Thermodynamics and Magnetic Resonance of Five-Coordinate Copper *t*-Butyl Acetoacetate–Pyridine Adducts in Cyclohexane[1a]

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Received July 24, 1968

Abstract: The equilibrium constants and enthalpies for 1:1 adduct formation of copper(II) bis(*t*-butyl acetoacetate) with a series of pyridine donors have been measured in cyclohexane by spectrophotometric methods and the 1:1 adducts studied by esr and nmr techniques. The spectrophotometrically determined thermodynamic values for the copper(II) *t*-butyl acetoacetate–pyridine system were found to agree with the calorimetrically determined values. This agreement was taken as evidence that the spectrophotometric method was a suitable technique for the systems studied. Measurement of the shift in OH stretching frequency of methanol upon hydrogen-bond formation with the series of pyridine donors established the order of donor ability as pyridine < 4-methylpyridine < 4-ethylpyridine < 4-*t*-butylpyridine. This order of donor ability was maintained in the thermodynamics of adduct formation with copper *t*-butyl acetoacetate. The copper isotropic hyperfine coupling constants $\langle a \rangle$ have been measured and found to decrease dramatically in the adducts. The adducts show an increase in isotropic $\langle g \rangle$ value. Proton contact shifts for the pyridine adducts are reported and are interpreted in terms of spin delocalization into the pyridine σ system.

The electronic and magnetic properties of copper(II) β-diketonates in solution are well known to be strongly dependent on the solution media. Coordinating solvents are found to have a particularly dramatic influence on the electronic spectra[2,3] and esr parameters.[4,6] Stoichiometric and equilibrium studies have shown that donor solvents interact with copper chelates to form both 1:1 and 2:1 adducts,[7-13] and a recent X-ray study of the $Cu(acac)_2 \cdot$quinoline adduct proves that axial coordination occurs.[14] Despite continued active interest in these systems, no systematic study has been reported relating the changes in electronic and magnetic properties with the nature of the adduct species in solution and the thermodynamics of axial coordination in a truly "inert" solvent environment.

In order to isolate and investigate those effects due solely to the specific interactions of adduct formation, a copper chelate capable of being fully characterized in "inert" alkane solvents was selected for investigation. This paper reports on the thermodynamics of adduct formation of copper(II) bis(*t*-butyl acetoacetate) [Cu(*t*-Buoac)$_2$] with a series of 4-substituted pyridines in cyclohexane and on the associated changes in the copper isotropic hyperfine coupling constants $\langle a \rangle$, isotropic $\langle g \rangle$ values, and pyridine proton contact shifts.

Experimental Section

Materials and Solutions. All the pyridines (reagent grade) were distilled through a Vigreux column under reduced pressure from Zn metal and then Cu(*t*-Buoac)$_2$, except pyridine (Fisher Spectrograde) which was first distilled under reduced pressure from Na metal. Middle fractions were collected over Linde 4A molecular sieves in tightly stoppered bottles for immediate use. Analyses carried out using an F & M Laboratory gas chromatograph with a Carbowax 20M column and helium carrier gas showed all pyridines to be gas chromatographically pure.

Fisher reagent grade methanol was refluxed for 2.5 hr over barium oxide and distilled through a Vigreux column, the middle fraction being collected.

Fisher Spectrograde carbon tetrachloride and Baker Spectrophotometric Quality cyclohexane were used without further purification. Storage of the cyclohexane over Linde 4A molecular sieves was found to be inconsequential to the experimental measurements and was thus discontinued.

All solutions were prepared in oven-dried glassware and used within a 1-hr period. No change in the electronic spectra of the solutions used in the spectrophotometric runs was observed over a 48-hr period. Infrared spectra of stock base solutions used in the spectrophotometric and infrared runs showed no absorptions due to water.

Copper Bis(*t*-butyl acetoacetate). *t*-Butyl acetoacetate was refluxed for 3 hr over anhydrous $CaCl_2$ and distilled through a Vigreux column under reduced pressure, the middle fraction being collected. The copper complex precipitated upon mixing aqueous solutions of $CuSO_4$ and *t*-butyl acetoacetate and NaOH. The green product was collected on a filter, thoroughly washed with water, and air-dried. The dried product was then recrystallized from *n*-hexane twice and placed in a vacuum dessicator over P_2O_5 for 3 days. Microanalysis results are as follows. *Anal.* Calcd for $C_{16}H_{26}CuO_6$: C, 50.85; H, 6.94; O, 25.40; Cu, 16.8; mol wt, 378. Found: C, 51.04; H, 6.91; O, 25.36; Cu, 16.7; mol wt, 387. Infrared spectra showed no absorptions due to water.

