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Preparation and Thermodynamic Data for Adducts of Bases with Some Copper(II) β -Diketonates

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The preparation of compounds of the type $\text{Cu}(\text{hfac})_2(\text{B})_n$ [hfac = hexafluoroacetylacetonate; B = N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), or pyridine (py) ($n = 1, 2$); B = trimethylamine N-oxide or triethylamine ($n = 1$)] is described. Enthalpies are reported for the interaction of the above bases, plus ethyl acetate ($\text{C}_2\text{H}_5\text{OAc}$), with $\text{Cu}(\text{hfac})_2$ in cyclohexane and/or carbon tetrachloride. Two systems were studied in *o*-dichlorobenzene to test further the feasibility of using this material as a poorly solvating solvent. Pronounced solvent effects are detected. The enthalpies for the formation of the 1:1 complexes in CCl_4 or cyclohexane correlate well with a previously derived four-parameter equation for predicting enthalpies. The acid parameters suggest that the copper complex is intermediate in its hard-soft character. In an attempt to ascertain quantitatively the inductive effect of substituents on the other ligands coordinated to copper, the enthalpy of interaction of bis(ethylacetoacetato)copper(II) ($\text{Cu}(\text{Eacac})_2$) with pyridine was determined and was found to be much less than that for $\text{Cu}(\text{hfac})_2$. The enthalpy of interaction of DMA with $\text{Cu}(\text{hfac})_2(\text{DMA})$ to form a 2:1 adduct is less than that of DMA with $\text{Cu}(\text{hfac})_2$ to form a 1:1 adduct. On the other hand, the enthalpy of interaction of pyridine with $\text{Cu}(\text{hfac})_2(\text{py})$ is surprisingly the same as that with $\text{Cu}(\text{hfac})_2$.

Introduction

We have been interested in a quantitative description of donor-acceptor interactions in poorly solvating solvents, where the measured enthalpy closely approximates that measured in the gas phase.² This paper describes a quantitative investigation of the acceptor properties of bis(hexafluoroacetylacetonato)copper(II). This is the first transition metal compound studied in poorly solvating solvents with a wide variety of bases. The number of suitable coordination compounds for this type of study are few due to the multiple coordination possibilities of such compounds, extensive association, and their lack of solubility in nonpolar solvents. The system described here is ideal in all of these respects.

The interaction of bases with copper(II) β -diketonates has been well established by preparation of a limited number of adducts,³⁻¹² by the effect of bases on the visible spectra,^{4,5,7,9-16} and by crystal structure determinations of bis(acetylacetonato)copper(II)¹⁶ and its adduct with quinoline.¹⁷ Two thermodynamic studies have been reported on these systems. These thermodynamic studies are not suitable for our purpose due to the solvent choice in one instance¹⁴ and the limited range of bases used¹² in the other.

Experimental Section

Materials.—Baker reagent grade cyclohexane and carbon tetrachloride and Eastman *o*-dichlorobenzene were dried over Linde 4A molecular sieves for at least 24 hr prior to use. Eastman White Label N,N'-dimethylacetamide (DMA), Mallinckrodt reagent dimethyl sulfoxide (DMSO), and Baker reagent pyridine were purified as previously described.¹⁸ Mallinckrodt reagent ethyl acetate was dried over 4A sieves for 24 hr, distilled over P_2O_5 at atmospheric pressure, and distilled once in the absence of a drying agent. Matheson Coleman and Bell triethylamine was stored overnight over LiAlH_4 and distilled twice from CaH_2 under argon atmosphere. Eastman Organic trimethylamine N-oxide dihydrate was heated to 120° at 10 mm for several hours to remove the water. The pressure was then gradually reduced to 1 mm, the temperature was raised to 150°, and the $(\text{CH}_3)_3\text{NO}$ was sublimed. The sublimation was repeated at 1 mm and 130°. The bis(hexafluoroacetylacetonato)copper(II), $\text{Cu}(\text{hfac})_2$, was prepared as previously described.⁹ The green monohydrate was sublimed at 90° at 1 mm and converted to the anhydrous complex by placing it over P_2O_5 in a desiccator for several days. The bis(ethylacetoacetato)copper(II), $\text{Cu}(\text{Eacac})_2$, was prepared as previously described¹⁹ and recrystallized from benzene. No bands were present in the infrared mull spectrum in the region 4000-3100 cm^{-1} indicating the absence of water.

All solutions were prepared in a drybox or drybag using thoroughly dried glassware. The calorimeter cells were thoroughly dried with nitrogen before use.

Apparatus and Procedure.—The apparatus used and the method of simultaneously determining enthalpies and equilibrium constants have been previously described.²⁰⁻²² The method for the simultaneous calculation of the equilibrium constant and change in extinction coefficient, between the acid and the 1:1 adduct, has also been previously described²³ and is analogous to the calorimetric measurement. The spectrophotometric measurements were made on a Cary 14 spectrophotometer, using a 1-cm thermostated cell which was held at 25° by a Kahl Scientific "Thermoboy" constant-temperature bath.

