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Thermodynamic Measurements of the *Cis* and *Trans* Effects in Alkylcobalt(III) Chelates

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Thermodynamic parameters for bonding a sixth ligand to a number of five coordinate alkylcobalt(III) complexes have been measured. The enthalpies of adduct formation demonstrate the magnitudes of the ground state trans *and* cis *effects in these systems. Substantial differences in the enthalpies of axial bond formation are caused by changes in both the* trans *and* cis *ligands. Unusual behavior is observed when tetrahydrofuran and tetrahydrothiophene are the entering ligands. Comparison of the equilibrium constants for these two bases indicates that the cobalt center prefers the more polarizable sulfur donor. On the other hand, the enthalpy measurements show that the metal ligand bond formed is stronger with the oxygen donor. This unusual behavior has been previously observed for the binding of these two bases to methylcobaloxime.*

Introduction

The study of the *trans* effect in cobalt(III) complexes has been a subject of considerable interest for most of the past two decades. The continuing interest in this topic is undoubtedly due primarily to the known *trans* effect in vitamin B_{12} derivatives, specifically the alkylcobalt(III) corrinoids. Underlying much of the current activity in this area is the suspicion that, during an enzymatic reaction, a change in ligation at an axial position of a B_{12} coenzyme could significantly alter the reactivity of the *trans* axial position and perhaps even alter the mechanism of the interconversion occurring at the active site. Aside from the possible benefit from current work on the cobalt(III) *trans* effect to questions of B_{12} biochemistry there are, for the inorganic chemist, sufficient inherently interesting questions to justify continued attention. A characteristic feature of the more recent work in this area is the fact that the nature of the *trans* effect in cobalt(III) is being addressed more quantitatively.

As was the case earlier with the platinum(II) *trans* effect (influence), the experimental approaches to the cobalt(III) *trans* effect have measured transition state parameters through a variety of kinetic analyses [1–5] or ground state parameters such as geometry [1, 3, 7–13], spectral characteristics [1, 14] or thermodynamic analyses [1, 15]. Several workers have addressed the question of the relationship between the ground state and transition state effects in the labilization of one cobalt(III) bound ligand by another *trans* to it. That is, how important is the *bond strength* (or change in bond strength as the *trans* ligand is varied) in determining the kinetic lability of a given ligand. Halpern has considered this in his analysis of ligand substitution reactions of sulfitopentaamminecobalt(III) [16]. Elder has considered this question in a comparison of the kinetic and structural *trans* effects in sulfitopentaamminecobalt(III) complexes [3]. Steward and Marzilli have recently shown that in nonaqueous solution alkylcobaloximes undergo axial ligand substitution by a strictly S_N1 dissociative mechanism [2]. That is, the bond breaking step is of overwhelming importance in determining the rate of ligand substitution. This result suggests that fundamental knowledge about bond strengths will be useful additional information in order to explain the nature of the cobalt *trans* effect. Such information is virtually non-existent in the large volume of literature associated with this area.

A second question of interest involves the Lewis acid nature of the cobalt. The cobalt center in alkylcobalt(III) chelates has been described as a class b acceptor [17, 18], a soft acid [19], and an acid capable of undergoing significant covalent and electrostatic bonding, with perhaps the electrostatic interaction dominating [20]. Because of the limited amount of quantitative data related to this subject, it was of interest to extend the thermodynamic data pertinent to this fundamental question.

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TABLE I. Thermodynamic Parameters for Formation RCo(chelate)–Ligand Adducts in *o*-dichlorobenzene Solvent.

