It appears reasonable to assume that the equilibrium constants k_{12}/k_{21} and k_{34}/k_{43} and the rate constant k are the same for various alkaline earth metal ions because the mutual effect of metals along the long bond sequence Cu-N-O-O-N-M seems to be unimportant.

The rate of the reaction path corresponding to k_1 is independent of the concentration of PAR. This fact suggests that hydroxyl ion in the OH-Cu(II)-EGTA-M complex prevents the coordination of PAR to copper in this complex. The rate constant for k_1^{Ca} is about one order of magnitude greater than k_1^{Ba} and k_1^{Sr}. The difference in rates for k_1 for alkaline earth metal ions corresponds to the difference in stability constants of complexes of alkaline earth metal ions with the segment of EGTA, *i.e.*, K_{ML} in Table VI. Thus the cleavage of the copper-nitrogen bond in (OH)Cu(egta)M is the rate-determining step in this reaction path. The resulting Cu(OH)$^+$ reacts rapidly with PAR under the present experimental conditions.

The reactivity of par^{2-} is about three orders of magnitude higher than that of Hpar$^-$. A similar result has been described by Kodama, *et al.*,[23] in the ligand-substitution reactions of Eriochrome Black T with cobalt(II) and nickel(II) complexes of 1,2-diaminocyclohexanetetraacetic acid and diethylenetriaminepentaacetic acid. This is understandable qualitatively in terms of the difference in constants for the relevant equilibria preceding the rate-determining step. More extensive electron donation of par^{2-} in (par)Cu(egta) than of Hpar$^-$ in (Hpar)Cu(egta) would make easier the cleavage of egta^{4-} from the intermediate (par)Cu(egta).

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Electron Spin Resonance Study of the Kinetics and Equilibrium of Adduct Formation by Copper(II) Dibutyldithiocarbamate with Nitrogen Bases[1a]

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The esr spectrum of copper (II) bis(di-*n*-butyldithiocarbamate) [Cu(DnBDC)$_2$] was measured as a function of temperature and solvent composition in mixtures of methylcyclohexane with piperidine, *n*-hexylamine, and pyridine. Evidence for the formation of a short-lived 1:1 adduct is presented. Equilibrium constants for the adduct formation reaction and adduct lifetimes were obtained from analysis of the line positions and line widths. The fast-exchange-limit solution of the modified Bloch equations was reexamined, and correction terms were derived permitting the application of the fast exchange limit to somewhat slower reactions than usual. Arrhenius plots of the equilibrium constants and the adduct lifetimes gave the thermodynamic parameters for the adduct formation equilibrium and kinetic parameters for the adduct dissociation reaction. In the case of the piperidine adduct at 25°, the equilibrium constant is $K = 3.9 \pm 0.1$ l./mol, $\Delta S° = -22 \pm 1$ eu; the rate of adduct dissociation is $k_r = (3.7 \pm 0.4) \times 10^8$ sec^{-1}, $\Delta H^{\ddagger} = 7.4 \pm 1.7$ kcal/mol, and $\Delta S^{\ddagger} = 5 \pm 3$ eu. In general, the rate of the adduct formation reaction seems to be almost entirely limited by entropy of activation, while the dissociation reaction is primarily limited in rate by enthalpy of activation.

Introduction

The past 15 years has seen a considerable amount of interest in the reaction of square-planar copper(II) complexes with nitrogen bases to form five-coordinate adducts. The principal effort has been on the characterization[2-5] and structure[6,7] of the adducts, on the interpretation of the electronic,[2,3,8-13] vibrational,[13] esr,[13-21] and nmr[21-23] spectra of the adducts, and on the

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[1] (a) Taken in part from the Ph.D. thesis of B. J. Corden, Brown University, Providence, R. I., 1970. (b) National Science Foundation Trainee, 1966-1969.

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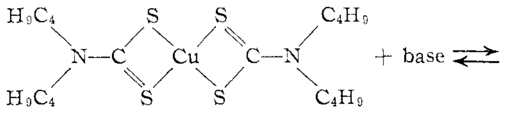
thermodynamics[3,5,10,19,24–27] of the adduct formation reactions. Most of the work has centered on β-diketonates and related bidentate chelates with oxygen donor atoms, although some work has been reported on chelates with nitrogen[7,8,10,13,21] and sulfur ligands.[15,16,20]

Knowledge of the thermodynamics of the adduct formation equilibria has contributed significantly to understanding of the nature of the adducts. However, since the process is apparently a very rapid equilibrium, the kinetic parameters, particularly the energy of activation for the adduct dissociation reaction, are expected to be most significant in understanding the true strength of the metal–nitrogen bond in the adducts.

Previously, Walker, *et al.*,[28] have observed esr line broadening in the pseudo-square-planar system VO(acac)$_2$–base. VO(acac)$_2$ gives an eight-line spectrum and the variation in line shape of the $m_I = +^7/_2$ line on the addition of pyridine, piperidine, or 2-picoline allowed the determination of the lifetime of the adduct in this system. Knowledge of the equilibrium constant from spectroscopic and calorimetric work,[29] together with the law of microscopic reversibility, yielded the forward rate constant which was close to that expected for a diffusion-controlled reaction. In the present work, we have extended this technique to adduct formation by copper(II) bis(*N*,*N*-di-*n*-butyldithiocarbamate) [Cu(DnBDC)$_2$]



five-coordinate adduct

The choice of this system for study was prompted primarily by the unusually narrow lines in the esr spectrum.[15] This factor is of considerable importance since the contribution to the line widths from chemical exchange is then much more easily measured.

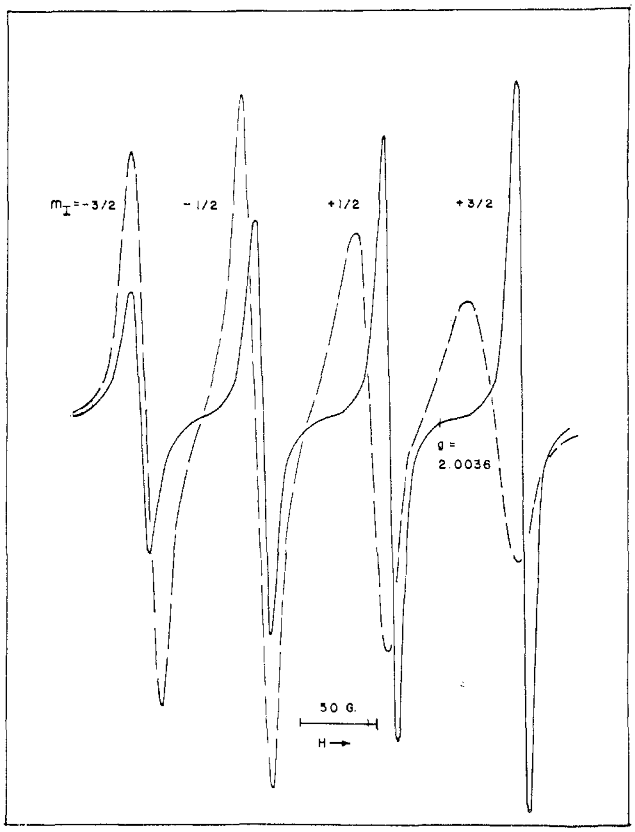


Figure 1.—Esr spectra of ^{63}Cu(DDC)$_2$ at 25° in benzene (solid line) and in 95% benzene–5% piperidine (dashed line); the spectrometer gain was different for the two spectra.