- (1) National Cancer Institute postdoctoral fellow. Grant No. 39147.
- (2) For a review of this work see R. S. Drago, *Chem. Brit.*, **3**, 516 (1967).
- (3) G. T. Morgan and J. D. M. Smith, *Trans. Chem. Soc.*, 912 (1926).
- (4) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).
- (5) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5399 (1963).
- (6) W. R. Walker, *Australian J. Chem.*, **14**, 161 (1961).
- (7) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5885 (1963).
- (8) N. C. Li, S. M. Wang, and W. R. Walker, *J. Inorg. Nucl. Chem.*, **27**, 2263 (1965).
- (9) W. R. Walker and N. C. Li, *ibid.*, **27**, 2255 (1965).
- (10) C. H. Ke and N. C. Li, *ibid.*, **26**, 2255 (1966).
- (11) L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).
- (12) A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, **91**, 866 (1969).
- (13) D. P. Graddon, *Nature*, **183**, 1610 (1959).
- (14) W. R. May and M. M. Jones, *J. Inorg. Nucl. Chem.*, **45**, 507 (1963).
- (15) D. P. Graddon and R. G. Schulz, *Australian J. Chem.*, **18**, 1731 (1965).
- (16) As reported by L. Dahl in *Mol. Phys.*, **5**, 169 (1962).
- (17) S. Ooi and Q. Fernando, *Chem. Commun.*, 532 (1967).

- (18) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3921 (1966).
- (19) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).
- (20) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965).
- (21) T. D. Epley and R. Drago, *ibid.*, **89**, 5770 (1967).
- (22) W. Partenheimer, T. D. Epley, and R. S. Drago, *ibid.*, **90**, 3886 (1968).
- (23) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

TABLE I
ANALYTICAL DATA

Compound	Mp, °C	% calcd				% found			
		C	H	N	Cu	C	H	N	Cu
Cu(hfac) ₂ ^a	95-100	25.15	0.42		25.30	25.15	0.65		25.25
Cu(hfac) ₂ (DMA)	78-80	29.77	1.97	2.48	11.25	30.52	1.90	2.51	11.25
Cu(hfac) ₂ (DMA) ₂	117-118	33.16	3.10	4.30	9.75	33.03	3.22	4.37	9.80
Cu(hfac) ₂ (DMSO)	106-107	25.93	1.45		11.43	26.10	1.49		11.32
Cu(hfac) ₂ (DMSO) ₂	138-139	26.52	2.23		10.02	26.55	2.32		10.01
Cu(hfac) ₂ ((CH ₃) ₃ NO)	51-55	28.24	2.01	2.53	11.47	28.38	2.05	2.63	11.16
Cu(hfac) ₂ (py) ^b	75-76	32.35	1.27	2.52	11.41	32.63	1.29	2.61	11.18
Cu(hfac) ₂ (py) ₂	152-153	37.77	1.91	4.41	9.99	38.19	2.07	4.47	10.00
Cu(hfac) ₂ ((C ₂ H ₅) ₃ N)	54-58	33.20	2.96	2.42		32.75	2.78	1.93	

^a Molecular weight in CCl₄ is 497 (theoretical 478). ^b Molecular weight in CCl₄ is 557 (theoretical 555).

Preparation of Adducts Cu(hfac)₂(B)_n.—All of the monoadducts ($n = 1$) were prepared by addition of stoichiometric amounts of purified acid and base in the appropriate solvent. Addition of DMA, DMSO, and py to Cu(hfac)₂ in CCl₄, evaporation of the solvent, and subsequent sublimation at 1 mm yielded the corresponding monoadducts. Slow evaporation of an equimolar (C₂H₅)₃N-Cu(hfac)₂ mixture in carbon tetrachloride yielded large green crystals that were consistently 1-3% low in carbon. Attempted recrystallization of these green crystals from carbon tetrachloride or cyclohexane yielded an oil. An oil also resulted from the slow evaporation of a CCl₄ solution of Cu(hfac)₂ containing excess triethylamine. A relatively pure sample was obtained by dissolving the impure crystals of Cu(hfac)₂((C₂H₅)₃N) in carbon tetrachloride, adding a small amount of triethylamine, and allowing a thin layer of the solution to evaporate and stand in the air for 48 hr. The monoadduct with trimethylamine N-oxide was prepared by addition of the acid and base in dichloromethane, evaporation of the solvent, and recrystallization from carbon tetrachloride. The resultant oil was crystallized by removal of the solvent and addition of a small amount of dichloromethane.

Cu(hfac)₂(DMSO)₂ was prepared by addition of an excess of DMSO to a concentrated solution of Cu(hfac)₂ in carbon tetrachloride. The resultant yellow precipitate was crystallized from carbon tetrachloride. The Cu(hfac)₂(py)₂ was prepared similarly and purified by sublimation at 1 mm and 110°, yielding a light green product. Cu(hfac)₂(DMA)₂ was prepared by the addition of an excess of DMA to Cu(hfac)₂ in carbon tetrachloride, evaporating the solution to dryness, and recrystallizing the yellow product from cyclohexane.

