$Cd(1,3-PDTA)^{2-}$ because a five-membered chelate ring is formed in $Cd(EDTA)^{2-}$.

Conclusions

If the noncoordinated nitrogen atom of a partially dissociated complex of a multidentate ligand of the EDTA type inverts (IV → V in Figure 4) at least once before it rebonds to the metal (IV → III), an AB pattern for the acetate methylenic protons is indicative of inert metal–nitrogen bonding, as has been assumed.[2] If, however, the noncoordinated nitrogen atom rebonds to the metal before at least one inversion occurs, an AB pattern can result due to the slowness of the nitrogen atom inversion even when the metal–nitrogen bonding is labile. The rate at which the noncoordinated nitrogen atom rebonds to the metal depends, on the basis of previous studies of complexation reactions of multidentate ligands, in part at least on the size of the

chelate ring formed. The previous studies suggest that, for the cadmium and zinc complexes of 1,3-PDTA, the rate of metal–nitrogen bond formation in IV is sufficiently less than the rate of noncoordinated nitrogen atom inversion so that the average lifetimes of the acetate methylenic protons before AB interchange are a measure of the rates of partial dissociation of these complexes.

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES, KENSINGTON, NEW SOUTH WALES, AUSTRALIA, THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA, NEDLANDS, WESTERN AUSTRALIA, AND THE DEPARTMENT OF CHEMISTRY, VICTORIA UNIVERSITY OF WELLINGTON, NEW ZEALAND

Temperature Dependence of the Proton Nuclear Magnetic Resonance Spectra of Some Diamagnetic N,N-Dialkyldithiocarbamate Complexes of Transition Metals

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Unusual structure and temperature dependent behavior of the proton nmr spectrum in a number of diamagnetic N,N-dialkyldithiocarbamate complexes of di- and trivalent transition metal ions, $[M(CS_2NR_2)_n]$, $n = 2, 3$ may be accounted for by a total line-shape analysis in terms of an appropriate and general two-proton exchange model using a density matrix formalism. This has been done in detail for a limited range of basic, well-defined, simple, and representative members of the above series, using the diethyl-, di-n-propyl-, diisopropyl-, diisobutyl-, and dibenzyldithiocarbamates of nickel(II) and cobalt(III). Where possible a tentative physical interpretation of the model is given.

Introduction

During studies of the temperature dependence of the proton nmr spectra of a variety of paramagnetic N,N-dialkyldithiocarbamate derivatives of trivalent transition metals, $[M(CS_2NR_2)_3]$,[2,3] the spectra of a range of diamagnetic analogs were determined to provide chemical shift references. In the latter, the protons near the nitrogen exhibit well-defined multiplets, some of which exhibit anomalies in structure and temperature dependence and worthy of independent study: the results are reported here, a range of di- and trivalent metals and alkyl substituents being selected which yield spectra which are well-defined, basic, and typical of the series in general. [A variety of work has recently appeared in the literature (1971) on a range of organic dialkyldithiocarbamate esters (Lemire and Thompson),[4,5] the thiuram disulfides (Wil-

son),[6] and a number of cobalt(III) dialkyldithiocarbamate derivatives (Siddall).[7] We refer to these in the Discussion.]

Experimental Section

Sodium salts of the N,N-dialkyldithiocarbamate anion, $CS_2^--NR_2$, are usually prepared by reacting the appropriate secondary amine with sodium hydroxide and carbon disulfide in stoichiometric amounts in ethanolic solution (the dithiocarbamate being usually formed in preference to the xanthate, CS_2^--OR)

$$Na^+OH^- + CS_2 + R_2NH \longrightarrow Na^+CS_2^-NR_2 + H_2O$$
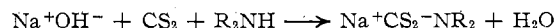
The salt is formed as a powder or crystals and may be recrystallized from ether–ethanol; neutral coordination complexes may then be made by the addition of an aqueous solution of the sodium salt to an aqueous solution of the appropriate di- or trivalent metal ion. The filtered and dried complex may be recrystallized from chloroform–ethanol. Using this basic method, a wide range of simple dialkyldithiocarbamate derivatives was prepared for a number of transition metals, namely, (i) $[M(CS_2-NR_2)_2]$ (M = Ni(II), Pd(II), Pt(II), Zn(II), Cd(II), and Hg(II)) and (ii) $[M(CS_2NR_2)_3]$ (M = Co(III), Rh(III), and Ir(III)). All of these complexes are diamagnetic and were made for the following ligand substituents: R = methyl, ethyl, n-propyl, n-butyl, n-amyl (*i.e.*, $CH_3-CH_2-CH_2R$), isopropyl, sec-butyl ($-CHR_2$, $-CHRR'$), isobutyl ($-CH_2-CHR_2$), and benzyl ($-CH_2-C_6H_5$). The compounds are air stable, soluble and monomeric in chloroform solution, easily prepared, and well characterized

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(2) R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, **45**, 2688 (1966); R. M. Golding, W. C. Tennant, J. P. M. Bailey, and A. Hudson, *ibid.*, **48**, 764 (1968).

(3) R. M. Golding, P. C. Healy, P. Newman, E. Sinn, W. C. Tennant, and A. H. White, *ibid.*, **52**, 3105 (1970).

(4) A. E. Lemire and J. C. Thompson, *Can. J. Chem.*, **48**, 824 (1970).

(5) A. E. Lemire and J. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 1163 (1971).

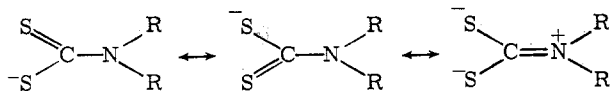(6) N. K. Wilson, *J. Phys. Chem.*, **75**, 1067 (1971).

