Registry No. $[RhCl(COD)]_2$, 12092-47-6; $[RhBr(COD)]_2$, 12092-45-4; $[RhI(COD)]_2$, 12092-49-8; $[RhCl(COD)py]$, 41812-78-6; $[RhBr(COD)py]$, 33271-94-2; $[RhI(COD)py]$, 33136-41-3; $[RhCl(COD)(P(C_6H_5)_3)]$, 31781-57-4; $[RhBr(COD)(P(C_6H_5)_3)]$, 33136-93-5; $[RhI(COD)(P(C_6H_5)_3)]$, 33136-94-6; $[RhCl(P(OC_6H_5)_3)_2]_2$, 25966-16-9; $[RhBr(P(OC_6H_5)_3)_2]_2$, 26309-79-5; $[RhI(P(OC_6H_5)_3)_2]_2$, 41777-37-1; $[RhCl(P(OC_6H_5)_3)_3]$, 16592-65-7; $[RhBr(P(OC_6H_5)_3)_3]$, 25966-18-1; $[RhI(P(OC_6H_5)_3)_3]$, 41777-40-6; $[Rh_2Cl_2(COD)(P(OC_6H_5)_3)_2]$, 31781-80-3; $[Rh_2Br_2(COD)(P(OC_6H_5)_3)_2]$, 31781-81-4; $[Rh_2I_2(COD)(P(OC_6H_5)_3)_2]$, 41812-86-6; $[PdCl_2(COD)]$, 12107-56-1; $[PdCl_2(P(OC_6H_5)_3)_2]$, 29891-44-9; C_6H_5CN, 100-47-0; C_5H_5N, 110-86-1; $P(C_6H_5)_3$, 603-35-0; $P(OC_6H_5)_3$, 101-02-0; COD, 111-78-4; $[PdCl_2(C_6H_5CN)_2]$, 14220-64-5; $[PdCl_2(py)_2]$, 14872-20-9; $[PdCl_2(P(C_6H_5)_3)_2]$, 13965-03-2; $[PdCl_2(COD)_2]$, 12257-74-8.

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Nature of the Cobalt Center in Methylcobaloxime

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Received January 10, 1973

There is considerable uncertainty in the literature about the nature of the cobalt center in methylcobaloxime and similar compounds. In trying to understand which bases will preferentially bind to the cobalt, various criteria which are not directly related to the strength of bonding have been used by various investigators to label the cobalt as a class B or soft center, while others have concluded that it is class A or hard. It is impossible reliably to infer anything about the strength of intermolecular interactions from data in which entropy and solvation contributions have not been factored out, so the often-raised question about the nature of the cobalt center remains unresolved. By using recently reported procedures for obtaining solvation-minimized enthalpies in CH_2Cl_2 and for factoring out constant contributions to measured enthalpies from dimerization or intramolecular interactions, we have been able to measure thermodynamic data which bear directly on the question of bond strength. The entropy term is seen to be the main cause for the poor coordination ability of oxygen donors to this acid. Accordingly, the poor coordination tendencies of oxygen donors compared to sulfur donors are not due to a weaker bond strength or soft character of the cobalt. The data obtained can be fit to our E and C equation and they indicate that methylcobaloxime is a strong acid in which both the E and C properties are large and important in describing the interaction. The C/E ratio is comparable to that found for the borderline acid boron trifluoride and considerably smaller than that for the soft acid iodine. This system is the first in which extra stabilization of an adduct (in this case with phosphite ligands) over that expected from the E and C parameters is found. A π-back-bonding interaction is considered as a potential cause.

Introduction

Methylatobis(dimethylglyoximato)cobalt(III), or methylcobaloxime,[1a] has aroused interest because of its possibilities as a model for vitamin B_{12}. Schrauzer[1b,c] has extensively investigated the chemistry of the cobaloximes and claimed they can be used as models for vitamin B_{12}. A crystal structure on a substituted alkylcobaloxime shows the in-plane Co–N and the Co–C bond lengths to be identical with those in coenzyme vitamin B_{12}.[2] Regardless of the ability of these compounds to model vitamin B_{12}, the cobaloximes merit study for they are unusual chemical compounds in that they form relatively stable compounds with alkyl groups bonded directly to a first-row transition metal atom.

The nature of the cobalt center in methylcobaloxime and related compounds has been the object of considerable speculation.[3-5] It has been compared to both cobalt(II) and cobalt(III) complexes. The lability of the attached ligand L in $CH_3Co(DMG)_2L$ is very atypical of Co(III) complexes. Some authors claim metal–ligand π back-bonding is important,[5b] in this class of compounds, while others claim it is not.[3]

Several authors[4,5b] have claimed that methylcobaloxime is a class B or soft acid. This assignment of the acid character provided further stimulation for our research because, in our E and C correlation of acids and bases,[6,7] very few class B or soft or large C/E ratio acids have been studied. Furthermore, the conflicting conclusions drawn in earlier work about the nature of the cobalt center in this novel transition metal system require a more definitive set of experimental results which bear more directly on the bond strength.

In this research, enthalpies of interaction of methylcobaloxime with various bases have been calorimetrically determined. In order for these values to be true measures of bond strength, the data must be free of significant solvation contributions; otherwise, they provide no information regarding the nature and strength of the metal–ligand bond. Because of the insolubility of methylcobaloxime in poorly solvating solvents such as cyclohexane and carbon tetrachloride, these studies must be carried out in the relatively polar solvent dichloromethane. However, previous work in this laboratory has led to a procedure for eliminating solvent effects for certain systems studied in polar solvents.[8-10] Utilizing this procedure, it is possible to correct the enthalpies measured in a polar solvent for solvation contributions.