Copper Bis(*t*-butyl acetoacetate)·Pyridine. The pyridine solutions from the spectrophotometric runs containing Cu(*t*-Buoac)$_2$ and pyridine in cyclohexane were saved, and an appropriate amount of pyridine was added to ensure complete adduct formation. The solutions were evaporated under reduced pressure at

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Table I. Spectrophotometric Data and Equilibrium Constants for 1:1 Adducts of the Pyridines with Copper *t*-Butyl Acetoacetate at 25° in Cyclohexane

Donor	C_A, M	C_B, M	$A - A^0$	$\epsilon_C - \epsilon_A$	λ, mμ	Temp, °C	K, l. mole^{-1}
Pyridine	0.02049	0.00683	0.088	32.16	700	25.0	37.2 ± 0.9
		0.02050	0.218				
		0.04099	0.352				
		0.1025	0.503				
	0.02049	0.00683	−0.070	−25.60	540	25.0	36.9 ± 0.9
		0.02050	−0.178				
		0.04099	−0.275				
		0.1025	−0.403				
4-Methylpyridine	0.01671	0.00761	0.129	37.84	700	25.0	60.8 ± 0.3
		0.01522	0.266				
		0.02283	0.302				
		0.04566	0.427				
		0.1142	0.543				
4-Ethylpyridine	0.01914	0.01536	0.273	39.15	700	25.0	67.9 ± 0.3
		0.03940	0.479				
		0.07680	0.605				
4-*t*-Butylpyridine	0.01880	0.01743	0.336	42.73	700	25.0	75.1 ± 0.3
		0.04358	0.559				
		0.08715	0.677				

room temperature and the bright green precipitate was collected. Microanalysis results are as follows. *Anal.* Calcd for $C_{16}H_{26}CuO_6 \cdot C_5H_5N$: C, 55.19; H, 6.84; N, 3.07; Cu, 13.9. Found: C, 55.16; H, 6.76; N, 3.12; Cu, 13.8. After 2 days under full vacuum, the analysis was unchanged. Infrared spectra showed no absorptions due to water.

Apparatus and Measurements. Optical absorption measurements were made with a Cary Model 14 spectrophotometer equipped with a red-sensitive photomultiplier detector and fluid thermostated cell holders. The temperature of the solutions was maintained constant within ± 0.1° and measured directly by inserting a thermocouple into the cell.

The methanol OH frequency shifts and Nujol spectra of Cu(*t*-Buoac)$_2$ and Cu(*t*-Buoac)$_2$·pyridine were measured on a Perkin-Elmer 421 infrared spectrometer.

The nmr spectra were determined on a Varian A60-A spectrometer. The shifts, $\Delta\nu_{obsd}$, were measured relative to the solvent cyclohexane and to a standard solution containing the same concentration of pyridine in cyclohexane.

The esr spectra were measured with a Varian Model V-4502 X-band spectrometer equipped with Fieldial Mark I, a Hewlett-Packard Model 70001A X-Y recorder, and a Hewlett-Packard frequency meter, Model X532B. Temperature control for room-temperature measurements was provided by a suitably modified Varian V-4457 variable-temperature accessory. The calibration of the spectra was checked using solid DPPH and an aqueous solution of Fremy's salt. Measurements were made on pyridine–cyclohexane solutions in which Cu(*t*-Buoac)$_2$ was completely complexed.

The calorimeter employed was similar to that used by Arnett[15] and will be reported in a future paper along with the experimental techniques.

Procedure. The spectrophotometric equilibrium constants were determined by analytical solution of the Rose–Drago equation[16]

$$K^{-1} = \frac{C_A C_B}{A - A^0}(\epsilon_C - \epsilon_A) - C_A - C_B + \frac{A - A^0}{\epsilon_C - \epsilon_A}$$

where C_A is the initial acid concentration, C_B is the initial base concentration, $A - A^0$ is the difference in the absorbance of a solution of acid at concentration C_A and a solution of acid and base at concentrations C_A and C_B, and $\epsilon_C - \epsilon_A$ is the difference in molar absorptivities of the complex (C) and acid (A). The reported equilibrium constants and differences in molar absorptivities were calculated using a computer program technique which gives K^{-1}, where the sum of the squares of the deviations of the experimental $(\epsilon_C - \epsilon_A)$ from their average was smallest.[17]

The spectrophotometric enthalpy measurements were made from the temperature dependence of the equilibrium constants. A single-solution technique that utilizes that Rose–Drago equation was used in the enthalpy calculations.[18] The ΔH values determined by the single-solution technique are insensitive to small errors in K and $\epsilon_C - \epsilon_A$. The value of ΔH is, however, very sensitive to the temperature dependence of $\epsilon_C - \epsilon_A$. The absorptivity difference $(\epsilon_C - \epsilon_A)$ was found to be temperature independent within experimental error.

The calorimetric equilibrium constants and enthalpies were evaluated simultaneously by the same techniques used in the spectrophotometric calculations. The appropriate form of the Rose–Drago equation is[19]

$$K^{-1} = \frac{C_A C_B V \Delta H^\circ}{\Delta H^1} - C_A - C_B + \frac{\Delta H^1}{V \Delta H^\circ}$$

where ΔH° is the heat of formation of 1 mole of adduct, V is the total volume of the solution, and ΔH^1 is difference between the heat observed upon adding the base to the acid solution and the heat of solution for an equal concentration of base.

