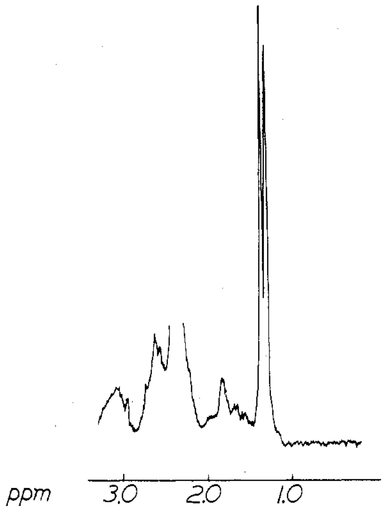

Figure 12. Pmr spectrum of *trans*-[Co((*RS*)-diMe-2,3,2)Cl_2]$^+$.

[Co(en)$_2$(H_2O)Cl]$^{2+}$ λ_{max} is 590[16]) and are quite dissimilar to the spectra of *cis*- and *trans*-diaquo complexes. Thus, the aquation of the *trans*-dichloro complex is in accord with the assigned structure.

Conclusion

The optically active isomers of diMe-2,3,2 coordinate stereospecifically in both *trans*- and *cis*-dichloro complexes. In the case of the trans structure there is strong evidence that the *SS* isomer yields a *RR* nitrogen configuration with the five-membered rings both in δ conformations and the six-membered ring in the λ skew-boat conformation. It is significant to note that the ligand appears to prefer to coordinate such as to yield a skew-boat six-membered ring with two equatorial methyl groups on the five-membered rings than to coordinate with the six-membered ring in the chair conformation and one of the methyl groups occupying an axial site on its ring.

For the cis structure the data indicate that the *SS* ligand yields a Λ-cis-β configuration with the six-membered ring in the chair conformation.

The *RS* (meso) isomer of the ligand coordinates stereospecifically, also, yielding the *trans-meso*-dichloro complex.

We see that the stereochemical behavior of the diMe-2,3,2 isomers is strongly in accord with the notions concerning the coordination chemistry of 2,3,2.

Registry No. 4,8-Diaza-2,10-undecanediamine, 36748-48-8; (*S,S*)-4,8-diaza-2,10-undecanediamine, 36749-49-2; *cis*-[Co((*R,R,S,S*)-diMe-2,3,2)Cl_2]Cl, 36841-26-6; *trans*-[Co((*R,S*)-diMe-2,3,2)Cl_2]ClO_4, 36841-27-7; *cis*-[Co((*S,S*)-diMe-2,3,2)Cl_2]Cl, 36841-28-8; *trans*-[Co((*S,S*)-diMe-2,3,2)Cl_2]-ClO_4, 36841-30-2.

Acknowledgment. The authors are grateful to the National Science Foundation for support of this research through Grant GP-28686. We also wish to acknowledge the Research Corp. and the National Science Foundation for grants through which the Cary 60 spectropolarimeter and JEOLCO PS100 nmr spectrometer were purchased.

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Contribution from the Department of Chemistry, State University
of New York at Buffalo, Buffalo, New York 14214

The Preparation and Characterization of the Dianion of the New Dithiolate Cyclopentadienedithiocarboxylate and Its Zinc and Copper Complexes

PAUL C. SAVINO and ROBERT D. BEREMAN*

Received June 12, 1972

The disodium salt of cyclopentadienedithiocarboxylic acid, $Na_2S_2CC_5H_4$, can be prepared from sodium cyclopentadienide and carbon disulfide in tetrahydrofuran. The salt is obtained as a 1:1 complex with either tetrahydrofuran or acetonitrile depending on the recrystallization solvent. Nuclear magnetic resonance studies indicate that a large amount of negative charge resides in the ring system. This novel 1,1-dithiolate reacts in acetonitrile with copper(II) bromide or zinc(II) bromide to form 2:1 ligand to metal complexes which can be isolated as the tetraethylammonium salts. Optical spectra coupled with electron spin resonance studies on the copper complex in the analogous zinc matrix and in a frozen glass indicate a very covalent out-of-plane metal–sulfur π bond.