(7) T. H. Siddall, *Inorg. Nucl. Chem. Lett.*, **7**, 545 (1971).

generically if not specifically (see the review of Coucouvanis for further references).[8]

Results

Proton nmr spectra of these derivatives at 60 MHz were obtained in CDCl$_3$ solution on a Varian A60 spectrometer with variable temperature probe (calibrated with methanol) in the range −60 to +60°. The multiplet of the proton group adjacent to the nitrogen is well-defined and is the feature of greatest interest according to the variations in structure and temperature dependence exhibited. The above range of compounds is large and there are many similarities in the system which make it possible to give a general description in terms of a number of restricted series which, with only minor variations in detail, are typical of the remainder. Among the alkyl groups above we describe only those members whose behavior is the simple archetype of each series. The divalent metals are describable in terms of the behavior of the nickel(II) complexes, and the trivalent metals likewise in terms of the cobalt(III) series.

The Spectra of the Nickel(II) and Cobalt(III) Complexes.—

In these derivatives all of the data at hand indicate that the planar ligand chelates through the two sulfur atoms, these being equivalent by virtue of extensive conjugation

$$\overset{S}{\underset{-S}{\diagup}}C{-}N\overset{R}{\underset{R}{\diagdown}} \leftrightarrow \overset{-S}{\underset{S}{\diagup}}C{-}N\overset{R}{\underset{R}{\diagdown}} \leftrightarrow \overset{S}{\underset{-S}{\diagup}}C{=}\overset{+}{N}\overset{R}{\underset{R}{\diagdown}}$$

The geometry of the complexes, with the exception of the outer atoms of the substituent, is a good approximation to D_{2h} in the nickel derivatives, or D_3 in the cobalt derivatives, the latter having *d* and *l* forms possible.

The spectra of the nickel(II) diethyl, di-*n*-propyl, diisobutyl, and dibenzyl derivatives are "normal," not markedly temperature dependent, and will not be discussed further. For reference, the spectra of the *N*-methylene protons are given in Figure 1, the spectral archetypes in the above cases being A$_2$X$_3$, A$_2$X$_2$, A$_2$X, and A$_2$, respectively. Chemical shifts are given in Table I.

TABLE I
60-MHz PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS[a]

R		a	b	c	J_{ab}	J_{bc}
Ethyl		−218	−75		7.3	
n-Propyl		−218	−98	−56	7.5	7.3
Isobutyl		−204	−132	−55	7.3	6.4
Benzyl		−284	−440			
Isopropyl	38°	−271	−84		7.3	
	−51°	$\begin{cases} −305 \\ −237 \end{cases}$	$\begin{cases} −97 \\ −74 \end{cases}$			

[a] σ_i and J_{ij} are in sec^{-1}, for the bis(*N,N*-dialkyldithiocarbamato)nickel(II) derivatives, [Ni(CS$_2$NR$_2$)$_2$]. The protons are denoted a, b, and c in order of increasing distance from the nitrogen atom. All chemical shifts are relative to tetramethylsilane and with the exception of the last entry are temperature independent in the range studied.

The 60° spectrum of the nickel(II) diisopropyl derivative is the usual septet–doublet combination characteristic of the AX$_6$ system. However, as the temperature is lowered, the fine structure collapses and toward −50°, two distinct sets of doublets and
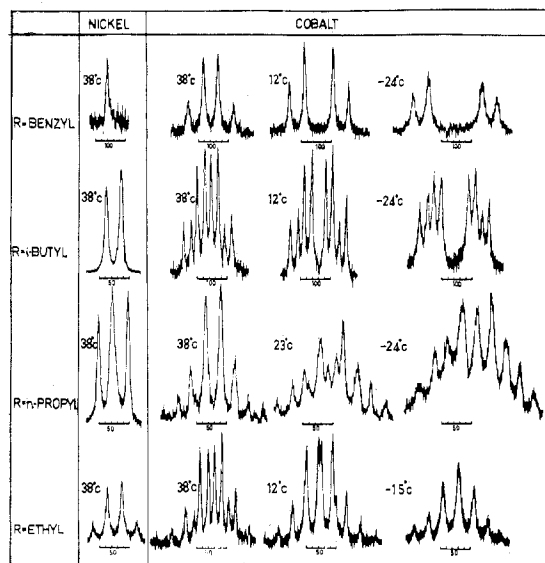
(8) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

Figure 1a.—Proton nmr spectra for a variety of dialkyldithiocarbamate complexes of nickel [(Ni(CS$_2$NR$_2$)$_2$)] and cobalt [(Co(CS$_2$NR$_2$)$_3$] illustrating the temperature dependence of the multiplet generated by the methylene protons adjacent to the nitrogen atom in the ligand. Chemical shifts in hertz.
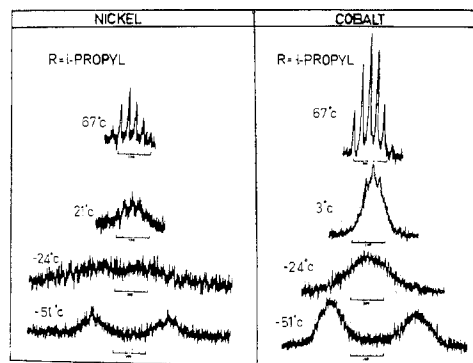

Figure 1b.—Proton nmr spectra of diisopropyldithiocarbamate complexes of nickel [Ni(CS$_2$N(CH(CH$_3$)$_2$)$_2$)$_2$] and cobalt [Co(CS$_2$N(CH(CH$_3$)$_2$)$_2$)$_3$], showing the temperature dependence of the multiplet for the proton on the carbon adjacent to the nitrogen atom in the ligand.

septets emerge. The cobalt(III) diisopropyl analog behaves similarly but at −50°, the two emergent sets of peaks are unresolved into multiplets and appear to be of unequal intensity. The spectra of these two derivatives are given in Figure 1.