No.	Acceptor Complex	Ligand [22]	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}	K_a, L mol^{-1} ^{a}
1	$CF_3Co(bae)$	PY	–15.4 ± 0.5	–31.2 ± 1.0	2.9×10^4
2		DMA	–5.9 ± 0.1	–17.2 ± 0.2	3.7
3		THF	–9.0 ± 0.5	–26.9 ± 1.5	5.3
4		THT	–7.1 ± 0.4	–18.2 ± 1.0	17
5		AN	–7.6 ± 0.1	–24.0 ± 0.4	2.1
6		TMP	–10.1 ± 0.1	–26.7 ± 0.3	37
7	$CF_3Co(F_3\text{-}bae)$	DMA	–11.8 ± 0.1	–25.8 ± 0.1	1.0×10^3
8		THF	–9.4 ± 0.7	–21.2 ± 1.7	1.8×10^2
9		THT	–7.0 ± 0.1	–11.1 ± 0.1	5.1×10^2
10		AN	–11.3 ± 0.3	–30.3 ± 0.7	46
11		TMP	–17.7 ± 0.8	–40.5 ± 1.8	1.3×10^4
12		EA	–10.0 ± 0.4	–27.5 ± 1.1	21
13	$CH_3Co(bae)$	PY	–9.1 ± 0.1	–22.6 ± 0.2	54
14	$C_6H_5Co(bae)$	PY	–8.1 ± 0.3	–20.5 ± 0.2	29
15	$CH_3Co(F_3\text{-}bae)$	PY	–11.1 ± 0.1	–22.6 ± 0.6	1.6×10^3
16	$(CHCl_2)Co(F_3\text{-}bae)$	PY	–10.9 ± 0.3	–17.4 ± 0.5	1.5×10^4
17	$CH_3Co(salen)$	PY	–10.4 ± 0.2	–23.9 ± 0.3	2.5×10^2
18	$(CHCl_2)Co(salen)$	PY	–4.9 ± 0.2	–6.5 ± 0.3	1.5×10^2

^{a}Calculated values for 298 °K.

Throughout the more recent work on the *trans* effect in cobalt(III) one finds few experiments addressing the effect which one ligand exerts on another *cis* to it, *i.e.* the cobalt(III) *cis* effect. Pratt and Thorp have discussed this question pointing out that while by some measurements the *cis* and *trans* effects appear to be equally important, by other measurements the effect of a given ligand on the others seems to be directed only to the *trans* ligand [1]. Thus structural work often indicates a distinct *trans*-directional influence of a given ligand on the others. Recent structural work, for example by Elder, has shown a marked lengthening of the *cis* ligands [3]. Richards has also determined a specific kinetic *trans* labilization in sulfitocobalt(III)ammine complexes [6]. Randaccio *et al.*, have carried out a number of structural analyses related to the cobalt(III) *trans* effect [9–13]. On the other hand, infrared analysis of pentacyanides shows considerable variation in the cyanide stretching frequency with changes in the sixth ligand. However, only one i.r. band is observed, suggesting identical bond strengths for the five cyanide ligands [21]. After an analysis of a large volume of data on formation constants, Pratt and Thorp have stated that no conclusion could be drawn about the relative effects of a given ligand on the *cis* and *trans* positions [1]. Once again, lacking in this area is a knowledge of the bond energy changes. Aside from a comparison of the enthalpy of pyridine binding to methylcobaloxime [20] and to $CH_3Co(bae)$ [15], each determined by different workers in different solvents, no thermodynamic data of the type needed has been reported relative to the *cis* effect.

In this work we report thermodynamic parameters for binding of a variety of ligands to the axial position of alkylcobalt(III) chelates. The systems which were investigated were chosen to address the questions described above, *i.e.* the *cis* and *trans* effects and the nature of the cobalt center.

Results

The alkyl cobalt(III) chelates were prepared by modification of previously reported procedures (see Experimental). The thermodynamic data reported are for addition of a sixth axial ligand to the five coordinate species. Equilibrium constants were calculated as described in the Experimental section. Enthalpy and entropy parameters were determined from the temperature dependence of the equilibrium constant. Table I summarizes the thermodynamic parameters obtained for the various systems. Table II gives the individual equilibrium constants at each temperature for each acid base pair along with statistical parameters which reflect the quality of the

TABLE II. Equilibrium Constants, Conditional Standard Deviation of K, and (Marginal Std. Dev./Conditional Std. Dev.) for Each Acid–Base Pair at Each Temperature.

