had reported the first, neutral *cis*-$Fe(NO)(S_2CN(CH_3)_2)_2X$ complexes (where $X = I^-$, Br^-, or Cl^-) in 1972. Later in 1977, Ileperuma and Feltham [29] described *cis* and *trans* derivatives of the general formula $Fe(NO)(S_2CN(CH_3)_2)_2X$. Complexes of *cis*-$Fe(NO)(S_2CN(CH_3)_2)_2X$ were prepared with $X = I^-$, Br^-, NO_2^-, or CH_3NC, along with a low temperature stable *trans* isomer of the NO_2^- derivative. Other, stable *trans* isomers were prepared with $X = CH_3CN$, pyridine, or SCN^-. For the iodo derivative, they reported a ν_{NO} (1815 cm^{-1}, KBr; 1848 cm^{-1}, $CHCl_3$), a ^1H NMR spectrum ($\tau = 6.63$, 6.70, 6.80 and 6.87 (1:1:1:1)), and a rate of NO exchange.

In 1979, Fitzsimmons and Hume [30] reported the preparation of nine *cis*-$Fe(NO)(S_2CNRR')_2I$ complexes (where R and R′ are organic substituents) along with *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2Br$. They reported the Mössbauer parameters (77 K), ν_{NO} (Nujol) and solid magnetic moments (0.44–1.12 μ_B, which were explained on the basis of some temperature-independent paramagnetism and some possible small amounts of impurities). The Mössbauer data were consistent with a *cis* geometric arrangement of the NO^+ and I^- in the first coordination sphere.

We now report herein the ^1H and $\{^1H\}^{13}C$ NMR spectra of several derivatives of the *cis*-$Fe(NO)(S_2CNR_2)_2I$ series as a variation on *cis*-$Fe(S_2CNRR')_2(CO)_2$ in which the two CO ligands have been replaced by NO^+ and a halide. We have expanded the *cis*-$Fe(NO)(S_2CNR_2)_2I$ series to include other *cis*-$Fe(NO)(E_2CNR_2)_2X$ complexes (where R is an organic substituent, E = S and/or Se and $X = Cl^-$, Br^- or I^-) by changing the halide, or by replacing the dithiocarbamate with a thioseleno- or diselenocarbamate analogue. In addition, these complexes provide insight into the interpretation of the NMR data of the $Co(SSeCNR_2)_3$ complexes reported in Dietzsch et al. Natural abundance ^{15}N NMR spectra are reported for a representative compound.

2. Experimental

2.1. Syntheses

2.1.1. General

The dithio-, thioseleno- and diselenocarbamate ligands (dtc, tsc and dsc) were prepared by standard procedures. The dithiocarbamates were synthesized by CS_2 addition to the deprotonated parent amine to form NaS_2CNR_2 products [21]. The tsc and dsc ligands were synthesized in *n*-heptane, by dropwise addition of a CE_2 solution ($CE_2 = CSSe$ or CSe_2) to a solution of the parent amine in a 1:2 ratio [16,17]. The $Fe(dtc)_3$ complexes were prepared similar to the method of White et al. [31], while the $Fe(tsc)_3$ and $Fe(dsc)_3$ complexes were prepared by the method of Dietzsch et al. [16] as modified from earlier syntheses [32]. $Fe(SSeCN(C_2H_5)_2)_2(CO)_2$ has been reported previously [16]. Nitrogen and argon gases were 99+% purified from cylinders provided by local distributors. NO(g) was purchased in cylinders from local distributors. Tetraethylthiuram disulfide (Matheson, Coleman and Bell, Norwood, OH) was used as received. The complex $Co(S_2CN(C_2H_5)_2)_3$ was prepared by a published method, recrystallized from dichloromethane/hexane and gave a satisfactory elemental analysis [33].

2.1.2. Synthesis of coordination complexes

$Fe(S_2CNR_2)_2I$. The $Fe(S_2CNR_2)_2I$ complexes that are precursors for the $Fe(NO)(S_2CNR_2)_2I$ compounds were all prepared by previously reported synthetic methods [34,35]. The synthesis of $Fe(S_2CN(CH_2CH_3)_2)_2I$ is illustrative. A saturated solution of $Fe(S_2CN(C_2H_5)_2)_3$ in 200 ml of benzene was prepared from 2.00 g of

$Fe(S_2CN(C_2H_5)_2)_3$. After filtering off residual, solid $Fe(S_2CN(C_2H_5)_2)_3$ from the $Fe(S_2CN(C_2H_5)_2)_3$/benzene solution, 2 ml of 57% HI(aq) were added dropwise to the vigorously stirring $Fe(S_2CN(C_2H_5)_2)_3$/benzene solution. Solid $Fe(S_2CN(C_2H_5)_2)I$ precipitated from the resulting green-black solution. After 90–120 s had elapsed, the precipitated product was collected on a sintered glass funnel. The product was rinsed twice with 15 ml portions of benzene. This product was sufficient for the next step of the $Fe(NO)(S_2CN(C_2H_5)_2)_2I$ synthesis without further purification.

$Fe(S_2CNR_2)_2Br$. The $Fe(S_2CNR_2)_2Br$ complexes were synthesized by the same method as $Fe(S_2CN(CH_2CH_3)_2I$. 48% HBr(aq) was substituted for 57% HI(aq). These $Fe(S_2CNR_2)_2Br$ products were used without further purification.

$Fe(Se_2CN(C_2H_5)_2)_2X$. The $Fe(Se_2CN(C_2H_5)_2)_2X$ (where $X = Cl^-$, Br^-, or I^-) compounds have been reported previously [36–38]. The synthesis of $Fe(Se_2CN(C_2H_5)_2)_2I$ is illustrative. A concentrated, filtered solution of $Fe(Se_2CN(C_2H_5)_2)_3$ (0.001 mol, 810 mg) was prepared in 80–100 ml benzene. The resulting benzene solution was shaken in a separatory funnel with 2 ml of 57% HI(aq) for 60–120 s. The precipitated $Fe(Se_2CN(C_2H_5)_2)_2I$ product was quickly collected on a sintered glass funnel and rinsed with 20–30 ml of distilled H_2O, and was then rinsed by the same volume of MeOH. The solid product was then dried in vacuo in a dessicator. The $Fe(Se_2CNR_2)_2Br$ and $Fe(Se_2CNR_2)_2Cl$ derivatives were prepared by the same method by substituting 48% HBr(aq) or conc. HCl for 57% HI(aq), respectively. The $Fe(Se_2CN(C_2H_5)_2)_2X$ complexes were sufficient for use in the succeeding synthetic process without further purification.

