ENTHALPIMETRIC TITRATION OF COPPER CHELATES WITH SOME ADDUCT-FORMING LIGANDS

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ABSTRACT

Thermodynamic functions and stability constants for 1:1 adduct formation of bis-(thenoyltrifluoroacetonato) copper(II) and bis-(benzoyltrifluoroacetonato) copper(II) with pyridine, 1,10-phenanthroline, 2,2′-bipyridyl, 4-methylpyridine N-oxide, tributylphosphate, trioctylphosphineoxide and dibenzylsulphoxide have been obtained in benzene at 35°C by direct titration calorimetry. The enthalpy changes (ΔH) are exothermic while the entropy changes (ΔS) are unfavourable for all the reactions studied. The values of ΔH and K have been correlated with the nature of the ligands (i.e., basicity, structure, etc.) wherever possible.

INTRODUCTION

The extractability of a metal chelate has often been found to be enhanced when a neutral base is added to the solvent extraction system. The so-called synergistic effect is usually interpreted through the formation of an adduct with the base which has a higher solubility in the organic phase as compared to the parent metal chelate [1]. Most of the thermodynamic studies in synergistic adduct formation have been carried out by means of solvent extraction [2]. This method of obtaining thermodynamic data from the temperature dependence of the equilibrium constants of the adduct forma-tion reaction involves complexities inherent to the heterogeneous equi-librium, e.g., the replacement of water molecules from the metal chelate by the base molecules. A direct determination of the thermodynamic functions of the adduct formation reaction in a nonsolvating solvent using calorimetry will be free from such complications and will therefore yield more reliable results. Some investigations of the adduct formation equilibria using calori-metric [3–7], spectrophotometric [4,8–10], ESR and NMR [11] techniques have been reported.

Calorimetric determination of enthalpy changes of the adduct formation reaction would give direct evidence of adduct formation and would provide a better understanding of the nature of the interaction of the metal chelate with the donor. This type of study would also provide quantitative informa-

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tion on factors affecting the stability of the adduct formed in non-aqueous solvents.

In the present work thermodynamic data for the adduct formation of bis-(thenoyltrifluoroacetonato)copper(II) with pyridine (PY), 1,10-phenanthroline (Phen), 2,2'-bipyridyl (BiPY), 4-methylpyridine N-oxide (4MPO), tributylphosphate (TBP), trioctylphosphineoxide (TOPO), dibenzylsulphoxide (DBSO) and bis-(benzoyltrifluoroacetonato) copper(II) with BiPY, 4MPO, TBP, TOPO and DBSO in benzene have been obtained at 35°C by direct titration calorimetry.

EXPERIMENTAL

The compounds thenoyltrifluoroacetone (HTTA), benzoyltrifluoroacetone (HBTA), Phen and BiPY obtained from Fluka, DBSO from Aldrich, and TOPO from Eastman Organic Chemicals were used without further purification.

Pyridine (BDH) was distilled from potassium permanganate and dried over anhydrous potassium carbonate. TBP (BDH) was purified by the method described in the literature [12]. Analar grade benzene (BDH) was distilled and dried by standard methods. 4-Methylpyridine N-oxide was recrystallized from benzene prior to use.

Preparation of β-diketonates of copper(II)

The β-diketonates of copper(II) were prepared by mixing an aqueous solution of analar grade copper(II) acetate with an ethanolic solution of the β-diketone in a 1 : 2 molar ratio. The mixture was heated on a water bath for 5 min. The green precipitate that separated out was filtered under suction and dried in vacuum over P_2O_5. The dried chelate was recrystallized from benzene. The purity of the metal chelates was ascertained by chemical analysis.

Apparatus and operational procedure

The instrument used for measuring enthalpy changes was a Tronac (Model 450) titration calorimeter (Tronac, Inc., U.S.A.). The instrument and the general procedure for operation are described in detail in the manufacturer's manual.

Typical ΔH measurement precision is $\pm 0.5\%$ on 2 cal using a standard instrument with a 50-ml reaction vessel. Temperature resolution is ± 100 $\mu°C$ with a 1-mV recorder (input impedance at least 100 kΩ). The response time limited by the thermistor is 3 s.

The instrument performance was verified by carrying out the titration of THAM (tris(hydroxymethyl)aminomethane) with HCl. The ΔH^0 value of

-11.28 ± 0.05 kcal mol^{-1} agreed well with the accepted literature value [13] of -11.33 kcal mol^{-1}.

In a typical run 20 ml of benzene solution (0.005 M) of the copper(II)–β-diketonate was introduced into the reaction vessel which was then placed in a constant-temperature bath (35°C). The buret was filled with a 0.05–0.1 M solution of the auxiliary ligand (e.g., pyridine in benzene) and placed in the bath. Electrical calibration was then carried out which was a combined electrical calibration and initial heat capacity run. After the attainment of thermal equilibrium a constant heat of stirring was achieved and the auxiliary ligand solution was continuously delivered from the buret for about 2 min. The heat change during the addition and the trail slope were recorded. The combined heat capacity and electrical calibration run was then carried out. The calibration allowed each heat of reaction to be directly compared with a known amount of electrical energy. Control experiments for correction due to heat of dilution were run separately.

