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(Diorganodithiocarbamato)iron Complexes. Effect of Organic Substituents

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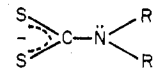
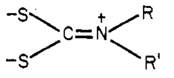
A series of $Fe(CO)_2(S_2CNRR')_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ complexes have been prepared, where R and R′ are organic substituents, both aliphatic and aromatic. The Mössbauer, infrared, and (for the second series) proton NMR spectra have been determined. For each series the ^{57}Fe Mössbauer parameters are essentially constant when R and R′ are varied. In contrast, the CO force constants (k_{CO}) in each series exhibit a linear dependence on the aqueous pK_a values of $H_2NRR'^+$ for the separate cases of R = R′ = alkyl, R = alkyl, R′ = aryl, and R = R′ = aryl. This separation into three groups is explained by the resonance, base-weakening effect of phenyl substituents in aqueous solutions of amines. Examination of the ^1H NMR of $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ and the literature x-ray structure of $Fe(S_2CN(C_2H_5)(C_6H_5))_3$ suggest that this resonance base-weakening effect does not take place in coordinated dithiocarbamates. When the resonance base-weakening effect of the phenyl substituents is taken into account, a single linear dependence of k_{CO} on pK_a is observed. These results indicate that inductive effects of R and R′ play a major role in the bonding of these carbonyls of iron dithiocarbamates. Furthermore, the aryl resonance base-weakening effect considerations allow a reinterpretation of the solution magnetic moment vs. pK_a data in the $Fe(S_2CNRR')_3$ series.

Introduction

Since the early 1930s it has been known[1] that the dithiocarbamates of iron(III) [$Fe(dtc)_3$, dtc = $S_2CNRR'^-$, where R and R′ are organic substituents] exhibit magnetic moments (μ_{eff}) intermediate between the high-spin (μ_{eff} = 5.9 μ_B) and low-spin ($\mu_{eff} \simeq 2\ \mu_B$) states for d^5 complexes in octahedral symmetry. The exact value of the magnetic moment depends, in part, on the identity of R and R′. The intermediate magnetic moments, both in the solid state and in solution, are believed to arise from an equilibrium involving iron atoms in these two different electronic configurations.[2-4] The ligand itself may be described as a resonance hybrid with two limiting resonance structures (A and B) being the major contributors to the description of the bonding. The variation of the intermediate magnetic moment value with changing R and R′ is taken to indicate that the relative contribution of structures A and B to the resonance hybrid depends on the identity of R and R′. One explanation[5] has proposed that R and R′ affect the ligand field strength according to the steric requirements of the substituents and has assigned form A above as the low ligand field form of the ligand. A second explanation has proposed that the effect of the organic groups is inductive.[6] An extension of this explanation by Eley, Myers, and Duffy[7] proposed that the inductive effect may be quantified by use of the aqueous pK_a of the protonated form of the parent secondary amine (pK_a of $H_2NRR'^+$). Eley et al. assigned form A above as the high ligand field form. This assignment was shown to be incorrect by a temperature-dependent structure determination of $Fe(S_2CN(C_2H_5)_2)_3$.[8] The data of Eley et al.[7] were reinterpreted by Chant et al.[9] who reported that the incorporation of an aryl group displaces the pK_a of the free amine to lower values and proposed that such dithiocarbamates of iron(III) are subject to the "exceptional π-mesomeric effects", such as limiting resonance form C.



A



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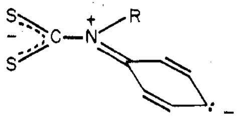

C

This study concentrates on the nature of these "exceptional π-mesomeric effects" when R and/or R′ are aryl. Two series of complexes, *cis*-$Fe(CO)_2(dtc)_2$ (hereafter called the dicarbonyls) and $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$ (hereafter the monocarbonyls), were prepared and studied by various spectroscopic techniques. In addition $Fe(S_2CNCH_3(OCH_3))_3$ was prepared and its measured properties support a reinterpretation of the $Fe(dtc)_3$ data suggested by measurements presented herein for the dicarbonyls and monocarbonyls.