The proton resonance position of complexed pyridine relative to uncomplexed pyridine, $\Delta\nu_{com}$, was calculated from the relationship $\Delta\nu_{com} f_{com} = \Delta\nu_{obsd}$, where f_{com} is the fraction of pyridine complexed. No concentration dependence was noted in the values of $\Delta\nu_{com}$ within experimental error. The electron–nuclear coupling constants were calculated by substitution of the contact shift $(\Delta\nu_{com})$ into the equation $A/h = (\Delta\nu/\nu)g_H\beta_H(3kT)/g_e\beta_e S(S+1)h$, where $\Delta\nu$ is the nmr shift, A the electron–nuclear coupling constant, ν the resonance frequency (60 Mc), g_e the Lande g factor, β_e the electron Bohr magneton, S the electron spin, g_H the proton g value, and β_H the proton–nuclear magneton.

The isotropic $\langle g \rangle$ values and copper hyperfine coupling constants were determined from the transitions corresponding to $m_I = +1/2$ and $-1/2$.

Results

The spectrophotometric and thermodynamic data for the 1:1 adducts of Cu(*t*-Buoac)$_2$ with pyridine donors in cyclohexane are given in Tables I and II.

(15) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Am. Chem. Soc.*, **87**, 154 (1965).
(16) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).
(17) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).
(18) R. L. Carlson and R. S. Drago, *ibid.*, **84**, 2320 (1962).
(19) T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965).

Table II. Spectrophotometric Data and Thermodynamic Values for 1:1 Adducts of the Pyridines with Copper *t*-Butyl Acetoacetate at 700 mμ in Cyclohexane

Donor	C_A, M	C_B, M	$A - A^0$	$E_C - E_A$	Temp, °C	K, l. mole^{-1}	$-\Delta F \pm$ 0.02 kcal mole^{-1}	$-\Delta H \pm$ 0.3 kcal mole^{-1}	$-\Delta S \pm$ 0.8 cal mole^{-1}
Pyridine	0.02510	0.1569	0.656	31.30	25.0	37.3	2.15	7.1	16.6
	0.02499	0.1562	0.637		28.7	32.3			
	0.02488	0.1555	0.613		32.8	27.3			
	0.02475	0.1547	0.592		36.6	23.8			
	0.02463	0.1540	0.571		40.6	20.7			
4-Methylpyridine	0.01671	0.04567	0.427	37.84	25.0	60.4	2.43	7.9	18.3
	0.01659	0.04533	0.386		31.2	45.4			
	0.01645	0.04496	0.341		38.1	33.7			
	0.01640	0.04480	0.323		40.9	29.9			
4-Ethylpyridine	0.01914	0.07680	0.605	39.15	25.0	68.2	2.49	7.9	18.1
	0.01903	0.07633	0.573		30.2	54.0			
	0.01890	0.07582	0.538		35.7	42.9			
	0.01881	0.07547	0.517		39.5	36.7			
4-*t*-Butylpyridine	0.01880	0.04358	0.559	42.73	25.0	75.1	2.56	7.9	17.9
	0.01864	0.04222	0.502		32.1	55.9			
	0.01855	0.04301	0.478		35.5	47.7			
	0.01846	0.04279	0.442		40.1	39.3			

The recorded absorption curves for the Cu(*t*-Buoac)$_2$–pyridine system are shown in Figure 1 and correspond to the pyridine data listed in Table I. These curves form a family with a sharp isosbestic point at 604 mμ, indicating the presence of only two absorbing species in solution, the free and complexed Cu(*t*-Buoac)$_2$. The equilibrium constant calculated from these curves is independent of wavelength as shown in Table I by typical data for the widely separated wavelengths 540 and 700 mμ. This indicates only 1:1 and not 2:1 equilibria taking place between the two absorbing species.[20] Similar spectra with sharp isosbestic points were obtained for all the donors studied.

The reliability of the spectrophotometric method for determining thermodynamic values of these systems was studied by employing a calorimetric technique. The calorimetric and thermodynamic data for the Cu(*t*-Buoac)$_2$–pyridine system are given in Table III. The calorimetric data accurately obey the equations for 1:1 equilibria. The graphical solutions for the data listed in Tables I and III are illustrated in Figures 2 and 3, respectively, and comparison of the computed values of K and ΔH shows that the calorimetrically determined values are in excellent agreement with those determined spectrophotometrically.

The chemical analysis of the Cu(*t*-Buoac)$_2$·pyridine adduct isolated from the solutions used in the spectrophotometric study agrees with the stoichiometry calculated for a 1:1 Cu(*t*-Buoac)$_2$·pyridine adduct. This combined with the spectrophotometric and calorimetric results discussed above is virtually conclusive evidence for only 1:1 adduct formation occurring in cyclohexane solution. Steric requirements in the Cu(*t*-Buoac)$_2$ chelate may be an important factor in limiting the coordination number to five in the adduct.