In the cobalt(III) diethyl, di-*n*-propyl, diisobutyl, and dibenzyl derivatives, the chemical shifts of the protons of the *N*-methylene groups are nonequivalent, the difference exhibiting a strong temperature dependence (Figure 1). Nonequivalence is typical of methylene groups attached to asymmetric centers; basically their spectra are of the types ABX$_3$, ABX$_2$, ABX, and AB, respectively. However, it is unusual to find chemical shift differences attributable to this cause of the magnitude found here; moreover, the pronounced temperature dependence is unusual and the likely mechanism is probably not as simple as this. The spectral characteristics are summarized in Table II.

The dimethyl derivatives of both nickel(II) and cobalt(III) are normal in behavior, a tempeature independent singlet being found. At low temperatures

TABLE II

MULTIPLET CHEMICAL SHIFT DIFFERENCES (δ) AT
TEMPERATURES (°K) FOR THE
TRIS(N,N-DIALKYLDITHIOCARBAMATO)COBALT(III) COMPLEXES[a]

Temp, K	Ethyl ABX$_3$ spectrum	n-Propyl ABX$_2$ spectrum	Isobutyl ABX spectrum	Benzyl AB spectrum
222				91.7
231		28.8	55.2	81.6
240		27.3	51.1	74.5
249		26.0	46.4	67.3
258	18.5	24.2	42.2	59.1
267	17.6	22.5	38.5	52.9
275	16.6	20.9	36.4	46.6
285	15.3		32.1	41.9
294	14.1	18.3	28.8	36.0
302.5	13.1		26.0	30.5
311	12.6	16.3	24.2	26.0
E^{act}	~0	~0	~0	~0
ΔE	~75	~75	~250	~250

[a] The derived energy parameters E^{act} and ΔE ($= E_M - E_N$) are both in cm^{-1}. In all cases $J_{AB} \approx 14$ sec^{-1} and $J_{AX} = J_{BX} \approx 7.5$ sec^{-1}.
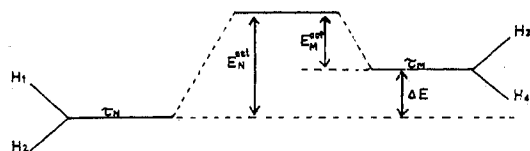

Figure 2.—Energy level scheme for the proton exchange mechanism discussed in the text.

these and many of the above spectra are badly resolved because of insolubility and/or solvent viscosity.

Theory

The calculation of the temperature dependence of nmr line shapes due to exchange mechanisms is well documented and clearly understood in terms of quantum mechanical principles, using either the treatment *via* the modified Bloch equations or the density matrix formalism which, in the slow passage limit, yields a series of linear algebraic simultaneous equations normally soluble by computer.[9] The absorption intensity at any frequency ω is derived from the imaginary part of the total magnetic moment. A general model of the latter type has been found appropriate to the spectra described above and is now discussed.

We consider the situation of a proton pair undergoing simultaneous exchange through a potential barrier between two sites of energy E_M and E_N, the mean lifetime in each state being τ_M and τ_N, respectively, as depicted in Figure 2 where site N has the lower energy. For the passage of the proton pair from site N to site M we postulate a potential barrier E_N^{act} and, for the reverse process E_M^{act}. Assuming a Boltzmann distribution, the fractional populations of sites M and N are

$$P_M = \tau_M/(\tau_M + \tau_N); \quad P_N = \tau_N/(\tau_M + \tau_N) \quad (1)$$

where

$$\tau_M = \tau_N \exp(-\Delta E/RT) \text{ and } \Delta E = E_M - E_N$$

The wave functions appropriate to the system are of

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959; R. M. Golding in "Physical Chemistry," Vol. 4, Academic Press, New York, N. Y., 1970; J. D. Swalen, *Progr. Nucl. Magn. Resonance Spectros.*, **1**, 205 (1966); C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

the form $|I_M{}^1 I_M{}^2 I_N{}^3 I_N{}^4\rangle$; the effect of an appropriate exchange operator R can be represented as

$$|I_M{}^1 I_M{}^2 I_N{}^3 I_N{}^4\rangle \xrightarrow{R} |I_M{}^3 I_M{}^4 I_N{}^1 I_N{}^2\rangle \quad (2)$$

For protons, the values appropriate to $I_M{}^n$, $I_N{}^n$ are $\pm^1/_2$; denoting $|^1/_2\rangle = \alpha$, $|-^1/_2\rangle = \beta$, we may write 16 possible wave functions for the system

$$\psi_1 = |\alpha\alpha\alpha\alpha\rangle \quad \psi_5 = |\alpha\beta\alpha\alpha\rangle \quad \psi_9 = |\beta\alpha\alpha\alpha\rangle \quad \psi_{13} = |\beta\beta\alpha\alpha\rangle$$

$$\psi_2 = |\alpha\alpha\alpha\beta\rangle \quad \psi_6 = |\alpha\beta\alpha\beta\rangle \quad \psi_{10} = |\beta\alpha\alpha\beta\rangle \quad \psi_{14} = |\beta\beta\alpha\beta\rangle$$

$$\psi_3 = |\alpha\alpha\beta\alpha\rangle \quad \psi_7 = |\alpha\beta\beta\alpha\rangle \quad \psi_{11} = |\beta\alpha\beta\alpha\rangle \quad \psi_{15} = |\beta\beta\beta\alpha\rangle$$

$$\psi_4 = |\alpha\alpha\beta\beta\rangle \quad \psi_8 = |\alpha\beta\beta\beta\rangle \quad \psi_{12} = |\beta\alpha\beta\beta\rangle \quad \psi_{16} = |\beta\beta\beta\beta\rangle$$