Experimental Section

The dicarbonyl complexes were prepared by two different routes (A and B). Synthesis A was the previously published synthetic method of Büttner and Feltham.[10] In this method the sodium salt of the dithiocarbamate ligand was prepared by the method of Delepine[11] and von Braun[12] (updated by Akerström)[13] if both substituents were aliphatic or by the method of Semon[14] if one or more substituents were aromatic. This sodium dithiocarbamate was then added to an acetone solution of ferrous sulfate, and carbon monoxide was bubbled through to form the desired product.

Synthetic route B involved first the preparation of the desired bis(diorganothiocarbamoyl) disulfide ($[RR'NC(S)S-]_2$) by published methods.[14] This compound was then added to stoichiometric amounts of triiron dodecacarbonyl ($Fe_3(CO)_{12}$) (3:1 ratio) also prepared according to a published method.[15] The mixture was refluxed in absolute ethanol for about 20 min until the solution was observed to change color from the green of the reactants to the brown or black of the products. The solution was cooled and the product isolated as a solid (sometimes partial removal of solvent was necessary). Table I shows in part the method used to prepare each of these compounds.

Table I. Infrared and Mössbauer Spectral Parameters of *cis*-$Fe(CO)_2(S_2CNRR')_2$ at Room Temperature

Organo substituents R	Organo substituents R′	Prepn meth[a]	pK_a[b]	CO str freq,[c] cm^{-1}	CO force const,[d] mdyn $Å^{-1}$ k_{cis}[e]	CO force const,[d] mdyn $Å^{-1}$ k_{int}	δ,[f] mm/s	ΔE_Q,[g] mm/s
pip		A	11.12[h]	2029.2, 1976.2	16.200	0.429	0.33	0.36
pyrr		B	11.11[h]	2030.0, 1976.3	16.207	0.436	--[i]	--[i]
2,6-Me_2pip		A	10.99[j]	2027.4, 1973.8	16.166	0.433	0.33	0.37
Et	Et	B	10.93[k]	--[l]	--[l]	--[l]	0.32	0.38
Me	Me	A, B	10.73[k]	2031.0, 1977.9	16.228	0.430	0.32	0.36
Bz	Et	B	9.68[m]	2031.2, 1978.0	16.230	0.431	0.32	0.30
Bz	Bz	B	8.52[h]	2033.2, 1990.2	16.344	0.439	--[i]	--[i]
morph		A	8.49[h]	2034.3, 1981.6	16.285	0.427	0.33	0.35
Ph	Et	B	5.11[n]	2029.3, 1976.0	16.199	0.431	0.35	0.45
Ph	Me	B	4.85[n]	2030.1, 1977.0	16.213	0.430	0.34	0.42
Bz	Ph	B	4.04[o]	2030.4, 1977.8	16.222	0.426	--[p]	--[p]
Ph	Ph	B	0.78[q]	2028.7, 1976.9	16.201	0.419	0.34	0.42
Ph	3-ClPh	B	−0.45[r]	2032.2, 1980.2	16.256	0.422	0.36	0.39

[a] Key: A, ref 10; B, this work, see text. [b] Aqueous pK_a of parent secondary amine, HNRR′. [c] CCl_4 solution. [d] Calculated according to ref 20. [e] Approximate error limits, ±0.003 mdyn/Å. [f] With reference to sodium nitroprusside, ±0.01 mm/s. [g] ±0.01 mm/s. [h] J. J. Christensen, R. M. Izatt, D. P. Wrothall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969). [i] Spectrum showed three peaks. [j] H. K. Hall, Jr., *J. Am. Chem. Soc.*, 79, 5444 (1957). [k] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, 54, 3469 (1932). [l] Three stretching frequencies noted: 2049.4, 2029.9; 1976.0. If the last two are presumed to be the cis CO stretches, the force constant is 16.204 mdyn/Å. [m] W. H. Carothers, C. F. Bickford, and G. J. Hurwitz, *J. Am. Chem. Soc.*, 49, 2908 (1927). [n] M. G. Gireault-Vexlearschi, *Bull. Soc. Chim. Fr.* 589 (1956). [o] E. Folkers and O. Runquist, *J. Org. Chem.*, 29, 830 (1964). [p] No usable spectrum obtained. [q] M. A. Paul, *J. Am. Chem. Soc.*, 76, 3236 (1954). [r] D. Dolman and R. Stewart, *Can. J. Chem.*, 45, 903 (1967).