$Fe(SSeCN(C_2H_5)_2)_2Br$. $Fe(SSeCN(C_2H_5)_2)_2Br$ was synthesized by the procedure of Dietzsch et al. [16] which is analogous to that described for $Fe(Se_2CNR_2)_2X$. $Fe(SSeCN(C_2H_5)_2)_2Br$ was of sufficient purity to be used without further purification.

$Fe(NO)(S_2CN(C_2H_5)_2)_2I$. The synthesis of $Fe(NO)(S_2CN(C_2H_5)_2)_2I$ typifies the preparation of all $Fe(NO)(S_2CNR_2)_2X$ complexes. The iodo intermediate (1.5 g), $Fe(S_2CNR_2)_2I$, was dissolved in 175 ml $CHCl_3$, which was then purged for 20 min with N_2(g). Nitric oxide gas was then bubbled into the $Fe(S_2CNR_2)_2I/CHCl_3$ solution at a steady, but slow, rate, over 5 min [18,39]. After NO(g) cessation, the reaction mixture was again purged with N_2(g) for 15 min. The resulting brown solid was isolated and recrystallized from absolute ethanol as per Fitzsimmons and Hume [30]. Yield: 0.3 g (19%) of $Fe(NO)(S_2CN(C_2H_5)_2)_2I$. Elemental analysis: Calc. for $C_{10}H_{20}FeIN_3OS_4$: C, 23.56; H, 3.92; N, 8.25. Found: C, 23.63; H, 4.05; N, 8.02%.

$Fe(NO)(S_2CN(C_2H_5)_2)_2Br$. $Fe(NO)(S_2CN(C_2H_5)_2)_2Br$ was prepared from 160 mg $Fe(S_2CN(C_2H_5)_2)_2Br$ in the manner described for $Fe(NO)(S_2CN(C_2H_5)_2)_2I$. Unlike $Fe(NO)(S_2CN(C_2H_5)_2)_2I$, $Fe(NO)(S_2CN(C_2H_5)_2)_2Br$ did not precipitate. The solvent was removed by vacuum, and the oily, brown residue was redissolved in 25 ml of CH_2Cl_2 to which an equal volume of *n*-heptane was then added. The solvent volume was reduced to half in vacuo, and the solid, dark brown product precipitated. The remaining solvent was decanted and the solid isolated and dried under vacuum. Yield: 50 mg (29%). Elemental analysis: Calc. for $Fe(NO)(S_2CN(C_2H_5)_2)_2Br \cdot 0.5\ CH_2Cl_2$, $C_{10.5}H_{21}FeClBrN_3OS_4$: C, 24.93; H, 4.19; N, 8.31. Found: C, 24.83; H, 4.36; N, 8.20%.

$Fe(NO)(S_2CN(CH_3)_2)_2I$. $Fe(NO)(S_2CN(CH_3)_2)_2I$ was prepared as per $Fe(NO)(S_2CN(C_2H_5)_2)_2I$ starting from $Fe(S_2CN(CH_3)_2)_2I$. This material was recrystallized by dissolving it in 20 ml of dichloromethane, followed by the addition of an equal volume of MeOH. The solvent volume was then reduced under vacuum to yield a brown solid. Yield: 0.09 g. Elemental analysis: Calc. for $C_6H_{12}FeIN_3OS_4$: C, 15.90; H, 2.67; N, 9.27. Found: C, 15.98; H, 2.73; N, 8.76%.

$Fe(NO)(S_2CN(CH_2)_5)_2I$. $Fe(NO)(S_2CN(CH_2)_5)_2I$ was prepared as per $Fe(NO)(S_2CN(C_2H_5)_2)_2I$ starting from $Fe(S_2CN(CH_2)_5)_2I$. Isolation was modified by redissolving the brown solid product in dichloromethane (approx. 20 ml) to which an equal volume of absolute ethanol was then added. The solution was evaporated in vacuo to one-half volume, and the precipitated product was collected on a sintered glass funnel. 0.08 g were recovered. Elemental analysis: Calc. for $Fe(NO)(S_2CN(CH_2)_5)_2I \cdot 0.33\ CH_2Cl_2$, $C_{12.33}H_{20.67}FeCl_{0.67}IN_3OS_4$: C, 26.37; H, 3.71; N, 7.48. Found: C, 26.32; H, 3.75; N, 7.27%.

$Fe(NO)(S_2CN(CH_2)_4)_2I$. $Fe(NO)(S_2CN(CH_2)_4)_2I$ was prepared as per $Fe(NO)(S_2CN(CH_2)_5)_2I$ starting from $Fe(S_2CN(CH_2)_4)_2I$. 0.2 g were recovered. Elemental analysis: Calc. for $Fe(NO)(S_2CN(CH_2)_4)_2I \cdot 1.25\ CHCl_3$, $C_{11.25}H_{17.25}Cl_{3.75}FeIN_3OS_4$: C, 20.68; H, 2.64; N, 6.43. Found: C, 20.61; H, 2.94; N, 6.42%.

$Fe(NO)(S_2CN(CH_2)_4O)_2I$. $Fe(NO)(S_2CN(CH_2)_4O)_2I$ was prepared as per $Fe(NO)(S_2CN(C_2H_5)_2)_2I$ from $Fe(S_2CN(CH_2)_4O)_2I$. 0.1 g were recovered. Elemental analysis: Calc. for $C_{10}H_{16}FeIN_3O_3S_4$: C, 22.35; H, 3.01; N, 7.82. Found: C, 22.52; H, 3.13; N, 7.21%.