Copper(II) bis(*N*,*N*-diethyldithiocarbamate) [Cu(DDC)$_2$] is well known and has found use in the gravimetric determination of copper.[30] The esr of this complex has been studied in solution,[15,16,20,31] in frozen glasses,[32,33] and doped into diamagnetic single crystals.[34,35] Aasa, *et al.*,[15] studied the room-temperature esr spectrum of Cu(DDC)$_2$ as a function of solvent composition using benzene–pyridine mixtures. They found that the line positions shifted with solvent composition but did not observe line width variations attributable to exchange and concluded that the shift in line positions was due to a solvent effect and not to formation of an adduct. Since the greatest line broadening occurs when the ratio of adduct to free complex is 1:2, this conclusion is not surprising since their spectra were observed in solutions where this ratio was somewhat larger. Gibson[16] considered the possibility of exchange line broadening but did not pursue the matter further.

We have found that the line widths do indeed show the effects of base exchange when the ratio of free complex to adduct is in the proper region. The magnitude of the observed line position shifts and line broadening is demonstrated in Figure 1 where the spectrum of ^{63}Cu(DDC)$_2$ is shown in pure benzene solution and in 95% benzene–5% piperidine solution. Unfortunately, the electronic spectrum of Cu(DDC)$_2$ is affected very little by adduct formation so that equilibrium constants could not be obtained from such measurements. However, esr line positions can be used to obtain accurate equilibrium constants when the exchange rate is sufficiently rapid.[36]

Naturally occurring copper consists of 69.9% ^{63}Cu and 30.1% ^{65}Cu. Both isotopes have a nuclear spin of $^3/_2$ but slightly different nuclear magnetic moments. Thus the esr spectrum of Cu(DDC)$_2$ consists of two overlapping sets of four lines with only the sharpest line visibly split. To avoid this complication, isotopically pure ^{63}Cu was used in the present work giving an undistorted four-line spectrum.

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$Cu(DDC)_2$ is soluble in the aromatic hydrocarbon or chlorinated solvents. However, since there may be complications due to solvent interactions with $Cu(DDC)_2$ or with the bases used—piperidine, pyridine, and *n*-hexylamine[20,26]—methylcyclohexane was chosen as the noninteracting solvent in this work. Methylcyclohexane also has the advantage of a wide liquid range, −126 to +100°. However, since $Cu(DDC)_2$ was found to be sparingly soluble in this solvent, the di-*n*-butyl derivative $Cu(DnBDC)_2$ was used. The esr spectra of these two complexes in benzene were nearly identical so that conclusions reached are probably not critically dependent on the choice of the complex.

Experimental Section

Copper(II) di-*n*-butyldithiocarbamate was synthesized following a modification of published procedures.[37] Isotopically pure ^{63}CuO, obtained from Oak Ridge National Laboratories, was dissolved in hot, concentrated HNO_3; the solution was cooled and neutralized with 6 *M* NaOH. The solution was concentrated to half-volume, and $NaNO_3$ was precipitated by the addition of cold methanol. Carbon disulfide, 8.4 g, was added to 13 g of freshly distilled di-*n*-butylamine in 200 ml of cold methanol. After cooling, 4.4 g of NaOH was added in a small amount of water. The copper solution (containing 100 mg of CuO) was added dropwise to about 40 ml of the NaDnBCD solution, the solution was cooled, and the brown precipitate was collected and dried *in vacuo* over refluxing acetone. The $^{63}Cu(DnBDC)_2$ was recrystallized from methanol in a rotary evaporator and dried in a vacuum desiccator; yield 300 mg (53%); mp 55–56°.

Methylcyclohexane was distilled from BaO and stored over molecular sieves. Pyridine, piperidine, and *n*-hexylamine were distilled from BaO prior to use.

Samples were prepared by weighing 6.0 mg of $^{63}Cu(DnBDC)_2$ into glass tubes having a bulb on one end and a side arm suitable for insertion into the variable-temperature dewar of the esr spectrometer. A solution containing the desired base concentration was prepared and 4.0 ml was pipetted into the sample tube. The sample was then promptly degassed by several freeze–pump–liquefy cycles, and the tube was sealed. The resulting concentration of copper complex, about 3.2 m*M*, was sufficiently low that spin exchange contribution to the esr line widths was negligible.

Some of the samples thus prepared, particularly those containing large concentrations of piperidine or *n*-hexylamine, were unstable at room temperature, undergoing slow decomposition. Samples were therefore stored under liquid nitrogen until immediately before recording the esr spectra. Spectra obtained in this way were reproducible.

The spectra were recorded using a Varian V-4502 spectrometer equipped with 100-kHz field modulation, a Fieldial field regulated magnet, and a Varian variable-temperature accessory. Magnetic field measurements relied on the Fieldial calibration which was checked periodically; *g* values were determined relative to DPPH, assumed to have a *g* value of 2.0036.[38] The variable-temperature accessory was calibrated with a thermocouple; temperature measurements were accurate to about ±2°.

Treatment of Data

Preliminary examination of the line width and line position data (Table I) indicated that the spectra of $Cu(DnBDC)_2$ in mixtures of methylcyclohexane and pyridine or *n*-hexylamine above 10° or methylcyclohexane–piperidine mixtures above 50° could be analyzed