The nonzero matrix elements of R, $R_{ij} = \langle\psi_i|R|\psi_j\rangle$, are then: $R_{1,2} = R_{2,5} = R_{3,9} = R_{9,3} = R_{4,13} = R_{13,4} = R_{6,6} = R_{7,10} = R_{8,14} = R_{14,8} = R_{11,11} = R_{12,15} = R_{15,12} = R_{16,16} = 1$.

The description of the system before exchange can be expressed using the density matrix formalism as

$$i\hbar\dot\rho = [\mathbf{H},\rho]$$

$$= (\mathbf{H}\rho - \rho\mathbf{H}) \quad (3)$$

$\mathbf{H}$ is the Hamiltonian matrix of the system and ρ the density matrix. To allow for the effect of exchange, a term of the form $\dot\rho = (R\rho R - \rho)/\tau$ is included in (3), which becomes

$$\dot\rho = (R\rho R - \rho)/\tau + (i/\hbar)[\mathbf{H},\rho] \quad (4)$$

Assuming the proton pair in each of the alternative site occupancies to be magnetically nonequivalent, and that spin–spin coupling is only possible within the pair we have

$$J_{12}, J_{34} \neq 0, J_{23} = J_{24} = J_{13} = J_{14} = 0$$

and the Hamiltonian operator $\mathcal{3C}$ has the form

$$\mathcal{3C} = \sum_{i=j}^{4} [-(\omega_i - \omega)I_z{}^i - \gamma_i H'(I_x{}^i)] + $$

$$2\pi[J_{12}(I^1 \cdot I^2) + J_{34}(I^3 \cdot I^4)] \quad (5)$$

Here $\gamma_i = (2\pi/h)g_N\beta_N(1 - \sigma^i)$, $\omega_i = \gamma_i H$, and H is the applied magnetic field (sec^{-1}), H' the applied radio frequency, $\omega = 2\pi\nu$ the angular frequency, and σ^i the chemical shift of the ith proton.

Calculation of the Hamiltonian matrix, $\mathbf{H} = \langle\psi_i|\mathcal{3C}|\psi_j\rangle$, followed by substitution in (4) and the assumption of "steady-state" condition ($\dot\rho = 0$) yields 120 complex simultaneous linear equations in the 120 unknown density matrix elements. Of these only eight obey the selection rule $\Delta M_I = \pm 1$

$$(\rho_{1,5} - \rho_{1,2})/\tau + i(\omega_4 - \omega)\rho_{1,2} + i\pi J_{34}(\rho_{1,3} - \rho_{1,2}) - $$
$$\rho_{1,2}/T_2 - i\gamma_4 H'(\rho_{1,1} - \rho_{2,2})P_M = 0$$

$$(\rho_{1,9} - \rho_{1,3})/\tau + i(\omega_3 - \omega)\rho_{1,3} + i\pi J_{34}(\rho_{1,2} - \rho_{1,3}) - $$
$$\rho_{1,3}/T_2 - i\gamma_3 H'(\rho_{1,1} - \rho_{3,3})P_M = 0$$

$$(\rho_{5,13} - \rho_{2,4})/\tau + i(\omega_3 - \omega)\rho_{2,4} + i\pi J_{34}(\rho_{2,4} - \rho_{3,4}) - $$
$$\rho_{2,4}/T_2 - i\gamma_3 H'(\rho_{2,2} - \rho_{4,4})P_M = 0$$

$$(\rho_{9,13} - \rho_{3,4})/\tau + i(\omega_4 - \omega)\rho_{3,4} + i\pi J_{34}(\rho_{3,4} - \rho_{2,4}) - $$
$$\rho_{3,4}/T_2 - i\gamma_4 H'(\rho_{3,3} - \rho_{4,4})P_M = 0$$

$$(\rho_{1,2} - \rho_{1,5})/\tau + i(\omega_2 - \omega)\rho_{1,5} + i\pi J_{12}(\rho_{1,9} - \rho_{1,5}) - $$
$$\rho_{1,5}/T_2 - i\gamma_2 H'(\rho_{1,1} - \rho_{5,5})P_N = 0$$

$$(\rho_{1,3} - \rho_{1,9})/\tau + i(\omega_1 - \omega)\rho_{1,9} + i\pi J_{12}(\rho_{1,5} - \rho_{1,9}) -$$
$$\rho_{1,9}/T_2 - i\gamma_1 H'(\rho_{1,1} - \rho_{9,9})P_N = 0$$

$$(\rho_{2,4} - \rho_{5,13})/\tau + i(\omega_1 - \omega)\rho_{5,13} +$$
$$i\pi J_{12}(\rho_{5,13} - \rho_{9,13}) - \rho_{5,13}/T_2 -$$
$$i\gamma_1 H'(\rho_{13,13} - \rho_{5,5})P_N = 0$$

$$(\rho_{3,4} - \rho_{9,13})/\tau + i(\omega_2 - \omega)\rho_{9,13} +$$
$$i\pi J_{12}(\rho_{9,13} - \rho_{5,13}) - \rho_{9,13}/T_2 -$$
$$i\gamma_2 H'(\rho_{13,13} - \rho_{9,9})P_N = 0$$