Table III. Calorimetric Data and Thermodynamic Values for the Pyridine Adduct of Copper *t*-Butyl Acetoacetate at 25° in Cyclohexane

C_A, M	C_B, M	V, ml	$-H^1$, cal	K, l. mole^{-1}	$-\Delta H$, kcal mole^{-1}
0.02013	0.03196	200.5	13.10	37.7	7.1 ± 0.2
0.02008	0.06376	201.0	18.80		
0.02002	0.09536	201.6	21.50		
0.01997	0.1268	202.1	23.00		

Pyridine proton contact shifts for the adducts were determined in cyclohexane. The contact shift data are summarized in Table IV. The shifts for pyridine are significantly smaller than the 4-alkyl-substituted pyridines which are all very similar.

The isotropic copper hyperfine coupling constants $\langle a \rangle$ and $\langle g \rangle$ values for the adducts are listed in Table V. The $\langle a \rangle$ values for the adducts decrease from the free acid Cu(*t*-Buoac)$_2$ value while the $\langle g \rangle$ values increase. The $\langle a \rangle$ and $\langle g \rangle$ values vary regularly with the thermodynamic values for adduct formation.

Discussion

Thermodynamics of Adduct Formation. The thermodynamic values of adduct formation represent changes occurring in the total energy of the system and are a sum of terms due to adduct bond formation and structural and electronic rearrangements occurring within the component donor or acceptor molecules. In the adducts reported here, the energy contributions from the electronic and structural rearrangements occurring in the acceptor Cu(*t*-Buoac)$_2$ are significant. That extensive electronic rearrangement does accompany adduct formation is simply evidenced in the large shift to lower energy of the electronic spectrum of Cu(*t*-Buoac)$_2$ shown in Figure 1. The structural rearrangement in the copper β-diketonate is shown by the X-ray structure of the chemically related copper acetylacetonate·quinoline adduct in which the copper atom is located above the plane of the acetylacetonate oxygens and the chelate rings are bent down and away

(20) G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, 87, 1655 (1965).

Table IV. Pyridine Proton Contact Shifts for 1:1 Adducts of Copper *t*-Butyl Acetoacetate[a] at 41° in Cyclohexane

Donor	C_A, *M*	C_B, *M*	f_{free}	f_{com}		$\Delta\nu_{obsd}$, cps	$\Delta\nu_{com}$, cps
Pyridine	0.004627	0.2527	0.9849	0.01509	α	−24.9 ± 0.2	−1650
					β	−9.6 ± 0.5	−636
					γ	−2.0 ± 0.3	−133
	0.004267	1.190	0.9966	0.003721	α	−6.2 ± 0.2	−1670
					β	−2.4 ± 0.1	−645
					γ	...	...
4-Methylpyridine	0.004627	0.9836	0.9954	0.004542	α	−10.2 ± 0.3	−2246
					β	−3.7 ± 0.2	−815
					γ-CH_3	+1.2 ± 0.1	+264
4-Ethylpyridine	0.004627	0.8489	0.9947	0.005255	α	−12.0 ± 0.2	−2284
					β	−4.6 ± 0.2	−875
					γ-CH_2–	+0.5 ± 0.1	+95
					γ-CH_3	−0.2	−38
4-*t*-Butylpyridine	0.004627	0.6482	0.9932	0.006836	α	−15.1 ± 0.5	−2209
					β	−5.3 ± 0.2	−775
					γ-CH_3	+0.2	+29

[a] f_{com} is the fraction of pyridine complexed as calculated from the equilibrium constant at 41°.

Table V. Electron Spin Resonance Isotropic Coupling Constants and *g* Values for 1:1 Pyridine Adducts of Copper *t*-Butyl Acetoacetate at 25° in Cyclohexane

	$-\langle a\rangle$, G	$\langle g\rangle$	P ($\langle g\rangle - g_e$)	$-K$
Cu(*t*-Buoac)$_2$	70.0	2.129	49.0	119.0
Cu(*t*-Buoac)$_2$ ·pyridine	47.3	2.155	59.1	106.4
Cu(*t*-Buoac)$_2$ ·4-methylpyridine	46.0	2.156	59.4	105.4
Cu(*t*-Buoac)$_2$ ·4-ethylpyridine	45.6	2.156	59.4	105.0
Cu(*t*-Buoac)$_2$ ·4-*t*-butylpyridine	45.0	2.157	59.8	104.8

from the axial coordination site.[14] Structural rearrangement is expected to inhibit adduct formation by making a positive contribution to the enthalpy.