Introduction

During the past decade, there has been a great deal of interest in sulfur complexes of transition elements.[1,2] Attention recently has centered on thiolate ligands which are of interest because of their bioinorganic importance (*i.e.*, in nitrogenase model systems) and on dithiolate complexes because of their extensive uses in a wide variety of practical applications.[2]

Gompper and Kutter[3] speculated that the dianion of cyclopentadienedithiocarboxylic acid (I) was an intermediate in organic preparations but it was never isolated. This dianion represents a unique dithiolate ligand because of its potential electronic properties. For this reason, we have undertaken a detailed characterization of the disodium salt of I and the preparation and characterization of zinc and copper complexes of I.

Experimental Section

Materials. Sodium hydride was obtained as a 50% dispersion in oil from Research Organic-Inorganic Chemical Corp. Carbon disulfide was dried over 4A molecular sieves. Acetonitrile was refluxed over and distilled repeatedly from phosphorus pentoxide. Tetrahydrofuran was distilled from $LiAlH_4$. Cyclopentadiene was prepared by the thermal cracking of dicyclopentadiene. Acetonitrile-d_3 was obtained from Norell Chemical Co. and dried over

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[1] J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).
[2] D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970).
[3] R. Gompper and E. Kutter, *Chem. Ber.*, 98, 2825 (1965).

4A molecular sieves. Pure nitrogen was obtained by passing commercial dry nitrogen through a BTS[4] column and subsequently through sodium hydroxide and 4A molecular sieve drying towers.

$Na_2C_5H_4CS_2 \cdot C_4H_8O$. This complex was prepared by causing 2 equiv of sodium cyclopentadienide to react with 1 equiv of carbon disulfide in anhydrous tetrahydrofuran. Typically 5.1 g of cyclopentadiene was distilled onto 1 equiv of NaH in tetrahydrofuran and 3.9 g of CS_2 was added slowly while keeping the reaction mixture at –30°. The total volume of the mixture was approximately 125 ml. The resulting bright yellow solid was filtered under a nitrogen atmosphere and dried under vacuum. *Anal.* Calcd for $Na_2C_5H_4CS_2 \cdot C_4H_8O$: C, 46.49; H, 4.68; S, 24.83. Found: C, 46.10; H, 4.67; S, 24.39.

$Na_2C_5H_4CS_2 \cdot CH_3CN$. This complex can be prepared by repeated crystallization of $Na_2C_5H_4CS_2 \cdot C_4H_8O$ from anhydrous acetonitrile. *Anal.* Calcd for $Na_2C_5H_4CS_2 \cdot CH_3CN$: C, 42.27; H, 3.11; S, 28.24; Na, 20.24. Found: C, 42.99; H, 3.00; S, 28.53; Na, 20.20.

$[(C_2H_5)_4N]_2Zn(C_5H_4CS_2)_2$. This complex was prepared by the action of the 1,1-dithiolate salt on 1 mol of zinc bromide, followed by 2 equiv of tetraethylammonium bromide.

Typically, 0.207 g of zinc bromide and 0.474 g of disodium cyclopentadienedithiocarboxylate were added to 100 ml of degassed anhydrous acetonitrile at –30°. The cold solution was stirred for 30 min and 0.385 g of tetraethylammonium bromide was added. The solution was stirred and allowed to warm to ambient temperature. The sodium bromide which had formed was removed by filtration under nitrogen. The filtrate was then cooled and bright yellow air-sensitive crystals precipitated. The product was isolated by filtration and dried under vacuum. *Anal.* Calcd for $[(C_2H_5)_4N]_2Zn(C_5H_4CS_2)_2$: C, 55.47; H, 7.98; N, 4.62; S, 21.15; Zn, 10.78. Found: C, 54.67; H, 7.83; N, 4.53; S, 20.64; Zn, 10.38.