Table II. Infrared, Proton NMR, and Mössbauer Spectral Parameters of $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ at Room Temperature

Organo substituents R	Organo substituents R′	Mp,[a] °C	pK_a[b]	CO str freq,[c] cm^{-1}	δ of C_5H_5 ^1H,[d] ppm	δ,[e] mm/s	ΔE_Q,[f] mm/s
n-Bu	*n*-Bu	Oil	11.25[g]	1933.5	4.378	--	--
pip		149–150	11.12[h]	1933.8	4.378	0.50	1.79
Et	Et	96–98	10.93[i]	1934.2	4.380	0.50	1.80
Me	Me	145–150	10.73[i]	1935.2	4.380	0.51	1.81
Bz	Et	82–85	9.68[j]	1935.9	4.413	0.52	1.89
Bz	Me	82–86	9.58[j]	1937.0	4.417	0.51	1.86
Bz	Bz	118–120	8.52[h]	1937.5	4.465	0.52	1.89
morph		132	8.49[h]	1937.6	4.412	0.51	1.79
Me	*p*-tol	130–135	5.33[i]	1935.8	4.477	0.51	1.84
Et	Ph	110–111	5.11[g]	1936.2	4.477	0.51	1.82
Me	Ph	126–128	4.85[g]	1935.9	4.487	0.51	1.81
Bz	Ph	100–105	4.04[k]	1937.2	4.412	0.50	1.80
Ph	Ph	194–196	0.79[l]	1937.9	4.393	0.50	1.80

[a] Uncorrected. [b] Aqueous pK_a of parent secondary amine, HNRR′. [c] CH_2Cl_2 solution approximate error limits ±0.5 cm^{-1}. [d] CS_2 solution. [e] With reference to sodium nitroprusside, ±0.01 mm/s. [f] ±0.01 mm/s. [g] M. G. Gireault-Vexlearschi, *Bull. Soc. Chim. Fr.*, 589 (1956). [h] J. J. Christensen, R. M. Izatt, D. P. Wrotholl, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969). [i] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932). [j] W. H. Carothers, C. F. Bickford, and G. J. Hurwitz, *ibid.*, 49, 2908 (1927). [k] R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966). [l] M. A. Paul, *J. Am. Chem. Soc.*, **76**, 3236 (1954).

The monocarbonyls were all prepared by the oxidation of dicyclopentadienyltetracarbonyldiiron(I) ($(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$) (Pressure Chemical Co.) by the appropriate bis(diorganothiocarbamoyl) disulfide[12–14] in cyclohexane or benzene using the method reported by Cotton and McCleverty.[6]

The compound $Fe[S_2CN(CH_3)(OCH_3)]_3$ was prepared by the method outlined by White et al.[16] The parent secondary amine was purchased as the hydrochloride from the Aldrich Chemical Co.

Satisfactory elemental analyses were obtained for all compounds reported in this study. Analyses of the dicarbonyls and the $Fe(S_2CNCH_3(OCH_3))_3$ complex were performed by Chemalytics, Tempe, Ariz., or Par-Alexander, South Daytona, Fla. The monocarbonyl compounds were analyzed by Galbraith Laboratories, Knoxville, Tenn.

Infrared spectra were recorded on the Perkin-Elmer 521 grating infrared spectrophotometer using an expanded abscissa feature. The spectra of the dicarbonyl compounds were recorded in carbon tetrachloride solution, those of the monocarbonyl compounds in dichloromethane solution.

Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer at an operating temperature of 35 °C and tetramethylsilane was used as the internal standard. All spectra were recorded for carbon disulfide solutions.

Solution magnetic moments were measured by the NMR method[17] using a Varian A60 NMR spectrometer at an operating temperature of 35 °C. Measurements were made in solution of 5% (v/v) Me_4Si in chloroform. A reference compound, $Fe[S_2CN(CH_3)_2]_3$, was prepared and its magnetic moment determined in the same manner; the result agreed with the literature value (4.19 μ_B).[7]

Solid magnetic measurements were made using a Faraday apparatus with a recording electrobalance which is commercially available from the Cahn Instrument Co. Solid $Hg[Co(SCN)_4]$ was used as the standard and measurements were repeated at two different field strengths. The error in the values reported here is estimated to be less than ±0.10 μ_B.

The Mössbauer spectra were obtained using a standard constant acceleration spectrometer[18] with a ^{57}Co source in a copper or palladium matrix. The instrument, calibration procedures, and treatment of data have been described previously.[19] The Mössbauer data of this paper are for the solid and were taken at room temperature.

Melting points for the monocarbonyl compounds were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The dicarbonyl compounds do not melt below 250 °C.

Results and Discussion

(a) $Fe(CO)_2(dtc)_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)dtc$. Table I lists the carbonyl stretching frequencies, calculated C–O bond force constant,[20] and Mössbauer parameters for the 13 dicarbonyl compounds successfully prepared in this work.

Table II similarly lists melting points, infrared stretching frequency, proton NMR resonance for the C_5H_5 ring, and Mössbauer parameters for the monocarbonyl complexes. As these complexes exhibited only one carbonyl stretching frequency, it was unnecessary to calculate C–O bond force

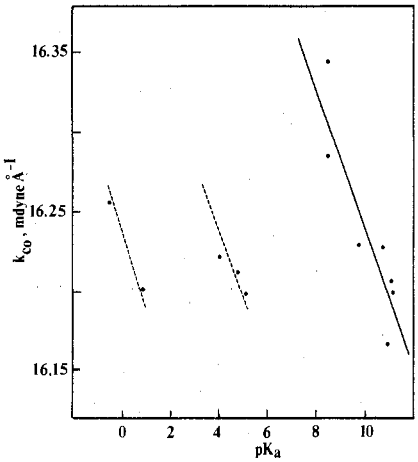

Figure 1. C–O stretch force constants for *cis*-$Fe(CO)_2(S_2CNRR')_2$ in CCl_4 solution at room temperature as a function of the aqueous pK_a of HNRR′.

constants for the monocarbonyl complexes.

Cotton and McCleverty[6] had originally proposed that the function of the –NRR′ group in the dtc ligand was that of a strong electron donor. Research on the general effects of substituents on redox potentials may be rationalized in terms of the electron-releasing or -withdrawing characteristics of the R group at nitrogen.[9,21,22] Eley et al.[7] postulated that the amount of this electron donation may be quantified by use of the aqueous pK_a of the protonated form of the parent secondary amine.

Leipoldt and Coppens[8] have demonstrated that limiting resonance form B is the higher field form of the ligand. Of the two limiting resonance structures, A and B, B is the form that can be associated with a highly basic nitrogen center. As the nitrogen atom donates more electron density toward the CS_2 end of the ligand, one would expect more electron density to be donated to the iron center. Note that in neither series of complexes is there an appreciable buildup of electron density on the nucleus because the isomer shift (δ) in each series is independent of the ligands. (See Tables I and II.) It is therefore reasonable to expect that as electron density is donated by the ligand this density flows through the iron center and into the carbonyl π^* (antibonding) orbitals, lowering the C–O bond force constant and, therefore, the C–O stretching frequency. (In the case of the monocarbonyls, electron density is also directed into vacant orbitals on the cyclopentadienyl ligand.) Thus, one would expect that an amine with a high pK_a value would give a carbonyl-substituted dithiocarbamate complex with a lowered C–O bond strength. Figures 1 and 2 confirm this expectation. These are plots of the C–O bond force constant vs. pK_a for the dicarbonyls and the C–O stretching frequency vs. pK_a for the monocarbonyls, respectively.