Pyridine adduct bond formation depends on the availability of the electrons at the nitrogen atom. As can be seen from the ionization potentials and Taft σ^* values for the substituents (Table VI), the donor ability of pyridine increases with increasing alkyl substitution at the 4 position. Since the 4-alkylpyridines have the same steric requirements and mode of donation as pyridine, any regular changes observed in the donor properties with a single reference acid may then be ascribed mainly to the alkyl substituent effect. This is confirmed in the shifts of the OH stretching frequency of methanol upon hydrogen-bond formation and in the

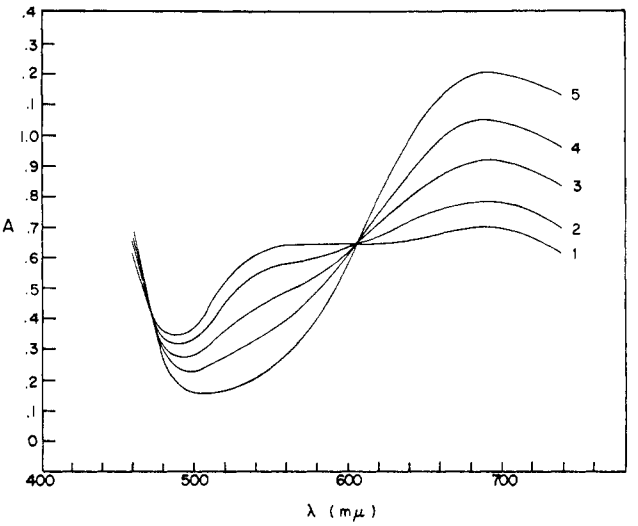

Figure 1. Electronic absorbtion spectra for Cu(*t*-Buoac)$_2$·pyridine system for C_A = 0.02049 and (1) C_B = 0.00; (2) C_B = 0.00683; (3) C_B = 0.02050; (4) C_B = 0.04099; and (5) C_B = 0.1025.

1:1 equilibria of I_2 (Table VI). The order of donor ability is then established to be pyridine < 4-methylpyridine < 4-ethylpyridine < 4-*t*-butylpyridine. This order is expected to be maintained for most reference acids as long as steric effects are not dominant. The

Table VI. Comparative Donor Property Data for Pyridines

	σ^* [a] 4-substituent	IP[b] 4-substituent free radical (eV)	$\Delta\nu_{OH}$, cm^{-1} [c] MeOH	K_{I_2},[d] l. $mole^{-1}$	$K_{Cu(t\text{-}Buoac)_2}$,[e] l. $mole^{-1}$
Pyridine	+0.49	13.6	285	109 ± 1.3	37.2 ± 0.9
4-Methylpyridine	0.00	9.9	296	216 ± 3.5	60.8 ± 0.3
4-Ethylpyridine	−0.10	8.7	300	248 ± 1.7	67.9 ± 0.3
4-*t*-Butylpyridine	−0.30	6.9	302	300 ± 4.3	75.1 ± 0.3

[a] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 660–665. [b] K. Higasi, I. Omura, and T. Tsuchiya, "Tables of Ionization Potentials of Molecules and Radicals," Monograph Series of the Research Institute of Applied Electricity, Hokkaido University, Hokkaido, Japan, 1956, No. 4, Appendix. [c] This work. Shift in the methanol O–H stretching frequency for methanol–base adducts in CCl_4 extrapolated to infinite dilution. Methanol = 0.054 *M*. Estimated error in frequency shift is ± 2 cm^{-1}. [d] Determined in CCl_4 at 25° (W. J. McKinney, M. K. Wong, and A. I. Popov, *Inorg. Chem.*, **7**, 1001 (1968)). [e] This work. Determined in cyclohexane at 25.0°.

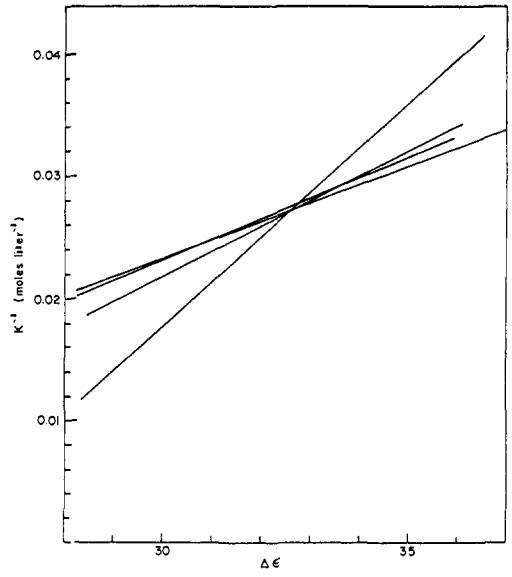

Figure 2. Graphical determination of K^{-1} and $\Delta\epsilon$ for Cu(t-Buoac)$_2$·pyridine spectrophotometric data listed in Table I.