Acid	Base	Temp. °C	K	Conditional Std. Dev.	Marginal Std. Dev. / Conditional Std. Dev.
$CF_3Co(bae)$	Py	30.0	17.9×10^3	1840	1.59
		39.0	8.45×10^3	326	1.81
		48.0	4.56×10^3	120	2.06
		56.6	2.23×10^3	25.9	2.42
	DMA	30.0	2.90	0.0383	3.05
		39.0	2.18	0.0163	3.20
		48.0	1.68	0.0100	3.35
	THF	30.0	4.33	0.0775	2.28
		39.0	2.70	0.0266	2.48
		48.0	1.87	0.0203	4.97
	THT	39.0	9.69	0.1090	3.11
		48.0	6.83	0.0582	3.26
		56.6	5.27	0.0712	3.41
	AN	30.0	1.63	0.0229	2.99
		39.0	1.16	0.0236	3.10
		48.0	0.82	0.0200	3.25
		56.6	0.59	0.0108	3.45
	TMP	30.0	30.0	0.100	1.87
		39.0	18.8	0.398	1.98
		48.0	11.7	0.259	2.24
$CF_3Co(F_3\text{-}bae)$	DMA	30.0	761	31.1	2.12
		39.0	434	24.9	2.17
		48.0	253	7.2	2.02
	THF	30.0	155	2.96	2.43
		48.0	76.5	3.72	2.49
		56.6	43.1	0.29	2.85
	THT	39.0	296	11.9	2.01
		48.0	216	4.43	2.04
		56.6	162	7.66	1.97
	AN	39.0	31.8	2.15	2.20
		48.0	19.2	0.92	2.04
		56.6	11.7	0.73	2.08
	TMP	39.0	3.2×10^3	182	1.95
		48.0	1.49×10^3	197	1.93
		56.6	6.82×10^2	32.1	2.05
	EA	39.0	9.77	0.347	2.20
		48.0	6.40	0.191	2.25
		56.6	4.13	0.150	2.30
$CH_3Co(bae)$	Py	30.0	44.0	0.493	1.61
		48.0	18.7	0.128	1.93
		56.6	13.0	0.113	2.50

(continued overleaf)

TABLE II. *(continued)*

Acid	Base	Temp. °C	K	Conditional Std. Dev.	Marginal Std. Dev. / Conditional Std. Dev.
$C_6H_5Co(bae)$	Py	30.0	22.4	0.0751	2.00
		39.0	15.3	0.0977	2.35
		48.0	10.6	0.103	2.87
$CH_3Co(F_3\text{-bae})$	Py	39.0	629	7.40	2.15
		48.0	382	4.55	2.57
		56.6	243	1.44	2.07
$CHCl_2Co(F_3\text{-bae})$	Py	30.0	11.1×10^3	189	2.72
		39.0	6.45×10^3	19.7	3.20
		48.0	4.04×10^3	737	2.18
$CH_3Co(salen)$	Py	30.0	222	1.66	2.18
		39.0	127	0.69	2.05
		48.0	85	0.96	1.92
		56.6	54	0.37	2.16
$CHCl_2Co(salen)$	Py	30.0	132	5.98	2.06
		39.0	99	2.67	1.99
		48.0	77	1.12	2.04

data. In the text, as well as in the tables, abbreviations* are used extensively.

One of the primary considerations in this effort was to chose alkylcobalt(III) chelates in which several types of entering ligands would bind sufficiently strongly so that thermodynamic parameters could be obtained. Thus, $CF_3Co(bae)$ and $CF_3Co(F_3\text{-bae})$ could be studied with oxygen, nitrogen, sulfur and phosphorus bases.

Discussion

As mentioned above, it is desirable to obtain this type of thermodynamic data in as noninteracting a solvent as possible. In this work it was considered important to collect all data in a common solvent. Normally alkanes or carbon tetrachloride are considered to be most suitable for this purpose but not all systems studied were soluble enough in these solvents. Therefore *o*-dichlorobenzene was chosen as a relatively noninteracting solvent in which all systems could be studied. The possible solvation effects in *o*-dichlorobenzene have been addressed [22, 23].

