concentration of $SnCl^+$ species (see eq 4) which can successfully compete as an electrophile with the ethylene for coordination sites on the metal complex through interaction with the filled, originally $5d_{z^2}$ platinum orbital. The increased concentration of $SnCl_2$ (see eq 4) may also be responsible for the observed effect since $SnCl_2$ can compete as nucleophile for the originally $6p_z$ platinum orbital. In fact there is considerable evidence that in some rhodium(I) four-coordinated complexes the attack of the olefin upon metal is mainly nucleophilic.[37]

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Axial Ligation of Copper(II) Bis(*t*-butylacetoacetate) by Pyridine Donors. Thermodynamics and Solvent Effects

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Equilibrium constants and enthalpies for 1:1 adduct formation of copper(II) bis(*t*-butylacetoacetate), Cu(*t*-Buoac)$_2$, with a series of pyridine donors have been measured in cyclohexane by calorimetric and spectrophotometric methods. Agreement between the two methods was found to be good. The equilibrium constants and enthalpies were found to correlate linearly with the corresponding shift in methanol OH stretching frequency, except for 2-methylpyridine, where a steric effect is proposed. Calorimetric studies in benzene, carbon tetrachloride, and chloroform have shown the thermodynamics of adduct formation with pyridine to be solvent dependent. Equilibrium constants and enthalpies decreased with change in solvent in the order $C_6H_{12} > C_6H_6 > CCl_4 > CHCl_3$. The epr parameters for Cu(*t*-Buoac)$_2$ are solvent dependent. The $\langle a \rangle$ values increase in the order $C_6H_{12} < CCl_4 < C_6H_6 < CHCl_3$, which is contrasted with the large decrease in $\langle a \rangle$ observed in donor solvents. Infrared spectra of copper(II) bis(trifluoroacetylacetonate) and copper(II) bis(trifluoroacetylacetonate)–pyridine show that upon adduct formation the pyridine ring vibrational frequencies increase and that the metal–oxygen stretching frequency decreases.

Introduction

Neutral bis chelates of Cu(II) are Lewis acceptors which have the ability to coordinate further with donor molecules to form mono and bis adducts.[2–7] Adduct formation is accompanied by large changes in electronic and magnetic properties.[7–13] An understanding of these changes can provide a basis for understanding the electronic structures and chemical bonding in metal chelates as well as revealing general properties of donor–acceptor complexes. The interpretation of metal chelate behavior in solution must begin with the characterization of the nature of the species in solution which can in part be accomplished by studying the thermodynamics of adduct formation. Thermodynamic studies are also a valuable means for locating and identifying regular changes in properties of the donor and acceptor fragments on adduct formation which are reflected by measurements such as the electronic spectra.

We recently reported a study of the formation and properties of five-coordinate adducts of copper(II) bis(*t*-butylacetoacetate) with a series of 4-alkylpyridines.[7] Evidence was presented that the observed electronic spectral and magnetic changes varied regularly with the thermodynamics of adduct formation.

This paper reports on a more complete study of the thermodynamics of 1:1 adduct formation of copper(II) bis(*t*-butylacetoacetate), Cu(*t*-Buoac)$_2$, with a series of alkyl-substituted pyridine donors in cyclohexane solvent. Thermodynamic data from both calorimetric and spectrophotometric studies are presented and compared. Thermodynamic studies of the Cu(*t*-Buoac)$_2$–py system in the series of solvents C_6H_{12}, CCl_4, C_6H_6, and $HCCl_3$ are reported and discussed in terms of the solvent interactions with pyridine, Cu(*t*-Buoac)$_2$, and the adduct. Heats of solution of pyridine are used as a means of reflecting the pyridine–solvent interactions. Solvent effects on the Cu(*t*-Buoac)$_2$ epr parameters $\langle a \rangle$ and $\langle g \rangle$ are taken as an indication of the solvent–Cu(*t*-Buoac)$_2$ interactions. Vibrational spectra for Cu(TFAcac)$_2$ and Cu(TFAcac)$_2$·py and the regular change in d–d spectral intensity for Cu(*t*-Buoac)$_2$·B with the donor ability of B are used to

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illustrate the changes that take place within the donor and acceptor fragments on adduct formation.

Experimental Section

Material and Solutions.—The pyridine bases were obtained from K & K Laboratories and were vacuum distilled from Zn dust and then from Cu(*t*-Buoac)$_2$ with the exception of pyridine, which was vacuum distilled from Na metal and then from Cu(*t*-Buoac)$_2$. They were stored at room temperature over Linde 4A Molecular Sieves. 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 Spectrograde carbon tetrachloride and Baker Spectrophotometric Quality cyclohexane were used without further purification. Baker reagent grade benzene was refluxed with P_2O_5 for 1 hr and distilled from P_2O_5. The middle fraction was collected. Baker reagent grade chloroform was stirred with molecular sieves for 24 hr and passed through a column 12 in. high and 1 in. in diameter of Woelm neutral alumina.[14] Fisher reagent grade methanol was refluxed for 2.5 hr over barium oxide and distilled through a Vigreux column, the middle fraction being collected. All solvents except cyclohexane were stored over Linde 4A Molecular Sieves.