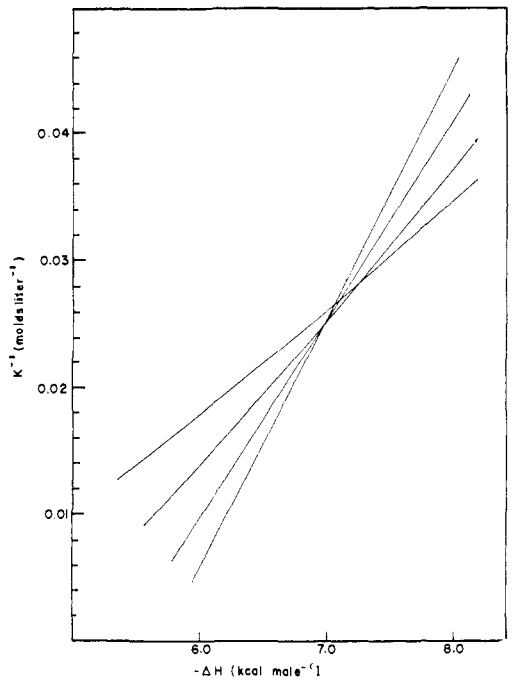

Figure 3. Graphical determination of K^{-1} and ΔH for Cu(t-Buoac)$_2$·pyridine calorimetric data listed in Table III.

equilibrium constants for 1:1 adduct formation of Cu(t-Buoac)$_2$ with this series of pyridine bases increase regularly from pyridine (K = 37.2) to 4-t-butylpyridine (K = 75.1), and a linear correlation of log K with alkyl σ^* value is obtained. The observed linear relationship between log K and σ^* demonstrates that the ligand steric requirements are constant throughout the series. As expected, the differences in the experimentally observed enthalpies for adduct formation for the 4-alkylpyridines with Cu(t-Buoac)$_2$ are not apparent, and, within the errors of this experiment, the enthalpies are equal. However, the observed enthalpy values reveal the largest difference in donor ability which occurs between pyridine (ΔH = −7.1) and any 4-alkylpyridine (ΔH = −7.9). Thus, Cu(t-Buoac)$_2$ is regularly sensitive to small changes in the donor properties of the pyridines, and adduct bond formation is enhanced by increased donor ability with this series of donors.

The change in molar absorbtivity at 700 mμ upon adduct formation is given in Table I as one of the parameters that results from the spectrophotometric determination of the equilibrium constants. The molar absorbtivity at 700 mμ is found to increase regularly as the thermodynamics for five-coordinate adduct formation increase. This correlation reflects the regular change in the z-axis perturbation on the effective adduct symmetry and the d-orbital energy levels.

Proton Contact Shifts. Contact shifts arising from unpaired electron density dominate the observed proton nmr shifts of pyridine coordinated to Cu(t-Buoac)$_2$. The observed shift ratios $\Delta\nu_\alpha/\Delta\nu_\beta$ and $\Delta\nu_\alpha/\Delta\nu_\gamma$ for the pyridine protons are 2.61 and 12.4, respectively. These values are similar to the shift ratios 3.40 and 13.0 for nickel acetylacetonate·2pyridine[21] and to the ratio of the α to β proton hyperfine interaction constants 2.83 for the isoelectronic phenyl cation radical;[22] however, the observed ratios are not comparable to the calculated pseudo-contact shift ratios $\Delta\nu_\alpha/\Delta\nu_\beta$ of 1.79 and $\Delta\nu_\alpha/\Delta\nu_\gamma$ of 1.97.[23] The small shift observed for the γ-pyridine proton is consistent with the near-zero value for the γ-proton hyperfine interaction constant of the phenyl cation radical. Also, the γ proton of pyridine is shifted downfield and the γ-methyl protons in 4-methylpyridine are shifted upfield; a dominant pseudo-contact shift would require a downfield shift for the γ-methyl protons in 4-methylpyridine.

The relatively large downfield shift for the α protons and the regularly attentuated downfield shifts for the β and γ positions suggest spin delocalization predominantly occurs into the pyridine σ molecular orbitals. σ-Spin delocalization has also been proposed for nickel acetylacetonate·2pyridine and the phenyl cation radical, which, as noted above, show shift ratios similar to Cu(t-Buoac)$_2$·pyridine.

The observed upfield 4-methyl proton shift is consistent with parallel spin in the σ system inducing antiparallel spin (negative spin density) in the π system by σ–π correlation effects. A π-hyperconjugative effect thus dominates the spin delocalization to the γ-methyl protons. This observation differs from that in the pseudo-tetrahedral complexes CoL_2X_2 and NiL_2X_2 (L = py, $4CH_3py$; X = Cl^-, Br^-, I^-), where unpaired electron density is in metal orbitals that can π-bond with pyridine and thus directly introduce parallel spin (positive spin density) into the pyridine π orbitals.[24]

The presence of pyridine proton contact shifts in the adduct requires unpaired electron spin density in the ligand molecular orbitals. In Cu(t-Buoac)$_2$, the mo-

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(22) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965).
(23) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).
(24) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4597 (1966).

lecular orbital containing the unpaired electron is predominantly d_{xy} in character and is orthogonal to the pyridine n-donor orbital. σ bonding between Cu(*t*-Buoac)$_2$ and pyridine requires the use of metal d_{z^2}, 4s, and $4p_z$ orbitals, and, in the adduct symmetry (C_2), admixtures of these metal orbitals and thus ligand σ orbitals with the d_{xy} are permitted. The presence of unpaired spin density in the pyridine σ orbitals thus gives evidence that the copper 4s, d_{z^2}, $4p_z$, and pyridine ligand orbitals make a significant contribution to the singly occupied MO of the adduct Cu(*t*-Buoac)$_2$·pyridine.