These solvation minimized enthalpies for methylcobal-

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(1) (a) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968), and references therein; (b) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, 90, 6541 (1968); (c) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *ibid.*, 92, 2997 (1970).

(2) P. G. Lenhert, *Chem. Commun.*, 980 (1967).

(3) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, 5, 156 (1969); Firth, *et al.*, *J. Chem. Soc. A*, 381 (1969), and references therein.

(4) D. N. Hague and J. Halpern, *Inorg. Chem.*, 6, 2059 (1967).

(5) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, 94, 384 (1972); (b) L. M. Ludwick and T. L. Brown, *ibid.*, 91, 5188 (1969).

(6) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971).

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

(8) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, 94, 90 (1972).

(9) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, 11, 280 (1972).

(10) M. S. Nozari, C. D. Jensen, and R. S. Drago, *J. Amer. Chem. Soc.*, 94, 3162 (1972).

oxime adducts allow us to compare this acid quantitatively with other acids we have studied by means of E and C parameters.[7] The enthalpies are related to the E and C parameters by

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

E_A and C_A are the empirically determined parameters for the acid, and E_B and C_B are for the base. Presently, there is only one transition metal compound, bis(hexafluoroacetylacetonato)copper(II), incorporated into the E and C correlation.[11] Methylcobaloxime extends the E and C correlation into an area where there is a lack of quantitative data and much speculation about bonding. Furthermore, the enthalpies of adduct formation obtained from our experiments provide the first really definitive information concerning the existence of an unusual stabilization in a metal-ligand interaction although such effects have been often claimed.

Experimental Section

Materials. The preparation of methylaquocobaloxime is described elsewhere.[12] The dehydration of methylaquocobaloxime was accomplished by heating the solid at a temperature of 100° at 5 mm pressure for a period of at least 24 hr. The slightly hygroscopic, light-sensitive methylcobaloxime was stored in a desiccator in the dark. Peninsular ChemResearch bis(hexafluoroacetylacetonato)-copper(II), Cu(hfac)$_2$, was purified as previously described.[9]

Baker Analyzed pyridine was fractionally distilled from barium oxide at atmospheric pressure. Aldrich tetrahydrothiophene (THTP) was purified as previously described.[13] Trimethylolpropanephosphine ester (TMPPE), from Arapahoe Chemicals, was sublimed once at 60°. Aldrich trimethyl phosphite (TMPP) was fractionally distilled at atmospheric pressure. Aldrich 1-methylimidazole (Columbia Chemicals) and dimethylcyanamide (DMCA) were fractionally distilled at 10 mm pressure. In all distillations, only the middle fraction was collected. Tetrahydrofuran was stored over CaH$_2$ for 24 hr, refluxed over CaH$_2$ for 2 hr, fractionally distilled, and used on the same day.

Baker Analyzed dichloromethane was kept over calcium sulfate, then fractionally distilled from calcium hydride in 1-l. quantities, and used within 3 days of purification. Fisher Certified 1,2-dichloroethane was dried over Linde 4A molecular sieves for at least 24 hr prior to use. Due to a suspected reaction with the sieves (the sieves discolored on standing), this solvent was stored no longer than 3 days over the sieves. Eastman *o*-dichlorobenzene was dried over Linde 4A molecular sieves for at least 24 hr prior to use. With the exception of dichloromethane, all solvents were used without further purification.

Calorimetry. Calorimetry was done as described elsewhere.[13,14] The reported procedure was somewhat modified by use of a calibrated gastight syringe for the introduction of reagents rather than glass bulbs. To be able to inject known volumes with the high precision required, a set of three finely machined brass plunger stops were made of varying lengths. The volumes, corresponding to the difference in plunger height between stops, were then accurately calibrated with distilled water. After six trials, the largest deviation was 0.22% in a 1.0-ml Hamilton gastight syringe. The syringe was calibrated to four significant figures. To prevent diffusion, special glass Luer tips with very small apertures were made for the syringe.

With the mechanical stirrer, it was not possible to place the syringe very deeply into the solution in the calorimeter cell. Consequently, the mechanical stirrer was replaced with a Teflon-coated magnetic stirring bar. The syringe barrel could then be immersed almost completely, ensuring faster and better thermal equilibration between the solution in the syringe and that in the cell.

When the syringe was used in a system where the equilibrium constant was infinite, each injection was treated as a separate determination of ΔH. If the system had a measurable K, each successive measured heat and the moles injected in a solution were added to the previous total measured heat and moles injected.

Because many of the acids and bases used in this research are hygroscopic, all solutions were transferred in a nitrogen-filled glove bag to the previously dried calorimeter cell.

Methylcobaloxime is known to dimerize both in solutions[15,16] and in the solid state.[17] Therefore, the equilibrium is represented by

$$A_2 + 2B \rightleftharpoons 2AB; K = [AB]^2/[A_2][B]^2 \quad (2)$$

However, all equilibrium constants reported in this study were so large that calorimetric method cannot distinguish them from infinity. Accordingly, the limiting reagent was used to calculate the enthalpy in units of kcal/mol of adduct.

