metrical absorption shifted to higher energy followed by an intense charge-transfer band in the near-UV region. The ϵ values are significantly higher than corresponding pentaamine complexes, demonstrating the dramatic influence coordinated thioether groups have on electronic spectra. The energy of the low-energy absorption band for these complexes is consistent with the normal spectrochemical series $Br^- < Cl^- < N_3^- < SCN^- < H_2O \ll NO_2^-$. Also, it demonstrates that the nitrogen atom in SCN^- and NO_2^- is coordinated.

As in similar stereochemical studies,[8-10] infrared spectra were found to be inconclusive in assigning the topological donor configuration for these complexes. In general, the N–H stretching region (3000–3400 cm^{-1}) exhibited three to five strong absorptions and a single strong N–H deformation band at $\sim$1575 cm^{-1}. $[Co(Q)NO_2](ClO_4)_2$ exhibited characteristic nitro (NO_2)[17] absorptions at 620, 825, 1320, and 1430 cm^{-1}. Terminal Co–NCS binding is supported by the C═N stretch at 2110 cm^{-1} for $[Co(Q)NSC](ClO_4)_2$.[18]

The synthesis and characterization of a new pentadentate ligand containing three nitrogen and two sulfur donors are reported. It coordinates to Co(III) giving a series of complexes $Co(Q)X^{n+}$, which we believe to possess the same $\alpha\alpha$ topology. This is a result of ligand design and stereochemical bonding angle requirements of both $CH_3N<$ and –S– donor atoms.

Registry No. $[Co(Q)Cl][CoCl_4]$, 67904-86-3; $[Co(Q)Cl](ClO_4)_2$, 67904-87-4; $[Co(Q)Br][CoCl_4]$, 64659-36-5; $[Co(Q)Br](ClO_4)_2$, 64659-37-6; $[Co(Q)N_3](ClO_4)_2$, 67904-89-6; $[Co(Q)NCS](ClO_4)_2$, 67904-91-0; $[Co(Q)NO_2](ClO_4)_2$, 67904-93-2; $Co(Q)H_2O^{3+}$, 67904-94-3; 1,5-dichloro-3-methyl-3-azapentane hydrochloride, 17027-23-5; 6-methyl-3,9-dithia-2,10-diimino-1,6,11-triazaundecane trihydrochloride, 63915-53-7; 4-methyl-1,7-dithia-4-azaheptane, 19031-92-6; 6-methyl-3,9-dithia-6-aza-1,11-bis(*N*-phthalimido)undecane, 67891-61-6; Q, 62121-70-4; *N*-methyl-2,2′-diethanolamine, 105-59-9; thionyl chloride, 7719-09-7; thiourea, 62-56-6; *N*-(2-bromoethyl)phthalimide, 574-98-1.

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Nitrosylbis(diorganodithiocarbamato)iron Complexes. Effect of Organic Substituents

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A series of 14 $Fe(NO)(S_2CNRR')_2$ complexes have been prepared, where R and R′ are either aliphatic or aromatic organic substituents. Room-temperature Mössbauer, infrared, and EPR measurements are included in this report. The N–O stretching frequency (both in chloroform solution and in Nujol) exhibits a nearly linear dependence on the "corrected" aqueous pK_a (pK_a(cor)) values of $H_2NRR'^+$, which confirms that the resonance effects which diminish the basicity of the nitrogen lone pair of electrons in HNRR′ in solution are absent in the aromatic dithiocarbamates. The change in each spectroscopic parameter, infrared NO stretching frequency, ^{57}Fe Mössbauer isomer shift and quadrupole splitting, and EPR g_{eff} value and ^{14}N hyperfine splitting with pK_a(cor) is explained on the basis of a single model which includes the inductive effects of R and R′, iron–nitrosyl back-bonding, and the occupation of the Fe d_{z^2} orbital by the unpaired electron.