$Fe(NO)(Se_2CN(C_2H_5)_2)_2I$. $Fe(NO)(Se_2CN(C_2H_5)_2)_2I$ was prepared from 200 mg (0.3 mmol) of $Fe(Se_2CN(C_2H_5)_2)_2I$ dissolved in 150 ml of Ar purged $CHCl_3$ to yield a deep violet colored solution. The $CHCl_3$ solution was then cooled to between 0 and −11 °C and purged with Ar for an additional 20 min. Following this, nitric oxide gas was bubbled through the solution at a slow but consistent flow for 3–4 min; the solution turned brown. After NO(g) cessation, the solution was again purged with Ar for 15 min. The temperature of the mixture was allowed to increase to room temperature and the solvent was removed under vacuum. The resultant brown

solid dissolved easily in 20 ml of dichloromethane, to which 20 ml of *n*-heptane was then added. The solution was reduced in volume to 20 ml or less under vacuum to induce precipitation. The supernatant liquid was then decanted. The resulting solid was dried in vacuo. This product was less stable than the dithiocarbamate derivative and was stored under vacuum. Yield: 200 mg (77%). Elemental analysis for $Fe(NO)(Se_2CN(C_2H_5)_2)_2I$: Calc. for $C_{10}H_{20}FeIN_3OSe_4$: C, 17.23; H, 2.90; N, 6.03. Found: C, 17.55; H, 2.70; N, 6.51%.

$Fe(NO)(Se_2CN(C_2H_5)_2)_2Cl$. $Fe(NO)(Se_2CN(C_2H_5)_2)_2Cl$ was prepared as per $Fe(NO)(Se_2CN(C_2H_5)_2)_2I$ starting from 380 mg of $Fe(Se_2CN(C_2H_5)_2)_2Cl$. Yield: 280 mg (70%). Elemental analysis: Calc. for $C_{10}H_{20}ClFeN_3OSe_4$: C, 19.84; H, 3.34; N, 6.94. Found: C, 20.08; H, 3.38; N, 6.66%.

$Fe(NO)(Se_2CN(C_2H_5)_2)_2Br$. $Fe(NO)(Se_2CN(C_2H_5)_2)_2Br$ was prepared as per $Fe(NO)(Se_2CN(C_2H_5)_2)_2I$ starting from 500 mg of $Fe(Se_2CN(C_2H_5)_2)_2Br$. Yield: 150 mg (29%). Elemental analysis: Calc. for $Fe(NO)(Se_2CN(C_2H_5)_2)_2Br \cdot 0.07$ n-C_7H_{14}, $C_{10.5}H_{21}BrFeN_3OSe_4$: C, 19.48; H, 3.11; N, 6.47. Found: C, 19.37; H, 3.26; N, 5.93%.

$Fe(NO)(SSeCN(C_2H_5)_2)_2Br$. $Fe(NO)(SSeCN(C_2H_5)_2)_2Br$ was prepared in a manner analogous to $Fe(NO)(Se_2CN(C_2H_5)_2)_2I$, starting from 290 mg of $Fe(SSeCN(C_2H_5)_2)_2Br$. The material was "gummy" but adequate for NMR, IR and elemental analysis. Elemental analysis: Calc. for $Fe(NO)(SSeCN(C_2H_5)_2)_2Br \cdot 0.2$ n-C_7H_{14}, $C_{11.5}H_{23}BrFeN_3OS_2Se_2$: C, 23.93; H, 4.04; N, 7.28. Found: C, 24.14; H, 4.09; N, 7.75%.

2.2. Methods

Proton-decoupled ^{13}C NMR spectra were measured on a GE 300 MHz FT-NMR or Brucker MSL 300 spectrometer. Typically, for ^{13}C, solutions were 72 mM in $CDCl_3$ with TMS added. Spectra were routinely run with a pulse width of 13.5 μs with a 5-s delay time. Usually 8000 scans were required, particularly to measure the carbon atom attached to the chalcogeno donor atoms.

For ^{15}N NMR spectra, the GE 300 MHz instrument was utilized and solutions were 120 mM in $CDCl_3$, with 0.10 M $Cr(acac)_3$ added as a relaxation agent in 10-mm tubes. Spectra were routinely run at a pulse width of 40 or 45 μs with a 500-ms delay time. These natural abundance spectra required 32,000 scans to attain an adequate signal. All spectra reported are referenced to an external sample of pure $CH_3{}^{15}NO_2$, which was run routinely before and after each of the samples. The maximum variation in reference calibration noted after a determination was 0.08 ppm.

The infrared spectra were obtained with a Nicolet 740 FT-IR spectrophotometer. NO stretching frequencies were determined for either chloroform solutions (3 mM) or KBr pellets and are reported with a precision of ± 2 cm^{-1}.

Elemental analyses were completed by either Galbraith Laboratories, Knoxville, TN, or by the elemental analysis facility at the Universität Leipzig.

3. Results and discussion

3.1. Syntheses

The $Fe(NO)(S_2CNR_2)_2X$ complexes reported herein were prepared in two steps by modifications of previous synthetic methods. Successful syntheses of $Fe(NO)(S_2CNR_2)_2X$ complexes resulted by reversing the order of addition for the halide and NO^+ ligands that form these complexes [28,30]. This method was then applied to prepare novel $Fe(NO)(E_2CNR_2)_2X$ complexes (where $X = Cl^-, Br^-, I^-$ and $E = S$ and/or Se). The members of this series of complexes were originally selected to be analogous to the series of the $Fe(dtc)_2(CO)_2$ complexes investigated by us previously, however, despite numerous attempts to prepare the dibenzyl and diphenyl dithiocarbamate $Fe(NO)(S_2CNR_2)_2X$ derivatives only impure products were obtained.

3.2. $\{^1H\}^{13}C$ Spectra

Table 1 reports the proton-decoupled ^{13}C NMR spectra of the diethyl derivative of *cis*-$Fe(NO)(S_2CNR_2)_2I$, the thioseleno- and diseleno-/halogeno-analogues, and, for comparison, the $\{^1H\}^{13}C$ NMR spectra of the corresponding *cis*-$Fe(S_2CNR_2)_2(CO)_2$, *cis*-$Fe(SSeCNR_2)_2(CO)_2$, *cis*-$Ru(NO)(S_2CNR_2)_2I$, $Co(S_2CNR_2)_3$ and $Co(SSeCNR_2)_3$. The $\{^1H\}^{13}C$ NMR spectrum of $Co(S_2CN(CH_2CH_3)_2)_3$ serves as a reference compound. The three peaks noted correspond to the 3 CS_2, 6 CH_2 and 6 CH_3 carbons in this highly symmetric complex. The values reported here are similar to those reported by Gregson and Doddrell [27].