TABLE I

EXPERIMENTAL LINE POSITION SHIFTS AND LINE WIDTHS

	$\omega - \omega_A$[a]		T_2^{-1}[b]		Temp, °C
[Base][c]	$^3/_2$	$^1/_2$	$^3/_2$	$^1/_2$	
	Methylcyclohexane–Piperidine				
0.000	0	0	56	74	50
0.051	50[d]	35	80[d]	88	
0.101	90	69	118	99	
0.202	155	116	137	136	
0.505	326	223	166	134	
1.01	475	319	153	126	
2.02	610	407	128	127	
5.05	729	486	100	125[e]	
0.000	0	0	56	74	65
0.051	43	24	70	84	
0.101	76	48	85	88	
0.202	122	80	102	96	
0.505	244	163	121	109	
1.01	381	255	120	114	
2.02	530	351	123	118	
5.05	659	438	98	114	
	Methylcyclohexane–*n*-Hexylamine				
0.000	0	0	62	83	10
0.151	259[d]	187	293[d]	181	
0.377	536	328	214	177	
0.754	. . .	417	. . .	157	
1.51	801	507	134	152	
3.77	878	573	102	149	
0.000	0	0	59	80	20
0.151	212	149	196	148	
0.377	463	298	188	158	
0.754	593	367	. . .	140	
1.51	698	462	134	140	
3.77	871	558	95	139	
0.000	0	0	57	78	30
0.151	188	126	143	122	
0.377	366	233	151	127	
0.754	482	322	118	129	
1.51	606	395	118	126	
3.77	771	499	91	124	
0.000	0	0	56	76	40
0.151	133	85	106	100	
0.377	283	192	118	121	
0.754	401	253	114	113	
1.51	536	353	114	113	
3.77	724	479	91	112	
0.000	0	0	56	76	50
0.151	122	55	83	89	
0.377	221	135	95	102	
0.754	333	228	100	105	
1.51	454	320	99	105	
3.77	. . .	475	. . .	121[e]	
	Methylcyclohexane–Pyridine				
0.00	0	0	62	83	10
0.62	264	158	151	133	
1.24	374	213	139	133	
2.48	489	282	109	121	
0.00	0	0	59	80	20
0.62	225	133	121	108	
1.24	321	199	124	121	
2.48	428	258	103	118	
0.00	0	0	57	78	30
0.62	164	115	94	98	
1.24	278	160	97	115	
2.48	351	212	100	105	

[a] Shifts of line positions from those in methylcyclohexane solution in units of 10^6 sec^{-1}; uncertainties are approximately $\pm 10^7$ sec^{-1}. [b] Line widths ($\sqrt{3}/2$ derivative width) in units of 10^6 sec^{-1}; uncertainties are approximately ±5%. [c] Base concentration in moles per liter; uncertainties are approximately 1%. [d] Data not included in analysis since the parameter Δ exceeds 0.8. [e] Data not included in analysis; line width measurement apparently in error.

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at least semiquantitatively using the solution of the modified Bloch equations in the fast-exchange limit. Data obtained for methylcyclohexane–piperidine solutions at 25° or below clearly could not be explained in terms of the fast-exchange approximation. Indeed, some spectra at 0 and 10° showed partial resolution of the $+^3/_2$ and $+^1/_2$ lines into separate lines for the four- and five-coordinate complexes. Thus, analyses of the two groups of data were carried out separately and by quite different methods.

Those experimental spectra in which the $+^3/_2$ and $+^1/_2$ lines appeared to be approximately Lorentzian were used in a straightforward least-squares fit of line positions to the usual fast-exchange-limit equation[39]

$$\langle\omega\rangle = p_A\omega_A + p_B\omega_B \tag{1}$$

where $p_A = 1/(1 + K[\text{base}])$ and $p_B = K[\text{base}]/(1 + K[\text{base}])$. The resulting least-squares parameters were K, the equilibrium constant for the adduct formation equilibrium, and $(\omega_A - \omega_B)$, the difference in resonance frequencies of the four- and five-coordinate species. These values were then used in an analysis of the line widths, again using the fast-exchange equation[39]

$$T_2^{-1} = T_{2,0}^{-1} + p_A^2 p_B \tau_B(\omega_A - \omega_B)^2 \tag{2}$$

to give a value of τ_B, the adduct lifetime, and an estimate of $T_{2,0}^{-1}$, the line width in the absence of exchange. These in turn give T_{2B}^{-1}, the line width of the adduct resonance since $T_{2,0}^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1}$.

The fast-exchange approximation relies on three conditions for applicability

$$\begin{aligned} \Delta &= \tau|\omega_A - \omega_B| \ll 1 \\ \delta &= \tau|T_{2A}^{-1} - T_{2B}^{-1}| \ll 1 \\ r &= \tau T_{2,0}^{-1} \ll 1 \end{aligned} \tag{3}$$

Preliminary analysis of the data showed that typical maximum values of δ and r were 0.05 and 0.1, respectively. The parameter Δ, on the other hand, was frequently greater than 0.5 and typically greater than 0.1. Consequently there was some doubt concerning the applicability of the fast-exchange approximation, and the matter was examined in some detail (see Appendix). It was concluded that the fast-exchange solution to the modified Bloch equations could still be employed, provided that certain correction terms were used. In general, the correction terms become significant for Δ, δ, or r greater than about 0.1, and are valid in the manner employed for values of the parameters up to about 0.8. Thus for these data, δ and r were neglected, but correction terms in Δ from eq A4 and A5 were used in the following procedure.

Using initial estimates of K, $(\omega_A - \omega_B)$, and τ_B, the parameter Δ was computed, and several iterations were carried out using the term in Δ^4 in (A5) to refine the estimate of τ_B. The resulting value of Δ was then used to correct the line positions using the terms in Δ^3 and Δ^5 in (A4), and the least-squares analysis was repeated to obtain new estimates of K and $(\omega_A - \omega_B)$. This process was continued until self-consistency was obtained. Throughout this process, data from both the $+^3/_2$ and $+^1/_2$ lines were employed, and, in the fitting procedures, all data for a given temperature were fitted to a single value of K or τ_B. In the course of analysis of the data, individual line width or position measurements were removed from the treatment if the value of Δ was found to be greater than 0.8. Data from the $-^3/_2$ and $-^1/_2$ lines were not useful in this procedure since the line widths in the absence of exchange were much greater and the resonance frequency differences were much smaller.

In adopting the above procedure, it was of course assumed that higher order terms in (A4) and (A5) would not lead to further significant corrections. This assumption seems justified since most of the corrections were small anyway, but, furthermore, comparison of the third- and fifth-order terms in (A4) suggests that higher order terms are indeed smaller, even for values of Δ approaching unity. The coefficients of higher powers of Δ are complicated combinations of the mole fractions p_A and p_B and tend to be smaller on the average by roughly a factor of 2 for each additional order in Δ. Thus, if only data with Δ less than 0.8 are retained, the next significant term in (A5), the sixth-order term, is at most about one-sixth of the fourth-order terms used in the corrections. In most cases, the higher order contributions would be even smaller.

The hyperfine splitting constant of the four-coordinate complex was found to be somewhat temperature dependent. Presumably the copper splittings of the five-coordinate adducts are similarly temperature dependent. Unfortunately, however, attempts to fit the line position data for each temperature independently to give values of $(\omega_A - \omega_B)$ for the $+^3/_2$ and $+^1/_2$ lines did not give results showing a statistically significant trend with temperature. For this reason, it was assumed in fitting the data that $(\omega_A - \omega_B)$ is temperature independent. This produces a consistent set of equilibrium constants and adduct lifetimes, though there may remain a systematic error as a result.

