Thermodynamics of Metal–Ligand Bond Formation. XXXIII. The Effects of Electron-withdrawing Groups on the Lewis Acidity of Copper(II) Complexes

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Abstract

Thermodynamic data are reported for the formation in benzene solution of addition compounds of selected copper(II) keto-enolate complexes with heterocyclic bases, tributyl phosphate, dimethylsulphoxide and trioctylphosphine oxide. The introduction of electron-withdrawing substituents, such as carbethoxy or F, into the copper complexes results in much increased adduct stabilities, largely attributable to entropy factors.

Introduction

Since it was first recognised that Lewis bases form 5-coordinate addition compounds with copper(II) keto-enolates [1], there have been many studies of the stabilities of these adducts [2–15]. In general adduct stabilities increase with increasing basicity of the Lewis base, increasing electronwithdrawing effect of the keto-enolate and decreasing polarity of the solvent.

There have been fewer studies of the enthalpy of adduct formation [9, 10, 13, 14], which show a broad correlation between adduct stabilities and enthalpies of adduct formation. Studies we have recently made on the solvent extraction of these compounds suggest that the effect on adduct stabilities of electron-withdrawing substituents in the keto-enolate is much greater than would be expected from corresponding changes in the enthalpies of adduct formation. These results are discussed in the present paper.

The copper(II) complexes studied include the compounds $((CH_3)_3CCOCHCOR)_2Cu$, when R = CH_3, $C(CH_3)_3$, CHF_2, CF_3, C_2F_5 and C_3F_7; and also $(C_6H_5COCHCOR)_2Cu$ where R = CH_3, H, and $COOC_2H_5$. Adduct formation has been studied in benzene solution using 4-methylpyridine as reference base; additional data have been obtained for the phenylpropanedionates with pyridine and 2-methylpyridine and for the fluorinated complexes with the O-donors tributylphosphate (TBP), dimethylsulphoxide (DMSO) and trioctylphosphine oxide (TOPO).

Results and Discussion

Data obtained calorimetrically for the formation of adducts of 4-methylpyridine with copper complexes of the diketonate ions RCOCHCOR′ are summarised in Table I; Figure 1 shows a plot of enthalpy against entropy change for these and some previously reported systems.

Data for the reactions of the non-fluorinated copper complexes with 4-methylpyridine or pyridine fit closely to a linear relationship between ΔH and ΔS; that is, these reactions belong to an isoequilibrium series. The fluorinated compounds however do not belong to this series.

For detailed discussion of the present results it is convenient to take as reference point the data for the complex with R = R′ = $C(CH_3)_3$ for which ΔH is least negative. Replacement of methyl by H in this series leads to more negative values of both ΔH and ΔS. Isoequilibrium series of this type are common; in these particular systems compensating changes in ΔH and ΔS lead to almost zero change in ΔG or K at room temperature. Relative to the simplest member of the series, bis(acetylacetonato)copper(II), further methylation thus has the effect of making the enthalpy of adduct formation less

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TABLE I. Thermodynamic Data for Formation of 1:1 Adducts of 4-Methylpyridine with $Cu(RCOCHCOR')_2$ in Benzene Solution at 30 °C ($\Delta H°$, $\Delta G°$ in kJ mol^{-1}. $\Delta S°$ in J K^{-1} mol^{-1}).

R	R'	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
CH_3	CH_3	5.4 ± 0.3	30.4 ± 0.8	4.25 ± 0.15	86 ± 3
CMe_3	CH_3	5.9 ± 0.1	23.0 ± 1.0	4.47 ± 0.04	61 ± 5
CMe_3	CMe_3	5.7 ± 0.7	19.0 ± 0.5	4.38 ± 0.33	48 ± 3
CMe_3	CHF_2	260 ± 4	25.4 ± 0.8	14.01 ± 0.04	38 ± 3
CMe_3	CF_3	1994 ± 220	26.8 ± 1.1	19.14 ± 0.30	25 ± 5
CMe_3	C_2F_5	2672 ± 347	30.3 ± 0.8	19.88 ± 0.35	34 ± 4
CMe_3	C_3F_5	3234 ± 278	31.6 ± 0.8	20.36 ± 0.25	37 ± 4