Results

Both 1:1 and 2:1 adducts of base to Cu(hfac)₂ form easily and are readily isolated. The analytical data for the parent acid and the adducts are given in Table I. Cu(hfac)₂ and Cu(hfac)₂(py) are monomers in carbon tetrachloride according to molecular weight measurements.

The calorimetric data are listed in Table II. In all determinations, except those for the Cu(hfac)₂-(CH₃)₃NO and Cu(hfac)₂(DMA)-DMA systems, the base was added to the acid solution. The limited solubility of Cu(hfac)₂ and Cu(hfac)₂((C₂H₅)₃N) in cyclohexane (0.01 *M*), Cu(Eacac)₂ in carbon tetrachloride (0.008 *M*), and (CH₃)₃NO in *o*-dichlorobenzene (0.005 *M*) necessitated care in the calorimetric determinations so that precipitation would not occur. The enthalpy of Cu(hfac)₂ with (CH₃)₃NO had to be measured in *o*-dichlorobenzene due to the insolubility of trimethylamine N-oxide in either carbon tetrachloride or cyclohexane. The low solubility of Cu(hfac)₂(py)₂ in cyclohexane necessitated that in order to compare

1:1 and 2:1 adducts the enthalpy of Cu(hfac)₂(py) with pyridine be measured in carbon tetrachloride, despite the inherent error of specific interaction of pyridine with the solvent. The enthalpy of the Cu(hfac)₂(DMSO)-DMSO system could not be measured due to the insolubility of Cu(hfac)₂(DMSO)₂ in carbon tetrachloride and cyclohexane.

The equilibrium constants and enthalpies calculated from the calorimetric data, assuming formation of a 1:1 adduct, are summarized in Table III. The enthalpies associated with the reaction of Cu(hfac)₂ with the various bases range from 5.9 to 16.9 kcal/mol. The large equilibrium constants associated with all of the bases, except ethyl acetate, made the addition of excess base (>1:1 for moles of base:moles of acid) unnecessary.

Table IV correlates the enthalpies of formation using the previously proposed four-parameter linear equation²⁷

$$-\Delta H = C_A C_B + E_A E_B \quad (1)$$

where E_A and C_A are two empirically derived parameters for the acid and C_B and E_B are the corresponding parameters for the base, with the standard acid iodine having E_A and C_A values of 1.00. The first four enthalpies listed in Table IV were fitted simultaneously, using the previously derived parameters for the four bases, to give the best least-squares fit between the calculated and experimental enthalpies. Values of E_A equal to 3.16 and a C_A value of 1.58 for Cu(hfac)₂ fit the data as shown in Table IV. The calculated enthalpy for (C₂H₅)₃N is considerably higher than the observed value.

The spectrophotometric data and resultant equilibrium constant calculation for the Cu(hfac)₂-C₂H₅OAc system are given in Table V. The effect of addition of ethyl acetate to Cu(hfac)₂ upon the visible spectrum is shown in Figure 1.

Discussion

Calorimetric Data.—Some comments should be made in regard to the method of determining the enthalpies reported in this study and the errors associated with the determinations. One possible complication with Cu(hfac)₂ is the possibility of simultaneous 2:1 and 1:1 adduct formation. In the concentration ranges reported in Table II the enthalpies and equilibrium con-