The adduct line widths T_{2B}^{-1} are clearly temperature dependent, increasing quite substantially below 30°. These parameters were not directly measurable and thus had to be estimated from the data. Preliminary estimates were made from manual manipulations of the data and were refined in the course of the above iterative procedure. However, the accuracy obtained was not high enough to engender much confidence in the final values. The uncertainties in the adduct lifetimes introduced from this source were therefore substantial, and, for this reason, data points with small p_B (and consequent smaller dependence of $T_{2,0}^{-1}$ on T_{2B}^{-1}) were weighted more heavily in the final data analysis.

In the case of data obtained using pyridine as the base the results are considerably less reliable than in the cases of piperidine and *n*-hexylamine. This is due to the rather smaller amount of data collected and the

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(39) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

generally smaller equilibrium constants found in the pyridine systems. The smaller equilibrium constants resulted in reliance on solutions with rather large amounts of the base in the analysis of the line position and line width data. These difficulties were exemplified most noticeably in the least-squares fit of line positions to (1). The values of $(\omega_A - \omega_B)$ obtained were regarded as unrealistically low, and the equilibrium constants were correspondingly too large to give results consistent with the observed line widths. A much more satisfactory fit to the line width data was obtained if the values of $(\omega_A - \omega_B)$ obtained from the piperidine data were employed in computation of the equilibrium constants for the pyridine adduct. Otherwise the procedure used to fit the pyridine data was identical with that described above including iterative refinements of K and τ_B.

Atherton and Luckhurst[40] have approached the problem of ligand-exchange line broadening from the point of view of relaxation matrix theory. In this approach, the same fast-exchange conditions, eq 3, are assumed as in the fast-exchange limit of the modified Bloch equations. They find that the contribution to the line widths from ligand-exchange modulation of the isotropic part of the spin Hamiltonian is

$$T_2^{-1}(\text{exchange}) = (\Delta g\beta H/h + \Delta a m_I)^2 p_A p_B \tau + [I(I+1) - m_I^2]/(1 + \omega_0^2\tau^2) p_A p_B \tau (\Delta a)^2 \quad (4)$$

where $\Delta g = g_A - g_B$, $\Delta a = a_A - a_B$, and $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$.

The first term in (4) is secular and corresponds to the solution of the modified Bloch equations.[41] The second, nonsecular term finds no counterpart in the solutions of the modified Bloch equations. However, in the present experiments with $\omega_0 = 57.5 \pm 10^9$ sec^{-1} and τ on the order of 10^{-9}–10^{-10} sec, the nonsecular contribution is negligible.

Atherton and Luckhurst[40] further pointed out a potential contribution to the line widths from ligand-exchange modulation of the anisotropic part of the spin Hamiltonian. They concluded, however, that so long as the rotational correlation times of the complexes are short compared with the average lifetime for ligand exchange, this contribution may be neglected with no important error. In the present case, with lifetimes ranging down to 10^{-10} sec and rotational correlation times on the order of 10^{-11} sec, neglect of the anisotropic contributions may be made only with a certain trepidation. Nevertheless, this contribution is probably still small compared with the deviations from the fast-exchange approximation which we have tried to correct.

The spectra obtained using piperidine as the base at low temperatures could not be interpreted in terms of the fast-exchange approximation even with correction terms included. In these cases, the spectra were fitted by computer-calculated line shape functions based on the complete solution to the modified Bloch equations in a manner very similar to that employed by Walker, *et al.*[28] In the computer-simulated spectra the line positions in the absence of exchange were assumed to be identical with those obtained from the fit of line positions to the fast-exchange equations at high temperatures. The line widths of the four-coordinate complex were measured in pure methylcyclohexane solution. Thus, in the computer simulations, it was necessary to adjust three parameters to fit the experimental spectra: the equilibrium constant, the adduct lifetime, and the adduct line widths in the absence of exchange. As in the treatment of the fast-exchange data, it was assumed that these parameters were independent of solvent composition at a given temperature. The fitting procedure was essentially one of trial and error, but, as discussed below, the final fit between calculated and experimental spectra was good, and the resulting parameters were entirely consistent with those determined at high temperatures.

Results

The measured line widths and line positions of the $+^3/_2$ and $+^1/_2$ hyperfine lines of the experimental spectra of $Cu(DnBDC)_2$ are given in Table I for solvent mixtures of methylcyclohexane and piperidine, n-hexylamine, or pyridine at various temperatures. Line widths and positions were most conveniently measured in the units of gauss in the experimental spectra. These were converted to angular frequency units and are expressed as T_2^{-1} and $\omega - \omega_A$, respectively, in Table I.

These data were analyzed as described above to give the equilibrium constants and adduct lifetimes listed in Table II. The uncertainties given in the table reflect both random errors in the least-squares fits and conservative estimates of possible systematic errors. The

TABLE II

PARAMETERS OBTAINED FROM DATA ANALYSIS

Temp, °C	K, l./mol	$10^9\tau_B$, sec	$10^{-6}T_{2B}^{-1}$,[a] sec^{-1}	
			$^3/_2$	$^1/_2$
		Piperidine		
0	12.4 ± 1.2[b]	9 ± 4[b]	118	143
10	7.9 ± 0.8[b]	5 ± 3[b]	105	125
25	3.9 ± 0.4[b]	2 ± 1[b]	95	111
50	1.43 ± 0.05	1.2 ± 0.6	91	110
65	0.90 ± 0.03	0.6 ± 0.3	91	110
		n-Hexylamine		
10	3.9 ± 0.3	1.5 ± 0.7	105	150
20	2.8 ± 0.2	1.1 ± 0.5	98	138
30	1.7 ± 0.1	0.8 ± 0.3	91	125
40	1.14 ± 0.06	0.5 ± 0.3	85	115
50	0.82 ± 0.05	0.3 ± 0.2	80	110
		Pyridine		
10	0.62 ± 0.11	0.8 ± 0.3	82	125
20	0.48 ± 0.07	0.6 ± 0.2	79	118
30	0.34 ± 0.05	0.4 ± 0.2	77	105

[a] Estimates of adduct line widths in the absence of exchange; see text for discussion of uncertainties. [b] Values obtained by fitting computer-simulated line shapes to experimental spectra; uncertainties are estimated.

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(40) N. M. Atherton and G. R. Luckhurst, *Mol. Phys.*, **13**, 145 (1967).

(41) This equation implies the high-field approximation and should be corrected to at least second order in perturbation theory before application to a problem involving large splitting constants.[42] The Bloch equation approach, which employs ω_A and ω_B, obviates this complication.