$[(C_2H_5)_4N]_2Cu(C_5H_4CS_2)_2$. This air-sensitive red-brown complex was prepared in the same manner as the above zinc complex. *Anal.* Calcd for $[(C_2H_5)_4N]_2Cu(C_5H_4CS_2)_2$: C, 55.68; H, 7.95; N, 4.64; S, 21.21; Cu, 10.52. Found: C, 54.51; H, 8.23; N, 4.56; S, 21.15; Cu, 8.23.

Analyses. All analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Methods. All reactions were carried out in an inert atmosphere (dry nitrogen) using standard Schlenk-tube techniques. Esr, nmr, and uv-vis samples were prepared by loading the chosen compound into specially constructed esr and nmr tubes and uv-vis cells in a glove bag and transferring the vessels to a vacuum line where the appropriate solvents were distilled onto the samples and the containers were sealed under vacuum.

Spectroscopic Measurements. The infrared spectra of the complexes were obtained by use of Nujol mulls, a Beckman IR-5A spectrophotometer, and a Perkin-Elmer Model 457 spectrophotometer. Ultraviolet-visible spectra were obtained in solution in acetonitrile and by use of Nujol mulls and a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were obtained by use of a Jeolco HA 100 spectrometer. X-Band electron spin resonance spectra were determined at 300 and 100°K by employing a Varian variable-temperature control apparatus with liquid nitrogen as coolant. A Varian V-4502-19 spectrometer was used in conjunction with a Magnion proton oscillator gauss meter and a Hewlett-Packard frequency meter to obtain accurate measurements of the magnetic field and microwave frequency. Spectra were scanned slowly to determine the hyperfine parameters accurately. Second-order corrections, although small, were employed to correct for the perturbation of the Zeeman transitions resulting from the hyperfine interactions.

Results and Discussion

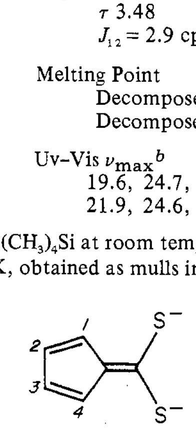
Disodium cyclopentadienedithiocarboxylate is a bright yellow air-sensitive crystalline solid. In hydroxylic solvents, it decomposes to form sulfide anion (as determined by precipitation with cobalt).

Table I summarizes the important physical parameters of the disodium salt of I complexed with CH_3CN and C_4H_8O. The nuclear magnetic resonance spectrum consists of two multiplets at τ 3.48 and 4.38 relative to $(CH_3)_4Si$. The multiplets are triplets as in an A_2X_2 type system with coupling constants $J_{12} = J_{13} = 2.9$ cps.

Table I. Physical Parameters of $Na_2C_5H_4CS_2 \cdot L$

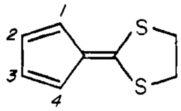
	Nmr Spectral Values[a]	
L = CH_3CN	τ 3.48 $J_{12} = 2.9$ cps	τ 4.38 $J_{13} = 2.9$ cps
	Melting Point	
L = CH_3CN	Decomposes at 240°	
L = C_4H_8O	Decomposes at 240°	
	Uv-Vis ν_{max}[b]	
L = CH_3CN	19.6, 24.7, 30.5, 32.8 sh	
L = C_4H_8O	21.9, 24.6, 30.8, 40.3, 44.3, 48.4	

[a] Relative to internal $(CH_3)_4Si$ at room temperature at 100 MHz in CD_3CN. [b] Values in kK, obtained as mulls in Nujol.



