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Multinuclear NMR of *cis*-Dicarbonylbis(dithiocarbamato)iron(II) Complexes in Chloroform Solution

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Abstract

The ^{13}C and ^{15}N NMR spectra of eleven *cis*-$Fe(S_2CNRR')_2(CO)_2$ complexes, where R and R′ are organic substituents, have been measured at ambient temperature in $CDCl_3$ (0.08–0.16 M). The ^{13}C absorptions for the carbonyl ligands correlate well with the force constants for the CO stretching vibrations in $CHCl_3$ solution. Each of the parameters (^{13}CO absorption and k_{cis} for CO) correlate well with the aqueous solution pK_a for $^+H_2NRR'$, corrected for the phenyl-containing substituents, high pK_a values corresponding to high ^{13}CO absorptions and low k_{cis} CO force constants.

Evidence was found in the ^{13}C NMR spectra for hindered rotation about the C–N bond in $S_2C{-}NC_2$ in complexes with higher p$K_{a(corr)}$ values and in the ^{13}C spectra of the corresponding thiuram disulfides.

The ^{15}N (natural abundance) NMR spectra for each of the complexes was determined. Each revealed a single sharp absorption in a region of the ^{15}N NMR spectrum which indicates substantial C–N double bond character, as one would expect for coordinated dithiocarbamate ligands.

Introduction

The *cis*-dicarbonylbis(diorganodithiocarbamato)iron(II) complexes, $Fe(S_2CNRR')_2(CO)_2$ (where R and R′ are organic substituents), were first prepared by Cotton and McCleverty [1] who reported the preparation and infrared spectrum of the dimethyl derivative. Several other derivatives have been prepared by a variety of methods [2–5]. An early crystal structure of the piperidyl derivative (NRR′ = piperidine) revealed [2] *cis* carbonyls (C–Fe–C: 92(1)°) and nearly planar S_2CNC_2 fragments coordinated to an iron in a roughly octahedral environment distorted by a limited ligand 'bite'. Infrared [1, 3–5] and ^{1}H NMR [3] spectra are in accord with this geometry in solution.

Zimmerman *et al.* [4] reported a correlation between the CO stretching force constant (CCl_4 solution) and the aqueous pK_a of the protonated secondary amine ($H_2NRR'^+$), corrected for phenyl substituents (*vide infra*). It was argued that the effect of the NRR′ group was primarily inductive in this series of compounds and the greater the pK_a of the $H_2NRR'^+$, the greater the importance of the $^{2-}S_2C{=}N^+RR'$ resonance form of the coordinated dithiocarbamate ligand. The greater ligand field strength of the dithiocarbamate ligand increased electron density on the Fe, resulting in increased backbonding (d–π*) to the coordinated carbonyls, lowering the CO stretching force constant, according to their interpretation [4].

This diamagnetic series of iron complexes provides an attractive system to investigate iron–dithiocarbamate bonding using multinuclear (^{1}H, ^{13}C and ^{15}N) NMR techniques. These results may further elucidate the bonding in the more complex, spin-crossover iron(III) system, $Fe(S_2CNRR')_3$, in which the ligand field strength of the coordinated dithiocarbamate ligand is influenced by inductive and a variety of steric effects [6–10].

Experimental

All compounds were prepared as previously described [4] and gave satisfactory elemental (C, H, N) analyses (Microanalytical Service, Chemistry Department, University of Queensland).

NMR

^{13}C spectra were measured in $CDCl_3$ solution (0.05–0.23 M) at ambient temperature using a JEOL FX-100 NMR spectrometer with complete proton decoupling. Results are reported in ppm with reference to an internal TMS standard.