The equatorial ligand systems were chosen because they maintain the same donor atoms while still providing enough variety in electron donating ability to make measurements which would be meaningful for a quantitative assessment of the *cis* effect. Relatively poor electron donating ligands (in both equatorial and axial positions) were chosen because it was of interest to carry out the thermodynamic measurements on a common Lewis acid which would bind oxygen, nitrogen, sulfur, and phosphorus donors well enough to allow accurate measurements. In this regard, both $CF_3Co(bae)$ and $CF_3Co(F_3\text{-bae})$ were suitable. However, the latter compound exhibited such strong binding to pyridine ($K > 5 \times 10^4$) that an enthalpy could not be measured by the technique which was employed.

Despite the numerous data from kinetics and from equilibrium constant measurements on the cobalt(III) *trans* effect, there is virtually no enthalpy data available pertinent to this subject. This has remained true even though the enthalpy should reflect internal bond energy changes most directly related to the *trans* effect. In the data presented here, one can compare the thermodynamic parameters for pyridine binding to several complexes. For example,

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*The abbreviations employed in the text and tables are as follows: bae, N,N'-bis(acetylacetone)ethylenediimine; salen, N,N'-bis(salicylaldehyde)ethylenediimine; F_3-bae, N,N'-bis(3-trifluoroacetylacetone)ethylenediimine; $(dmg)_2$, bis(dimethylglyoximato); PY, pyridine; DMA, N,N-dimethylacetamide; THF, tetrahydrofuran; THT, tetrahydrothiophene; AN, acetonitrile; TMP, trimethylphosphite; EA, ethylacetate.

comparison of pyridine binding to $CH_3Co(bae)$ and $CF_3Co(bae)$, shows equilibrium constants at 25 °C of 54 L mol^{-1} and 2.9×10^4 L mol^{-1} respectively. The enthalpies for bond formation are −9.1 kcal mol^{-1} and −15.4 kcal mol^{-1} respectively. These values are perfectly consistent with the greater electron withdrawing capacity of the *trans* CF_3 ligand as compared to CH_3. If one further considers the binding of pyridine to $C_6H_5Co(bae)$, K_{298} = 29 L mol^{-1} and $\Delta H = -8.1$ kcal mol^{-1}, the results appear to be anomalous. Both the equilibrium constant and the enthalpy of bond formation are smaller for the phenyl derivative than for the methyl derivative. The *trans* phenyl ligand is certainly less electron releasing than the methyl ligand and it therefore follows that the enthalpy of adduct formation with a sixth axial ligand should be larger for the phenyl than for the methyl derivative. The X-ray structure of $C_6H_5Co(bae)\cdot H_2O$ indicates the probable origin of the anomalous behavior for the phenyl derivatives [24]. In this compound the flexible bae ligand is bent away from the phenyl group. This would cause steric interference for the entering axial ligand. The bulk of the phenyl group is apparently responsible for this as the bae ligand in (vinyl) $Co(bae)\cdot H_2O$ is not distorted away from the organo ligands [25]. The $Co{-}OH_2$ distances in (vinyl) $Co(bae)\cdot H_2O$ and $C_6H_5Co(bae)\cdot H_2O$ also demonstrate this steric effect. In the former a $Co{-}OH_2$ distance of 2.22 Å is found while in the latter the bond has lengthened substantially to 2.33 Å. If a small ligand such as H_2O experiences this steric effect, certainly the pyridine ligand would be expected to encounter steric interference and the low enthalpy of formation for the $C_6H_5Co(bae)$–pyridine system appears to be due to this phenomenon.