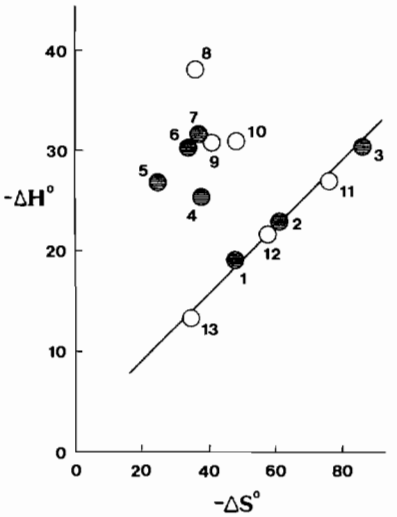

Fig. 1. Enthalpy–entropy relationship for formation of adducts of copper diketonates with 4-methylpyridine (or pyridine). Full circles refer to present work; empty circles are from literature. 1. CMe_3, CMe_3; 2. CMe_3, CH_3; 3. CH_3, CH_3; 4. CMe_3, CHF_2; 5. CMe_3, CF_3; 6. CMe_3, C_2F_5; 7. CMe_3, C_3F_7; 8. CF_3, CF_3/py [14]; 9. CH_3, CF_3 [14]; 10. CH_3, CF_3/py [14]; 11. CH_3, CH_3/py [12]; 12. $CHMe_2$, $CHMe_2$/py [16]; 13. 3-methyl-acetylacetonate/py [12].

negative without significant change in adduct stability.

Replacement of methyl by F also leads to more negative enthalpies of adduct formation and the changes due to F are rather greater than those due to H. The effect of replacement by F on the entropy term is however quite different: ΔS is almost unchanged when F replaces methyl. The combination of more negative ΔH with unchanged ΔS leads to the greatly increased adduct stabilities observed. Relative to the acetylacetonate the effect of replacement of H by F is a large increase in adduct stability with only a small change in the enthalpy of adduct formation, so that the effect of fluorination appears to be almost wholly entropic, as previously reported [14].

The changes in enthalpy of reaction when methyl is replaced by H or F can be readily understood in terms of inductive effects. In seeking to explain the corresponding entropy changes we may note that methyl and fluorine are isoelectronic and of comparable size, but H is much smaller than either; we may thus expect that when adduct formation occurs solvent displacement will be similar for the methyl- and fluoro- substituted compounds but much less for the H-substituted. This provides a simple explanation for the roughly similar values of ΔS for $-C(CH_3)_3$ and $-CF_3$ substituted compounds, compared to the much more negative values of ΔS for those with methyl substituents. This effect is evidently confined to the first carbon atom in the side chain, since further, more remote substitution has little further effect on the entropy term.

The non-fluorinated complexes show no evidence of adduct formation with O-donors: no colour change, no evolution of heat and no enhancement of solvent extraction, but all of these phenomena are observed with the fluorinated complexes. Data for adduct formation in these systems, obtained from calorimetric measurements, are summarised in Table II.

Adduct stabilities increase in the order TBP < DMSO < TOPO. This is due to increasingly negative enthalpies of adduct formation, corresponding to increasing basicity of the donor, though this is partly compensated by small increases in the negative entropy term. The enthalpies of formation of adducts with TOPO are similar to those with 4-methylpyridine, but the 4-methylpyridine adducts are much more stable due to a less negative entropy term. This implies that more solvent molecules are displaced when 4-methylpyridine is coordinated in the fifth site and may be related to the binding of the N atom to two C atoms, whereas in TOPO the O atom is bound only to one other atom.

Introduction into the keto-enolate of electron-withdrawing groups other than fluorine does not promote adduct formation with O-donors, but an increase can be observed in the stabilities of adducts

TABLE II. Thermodynamic Data for Formation in Benzene Solution at 30 °C of 1:1 Adducts of O-bases with Fluorinated Complexes $Cu(RCOCHCOCMe_3)_2$ ($\Delta H°$, $\Delta G°$ in kJ mol^{-1}, $\Delta S°$ in J K^{-1} mol^{-1}).