The $\{^1H\}^{13}C$ NMR of *cis*-$Fe(S_2CN(CH_2CH_3)_2)_2(CO)_2$ reported by Duffy and Appleton exhibited two CH_2 peaks, because of hindered rotation about the S_2C–NC_2 bond, which resulted in the α-C atoms being nonequivalent (one *cis* to a CO ligand and the other *cis* to the second dithiocarbamate ligand, see Fig. 1) [22]. *cis*-$Fe(NO)(S_2CN(CH_2CH_3)_2)_2I$ is similar to the corresponding dicarbonyl, with the two carbonyls replaced by an NO^+ and an I^- (Fig. 1). Four CH_2 signals are observed (Fig. 2), indicating both a difference in the two dithiocarbamate ligands in addition to differentiation as a result of hindered rotation about the S_2C–NC_2 bond. Furthermore, the $\{^1H\}^{13}C$ NMR spectrum of *cis*-$Fe(NO)(S_2CN(CH_2CH_3)_2)_2I$ provides an indication of the structural rigidity of this complex. Two CS_2 peaks were recorded, reflecting one sulfur of each dithiocar-

Table 1
$\{^1H\}^{13}C$ NMR spectra of selected diethyldichalcogenocarbamate complexes and tetraethylthiuram disulfide

Complex	CE_2 Carbon[a] (ppm)	α-Carbon (ppm)	β-Carbon (ppm)
$(S_2CN(C_2H_5)_2)_2$)[b]	192.63	52.01, 47.60	13.45, 11.47
$Co(S_2CNEt_2)_3$	204.4	42.7	12.6
$Co(SSeCNEt_2)_3$[c]	199.0, 198.5 198.0, 197.5	45.0, 44.8 43.4, 43.3 43.1, 43.0	12.7, 12.2
$Fe(S_2CNEt_2)_2(CO)_2$[d]	205.80	43.74, 43.33	12.51, 12.45
$Fe(SSeCNEt_2)_2(CO)_2$[e]	200.49, 200.00 199.08	46.03, 45.92 45.67, 44.16 43.87, 43.79	12.71, 12.66 12.59, 12.14 12.09
$Fe(NO)(S_2CNEt_2)_2$ Br	202.51, 199.81	45.12, 44.88 44.22, 43.60	13.27, 13.15 13.01, 12.71
$Ru(NO)(S_2CNEt_2)_2I$[f]	210.0, 201.7	44.9, 44.2, 43.4	12.7, 12.5
$Fe(NO)(S_2CNEt_2)_2I$	204.31, 199.34	44.32, 43.64 43.46, 43.04	12.91, 12.84 12.78, 12.48
$Fe(NO)(SSeCNEt_2)_2Br$	196.55, 194.08	47.76, 46.68 46.53, 45.94 45.35, 44.86 44.00, 43.59 42.90, 42.50	13.56, 13.50 12.77, 12.71 12.57, 12.33 12.22, 12.13
$Fe(NO)(Se_2CNEt_2)_2Br$	191.44, 191.31	47.55, 47.46 46.36	12.89, 12.66 12.55, 12.48
$Fe(NO)(Se_2CNEt_2)_2I$	192.82, 190.78	47.33, 47.08 46.59, 46.02	12.75, 12.55 12.35, 12.26

[a] E = S and/or Se.
[b] Ref. [22].
[c] Ref. [23].
[d] One peak in the CO region: 212.96 ppm; these values are very similar to those reported in [22].
[e] Three peaks in the CO region: 215.05, 214.70 and 214.53 ppm.
[f] Ref. [26].

bamate being *trans* to either an NO^+ or I^- ligand (the two other sulfur ligand atoms are, of course, *trans* to one another). The change from two strong field, π-accepting CO ligands to one strong field, π-accepting and one weak field, π-donor ligand does not result in a sufficient lowering of the C–N partial double bond character to allow rotation at room temperature [40]. The difference in the two dithiocarbamate ligands and the hindered rotation about the C–N bond is confirmed by the observation of the four CH_3 peaks as well, although the differences (0.43 ppm) between these β-carbons is much less than the α-carbons (1.28 ppm). Finally, Dubrawski and Feltham [26] reported similar $\{^1H\}^{13}C$ NMR results to those of *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$ for *cis*-$Ru(NO)(S_2CN(C_2H_5)_2)_2I$.

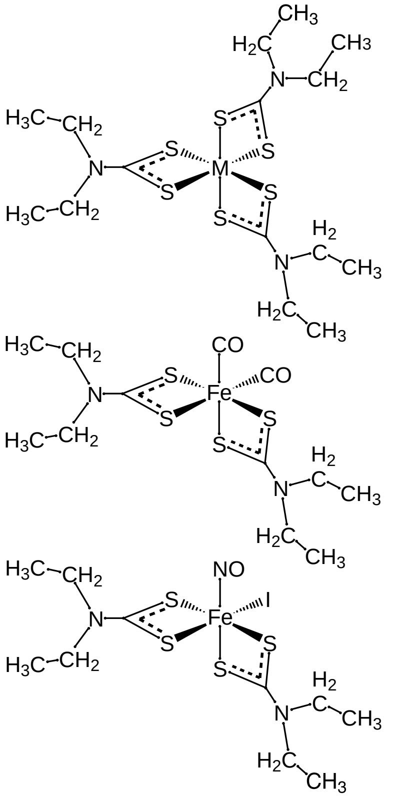

Fig. 1. Schematic representations of the structures of M(III)$(S_2CN(C_2H_5)_2)_3$ (M = Fe, Co, In), *cis*-$Fe(S_2CN(C_2H_5)_2)_2(CO)_2$, and *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$ (from top to bottom, respectively).