Here T_2 is the relaxation time introduced to provide the correct line width in the nonexchanging limit. Assuming no saturation, all driving terms $(\rho_{i,i} - \rho_{j,j})$ in these equations may be set equal and constant. If reasonable values of T_2, the chemical shifts, ω_i, and coupling coefficients J_{ij} can be obtained, either from a limit of the system under study, or from a comparable nonexchanging system, the above relations may be solved for $\rho_{i,j}$ in terms of τ, ω, and ΔE. The line shape may then be obtained by determining the intensity through the frequency range from

$$I(\omega) = \mathrm{Im}(\rho_{1,2} + \rho_{1,3} + \rho_{2,4} + \rho_{3,4} +$$
$$\rho_{1,5} + \rho_{1,9} + \rho_{5,13} + \rho_{9,13}) \quad (6)$$

The total line shape of ABX_n consists of a superposition of the $(n + 1)$ lines of the X_n protons upon the basic pattern generated by the exchange treatment of the group adjacent to the nitrogen atom.

The overall pattern of the two proton exchange model given above is similar to that for the one proton situation. For large values of τ, two separate multiplets are observed; as τ decreases, these broaden and coalesce until as $\tau \to 0$ one multiplet emerges which is an average of the original pair. If $\Delta E = 0$, the multiplet–multiplet separation c observed is temperature independent; if $\Delta E \neq 0$, the chemical shift difference of the multiplet is $\delta = (2c^2 - J)^{1/2}$ where J is the coupling coefficient, δ being strongly temperature dependent.

ΔE is readily calculable by a linear regression technique (the standard deviation being minimized) from the experimental spectra using the Boltzmann relation

$$\delta = \delta_{34} + (\delta_{12} - \delta_{34})/(1 + \exp(-\Delta E/RT)) \quad (7)$$

δ_{12} and δ_{34} being the chemical shift differences of H_1 and H_2 and H_3 and H_4, respectively.

Experimental and derived parameters are tabulated (Table II) and some typical computed line shapes given in Figure 3. Where ΔE is finite, the error is of the order of 10–15%, being large because it is possible to obtain an accurate fit over a wide range of ΔE.

Analysis of Results and Discussion

A simple model has been derived, which with suitable and reasonable parameters, may be easily adapted to reproduce all observations. It now remains to establish that the model itself has a physically reasonable interpretation in these adaptations. We note initially the following points.

(a)   In these complexes, it is well established structurally that the S_2CN fragment is highly conjugated and very resistant to out-of-plane distortion;[10] the
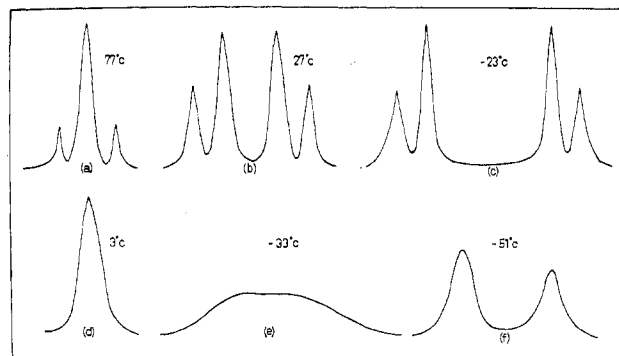
(10) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).

Figure 3.—Calculated spectra for typical dialkyldithiocarbamate complexes of cobalt, $[Co(CS_2NR_2)_3]$, as a function of temperature. a, b, c: $[Co(CS_2N(CH_2C_6H_5)_2)_3]$, $\tau \simeq 0$. d, e, f: $[Co(CS_2N(CH(CH_3)_2)_2)_3]$, $\tau = 8 \times 10^{-4}, 2.8 \times 10^{-3}, 9 \times 10^{-3}$ sec.
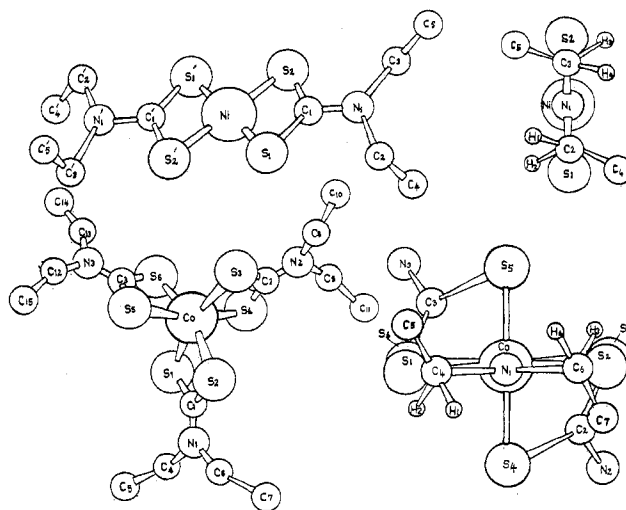

Figure 4.—A comparison of the ligand environments in the dialkyldithiocarbamate complexes of cobalt and nickel, illustrating the possibility of two possible environments for protons in the cobalt case.

MS_2CNC_2 fragment is also planar but less rigorously so, the small deviation observed being directly attributable to hydrogen–sulfur lattice interactions between molecules.[11] It is reasonable to expect that in solution deviations from planarity will be small as a time average.