TABLE II
CALORIMETRIC DATA^a

[Acid], M	[Base], M	H, cal	Vol, ml	[Acid], M	[Base], M	H, cal	Vol, ml
Cu(hfac) ₂ + C ₂ H ₅ OAc in CCl ₄				Cu(hfac) ₂ + py in Cyclohexane			
0.01933	0.00666	2.84	100.1	0.01122	0.00521	7.75	110.0
0.01874	0.00904	3.97	110.1	0.01121	0.00598	8.28	107.1
0.01525	0.01370	4.96	110.2	0.01121	0.00567	8.59	110.1
0.01874	0.01148	5.04	110.1	0.01121	0.00568	8.19	110.1
0.01874	0.01626	6.74	110.1	0.01121	0.00908	13.61	110.1
0.01524	0.02487	7.69	110.3	0.01121	0.00984	14.16	110.1
0.01872	0.01852	7.74	110.2	0.01121	0.01074	15.79	110.1
0.01521	0.04666	8.24	110.5	Cu(hfac) ₂ + py in CCl ₄			
0.01523	0.03522	8.37	110.4	0.01945	0.004735	6.43	110.0
Cu(hfac) ₂ + DMA in CCl ₄				0.01943	0.007658	9.89	110.1
0.01888	0.00537	4.55	110.0	0.01943	0.009146	11.67	110.1
0.01887	0.00800	6.59	110.0	0.01945	0.01080	13.10	110.1
0.01887	0.01166	9.31	110.1	0.01943	0.01236	16.23	110.1
0.01887	0.01358	11.11	110.1	0.01975	0.01512	19.78	110.0
0.01887	0.01683	12.82	110.1	0.01966	0.01600	20.66	110.1
Cu(hfac) ₂ + DMA in <i>o</i> -Dichlorobenzene				Cu(hfac) ₂ + (C ₂ H ₅) ₂ N in Cyclohexane			
0.02262	0.00788	5.79	111.1	0.009654	0.00306	5.53	110.0
0.02262	0.01150	8.11	111.1	0.009654	0.00508	9.00	110.0
0.02260	0.01612	11.1	111.2	0.009618	0.00654	11.13	107.1
0.02260	0.02114	14.5	111.2	0.009646	0.0641	11.15	110.1
0.02258	0.02586	15.6	111.3	0.009646	0.00880	14.56	110.1
Cu(hfac) ₂ + DMSO in CCl ₄				Cu(Eacac) ₂ + py in CCl ₄			
0.01843	0.005764	5.27	110.1	0.008024	0.01352	1.86	110.1
0.01843	0.009927	9.20	110.1	0.008123	0.03836	2.78	110.3
0.01843	0.01394	13.22	110.1	0.008109	0.06195	3.86	110.5
0.01843	0.01567	14.36	110.1	0.008094	0.07949	4.33	110.7
0.01843	0.01723	16.30	110.1	0.008065	0.1227	4.78	110.1
Cu(hfac) ₂ + (CH ₃) ₂ NO in <i>o</i> -Dichlorobenzene				Cu(hfac) ₂ (DMA) + DMA in CCl ₄			
0.004480	0.004571	5.48	110.0	0.01340	0.03927	1.90	110.4
0.005105	0.004571	5.35	110.0	0.01421	0.09026	3.55	110.9
0.005405	0.004571	5.42	110.0	0.01640	0.07589	3.61	110.0
0.007275	0.004571	5.58	110.0	0.01636	0.2911	6.69	110.0
0.007289	0.004571	5.70	110.0	0.01925	0.5069	8.86	110.0
0.007936	0.004571	5.73	110.0	0.01838	0.5988	8.76	110.0
0.01156	0.004571	5.89	110.0	0.01815	0.7995	9.10	110.0
0.01870	0.004571	5.75	110.0	Cu(hfac) ₂ (py) + py in CCl ₄			
				0.009718	0.00226	2.55	110.1
				0.009710	0.01348	9.64	110.2
				0.009783	0.05028	12.43	110.5
				0.009640	0.1047	12.73	111.0
				0.009750	0.1108	12.87	111.1
				0.009768	0.08738	12.96	110.9

^a H is total heat evolved, corrected for heat of solution of added acid or base, when acid and base are mixed together.

TABLE III
THERMODYNAMIC RESULTS

Acid	Base	$-\Delta H_f$, kcal mol ⁻¹	K, M ⁻¹
Cu(hfac) ₂	C ₂ H ₅ OAc	5.9 ± 0.3	195 ± 43
Cu(hfac) ₂	DMA	8.0 ± 0.2 ^c	1650 ± 430
Cu(hfac) ₂	DMA	6.6 ± 0.2 ^d	... ^a
Cu(hfac) ₂	DMSO	8.5 ± 0.3	... ^a
Cu(hfac) ₂	(CH ₃) ₂ NO	11.4 ± 0.3 ^d	... ^a
Cu(hfac) ₂	py	13.4 ± 0.3 ^b	... ^a
Cu(hfac) ₂	py	11.8 ± 0.4 ^c	... ^a
Cu(hfac) ₂	(C ₂ H ₅) ₂ N	16.9 ± 0.5	5000 ± 900
Cu(Eacac) ₂	py	6.1 ± 0.5 ^c	43.7 ± 12.0
Cu(hfac) ₂ (DMA)	DMA	5.2 ± 0.3	9.2 ± 0.3
Cu(hfac) ₂ (py)	py	12.1 ± 0.3 ^c	570 ± 150

^a K could not be measured. See Discussion. ^b Measured in cyclohexane. ^c Measured in carbon tetrachloride. ^d Measured in *o*-dichlorobenzene.

TABLE IV
CALCULATED AND EXPERIMENTAL ENTHALPIES FOR
Cu(hfac)₂ WITH SOME LEWIS BASES

Base	E _B	C _B	Calcd ^a , kcal/mol	Obsd
C ₂ H ₅ OAc	0.85	1.89	5.7	5.9
DMA	1.21	2.71	8.1	8.0
DMSO	1.26	2.87	8.5	8.5
py	0.91	6.66	13.4	13.4
(C ₂ H ₅) ₂ N	0.43	11.78	20.0	16.9

^a Using E_A = 3.16 and C_A = 1.58. Enthalpy for (C₂H₅)₂N is not used in the calculation of E_A and C_A.

stants were calculated from the calorimetric data, assuming formation of only a 1:1 adduct. The effect of all of the bases upon the visible spectrum of Cu(hfac)₂ has been studied and a sharp isosbestic point is