Results

The concentrations, volumes, and the measured enthalpies for the Cu(hfac)$_2$-TMPP system in specified solvents are available. (See paragraph at end of paper regarding supplementary material.) Also available are the moles of methylcobaloxime, the moles of base injected into the methylcobaloxime solution, the measured enthalpy from the injection of base, and the enthalpies calculated assuming that all base injected reacts with the excess methylcobaloxime (*i.e.*, K is infinite). The experimentally measured enthalpy H' which is reported is the total heat evolved corrected for the heat of solution of the added reagent at the corresponding concentration. In most instances, stock solutions were made up and heats of dilution were measured directly and applied as a correction to give H'. In certain instances, the enthalpies of solution of the pure base were determined and are reported in the microfilm edition. The thermodynamic data for the interaction of Cu(hfac)$_2$ and methylcobaloxime with various bases in various solvents are reported in Table I. Table II contains corrections for the base interactions with the acidic solvent dichloromethane and the final solvation-minimized enthalpies of interaction of methylcobaloxime with the specified bases. The E and C values of the bases used in this study are also listed in this table along with the enthalpies calculated from the E and C equation.

There were several bases which showed little or no measurable interaction with methylcobaloxime by the calorimetric procedure. Several of these were oxygen donors: *N*,*N*-dimethylacetamide (DMA), trimethylphosphine oxide, 4-methylpyridine *N*-oxide, hexamethylphosphoramide (HMPA), and 7-oxabicyclo[2.2.1]heptane. The nitrogen donors triethylamine and quinuclidine (1-azabicyclo[2.2.2]octane), which would have been interesting to study, undergo some complex reaction with the solvents dichloromethane and 1,2-dichloroethane. The pyridine solutions in dichloromethane were made up just prior to use because a white solid formed in these solutions on standing for several hours.

Discussion

Solvation Corrections. In order to obtain meaningful thermodynamic data concerning the bond strength of Lewis bases coordinating to methylcobaloxime, it is necessary that there be minimal contributions to the measured enthalpies from solvation energies. Ideally, the system should be studied in the gas phase, but poorly solvating media, *e.g.*, CCl$_4$ and saturated hydrocarbons, have been used with success in approximating gas-phase enthalpies. The insolubility of methylcobaloxime in these nonpolar solvents has made quantitative studies on the acceptor strength of this acid and comparisons with other acids impossible in the past. Recent work in this laboratory has led to a procedure, ESP, for correcting data obtained in polar solvents[8-10] for the

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[11] W. Partenheimer and R. S. Drago, *Inorg. Chem.*, 9, 47 (1970).

[12] G. N. Schrauzer, *Inorg. Syn.*, 11, 61 (1968).

[13] T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, 89, 5770 (1967).

[14] M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, 92, 7086 (1970).

[15] L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, 91, 5188 (1969).

[16] A. W. Herlinger and T. L. Brown, *J. Amer. Chem. Soc.*, 94, 388 (1972).

[17] G. D. Stucky and J. Swanson, to be submitted for publication.

Table I. Thermodynamic Results for the Interaction of Methylcobaloxime and Cu(hfac)$_2$ with Several Bases in Various Solvents at 24 ± 1°

Acid	Base	Solvent	$-\Delta H^{a,b}$	$K^{c,d}$
Methylcobaloxime	Pyridine	Dichloromethane	12.0 ± 0.2	
Methylcobaloxime	Pyridine	1,2-Dichloroethane	11.7 ± 0.3	
Methylcobaloxime	Pyridine	Tetrahydrofuran	4.9 ± 0.1	
Methylcobaloxime	THTP	Dichloromethane	8.0 ± 0.1	
Methylcobaloxime	THTP	1,2-Dichloroethane	7.8 ± 0.2	
Methylcobaloxime	1-Methylimidazole	Dichloromethane	13.8 ± 0.2	
Methylcobaloxime	TMPPE	Dichloromethane	12.1 ± 0.2	
Methylcobaloxime	TMPP	Dichloromethane	11.6 ± 0.2	
Methylcobaloxime	TMPP	1,2-Dichloroethane	12.0 ± 0.3	
Methylcobaloxime	DMCA	Dichloromethane	4.3 ± 0.1	
Cu(hfac)$_2$	TMPP	Dichloromethane	6.0 ± 0.1	260 ± 10
Cu(hfac)$_2$	TMPP	*o*-Dichlorobenzene	5.5 ± 0.1	420 ± 30

[a] For methylcobaloxime, these are the actual measured enthalpies uncorrected for the enthalpy of dimerization and solvent interactions. [b] In units of kcal mol^{-1}. [c] In units of l. mol^{-1}. [d] For methylcobaloxime, all *K*'s were too large to evaluate with our procedure.

Table II. Measured Enthalpies, Solvation-Minimized Enthalpies, and *E* and C^a Calculated Enthalpies for Methylcobaloxime-Donor Systems (All enthalpy units in kcal mol^{-1})

Base	E	C	$-\Delta H_{\text{measd}}{}^b$	Base cor^c	$-\Delta H_{\text{cor}}{}^d$	$-\Delta H_{\text{calcd}}{}^e$
DMCA	1.10	1.81	4.3 ± 0.1	−1.7	12.7	12.8
Pyridine	1.17	6.40	12.0 ± 0.3	−2.1	20.8	20.5
1-Methylimidazole^c	0.895	9.29	13.8 ± 0.2	−1.6	22.1	22.4
THTP	0.341	7.90	8.0 ± 0.1	−0.6	15.3	15.2
TMPPE^f	0.515	6.60	12.1 ± 0.2	−0.9	19.7	14.8
TMPP	g	g	11.6 ± 0.2	−0.9	19.2	
THF	0.978	4.27			15.8	15.5