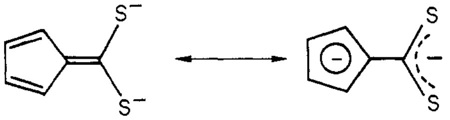
I

These values can be compared to those of a quite similar compound, *S,S′*-ethylene-6,6′-dimercaptofulvene (II) originally prepared by Gompper and Kutter,[3,5] who reported two singlets in the nmr spectrum at τ 6.47 and 3.61. We find a singlet at τ 6.48 for the ethylene protons and a complex multiplet centered at τ 3.82. The coupling constants are $J_{12} = 4$ cps, $J_{23} = 1.3$ cps, $J_{13} = 2$ cps, and $J_{14} = 1.3$ cps. These spectra were analyzed using normal procedures.[6,7]



II

It is important to note that the J_{12} and J_{23} values of II are significantly higher and lower, respectively, than the J_{12} values of I. With the considerations presented by Smith, Watson, and Chiranjeevi[8] and more recently by Ammon and Wheeler[9] and by Ammon and Plastas[10] concerning the vicinal proton coupling constant-bond length relationship for five-membered rings, it is obvious that in going from II to I, there is some degree of electron charge delocalization into the ring system of I, that is



The major infrared peaks for I and II are summarized in Table II for comparison along with tentative assignments.

This dithiolate when bonded to transition elements should result in very covalent metal π bonds to a greater extent than other known dithiolates. To test this premise, both the zinc

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(4) A. D. Broadbent, *J. Chem. Educ.*, 44, 145 (1967).

(5) This compound was also prepared as a derivative of the sodium dithiolate. The compound was prepared by the reaction with 1,2-dibromoethane and purified by chromatographing the product mixture over Brockman Activity 1 basic alumina. *Anal.* Calcd for $C_8H_8S_2$: C, 57.10; H, 4.78. Found: C, 57.34; H, 5.00. Mp[3] 92°, lit. mp 93–95°.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(7) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, New York, N. Y., 1962.

(8) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 89, 1438 (1967).

(9) H. L. Ammon and G. L. Wheeler, *Chem. Commun.*, 1032 (1971).

(10) H. L. Ammon and L. A. Plastas, *Chem. Commun.*, 356 (1971).

Table II.[a] Infrared Spectroscopic Features of I[b] and II

I

657 s [C—S], 760 vs, 788 vs, 822 s, 887 vs, 1020 s, 1053 s, 1197 s (C—O), 1322 vs, 1378 m, 1392 m, 1455 s, 1622 vvs (C=C).

II

600 s (C—S), 665 s, 805 vvs, 850 m, 925 s, 975 w, 1010 m, 1075 s, 1150 vw, 1214 vvs, 1280 s, 1360 vs, 1420 sh, 1440 s, 1550 vvs (C=C).

[a] Values in cm^{-1}. [b] The complex of I with C_4H_8O.

Table III. Infrared and Optical Spectroscopic Features of $[(C_2H_5)_4N]_2M(C_5H_4CS_2)_2$

Infrared[a]

M	ν
Zn	353 m (Zn–S), 648 s, 722 sh, 750 s, 780 s, 796 s, 827 w, 905 s, 998 w, 1023 w, 1051 m, 1157 s, 1205 w, 1345 s, 1375 s, 1405 w, 1460 vs, 1585 w
Cu	339 m (Cu–S), 648 m, 720 sh, 748 s, 781 m, 805 s, 827 w, 915 s, 1000 w, 1028 w, 1063 m, 1172 s, 1204 w, 1347 s, 1388 m, 1475 vs, 1590 sh, 1614 m

Uv-Vis[b]

M	ΔE_z	ΔE_{xy}	ΔE_{xz}
Cu[c]	11.0	23.5	25.6
Cu[d]	Not obsd[e]	21.2	26.0

[a] Values in cm^{-1}, obtained as Nujol mulls. [b] Values in kK. [c] Obtained as Nujol mull. [d] Obtained as solution in CH_3CN. [e] Poor base line resolution in this area prevented the resolution.