Computation of thermodynamic functions

The thermodynamic functions K, ΔH, ΔG and ΔS are not independent quantities but are related by the equation

$$-RT \ln K = \Delta G = \Delta H - T\Delta S$$

It can be seen that a determination of K and ΔH is sufficient to compute the rest.

For the simple reaction of a reactant A with a reactant B forming a product AB (i.e., $A + B \rightleftharpoons AB$) the thermogram obtained can be described by the following equations. At any point b on the thermogram

$$Q_b = \Delta H [AB]_b V_b$$

where V is the volume of solution in the calorimeter

$$K = [AB]_b / [A]_b [B]_b$$

$$[A_{total}]_b = [A]_b + [AB]_b$$

$$[B_{total}]_b = [B]_b + [AB]_b.$$

Since the concentrations of both A and B were very low, a value of 1 has been assumed for the activity coefficients.

The above equation can be combined to produce a single equation

$$\frac{Q_b^2}{\Delta H V_b} - \left(\frac{1}{K} [A_{total}]_b + [B_{total}]_b \right) Q_b + [A_{total}]_b [B_{total}]_b \Delta H V_b = 0 \qquad (1)$$

This equation has two variables (ΔH and K) and, hence, cannot be solved directly. Of course, it can be solved [14] by considering any two points on the thermogram and obtaining two simultaneous equations. The solution may be obtained analytically [14] or graphically [15], both of which will yield

the same results. Izatt et al. [16] have compared different methods for the computation of K and ΔH and suggest a technique based on a least-squares analysis. An error function, $U(K_i, \Delta H_i)$, given by

$$U(K_i, \Delta H_i) = \sum_{i=1}^{N} \omega_i \left(Q_{\mathrm{cal}_i} - Q_{\mathrm{exp}_i}\right)^2$$

is minimised over a large domain of K and ΔH. The values of K and ΔH yielding a minimum error are taken as the actual values.

In the present work, the above technique was used. Three points were taken ($N = 3$) on the thermogram and the above error function was evaluated on these points for all combinations of ΔH and K. Q_{cal} was computed by solving eqn. (1) which can be written as $Dx^2 + Ex + F = 0$. Solution of this equation gives two values for Q_{cal}, but it was seen that one of them, say, Q_{c1}, was always unrealistic in the sense that with the value of ΔH used for the computation, Q_{c1} was greater than the amount of heat which would have been produced with $K = \infty$. Hence, unique solutions were always obtained for eqn. (1). All these computations and minimisations were done with a microcomputer using a program developed in BASIC *.

RESULTS AND DISCUSSION

The thermodynamic functions and the equilibrium constants for the formation of 1:1 adducts of $Cu(TTA)_2$ or $Cu(BTA)_2$ with the various auxiliary ligands are listed in Table 1. It can be seen from the results that the adduct formation reactions studied here are exothermic and the entropy changes are unfavourable for them.

A definite enthalpy change associated with all the reactions studied here offers direct evidence for adduct formation. The auxiliary ligands studied here can be considered separately on the basis of their donor groups.

Thus, PY, Phen and BiPY, all of which donate through heterocyclic nitrogen, can be considered together for comparison. The ΔH and K values obtained with PY are much smaller than those obtained with Phen and BiPY. These results suggest that Phen and BiPY coordinate through both the nitrogens giving rise to hexacoordinate complexes. The higher stability of the Phen over the BiPY adduct seems to be the result of two factors. One is its slightly higher basicity [6] and the other is the rigid architecture of its molecule, which should give its adduct a higher stability than that of BiPY in which free rotation is possible about the bond between two phenyl groups. This is shown by a more negative entropy change in the formation of the BiPY adduct as a result of a loss of rotational freedom. The steric factor

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* The listing of the program is available on request.

TABLE 1

Thermodynamic data for adduct formation in benzene at 35°C

Acid	Base	$-\Delta H$ [a] (kcal mol^{-1})	$-\Delta S$ (cal K^{-1} mol^{-1})	$-\Delta G$ (kcal mol^{-1})	Log K (1 mol^{-1})
Cu(TTA)$_2$	PY	10.62	22.04	3.83	2.72
Cu(TTA)$_2$	Phen	14.2	24.14	6.76	4.8
Cu(TTA)$_2$	BiPY	14.36	28.14	5.69	4.04
Cu(BTA)$_2$	BiPY	12.20	23.32	5.02	3.56
Cu(TTA)$_2$	4MPO	8.49	17.49	3.10	2.2
Cu(BTA)$_2$	4MPO	8.34	16.66	3.21	2.28
Cu(BTA)$_2$	TBP	10.17	28.45	1.41	1.00
Cu(BTA)$_2$	TOPO	15.14	40.00	2.82	2.00
Cu(TTA)$_2$	TOPO	14.49	37.90	2.82	2.00
Cu(TTA)$_2$	DBSO	14.61	42.86	1.41	1.00
Cu(BTA)$_2$	DBSO	10.22	28.61	1.41	1.00

[a] Corrected for heat of dilution.

must play a more dominant role here as the ΔH values are very similar.