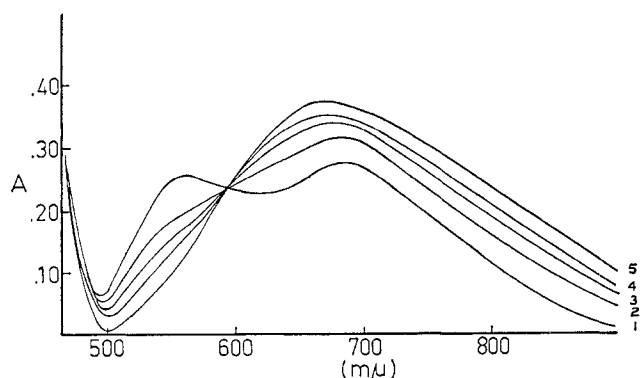


Figure 1.—Electronic absorption spectra for the $\text{Cu}(\text{hfac})_2\text{-C}_2\text{H}_5\text{OAc}$ system. $[\text{Cu}(\text{hfac})_2] = 0.02245 M$; $[\text{EtOAc}]$: (1) = 0.00 M, (2) = 0.00879 M, (3) = 0.01724 M, (4) = 0.2398 M, (5) = 0.4356 M.

TABLE V
SPECTROPHOTOMETRIC DATA FOR THE
 $\text{Cu}(\text{hfac})_2\text{-C}_2\text{H}_5\text{OAc}$ SYSTEM^a

$[\text{C}_2\text{H}_5\text{OAc}]$, M	$A - A_0^b$	$E_0 - E^c$	λ , m μ	K , M ⁻¹
0.00879	-0.119	-17.3 ± 0.3	560	205 ± 17
0.01724	-0.201			
0.02398	-0.250			
0.03262	-0.297			
0.04356	-0.321			
0.00879	0.090	12.5 ± 0.6	860	206 ± 41
0.01724	0.142			
0.02398	0.181			
0.03262	0.207			
0.04356	0.234			

^a $[\text{Cu}(\text{hfac})_2] = 0.02245 M$. Temperature 25°. ^b A is observed absorption; A_0 is absorption of acid before base is added. ^c $E_0 - E_A$ is the difference in extinction coefficients between the acid and acid-base adduct.

observed indicating only two absorbing species, the 1:1 adduct and $\text{Cu}(\text{hfac})_2$, in the concentration range used in the calorimetric work. Except for $\text{C}_2\text{H}_5\text{OAc}$, addition of an excess of base after an equimolar amount of base has been added to the $\text{Cu}(\text{hfac})_2$ solution results in loss of the isosbestic point and a decrease in the intensity of the entire spectrum, both indicating formation of a 2:1 complex.

An excess of base over the stoichiometric amount had to be added in the $\text{Cu}(\text{hfac})_2\text{-C}_2\text{H}_5\text{OAc}$ system to complex the acid sufficiently. Significant 2:1 complexation is not occurring in this system in the range of acid and base concentrations used for two reasons. (1) The calorimetric data fit a 1:1 equilibrium system throughout the concentration range used. (2) A sharp isosbestic point is observed in the visible spectrum (see Figure 1).

It was not possible, from our calorimetric data, to calculate the large equilibrium constants for the interaction of most bases with $\text{Cu}(\text{hfac})_2$. Accurate equilibrium constants could have been calculated if the sums of the initial concentrations were varied over a larger range. Since we were primarily concerned with the determination of the enthalpy, this was not done.

The large values for the equilibrium constants encountered here are manifested by the constancy within

experimental error²⁴ of the ratio of the heat given off in a calorimetric experiment to the moles of base added when the acid is present in excess. This ratio is found to be constant over a range of added pyridine concentration to fixed metal complex concentration and over a wide range of excess metal complex concentrations at fixed $(\text{CH}_3)_3\text{NO}$ concentration.

The difference in the enthalpies measured in the $\text{Cu}(\text{hfac})_2\text{-py}$ system in carbon tetrachloride and cyclohexane (1.5 kcal/mol) is probably due to the specific interaction of pyridine with carbon tetrachloride.²⁵ The enthalpy was measured in carbon tetrachloride in this study so that the enthalpies of both the 1:1 and 2:1 adducts with the pyridine could be compared, since $\text{Cu}(\text{hfac})_2(\text{py})_2$ is insoluble in cyclohexane.

The insolubility of trimethylamine N-oxide in carbon tetrachloride and cyclohexane prompted the corresponding enthalpy measurement to be done in *o*-dichlorobenzene. It has been suggested previously that this *may* be a good "inert" solvent.²² The difference in the enthalpies of the $\text{Cu}(\text{hfac})_2\text{-DMA}$ system measured in carbon tetrachloride and *o*-dichlorobenzene is 1.4 kcal/mol indicating that *o*-dichlorobenzene is a poor "inert" solvent for this work.

The Acceptor Properties of $\text{Cu}(\text{hfac})_2$.—Table IV incorporates $\text{Cu}(\text{hfac})_2$ into the previously proposed relationship (eq 1). A very good correlation is observed for ethyl acetate, DMA, py, and DMSO. The large discrepancy between the observed and calculated enthalpies involving triethylamine can be ascribed to front strain similar²⁶⁻²⁸ to that in $\text{B}(\text{CH}_3)_3$. Steric effects, as manifested through the enthalpy, should be minimized with the other donors and their incorporation into the correlation suggests their absence.