The effect of a bulky axial ligand can be seen even more dramatically by comparing the binding of pyridine to $CH_3Co(salen)$ and $(CHCl_2)Co(salen)$. The dichloromethyl ligand is obviously more electron withdrawing than the methyl group. Nevertheless, the enthalpy of pyridine binding to $(CHCl_2)$-Co(salen) is very low. This can only be understood by assuming that the bulky dichloromethyl group causes the salen ligand to bend away from it which, in turn, causes the entering pyridine ligand to experience substantial steric hindrance. This same effect is apparent, but less pronounced when one compares pyridine binding to $CH_3Co(F_3\text{-bae})$ and $(CHCl_2)$-$Co(F_3\text{-bae})$.

With respect to the two dichloromethyl derivatives, Brown *et al.*, have observed a rather dramatic decrease in trimethylphosphite exchange with alkylcobaloximes with chloro- or bromomethyl derivatives [5]. For example exchange is slower with bromomethyl- and dibromomethylcobaloxime than with trifluoromethylcobaloxime. Trimethylphosphite exchange with dichloromethylcobaloxime occurs at about the same rate as with trifluoromethylcobaloxime. The origin of this unexpectedly slow exchange in the chloro- and bromomethylcobaloximes has been attributed to steric repulsion between the alkyl ligand and the d_{xz}, d_{yz} electrons. One consequence of this is suggested to be enhanced π bonding to the sixth axial ligand providing added stability to the cobalt–axial ligand bond. The data reported here indicate that the ground state cobalt–pyridine bond energy is considerably weaker in dichloromethylcobalt(III)salen than with the methyl derivative. It is true, of course, that pyridine will undergo metal-ligand π bonding to a considerably lesser degree than will trimethylphosphite. The π bonding to pyridine may, in fact, be weak enough that the effect observed for trimethylphosphite is unobservable. It will be of interest in the future to investigate the thermodynamics of trimethylphosphite binding to complexes with bulky alkyl groups to ascertain if there is some enhanced stability in the ground state.

The effects of changing a *cis* ligand are also demonstrated by the data in Table I. This is best noted by comparing ligand binding to $CF_3Co(bae)$ and $CF_3Co(F_3\text{-bae})$, two complexes in which the only difference is the electron donating ability of the equatorial ligand. Several axial ligands have been studied with both complexes. For each of the ligands studied with both Lewis acids one observes substantially enhanced binding (larger K) to the complex with the F_3-bae equatorial ligand system. For the axial ligands DMA, AN, and TMP one also observes a considerably larger value for the enthalpy of adduct formation as expected. However, the enthalpies for THF and THT are no different, within experimental error, between $CF_3Co(bae)$ and $CF_3Co(F_3\text{-bae})$. Thus, in going from $CF_3Co(bae)$ to $CF_3Co(F_3\text{-bae})$ one observes an enhancement in the equilibrium constant by a factor of 34 for the THF and 20 for THT, but no significant increase in the enthalpy of formation. This surprising behavior is only observed for these two donors with the same geometry. Significantly, the same behavior is observed for both donors so that the possibility of an experimental artifact seems highly unlikely. For these two donors, at least, the entropy term is totally responsible for the enhanced binding (*i.e.* larger K) to $CF_3Co(F_3\text{-bae})$. Note especially for the THT-$CF_3Co(F_3\text{-bae})$ adduct the extremely low entropy of formation. This is much lower than we have normally observed for adduct formation of this type. However, in 1:1 adduct formation of several bases to bis(hexafluoroacetylacetonate)copper(II), entropy values similar to this were observed [26]. We are currently expanding this investigation to a number of analogous sulfur and oxygen donors in hopes of gaining more insight into this situation. Furthermore, a number of solvents will be employed to ascertain how important solvation effects are in determining the entropy parameters.

Additional information on the *cis* effect is available in Table I by comparing the enthalpies of formation of pyridine adducts with $CH_3Co(bae)$ (−9.1 kcal mol^{-1}), $CH_3Co(salen)$ (−10.4 kcal mol^{-1}), and $CH_3Co(F_3\text{-}bae)$ (−11.1 kcal mol^{-1}). The variation in enthalpies here is rather small. The order of electron withdrawing ability of the *cis* ligands is bae $<$ salen $<$ F_3-bae. This same order has been observed through an entirely different measurement in a series of *o*-semiquinone adducts of cobalt(III) complexes containing these same tetradentate ligands [27].