(b)   As a result, with the exception of some of the terminal substituent groups, the complexes $[Ni(S_2CNR_2)_2]$ are expected to be planar and centrosymmetric in solution as in the solid. The complexes $[Co(S_2CNR_2)_3]$, on the other hand, are noncentrosymmetric conforming closely to a d or l D_3 propeller configuration. Thus, in the former, the N-methylene protons would be expected to be magnetically equivalent; in the latter they will be nonequivalent (Figure 4).

With the exception of the diisopropyl derivative, the behavior of the nickel(II) series is unexceptionable; we discuss this derivative first, together with the cobalt(III) analog, in which there is no added complication due to magnetic nonequivalence so that its behavior is similar.

The Diisopropyldithiocarbamate Derivatives.—The concurrent determination of the crystal structure of $[Ni(CS_2N(CH(CH_3)_2)_2)_2]$[11] provides an immediate hy-

(11) P. W. G. Newman and A. H. White, submitted to *J. Chem. Soc. A*.
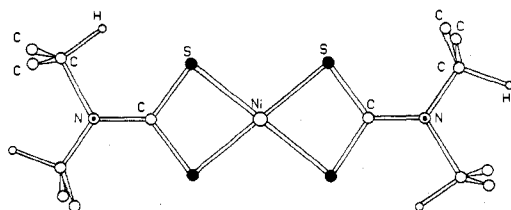
Figure 5.—Molecular configuration of [Ni(CS$_2$N(CH(CH$_3$)$_2$)$_2$)$_2$] in the crystalline state.

pothesis which is a plausible and satisfying interpretation of the spectrum of the complex and its cobalt(III) analog in chloroform solution. The molecular configuration is shown in Figure 5, the salient feature being the nonequivalence of the adjacent isopropyl groups on the same ligand, the CH proton being directed either toward or away from the nearby sulfur atom. Distortions observed in the geometries of the nitrogen atom and the isopropyl groups suggest that the origin of the observed disposition arises from mutual interference between the methyl groups on the adjacent substituents, and also, perhaps, between the methyl groups and sulfur atoms; a strong interaction between the secondary hydrogen atoms and the sulfur is also a likely participating factor. If, as seems likely, this is assumed to be the molecular configuration in solution at low temperature, the origin of the two independent sets of methyl and CH proton signals is clearly explained since their environments within the two isopropyl substituents differ. As the temperature increases the collapse and emergence of the single CH and CH$_3$ multiplets is explicable in terms of rotation about the isopropyl-nitrogen bond being induced. (It is most unlikely, as other work might tend to suggest, that the cause is rotation about the C–N conjugated bond; free rotation about this would still require two independent CH and CH$_3$ environments and the expected spectrum would be different.) It is reasonable that this should be a simultaneous and synchronous effect for the two isopropyl substitutents on the nitrogen atom. Hence, the above theoretical two-proton exchange model may be readily applied to the pair of CH protons within the one ligand, by the assumption that they are uncoupled and that the two sites available for each proton concur in energy with those available to the other; *e.g.*, $E_1 = E_3 \neq E_2 = E_4$ and $J_{AB} = 0$. The overall energy of the system will not change and we would expect $E_{1,2} = E_{3,4}$ ($=E_N = E_M$), ΔE emerging directly from the relative areas of the two multiplets observed in the spectrum when exchange is slow (τ large), using the Boltzmann relation $A_M = A_N$ exp $(-\Delta E/RT)$. The activation energy E^{act} may be derived from the temperature dependence of τ by the Arrhenius relation

$$\log \tau = E^{act}/2.303RT - \log 2A$$

We find in this case that $\Delta E = 0$, and $E^{act} \approx 1600$ cm^{-1}, *i.e.*, 4.6 kcal mol^{-1}.

(As would be expected in this case, the two-proton exchange model is similar in the result it yields to that obtained by treating one isopropyl group only, *i.e.*, as the classical one-proton exchange system.)

The behavior of the cobalt(III) derivative is similar, a value for E^{act} of $\sim$1750 cm^{-1} (5.0 kcal mol^{-1}) being obtained. The two envelopes at low temperature
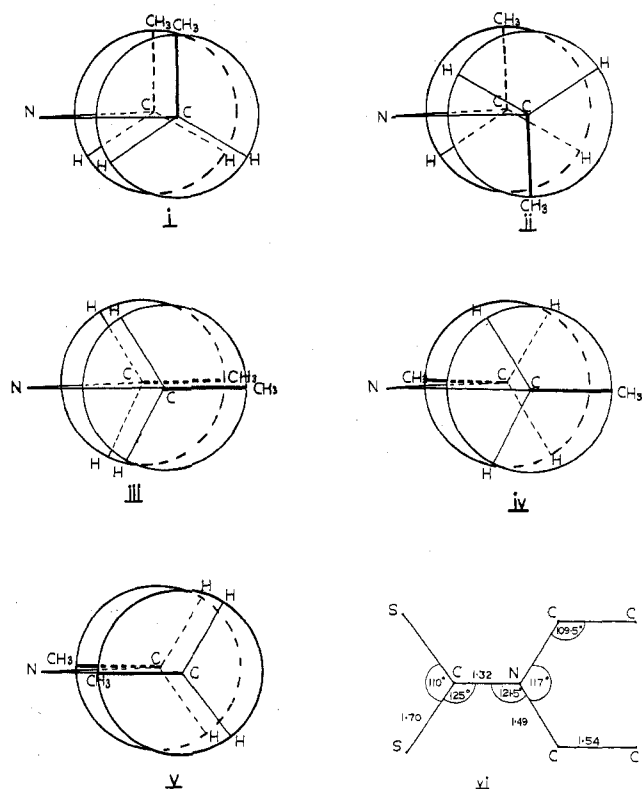

Figure 6.—i–v show possible configurations of the N-Et$_2$ ligand fragments. vi gives the assumed geometry which refutes iii, iv, and v as reasonable and likely actualities.

differ slightly in area; this can be accounted for by the introduction of a ΔE of $\sim$10 cm^{-1} (30 cal mol^{-1}).