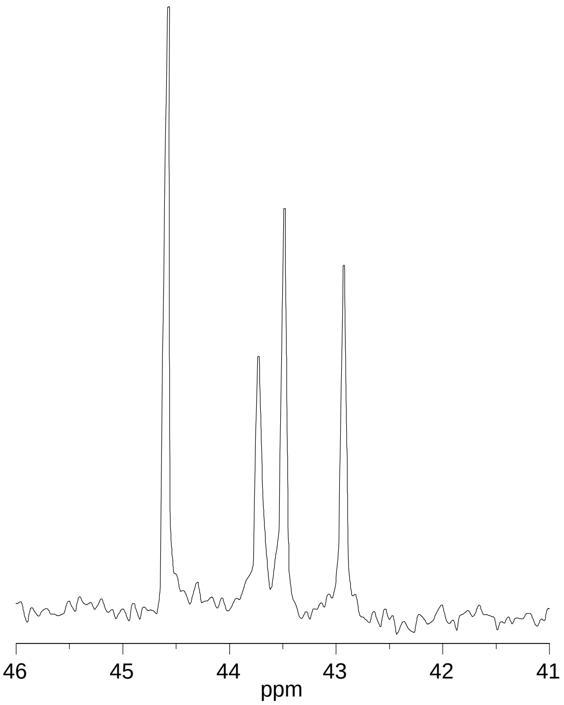

Fig. 2. ^{13}C NMR signals for the alkyl C α to the N in *cis*-Fe(NO)$(S_2CN(C_2H_5)_2)_2I$ ($CDCl_3$).

The complex *cis*-$Fe(SSeCN(CH_2CH_3)_2)_2(CO)_2$ exhibits a more complex pattern than *cis*-$Fe(S_2CN(C_2H_5)_2)_2(CO)_2$, Table 1. Three CE$_2$ and three CO signals are observed. This result is consistent with a structurally rigid complex, existing as three isomers (carbonyls *trans* to two S, a S and Se, or two Se, Fig. 3) in an approximately statistical ratio (1:2:1). There are six signals for the α-carbons, similar in location and relative intensity to that of the $Co(SSeCN(C_2H_5)_2)_3$ complex, because each α-carbon is proximate to a S or Se (Fig. 4) which, in turn, is *trans* to a S, CO or Se ligand in an approximately 1:2:1 ratio. The multiple β-carbon signals reflect the hindered rotation about the SSeC–NC$_2$ bond, resulting in the CH_3 being either on the same side of the approximately planar ligand as a S or Se and next to another CH_3 or CO.

In the $\{^1H\}^{13}C$ NMR of the $Co(SSeCN(CH_2CH_3)_2)_3$ derivative, reported by Dietzsch et al. [23], four CSSe peaks were observed, reflecting the *fac* isomer and the three different environments of the CSSe carbons in the *mer* isomer (Fig. 5). Six α-C CH$_2$ peaks were observed. Interpreted in terms of the α-C orientation with respect to the proximate chalcogens and to the other chalcogens in the first coordination sphere, Dietzsch et al. presented two alternative explanations for the six α-carbon signals. The $\{^1H\}^{13}C$ spectra of the *cis*-$Fe(NO)(E_2CNR_2)_2X$ complexes yield new insight into the interpretation of the $Co(SSeCNR_2)_3$ spectra.

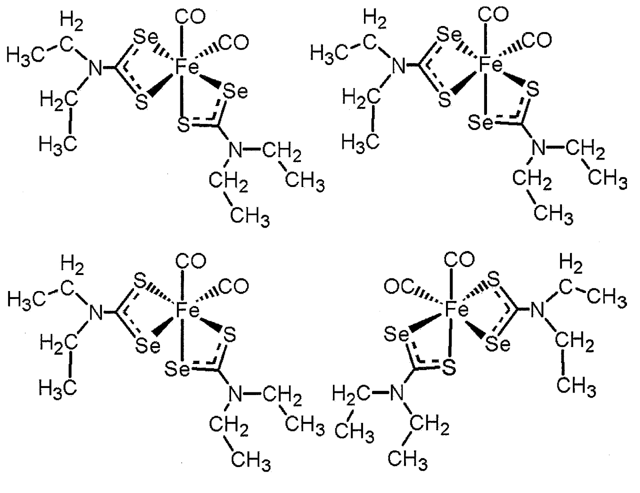

Fig. 3. Schematic representations of the structural isomers of *cis*-$Fe(SSeCN(C_2H_5)_2)_2(CO)_2$.

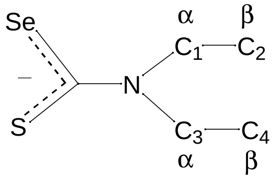

Fig. 4. Scheme of the ligand $^-SSeCN(CH_2CH_3)_2$ depicting the text terminology: C_1 is the carbon atom α to the N of the parent amine, and proximate to the Se donor atom. C_2 is the β-carbon atom and proximate to Se. Likewise, C_3 is the α-C and proximate to S, while C_4 is the β-C and proximate to S.

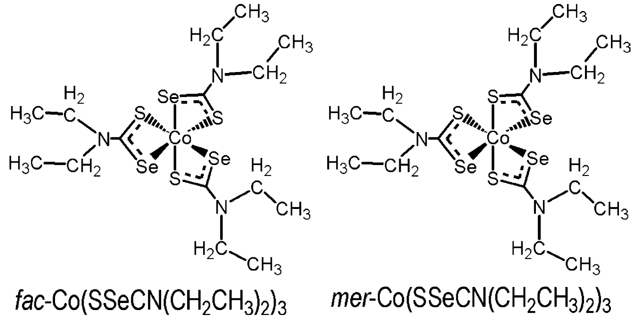

Fig. 5. Schematic representations of *fac*-$Co(III)(SSeCN(CH_2CH_3)_2)_3$ and *mer*-$Co(III)(SSeCN(CH_2CH_3)_2)_3$.