Base	R	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
TBP	CHF_2	6.0 ± 1.1	15.4 ± 0.6	4.51 ± 0.51	36 ± 4
	CF_3	22.1 ± 0.9	18.9 ± 0.5	7.80 ± 0.11	37 ± 2
	C_2F_5	20.4 ± 1.8	19.9 ± 0.2	7.60 ± 0.24	41 ± 2
	C_3F_7	18.9 ± 1.0	19.1 ± 0.1	7.40 ± 0.13	39 ± 1
DMSO	CHF_2	29.3 ± 2.9	17.8 ± 0.6	8.51 ± 0.26	31 ± 3
	CF_3	56.7 ± 5.3	23.1 ± 0.3	10.17 ± 0.25	43 ± 2
	C_2F_5	66.0 ± 8.3	24.7 ± 0.5	10.55 ± 0.34	47 ± 3
	C_3F_7	51.6 ± 5.1	23.1 ± 0.1	9.93 ± 0.26	43 ± 2
TOPO	CHF_2	83 ± 6	23.8 ± 0.4	11.13 ± 0.19	42 ± 2
	CF_3	349 ± 54	28.9 ± 1.0	14.75 ± 0.43	47 ± 5
	C_2F_5	353 ± 65	30.3 ± 0.9	14.78 ± 0.52	51 ± 5
	C_3F_7	362 ± 28	30.0 ± 1.1	14.84 ± 0.20	50 ± 4

TABLE III. Thermodynamic Data for Formation in Benzene Solution at 30 °C of 1:1 Adducts of Heterocyclic Bases with Complexes $Cu(RCOCHCOC_6H_5)_2$ ($\Delta H°$, $\Delta G°$ in kJ mol^{-1}, $\Delta S°$ in J K^{-1} mol^{-1}).

R	Base	K	$-\Delta H°$	$-\Delta G°$	$-\Delta S°$
CH_3	4-mepy	41.0 ± 3.0	29.6 ± 0.8	9.14 ± 0.19	69 ± 3
	py	21.3 ± 1.3	25.5 ± 0.7	7.53 ± 0.16	61 ± 3
	2-mepy	6.6 ± 0.5	21.8 ± 1.7	4.64 ± 0.19	58 ± 6
H	4-mepy	124 ± 18	26.2 ± 1.1	11.86 ± 0.38	48 ± 5
	py	63 ± 6	26.2 ± 1.7	10.20 ± 0.25	54 ± 6
	2-mepy	11.5 ± 0.5	24.0 ± 0.4	6.01 ± 0.11	61 ± 2
$CO_2C_2H_5$	4-mepy	593 ± 60	25.9 ± 2.2	15.72 ± 0.27	34 ± 8
	py	250 ± 30	25.7 ± 0.6	13.59 ± 0.31	41 ± 3
	2-mepy	48 ± 4	21.8 ± 0.5	9.53 ± 0.22	41 ± 3

with N-donors. Table III summarises thermodynamic data for the addition of N-bases to the complexes $(C_6H_5COCHCOR)_2Cu$.

In these systems K was determined spectrophotometrically and ΔH calorimetrically, both at 23 °C. The results show the steric effect of 2-substitution in the N-base and the increased adduct stabilities as CH_3 is replaced by H or $CO_2C_2H_5$. These increased stabilities occur without significant changes in the enthalpy of adduct formation and are due almost entirely to less negative entropy terms, presumably because of increasing solvent displacement.

Experimental

Pentane-2,4-dione, 2,2,6,6-tetramethylheptane-3,5-dione, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dione and 1-phenylbutane-1,3-dione were obtained commercially. Copper complexes were prepared by the reaction of a solution of the diketone in methanol with an aqueous solution of copper(II) acetate and sodium acetate and purified by crystallisation from methanol or toluene, followed by drying over phosphorus pentoxide *in vacuo* at 80 °C.

2,2-Dimethylhexane-3,5-dione, 2,2-dimethyl-6,6-difluorohexane-3,5-dione, 2,2-dimethyl-6,6,6-trifluorohexane-3,5-dione and 2,2-dimethyl-6,6,7,7,7-pentafluoroheptane-3,5-dione were prepared by the reaction of 3,3-dimethyl-2-butanone with ethyl acetate, ethyl difluoroacetate, ethyl trifluoroacetate or ethyl pentafluoropropionate in dry ether in the presence of sodium; copper complexes were obtained by reaction with copper acetate without isolation of the diketone, purified by crystallisation from methanol and dried over phosphorus pentoxide *in vacuo* at 80 °C.