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TABLE I. ^{13}C Parameters for $Fe(S_2CNRR')_2(CO)_2$ in $CDCl_3$[a]

NRR'	^{13}CO	$^{13}CS_2$	N-^{13}C	Other ^{13}C absorptions
2,6-Dimethylpiperidyl	213.04	206.28	49.45, 48.87	29.45, 19.49, 13.96
Piperidyl	212.77	204.82	47.30, 46.72	25.25, 24.06
R = Et, R' = Bz	212.73	207.44	51.60, 51.02 Bz; 43.51, 43.07 Et	134.89, 134.76, 128.82, 128.00 Bz; 12.00 Et
R,R' = Me	212.70	206.79	38.56, 38.19	
R,R = Et	212.64	205.38	43.49, 43.05	12.23
R = Et, R' = Ph	212.60	208.77	142.85, 140.29 Ph; 47.71, 47.30 Et	129.67, 128.68, 128.27, 127.86, 120.83 Ph; 12.69 Et
R,R' = Bz	212.49	208.84	50.67, 50.09	140.70, 134.45, 130.39, 129.54, 128.96, 128.21
R = Me, R' = Ph[b]	212.42	209.25	143.97, 142.13, 140.01, Ph; 48.18, 40.37 Me	129.98, 129.64, 128.48, 127.25, 126.50, 122.98
R,R' = Ph	212.22	211.23	141.62	129.50, 128.21, 127.63
Morpholino	212.08	206.59	66.06	46.41, 46.93
R = Ph, R' = 3ClPh	211.88	211.67	142.44, 141.17	134.96, 130.42, 129.71, 128.58, 128.41, 127.76, 125.92

[a] ppm; TMS reference; conc. 0.08–0.15 M; room temperature. [b] Probable contamination by $(S_2CNMePh)_2$.

^{15}N spectra (natural abundance) were measured in $CDCl_3$ solution (0.10–0.16 M) in 10 mm diameter tubes at ambient temperature using a JEOL GX-400 NMR spectrometer. A relaxation agent (0.10 M $Cr(acac)_3$) was added to each sample and results are reported in ppm with reference to a 2.5 M solution of $(^{15}NH_4)_2SO_4$ in 1 M H_2SO_4 in a 1.7 mm coaxial capillary. Overnight accumulation (about 22 000 scans) was required.

IR

Infrared spectra were measured using a Mattson SIRIUS 100 FT-IR spectrophotometer using the peak-pick option. Spectra were measured at ambient temperature in $CHCl_3$ solution (0.008–0.010 M).

Results and Discussion

Table I lists the ^{13}C NMR parameters for eleven members of the series $Fe(CO)_2(S_2CNRR')_2$. The ^{13}CO chemical shifts are in the expected region of the spectrum [11] and show a dependence on the organic substituents of the dithiocarbamate ligand (*vide infra*). The $^{13}CS_2$ chemical shifts are in the expected region [12–14] and are 1–3 ppm greater than the corresponding d^6 system $Co(S_2CNRR')_3$ [12]. The ^{13}C NMR of eight of the eleven corresponding thiuram disulfides indicates a 12–14 ppm increase in chemical shift of the $^{13}CS_2$ on oxidation and coordination (Table II).

The ^1H NMR of the dimethyl and diethyl derivatives of $Fe(CO)_2(S_2CNRR')_2$ in $CDCl_3$ revealed nonequivalence of the organic substituents [3], indicative of hindered rotation about the $S_2C{-}NC_2$ fragment [15, 16]. As shown in Table I, two ^{13}C absorptions for carbons α to the N for each different R substituent was found for each $Fe(CO)_2(S_2CNRR')_2$ at room temperature in $CDCl_3$ except the diphenyl; phenyl, *m*-chlorophenyl, phenyl, methyl (*vide infra*) and morpholine derivatives. Similar results were found for the corresponding thiuram disulfides Table II). These splittings are taken as evidence of hindered rotation about the $S_2C{-}NRR'$ fragment and this is further supported by similar splitting of ^{13}C signals more distant from the nitrogen.