The first explanation for the $Co(SSeCN(C_2H_5)_2)_3$ $\{^1H\}^{13}C$ NMR spectrum is predicated on the chalcogen to which the α-C is proximate in the ligand, and the two chalcogens in the first coordination sphere that are perpendicular to the plane of the ligand containing that particular α-C atom. Thus, for the *mer* isomer (Fig. 5), this approach predicts six different signals for the six different kinds of α-carbons: S(SSe), Se(SSe), S(SS), Se(SS), S(SeSe) and Se(SeSe) – where the first chalcogen is the chalcogen proximate to the α-carbon and the chalcogens in parentheses are the two chalcogen atoms which are perpendicular to the plane of the coordinated thioselenocarbamate. There are only two different kinds of α-carbon atoms in the *fac* isomer: carbon atoms proximate to S and carbon atoms proximate to Se (Fig. 5). Every coordinated thioselenocarbamate ligand has a coordinated S and Se (from the other ligands) perpendicular to the ligand plane. This first explanation predicted a 2:2:1:1:1:1 ratio of intensities, which was in accord with the experimental results.

The second explanation predicts eight different signals for the α-carbons. Each α-C is influenced by the chalcogen to which it is proximate, the chalcogen *trans* to that donor atom in the first coordination sphere, and the other, second, chalcogen in the same ligand of that specific α-carbon (always different from the proximate chalcogen) and the chalcogen *trans* to this second chalcogen in the first coordination sphere. In the *fac* isomer of $Co(SSeCN(C_2H_5)_2)_3$, there are again only two different kinds of α-carbons: each α-C atom that is proximate to a S atom has a Se atom *trans* to that S atom (Fig. 5). The other coordinating atom in that same ligand is a Se atom that is *trans* to a S atom. Likewise, each α-C atom that is proximate to a Se has a S atom *trans* to that Se atom, whilst the other coordinating atom in that same ligand is a S atom that is *trans* to a Se atom. For the *mer* isomer, there exist six unique α-C atoms by this method (Fig. 5). Despite the second explanation predicting eight peaks of equal intensity, combined, for the *fac* and *mer* isomers, only six $C\mathrm{H}_2$ signals were observed. Degeneracy, however, could have caused the experimentally observed 2:2:1:1:1:1 intensity ratio.

When applied to the *cis*-Fe(NO)(S_2CNR_2)$_2$I complexes, the first explanation predicts only two α-^{13}C NMR signals. On the first ligand, both α-carbons are proximate to S atoms and the ligands perpendicular to the plane of the dithiocarbamate ligand are NO and a S from the other dithiocarbamate ligand (Fig. 1). On the second dithiocarbamate ligand, both α-carbons are proximate to S atoms, with I and S (from the first dithiocarbamate ligand) perpendicular to the ligand plane. This explanation is clearly inadequate.

The second explanation is in accord with the experimental results. There are four different α-carbon atoms (Fig. 1): S(S)S(I), S(I)S(S), S(NO)S(S) and S(S)S(NO); using the notation: proximate chalcogen (ligand *trans* to it in the coordination sphere), second chalcogen of the ligand (ligand *trans* to it in the coordination sphere). The four different α-carbon atoms, Se(Se)Se(I), etc., in the diselenocarbamate derivatives further confirm this interpretation.

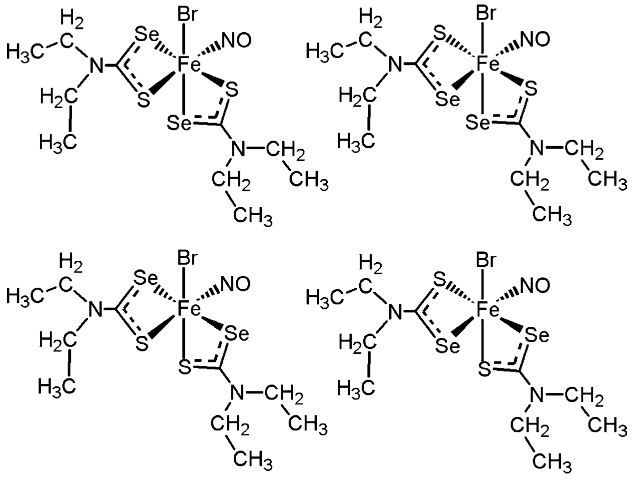

Fig. 6. Schematic representation of the structural isomers of *cis*-Fe(NO)(SSeCN(C_2H_5)$_2$)$_2$Br.

The thioselenocarbamate derivative, *cis*-Fe(NO)(SSeCN(C_2H_5)$_2$)$_2$Br, would exhibit eight α-C peaks, in accord with the first interpretation, due to eight different permutations of S or Se with S, Se, NO or Br (Fig. 6). The *cis*-Fe(NO)(SSeCN(C_2H_5)$_2$)$_2$Br spectrum clearly exhibits more than eight signals (Table 1). If the second interpretation is correct, there are 16 different permutations of S(A)Se(B) and Se(A)S(B), wherein A and B may be either S, Se, Br, or NO, e.g., S(Se)Se(NO) or Se(Br)S(S) (excluding, of course, any double entries and E(Br)E(NO) permutations). The reduced number of peaks probably arises from accidental degeneracies.

Table 2 summarizes the {^{1}H}^{13}C NMR spectra of the dimethyl, morpholyl, piperidyl and pyrrolidyl *cis*-Fe(NO)(S_2CNR_2)$_2$I derivatives and the corresponding dicarbonyl complexes for the first three. The pattern of peaks observed for the diethyl derivatives in Table 1 is repeated for these derivatives as well: the change from two CO ligands to NO$^+$ and an I$^-$ results in two $C\mathrm{S}_2$ peaks and an average decrease of 5 ppm in the $C\mathrm{S}_2$ signal, a differentiation in the α-carbons into four signals whose average value was ±0.5 ppm of the average value of the corresponding α-C of the dicarbonyl derivatives. The remaining carbons also evidenced the effects of the decrease in symmetry upon replacement of the two CO by NO$^+$ and I$^-$, but to a lesser extent.

3.3. ^{15}N spectra

Table 3 presents the ^{15}N NMR data for the *cis*-Fe(NO)($S_2CN(C_2H_5)_2$)$_2$I derivative along with the values of several related compounds. The ^{15}N signals for the dithiocarbamate nitrogen atoms of the complex are

Table 3
^{15}N NMR spectra of compounds containing the diethyldithiocarbamate moiety

Compound	^{15}N signal[a] (ppm)
($S_2CN(C_2H_5)_2$)$_2$	214.85
Co($S_2CN(C_2H_5)_2$)$_3$	215.07
Fe($S_2CN(C_2H_5)_2$)$_2$(CO)$_2$[b]	213.35
Fe(NO)($S_2CN(C_2H_5)_2$)$_2$I	210.92, 210.09, 29.28

[a] Relative to CH$_3$^{15}NO$_2$ reference.