Introduction

The nitrosylbis(diorganodithiocarbamato)iron complexes $(FeNO(dtc)_2$, where dtc is $S_2CNRR'^-$ and R and R′ are organic substituents) are a series of compounds in which several spectroscopic techniques can probe the effect of varying R and R′ on the ligand field strength of $^-S_2CNRR'$. Only a few of these derivatives (usually R,R′ = Me or R,R′ = Et) have been investigated by IR,[1,2,5] EPR,[2-6] UV–vis,[5] and Mössbauer[1,7] techniques, even though they were first synthesized in 1931.[8] Recently, Ileperuma and Feltham[9] reported the preparation, IR spectra, and reactions of four derivatives (R,R′ = Me; Et; Ph; R = Me, R′ = Ph). These results combined with X-ray structure determinations[10-12] yield the picture of a square-pyramidal complex with the NO bond axis perpendicular to the plane of the four sulfurs. The similarity of the trends of N–O stretching frequencies in $CHCl_3$ solution and Nujol mulls reported below supports our expectation that the square-pyramidal configuration is maintained. These complexes, however, are probably not sterically rigid in solution; indeed, the corresponding $Fe(dtc)_3$ complexes exhibit two distinct kinetic processes, a trigonal twist and a cis–trans isomerization, in CH_2Cl_2 at −20 °C and below.[13] The unpaired electron in these spin = $^1/_2$ compounds has been presumed to occupy an a_1 (d_{z^2}) molecular orbital.[9]

Little attention has been paid to the effect of changing organic substituents (R,R′) on the dithiocarbamate ligand in this set of complexes. In the corresponding iron(III) series, $Fe(dtc)_3$, changing the organic substituents causes a change in the magnetic moments[14] and, hence, a set of spin-crossover

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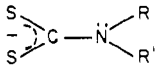
Table I. Infrared, Mössbauer, and EPR Parameters of $Fe(NO)(S_2CNRR')_2$ at Room Temperature

organic substituents		pK_a(cor)[a]	ν_{N-O},[b] cm^{-1}		IS,[c] mm/s	ΔE_Q,[d] mm/s	g_{eff}[e]	A,[f] G
			$CHCl_3$ soln	Nujol				
1	piperidine	11.12	1717	1693	0.507	0.85	2.041	12.8
2	pyrrolidine	11.11	1718	1686	0.524	0.87	2.043	12.7
3	Et, Et	10.93	1716	1683	0.514	0.80	2.040	12.8
4	Me, Me	10.73	1718	1690[g]	0.521	0.92	2.040	12.5
5	Ph, Ph	10.38	1721	1700[g]	0.542	0.72	2.042	12.4
6	Ph, Et	9.91	1719	1714	0.526	0.81	2.042	12.7
7	Bz, Et	9.68	1718	1709	0.528	0.76	2.041	12.8
8	Ph, Me	9.65	1721	1708	0.528	0.83	2.044	12.5
9	Bz, Me	9.58	1719	1707	0.535	0.77	2.041	12.7
10	Ph, 3-ClPh	9.15	1725	1710	0.515	0.83	2.042	12.6
11	Bz, Ph	8.84	1721	1713	0.531	0.75	2.042	12.8
12	morpholine	8.49	...[h]	1712	0.534	0.74	2.042	12.7
13	Et, EtO	4.91	1724	1712	0.545	0.72	2.045	12.9
14	Me, MeO	4.75	1727	1724	0.552	0.66	2.044	13.0

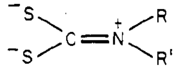
[a] Aqueous pK_a of parent amine plus 4.80 pK_a units per phenyl substituent (for sources of pK_a values, see ref 18). [b] $CHCl_3$ solution and Nujol, error limits ±1 cm^{-1}. [c] With reference to sodium nitroprusside, ±0.01 mm/s. [d] ±0.01 mm/s. [e] $CHCl_3$ solution, error limits ±0.001. [f] ±0.1 G, $CHCl_3$ solution. [g] ±5 cm^{-1}. [h] Not sufficiently soluble in $CHCl_3$.

complexes. The effect of changing R and R′ on the ligand field strength has been proposed to be either steric[15] or inductive.[16,17]

The ligand itself may be described as a resonance hybrid in which two limiting resonance structures (A and B) are the contributors to the ligand bonding.



A



B

Eley et al.[17] proposed the use of the pK_a as an indication of the tendency of the lone pair on the nitrogen of the dithiocarbamate ligand to participate in a carbon–nitrogen double bond as shown in limiting resonance structure B. Leipoldt and Coppens[18] have presented evidence that limiting resonance structure B is the high-field structure via a temperature-dependent X-ray structure determination of $Fe(S_2CN(C_2H_5)_2)_3$. In particular, the bond lengths averaged over chemically equivalent bonds were S–C = 1.708 (4) Å and C–N = 1.337 (6) Å at 297 K (μ = 4.3 μ_B) and S–C = 1.721 (2) Å and C–N = 1.323 (4) Å at 79 K (μ = 2.2 μ_B). These results correspond to the identification of the low moment, high-field resonance structure as limiting resonance structure B.