Both Figure 1 and Figure 2 show that the relationship between pK_a and the measure of C–O bond strength is not completely linear but, rather, divided into three distinct regions. (A similar division into three regions is obtained if one plots pK_a vs. the proton NMR chemical shift of the cyclopentadienyl protons.) The three lines in Figure 1 are described by (from right to left) (1) those compounds where neither R nor R′ is aromatic, (2) those compounds where R is aromatic but R′ is not, and (3) those compounds where both R and R′ are aromatic. Figure 2 shows the same separation by substituents, where the single point at the left is the point R = R′ = phenyl. In both Figure 1 and Figure 2 the rightmost solid line is a least-squares fit of a straight line to the non-phenyl-containing points. The other line or lines have been drawn parallel to this line but through the respective groups of points.

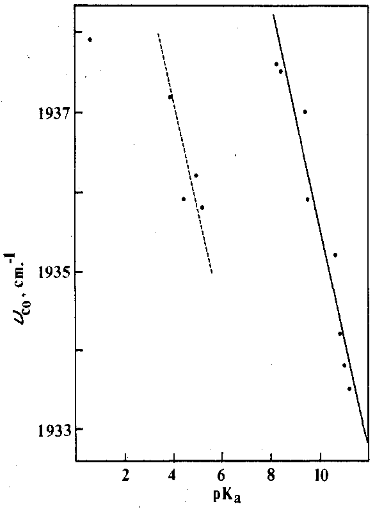

Figure 2. C–O stretching frequency of $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNRR')$ in CH_2Cl_2 solution at room temperature as a function of aqueous pK_a of HNRR′.

Table III

Compd	Chemical shifts of phenyl protons, ppm
$PhNH_2$	6.457, 7.008, 6.619[a,b]
$PhNH(CH_3)$	6.434, 7.042, 6.578[a,b]
$PhN(CH_3)_2$	6.590, 7.085, 6.598[a,b]
$[PhN^+(CH_3)_3]I^-$	7.979, 7.658, 7.604[a,c]
$(Ph(CH_3)NCS_2)Fe(CO)Cp$	7.26_7–7.14_7[d,e]
$(Ph(C_2H_5)NCS_2)Fe(CO)Cp$	7.36_0–6.99_0[d,e]
$(Ph_2NCS_2)Fe(CO)Cp$	7.18_7[d]

[a] S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, **51**, 5205 (1967); ortho, meta, para, respectively. [b] 10% w/w CCl_4 solution. [c] 15% w/w CH_3OH solution. [d] CS_2 solution. [e] Poorly resolved multiplet.

This separation into three groups can be attributed to the phenyl substituent(s) bonded directly to the nitrogen. The exact effect of replacing a nonaromatic group with a phenyl group in amines has been discussed by Condon.[23] After a detailed consideration of the effect of the phenyl group in substituted anilines, Condon estimated that the overall base-weakening effect of phenyl–nitrogen conjugation in anilines is 4–6 pK_a units. If one could show that resonance structures like C made little or no contribution to the description of the bonding in phenyl-containing dithiocarbamates, then one could compute a "corrected pK_a" for the parent secondary amine which would omit the contribution of phenyl–nitrogen conjugation in the amine.

There are two different types of evidence which show that resonance structures such as C are of little importance in the description of the bonding in the dithiocarbamate ligand. First, Hoskins and Kelly[24] have reported that in the x-ray crystal structure of $Fe(S_2CN(CH_3)(C_6H_5))_3$ the phenyl rings are twisted an average of 67° out of the S_2C–NC_2 plane, thus preventing the planarity required in extended conjugated systems such as limiting resonance form C. This evidence is, of course, for the solid state.

Second, in any phenyl-containing compound in which there is a marked difference in the amount of electron density which is resident upon the three distinguishable positions of the ring (ortho, meta, para), one would expect the proton NMR spectrum of the phenyl ring to show three distinct, separable peaks. In the case of a phenyl ring where there is no large difference in the amount of charge resident on the various positions, the three signals should be either close to each other or merge into one signal. The data in Table III will help clarify this point.