[a] *E* and *C* numbers taken from ref 6. [b] Measured enthalpy in units of kcal/mol of base (which was the limiting reagent). [c] J. A. Nusz and R. S. Drago, to be submitted for publication. This correction can be estimated by using an *E* parameter of 1.66 and a *C* parameter of 0.01 for the CH_2Cl_2 solvation. [d] Enthalpy has been corrected for half the enthalpy of dimerization of methylcobaloxime (−6.7 kcal mol^{-1}) and for the base interaction with methylene chloride, *i.e.*, the units are in kcal/mol of adduct formed. [e] Calculated using *E* and *C* numbers of 9.14 and 1.53, respectively, for methylcobaloxime. [f] This base was not included in the determination of *E* and *C* numbers of methylcobaloxime. [g] These *E* and *C* numbers have not been determined but are probably very similar to those of TMPPE (see footnote 19).

solvation contributions to the energy. Essentially, it was found that if one studied the displacement reaction

$$AB + B' \rightleftharpoons AB' + B \qquad (3)$$

in a basic solvent that did not interact specifically with free base, solvation contributions to the enthalpy of the displacement reaction were minimal in benzene and *o*-dichlorobenzene. This was shown to be consistent with the requirement that all enthalpies of reaction of various bases (B, B', etc., which do not interact with the solvent) with the same A in a given polar solvent would differ from those in poorly solvating media by a constant amount. This constant amount hereafter will be referred to as the solvent correction. In a basic solvent,[8] free A is eliminated in the displacement reaction (eq 3) to prevent specific interaction of the acid with the basic solvent. The same idea has been extended to the acidic solvent methylene chloride.[10] In an acidic solvent, B must be eliminated from the displacement reaction; *i.e.*, the following reaction should be studied

$$BA + A' \rightleftharpoons BA' + A \qquad (4)$$

The acids A and A' should not interact with the acidic solvent unless this interaction is the same in A and BA or in A' and BA'. The solvent correction for a given base is determined by studying several acids with this base in both CH_2Cl_2 and a nonpolar solvent. The various solvent corrections in dichloromethane for the bases used in this study have been determined elsewhere[18] and are listed in Table II. Because of various complications, it was not possible directly to measure the corrections for THTP, TMPP, and TMPPE by studying the same system in both CH_2Cl_2 and a nonpolar solvent. However, we have found that *E'* and *C'* values can be obtained for the solvation correction of bases by dichloromethane[18] (*i.e.*, the enthalpy solvent corrections for CH_2Cl_2 can be correlated and predicted using our *E* and *C* parameters for the bases and *E'* and *C'* values for CH_2Cl_2 in eq 1) making it possible to calculate what the solvation corrections are. The corrections calculated using eq 1 are also listed in Table II. For TMPP and TMPPE (which are almost identical in the basic properties of the phosphorus bonding site[19,20]), the solvent correction could be measured indirectly using Cu(hfac)$_2$ as the acid[18] and the result is in excellent agreement with the value predicted from the *E'* and *C'* numbers.

The Relative Coordinating Abilities of Oxygen and Sulfur Donors. The results of these studies bear out the observations of other workers regarding the strong preference by methylcobaloxime for coordination of sulfur instead of oxygen donors. However, before these observations can be attributed to hard-soft or class A-class B behavior, the strength of bonds formed with these two classes of donors must be ascertained. For example, the observed differences in behavior could be entropic in nature.

We attempted to measure the enthalpy of adduct formation toward several oxygen donors in CH_2Cl_2 by our calorimetric procedure without much success. This is surprising because the *E* and *C* equation (*vide infra*) predicts that the enthalpies should be as large for these donors as for the analogous sulfur donors and, barring an unusual entropy effect, a large *K* is expected. We were able to obtain crude data in 1,2-dichloroethane with *N,N*-dimethylacetamide as the donor which indicate the source of the difficulty. A low

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(18) J. A. Nusz and R. S. Drago, to be submitted for publication.

(19) They are structurally very similar; TMPPE simply has a carbon with an ethyl group tying together the three methyls of TMPP. The enthalpies of interaction of TMPP and TMPPE with chloroform were found to be identical (see ref 20). Also the enthalpies of both with methylcobaloxime are very nearly the same. These two enthalpies do not permit us to obtain reliable *E* and *C* parameters for TMPP.

(20) F. L. Slejko, D. G. Brown, and R. S. Drago, *J. Amer. Chem. Soc.*, **94**, 9210 (1972).

equilibrium constant was obtained and we were not able to convert a significant fraction of the free acid to complex in dilute solutions of the polar base. As a result, our thermodynamic values are only very approximate for this donor. An equilibrium constant of ~2 l. mol^{-1} and an enthalpy of ~5 kcal mol^{-1} lead to a corrected (see Table II) enthalpy value of ~14 kcal mol^{-1}. To be sure that what we were measuring was the complexation of DMA, we carried out a series of infrared studies which confirmed a low K for this system. The low K from the ir studies coupled with the observed heat evolution (H') from the calorimetric study of this system, supports a $\Delta H°$ consistent with the E and C prediction. The calorimetric data were obtained in 1,2-dichloroethane, a solvent we previously have found to cause solvent complications of ~1 kcal mol^{-1}. However, the solvent change is not the source of the low equilibrium constant, for when cobaloxime adducts of tetrahydrothiophene and TMPPE were studied in 1,2-dichloroethane, the equilibrium constants were infinite and the uncorrected enthalpies comparable to the uncorrected enthalpies in CH_2Cl_2.