Copper(II) Bis(*t*-butylacetoacetate).—The preparation of this compound has been described.[7] *Anal.* Calcd for Cu(*t*-Buoac)$_2$: 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, 382 in cyclohexane, 387 in benzene, and 383 in chloroform.

Copper(II) Bis(trifluoroacetylacetonate).—Trifluoroacetylacetone was mixed with an aqueous solution of sodium acetate. The copper complex precipitated upon mixing of this solution with an aqueous solution of cupric nitrate. The pale purple product was collected on a filter, washed thoroughly with water, air dried, and then recrystallized from carbon tetrachloride. *Anal.* Calcd for Cu(TFAcac)$_2$: C, 32.49; H, 2.18. Found: C, 32.41; H, 2.15.

Copper(II) Bis(trifluoroacetylacetonate)-Pyridine.—To a solution of Cu(TFAcac)$_2$ in carbon tetrachloride was added enough pyridine for a pyridine:Cu(TFAcac)$_2$ ratio of 1.3:1. The solution was filtered and evaporated under reduced pressure at room temperature. The medium green precipitate was collected and subjected to vacuum for 6 hr. *Anal.* Calcd for Cu(TFAcac)$_2$·py: C, 40.14; H, 2.92; N, 3.12. Found: C, 39.89; H, 3.00; N, 3.10.

Apparatus.—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 the Nujol mull spectra of Cu(TFAcac)$_2$ and Cu(TFAcac)$_2$·py were measured on a Perkin-Elmer 421 infrared spectrometer.

The esr spectra were measured with a Varian Model V-4502 X-band spectrometer equipped with a Fieldial Mark I, a Hewlett-Packard Model 7001A 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-4557 variable-temperature accessory. The calibration of the spectra was checked using solid DPPH and an aqueous solution of Fremy's salt.

The calorimeter was similar to that described by Arnett.[15] A 265-ml silvered dewar flask from the Ace Glass Co. was fitted with a Teflon top, from which were suspended a heating coil, a thermistor, a thermocouple, and a cooling tube. The cooling tube was an 8-mm o.d. Pyrex tube, closed at the bottom, into which a solid glass rod cooled in Dry Ice could be inserted. It was closed with a rubber stopper when not in use.

Magnetic stirring was found to cause less vibration problems than mechanical stirring, as well as leaving more room in the calorimeter because of the absence of the bulky impellors. A Thermolyne SP-A1025B stir plate was used with a modified stirring bar made by insertion of a Teflon-coated magnetic bar into a piece of perforated Teflon tubing, forming a cross-shaped stirrer which was more effective than the commercial stirring bar alone. An asbestos square between the stir plate and the dewar flask reduced heat transfer.

Absolute temperature measurements were made with an iron-constantan thermocouple and a Leeds and Northrup Model 8687 potentiometer. Temperature changes were measured with a thermistor in conjunction with a recorder.

The syringe for injection of bases was a Hamilton 1001 LLCH gas-tight syringe, having a capacity of 1 ml and equipped with a Chaney adapter. It was modified in the following manner. A piece of Tygon tubing, softened in acetone, was pulled over the syringe, and Fisher Flexaframe end-to-end joint was screwed on over this. The Tygon formed a tight seal to the syringe when the acetone dried. The bottom of the Chaney adapter rod then made contact with the metal of the Flexaframe joint when an injection was made. The reproducibility of delivery of the base by the syringe was improved from approximately 1% without the modification to approximately 1 part per thousand with it. In addition, the modification made the syring easier to clamp in to place and made it possible to handle the syringe for a few seconds without heating the contents.

By thermostating the room and use of the heater and cold rod, the temperature in the calorimeter was held at 25 ± 0.2°. After each experiment at least three determinations were made of the weight of base delivered by the syringe.

The electrical calibration was checked by measuring the heat of neutralization of aqueous HCl with aqueous NaOH. Agreement with literature values was found within 2%.

Procedures.—The procedures and calculations for the spectrophotometric method have been reported previously.[7,16]

The calorimetry experiment was carried out using the following procedure. Two hundred milliliters of pure solvent was pipetted into the dewar flask. The heat of solution of base in the solvent in the concentration range of interest, as well as concentration dependence of this heat, was determined by four successive additions of base to the solvent. The heat capacity of the calorimeter system was redetermined after each addition of base. This procedure was then repeated using a solution of Cu(*t*-Buoac)$_2$.

Equilibrium constants and enthalpies of adduct formation were obtained by analytical or graphical solution of the Bolles–Drago equation[17]

$$K^{-1} = \frac{H_i'}{V_i \Delta H} - C_A - C_B + \frac{C_A C_B V_i \Delta H}{H_i'}$$

where ΔH is the enthalpy of adduct formation in kcal mol^{-1}, V_i is the total volume of solution after i additions of base, and H_i' is the heat of reaction corresponding to mixing acid with base at respective initial concentrations C_A and C_B. The value for H_i' is the heat observed for addition of base to acid solution corrected for the heat of solution of base.