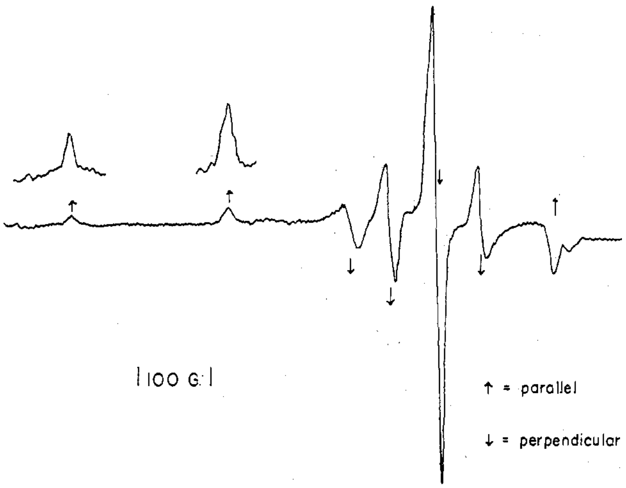

Figure 1.

and copper complexes were prepared and characterized. Table III summarizes the major infrared peaks for both metal complexes and the uv-vis peaks for the copper complex which are not also present in the zinc complex.

The nuclear magnetic resonance spectrum of the zinc complex consisted of the peaks normally attributed to the tetraethylammonium ion and two multiplets at τ 4.07 and 3.52 relative to TMS. The complex was not soluble enough, however, to obtain accurate J coupling constants in order to obtain an idea of the delocalization of electron density in the complexed ligand.

Fortunately, the copper dithiolate complex lends itself ideally to a more sensitive spectroscopic tool which can give similar information, electron spin resonance spectroscopy. Esr spectra were obtained in acetonitrile solutions at 300°K and as glasses at 100°K. Spectra were also obtained as a diluted powder in the corresponding zinc host lattice. A typical glass spectrum is shown in Figure 1. The esr parameters for the copper complex in the zinc lattice and in a frozen CH_3CN glass were virtually identical and are $g_\parallel = 2.094$, $g_\perp = 2.022$, $|A_\parallel| = 177.1 \times 10^{-4}$ cm^{-1}, and $|A_\perp| = 47.6 \times 10^{-4}$ cm^{-1}. Solution esr parameters in CH_3CN are $\langle g \rangle = 2.046$ and $\langle a \rangle = 85.2 \times 10^{-4}$ cm^{-1}.

The observed g and A values are used to calculate the coefficients for the antibonding molecular orbitals of interest in a simple molecular orbital scheme. While the gross symmetry of the copper complex is D_{2h} or lower, the observation of only parallel and perpendicular components in both the frozen glass and the diluted powders indicates that the effective local electronic symmetry at the copper must be near D_{4h}. With this in mind, the molecular orbitals of interest are LCAO-MO functions of the form[11,12]

$$\psi_{\mathrm{B_{1g}}} = \alpha \mathrm{d}_{x^2-y^2} - {}^1\!/_2\alpha'[-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}] \quad (1)$$

$$\psi_{\mathrm{B_{2g}}} = \beta \mathrm{d}_{xy} - {}^1\!/_2(1-\beta^2)^{1/2}[\mathrm{p}_y^{(1)} + \mathrm{p}_x^{(2)} - \mathrm{p}_y^{(3)} - \mathrm{p}_x^{(4)}] \quad (2)$$

$$\psi_{\mathrm{A_{1g}}} = \gamma \mathrm{d}_{z^2} - {}^1\!/_2(1-\gamma^2)^{1/2}[\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}] \quad (3)$$

$$\begin{aligned}\psi_{\mathrm{E_g}} &= \delta \mathrm{d}_{xz} - (1-\delta^2)^{1/2}[\mathrm{p}_z^{(1)} - \mathrm{p}_z^{(3)}]/\sqrt{2} \\ &= \delta \mathrm{d}_{yz} - (1-\delta^2)^{1/2}[\mathrm{p}_z^{(2)} - \mathrm{p}_z^{(4)}]/\sqrt{2} \quad (4)\end{aligned}$$

Following Gersmann and Swalen,[12] overlap was included only for the $\psi_{\mathrm{B_{1g}}}$ state, where α and α' are related by

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \quad (5)$$

where S is the metal-ligand overlap term $(0.005)^{12}$ and the σ orbitals are hybridized sp orbitals.