(42) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

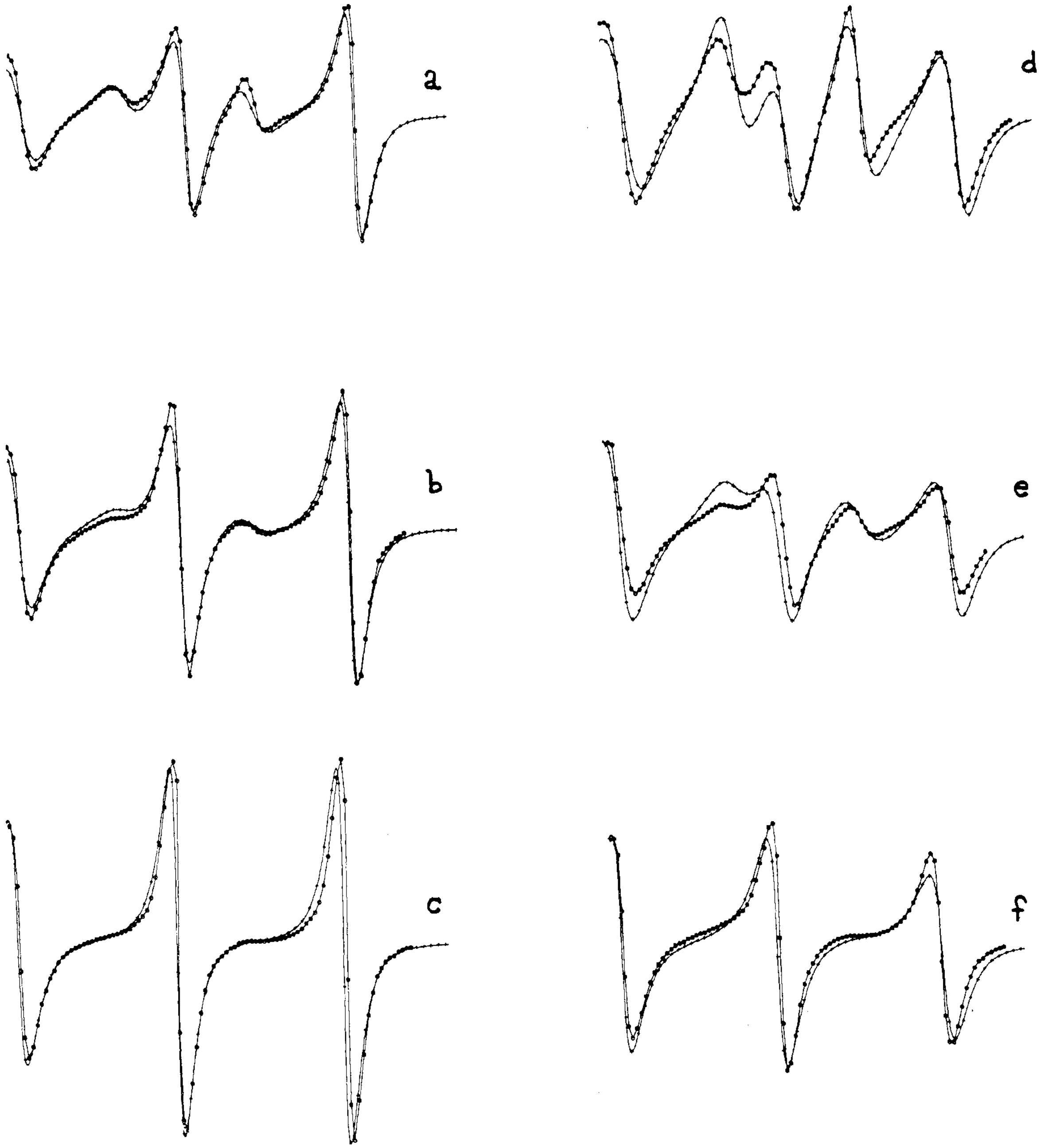

Figure 2.—Comparison of experimental (circles) and calculated (crosses) spectra of $Cu(DnBDC)_2$ in methylcyclohexane solutions of piperidine at the following base concentrations and temperatures: (a) 0.051 *M*, 0°; (b) 0.051 *M*, 10°; (c) 0.051 *M*, 25°; (d) 0.101 *M*, 0°; (e) 0.101 *M*, 10°; (f) 0.101 *M*, 25°. Only the $+^3/_2$ and $+^1/_2$ lines (and part of the $-^1/_2$ line) are shown. The magnetic field increases to the right.

line widths estimated for the adducts are also given in Table II. Those spectra obtained in methylcyclohexane–piperidine mixtures at low temperatures which could not be interpreted in terms of the fast-exchange approximation were computer fitted with the results at 0, 10, and 25° for [piperidine] = 0.051 and 0.101 *M* shown in Figure 2. The agreement is seen to be quite good. The parameters used are given in Table II.

Arrhenius plots of the equilibrium constants and adduct lifetimes yielded the standard enthalpy and entropy changes for the adduct formation equilibria as well as the activation parameters for the adduct dissociation reactions. These parameters are given in Tables III and IV. The uncertainties given for *K* and k_r in Tables III and IV reflect the standard deviations in the least-squares fits to the Arrhenius equation. These fits are much better than might have been expected from the uncertainities in *K* and τ_B given in Table II and it is possible that the uncertainties in Table II are overly conservative.

The *g* values and copper nuclear hyperfine splitting constants measured for four-coordinate $Cu(DnBDC)_2$ in methylcyclohexane solution and the extrapolated values for the five-coordinate adducts are given in Table V. The copper splitting of $Cu(DnBDC)_2$ in methylcyclohexane was found to be temperature dependent

TABLE III

THERMODYNAMIC PARAMETERS

Base	pK_B[a]	K,[b] l./mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
		$Cu(DnBDC)_2 \cdot$base		
Piperidine	11.0	3.9 ± 0.1	−7.5 ± 0.4	−22 ± 1
n-Hexylamine	10.6	2.1 ± 0.1	−7.3 ± 1.2	−23 ± 2
Pyridine	5.2	0.40 ± 0.02	−5 ± 2	−19 ± 3
		$Cu(\textit{tert}\text{-}C_4H_9OAc)_2 \cdot$base[c]		
Pyridine	5.2	37.3	−7.1 ± 0.3	−17 ± 1
		$Cu(acac)_2 \cdot$base[d]		
Pyridine	5.2	7.4	−6.0 ± 1.0	−16 ± 4

[a] In aqueous solution at 25°; D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965. [b] At 25°. [c] From ref 21. [d] From ref 24.

TABLE IV

KINETIC PARAMETERS

Base	10^9k_r,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Piperidine	0.37 ± 0.04	7.4 ± 1.7	5 ± 3
n-Hexylamine	1.3 ± 0.1	6.6 ± 2.0	5 ± 3
Pyridine	2.0 ± 0.2	5 ± 2	−1 ± 5

[a] At 25°.