The study described herein with $\text{Cu}(\text{hfac})_2$ is somewhat unusual for a transition metal system in that the study has been done in poorly solvating solvents with nonionic species, instead of with a metal cation in some highly polar solvent. Consequently it is of considerable interest to compare $\text{Cu}(\text{hfac})_2$ with other nonionic acids in terms of its interaction with hard and soft donors.²⁹

If the C parameters represent the susceptibility of the acid or base to interact in covalent bonding (softness) and the E parameters represent the susceptibility of the acid or base to undergo electrostatic bonding (hardness), then one could compare the relative covalent character of acid-base adducts by comparing their $C_A C_B / E_A E_B$ ratios.³⁰ These ratios for the reference base pyridine with the acids I_2 , $\text{Cu}(\text{hfac})_2$, and $\text{B}(\text{CH}_3)_3$ are 7.3, 3.8, and 2.3 respectively. In terms of covalent character or softness, $\text{Cu}(\text{hfac})_2$ is between iodine and $\text{B}(\text{CH}_3)_3$ according to this interpretation.

(24) The error in the measured heat is estimated to be 5%.

(25) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **62**, 2068 (1966), and references therein.

(26) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **75**, 1 (1953); H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953).

(27) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

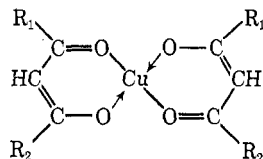
(28) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

(29) R. G. Pearson, *J. Chem. Educ.*, **45**, 581 (1969); R. G. Pearson, *ibid.*, **45**, 643 (1969), and references therein.

(30) This idea has been suggested by G. C. Vogel of this laboratory.

It should be emphasized that the strength of the interaction (*i.e.*, the enthalpy of adduct formation) is not a function of the ratio. Contrary to popular belief, weak adduct formation does not primarily involve electrostatic bonding, and strong adduct formation does not necessarily imply covalent bonding.

The Lewis acidity of copper(II) β -diketonates is affected by the relative electron-withdrawing power of the chelate substituent groups R_1 and R_2 . It has



been previously shown that the equilibrium constants associated with tri-*n*-octylphosphine oxide and $\text{Cu}(\text{hfac})_2$ ($R_1 = R_2 = \text{CF}_3$), $\text{Cu}(\text{tfac})_2$ ($R_1 = \text{CF}_3$; $R_2 = \text{CH}_3$), and $\text{Cu}(\text{acac})_2$ ($R_1 = R_2 = \text{CH}_3$) decrease in this order. A similar result is obtained in this work when comparing the equilibrium constants of $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{Eacac})_2$ ($R_1 = \text{CH}_3$; $R_2 = \text{OC}_2\text{H}_5$). It would be more instructive to ascertain the effect upon the enthalpy of interaction associated with varying the substituent groups in poorly solvating media. The enthalpy of interaction of pyridine with $\text{Cu}(\text{hfac})_2$ (11.8 kcal/mol in CCl_4) is twice as large as that for pyridine with $\text{Cu}(\text{Eacac})_2$ (6.1 kcal/mol in CCl_4). A similar result is observed in the enthalpy of interaction of pyridine toward $\text{Cu}(\text{hfac})_2$ (13.4 kcal/mol in cyclohexane) and $\text{Cu}(\text{Bacac})_2$ (7.1 kcal/mol in cyclohexane; $R_1 = \text{CH}_3$; $R_2 = \text{OC}(\text{CH}_3)_3$).¹² Thus, there is very convincing evidence for the transmission of substituent effects from ligands in the *xy* plane through the copper to the ligand bonding on the *z* axis.

Since the C_B and E_B parameters used for DMSO correspond to this base bonding through the oxygen, the correct prediction of the enthalpy indicates that the mode of attachment to $\text{Cu}(\text{hfac})_2$ involves oxygen. This mode of bonding is supported by the reduction upon coordination of the coupled "S-O" stretching frequency.³¹⁻³⁴

We became interested in the interaction of $(\text{CH}_3)_3\text{NO}$ with $\text{Cu}(\text{hfac})_2$ since this base has a very high reported enthalpy of interaction with $\text{VO}(\text{acac})_2$ ³⁵ (38 kcal/mol in dichloromethane). The enthalpy of interaction of $\text{VO}(\text{acac})_2$ with pyridine N-oxide is reported to be 6.2 kcal/mol, in dichloromethane, while that for the same base with $\text{Cu}(\text{hfac})_2$ in CCl_4 is predicted from the *E* and *C* correlation to be 11.0 kcal/mol. Therefore one might expect the enthalpy of interaction of trimethylamine N-oxide with $\text{Cu}(\text{hfac})_2$ to be very large. It was of interest to extend our studies to such a strong adduct.