Our interest is in determining the bonding parameters α, β, and δ in eq 1-4 which can be related to the observable esr parameters. Since we are particularly interested only in comparing the bonding parameters in this copper-dithiolate system to other copper-dithiolate systems, we used a slightly simplified set of equations developed by Kivelson and Neiman[13]

$$g_\parallel = 2.0023 - (8\lambda/\Delta E_{xy})\alpha^2\beta^2 \quad (6)$$

$$g_\perp = 2.0023 - (2\lambda/\Delta E_{xz})\alpha^2\delta^2 \quad (7)$$

$$A_\parallel = P\alpha^2 - \left\{(\frac{4}{7} + K) - 2\lambda\left[\frac{4\beta}{\Delta E_{xy}} + \frac{3}{7}\,\frac{\delta^2}{\Delta E_{xz}}\right]\right\} \quad (8)$$

λ is the spin-orbit coupling constant for the free ion and was taken as -828 cm^{-1}. The constant K corrects for the Fermi contact term of excited configurations of copper and was taken as equal to $^3/_7$.[13] P was taken as 0.0360 cm^{-1}.

The procedure for evaluating eq 6-8 for α, β, and δ was an iterative one and was carried out with the aid of a desk calculator. Normally, six iterations were needed for convergence, the requirement being that successive values of the molecular orbital coefficients differ by less than 0.002. Table IV lists values for α, α', β, and δ for this system studied and for another, the copper-diethyldithiocarbamate system, for comparison. Both sets of parameters were obtained using modified eq 6-8 and the values compare favorably to those obtained by Gersmann and Swalen using a more rigorous form of the same equations.[12]

(11) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

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(13) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 149, 156, 162 (1961).

Table IV. Bonding Parameters for $CuL_2{}^{2-}$ Systems

	α	β	δ	α'
Diethyldithiocarbamate[a]	0.73	0.72	0.92	0.69
Cyclopentadienedithiocarboxylate	0.77	0.70	0.72	0.64

[a] Experimental parameters needed for calculations are taken from ref 12.

It is quite obvious that the out-of-plane π bonding is much more covalent in the system investigated than in the copper-diethyldithiocarbamate system. The in-plane π and σ bondings are quite similar. Since this out-of-plane π bond is antibonding in character and is very covalent, the bonding molecular orbital is similar indicating that the dithiolate is a strong π-bonding ligand and is, in fact, a good π-acceptor ligand.[14,15] It should be noted that in Cu^{2+}, the π-bonding and antibonding molecular orbitals have two electrons each so that the transfer of electrons from metal to ligand in the antibonding orbitals is canceled by the reverse transfer in the bonding orbitals. The only effective electron transfer occurs in the B_{1g} orbital where the net transfer is toward the metal cation since the bonding molecular orbital has two electrons and the antibonding molecular orbital only one electron.

This dithiolate also forms 2:1 and 3:1 ligand to metal complexes with a large number of transition and nontransition elements. We observe in a qualitative way that the stability of these complexes decreases with decreasing number of d electrons indicating the importance of the covalent π bonding in stabilizing the metal-sulfur bond.[16,17]

Registry No. $Na_2C_5H_4CS_2 \cdot C_4H_8O$, 36487-17-9; $Na_2C_5H_4CS_2 \cdot CH_3CN$, 36487-18-0; $[(C_2H_5)_4N]_2Zn(C_5H_4CS_2)_2$, 36544-15-7; $[(C_2H_5)_4N]_2Cu(C_5H_4CS_2)_2$, 36544-16-8.