Pratt and Thorp have previously suggested an order for the *cis* effect as follows: $(H_2O)_4 \gg (NH_3)_4 \sim en_2 \sim (dmg)_2 \sim$ corrin $\sim (CN)_4$ [1]. Here $(H_2O)_4$ is the *cis* ligand system which results in the most stable axial cobalt–ligand bond while $(CN)_4$ is the most labilizing *cis* ligand system. From our data and the earlier work of Courtright and Drago [20], we would suggest the order of *cis* effect is $(dmg)_2 >$ $(F_3\text{-}bae) >$ salen $>$ bae where $(dmg)_2$ causes the strongest axial cobalt ligand bonds and bae the weakest.

The thermodynamic results on formation of the sixth metal–ligand bond in these systems has raised a number of interesting questions about the nature of the cobalt. The cobalt center in methylcobinamide has been described as a class b center [17, 18]. Methylcobaloxime has been described as a 'soft' Lewis acid [19]. Exception has been taken to the soft classification by Drago who argues that methylcobaloxime undergoes both moderately strong electrostatic and covalent bonding [20]. Within the technical definition of each classification all descriptions appear to be correct. The current results provide new information on the nature of the cobalt center and raise additional interesting questions. The equilibrium constants for the binding of THF and THT indicates that THT binds to the cobalt in CF_3-Co(bae) three times as readily as THF. That is, the cobalt 'prefers' the soft sulfur ligand to the hard oxygen ligand. On the other hand, the bond formed with the oxygen donor is 2 kcal stronger than that with the sulfur donor. That is, the cobalt seems to form stronger bonds with the base that more readily undergoes electrostatic bonding. The same contradicting conclusions can be drawn from the data for THF and THT with $CF_3Co(F_3\text{-}bae)$. Unfortunately, these two Lewis bases appear to be anomalous as discussed earlier so that these comparisons are open to question. They do indicate clearly that additional work is in order in which binding of analogous oxygen and sulfur donors to the same cobalt center is measured. It has been suggested that TMP binding to methylcobaloxime is anomalously strong [20]. The enthalpy of binding of TMP to methylcobaloxime is as large as for pyridine binding to the same cobalt center. The results presented here do not show the same phenomenon. $CF_3Co(bae)$ clearly favors pyridine binding over the TMP although TMP is the second strongest base employed in this work.

Aside from cobalt chelates studied by us, the other system for which thermodynamic information is available is methylcobaloxime [20]. Comparison of the cobaloxime system with the bae or salen chelates deserves comment. The obvious differences between the bis dimethylglyoximato equatorial ligand and the bae or salen ligand are the nature of the 4 donor atoms (4N *vs.* 2N and 2O) and the rigidity of the $(dmg)_2$ ligand system compared with the flexibility of the bae or salen ligand [28]. In general the cobaloxime always appears to be a stronger Lewis acid than either $CH_3Co(bae)$ or CH_3-Co(salen). Methylcobaloxime, even with a strongly electron releasing axial ligand is more acidic than $CF_3Co(bae)$, with a much more electron withdrawing axial ligand. Thus the strong *cis* effect of the $(dmg)_2$ equatorial ligand dominates substantial differences in *trans* axial ligands.