TABLE V

ESR PARAMETERS

Species	g	$-a$, G
$Cu(DnBDC)_2$[a]	2.0456 ± 0.0002	77.8 ± 0.3
$Cu(DnBDC)_2 \cdot$piperidine[a]	2.0608 ± 0.0005	60.8 ± 0.8
$Cu(DnBDC)_2 \cdot$*n*-hexylamine[a]	2.0612 ± 0.0007	58.5 ± 1.0
$Cu(HD)_2$[b]	2.069	89
$Cu(HD)_2 \cdot$pyridine[b]	2.081	71
$Cu(\textit{tert}\text{-}C_4H_9OAc)_2$[c]	2.129	70.0
$Cu(\textit{tert}\text{-}C_4H_9OAc)_2 \cdot$pyridine[c]	2.155	47.3

[a] In methylcyclohexane solution at 25°. [b] In benzene solution; data from ref 19. [c] In cyclohexane solution; data from ref 21.

over the range 0–50°; the splitting decreases in absolute value by 0.027 ± 0.007 G/deg over this range. The g value, on the other hand, is nearly temperature independent, increasing by only 0.0004 ± 0.0003 when the temperature is increased from 0 to 50°.

Discussion

Aasa and coworkers[15] concluded from the esr spectra of $Cu(DDC)_2$ in pyridine–benzene solutions that no specific adduct was formed in this system but that the effects on the esr spectrum were due to a solvent effect. Therefore we must first consider whether we are dealing with a well-defined, though short-lived, adduct of the metal complex with the nitrogen bases or merely with a loose solvate of indeterminant structure.

The esr parameters obtained for the presumed adducts of $Cu(DnBDC)_2$ are very similar to those obtained with adducts of other square-planar copper complexes.[19,21] The g values and copper hyperfine splittings of copper(II) bis(*tert*-butylacetoacetate) [$Cu(\textit{tert}\text{-}C_4H_9OAc)_2$][21] and copper(II) dimethylglyoxime [$Cu(HD)_2$][19] and the corresponding pyridine adducts are given in Table V for comparison. The splitting constant of $Cu(DnBDC)_2$ decreases by nearly the same amount on adduct formation as do the splittings in the other systems. Similarly the g values shift in the same way on adduct formation. The shift in line positions is well explained by the fast-exchange approximation, eq 1, which is based on a two-jump model. The equilibrium constants so derived follow the basicity of the nitrogen bases (see Table III) in the same way as has been observed previously.[21,24,26–29] Finally and most conclusively, two separate resonances are seen at low temperatures, the ratios of intensities of which are entirely consistent with equilibrium constants extrapolated from higher temperatures. Thus we conclude that the $Cu(DnBDC)_2$ does indeed form nitrogen base adducts of character similar to those formed by complexes with oxygen ligands.

There is evidence for the formation of six-coordinate bis adducts in the case of more strongly acidic complexes such as copper(II) bis(trifluoroacetylacetonate).[9] Furthermore, bis adducts of square-planar nickel(II) complexes are common.[43] The esr spectrum at 0° of $Cu(DnBDC)_2$ in methylcyclohexane containing 0.101 M piperidine exhibited an asymmetric high-field ($m_I = +{}^3/_2$) line which could not be explained in terms of two species interconverting at rates consistent with the remainder of the data. This effect is only barely detectable in Figure 2d, which is computer drawn; the original trace is more convincing. This asymmetry is almost certainly due to an additional monomeric copper species, perhaps to a small amount of a six-coordinate adduct with splitting constant intermediate between the four- and five-coordinate species. Attempts to confirm this interpretation were unsuccessful, however, since, at lower temperatures, where the six-coordinate species would have been expected to be more highly favored, the lines were much broader and the asymmetry could not be detected, while at higher temperatures, even in solutions containing much higher concentrations of piperidine, no evidence for such a species could be found. Similarly, no evidence for a six-coordinate adduct was seen in the cases of the other two bases studied.

The variation of the copper hyperfine splitting of four-coordinate $Cu(DnBDC)_2$ with temperature is very similar to that observed by Falle and Luckhurst,[44] who studied $Cu(acac)_2$ in liquid mesitylene and *o*-terphenyl from room temperature up to 450°. They ascribed the variation to contributions of excited vibrational states having smaller splitting constants. This effect is most likely due to vibronic mixing of states having a contribution from the copper 4s orbital into the molecular orbital containing the odd electron. Spin density in the 4s orbital would be expected to make a positive contribution to the splitting. Such admixtures have been proposed to account for variations of the splittings in other copper complexes.[17,21,45]

As shown in Table II, the line widths of the esr spectrum of four-coordinate $Cu(DnBDC)_2$ are constant at higher temperatures, but increase below 20°. This is in contrast with the results of Aasa, *et al.*,[15] who found somewhat narrower lines in the esr spectrum of Cu-

(43) G. N. La Mar, *Inorg. Chim. Acta*, **3**, 183 (1969); R. L. Carlin and A. E. Siegel, *Inorg. Chem.*, **9**, 1587 (1970).

(44) H. R. Falle and G. R. Luckhurst, *Mol. Phys.*, **10**, 587 (1966).

(45) T. Chiang, *J. Chem. Phys.*, **48**, 1814 (1968).

(DDC)$_2$ with constant line widths from −40° to +40°, the line widths increasing both at higher and at lower temperatures. This effect has been interpreted[46] as indicating comparable contributions to the widths from the spin–rotation interaction and from incomplete averaging of anisotropies in the g and hyperfine tensors. The first contribution decreases, while the second increases, with increasing rotational correlation time. Since the correlation time is expected to increase with η/T, where η is the solution viscosity, the two effects balance over a considerable range of temperature. However, since the rotational correlation time depends upon the size of the complex, one expects that with the bulkier n-butyl groups the correlation time of Cu(DnBDC)$_2$ will be longer than that of Cu(DDC)$_2$ at a given temperature so that the minimum in the line width–temperature curve would be shifted to larger line widths and to higher temperatures. Everything else being equal, one would expect this shift to be still greater for the adducts, and, to the extent that the T_{2B}'s in Table II are meaningful, this expectation seems to be fulfilled. Somewhat larger values of T_{2B}^{-1} were required to fit the n-hexylamine data at lower temperatures than in the cases of piperidine or pyridine; this may reflect the expected larger size of this adduct.

Since the line widths depend upon the solution viscosity through the rotational correlation times and since the solution viscosities are not constant with varying solvent composition, there is a serious problem in the data analysis method employed in this work. It was assumed that the T_{2A}'s were constant at constant temperature and the T_{2B}'s were chosen to fit all the data for a given base at a given temperature. Unfortunately, however, without a much more thorough study of the line widths as functions of viscosity and temperature it is impossible to improve on this procedure. Thus, the values of T_{2B} which fit the data represent some kind of average which best accounts for the variation of T_{2A} and T_{2B} with solution viscosity; this is, of course, further reason for discounting the significance of the values of T_{2B}^{-1} which are listed in Table II.