The equilibrium constants for most of the systems reported here were calculated using a computer program technique which gives K^{-1} for which the sum of the squares of the deviations of the experimental H_i' from their average was smallest.[17] This technique proved unsatisfactory for the systems using solvents other than cyclohexane, and for the 2-methylpyridine–copper(II) bis(*t*-butylacetoacetate)–cyclohexane system. In these cases graphical solution for K was used, averaging all intersections. In all cases the reported enthalpies of adduct formation are the average of enthalpies calculated from the observed heats and the calculated K's. For a given experiment, the reproducibility of these calculated enthalpies was ±0.07 kcal mol^{-1} or better.

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Table I

Calorimetric Data and Thermodynamic Values for 1:1 Adducts of Copper(II) Bis(t-butylacetoacetate) in Cyclohexane (25°)

Donor	C_A, M	C_B, M	V, ml	$-H^1$, cal[a]	$-H^2$, cal[b]	$-H^3$, cal[c]	K,[d] M^{-1}	$-\Delta F$,[e] kcal mol^{-1}	$-\Delta H$,[f] kcal mol^{-1}	$-\Delta S$,[g] cal mol^{-1} deg^{-1}
Pyridine	0.02013	0.03196	200.5	1.01	−12.11	13.12	37.7	2.15	7.1	16.5
	0.02008	0.06376	201.0	−6.18	−11.89	5.71				
	0.02003	0.09541	201.5	−9.08	−11.72	2.64				
	0.01998	0.1269	202.0	−9.98	−11.48	1.50				
2-Methylpyridine	0.01827	0.02506	200.5	−4.11	−7.94	3.83	9.2	1.32 ± 0.07	6.3	16.7 ± 0.9
	0.01823	0.04999	201.0	−4.84	−7.85	3.01				
	0.01818	0.07480	201.5	−5.64	−7.58	1.94				
	0.01814	0.09949	202.0	−5.83	−7.46	1.63				
3-Methylpyridine	0.01846	0.02051	200.5	2.65	−9.50	12.45	41.5	2.21	7.5	17.7
	0.01842	0.05288	201.0	−3.65	−9.12	5.47				
	0.01837	0.07913	201.5	−6.26	−9.12	2.86				
	0.01833	0.1053	202.0	−7.68	−9.12	1.44				
3-Ethylpyridine	0.01802	0.02255	200.5	3.62	−7.40	11.06	44.0	2.24	7.6	17.9
	0.01797	0.04489	201.0	−2.12	−7.48	5.32				
	0.01793	0.06730	201.5	−4.64	−7.42	2.80				
	0.01788	0.08951	202.0	−5.48	−7.46	1.96				
4-Methylpyridine	0.01828	0.02539	200.5	4.15	−9.16	13.31	54.3	2.37	7.6	17.6
	0.01823	0.05065	201.0	−3.60	−9.15	5.55				
	0.01819	0.07579	201.5	−6.46	−9.06	2.60				
	0.01814	0.10081	202.0	−7.39	−8.96	1.57				
4-Ethylpyridine	0.01915	0.02178	200.5	5.80	−7.79	13.49	61.0	2.44	7.9	18.2
	0.01910	0.04346	201.0	−1.26	−7.46	6.20				
	0.01905	0.06502	201.5	−4.18	−7.31	3.13				
	0.01901	0.08648	202.0	−5.53	−7.20	1.67				
4-t-Butylpyridine	0.01854	0.01692	200.5	6.82	−4.65	11.47	68.5	2.51	7.8	17.9
	0.01849	0.03376	201.0	1.52	−4.66	6.17				
	0.01845	0.05051	201.5	−1.40	−4.65	3.25				
	0.01840	0.06718	202.0	−2.79	−4.59	1.86				

[a] H^1 is the heat observed for addition of base to Cu(t-Buoac)$_2$ solution. [b] H^2 is the heat observed for addition of base to solvent alone. [c] $H^3 = H^1 - H^2$. H_i' values are obtained by successive additions of H^3 values. [d] Deviation ±1 M^{-1}. [e] Deviation ±0.02 kcal mol^{-1}. [f] Deviation ±0.2 kcal mol^{-1}. [g] Deviation ±0.7 cal mol^{-1} deg^{-1}.

The error limits given in the tables are average deviations between different experiments.

Results and Discussion

Thermodynamics of 1:1 Adduct Formation in Cyclohexane. Comparison of Calorimetry with the Spectrophotometric Method. The thermodynamic values for adduct formation of Cu(t-Buoac)$_2$ with pyridine donors in cyclohexane determined by both calorimetric and spectrophotometric techniques are given in Tables I and II. Data from both techniques fit a 1:1 equilibrium expression accurately, which taken along with sharp isosbestic points in the electronic spectra and isolation of only 1:1 adducts give compelling evidence that only the 1:1 adduct forms in measurable quantity in cyclohexane solution.