Zimmerman et al.[19] provide data which agree (from the inductive point of view) that the limiting resonance structure B possesses the stronger ligand field. Their conclusions[19] are based on correlations between spectroscopic parameters and changes in the ligand field strength of the dtc ligand as measured by the pK_a of $H_2NRR'^+$. In particular, for $Fe(dtc)_3$, *cis*-$Fe(CO)_2(dtc)_2$, and $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$, they show that the inductive effect as observed by IR, Mössbauer, and proton NMR depends on the basicity of the lone pair on the nitrogen in the dtc ligand. The study of this inductive effect is now extended to the five-coordinate, paramagnetic, iron nitrosyl series. We employ IR, EPR, and Mössbauer spectroscopy in this report and we discuss the experimental results in the following sections.

Experimental Section

All reactions were carried out under a N_2 atmosphere. Solvents were deaerated by purging them with N_2. Nitric oxide was purified by trapping impurities in dry ice–acetone cold traps.

Each complex was prepared from a solution of 20 mmol of $FeSO_4 \cdot 7H_2O$ in 100 mL of water cooled to 0 °C and saturated with purified NO. To this mixture was added dropwise 40 mmol of the sodium salt of the appropriate dithiocarbamate dissolved in 50 mL of water.[9] The green precipitate was filtered, washed with small quantities of water and methanol, and dried under vacuum. The complexes were recrystallized from chloroform solution by addition of methanol, yielding black-green crystalline solids.

Each compound gave satisfactory elemental analyses (C, H, and N). Analyses were performed by Chemalytics, Inc., Tempe, Ariz.

O,N-Diethylhydroxylamine was prepared by published methods[20] and the pK_a of $H_2N(C_2H_5)OC_2H_5^+$ was determined by titration.[21]

Infrared Spectra. Nujol mull and chloroform solution infrared spectra were obtained using a Perkin-Elmer 521 grating infrared spectrophotometer. The N–O stretching frequencies which we report are accurate to ±1 cm^{-1}.

Mössbauer Spectra. The Mössbuaer spectra were obtained using a standard constant-acceleration spectrometer.[22] The source was ^{57}Co in either a copper or rhodium matrix. All the measured isomer shifts are reported relative to sodium nitroprusside. The spectrometer, calibration procedures, and the treatment of the data have been described previously.[19] The Mössbauer data of this paper are from room-temperature measurements of the $Fe(NO)(dtc)_2$ compounds in the solid state. The isomer shifts (IS) and quadrupole splittings (ΔE_Q) are accurate to ±0.01 mm/s.

EPR Spectra. EPR spectra were obtained using a Varian V4500 X-band spectrometer and a Magnion magnet with a FFC-4 field control. A deMornay-Bonardi secondary standard wavemeter was used to measure the frequency to four significant figures, and the magnetic field was measured to 0.1 G. The absolute corrected value of the magnetic field was obtained using a nitroxide spin probe of known *g* value as a standard. Our *g* values which were measured in solution at room temperature are accurate to ±0.001 and the hyperfine values (A) are accurate to ±0.1 G. The A values result from the N nucleus (I = 1)–unpaired electron electron hyperfine interaction.

Results and Discussion

Table I lists the NO stretching frequencies and Mössbauer and EPR parameters for the 14 $Fe(NO)(dtc)_2$ complexes prepared for this work.

IR Data. Figure 1 shows a plot of the NO stretching frequencies (ν_{NO}) of these compounds in chloroform vs. the aqueous pK_a value of the protonated form of the parent secondary amine, $H_2NRR'^+$.