Perhaps the most noteworthy feature of the results given in Tables II and III are the generally small values of the equilibrium constants for adduct formation. For comparison, results on pyridine adduct formation with Cu(acac)$_2$[24] and Cu(*tert*-C$_4$H$_9$OAc)$_2$[21] are given in Table III. Clearly, Cu(DnBDC)$_2$ is substantially less acidic than are the copper complexes with oxygen ligands. This is most likely due to the more covalent character of the copper–sulfur bonds of the complex and consequent higher electron density on copper. Furthermore, the more covalent bonds would be expected to be more resistant to deformation to the geometry which seems to be characteristic of the five-coordinate adducts—a square pyramid with the copper atom appreciably above the plane of the equatorial ligands.[6,7]

In discussing the rates of adduct dissociation in the VO(acac)$_2$–base system, Walker, *et al.*,[28] speculated that the forward rate was primarily entropy limited. The argument was that an orientational factor was involved in the reaction of the base with the metal complex. This supposition is supported by the present data. Indeed, in comparing the thermodynamic and kinetic parameters of Tables III and IV, one is struck by the fact that the enthalpy of activation for the dissociation reaction is identical within experimental error with the overall enthalpy change for the reaction. Application of the law of microscopic reversibility indicates near-zero enthalpy of activation for the forward reaction. Thus the forward reaction is apparently limited in rate almost entirely by activation entropy, whereas the reverse reaction is primarily enthalpy limited.

A diffusion-controlled reaction is expected to have an enthalpy of activation on the order of 1–3 kcal/mol, essentially the activation energy for the diffusion process.[47] The near-zero enthalpy of activation for the forward process indicated by the present data thus seems anomalous. On the other hand, the theory of diffusion-controlled reactions would not really be expected to apply to the present case since the concentration of base was quite high for all solutions from which significant data were obtained. Indeed, the reaction partners are virtually always within a few molecular diameters of one another in the solutions studied. It would be interesting to study the Cu(DnBDC)$_2$–base system at much lower temperatures where larger equilibrium constants would permit working with more dilute solutions of base. Under these conditions, one would expect to find a nonzero enthalpy of activation for the forward reaction. Unfortunately, the much larger line widths in the absence of chemical exchange limit the accuracy of the equilibrium constant and adduct lifetime measurements at lower temperatures, so that, with the added complication of a possible six-coordinate adduct at low temperatures, this small effect would probably be extremely difficult to find and prove conclusively.

The application of esr line broadening to measurement of rate constants used in this work seems promising on first thought, and the apparent success in the present case would seem to encourage further applications. A word of caution is in order, however, for the rates found in the Cu(DnBDC)$_2$–base system are in a rather narrow range of ideality. If, on the one hand, the rates had been much greater, the adduct lifetimes would have been sufficiently short that a serious attempt would have to be made to deal with chemical exchange modulation of the line width contributions from incomplete rotational averaging of the g and hyperfine tensor anisotropies.[40] On the other hand, longer lifetimes would have put all the data analysis in the intermediate exchange region where extraction of the rate and equilibrium parameters is both more tedious and less precise.

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(47) E. F. Caldin, "Fast Reactions in Solution," Blackwell, 1964, Oxford.

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Appendix

The Fast-Exchange Approximation

The Bloch equations are commonly and conveniently modified to take into account exchange of the unpaired electron between two sites, A and B, which are characterized by resonance frequencies ω_A and ω_B and transverse relaxation times T_{2A} and T_{2B}. The slow-passage solution of the modified Bloch equations is the complex magnetization[39]

$$G = -i\gamma H_1 M_0 T_{2,0} \times \frac{1 + r(1 + ix) - (p_A - p_B)(\delta - i\Delta)}{r(1 + ix)^2 + (1 + ix)[1 - (p_A - p_B)(\delta - i\Delta)] - p_A p_B(\delta - i\Delta)^2/r} \qquad \text{(A1)}$$

where $x = T_{2,0}(\omega - \langle\omega\rangle)$, $r = \tau/T_{2,0}$, $\Delta = \tau(\omega_A - \omega_B)$, $\delta = \tau(T_{2A}^{-1} - T_{2B}^{-1})$, $\langle\omega\rangle = p_A\omega_A + p_B\omega_B$, $T_{2,0}^{-1} = p_A T_{2A}^{-1} + p_B T_{2B}^{-1}$, and $\tau = \tau_A\tau_A/(\tau_B + \tau_B)$; τ_A, τ_B and p_A, p_B are, respectively, the residence times of the electron on sites A and B and the fractional populations of sites A and B.

Equation A1 is subject to simple interpretation when the parameters r, Δ, and δ are all very much less than unity, that is, when the average lifetime of the electron at one site is very much less than the average transverse relaxation time in the absence of exchange and also much less than the reciprocals of the difference of the resonance frequencies and the difference in the no-exchange relaxation times. The usual procedure in deriving the fast-exchange approximation is to assume a Lorentzian line shape and then to identify T_2 with the intensity at the center of the absorption line, assumed to occur at $\langle\omega\rangle = p_A\omega_A + p_B\omega_B$. In this way one obtains the usual expression for T_2^{-1}

$$T_2^{-1} = T_{2,0}^{-1} + p_A p_B \tau(\omega_A - \omega_B)^2 \qquad \text{(A2)}$$

As is evident from the data presented above, many of the spectra analyzed to obtain equilibrium and kinetic parameters gave values of τ large enough to be perilously close to the limits of applicability of the fast-exchange solution, if not already beyond those limits. From the method of derivation of (A2) it is difficult to estimate the accuracy of the equation near the limits of applicability. Although it is always possible to use the complete solution (A1) and determine the kinetic parameters by fitting the experimental spectra to computer-simulated spectra, this procedure is extremely tedious and of doubtful precision. Thus it was thought necessary to examine the fast-exchange approximation more closely.

Since one of the most experimentally obvious characteristics of the transition from fast exchange to the more complex intermediate exchange region is a marked non-Lorentzian line shape, it would seem fruitless to assume a Lorentzian line shape in attempting to improve on the fast-exchange equations or even to estimate their accuracy. Rather, a more direct approach was attempted, assuming only the accuracy of the modified Bloch equations.