A few spectra require comment – slightly broadened, split ^{13}C absorptions were noted for Et_4tds (tds = $NC(S)S_2C(S)N$), α-C: 52.01 and 47.60 ppm; β-C: 13.45 and 11.47 ppm. Van Gaal *et al.* reported single absorptions: α-C: 49.2 ppm; β-C: 12.0 ppm under similar conditions [14]. Proton NMR of Et_4tds indicate [15, 17] a coalescence temperature for the $-N{-}CH_2-$ proton resonances of 10 °C and, at 30 °C, the methyl chemical shift has been reduced to only one signal without detectable fine structure. At lower temperatures (–20 °C), this rotation is frozen out on the NMR time scale.

In general, the reduced, coordinated ligand, $^-S_2CNRR'$, exhibits N-^{13}C absorptions at 6.4–7.3 ppm less than the corresponding tds when R and/or R' = Me, Et or Bz, except in the case of the methyl

TABLE II. ^{13}C Parameters for $(S_2CNRR')_2$ in $CDCl_3$ [a]

NRR'	$^{13}CS_2$	N-^{13}C	Other ^{13}C absorptions
Piperidyl	192.63	53.71[b]	26.07, 26.00, 24.19
R,R' = Me	193.66	47.50[c], 42.01[c]	
R,R' = Et	192.63	52.01[c], 47.60[c]	13.45, 11.47[c]
R = Et, R' = Ph	195.12	142.20 Ph; 54.80 Et	129.81, 129.60, 128.24 Ph; 11.67 Et
R,R' = Bz	196.22	58.97[c], 54.91[c]	134.76, 134.25, 128.92, 127.76[c]
R = Me, R' = Ph	195.60	143.97 Ph; 48.05 Me	129.91, 129.50, 127.22
Morpholino	193.79	66.37	52.82[c]
R = Ph, R' = 3ClPh	197.31	146.46, 144.24	135.00, 130.49, 129.88, 129.09 128.58, 127.97, 125.95

[a] ppm; TMS reference; conc. 0.05–0.23 M; room temperature. [b] Broadened considerably. [c] Slightly broadened.

TABLE III. CO Stretching Frequencies and Force Constants for $Fe(S_2CNRR')_2(CO)_2$ [a]

NRR'	CO stretching frequencies (cm^{-1})	k_{cis} [b] (mdyne/Å)	pK_a [c]
2,6-Dimethylpiperidyl	2022.9, 1966.1	16.068	10.99
Piperidyl	2025.6, 1969.2	16.144	11.12
R = Et, R' = Bz	2026.9, 1971.3	16.142	9.68
R,R' = Me	2027.7, 1971.9	16.153	10.73
R,R' = Et	2028.6, 1973.7	16.175	10.93
R = Et, R' = Ph	2026.4, 1970.7	16.133	5.11
R,R' = Bz	2028.6, 1973.7	16.175	8.52
R = Me, R' = Ph	2027.5, 1972.2	16.154	4.85
R,R' = Ph	2027.4, 1972.9	16.158	0.78
Morpholino	2030.4, 1975.7	16.205	8.49
R = Ph, R' = 3ClPh	2029.7, 1976.1	16.203	−0.45

[a] $CHCl_3$, +/−0.1 cm^{-1}, room temperature, conc. 0.008–0.010 M. [b] Calculated using equations from ref. 23. [c] See ref. 4 and refs. therein.

signal for $Fe(CO)_2(S_2CNMePh)_2$ (decrease of 3.8 ppm). The splitting of these α-^{13}C signals for these $Fe(CO)_2(S_2NRR')_2$ complexes is 0.37–0.58 ppm except in the case of the methyl signal for $Fe(CO)_2(S_2CNMePh)_2$ (splitting 7.81 ppm). These factors, in addition to the suspicious three α-^{13}C phenyl signals, suggest that the sample of $Fe(CO)_2(S_2CNMePh)_2$ is contaminated with $(S_2CNMePh)_2$ in spite of the satisfactory elemental analysis results and no measurable peak for the $^{13}CS_2$ for $(S_2CNMePh)_2$ being observed.