Figure 1 shows a decrease in ν_{NO} with increasing pK_a in three distinct groups: R,R′ = alkyl; R = alkyl, R′ = aryl; R,R′ = aryl. Zimmerman et al.[19] observed a similar correlation for ν_{CO} vs. pK_a for $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ and k_{cisCO} vs. pK_a for *cis*-$Fe(CO)_2(dtc)_2$. They attributed this separation into three groups to the absence in aromatic dithiocarbamates of the resonance effects which diminish the basicity of the nitrogen lone pair of electrons in HNRR′ in solution. The absence of this resonance effect of the phenyl substituents in the dtc complexes was corrected for by adding 4.8[19,23] pK_a units per *N*-phenyl substituent to the measured pK_a values. The plots of ν_{CO} or k_{cisCO} values vs. corrected pK_a values for $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ and $Fe(CO)_2(dtc)_2$ are very nearly linear.[19] In Figure 2, ν_{NO} exhibits a similar correlation when plotted vs. the corrected pK_a values for our 14 $Fe(NO)(dtc)_2$ com-

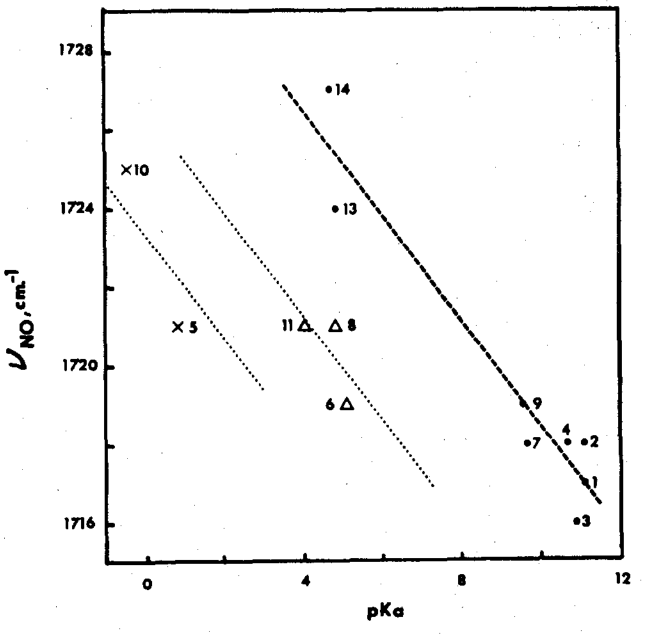


Figure 1. A plot of the N–O stretching frequency of $Fe(NO)(S_2CNRR')_2$ in $CHCl_3$ solution at room temperature vs. the aqueous pK_a of $H_2NRR'^+$: ●, R,R′ = nonaryl; △, R = aryl, R′ = nonaryl; ×, R,R′ = aryl. The best linear fit of the nonaryl data using the least-squares method is indicated by the dashed line. The dotted lines are parallel to this line and are drawn through the other two sets of data points. Each line is drawn to indicate the trend of the data. Numbers refer to the identity of each complex as given in Table I.

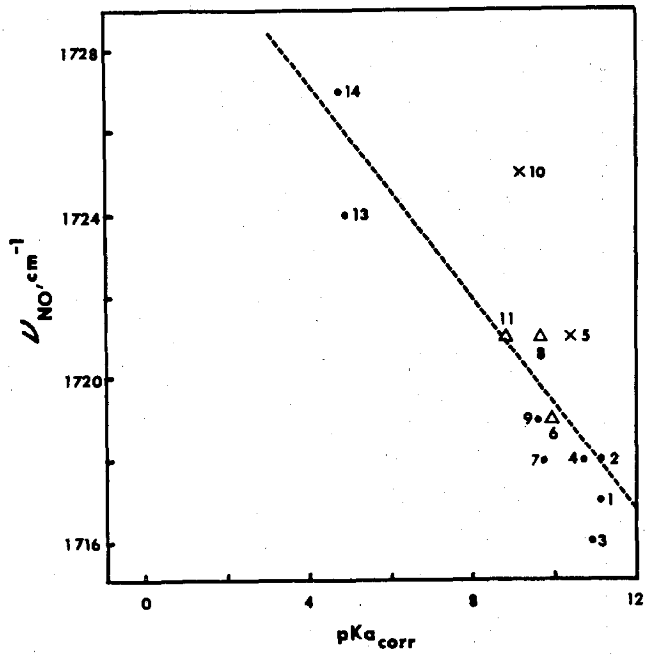


Figure 2. A plot of the N–O stretching frequency of $Fe(NO)(S_2CNRR')_2$ in $CHCl_3$ solution at room temperature vs. the corrected pK_a of $H_2NRR'^+$: ●, R,R′ = nonaryl; △, R = aryl, R′ = nonaryl; ×, R,R′ = aryl. The best linear fit of all the data obtained using the least-squares method is indicated by the dashed line. This line is drawn to indicate the trend of the data. Numbers refer to the identity of each complex as given in Table I.

pounds. The increase in pK_a and therefore the dtc ligand field strength results in a weakening of the N–O bond strength.