The α-proton contact shift of -1650 cps corresponds to a coupling constant $A/h = +1.0 \times 10^6$ cps (0.33G) or an α-proton spin density of $+0.00071$. Assuming that the α-proton shift results entirely from spin delocalization in the highest occupied pyridine σ MO which contains a total of $\sim$8.2% proton 1s character, the total spin density on pyridine may be crudely estimated as $+0.017$.

The significance of comparing differences in the magnitudes of ligand contact shifts even within a series of closely related donors is at present uncertain. The concomitant changes in the thermodynamics of adduct formation, ligand steric requirements, and the modification of the ligand molecular orbitals makes isolation of the dominant source of the differences hazardous. The apparent absence of a steric influence by the 4-alkyl substituent on the thermodynamics of adduct formation suggests that steric effects can be safely eliminated as a dominant influence on the contact shifts. The smaller α- and β-proton contact shifts for the pyridine adduct compared to the adducts of 4-alkyl-substituted pyridines is consistent with the thermodynamic values for the pyridine adduct; however, more detailed studies in this area are required before a definitive interpretation can be given.

Coordination Effects on the Isotropic Hyperfine Coupling Constants and *g* Values. The isotropic copper hyperfine coupling constants $\langle a \rangle$ and $\langle g \rangle$ values for the free acid Cu(*t*-Buoac)$_2$ and the 1:1 adducts with pyridine bases have been determined in cyclohexane. Thermodynamic studies on these systems in cyclohexane assure that the observed esr parameter changes are due to specific 1:1 adduct formation and are not significantly complicated by medium effects and 2:1 adduct formation.

Formation of the five-coordinate pyridine adduct produces a dramatic decrease in the magnitude of $\langle a \rangle$ and an increase in $\langle g \rangle$ from the corresponding values for the free acid Cu(*t*-Buoac)$_2$ (Table IV), and the decrease in $\langle a \rangle$ for the series of 4-alkylpyridine adducts correlates regularly with the corresponding thermodynamic changes. The esr parameters are thus found to quantitatively reflect small changes in the axial perturbation.

The isotropic hyperfine coupling constant $\langle a \rangle$ was demonstrated to be negative for copper acetylacetonate from the intensity and spacings of the hyperfine lines.[25] The variation in the line widths and positions for Cu(*t*-Buoac)$_2$ are the same, and thus $\langle a \rangle$ for Cu(*t*-Buoac)$_2$ is taken to be negative. The isotropic coupling constant $\langle a \rangle$ is given as the sum of indirect dipolar and Fermi contact terms by the relationship[26]

$$\langle a \rangle = P(g_{av} - 2.0023) + K \qquad (1)$$

where $P = \langle 1/r^3 \rangle_{3d} g_e \beta_e g_n \beta_n$ and K is the contact term. The value of P for Cu(II) is commonly taken as 0.036 cm^{-1} (386 G). From a knowledge of $\langle g \rangle$, the contributions to $\langle a \rangle$ from the indirect dipolar term and the contact term can be separately evaluated (Table VI). The indirect dipolar term is always positive for Cu(II), so that the negative sign for $\langle a \rangle$ results from the contact term. The contribution of the contact term to $\langle a \rangle$ can result from both positive and negative terms. The unpaired electron in these systems resides in an MO predominantly $3d_{xy}$ in character. The positive spin density in the d orbitals does not directly contribute to $\langle a \rangle$ but indirectly through core polarization leading to negative spin density at the nucleus and thus a negative contribution to $\langle a \rangle$.[27] A positive contribution to $\langle a \rangle$ can arise through admixture of copper 4s character into the singly occupied MO, which is allowed in the adduct symmetry (C_2). Equation 1 can then be rewritten to express the indirect 3d and direct 4s contributions to the Fermi contact term[6,28]

$$\langle a \rangle = P(g_{av} - 2.0023) + \alpha^2 K_{3d} + C^2 K_{1s} \qquad (2)$$

where α^2 and C^2 are respectively the 3d and 4s contributions to the singly occupied MO, and K_{3d} and K_{1s} are the Fermi contact hyperfine interactions arising from unit spin density in the copper 3d and 4s orbitals. The value for K_{3d} (-166 G) has been used in previous studies of Cu(II) complexes.[15] A theoretical value for K_{4s} ($+1046$ G) has been obtained from Hartree–Fock calculations.[17] The negative sign for $\langle a \rangle$ in Cu(*t*-Buoac)$_2$ and its monopyridine adduct shows that the indirect contribution from d-orbital spin density is dominant in both cases. However, the reduction in the magnitude of the negative $\langle a \rangle$ upon adduct formation could be the result of reduced d-orbital spin density or increased 4s spin density, or both.