[b] Ref. [22] reports 150.0 ppm referenced to 2.5 M (^{15}NH$_4$)$_2$SO$_4$.

Table 2
Comparison of the ^{13}C NMR spectra of Fe(NO)(S_2CNR_2)$_2$I and Fe(S_2CNR_2)$_2$(CO)$_2$

Compound	$C\mathrm{S}_2$ (ppm)	α-*C* (ppm)	Other C (ppm)
Fe(NO)($S_2CN(CH_3)_2$)$_2$I	203.03, 197.94	38.82, 38.20 37.88, 37.66	
Fe($S_2CN(CH_3)_2$)$_2$(CO)$_2$[a]	206.79	38.56, 38.19	
Fe(NO)($S_2CN(CH_2)_5$)$_2$I	203.03, 197.94	47.84, 47.34 46.95, 46.64	25.40, 25.36 25.25, 24.18 23.93
Fe($S_2CN(CH_2)_5$)$_2$(CO)$_2$[a]	204.82	47.30, 46.72	25.25, 24.06
Fe(NO)($S_2CN(CH_2)_4O$)$_2$I	205.06, 199.93	46.81, 46.33 45.93, 45.70	66.05, 65.96 65.82
Fe($S_2CN(CH_2)_4O$)$_2$(CO)$_2$[a]	206.59	46.93, 46.41	66.06
Fe(NO)($S_2CN(CH_2)_4$)$_2$I	200.32, 196.16	49.49, 48.91 48.67, 48.44	24.66, 24.55 24.44

[a] Ref. [22].

in the same range as the other diethyldithiocarbamato derivatives, but the two ^{15}N signals indicate that the two nitrogen atoms of the two dtc ligands experience different chemical environments, one ligand being *trans* to an NO^+, the second *trans* to an iodide. A single ^{15}N signal is noted for the nitrosyl ligand. This value is in accord with other linear nitrosyl complexes [41–44].

The values in Table 3 indicate that the nitrogen atom in the $(C_2H_5)_2NCS_2^-$ moiety is considerably deshielded compared to the parent secondary amine, $HN(C_2H_5)_2$ [45]. Attempts have been made to correlate the ^{15}N chemical shifts in a series of closely related molecules where the possible delocalization of a lone pair of electrons on a nitrogen atom to an adjacent atom can result in a rotational barrier [41]. The general trend of the data gathered in these studies indicates increasing deshielding (more positive ^{15}N chemical shifts) with an increase in delocalization of the lone pair of electrons. Therefore, a more positive ^{15}N chemical shift would correspond to greater partial double bond character and a larger energy barrier to rotation. That correlation would not account for steric effects, however [41].

Thus, based on the data in Table 3, the barrier to rotation of the $S_2C{=}N(C_2H_5)_2$ bond would increase in the order: $Co(S_2CN(C_2H_5)_2)_3 <$ $(S_2CN(C_2H_5)_2)_2 <$ *cis*-$Fe(S_2CN(C_2H_5)_2)_2(CO)_2 <$ *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$. Although few rotational barriers for dithiocarbamate complexes have been reported in the literature, the ΔG^{error} for rotation about the C–N bond has been reported to be 18.5 kcal/mol for $(S_2CN(C_2H_5)_2)_2$ [46] and estimated as 15–20 kcal/mol (60–85 kJ/mol) for $Co(S_2CN(C_2H_5)_2)_3$ [24]. The general trend in our limited ^{15}N NMR data is consistent with these data.

3.4. ^1H spectra

The ^1H NMR of *cis* -$Fe(NO)(S_2CN(CH_3)_2)_2I$ is the most straightforward ^1H NMR spectrum recorded for this series of complexes. The *cis*-$Fe(NO)(S_2CN(CH_3)_2)_2I$ spectrum exhibits four peaks (3.38, 3.31, 3.22 and 3.14 ppm) of equal intensity, indicating that each set of protons experiences a different environment. This data set is also in good agreement with the results reported by Ileperuma and Feltham [29]. The ^1H NMR of *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$ exhibits a complex multiplet consisting of at least 16 discernible peaks from 3.82 to 3.45 ppm (which may be interpreted as four overlapping ABX_3 systems) and two triplets of different intensities centered at 1.33 and 1.26 ppm. Similar spectra were reported for $Co(SSeCN(C_2H_5)_2)_3$ with complex multiplets at 3.74 and 3.60 ppm and a single triplet at 1.27 ppm [23]. The piperidyl derivative, *cis*-$Fe(NO)$ $(S_2CN(CH_2)_5)_2I$, exhibited a broad multiplet centered at 3.7 ppm and a broad single peak at 1.71 ppm, while the morpholyl derivative, *cis*-$Fe(NO)(S_2CN(CH_2)_4O)_2I$, exhibited two broad overlapping multiplets centered at 3.92 and 3.77 ppm. Each of these ^1H NMR spectra was quite similar to that reported for the corresponding Co(III) thioselenocarbamato complex [23]. Thus, the ^1H NMR spectra are consistent with the $\{^1H\}^{13}C$ and ^{15}N NMR spectra reported above, further supporting the assertion that each α-C "occupies" a different environment within these structurally rigid complexes.

The ^1H NMR data of the dimethyl and diethyl *cis*-$Fe(NO)(S_2CNR_2)_2I$ derivatives also correlate well with data recorded for other structurally similar complexes. In the *cis*-$M(NO)_2(S_2CNR_2)_2$ complexes ($R = CH_3$, $M = Mo$ or W; $R = C_2H_5$, $M = Mo$), the dimethyl derivatives exhibit two lines (center of doublet: 3.34 ppm, Mo; 3.33, W), while the diethyl derivative exhibits eight lines centered at 3.81 ppm and six lines centered at 1.29 ppm [47]. *cis*-$Ru(NO)(S_2CN(C_2H_5)_2)_2I$ exhibits a complex multiplet between 3.88 and 3.43 ppm and several signals between 1.47 and 1.10 ppm [26].