Acknowledgment. We wish to thank Professor Fred Wudl of this department for many very helpful and stimulating suggestions. This work was supported by a grant (2385-G3) from the Petroleum Research Fund, administered by the American Chemical Society.

(14) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 3, 1398 (1964).

(15) R. R. Eley, R. R. Meyers, and N. V. Duffy, *Inorg. Chem.*, 11, 1128 (1972).

(16) B. J. Kalbacher and R. D. Bereman, in preparation.

(17) P. Savino and R. D. Bereman, in preparation.

Contribution from the Wm. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801

Calorimetric and Nuclear Magnetic Resonance Studies of Hydrogen Bonding. Quinuclidine with Various Lewis Acids[1a]

FRANK L. SLEJKO[1b] and RUSSELL S. DRAGO*

Received May 22, 1972

The nmr chemical shift differences ($\Delta\omega°$) between "free" hydrogen-bonding acids and their 1:1 complexes with a Lewis base have been measured with the Lewis base quinuclidine (1-azabicyclo[2.2.2]octane) in nonpolar solvents such as cyclohexane. Enthalpies of adduct formation for this base with a series of Lewis acids enabled us to incorporate quinuclidine into our double-scale enthalpy equation. The E_B and C_B values thus obtained allowed us to predict enthalpies of adduct formation for quinuclidine with a large series of hydrogen bonding acids whose E_A and C_A numbers are known and whose nmr hydrogen bonding chemical shifts were measured. A straight-line correlation between $-\Delta H$, the enthalpy of adduct formation, and $\Delta\omega°$ was obtained for quinuclidine interacting with all the Lewis acids studied, having the form $-\Delta H = (0.95 \pm 0.04)\Delta\omega° + 3.2 \pm 0.2$ kcal/mol. This correlation is considered in light of other reported relationships between $-\Delta H$ and $\Delta\omega°$ which were obtained by keeping the acid constant and varying the base. Failure of quinuclidine to fall on these constant acid lines is discussed. This base also fails to obey constant acid enthalpy-infrared frequency shift correlations. The magnitudes of $\Delta\omega°$ for the protons in the Lewis acids upon hydrogen bonding to quinuclidine are rationalized in terms of an "electric field effect" arising from the lone-pair electrons on the nitrogen atom and the polarizability components of the Lewis acids along the hydrogen bond.

Introduction

The ability of changes in spectroscopic properties to reflect the strength and nature of the coordination of Lewis acids to Lewis bases is of considerable importance to the reliability of many conclusions drawn in inorganic chemistry. In much of the inorganic literature, it is tacitly assumed that a direct relationship exists between the strength of interaction and some spectroscopic change. Very little research has been published to verify, negate, or indicate the limitations of such assumptions. The possibility of obtaining both enthalpy data and the corresponding chemical shifts on hydrogen-bonding systems makes them particularly attractive in this regard.

It has long been known that upon hydrogen bonding of an acid to a donor, the proton magnetic resonance of the acid experiences a significant downfield contribution to the shift relative to the position of the "free" acid.[2] At room temperature, the observed chemical shift, ω_{obsd}, corresponds to the mole fraction weighted average of the complexed and free protons as indicated in

$$\omega_{\text{obsd}} = \frac{[\text{AB}]}{[\text{A}] + [\text{AB}]}\,\omega_{\text{complex}} + \frac{[\text{A}]}{[\text{A}] + [\text{AB}]}\,\omega_{\text{free}} \qquad (1)$$

for $A + B \rightleftarrows AB$, where A denotes a hydrogen-bonding

(1) (a) Abstracted in part from the Ph.D. thesis of F. L. S., University of Illinois. (b) National Science Foundation predoctoral fellow, 1969-1972.

(2) See, for instance, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR," Pergamon Press, Oxford, 1965.