Nmr studies in methylene chloride on the cobaloxime-dioxane system with a tenfold excess of base indicated an approximate equilibrium constant of 2 at −30°. This result was obtained by integration of the free and complexed O-H-O resonances. If the enthalpy is as large as the DMA experiments suggest and the E and C equation predicts (*vide infra*), some unusual entropy effect exists with these oxygen donors and most probably with many other oxygen donors leading to a small equilibrium constant even though the strength of interaction is appreciable.

In light of the implications of the above discussion, it is desirable to be more certain that the enthalpy toward these oxygen donors is large even though the equilibrium constant is small. This is also desirable from the standpoint of verifying the applicability of the E and C equation to methylcobaloxime. If cobaloxime is dissolved in pure THF, it is almost completely complexed to the THF ($K \approx 2$). However, the equilibrium constant toward pyridine is so large as to displace completely THF at low pyridine concentrations in THF (*vide infra*). The enthalpy measured in THF solvent is that for the displacement reaction

$$CH_3Co(DMG)_2{\cdot}THF + C_5H_5N \rightarrow CH_3Co(DMG)_2C_5H_5N + THF \quad (5)$$

Tetrahydrofuran was selected as both the solvent and oxygen base because it has a low dielectric constant ($\epsilon \approx 7$) and nonspecific solvation contributions to the measured thermodynamic data for the displacement reaction are expected to be minor. Adding a 15-fold excess of pyridine to ~2×10^{-4} M methylcobaloxime monomer in pure THF completely converted all of the cobalt to the pyridine complex as evidenced by the fact that the second addition of pyridine to this solution gave no detectable heat evolution after correction for the heat of solution of pyridine in THF. Based on methylcobaloxime as the limiting reagent, an enthalpy of 4.9 kcal mol^{-1} of 1:1 adduct was obtained. Since the solvation-minimized enthalpy for formation of the pyridine adduct is −20.8 kcal mol^{-1} (Table II), the enthalpy of formation of the THF adduct is calculated to be 15.8 kcal mol^{-1} in excellent agreement (considering that there may be minor solvation effects from THF) with the value of 15.5 kcal mol^{-1} predicted with the E and C equation. There can be no doubt that the low equilibrium constant for THF and very probably for the other oxygen donors studied is due to an entropy effect.

Before speculating on a potential cause of this unusual entropy effect, we should comment upon another result from the nmr experiment which, by using the kind of criteria often employed in the HSAB work,[21] led to the inference that methylcobaloxime is soft.[5] When $S(CH_2CH_2)_2O$ was used as a donor toward methylcobaloxime, the nmr spectra indicated that exclusively sulfur-bonded complex was obtained in preference to oxygen. The nmr spectra at −30°, in the region of the oxime methyl groups, is a singlet in both pure THF and a 50:50 dioxane-CH_2Cl_2 mixture, indicating nearly complete complexation of the methylcobaloxime by these bases. Addition of tetrahydrothiophene to pure THF solution showed a strong preference of the acid for the sulfur donor consistent with previous reports.[5] At about 0.05 M methylcobaloxime dimer and 0.09 M tetrahydrothiophene in pure THF solvent (12 M), about 60% of the cobalt was shown to be coordinated to the sulfur donor by integration of the O-H-O proton resonances. However, contrary to the conclusion drawn, as encouraged by reading the HSAB literature, these findings are not evidence that the strength of interaction is dominated by soft-acid behavior. Admittedly, the HSAB concept is loosely defined,[21] but the interpretation of hardness and softness is pseudo quantum mechanical (*i.e.*, ionic-covalent bonding, electron correlation, π bonding) and consequently is mainly based on the strength of interaction between the acid and the base. The oxygen donor, THF, interacts more strongly than the analogous sulfur donor, but the amount of complexation is much lower. Clearly, the complication arises because the nmr experiment is dependent upon free energy considerations and counts the number of adducts formed and not the strength with which the acid and base are bound. Often the free energy and enthalpy change in a parallel fashion,[22] but, if, as in this case, they do not, the free energy and enthalpy give conflicting orders of HSAB character. When the enthalpy is not known as in many of the HSAB examples, one may realistically question whether or not the free energy parallels the enthalpy. The free energy is important for many applications, but contrary to what one is encouraged to do with HSAB, one must remember the limitations on the information that free energies alone provide about the nature and strength of interaction.

In contrast to an excellent understanding of the factors influencing enthalpies, relatively little is known about the factors (including solvent effects) influencing entropies. In the present case, it is tempting *to speculate* on the nature of the unusual entropy effect associated with the oxygen donors. One could view the reaction of donors with methylcobaloxime as a competition between the base coordinating to the metal in a displacement reaction and the base weakly hydrogen bonding (*i.e.*, a low enthalpy) to the O-H-O proton. The observed equilibrium constant would describe the competitive equilibria. If the K for hydrogen bonding to oxygen donors is large while that for sulfur donors and acetonitrile is small (as is observed toward phenol[23]), larger net equilibrium constants for the cobalt center would be observed for sulfur donors than for oxygen donors. The hydrogen bonding, if it exists, must be a very small enthalpy effect because the O-H-O proton resonance of the dimer in CH_2Cl_2 solution containing excess dioxane is not shifted from that found in pure CH_2Cl_2. This would imply a long distance and a weak interaction, so the term hydrogen bonding is being used loosely here for an essentially dipole-dipole association. This effect cannot be the whole story

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[21] See, for example, R. G. Pearson, *J. Amer. Chem. Soc.*, **89**, 1827 (1967), and the references therein.

[22] W. B. Pearson, *J. Amer. Chem. Soc.*, **84**, 536 (1962).