It has been suggested for oxygen donors binding to methylcobaloxime that there is an anomalous entropy effect causing artificially low equilibrium constants [20]. Unfortunately this was based on data for THF, a base which seems to be anomalous, at least in our systems. In an earlier report we concluded that there was no anomalous entropy effect and, if fact, for a series of adducts found a relatively good correlation between ΔH and ΔS [15]. However, most of the data in that correlation were for pyridine binding to RCo(bae) in which only R was varied. In this work much more data is available which includes complexes with a variety of *cis* ligands as well as a larger variety of entering ligands. Figure 1 shows a plot of $-\Delta H$ *vs.* $-\Delta S$ for all the data reported in Table I. Initial inspection of Fig. 1 shows at best a very qualitative correlation between ΔH and ΔS. Closer inspection also reveals that if one compares data only for one Lewis acid or one Lewis base no good correlation is found. With respect to oxygen donors, we do not find a consistently large negative entropy as suggested by Drago for methylcobaloxime but rather find the data for oxygen bases scattered throughout the grid in Fig. 1. Thus the unusually large negative entropies are apparently unique to methylcobaloxime and not a function of only the cobalt center in this type complex.

Experimental

Chemicals and Preparation of Complexes

Ortho-dichlorobenzene was obtained from J. T. Baker Company. Before using for spectral work it was distilled from barium oxide and stored over Linde 4A molecular sieves. Tetrahydrofuran used

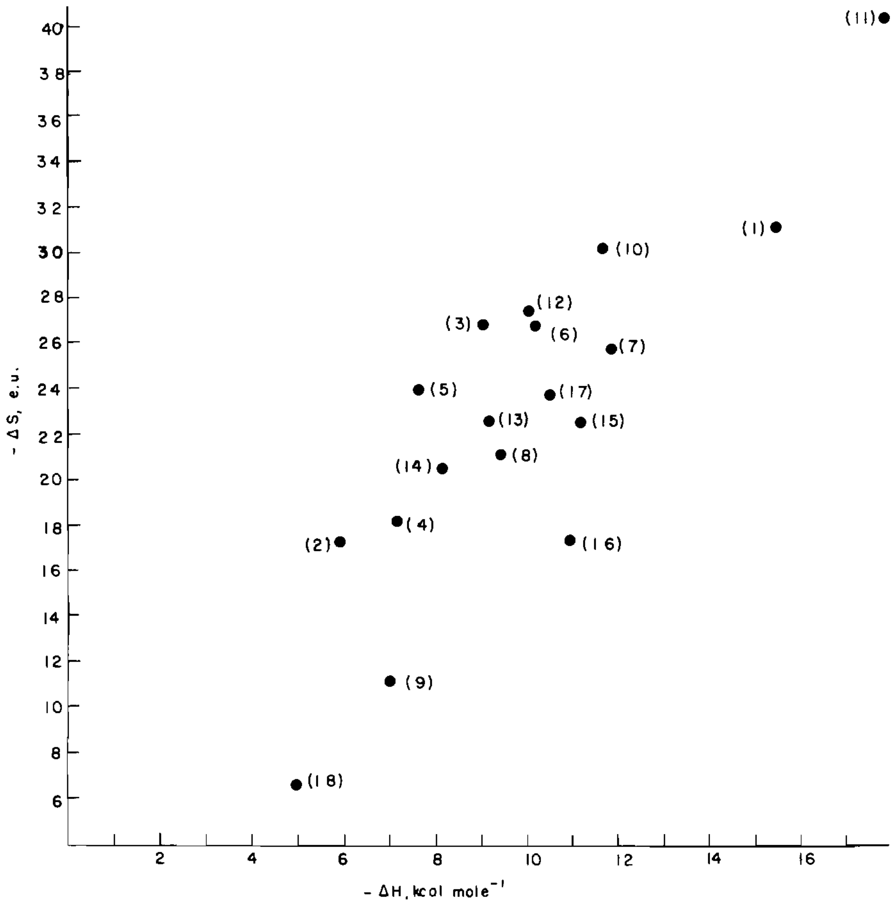

Fig. 1. Plot of $-\Delta H$ vs. $-\Delta S$ for all systems studied. Adducts are identified by numbers listed in Table I.

in preparation of some of the complexes was from J. T. Baker Company. It was dried over fused sodium hydroxide, then over sodium wire, and finally distilled from lithium aluminum hydride. All of the bases used as ligands were distilled prior to use. The equatorial ligands $baeH_2$, and $salenH_2$ were prepared by a modification of the method of Martell *et al.* [29].