The observed enthalpy (in *o*-dichlorobenzene) is much less than this, indicating either the reported value for the enthalpy of trimethylamine N-oxide with $\text{VO}(\text{acac})_2$ is in error or important electronic differences exist between these two acids.

The Acceptor Properties of $\text{Cu}(\text{hfac})_2(\text{B})$.—The ability of $\text{Cu}(\text{hfac})_2$ to form diadducts makes it possible to compare the acceptor strengths of $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{hfac})_2(\text{B})$; *i.e.*, steps corresponding to formation of 1:1 and 2:1 adducts. The enthalpy of interaction of DMA with $\text{Cu}(\text{hfac})_2$ is 8.0 kcal/mol, and that of DMA with $\text{Cu}(\text{hfac})_2(\text{DMA})$ to form a 2:1 adduct is 5.2 kcal/mol. Thus the acceptor strength, using the enthalpy as the defining parameter, is reduced considerably upon axial ligation with DMA as would be expected if charge were transferred into the metal upon complexation by base. The equilibrium constant is also reduced considerably. The equilibrium constant for the analogous pyridine system is also reduced, but the enthalpies of pyridine toward $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{hfac})_2(\text{py})$ are the same, within experimental error. The increased acceptor ability in the sixth coordination position for $\text{Cu}(\text{hfac})_2(\text{py})$ could result if upon addition of two pyridines the formal positive charge on the metal was reduced so that metal to ligand back-bonding was more important in the 2:1 than in the 1:1 complex. Metal-pyridine back-bonding in $\text{Co}(\text{acac})_2(\text{py})_2$ and $\text{Ni}(\text{acac})_2(\text{py})_2$ has been proposed from a single-crystal X-ray study^{36,37} on the basis of a short metal-nitrogen bond. Another possibility is that larger steric effects exist in the six-coordinate adduct with DMA than in the one with pyridine.

Preparation of Adducts of Copper(II) β -Diketonates.

—The ability to prepare isolable 1:1 and 2:1 base adducts of $\text{Cu}(\text{hfac})_2$ with a variety of bases is illustrated in this work. The *E* and *C* correlation provides a number of predicted enthalpies of formation which can serve as a guide to selecting donors which should form stable adducts. In our experience, adducts with $\text{Cu}(\text{hfac})_2$ which are stable at room temperature can be isolated with bases having enthalpies of formation greater than 8 kcal/mol. This enthalpy is associated with the $\text{Cu}(\text{hfac})_2$ -DMA adduct. The enthalpy values predicted for some of the amines and ethers are expected to be somewhat higher than is actually the case due to steric effects.

It is interesting that the available preparative data on adducts involving copper(II) β -diketonates are consistent with the calorimetric data discussed in the previous section. It was shown that the Lewis acidity of these copper compounds can be related to the inductive effects of the acetylacetonate substituent groups. Accordingly, $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{tfac})_2$ form isolable adducts of pyridine^{7,11} at room temperature while the pyridine adducts of $\text{Cu}(\text{acac})_2$ ⁹ and $\text{Cu}(\text{Eacac})_2$ ⁴ are unstable, losing pyridine readily when exposed to the air. Furthermore, $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{tfac})_2$ form isolable 2:1 adducts,^{7,11} while $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{Eacac})_2$

(31) J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1960).

(32) F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).

(33) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960).

(34) R. S. Drago and D. W. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

(35) C. J. Popp, J. H. Nelson, and R. O. Ragsdale, *J. Am. Chem. Soc.*, **91**, 610 (1969).

(36) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(37) R. C. Elder, *ibid.*, **7**, 2316 (1968).

form only 1:1 adducts even in the presence of large excesses of base.^{3,4,12} This constitutes an interesting body of chemical information which is now understood and can be interpreted in terms of acid-base concepts with relatively little considerations from lattice effects.

Recent X-ray analyses have elucidated the structure of the 1:1 adducts.^{17,26} The new adducts prepared in this work are probably analogous, having a square-pyramidal geometry about the copper atom. The

structures of the dipyridine adducts of $\text{Co}(\text{acac})_2$ ³⁷ and $\text{Ni}(\text{acac})_2$ ³⁸ involve a *trans*-octahedral configuration, and the 2:1 adducts of the copper(II) β -diketonates are probably the same.

Acknowledgment.—This investigation was supported in part by the National Science Foundation, Grant No. GP 5498.

(38) V. F. Duckworth, D. P. Graddon, G. M. Mockler, and N. C. Stephenson, *Inorg. Nucl. Chem. Letters*, **3**, 471 (1967).