So, in a manner similar to $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ and $Fe(CO)_2(dtc)_2$, the increased importance of limiting resonance structure B results in increased iron back-bonding through the interaction of d orbitals on the iron and empty π^* molecular orbitals on the NO. The range of the observed NO stretching frequencies (1710–1730 cm^{-1}) is consistent with other five-coordinate "$\{FeNO\}^7$" complexes.[23]

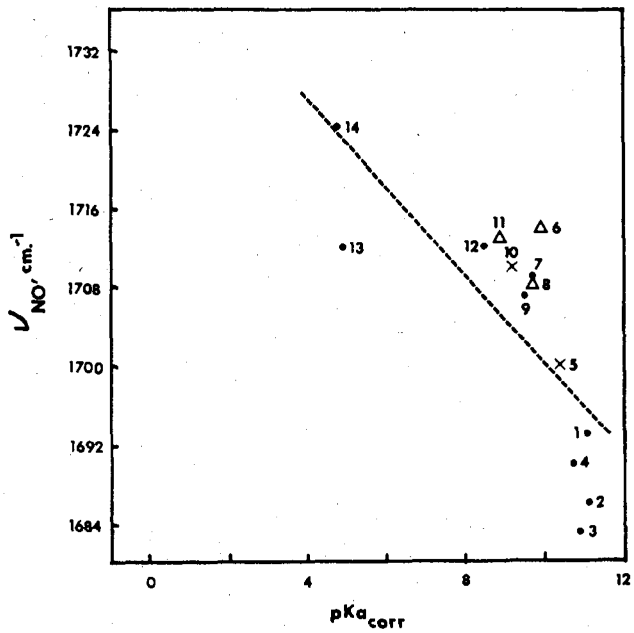


Figure 3. A plot of the N–O stretching frequency of $Fe(NO)(S_2CNRR')_2$ in Nujol mulls at room temperature vs. the corrected pK_a of $H_2NRR'^+$: ●, R,R′ = nonaryl; △, R = aryl, R′ = nonaryl; ×, R,R′ = aryl. The best fit of the data obtained using the least-squares method is indicated by the dashed line, drawn to indicate the trend of the data. Numbers refer to the identity of each complex as given in Table I.

Figure 2 indicates the importance of the methyl, methoxy and ethyl, ethoxy derivatives, whose parent secondary amines contain strong electron-withdrawing substituents ($H_2N(CH_3)OCH_3^+$, $pK_a = 4.75$;[25] $H_2N(C_2H_5)OC_2H_5^+$, $pK_a = 4.91$) which are without resonance effects. Hall[26] has reported that the aqueous pK_a of $H_2NRR'^+$ (where R and R′ are aliphatic substituents) could be calculated by the equation

$$pK_a = 12.13 - 3.23\sum\sigma^* \qquad (1)$$

where $\sum\sigma^*$ is the sum of the polar substituent constants of HNRR′. For $HN(CH_3)OCH_3$, with $\sigma^*_{CH_3} = 0.00$ and $\sigma^*_H = 0.49$, eq 1 gives the polar substituent constant $\sigma^*_{OCH_3} = 1.79$. While no value for $\sigma^*_{OCH_3}$ could be found in the literature, the two reported values of $\sigma^*_{CH_2OCH_3}$ are 0.520[27] and 0.66.[28] The reported attenuation factor of the inductive effect

$$\text{attenuation factor} = \sigma^*_{CH_2R}/\sigma^*_R \qquad (2)$$

by one methylene group is 0.34 ± 0.05,[29] which predicts $\sigma^*_{OCH_3}$ = 1.3–1.8 and 1.7–2.3, respectively. This alternate determination of $\sigma^*_{OCH_3}$ confirms the grouping together of N-alkoxyamines with the corresponding aliphatic secondary amines.

From the pK_a of $H_2N(C_2H_5)OC_2H_5^+$, eq 1 yields $\sigma^*_{OC_2H_5} = 1.85$.