3.5. IR spectra

The ν_{NO} of these complexes are consistent with a bound NO molecule. Coupling the ^{15}N NMR data with the structure of *cis*-$Fe(NO)(S_2CN(CH_3)_2)_2(NO_2)$ [29], the Mössbauer data [30] and ν_{NO}, a linear Fe–NO moiety is predicted. In addition, the data collected for this study indicate and corroborate earlier reports that the solution IR spectra of the *cis*-$Fe(NO)(S_2CNR_2)_2I$ complexes yield higher ν_{NO} values than in KBr or Nujol mulls. For example, *cis*-$Fe(NO)(S_2CN(CH_2)_5)_2I$, 1840 cm^{-1}; *cis*-$Fe(NO)(S_2CN(CH_3)_2)I$, 1842 cm^{-1}; and *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$, 1844 cm^{-1} in $CHCl_3$ were higher than the range of values (1804–1829 cm^{-1}) reported by Fitzsimmons and Hume [30] for their Nujol mulls. Samples analyzed as KBr pellets, however, were consistent with the Nujol mulls: *cis*-$Fe(NO)$ $(S_2CN(C_2H_5)_2)_2I$ in KBr at 1805 cm^{-1} versus 1800 cm^{-1} in Nujol. Similar data were reported by Ileperuma and Feltham [29], but without comment. They recorded the ν_{NO} of *cis*-$Fe(NO)(S_2CN(CH_3)_2)_2I$ in both $CHCl_3$ and KBr and reported values of 1848 and 1815 cm^{-1}, respectively, compared to 1842 cm^{-1} ($CHCl_3$) in this study. For the *cis*-$Fe(NO)(E_2CN(C_2H_5)_2)_2Br$ series of complexes, the following ν_{NO} were recorded in KBr: *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2Br$, 1825 cm^{-1} (1813 and 1810 cm^{-1} in previous reports [28,30]); *cis*-$Fe(NO)(SSeCN(C_2H_5)_2)_2Br$, 1820 cm^{-1}; and *cis*-$Fe(NO)(Se_2CN(C_2H_5)_2)_2Br$, 1805 cm^{-1}. Although the diseleno/chloro derivative, *cis*-$Fe(NO)(Se_2CN(C_2H_5)_2)_2Cl$, suffered from solubility problems with respect to NMR data collection, an IR spectrum was obtained, with $\nu_{NO} =$ 1800 cm^{-1}. Previously, Büttner and Feltham [28] reported an impure preparation of *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2Cl$ with $\nu_{NO} = 1840$ cm^{-1}. Based on these data, it would be tempting to speculate on a trend, namely that as more polarizable, or "electron-rich", donor atoms like Se are added to the first coordination sphere, that more electron density is involved in π-backbonding to the NO^+ ligand, thereby causing the downward shift in the reported ν_{NO} observed for the chloro and bromo series of complexes. However, the complex *cis*-$Fe(NO)(Se_2CN(C_2H_5)_2)_2I$ was measured at $\nu_{NO} = 1840$ cm^{-1}, which is only a slight shift from 1844 cm^{-1} reported for the dithiocarbamate derivative, *cis*-$Fe(NO)(S_2CN(C_2H_5)_2)_2I$. This is consistent with the literature perspective that indicates that within metal-nitrosyl chemistry it is often difficult to establish trends for a series of molecules as to whether or not the ν_{NO} is varying with respect to electron density on the central metal atom [42,48]. Thus, a larger series of samples would be required to establish whether or not a trend exists for *cis*-$Fe(NO)(E_2CNR_2)_2X$. Currently, no clear trend is evident in the IR data to suggest that the change from S to Se leads to a downshift in ν_{NO} as a result of increased electron density.

As a final note, the similarity of the NO stretching frequencies is in accord with the very similar force constants of the three corresponding dicarbonyl derivatives (16.21 ± 0.01 mdyne $Å^{-1}$). The force constants for the NO stretching frequencies range from 13.67 to 12.97 ± 0.01 mdyne $Å^{-1}$ [49].

4. Conclusion

All of the results reported herein are consistent with a series of *cis*-$Fe(NO)(E_2CNR_2)_2X$ complexes that are stereochemically rigid at room temperature and that retain a *cis* geometry. The kinetic processes which would involve a trigonal twist mechanism and a C⩦N bond rotation are shown to be slow on the NMR time scale: a trigonal twist would render the two CE_2 peaks equivalent (which they are not) and rapid C⩦N bond rotation would reduce the number of α-carbon signals from four to two. The $\Delta G^{\ddagger}$ values for rotation about the E_2C–NR_2 bond support hindered rotation, which does not allow for equilibration on the NMR time scale. Furthermore, the results are consistent with observation of only *cis*-$Fe(NO)(E_2CNR_2)_2X$ complexes. Were a mixture of *cis* and *trans* isomers present, either three or five α-C signals would be observed, but not four. This is clearly not the case for complexes like $Fe(NO)(S_2CN(CH_3)_2)_2I$. More than two CE_2 signals would also be predicted. Indeed, for the complex $Ru(NO)(S_2CN(CH_3)_2)_2L$, $L = SCN^-$ or N_3^-, for which both *cis* and *trans* isomers were analyzed by ^{13}C NMR, the α-Cs yield a single signal for the *trans* isomer, while four signals were observed for the α-Cs in the *cis* isomer [26]. Three CE_2 signals were reported for $Ru(NO)(S_2CN(CH_3)_2)N_3$: a single signal for *trans*-$Ru(NO)(S_2CN(CH_3)_2)_2N_3$ at 213.3 ppm, versus two CE_2 signals for *cis*-$Ru(NO)(S_2CN(CH_3)_2)_2N_3$ at 210.4 and 204.3 ppm. Finally, the ^{15}N NMR data also clearly indicate that the two dithiocarbamate ligands are in different environments, eliminating the possibility of a rapid trigonal twist mechanism. Were *cis* and *trans* isomers present, a second NO signal in the NMR spectrum would be predicted. Thus, all of these data support the stereochemical rigidity of these *cis*-$Fe(NO)(E_2CNR_2)_2X$ complexes.

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