The agreement between thermodynamic values determined by calorimetry and the spectrophotometric method is generally quite good and the same order of equilibrium constants is obtained from both methods (Table III).

Table II

Spectrophotometric Data and Equilibrium Constants for 1:1 Adducts of 2- and 3-Alkylpyridines with Copper(II) Bis(t-butylacetoacetate) at 700 mμ in Cyclohexane at 25.0°

Donor	C_A, M	C_B, M	$A - A_0$	$\epsilon_C - \epsilon_A$, abs l. mol^{-1}	K, M^{-1}
2-Methylpyridine	0.008136	0.03970	0.0496	23.1	9.5 ± 0.4
		0.07941	0.0785		
		0.1191	0.0982		
		0.19853	0.1214		
3-Methylpyridine	0.02020	0.02005	0.258	36.4	41.5 ± 0.3
		0.05011	0.449		
		0.1002	0.573		
3-Ethylpyridine	0.01914	0.02763	0.336	37.2	47.0 ± 0.9
		0.04604	0.434		
		0.09208	0.559		
		0.13812	0.606		

The spectrophotometric method for studying adduct formation is based upon the assumptions that changes in the electronic spectra of the copper β-diketonate upon addition of base result only from adduct formation and that all absorbing species obey Beer's law. This method is thus subject to uncertainties from possible electronic spectral changes resulting from changes in the solution media such as the dielectric constant which occur upon addition of base. Similarly the calorimetric method assumes that the heat evolved upon addition of base to acid after correction for the heat of solution of the base in the pure solvent results solely from adduct formation and that the observed heat is a linear function of the amount of adduct formed. In this method, the effects of various solvation terms, such as how the presence of the acid affects the heat of solution of the base, are unknown. Although the uncertainties in these methods are not expected to be very large in an alkane solvent such as cyclohexane, neither method alone can be considered as yielding

TABLE III

COMPARISON OF THERMODYNAMIC VALUES OBTAINED FROM CALORIMETRIC AND SPECTROPHOTOMETRIC MEASUREMENTS FOR ADDUCT FORMATION BETWEEN COPPER(II) BIS(t-BUTYLACETOACETATE) AND PYRIDINE BASES IN CYCLOHEXANE AT 25°

	Calorimetric		Spectrophotometric		$\epsilon_C - \epsilon_A$
Donor	K, M^{-1}	$-\Delta H$, kcal mol^{-1}	K, M^{-1}	$-\Delta H$, kcal mol^{-1}	(700 mμ), abs l. mol^{-1}
Pyridine	37.7	7.1	37.2[a]	7.1[a]	32.2[a]
2-Methylpyridine	9.2	6.3	9.5	. . .	23.1
3-Methylpyridine	41.5	7.5	41.5	. . .	36.4
3-Ethylpyridine	44.0	7.6	47.0	. . .	37.2
4-Methylpyridine	54.3	7.6	60.8[a]	7.9[a]	37.8[a]
4-Ethylpyridine	61.0	7.9	67.9[a]	7.9[a]	39.2[a]
4-t-Butylpyridine	68.5	7.8	75.1[a]	7.9[a]	42.7[a]

[a] Previously presented: A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, **91**, 866 (1969).

unequivocal thermodynamic data. However, the use of these two distinctly different methods in conjunction with each other as in this study allows an accurate description of the thermodynamics of adduct formation to be formulated. The agreement between thermodynamic values resulting from calorimetric and spectrophotometric studies indicates that the basic assumptions for the application of these methods are valid for the systems reported here. It is of particular importance in this respect that the changes in the electronic spectra resulting from addition of base to a cyclohexane solution of Cu(t-Buoac)$_2$ accurately reflect adduct formation, and these changes may thus be used in understanding the effects of axial ligation on the electronic structure of the copper β-diketonate.

TABLE IV

COMPARATIVE DONOR PROPERTY DATA FOR PYRIDINES

Donor	K[Cu(t-Buoac)$_2$],[a] M^{-1}	$-\Delta H$[Cu(t-Buoac)$_2$],[a] kcal mol^{-1}	$\Delta\nu_{OH}$ (CH$_3$OH),[b] cm^{-1}	K(I$_2$),[c] M^{-1}	$-\Delta F$[Ni-(DBH)],[d] kcal mol^{-1}	$-\Delta H$[Ni-(BDH)],[d] kcal mol^{-1}	IP,[e] eV
Pyridine	37.7 ± 1	7.1 ± 0.2	285	1.09 ± 1.3	5.15	14.95	9.76 ± 0.05
2-Methylpyridine	9.2 ± 1	6.3 ± 0.2	302		0.65	12.83	9.66 ± 0.05
3-Methylpyridine	41.5 ± 1	7.5 ± 0.2	290	2.07 ± 3.0	5.32	15.17	9.71 ± 0.05
4-Methylpyridine	54.3 ± 1	7.6 ± 0.2	296	2.16 ± 3.5	6.03	15.65	9.56 ± 0.05

[a] This work. Determined in cyclohexane at 25°. [b] This work. Shift in the methanol O–H stretching frequency for methanol–base adducts in CCl$_4$ extrapolated to infinite dilution. Methanol concentration is 0.015 M. Estimated error in frequency shift is ±2 cm^{-1}. [c] Determined in CCl$_4$: W. J. McKinney, M. K. Wong, and A. I. Popov, *Inorg. Chem.*, **7**, 1001 (1968). [d] Thermodynamic functions for 2:1 adduct formation between the pyridine bases and (biacetylbisbenzoylhydrazone)nickel II: L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958). [e] Ionization potential of the molecules: H. Baba, L. Omura, and K. Higasi, *Bull. Chem. Soc. Japan*, **29**, 521 (1956).