Figure 3 exhibits a plot of ν_{NO} vs. corrected pK_a for Nujol mulls of these compounds. Although the absolute values of the NO stretching frequencies are shifted to lower values when compared to the solution data, the general trend of lower NO stretching frequencies with higher pK_a values remains. The parameter variations in solution and solid state are, therefore, comparable in this series of compounds. In particular, we will show correlations between solid-state Mössbauer measurements of isomer shifts and ΔE_Q and the corrected solution pK_a values for the $Fe(NO)(dtc)_2$ compounds (vide infra).

In contrast to the results of this paper, we have previously observed no correlation between the solid-state Mössbauer parameters (isomer shift and ΔE_Q) and the corrected aqueous

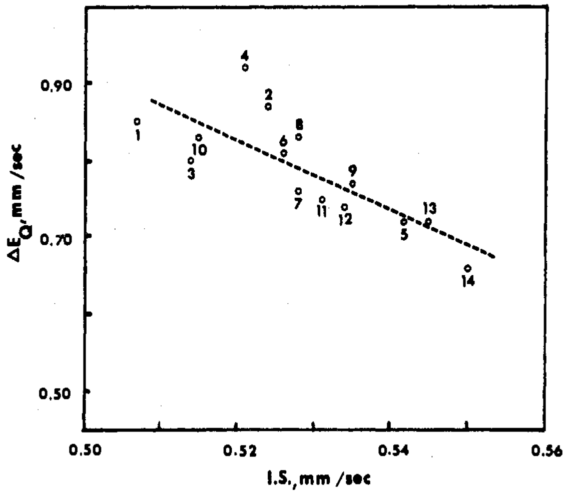


Figure 4. A plot of the ^{57}Fe quadrupole splitting (ΔE_Q) of Fe(NO)(S$_2$CNRR$'$)$_2$ vs. the isomer shift (IS) from room temperature, solid-state Mössbauer spectra. Numbers refer to the identity of each complex as given in Table I. The compounds labeled number 5 and 10 appear to violate the general trend of increasing pK_a(cor) as ΔE_Q decreases and the IS increases. These two compounds, however, are the R,R$'$ = Ph and R = Ph, R$'$ = 3Cl-Ph complexes which require the maximum correction in the determination of their pK_a(cor) values. The best linear fit of the data obtained using the least-squares method is indicated by the dashed line, drawn to indicate the trend of the data.

pK_a of the parent secondary amine of the dtc ligand in three other dithiocarbamate series [Fe(dtc)$_3$;[30] *cis*-Fe(CO)$_2$(dtc)$_2$;[19] and (η^5-C$_5$H$_5$)Fe(CO)(dtc)[19]]. In the carbonyls, the CO group is such a good π acceptor that it accepts any excess charge on the iron atom.[31] The lack of correlation between isomer shift and ΔE_Q and pK_a was therefore expected for both carbonyl series.

The Fe(dtc)$_3$ are spin-crossover compounds[14] in which the magnitude of the effective magnetic moment (μ_{eff}) depends on whether the sample is crystalline or in solution (e.g., Fe(S$_2$CNRR$'$)$_3$: for R = Et and R$'$ = Ph, μ_{eff}(solid) = 4.70 μ_B, μ_{eff}(solution) = 3.45 μ_B; for R = Me and R$'$ = Ph, μ_{eff}(solid) = 2.99 μ_B, μ_{eff}(solution) = 3.47 μ_B).[15] As expected, therefore, solution parameters (pK_a) and solid-state parameters (isomer shift and ΔE_Q) did not correlate. Correlations between the Mössbauer solid-state parameters and μ_{eff}(solid) were observed, however.[30]

Mössbauer Data. The room-temperature Mössbauer isomer shifts (IS) and quadrupole splittings (ΔE_Q) for the 14 Fe(NO)(dtc)$_2$ compounds are listed in Table I. The isomer shift is plotted vs. ΔE_Q in Figure 4, showing an approximately linear decline of the isomer shift as ΔE_Q increases. Upon comparison of the data points in Figure 4 with the corrected pK_a values (see Table I), one observes that the corrected pK_a tends to increase from right to left, i.e., the isomer shift decreases and ΔE_Q increases as the corrected pK_a increases.