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The Synthesis and Aquation Kinetics of *cis*- and *trans*-Dichlorotriaquoamminechromium(III) and Blue-Violet Chlorotetraquoamminechromium(III) Cations^{1a,b}

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The new complexes *cis*- and *trans*- $\text{Cr}(\text{NH}_3)(\text{OH}_2)_3\text{Cl}_2^+$ have been synthesized, and spectrophotometric and chromatographic evidence has been obtained supporting the isomeric assignments (the location of the NH_3 ligand is uncertain in the *cis* isomer). The aquation of both isomers was studied at 30–45° by spectrophotometry and by Cl^- release. For both isomers the same product, previously unreported blue-violet $\text{Cr}(\text{NH}_3)(\text{OH}_2)_4\text{Cl}^{2+}$ (tentatively assigned as the *cis*-chloroammine isomer), is formed. In 0.3–1 *F* HClO_4 ($\mu = 1$ *M*, NaClO_4) at 25° (by extrapolation) the first-order rate constant for *cis*- $\text{Cr}(\text{NH}_3)(\text{OH}_2)_3\text{Cl}_2^+$ is $k_{1c} = 2.8 \times 10^{-5}$ sec^{-1} , with $E_a = 23.1 \pm 0.5$ kcal mol^{-1} and $\log PZ$ (sec^{-1}) = 12.47 ± 0.31 , and for *trans*- $\text{Cr}(\text{NH}_3)(\text{OH}_2)_3\text{Cl}_2^+$ the first-order rate constant is $k_{1t} = 4.8 \times 10^{-5}$ sec^{-1} , with $E_a = 20.2 \pm 0.2$ kcal mol^{-1} and $\log PZ$ (sec^{-1}) = 10.38 ± 0.13 . The aquation of blue-violet $\text{Cr}(\text{NH}_3)(\text{OH}_2)_4\text{Cl}^{2+}$ to $\text{Cr}(\text{NH}_3)(\text{OH}_2)_5^{3+}$ was studied spectrophotometrically and by Cl^- release in 0.25–1.5 *F* HClO_4 ($\mu = 0.25$ – 1.5 *M*, NaClO_4) at 45–70°. For $\mu = 1.5$ *M*, the observed hydrolysis rate constant, $k_{2,\text{obsd}}$ has the form $k_{2,\text{obsd}} = k_2 + (k_2'/[\text{H}^+])$, where k_2 is the first-order constant for the aquation of blue-violet $\text{Cr}(\text{NH}_3)(\text{OH}_2)_4\text{Cl}^{2+}$ and k_2' has been interpreted as $k_{2h}K_a$, with k_{2h} being the first-order rate constant for aquation of $\text{Cr}(\text{NH}_3)(\text{OH}_2)_3(\text{OH})\text{Cl}^+$ and K_a the first acid dissociation constant of blue-violet $\text{Cr}(\text{NH}_3)(\text{OH}_2)_4\text{Cl}^{2+}$. At 45° $k_2 = 7 \times 10^{-6}$ sec^{-1} , with $E_a = 25.0 \pm 0.7$ kcal mol^{-1} and $\log PZ$ (sec^{-1}) = 11.94 ± 0.48 , and $k_2' = 8 \times 10^{-7}$ M sec^{-1} . There is little or no aquation of these complexes *via* Cr–N bond rupture. The visible absorption spectra of the new complexes are reported.

Introduction

Only ten monoamine complexes of chromium(III) have been reported, in sharp contrast with the numerous chromium(III)–amine complexes with two, three, and four Cr–N bonds; of the reported monoamine complexes, only two are halo complexes and they have pyridine as the amine ligand.

We report here the synthesis of three new monoamine complexes of chromium(III), namely, *cis*- and *trans*-dichlorotriaquoamminechromium(III) cations, $\text{Cr}(\text{NH}_3)(\text{OH}_2)_3\text{Cl}_2^+$, and a blue-violet isomer of chlorotetraquoamminechromium(III) cation, $\text{Cr}(\text{NH}_3)(\text{OH}_2)_4\text{Cl}^{2+}$. We also report our studies of the kinetics of aquation of the dichloro complexes to form the monochloro complex and aquation of the latter to pentaquoamminechromium(III) cation, $\text{Cr}(\text{NH}_3)(\text{OH}_2)_5^{3+}$. These chloro complexes are of especial interest for

comparison of their aquation rates with those of certain related dichloro and monochloro complexes of chromium(III), since these new complexes serve as links between the numerous chloroamine complexes with more than one amine ligand and the chloroquo complexes of chromium(III) without amine ligands. Moreover, these aquation studies provide another opportunity to examine the possibility of Cr–N bond rupture in competition with Cr–Cl bond rupture, a phenomenon which has been reported in a variety of chromium(III)–amine complexes.

Experimental Section

Pentaquoamminechromium(III) Cation.—The method of Ardon and Mayer,² modified as follows, was used to give a solution of this complex in *ca.* 6 *F* HCl . Electrolytic Cr metal (*ca.* 0.5 g) was added under N_2 to 25 ml of 3 *F* HCl which had been freed of dissolved O_2 by scrubbing with N_2 , and the Cr was dissolved by heating at *ca.* 80°. Enough 0.1 *F* NaN_3 was added dropwise to the vigorously stirred Cr(II) solution at *ca.* 20° to give a Cr: N_3^- mole ratio of 2, producing $\text{Cr}(\text{NH}_3)(\text{OH}_2)_5^{3+}$ and

(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-5 to the AEC. (b) Abbreviations used: en, ethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine.

(2) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).