The calorimetric method has the advantage of simultaneous determination of K and ΔH, and, unless otherwise noted, the thermodynamic functions referred to in the following discussions will be those determined by calorimetry.

Donor Properties of Pyridine Bases.—The order of donor ability for methyl-substituted pyridines suggested by ionization potentials,[18] nqr studies,[19] mo calculations,[20] and $\Delta\nu_{OH}$(CH$_3$OH) is 2-CH$_3$py $\gtrsim$ 4-CH$_3$py > 3-CH$_3$py $\gtrsim$ py (Table IV). The free energy change on 1:1 adduct formation of Cu(t-Buoac)$_2$ with a series of pyridine bases is found to correlate linearly with $\Delta\nu_{OH}$(CH$_3$OH), the shift in OH stretching frequency for the methanol–base interaction in CCl$_4$, for the monosubstituted 3- or 4-alkylpyridines (Figure 1). The enthalpy changes, although less sensitive, also change regularly with $\Delta\nu_{OH}$(CH$_3$OH) for the base. The presence of these relationships suggests that the observed basicity order toward Cu(t-Buoac)$_2$ (4-CH$_3$py > 3-CH$_3$py) is principally an electronic effect, presumably caused by the more effective transmission of the substituent effects through the π orbitals from the 4 position than from the 3 position. 2-Methylpyridine has relatively small ΔF and ΔH values and deviates dramatically from the correlation of ΔF with $\Delta\nu_{OH}$ (Figure 1). The small values of ΔH and ΔF for the 1:1 Cu(t-Buoac)$_2$ adduct with 2-methylpyridine almost certainly arise from a steric effect. Similar deviations from the normal basicity order for this donor in adducts of VO(acac)$_2$[21] and Ni(DBH)[22] have been previously observed.

Comparison of the thermodynamic data for the 2-methylpyridine–copper(II) bis(t-butylacetoacetate) system with the results for other pyridine donors indicates that the steric effect manifests itself primarily as an enthalpy, rather than entropy, effect. The enthalpy reduction presumably occurs because of restricted approach of the base to the metal.

It is interesting to note that the molar absorptivities (700 mμ) of the adducts correlate regularly with the thermodynamics of adduct formation (Table III) and that 2-methylpyridine is included in the correlation.

Electronic and Structural Reorganizations on Adduct Formation.—Formation of the 1:1 adduct of Cu(t-Buoac)$_2$ with pyridine results in large structural and electronic reorganization. The structural rearrangement for the copper(II) β-diketonate fragment on

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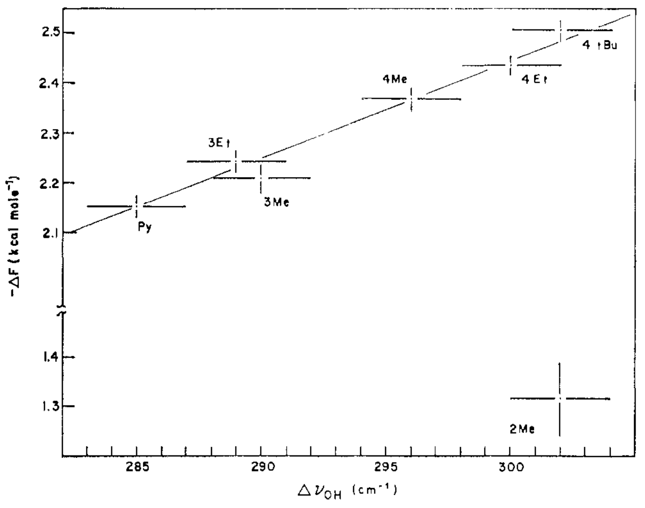

Figure 1.—$\Delta\nu_{OH}(CH_3OH)$ plotted *vs.* the free energy change for $Cu(t\text{-}Buoac)_2 \cdot py$ base adduct formation.

adduct formation is illustrated by the results of the X-ray structure determination of $Cu(acac)_2 \cdot quin$ (quin = quinoline). In this adduct the copper atom is displaced 0.21 Å above the plane of acetylacetonate oxygens and the chelate rings are bent down and away from the axial coordination site.[23,24] This structural rearrangement is similar in kind to that observed for adduct formation with other acceptors such as BF_3 and $(CH_3)_3SnCl$.[25,26] Changes in the intensities and positions of the d–d transitions, shifts in the chelate and Cu–O vibrational frequencies, and changes in the epr parameters $\langle a \rangle$ and $\langle g \rangle$ are all manifestations of the electronic and structural reorganization of the Cu chelate fragment on adduct formation. As an example, we have found that the Cu–O stretching frequency for $Cu(TFAcac)_2$ is reduced from 442 to 430 cm^{-1} on forming the monopyridinate, suggesting a weakening of the Cu chelate bonding in the adduct.