The imaginary part v of the complex magnetization G, corresponding to the magnetic resonance absorption, may be written

$$v = \gamma H_1 M_0 T_{2,0} \sum_{i=0}^{2} v_{ni}x^i \Big/ \sum_{i=0}^{4} v_{di}x^i \qquad \text{(A3)}$$

where each of the coefficients may be expressed as a function of the parameters r, Δ, and δ

$$v_{n0} = (1 + r)^2 - 2(p_A - p_B)(1 + r)\delta + p_A p_B(1 + r)(\Delta^2 - \delta^2)/r + (p_A - p_B)^2(\Delta^2 + \delta^2) + p_A p_B(p_A - p_B)\delta(\Delta^2 + \delta^2)/r$$

$$v_{n1} = 2\Delta[(p_A - p_B)r + p_A p_B\delta]$$

$$v_{n2} = r^2$$

$$v_{d0} = (1 + r)^2 - 2(p_A - p_B)(1 + r)\delta + 2p_A p_B(1 + r)(\Delta^2 - \delta^2)/r + (p_A - p_B)^2(\Delta^2 + \delta^2) + 2p_A p_B(p_A - p_B)\delta(\Delta^2 + \delta^2)/r + p_A^2 p_B^2(\Delta^2 + \delta^2)^2/r^2$$

$$v_{d1} = 2\Delta[(p_A - p_B)r + 2p_A p_B(1 + 2r)\delta/r - 2p_A p_B(p_A - p_B)(\Delta^2 + \delta^2)/r]$$

$$v_{d2} = (1 + 2r + 2r^2) - 2(p_A - p_B)(1 + r)\delta + (\Delta^2 + \delta^2) - 2p_A p_B(3\Delta^2 + \delta^2)$$

$$v_{d3} = 2(p_A - p_B)r\Delta$$

$$v_{d4} = r^2$$

Differentiating v with respect to x and setting the derivative equal to zero, one can obtain an expression for the position of the maximum of the absorption curve or the zero crossing of the first derivative as a power series in the three parameters Δ, δ, and r. The result, to fifth order, is

$$\langle\omega\rangle = (p_A\omega_A + p_B\omega_B) - p_A p_B \tau^{-1}\{\delta(2 + 3r)/(1 + r)^2 - (p_A - p_B)(\Delta^2 - \delta^2/3)(1 + 2r)/(1 + r)^3 + \delta(\Delta^2 - \delta^2) \times [p_A p_B(3 + 10r + 8r^2) - 2(p_A - p_B)^2(2 + 7r + 5r^2)]/(1 + r)^5 + p_A p_B(p_A - p_B)[\Delta^4(2 + 7r + 6r^2) - [\Delta^2\delta^2(7 + 40r + 42r^2) + \delta^4(11 + 49r + 48r^2)]/(1 + r)^6 - (p_A - p_B)^3\Delta[\Delta^4(1 + 3r) - 2\Delta^2\delta^2(7 + 18r) + 5\delta^4(1 + 3r)]/(1 + r)^5\} \qquad \text{(A4)}$$

Differentiating again and setting the second derivative equal to zero, one obtains the width between first-derivative extrema. This calculation, which is far more tedious than the first, gives the following result, to fourth order, for $T_{2,\mathrm{obsd}}^{-1} = (\sqrt{3}/2) \times$ derivative width

$$T_2^{-1} = T_{2,0}^{-1} + \tau^{-1}p_Ap_B[(\Delta^2 - \delta^2) + (p_A - p_B) \times \delta(3\Delta^2 - \delta^2) + (5p_Ap_B - 1)(\Delta^4 - 6\delta^2\Delta^2 + \delta^4)] \quad \text{(A5)}$$

Each of the terms within the brackets of (A5) multiplies a power series in r; however, in the second- and third-order terms, the lowest power (other than zero) of r occurring with a nonzero coefficient is fourth order, and in the fourth order term, the lowest nonzero term in r is third order.

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Cuprous Complex of Methyldiazene

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The reaction of methyldiazene with aqueous cuprous chloride yields an air-sensitive, moderately stable, diamagnetic, red-brown solid with the formula $(CH_3N{=}NH)CuCl$ (I). The electronic spectrum shows transitions at 360 and 470 nm. Solubility characteristics suggest a polymeric structure, and two possibilities are discussed. The integrity of the nitrogen–nitrogen bond in the diazene is maintained both in the reaction of the compound with oxygen and in the thermal decomposition at 70–72°. Methyldiazene can be recovered from the compound by dissolving it in a medium which coordinates cuprous ion. The reaction of methyldiazene with cupric ion is examined in relationship to the failure of an alternate synthetic route to I.

Introduction

A number of monosubstituted diazenes ($RN{=}NH$), including alkyl-,[1] aryl-,[2] and alkenyldiazenes,[3] are now known. These molecules are highly reactive and inherently unstable, reacting with themselves *via* a bimolecular mechanism.[1-3] Stabilization of several monosubstituted aryldiazenes in complexes with platinum is possible.[4,5] An even greater variety of complexes of deprotonated monosubstituted aryldiazenes with platinum,[4,5] molybdenum,[5-8] and tungsten[7-9] have been prepared. One report of a platinum complex of deprotonated diazene itself has appeared,[10] as has one report of molybdenum and tungsten complexes of a deprotonated monosubstituted alkyldiazene.[11]

Most recently Balch, *et al.*, synthesized a cuprous chloride complex of phenyldiazene, $(C_6H_5N{=}NH)Cu_4Cl_4$, from the reaction of phenylhydrazine with aqueous cupric chloride.[12] This reaction parallels the established synthesis of the azomethane–cuprous chloride complex $(CH_3N{=}NCH_3)Cu_2Cl_2$.[13] They did not obtain a methyldiazene complex when methylhydrazine was substituted for phenylhydrazine. This paper is a report of the successful synthesis of a methyldiazene–cuprous chloride complex through the direct reaction of methyldiazene with aqueous cuprous chloride. This is the first synthesis of a monosubstituted alkyldiazene complex.

Experimental Section

Preparation of Compounds.—Hydroxylamine-*O*-sulfonic acid was prepared as described by Smith[14] and analyzed to be 98+% pure by iodometry.

N-Methylhydroxylamine was obtained as the oxalate salt by hydrogenation of nitromethane on 5% palladium on barium sulfate catalyst (Matheson Coleman and Bell) at atmospheric pressure.[15] Data for $(CH_3NH_2OH)_2C_2O_4$ follow: mp 158–160° (uncor), lit.[15] mp 158°; neutralization equivalent: calcd, 92.1; found, 93.3.

Cuprous chloride was prepared by the literature method.[16]

trans-**Methyldiazene.**—This substance was obtained from the reaction of hydroxylamine-*O*-sulfonic acid with *N*-methylhydroxylamine in aqueous sodium hydroxide.[1a] In a typical synthesis 0.37 g (3.3 mmol) of hydroxylamine-*O*-sulfonic acid and a magnetic stirring bar were placed in a flask on a vacuum line. This flask was connected to a side-arm flask *via* a standard taper arrangement. Into the side-arm flask was placed 40 ml of 1 *M* sodium hydroxide solution containing 0.51 g (5.5 mmol of *N*-methylhydroxylamine) of *N*-methylhydroxylammonium oxalate. After pumping for several minutes to remove air from the two flasks, the side-arm flask was rotated to add the sodium hydroxide solution to the solid hydroxylamine-*O*-sulfonic acid which dissolved within a few seconds after stirring commenced. Over

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