In the first three entries in Table III, the chemical shifts of the phenyl ring protons of the aniline and *N*-methylaniline derivatives are significantly separated (0.5–0.6 ppm). These large spectral separations are due to contributions from resonance forms in which there is a double bond between the nitrogen and the phenyl ring and in which there is a negative charge localized on either the ortho or para position in the phenyl ring. The fourth entry, *N,N,N*-trimethylanilinium iodide (with no resonance[25] involving nitrogen to phenyl double bond formation), has a substantially smaller difference of the chemical shifts (~0.37 ppm) for the phenyl ring protons and demonstrates also a substantial shift to higher values of δ.

The last three entries of Table III are compounds of the type of interest here, phenyl-containing dithiocarbamate complexes. If resonance forms such as C are of importance in describing the bonding in these complexes, one would expect a spread of δ values like those found for aniline and *N*-methylanilines. If resonance forms such as C are not of importance in describing the bonding in these complexes, then one would expect a much smaller difference in δ values. The data support the interpretation that resonance forms such as C are comparatively unimportant in the description of the bonding of these complexes. The chemical shift values found for the *N*-methyl, *N*-phenyl derivative are separated by 0.12 ppm, those for the *N*-ethyl, *N*-phenyl derivative are separated by 0.37 ppm, and the spectrum of the diphenyl derivative reveals a single sharp peak. The evidence for these iron(II) complexes is particularly important, since it supports the interpretation that resonance forms such as C do not figure significantly in the dithiocarbamates even in solution.

These proton NMR data are not subject to the same criticisms as the x-ray structure determination of the tris-*N*-methyl, *N*-phenyl derivative in the solid state, namely, that there are unknown variations between the solid state and solution and between an Fe(III) bonded to three dithiocarbamate ligands and an Fe(II) bonded to one dithiocarbamate ligand. It is clear that these two sets of data mutually reinforce each other, showing that neither in the solid state nor in solution are resonance forms such as C important in describing the bonding of the dithiocarbamate ligand. This contradicts the proposal by Chant et al.[9] that four aryl substituent anomalies in their correlation of $(\mu_{\mathrm{eff}}(\mathrm{soln}))^2$ and oxidation potentials of 20 iron(III) dithiocarbamates could be explained on the basis that "such dithiocarbamates are subject to exceptional π mesomeric effects." It should be noted that one of these anomalies was the dibenzyl derivative which has no direct nitrogen–aryl bond and which may not participate in resonance forms such as C. Since resonance forms such as C are of little importance in the overall bonding of the dtc ligand to iron(II) or -(III), the aqueous pK_a values appearing in Tables I and II and used in Figures 1 and 2 must be modified to separate out the base-weakening effects of these resonance forms. As noted earlier, Condon[23] estimated the overall base weakening effect of phenyl nitrogen conjugation to be 4–6 pK_a units. The data in Figure 1 lead us to estimate this effect to be 4.8 pK_a units per phenyl substituent. Replotting Figures 1 and 2 with these corrected pK_a values yields Figures 3 and 4.

Figures 3 and 4 show that, for both $\mathrm{Fe(CO)_2(dtc)_2}$ and $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)dtc}$, an increase in the p$K_a$ of the parent secondary amine in the dithiocarbamate ligand results in a weaker CO bond in a carbonyl bonded to the iron.

The variation of the chemical shift of the cyclopentadienyl proton of $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)dtc}$ as a function of these corrected pK_a values is in accord with this interpretation.

(b) Fe(dtc)$_3$. In an earlier study,[7] the solution magnetic moments of the tris(diorganodithiocarbamato)iron(III) complexes were interpreted as a function of the aqueous pK_a of parent secondary amine. The initial interpretation of increasing magnetic moments with increasing pK_a was questioned by Chant et al.[9] on the basis of the effect of phenyl substituents.