Electronic and structural reorganization is not limited to the acceptor but also occurs in the donor fragment. Pyridine and related nitrogen heterocycles are interesting donors in this respect, for complexation results in shifts to higher frequency for most of the donor vibrations.[27,28] For example, we have found that the ring-breathing vibration which occurs at 991 cm^{-1} in free pyridine shifts to 1002 cm^{-1} in $Cu(TFAcac)_2 \cdot py$.

A structural determination of *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II) reveals a contraction of the pyridine ring which shortens all of the skeletal bond distances.[29] Similar observations have been made for the related quinoline donor in $Cu(Acac)_2 \cdot quin$ adduct.[23,24] These results clearly suggest a stabilization of the pyridine framework through adduct formation.

For the purpose of discussing the changes that occur in the acid and base fragments on complex formation, it is useful to consider the enthalpy of complex formation as containing contributions from the reorganization energies for the acid and base as well as the enthalpy of bond formation. In the case of $Cu^{II}(\beta\text{-dik})_2 \cdot py$ (β-dik = β-diketonate) the ir evidence presented above suggests that the enthalpy of adduct formation contains a positive (destabilizing) contribution from the reorganization of $Cu(t\text{-}Buoac)_2$ and a negative contribution from changes that occur in the pyridine fragment. The accumulation of data on adduct formation strongly indicates that the structural and electronic reorganization within the donor and acceptor are not constant terms, but instead vary regularly with over-all thermodynamic values for adduct formation.[30] The regular increase in the $Cu(t\text{-}Buoac)_2$ d–d spectral band intensity (700 mμ) with increase in ΔH or ΔF of adduct formation may be interpreted as a manifestation of regular structural changes in the $Cu(t\text{-}Buoac)_2$ fragment.

Solvent Effects on the Thermodynamics of Adduct Formation.—The thermodynamics of adduct formation between pyridine and $Cu(t\text{-}Buoac)_2$ in the presumed less ideal solvent media benzene, carbon tetrachloride, and chloroform are compared with the cyclohexane data in Table V. These systems were selected for investigation because they are representative of the solvents used in previous studies and are used here to illustrate the medium effect on the thermodynamics. The one feature that these solvents all have in common is that both the equilibrium constants and enthalpies for formation of $Cu(t\text{-}Buoac)_2 \cdot py$ are reduced from the values measured in cyclohexane. Equilibrium constants and enthalpies decreased in the solvent order $C_6H_{12} > C_6H_6 > CCl_4 > CHCl_3$ (Table V). A previous spectrophotometric study of $Cu(\beta\text{-dik})_2 \cdot py$ adduct formation reported larger equilibrium constants in benzene than in chloroform which is in agreement with our results.[2]

The effect of solvent media on the thermodynamics is very complicated, for solvation of acid, base, and adduct as well as differences in the solvent structure may significantly contribute to the final net effect. A semiquantitative appreciation of the solvent–base interactions can be obtained from the pyridine heats of solution in the solvents studied (Table V). The large differences in the heat of solution of pyridine reflect differences in the pyridine–solvent interactions. The relatively large positive value for heat of solution of pyridine in cyclohexane ($\Delta H_{soln} = +1.84$ kcal mol^{-1}) reflects the relatively small solvent–base interaction when compared to the other solvents CCl_4 ($\Delta H_{soln} = +0.17$ kcal mol^{-1}), C_6H_6 ($\Delta H_{soln} = -0.01$ kcal mol^{-1}), and $CHCl_3$ ($\Delta H_{soln} = -1.82$ kcal mol^{-1}). The near-zero ΔH_{soln} in benzene could be the result of similar solution structure and intramolecular interactions in pyridine and benzene. Carbon tetrachloride is known to form a weakly bound adduct with pyridine[31] which

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TABLE V

CALORIMETRIC DATA AND THERMODYNAMIC VALUES FOR PYRIDINE–COPPER(II) BIS(t-BUTYLACETOACETATE) ADDUCT FORMATION IN VARIOUS SOLVENTS