[23] G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970).

for at most one would expect K to be lowered by 10^2 from this effect if indeed it exists at all.

One other potential explanation of this large negative entropy for the oxygen donors is steric in nature. If the oxygen donor in THF remains approximately sp^3 hybridized and that in DMA approximately sp^2 hybridized in the adduct, other atoms in these molecules (*e.g.*, the O-CH_2 group of THF and the acetyl methyl of DMA) may encounter steric repulsion from atoms of the oxime ligand for all but a very specific orientation of the oxygen-donor molecule in the adduct. Courtland atomic models indicate that if the cobalt is in the plane of the oxime nitrogens, little steric effect is encountered for most orientations of THF. If, in the THF adduct, the cobalt is on the methyl group side of this plane, then the only orientation which may be allowed when oxygen is bound is the one in which the oxygen and two carbons of the THF molecule and the two oxime hydrogens in the adduct form a plane perpendicular to that of the four oxime nitrogens. If there is no steric effect only in this orientation, a lower enthalpy for the formation of the oxygen-donor adduct would not be expected, but a large negative entropy of formation would be expected. A similar effect would be operative in the DMA adduct for coordination on the acyl methyl side of the carbonyl. No such entropy effect would be present in the acetonitrile adduct for the nitrile nitrogen donor site has a small steric requirement. The absence of this entropy effect in the pyridine adduct could be a consequence of the 120° angles in the Co-N-C framework. An additional effect which could minimize the steric repulsions in the pyridine adduct involves the position of the cobalt relative to the oxime nitrogen plane. The cobalt atom in the methylcobaloxime dimer is[24] 0.1 Å above the mean plane consisting of the dimethylglyoxime nitrogens. If covalency in the interaction causes the cobalt to move toward the donor, it may be possible for those nitrogen and sulfur donors with large C numbers to bind without steric repulsion from the oxime ligand atoms. However, oxygen donors with smaller C numbers could have serious steric problems for certain orientations if the cobalt atom is located in or on the opposite side of the plane away from the incoming ligand.

***E* and *C* Parameters for Methylcobaloxime.** As mentioned earlier, the possibility of adding another transition metal ion type Lewis acid to the systems incorporated by the E and C equation provided some of the motivation for carrying out these thermodynamic measurements. Since methylcobaloxime exists as a dimer in solution, the calorimetrically measured enthalpies of interaction of methylcobaloxime with various bases must be corrected for the enthalpy of dimerization in order to cast the measured enthalpies into a form amenable to the E and C equation (*i.e.*, $A + B \rightarrow AB$).

We have recently reported a procedure[25] which enables one to solve a series of equations of the form

$$-\Delta H - W = E_A E_B + C_A C_B \qquad (6)$$

for the best set of acid (or base) parameters and W as long as the E_B and C_B parameters for a series of different bases (*i.e.*, different E/C ratio) are well known. In this instance, W is the constant contribution to the enthalpy from dissociation of the dimeric methylcobaloxime. The four solvent-corrected enthalpies of adduct formation of cobaloxime with *N,N*-dimethylcyanamide, pyridine, 1-methylimidazole, and tetrahydrothiophene are employed. We obtain values of $E = 9.14$, $C = 1.53$, and $W = -6.7$ with marginal standard deviations of 0.8, 0.09, and 1.1, respectively. The W value of 6.7 kcal mol^{-1} is in excellent agreement with the reported[16] nmr value for the enthalpy of activation of the exchange processes occurring in the methylcobaloxime dimer. This confirmation is valuable because the E, C, and W values are very highly correlated.

Since bases with a wide range of C_B/E_B were used, the deviation of 1.1 in W will not affect the internal consistency of base-methylcobaloxime monomer predictions with the E and C equations. However, this constant source of uncertainty must be taken into account when methylcobaloxime monomer is compared to other acids.

If we employ the W value of 6.7, we can use the E and C numbers listed for the first four bases in Table II to substitute into eq 1 to give a series of simultaneous equations which, when solved, give the calculated values of $E = 9.14 \pm 0.27$ and $C = 1.53 \pm 0.02$ for the monomeric methylcobaloxime. A plot of the simultaneous equations which were solved to produce the E and C fit is shown in Figure 1. The minimum was obtained using the SIMPLEX minimization subroutine.[26] As can be seen in Figure 1, the slopes of the various lines for the bases employed are significantly different indicating that bases with a wide range of C/E ratios were used. Consequently, reasonable confidence may be placed in the E and C values found for the acid. Using these E and C values for methylcobaloxime, one calculates an enthalpy of 16 kcal mol^{-1} for the DMA adduct compared to a measured value of ~14 kcal mol^{-1}. With THF, the calculated value is 15.5 kcal mol^{-1} compared to a measured value of 15.8 kcal mol^{-1}. Indeed, it was this large predicted enthalpy for THF from the E and C equation which prompted us to design the displacement experiment in pure THF to test the predictive power of eq 1 and to obtain evidence for the existence of unusual entropy effects.