Table III reports the CO stretching frequencies and force constants ($CHCl_3$ solution) for $Fe(CO)_2(S_2CNRR')_2$. The order of compounds in Table I (decreasing ^{13}CO) is maintained in Table III. Also listed in Table III are the pK_a values for the protonated form of the parent secondary amine ($^+H_2NRR'$). Figure 1 shows a plot of the CO force constant in $CHCl_3$ solution *versus* $pK_{a(corr)}$ (4.8 pK_a units added for each N-phenyl substituent) [4]. These results are quite comparable to those obtained by Zimmerman *et al.* [4] for the same compounds in CCl_4 solution. The force constants in $CHCl_3$ are 0.04–0.10 mdyne/Å lower than in CCl_4 solution. (The CO stretching frequencies reported by Zimmerman *et al.* for $Fe(CO)_2S_2CNBz_2)_2$ in CCl_4 are incorrect; the corrected results are: CO stretching frequencies, 2033.2, 1980.2; k_{cis}, 16.264 mdyne/Å; k_{int}, 0.430 mdyne/Å).

Figure 2 shows a plot of ^{13}CO absorptions (from Table I) *versus* $pK_{a(corr)}$ of $^+H_2NRR'$. A correlation similar to Fig. 1 is observed; the higher the $pK_{a(corr)}$, the greater the ^{13}CO NMR absorption. This result is not unexpected since ^{13}CO NMR chemical shifts and carbonyl force constants are inversely correlated in series of substituted metal carbonyls [18].

These NMR results support the conclusions reached by Zimmerman *et al.* [4] concerning the relative importance of two limiting resonance structures

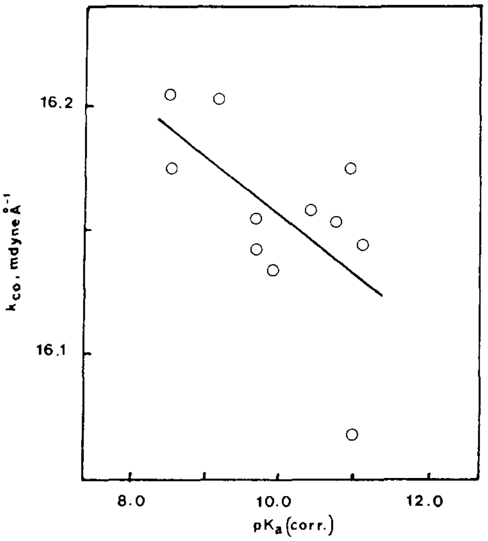


Fig. 1. CO stretch force constants for *cis*-$Fe(CO)_2(S_2CNRR')_2$ in $CHCl_3$ solution at room temperature as a function of the corrected aqueous pK_a of $H_2NRR'^+$.

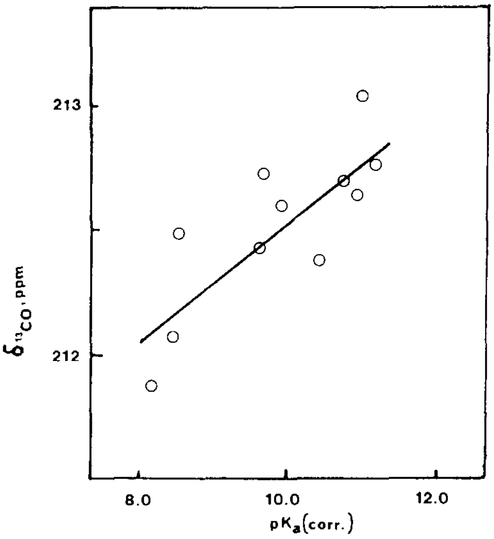
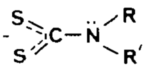


Fig. 2. ^{13}CO chemical shift (reference TMS) for *cis*-$Fe(CO)_2(S_2CNRR')_2$ in $CDCl_3$ solution at room temperature as a function of the corrected aqueous pK_a of $H_2NRR'^+$.