The admixture of 4s with the d_{xy} is possible in both the acid (C_{2h}) and the adduct (C_2) symmetries. The Fermi contact term for the copper 4s orbital corresponds to a hyperfine coupling constant of $+1046$ G per unit 4s spin density, so that if admixing of 4s with d_{xy} were solely responsible for changes in $\langle a \rangle$, then an increase in 4s spin density of less than 0.015 would be required. The observation of pyridine contact shifts is consistent with there being a modest spin density along the z axis in metal orbitals (d_{z^2}, 4s, 4p) appropriate for σ bonding with pyridine. Vibronic admixing of the 4s into the singly occupied MO has been proposed to account for changes in $\langle a \rangle$ for higher symmetry complexes[6,28] and may also be operative in the systems reported here.

The effect of the known structural rearrangement accompanying adduct formation on the d-orbital spin density is currently being studied by extended Hückel calculations. The structural rearrangement around the copper atom is expected to increase the d_{xy} orbital coefficient through the moving of the copper atom above

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(27) A. J. Freeman and R. E. Watson, *Phys. Rev.*, **41**, 2027 (1961).
(28) T. Chiang, *J. Chem. Phys.*, **48**, 1814 (1968).

the plane of the chelate oxygens and the lengthening of the copper–oxygen bond distance. However, the oxygen p orbital contribution to the singly occupied MO is highly sensitive to the choice of coordinates for for the adduct and may lead to a decrease in the d_{xy} contribution.

Conclusion

(1) Cu(*t*-Buoac)$_2$ forms well-defined 1:1 pyridine adducts in cyclohexane over the range of concentrations studied.

(2) The spectrophotometric technique employed is suitable for studying the thermodynamics of adduct formation for copper(II) β-diketonates.

(3) The order of donor ability is pyridine < 4-methylpyridine < 4-ethylpyridine < 4-*t*-butylpyridine and is maintained with Cu(*t*-Buoac)$_2$. The pyridine ligand steric requirements are constant throughout the series.

(4) The pyridine proton contact shifts predominantly occur by spin delocalization into the pyridine σ system and are free of steric effects. A small $\sigma-\pi$ hyperconjugative effect is present, dominating at the γ position. Evidence is given that the contact shifts may follow the thermodynamics of adduct formation.

(5) The isotropic copper hyperfine coupling constant decreases dramatically upon adduct formation and does follow the thermodynamics of adduct formation. This decrease may be due to both decreasing d-orbital spin density and admixing of 4s character into the singly occupied MO.

Acknowledgments. The authors are grateful to Dr. Heinze Schleyer of the Johnson Foundation, Department of Biophysics, University of Pennsylvania, for the generous use of his esr facilities in the preliminary phases of this study, and to Mr. B. L. Libutti for assistance in the calorimetric measurements. They wish to acknowledge the Advanced Research Projects Agency for their support of this research through Contract No. SD-69, and the National Science Foundation through Grant No. GP-3651.

Proton Nuclear Magnetic Resonance Study of Metal–Glycine Peptide Complexes. Copper(II) and Nickel(II) Complexes[1,2]

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Received August 9, 1968

Abstract: Glycine peptides and their complexes with copper(II) and nickel(II) have been studied by aqueous (D_2O) proton nmr spectral measurements. For each dissociation step, as the pH is increased, the proton nmr peaks of the ligand methylene group nearest to the site of proton dissociation shift to higher field. In the presence of relatively small amounts of copper(II) or nickel(II) ion, these peaks disappear or broaden and the order of such change with increasing concentration of metal ion suggests the manner in which metal ion coordinates to the ligand and the sequence of coordination under changing solution conditions. Paramagnetic octahedral nickel(II) complexes undergo transition to diamagnetic planar forms with displacement of protons from the peptide linkages present in triglycine and tetraglycine. Direct evidence for the nature of this diamagnetic complex is obtained by proton nmr spectra. Contrary to the line broadening observed for paramagnetic metal complexes, three methylene peaks are observed for the nickel–triglycine complex and four methylene peaks, of which two peaks overlap, are observed for the nickel(II)–tetraglycine complex.

Copper(II) and nickel(II) complexes of glycine peptides have been studied by potentiometric pH measurements together with aqueous (D_2O) infrared absorption spectral techniques.[4–6] The purpose of the present aqueous (D_2O) proton nmr study is to obtain further information about the structures and the coordination sites of the metal peptide chelate species in solution.

Li and his coworkers[7–9] have already employed proton nmr measurements in studying metal complexes of diglycine and triglycine using heavy water as solvent, and proved this technique to be useful in obtaining

(1) This investigation was supported by Research Grants AM05217 and AM11694 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) Abstracted in part from a thesis submitted by M. K. Kim to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

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