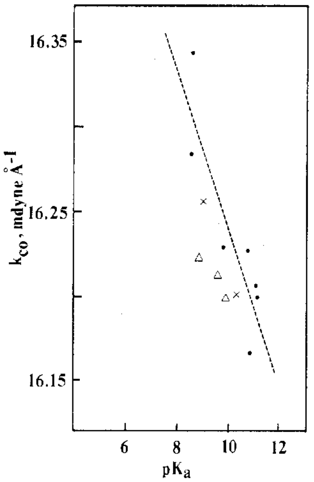

Figure 3. C–O stretch force constants for *cis*-$\mathrm{Fe(CO)_2(S_2CNRR')_2}$ in $\mathrm{CCl_4}$ solution at room temperature as a function of corrected aqueous pK_a of HNRR′: ●, R,R′ = nonaryl; Δ, R = aryl, R′ = nonaryl; ×, R,R′ = aryl.

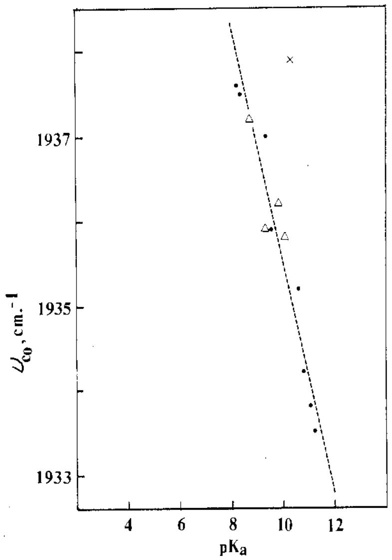

Figure 4. C–O stretching frequency of $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)(S_2CNRR')}$ in $\mathrm{CH_2Cl_2}$ solution at room temperature as a function of corrected aqueous pK_a of HNRR′: ●, R,R′ = nonaryl; Δ, R = aryl, R′ = nonaryl; ×, R,R′ = aryl.

Although these are Fe(III) complexes with three coordinated dithiocarbamate ligands, one may correct for the base-weakening effect of phenyl nitrogen conjugation which appears in the amine but not in the ligand. If the correction factor (4.8 pK_a units per phenyl group) is applied to the amine basicities, one may use these corrected basicities to plot Figure 5. This figure indicates that in the "spin-crossover" region, increasing pK_a corresponds to decreasing solution magnetic moment.

Additional support of this interpretation (increasing pK_a decreases $\mu_{\mathrm{eff}}(\mathrm{sol})$) is indicated by the compound $\mathrm{Fe(S_2CN(CH_3)(OCH_3))_3}$. Its parent secondary amine does not contain an N-bonded phenyl substituent and it has a low pK_a value (4.75).[26] The solution magnetic moment of this iron(III) complex is 5.36 μ_B, close to the high-spin limit for a d^5 system. This value fits well with the reinterpretation of the earlier data[7] and supports the idea of μ_B approaching the high-spin limit

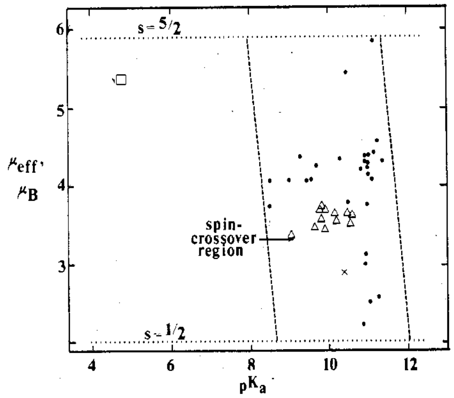

Figure 5. Solution magnetic moments of $Fe(S_2CNRR')_3$ in $CHCl_3$ or C_6H_6 solution at room temperature as a function of corrected aqueous pK_a of HNRR′: ●, R,R′ = nonaryl; Δ, R = aryl, R′ = nonaryl; ×, R,R′ = aryl; □, R = CH_3, R′ = OCH_3.

at low pK_a values of the parent secondary amine.