Solvent	C_A, M	C_B, M	V, ml	$-H^1$, cal[a]	$-H^2$, cal[b]	$-H^3$, cal[c]	K, M^{-1}	$-\Delta F$, kcal mol^{-1}	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, cal mol^{-1}
Cyclohexane	0.02013	0.03196	200.5	1.01	−12.11	13.12	37.7 ± 1	2.15 ± 0.02	7.1 ± 0.2	16.5 ± 0.7
	0.02008	0.06376	201.0	6.18	−11.89	5.71				
	0.02003	0.09541	201.5	−9.08	−11.72	2.64				
	0.01998	0.1269	202.0	−9.98	−11.48	1.50				
Benzene	0.01884	0.03079	200.5	8.17	0.07	8.10	20.5 ± 1	1.79 ± 0.03	6.4 ± 0.2	15.5 ± 0.8
	0.01879	0.06142	201.0	4.45	0.07	4.38				
	0.01875	0.09191	201.5	2.58	0.07	2.51				
	0.01870	0.12224	202.0	1.67	0.07	1.60				
Carbon tetrachloride[d]	0.01901	0.03086	200.5	6.39	−1.00	7.39	18.9 ± 1	1.74 ± 0.03	6.0 ± 0.2	14.3 ± 0.8
	0.01896	0.06156	201.0	2.86	−1.04	3.90				
	0.01891	0.09212	201.5	1.32	−1.07	2.39				
	0.01887	0.12252	202.0	0.61	−1.07	1.68				
Chloroform	0.01862	0.3078	200.5	13.63	11.50	2.13	4.8 ± 1	0.93 ± 0.1	4.8 ± 0.2	13.0 ± 1
	0.01857	0.06140	201.0	13.02	11.29	1.73				
	0.01853	0.09187	201.5	12.45	11.17	1.28				
	0.01848	0.12219	202.0	12.38	11.16	1.22				

[a] H^1 is the heat observed for addition of base to Cu(t-Buoac)$_2$ solution. [b] H^2 is the heat observed for addition of base to solvent alone. [c] $H^3 = H^1 - H^2$. H_i' values are obtained by successive additions of H^3 values. [d] Slight precipitation occurred during the experiment.

accounts for the smaller positive heat of solution in CCl_4 than in cyclohexane while $HCCl_3$ interacts strongly with pyridine resulting in a large exothermic ΔH_{soln}. These data clearly indicate that thermodynamic studies in cyclohexane are less subject to complications due to base–solvent interactions than those in benzene, carbon tetrachloride, and chloroform, which have been most frequently used in previous studies. The hydrogen-bonding properties of chloroform with metal acetylacetonates[32] as well as with bases like pyridine make $CHCl_3$ the most complicated solvent media. The significant changes in both the electronic spectra and epr parameters in $CHCl_3$ compared with C_6H_{12} may be taken as indications of $CHCl_3$ hydrogen bonding with the Cu chelate (Figure 2, Table VI).

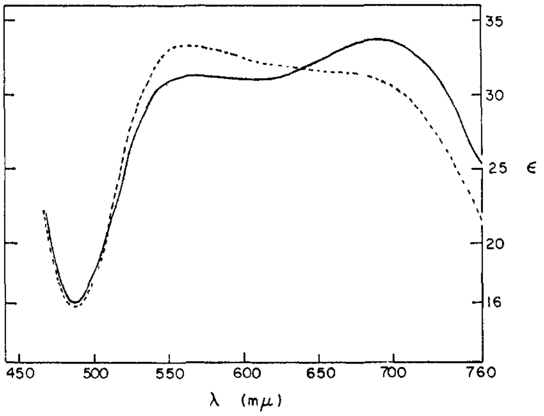

Figure 2.—Solvent effects on electronic absorption spectra of Cu(t-Buoac)$_2$: ——, 0.01407 M Cu(t-Buoac)$_2$ in cyclohexane; - - - -, 0.01881 M Cu(t-Buoac)$_2$ in chloroform.

Solvent Effects on Epr Parameters for Cu(t-Buoac)$_2$.—Solution epr spectra of copper(II) β-diketonates and related Cu(II) chelates have been thoroughly investigated.[11–13] These studies have been limited to chloroform and donor solvents. The solubility of Cu(t-Buoac)$_2$ in cyclohexane allows investigation of its epr spectrum in this comparatively inert alkane solvent. The epr parameters for Cu(t-Buoac)$_2$ have been determined in cyclohexane, carbon tetrachloride, benzene, and chloroform (Table VI) in order to examine the effects of some common solvents which have frequently been assumed to be virtually noncoordinating. The isotropic copper hyperfine coupling constant was found to be significantly different in each of these solvents and follows the solvent order $C_6H_{12} < CCl_4 < C_6H_6 < CHCl_3$ (Table VI). The $\langle g \rangle$ value, however, was found to be virtually constant, which is consistent with only the electronic spectral intensities and not position being significantly solvent dependent.

TABLE VI

SOLVENT EFFECTS ON ELECTRON SPIN RESONANCE PARAMETERS OF COPPER(II) BIS(t-BUTYLACETOACETATE)

Solvent	$-\langle a \rangle$, G[a]	$\langle g \rangle$[b]
Cyclohexane	70.0	2.129
Carbon tetrachloride	71.3	2.126
Benzene	72.4	2.129
Chloroform	74.8	2.130
Pyridine–cyclohexane	47.3	2.155

[a] Deviation ±0.5 G. [b] Deviation ±0.004.

The increase in $\langle a \rangle$ of ~5 G in changing the solvent from cyclohexane to chloroform illustrates the large effects that even relatively weakly interacting solvents can have on the epr parameters.