$CH_3Co(bae)$, $C_6H_5Co(bae)$, and $CF_3Co(bae)$ were prepared as reported previously [10]. $CH_3Co(salen)$, $CH_3Co(F_3\text{-}bae)$ were prepared in the same manner as $CH_3Co(bae)$. $(CHCl_2)Co(salen)$ and $(CHCl_2)Co(F_3\text{-}bae)$ were prepared also following the procedure used for $CH_3Co(bae)$ but with chloroform as the alkylating agent. All compounds were characterized spectrally and by elemental analyses. $CF_3Co(F_3\text{-}bae)$ was prepared as follows. To 500 ml anhydrous methanol under argon were added 9.66 g (0.030 mol) $F_3\text{-}baeH_2$ and 7.14 g (0.030 mol) $CoCl_2 \cdot 6H_2O$. After the $CoCl_2J6H_2O$ had completely dissolved, 4.8 g of 50% aqueous NaOH solution dissolved in 30 ml methanol was added. The reduction was carried out by addition of 3.0 g sodium borohydride in 30 ml H_2O, followed immediately by 0.24 g $PdCl_2$. After 10 min stirring, 9.3 g (0.062 mol) trifluorobromomethane contained in a rubber balloon attached to the top of the reaction flask was added. The solution was stirred at room temperature for 1.5 hours at which time 30 ml acetone was added. This was followed immediately by filtration. To the filtrate was added 500 ml H_2O and the resulting solution was cooled at 0 °C for 24 hours. The resulting orange precipitate, $CF_3Co(F_3\text{-}bae)H_2O$, was collected by filtration. The orange powder was dried at 100 °C (1 Torr) over P_2O_5 until it was completely converted to the five coordinate $CF_3Co(F_3bae)$. *Anal.* Calc. for $C_{13}H_{12}F_9N_2O_2Co$: C, 34.06; H, 2.62; N, 6.11. Found: C, 34.15; H, 2.91; N, 6.05. This compound is extremely hygroscopic. Prior to all solution preparations it was again dried at 100 °C (1 Torr) over P_2O_5 and placed in an argon atmosphere. Subsequent solution preparations were carried out under argon.

Spectral Measurements and Calculations of Thermodynamic Results

All absorbance measurements were carried out on a Beckman Acta M-VII UV–visible spectrometer equipped with a temperature regulated cell compartment. The temperature was controlled with a HAAKE FJ constant temperature circulator to within ±0.1 °C. All absorbance measurements were obtained in the region of 650 nm where the free acids have an absorption maximum.

The equilibrium constants were obtained by a computer solution of the Rose-Drago equation [15, 30].* The method involves measurement of changes in absorbance of the system with addition of various amounts of ligand. The data is analyzed to simultaneously deduce the equilibrium constant and ($\epsilon_C - \epsilon_A$) where ϵ_C and ϵ_A are the molar absorptivities of the 1:1 complex and free Lewis acid, respectively. For each acid–base pair a series of simultaneous equations is solved and displayed graphically as plots of K^{-1} *vs.* ($\epsilon_C - \epsilon_A$) to allow visual assessment of the quality of the data, in addition to statistical parameters obtained from the calculation. The reader is referred to ref. 31 for a useful discussion of the technique. Enthalpies and entropies for complex formation were determined from the temperature dependence of the equilibrium constant using a least-squares routine. Because of the large amount of data collected in this type of work it is necessary to condense it to a manageable form which still allows the reader to assess its quality. Table II summarizes the data as follows: for each equilibrium constant determination (one acid–base pair at a given temperature) the equilibrium constant, the conditional standard deviation for K, and the ratio of the marginal standard deviation to the conditional standard deviation are given. This information will allow the reader to appreciate the nature of the K^{-1} *vs.* ($\epsilon_C - \epsilon_A$) without the necessity of reproducing all the plots [31].

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*The general minimization routine, SIMPLEX, has been copyrighted by J. P. Chandler, University of Indiana Physics Department, (1965).