The solid magnetic moment (μ = 5.34 μ_B) and room temperature isomer shift (δ = 0.664 mm/s) for $Fe(S_2CN(CH_3)(OCH_3))_3$ correlate well with earlier data[19] and show that it is a normal $Fe(dtc)_3$.

The large scatter of data points in the spin-transition region shown in Figure 5 is probably due to second-order effects caused by steric interaction of the R and R′ groups. A fair correlation of E_s (Hammett's steric parameter)[27] with solution magnetic moment is taken as an indication that steric factors may be a major second-order effect. Attempts to fit an equation of the type $\mu_{eff} = A + B(pK_a) + C(E_s)$ were inconclusive for lack of E_s data for such heterocycles as pyrrolidine.

The steric explanation of Martin et al.,[5] however, cannot accommodate the compound $Fe(S_2CN(CH_3)(OCH_3))_3$. The solution magnetic moment of this compound is close to that of steric group I[5] (μ_{eff} = 5.8 ± 0.1 μ_B, NRR′ is a small strained ring) and substantially greater than steric group II (μ_{eff} = 4.3 ± 0.2 μ_B, R and R′ are *n*-alkyl groups).

Conclusions

The results of this study are consistent with or reaffirm the following generalizations concerning iron dithiocarbamates. (1) A major function of the –NRR′ portion of the dithiocarbamate ligand is its "strong mesomeric electron-releasing effect";[6] (2) In describing the iron dithiocarbamate coordination in terms of two limiting resonance forms (see above), limiting resonance form B is the high ligand field form. (3) The mesomeric electron-releasing ability of the nitrogen lone pair may be quantified by the pK_a of $H_2NRR'^+$ when R and R′ are alkyl. (4) Nitrogen–phenyl conjugation, which substantially lowers the aqueous pK_a of phenyl amines, is insignificant in coordinated phenyl dithiocarbamates; (5) When this absence of nitrogen–phenyl conjugation is corrected for, the relationship described in three applies to dithiocarbamates in general.

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Registry No. *cis*-$Fe(CO)_2(S_2CNpip)$, 35816-66-1; *cis*-$Fe(CO)_2(S_2CNpyrr)$, 63989-14-0; *cis*-$Fe(CO)_2(S_2CN(2,6\text{-}Me_2pip))$, 63796-67-8; *cis*-$Fe(CO)_2(S_2CNEt_2)$, 36309-90-7; *cis*-$Fe(CO)_2(S_2CNMe_2)$, 36309-89-4; *cis*-$Fe(CO)_2(S_2CNBzEt)$, 63796-64-5; *cis*-$Fe(CO)_2(S_2CNBz_2)$, 63989-15-1; *cis*-$Fe(CO)_2(S_2CNmorph)$, 63796-66-7; *cis*-$Fe(CO)_2(S_2CNPhEt)$, 63796-69-0; *cis*-$Fe(CO)_2(S_2CNPhMe)$, 63796-70-3; *cis*-$Fe(CO)_2(S_2CNBzPh)$, 63989-00-4; *cis*-$Fe(CO)_2(S_2CNPh_2)$, 63796-68-9; *cis*-$Fe(CO)_2(S_2CNPh(3\text{-}ClPh))$, 63989-01-5; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CN(n\text{-}Bu)_2)$, 63989-02-6; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNpip)$, 63989-03-7; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNEt_2)$, 63989-04-8; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNMe_2)$, 12128-65-3; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNBzEt)$, 63989-05-9; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNBzMe)$, 63989-06-0; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNBz_2)$, 63989-07-1; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNmorph)$, 63989-08-2; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNMe(p\text{-}tol))$, 63989-09-3; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNEtPh)$, 63989-10-6; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNMePh)$, 63989-11-7; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNBzPh)$, 63989-12-8; $(\eta^5\text{-}C_5H_5)Fe(CO)(S_2CNPh_2)$, 63989-13-9; $Fe[S_2CN(CH_3)(OCH_3)]_3$, 60282-50-0.

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