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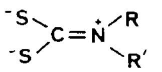
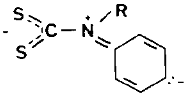


B

in describing the bonding in these Fe(II) dithiocarbamates. In this series of Fe(II) complexes, it appears that inductive effects within the dithiocarbamate ligand are important to the overall bonding within the complex and, as proposed by Cotton and McCleverty [1], the function of the –NRR′ group in the dithiocarbamate ligand was that of a strong electron donor.

The greater the basicity of the lone pair on the N (as measured by the aqueous pK_a of $^+H_2NRR'$), the greater the importance of limiting resonance structure B in describing the bonding of the complex, the greater the C–N double bond character, the greater the formal charge on the S atoms. Whether limiting resonance structure B is the high-field form (because of the strong electron donation to the Fe) [4] or the low-field form (because of the reduced capacity of the S to participate in dπ–dπ backbonding from the Fe because of the increased negative charge on the S) [7] is moot; either explanation will result in an increased dπ–π* backbonding from Fe to the C of the CO, yielding low CO force constants and high ^{13}CO chemical shifts. As postulated by Zimmerman *et al.* the pK_a of $^+H_2NRR'$ must be corrected for the proposed absence of the base-weakening limiting resonance structure



of N-phenyl secondary amines in aqueous solution. The similarity of the *ortho*-, *meta*-, and *para*-^{13}C chemical shifts in $Fe(CO)_2(S_2CNPh_2)_2$ appears to support this contention.

It is significant to note that hindered rotation about the S_2C–NRR′ bond is observed only for δ $^{13}CO > 212.49$ ppm and correspondingly higher $pK_{a(corr)}$ values. This is taken as substantial indication of the relative importance of the inductive effects of R and R′ in the overall bonding of these $Fe(CO)_2(S_2CNRR')_2$.

Table IV reports the ^{15}N NMR chemical shifts (natural abundance) for this series of compounds.

TABLE IV. ^{15}N Parameters for $Fe(S_2CNRR')_2(CO)_2$ in $CDCl_3$[a]

NRR′	^{15}N (ppm)[b]	pK_a[c]
2,6-Dimethylpiperidyl	160.0	10.99
Piperidyl	144.3	11.12
R = Et, R′ = Bz	148.1	9.68
R,R′ = Me	122.5	10.73
R,R′ = Et	150.0	10.93
R = Et, R′ = Ph	154.9	5.11
R,R′ = Bz	146.7	8.52
R = Me, R′ = Ph	137.7[d]	4.85
R,R′ = Ph	158.9	0.78
Morpholino	133.6	8.49
R = Ph, R′ = 3ClPh	156.6	−0.45

[a] $CDCl_3$ solution, 0.10–0.16 M, 0.10+/−0.01 M $Cr(acac)_3$ added, room temperature. [b] Reference: 2.5 M $(^{15}NH_4)_2SO_4$ in 1 M H_2SO_4. [c] See ref. 4 and refs. therein. [d] Poor spectrum, apparent decomposition with the appearance of a second peak at 140.1 ppm.

The addition of the relaxation agent, Cr(acac)$_3$, does result in an δ ^{15}N shift of about 3.5 ppm to lower shielding [19], but this shift should be approximately constant for the results in Table IV. The chemical shifts are in a region of the ^{15}N spectrum appropriate for a N with partial double 'iminium' character [20]. The ^{15}N spectra for the methyl ester of the dimethyl and diethyl dithiocarbamates have been reported: −244.3 and −215.8 ppm respectively (3 M, CDCl$_3$, CH$_3$NO$_2$ reference) [21]. Converted to (^{15}NH$_4$)$_2$SO$_4$ reference, these values are comparable (113.8 and 142.3 ppm, respectively) to the results reported in Table IV. No correlation between ^{15}N chemical shifts and ^{13}CO chemical shifts, CO force constants or pK_a values is observed, since the organic substituents, R and R′, will also affect the ^{15}N chemical shifts [22].

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