The phosphite donors were not included in our final calculation of the E and C numbers for methylcobaloxime. These systems now constitute the first exception to our correlation in which the calculated enthalpy is substantially lower (by 4.8 kcal mol^{-1}) than that measured. We can conclude that either the E and C equation is fundamentally of the wrong functional form and has broken down for this particular combination of donor and acceptor properties or, for this particular donor and acceptor, there is enhanced stabilization from some additional bonding effect. One result would hardly enable one to draw the former conclusion. In the latter regard, it is tempting to invoke enhanced stabilization from a metal to ligand π-back-bonding interaction. Assuming our E and C parameters for the cobaloxime and phosphite have been defined on systems where this effect is not operative, they would predict an enthalpy of interaction devoid of this contribution. Consequently, a third term, $\pi_A\pi_B$, would have to be added *to attempt to* accommodate this additional effect when it is present. Should π back-bonding be the cause of the discrepancy in our calculated and experimental results, it is somewhat surprising that it is not manifested in the DMCA adduct. However, π back-bonding is invoked in such a whimsical way in the literature (*i.e.*, few fixed rules exist and π back-bonding is usually an after the fact rationalization) it is difficult to know when it should or should not exist. The infrared spectrum of the DMCA adduct showed

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[24] G. D. Stucky and R. Swanson, work in preparation.

[25] M. A. Guidry and R. S. Drago, *J. Amer. Chem. Soc.*, 95, 759 (1973).

[26] The general minimization routine, SIMPLEX, has been copyrighted by J. P. Chandler of the University of Indiana Physics Department, 1965.

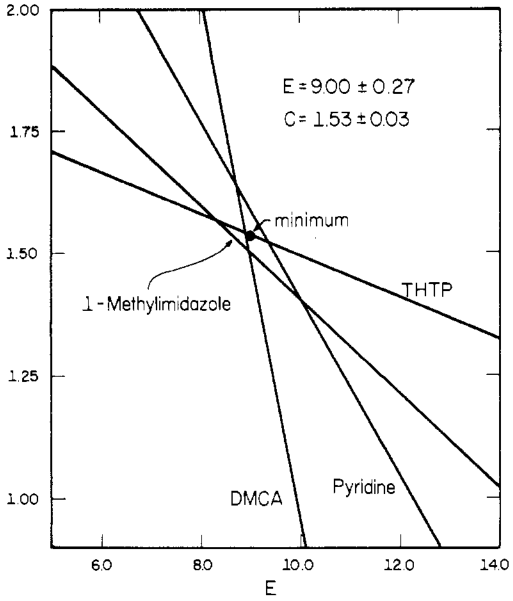

Figure 1. Plot of the two variables in eq 1 for methylcobaloxime.

an increase in $\Delta\nu_{C\equiv N}$ of 50 cm^{-1}, consistent with a mainly σ-bonding interaction.[27]

The C/E ratio of 0.17 for methylcobaloxime is clearly inconsistent with the labeling of this acid as class B[3] or soft.[4,5] The ratio is close to that of phenol (0.10) (class A), comparable to that of boron trifluoride (0.16), and very different from that of iodine (1.0) or SO_2 (0.88) (class B or soft). The difficulty with inferring the nature of the acid center from the earlier literature studies is twofold. First, if one is studying a reaction in some solvent which interacts specifically with the acid, the enthalpies including this specific interaction will be given by

$$-\Delta H = E_A(E_B - E_S) + C_A(C_B - C_S) \qquad (7)$$

where E_S and C_S are the E and C values for the specific interaction by the solvent. For example, if the E number of the solvent is large and similar to those of the bases and the C number of the solvent small, the observed trends in reactivity will be dominated by the C term of the bases even if the C_A/E_A ratio of the acid is small (*i.e.*, the acid will really be class A, but will appear soft). This situation can pertain to equilibria in water where additional complications are encountered due to the fact that the hydrogen bonding of the bases to water will be greater for oxygen and nitrogen donors than for donors with comparable or slightly larger C values, but small E numbers. For example, let us assume that the E and C numbers of water in the hydrogen bonding interaction are similar to those of phenol (*i.e.*, 0.4 and 4.0). With such a guess, pyridine enthalpies are predicted to be 6.8 kcal mol^{-1} less exothermic from the specific hydrogen-bonding interaction with the solvent, but diethyl sulfide will only be less exothermic by 4.2 kcal mol^{-1}. Thus, even toward a class A acid, the sulfur donor could interact more strongly. Water is a complex solvent and many more complications than those described above make the reported interpretation of data[3,4] obtained in this solvent impossible. Clearly, by expressing these competition reactions with equations similar to those described above, one can see that, depending on the E and C property of the solvent, the E property of an acid or base could be leveled by the solvent. The second criticism that can be leveled against earlier literature inferences of the nature of the cobalt involves the use of kinetic rate data. Rates or relative rates of substitution reactions have contributions from both the enthalpy and entropy of activation. Consequently, even for first-order dissociation processes, rate constants are as unreliable as equilibrium constants in providing information about the strength of bonding.

We might comment briefly on the potential use of enthalpies of activation from nmr to make inferences about metal-ligand interaction. Uncertainties in the reported values of the activation energies for ligand-exchange reactions from nmr methods have large error limits assigned[5,15,16] to the data. For example, with trimethyl phosphite, a value of −22.4 ± 2.7 kcal mol^{-1} was reported.[5] This is to be compared to the value of −19.1 ± 0.2 kcal mol^{-1} found in this study (neglecting error in the constant value used for the dissociation energy). The ~3-kcal mol^{-1} uncertainty in the nmr result is large enough to mask most of the differences in the donor strength of the bases in Table II toward this acid. With uncertainties of this magnitude, one can make few inferences about the nature of the cobalt center. For example, it can be shown mathematically that it would have been difficult to ascertain anything inconsistent about the phosphite donors with a 3-kcal mol^{-1} error in the enthalpies. If all the data in Table II are used to obtain E and C parameters for the cobalt complex, values of 8.3 and 1.8, respectively, result. These E and C parameters would fit all the enthalpies, including TMPPE, to within the 3-kcal mol^{-1} error. Clearly, one cannot ascertain anything unusual about the phosphite ligand at this level of error. It is interesting to point out, though, that even with the phosphorus donor included and an error of ~3 kcal mol^{-1} accepted, the C/E ratio is clearly not that expected for blass B or soft behavior. In view of this discussion, the need for considerable improvement in the precision of the nmr experiment is evident as is the need for a quantitative assessment of the different factors contributing to bond strength.