The compounds TOPO and TBP, both of which donate through phosphoryl oxygen, can be considered together. The ΔH and K values obtained with the TBP adduct are lower than those of the TOPO adduct. This is to be expected, since with an organophosphorous compound as the neutral ligand, the order of synergistic enhancement is that of increasing base strength, i.e., phosphate < phosphonate < phosphinate < phosphine oxide [17]. This is also the order of decreasing ester linkage, increasing carbon-to-phosphorus linkage and increasing extractive efficiency [17].

Sulphoxides have many similarities with phosphine oxides [18], therefore, the results obtained with DBSO can be compared with those obtained for TOPO and TBP. It can be seen from the results that the adducts formed by DBSO are weaker than those formed with TOPO, but are very similar to the TBP adduct, both with respect to bond strength and stability. A similar trend was observed by Subramanian and Viswanatha [18] for the synergistic extraction of UO$_2$(TTA)$_2$ with aromatic sulphoxides.

It is known that the pyridine N-oxides are less basic than the pyridines as is shown by their pK_{BH} values [19]. Therefore, pyridine N-oxides are expected to form weaker adducts if certain other factors which increase the bond strength (back bonding, etc.) are less significant. The ΔH and K values observed for the Cu(TTA)$_2$4MPO adduct are lower than those of the Cu(TTA)$_2$PY adduct. This result is in accordance with the observations of Al-Niami and Rasoul [20] who determined the equilibrium constants of adduct formation between Cu(TTA)$_2$ and a series of pyridines and pyridine N-oxides by spectrophotometry in chloroform. It can be noted that the values of K obtained by these authors are lower than those obtained in the present study. This is due to the fact that synergistic effects are lower in

polar solvents like chloroform as compared to those in solvents like benzene.

It is known that the stability of such synergistic adducts depends on the acidity of the β-diketone, the basicity of the donor atom in the organic base, steric hindrance, and the size and coordination tendency of the metal ion. Comparing the ΔH and K values obtained here for the formation of Cu(TTA)$_2$PY with those [3] for a nonfluorinated β-diketone, i.e., acetylacetone (ACAC), it can be seen that ΔH is more negative and K is much higher in the case of Cu(TTA)$_2$PY. This can be explained by the fact that the replacement of the $-CH_3$ group by a $-CF_3$ group decreases the electron density around the central copper ion, thereby increasing its ability to attract the auxiliary ligand.

Out of all the auxiliary ligands studied here, Phen and BiPY form the most stable adducts and, therefore, can conveniently replace costlier ligands like TOPO in extraction work.

The ΔH values obtained for the adducts of PY, BiPY and Phen are of the same order as the ΔH values [21] for the formation of copper(II) complexes of PY (-4.02 kcal mol^{-1}), BiPY (-11.9 kcal mol^{-1}) and Phen (-11.7 kcal mol^{-1}) in an aqueous medium. This feature broadly indicates that the new bonds formed in the adducts are of a similar nature to those in the complexes of copper with the auxiliary ligands themselves.

Crystal structure data for monomeric five-coordination species containing two bidentate ligands indicate the predominance of the square pyramidal geometry or arrangements slightly distorted from it [20]. Thus, in the adduct of Cu(ACAC)$_2$ with quinoline the copper atom is pentacoordinated to the four oxygen atoms of the two ACAC anions and the nitrogen atom of the quinoline (qu) molecule [22]. Crystal data [23] for the adduct of hexafluoroacetylacetonatocopper(II) with BiPY have shown that it is a *cis*-octahedral molecule with four close coplanar and two more distant donor atoms. The two copper–oxygen bonds in the plane defined by the copper and nitrogen atoms are slightly shorter than the copper–nitrogen bonds as is usually the case. Both the copper–oxygen bond length of 1.967 ± 0.004 Å and the copper–nitrogen bond length of 1.998 ± 0.004 Å are similar to the distance found in other complexes with both nitrogen and oxygen atoms coordinated to the copper atom. However, the copper–oxygen bonds to the second oxygen of each β-diketone ring are much longer (2.296 ± 0.004 Å).

The adducts with the unidentate bases studied in the present work are expected to have structures similar to the Cu(ACAC)$_2 \cdot$ qu adduct, while the structures of the adducts with BiPY and Phen are likely to be similar to that of the BiPY adduct of Cu(HFACAC)$_2$, but crystal structure data are necessary to confirm such assumptions.

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