The rather small trend in the isomer shift is indicative of increasing s-electron density on the iron nucleus as the dtc ligand field strength increases. The buildup of s-electron density with increased ligand field strength is consistent with the postulation that structure B is the one of higher field strength. As limiting resonance structure B becomes increasingly more important, one expects a flow of electron density from the ligand to the sulfurs and a corresponding increase in σ bonding from the sulfurs into the metal dsp^3 hybrid orbitals.[19] The isomer shift is known to be more sensitive to changes in 4s population than to p or d augmentation and a net decrease in the isomer shift is expected.[31,32] Further, the good π-acceptor strength of the NO ligand produces a greater delocalization of the d$_{xz}$,d$_{yz}$ electrons (assigning Fe–N as the z axis) as the dtc ligand field increases. The resultant decreased shielding by the d electrons allows the s electron density on the iron to increase and reinforces the effect caused by the dtc σ donation.

Johnson et al.[7] determined that the sign of the electric field gradient (efg) in Fe(NO)(S$_2$CNEt$_2$)$_2$ is positive by observing the Zeeman splitting of the quadrupole doublet lines in a large magnetic field at 1.8–4.2 K. They further deduced via measurements of the hyperfine fields that the unpaired electron occupied the d$_{z^2}$ orbital. Since an unpaired electron in the d$_{z^2}$ orbital gives a negative contribution to the efg, they concluded that the major contribution to the efg came from bonding electron inequalities and from the lattice.

An increase in ΔE_Q and, therefore, the magnitude of the efg accompanies the decrease in isomer shift with increasing ligand field strength of the dtc ligand (higher pK_a). The d component of the iron dsp^3 hybrid orbitals is d$_{x^2-y^2}$.[24] The σ donation from the sulfurs into hybrid orbitals with this d character will increase the positive efg value since d$_{x^2-y^2}$ gives a positive contribution to the efg.[33] The coincident backbonding into the NO π^* orbitals comes from the iron d$_{xz}$,d$_{yz}$ orbitals, both of which give a negative contribution to the efg.[33] The back-donation thus reduces this negative contribution and favors a more positive efg for higher ligand fields (high pK_a).[31] The measured increase in ΔE_Q with increased pK_a is therefore consistent with both increased σ donation from the sulfurs to the iron and increased back-donation from the iron to the NO ligand.

Finally, the Fe(NO)(dtc)$_2$ compounds exhibited the maximum ΔE_Q and minimum isomer shift for those dtc with high ligand field strength (high pK_a). These results are in accord with the Fe(dtc)$_3$ results which gave maximum ΔE_Q and minimum isomer shift for the low-spin high-field members of the series.[30]

EPR Data. The EPR g_{eff} values and the isotropic hyperfine coupling constants (A) are shown in Table I. Both g_{eff} and A have extreme values for R,R$'$ = Me,MeO and Et,EtO as do all the other parameters. A is plotted vs. the corrected pK_a value in Figure 5a. One notes a weak general downward trend of A with increasing pK_a (as shown by the least-squares fitted line). This trend may be explained in terms of current ideas on the position of the unpaired electron[2,6,7,9,34] which is generally believed to occupy the d$_{z^2}$ orbital. As the ligand field strength of the dtc ligand increases, the NO π^* orbitals become increasingly populated (see above). Increased d–π^* backbonding results in greater double bond character in the Fe–N bond which increases the coulombic repulsion between the dsp^3 hybrid orbital (into which the nitrogen lone pair electrons (from the NO ligand) are donated) and the d$_{z^2}$ Fe orbital. As a result, there is a shift of the d$_{z^2}$ electron density away from the NO ligand to the (vacant) sixth coordination position of the iron and this corresponds to the observed decrease in A and the decrease in g_{eff} (toward the free electron value, 2.0023) as the corrected pK_a of the dtc ligand increases. The latter occurs because as the d$_{z^2}$ orbital is increased in energy relative to the hybridized orbitals, the angular momentum of the unpaired electron is more effectively quenched.

A similar observation was made for Fe(NO)(S$_2$CNEt$_2$)$_2$ dissolved in 25 different solvents.[2] In this case, g_{eff} was correlated with the solvent parameter E_T (kcal/mol). It was found that as the solvent interaction increased, the unpaired electron density was shifted more toward the vacant sixth coordination position, destabilizing the d$_{z^2}$ orbital with an accompanying trend of the g_{eff} toward the free electron value. This interpretation is in accord with the EPR observations of this paper.