We conclude that the nature of the cobalt center is best described on the basis of the E and C numbers, *as a rather strong acid in which both the E and C parameters are relatively large.* (E and C are 9.14 and 1.53, respectively, compared to 4.33 and 0.442 for phenol and 1.00 and 1.00 for iodine.) The large C number accounts for the strong interaction with sulfur donors while the large E *predicts* strong interaction with oxygen donors. Our E and C parameters predict that the enthalpy of interaction toward tetrahydrofuran will be slightly larger than that toward tetrahydrothiophene. Using this criterion, one could assign this complex to a borderline category in the HSAB description or as being between class A and class B behavior. *We prefer a more complete description which states it has moderately large values for both the C and E property.* This is more complete because it gives an indication of the magnitudes as well as the nature of the interaction, whereas the HSAB description only indicates the latter as previously discussed.[28]

Acknowledgment. The authors acknowledge the generous support of this research by the National Science Foundation through Grant 31431X. Mr. Charles Schramm measured the pyridine-methylcobaloxime enthalpy in THF solvent.

Registry No. Methylcobaloxime, 36609-02-6; pyridine, 110-86-1; 1-methylimidazole, 616-47-7; THTP, 110-01-0; TMPPE, 824-11-3;

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TMPP, 121-45-9; DMCA, 1467-79-4; THF, 109-99-9; $Cu(hfac)_2$, 14781-45-4.

Supplementary Material Available. The concentrations, volumes, and measured enthalpies for the $Cu(hfac)_2$-TMPP system in specified solvents will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2809.

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Comparative Study of Base Interactions with Three Methylatocobalt(III) Chelate Complexes[1]

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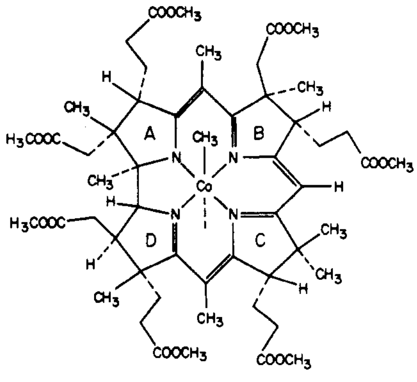
Received March 30, 1973

Proton magnetic resonance studies of ligand exchanges have been carried out for adducts of methylatobis(dimethylglyoximato)cobalt(III), $CH_3Co(dh)_2$, methylato-*N,N'*-ethylenebis(acetylacetoniminato)cobalt(III), $CH_3Co(bae)$, and methylato-[cobyrinic acid heptamethyl ester], I. Trimethyl phosphite, 1-(2-trifluoromethylphenyl)imidazole ($ImCF_3$), and 3-fluoropyridine were employed as bases. The rates of dissociation of $ImCF_3$ from the cobalt compounds are in the order $CH_3Co(bae) > I > CH_3Co(dh)_2$. The results reported here are the first quantitative data for base dissociation from $CH_3Co(bae)$ or from any alkylcobalt(III) corrinoid system.

The chemistry of cobalt(III) complexes containing an alkyl-cobalt bond and (in some instances) a base coordinated in the trans position is of interest because of the analogy with alkylcobinamides and cobalamins.[2-4] Complexes involving coordination by a planar, tetradentate ligand, such as bae = *N,N'*-ethylenebis(acetylacetoniminato),[5,6] salen = *N,N'*-ethylenebis(salicylideniminato),[7-9] saloph = *N,N'*-*o*-phenylenebis(salicylideniminato),[10,11] α-Me-salen = *N,N'*-ethylenebis-(α-methylsalicylideniminato),[10,11] $(dh)_2$ = bis(dimethylglyoximato),[12,13] and 1-(diacetyl monoxime iminato)-3-(diacetyl monoximato iminato)propane,[14,15] (DO)(DOH)pn, have been studied.

The axially coordinated base has been shown to affect certain physical properties of the ligands in the cis position,[16] but the most interesting chemical effects result from its influence on the trans cobalt-ligand bond. Conversely, both the planar ligand system and trans ligand affect the tendency of the cobalt to bind a base in the sixth coordination position. Thus, for example, displacement of water from aquocobalamin[17] is several orders of magnitude more facile than the analogous reaction in aquocobaloxime complexes.[18]

We have been interested in the kinetics parameters for exchanges of ligands trans to the methyl groups in alkylcobalt chelate complexes.[19,20] The presence of an alkyl group clearly labilizes the sixth coordination position in both a kinetic and thermodynamic sense, but few data are available to assess the effect of the planar ligand on the kinetics of base exchange or the thermodynamics of the base-cobalt interaction. In this contribution we present comparative data for methylatobis(dimethylglyoximato)cobalt(III) adducts, $CH_3Co(dh)_2L$, adducts of methylato-*N,N'*-ethylenebis(acetylacetoniminato)cobalt(III), $CH_3Co(bae)L$ (Figure 1), and limited but highly significant data for methylato[cobyrinic acid heptamethyl ester], I.



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Results

Although data on the kinetics of axial base exchange are

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[1] This research was supported by The National Science Foundation through Contract NSF-GH-33634 and Research Grant GP 30256X.

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