The difference in $\langle a \rangle$ value for this series of solvents could result from variations in the extent of dimerization of Cu(t-Buoac)$_2$. Dimerization is expected to reduce the value of $\langle a \rangle$ in a manner similar to that of donor solvents, so that if dimerization were present in these systems, it would be most important in the least interacting solvent cyclohexane and produce the observed solvent trend. However, molecular weight determinations, the absence of significant temperature dependence of the electronic spectra, and accurate adherence to Beer's law over a moderate range of concen-

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trations are good indications that Cu(*t*-Buoac)$_2$ is not significantly self-associated in cyclohexane in the vicinity of 25°. The change in epr parameters can thus be ascribed to differences in the solvent–Cu(*t*-Buoac)$_2$ interactions and not to partial dimerization. Assuming that the epr parameters measured in cyclohexane best reflect the true molecular values, then the solvents CCl_4, C_6H_6, and $HCCl_3$ cause an increase in $\langle a \rangle$ which can be contrasted with the large decrease in $\langle a \rangle$ caused by basic solvents like pyridine. The opposite directions for changes in $\langle a \rangle$ could result from different sites for the solvent–Cu(β-dik)$_2$ interactions. Chloroform is known to hydrogen bond with chelate ligand, and the known weak acceptor properties of carbon tetrachloride and the π-complex forming ability of benzene also suggest that these solvents may interact more with the chelate ligand than with the metal. Donor solvents are distinctly different in that they form well-defined complexes through bonding with the metal.

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Oxidation–Reduction Chemistry of Coordination Complexes with Macrocyclic Ligands. The Cu(*trans*[14]diene)$^+$–Cu(*trans*[14]diene)$^{2+}$ System. Electrochemical, Spectral, and Solution Studies[1a,b]

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The very careful electrolytic reduction of the macrocyclic Schiff base amine–copper(II) complex Cu(*trans*[14]diene)$^{2+}$ yields a highly reactive yellow complex which appears to be Cu(*trans*[14]diene)$^+$. The cathodic reduction of Cu(*trans*[14]diene)$^{2+}$ has been examined polarographically and by controlled-potential electrolysis and the conditions for the formation of Cu(*trans*[14]diene)$^+$ are described. The Cu(*trans*[14]diene)$^{2+,+}$ couple is strongly reducing, probably indicating that the ligand provides a somewhat unfavorable coordination environment for copper(I). Comparison of the ultraviolet spectra of Cu(*trans*[14]diene)$^{2+}$, Cu(*trans*[14]diene)$^+$, and several M(*trans*[14]diene)$^{2+}$ complexes reveals some systematic variations in the energies of absorption maxima; it is suggested that these ultraviolet and near-ultraviolet absorption bands should be assigned to metal-to-ligand charge-transfer transitions.

The chemistry of simpler inorganic systems which can mimic certain of the properties of naturally occurring complexes has been of long and continuing interest.[2–4]

Among the simplest of macrocyclic ligands are the cyclic tetramines.[5–7] A particularly elegant and fascinating series is the complexes containing 14-, 15-, and 16-membered cyclic amine ligands and their Schiff base precursors which have been prepared and characterized by Curtis and his coworkers.[7] The most stable and best characterized complexes of this series are those containing the 14-membered macro rings: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[8] and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.[9] (See Figure 1.) Complexes of these particular ligands generally have the nitrogen atoms almost coplanar;[7] removal of the metal atom from coordination to any of the cyclic complexes is generally a relatively slow process. Thus the Ni(*trans*[14]diene)$^{2+}$, Ni(teta)$^{2+}$, Cu(*trans*[14]diene)$^{2+}$, and Cu(teta)$^{2+}$ complexes are all kinetically stable in acidic aqueous solution at room temperature and all four complexes appear to exhibit only weak interaction with the solvent along the axial coordination positions.[7] Therefore in a sense with these ligands the metal ion is in a coordination "trap." In principle, it should be possible to oxidize or reduce the metal center with little change in coordination geometry. Curtis has reported[7,10,11] that Ni^{III}-

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[1] (a) Research partially supported by the Public Health Service through Research Grant AM 08737 and a grant-in-aid from the Boston University Graduate School. (b) Taken in part from the M.A. Thesis of J. M. Palmer, Boston University, 1968. (c) Graduate Fellow (1966–1967) under the Prospective Teacher Program of the Higher Educational Act of 1965, Title V,C. (d) Author to whom inquiries should be addressed.

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[9] Following Curtis' suggestion,[7] this ligand will hereafter be referred to as the *trans*[14]diene. The two isomeric complexes which can be formed from this ligand (see below) will be distinguished only when necessary for clarity. The studies reported here were performed with isomerically pure complexes. When referring to studies in which Cu(*dl-trans*[14]diene)$^{2+}$ and Cu(*meso-trans*[14]diene)$^{2+}$ exhibit similar chemical behavior, we will simply refer to Cu(*trans*[14]diene)$^{2+}$.

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