The *N*-Methylene Derivatives of Cobalt(III).— Whereas the spectra of the diisopropyl derivatives may be adequately reproduced by suitable usage of a one- or two-proton exchange model, we have not found it possible to give a satisfactory derivation of the temperature dependence of the *N*-methylene protons in the cobalt(III) derivatives using a simpler analysis than the coupled two-proton exchange system described above. Magnetic nonequivalence of the *N*-methylene group is fully expected because of the asymmetric nature of the molecular core; nevertheless, we find that the *N*-methylene multiplet-multiplet separations in these complexes $\sim$300 $\pm$ 30 K may be typically as much as 100 Hz. This value is much larger than would be commonly expected for a simple magnetic nonequivalence within the pair; moreover, the temperature dependence of the separation is most unusual (Figure 1). The above theoretical model requiring a proton-pair exchange between two sites of different energy reproduces the spectra in detail. A survey of the available solid state structural data on *N,N*-diethyldithiocarbamate derivatives provides a satisfying physical interpretation. In these derivatives the S$_2$CNC$_2$ entity is usually planar to within 0.01 Å, as a consequence of conjugation within the S$_2$CN fragment. The terminal methyl groups are unaffected by the conjugation and may project at any angle from the S$_2$CNC$_2$ plane, within the limits of the steric constraints imposed by the ethyl group itself. Five plausible conformational types for the NEt$_2$ group are shown in Figure 6. Using the geometrical parameters of Figure 6 (vi), calculation shows that iii is unlikely, since the distance
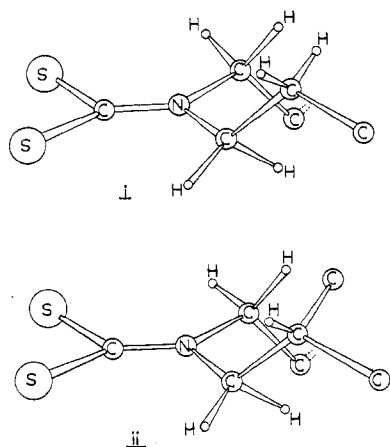
Figure 7.—Showing the influence of more than one substituent on the β-carbon atom in the NR_2 fragments on the environment of the N-methylene proton pair on the alternate alkyl group.

between the terminal methyl carbons in the S_2CNC_2 plane is only of the order of 1.9 Å. Likewise in iv and v the sulfur–terminal carbon distance is of the order of 2.6 Å and this is similarly unlikely. This leaves i and ii as reasonable possibilities and, in fact, it is only these types or close variants which have been observed in the numerous structure determinations on these complexes. Only two examples of i appear to be known in the structures of $[FeCl(CS_2NEt_2)_2]$[12] and $[ReN-(CS_2NEt_2)_2]$.[13] The overwhelming majority of diethyl-dithiocarbamate structures are of type ii in Figure 6.[14] Depending on whether the conformation is that of type ii or its mirror image, the methylene proton pair can exist in two distinct sites, presumably of different energies, in the cobalt(III) derivatives. The cause of the phenomenon thus may well be proton pair exchange between these two sites by rotation about the N-methylene bond; the parameters derived from the model suggest that this energy difference is of the order of ~75 cm^{-1} (~0.2 kcal mol^{-1}) for the isobutyl and

dibenzyl derivatives, *i.e.*, where the substituent type is N–C–C(–C), and ~250 cm^{-1} (~0.7 kcal mol^{-1}) for the diethyl and di-n-propyl derivatives, *i.e.*, where the substituent type is C–C(–C). There is no measurable activation energy for the process. (If $\Delta E \rightarrow 0$, the spectrum will reduce to that of a normal hindered rotation situation, as exemplified by the spectrum of the diisopropyl derivative, the exact form of the spectrum depending on the magnitude of E^{act} and the temperature. The spectra of the nickel derivatives are normal and this suggests that E^{act} is small and not large enough to be relevant in the cobalt situation as, in fact, we find.) Although it is not possible to obtain an appreciation of the magnitude of these quantities from the physical model, it is not unreasonable that the two cases differ since in ii in the diethyl case the methylene pair of one ethyl group is in the vicinity of the terminal methyl groups on the other. When this methyl group is monosubstituted, as in n-propyl, there is no necessity for the additional carbon atom to influence the conformation; with two substituents on the β carbon, however, the environment of the N-methylene protons may well be influenced by the presence of the two substituents (Figure 7).

Siddall[7] has recently reported the study of a number of similar derivatives of type $[Co(CS_2NRR')_3]$, these yielding even more complex spectra by virtue of the increased asymmetry. As in previous studies of related derivatives,[4-6] he postulates rotation about the C–N bond as the mechanism for certain of his observations. In our model, this is tantamount to exchange between the two N-methylene pairs. Because of molecular symmetry these proton pairs as pairs are magnetically and sterically equivalent and only a single AB multiplet should result; *i.e.*, expectations from the physical model are $\Delta E = 0$, and the chemicals shifts $\omega_1 = \omega_3$, $\omega_2 = \omega_4$.