Summary

The three different spectroscopic probes (IR, Mössbauer, and EPR) provide data which are interpreted in terms of a

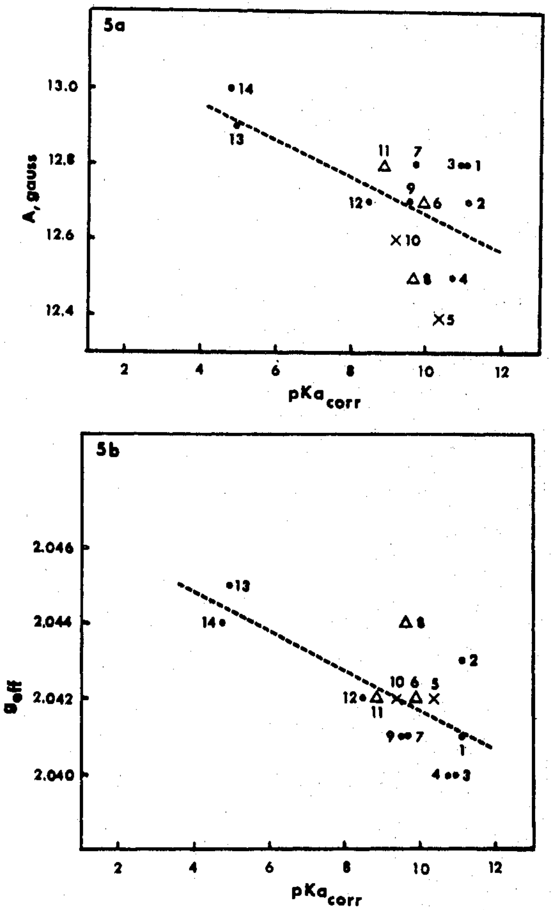


Figure 5. Plots of both the hyperfine splitting (a) and g_{eff} (b) of $Fe(NO)(S_2CNRR')_2$ vs. the corrected pK_a of $H_2NRR'^+$: ●, R,R′ = nonaryl; △, R = aryl, R′ = nonaryl; ×, R,R′ = aryl; from room temperature, $CHCl_3$ solution EPR spectra. The best linear fit of the data using the least-squares method is indicated by the dashed lines, drawn to indicate the trends of the data. Numbers refer to the identity of each complex as given in Table I.

bonding description which is internally consistent and in accord with earlier studies involving iron dithiocarbamates. We conclude the following: (1) the major property of the –NRR′ portion of the dithiocarbamate ligand is its "strong mesomeric electron-releasing effect"[16] which may be quantified by the pK_a of $H_2NRR'^+$ when R and R′ are alkyl substituents (or as corrected when R and/or R′ are phenyl substituents);[18] (2) limiting resonance form B is the high-field limiting resonance form and corresponds to high pK_a;[19] (3) greater relative importance of high field resonance form B corresponds to (a) more σ donation from S ligands into empty Fe dsp^3 hybrid orbitals (lower isomer shift, higher ΔE_Q), (b) more d–π^* back-bonding to the NO (higher ΔE_Q, lower ν_{NO}, lower isomer shift), (c) shorter Fe–N bond and, therefore, a greater coulombic repulsion between the lone pair on N (of the NO ligand) and the unpaired electron density in the d_{z^2} orbital (lower g_{eff}), and, (d) the greater probability of the unpaired electron density shifting away from N (lower A).

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Registry No. $Fe(NO)(S_2C(piperidine))_2$, 68000-88-4; $Fe(NO)(S_2C(pyrrolidine))_2$, 65703-90-4; $Fe(NO)(S_2CNEt_2)_2$, 36656-66-3; $Fe(NO)(S_2CNMe_2)_2$, 14263-11-7; $Fe(NO)(S_2CNPh_2)_2$, 67988-78-7; $Fe(NO)(S_2CN(Ph)(Et))_2$, 67988-79-8; $Fe(NO)(S_2CN(Bz)(Et))_2$, 67988-80-1; $Fe(NO)(S_2CN(Ph)(Me))_2$, 62637-78-9; $Fe(NO)(S_2CN(Bz)(Me))_2$, 67988-81-2; $Fe(NO)(S_2CN(Ph)(3\text{-}ClPh))_2$, 67988-82-3; $Fe(NO)(S_2CN(Bz)(Ph))_2$, 67988-83-4; $Fe(NO)(S_2C(morpholine))_2$, 67988-84-5; $Fe(NO)(S_2CN(Et)(OEt))_2$, 67988-85-6; $Fe(NO)(S_2CN(Me)(OMe))_2$, 67988-86-7.

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