1-Phenylpropane-1,3-dione and ethyl 3-phenyl-1,3-diketobutyrate were prepared by the reaction of acetophenone with ethyl formate or ethyl oxalate in dry ether in the presence of sodium; copper complexes were obtained by reaction with copper acetate without isolation of the diketo compounds and purified by crystallisation from ethanol followed by drying over phosphorus pentoxide *in vacuo* at 80 °C. The purity of all copper complexes was checked by carbon and hydrogen analyses.

Chromatographically pure pyridine, 4-methylpyridine and 2-methylpyridine (Tokyo Kasei) were redistilled and stored on anhydrous potassium carbonate. Reagent grade tributyl phosphate and dimethylsulphoxide were purified by fractional distillation and dimethylsulphoxide was stored over calcium hydride; trioctylphosphine oxide (PCR Chemicals) was used without further purification. Benzene for use as solvent was purified by freezing and distillation and dried over calcium hydride.

Calorimetric titrations were done in a LKB 8700 titration calorimeter at 30 °C, using the previously described technique [13]. Briefly, a solution of the base was added incrementally to a solution of the copper complex and the heat change measured after the addition of each increment. Control titrations were made to determine the heat of dilution of the titrant. Enthalpograms were obtained by plotting the cumulative, corrected heat of reaction against the total base concentration. The enthalpy of reaction was obtained from the extrapolated, integrated heat of reaction and equilibrium constants then calculated at each experimental point; the enthalpy was then refined iteratively until constant values of K were obtained throughout the titration. At least three titrations were done for each system and the data in Tables I and II are the averages of these results. Uncertainties quoted for ΔH are mean deviations and uncertainties for K are the sum of average standard deviations in individual titrations and mean deviations for different titrations.

Spectrophotometric equilibrium constants in Table III were determined on a Perkin–Elmer model 124 spectrophotometer using the previously reported method [2]. Values of K are the average of 10–20 experimental points with standard deviations typically ±5%, increasing to ±10% when $K > 100$. Enthalpy data in Table III were obtained calorimetrically by the ampoule technique in a LKB 8700 calorimeter: ampoules containing 10–40 mg of copper complex were broken into solutions of base of various concentrations; control experiments were made by breaking ampoules containing complex into pure solvent. The enthalpy change was obtained from the corrected heat of reaction using the spectrophotometric values of K. Reproducibilities of ΔH for 3–10 experiments were typically ±1 kJ mol^{-1}. Uncertainties quoted for K are standard deviations and for ΔH are mean deviations.

References

1 D. P. Graddon, *Nature (London), 183,* 1610 (1959).
2 D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem., 21,* 49 (1961).
3 W. R. May and M. M. Jones, *J. Inorg. Nucl. Chem., 25,* 507 (1963).
4 W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem., 27,* 2255 (1965).
5 D. P. Graddon and R. A. Schulz, *Aust. J. Chem., 18,* 1731 (1965).
6 D. P. Graddon and G. M. Mockler, *Aust. J. Chem., 21,* 617 (1968).
7 P. E. Rakita, S. J. Kopperl and J. P. Fackler, Jr., *J. Inorg. Nucl. Chem., 30,* 2139 (1968).
8 T. Shigematsu, M. Tabushi, M. Matsui and M. Munakata, *Bull. Chem. Soc. Jpn., 41,* 2656 (1968).
9 B. L. Libutti, B. B. Wayland and A. F. Garito, *Inorg. Chem., 8,* 1510 (1969).
10 A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc., 91,* 866 (1969).
11 W. Partenheimer and R. S. Drago, *Inorg. Chem., 9,* 47 (1970).
12 D. P. Graddon and K. B. Heng, *Aust. J. Chem., 24,* 1059 (1971).
13 D. P. Graddon and K. B. Heng, *Aust. J. Chem., 24,* 1781 (1971).
14 D. P. Graddon and W. K. Ong, *Aust. J. Chem., 27,* 741 (1974); *J. Inorg. Nucl. Chem., 37,* 469 (1975).
15 E. Kwiatkowski and J. Trojanowski, *J. Inorg. Nucl. Chem., 38,* 131 (1976).
16 D. P. Graddon and T. T. Nyein, unpublished data.