It has been experimentally demonstrated that inversion of the MS_6 core between d and l isomeric forms may occur in some tris(dithiocarbamato)metal complexes.[15] This phenomenon results in interchange of the chemical shift parameters of the methylene protons, the proton pair being energetically the same in the two possibilities, *i.e.*, $\Delta E = 0$. Thus the observed spectrum should be dependent only on the activation energy of the process, and as we have shown, such a model will not reproduce the temperature dependence of the spectrum observed experimentally.[16]

(12) B. F. Hoskins and A. H. White, *J. Chem. Soc. A*, 1668 (1970).

(13) S. R. Fletcher, J. F. Rowbottom, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1572 (1970).

(14) The following list is not exhaustive, but the examples given clearly illustrate the prevalence of this conformation in the N,N-diethyl- and other N,N-di-n-alkyldithiocarbamate complexes: (1) [Ni(CS₂NEt₂)₂], M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 619 (1965); (2) [Ni(CS₂N-n-Pr₂)₂], G. Peyronel and A. Pignedoli, *ibid.*, **23**, 398 (1967); (3) [Ni(CS₂N-n-Bu₂)₃]Br, A. Avdeef, J. Fackler, and R. Fischer, *J. Amer Chem. Soc.*, **92**, 6972 (1970); (4) [Ni(CSe₂NEt₂)₂], M. Bonamico and G. Dessy, *Chem. Commun.*, 1114 (1967); (5) [Cu(CS₂NEt₂)₂], M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 886 (1965); (6) [Cu(CS₂N-n-Pr₂)₂], A. Pignedoli and G. Peyronel, *Gazz. Chim. Ital.*, **92**, 745 (1962); (7) [Cu(CS₂NEt₂)₂]₆, R. Hesse, *Ark. Kemi*, **20**, 481 (1963); (8) [Cu(CSON-n-Pr₂)₂]₆, R. Hesse and U. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970); (9) [Cu(CS₂N-n-Bu₂)Br₂], P. Beurskens, J. Cras, and J. Steggerda, *Inorg. Chem.*, **7**, 810 (1968); (10) (S₂CNEt₂)₂, I. L. Karle, J. A. Estlin, and K. Britts, *Acta Crystallogr.*, **22**, 273 (1967); (11) Na(CS₂NEt₂), M. A. Colapietro, A. Domenicano, and A. Vaciago, *Chem. Commun.*, 572 (1968); (12) Cs(CS₂N-n-Bu₂), U. Aava and R. Hesse, *Ark. Kemi*, **30**, 149 (1968); (13) [Zn(CS₂NEt)₂]₂, M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 898 (1965); (14) [Cd(CS₂NEt₂)₂]₂, A. Domenicano, L. Torrelli, A. Vaciago, and L. Zambonelli, *J. Chem. Soc. A*, 1351 (1968); (15) [Au(S₂CN-n-Bu₂)₂]-[AuBr₂], P. Beurskens, J. Blaauw, J. Cras, and J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968); (16) [Ag(CS₂N-n-Pr₂)]₆, R. Hesse and L. Nilson, *Acta Chem. Scand.*, **23**, 825 (1969); (17) [Ag(CSON-n-Pr₂)]₆, P. Jennische and R. Hesse, *ibid.*, **25**, 423 (1971); (18) [Tl(CS₂N-n-Pr₂)]₂, L. Nilson and R. Hesse, *ibid.*, **23**, 1951 (1969); (19) [(C₆H₅)As(CS₂NEt₂)₂], P. Bally, *Acta Crystallogr.*, **23**, 295 (1967); (20) [Mo(CS₂N-n-Bu₂)₃NO], T. Brennan and I. Bernal, *Chem. Commun.*, 139 (1970); (21) [Re₂O₃(CS₂NEt₂)₄], S. Fletcher, J. Rowbottom, A. Skapski, and G. Wilkinson, *ibid.*, 1572 (1970); (22) [Fe(CS₂NEt₂)₂-(S₂C₂(CF₃)₂)], D. Johnston, W. Rohrbaugh, and W. Horrocks, *Inorg. Chem.*, **10**, 1474 (1971); and (23) [Co(CS₂NEt₂)₃], T. Brennan and I. Bernal, *J. Phys. Chem.*, **73**, 443 (1969).

(15) M. C. Palazzotto and L. H. Pignolet, *Chem. Commun.*, 6 (1972).

(16) NOTE ADDED IN PROOF.—Work since carried out in other solvent systems, in particular benzene-d_6 and carbon tetrachloride, on tris(N,N-diethyldithiocarbamato)cobalt(III) has shown no evidence for the existence of the anomalous spectra reported above for chloroform solution, the spectra being the normal quartet/triplet over the accessible temperatures. While this does not invalidate the theoretical model it does suggest the necessity for explaining the different energy levels in terms of a specific chloroform-complex interaction in this and the other methylene derivatives. Perry and Drago [W. D. Perry and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 2183 (1971)] have suggested the possibility of such an interaction occurring at the nitrogen atom influencing the hyperfine constants in the paramagnetic analogs; in these derivatives the proximity of such a solvent molecule may well affect the rotation of the methylene groups. Further experimental work is proceeding involving pure and mixed solvent systems; it is a common observation, moreover, that many of these solid derivatives form chloroform solvates, and we are currently endeavoring to obtain structural data on such a system in an attempt to determine the nature of the interaction. Previous work on the paramagnetic complexes is also being reexamined and extended in the light of the obviously important role of the solvent. The data concerning the diisopropyl species do not appear to be appreciably influenced by the solvent and the validity of the above interpretation remains unimpaired.