THERMODYNAMICS OF METAL–LIGAND BOND FORMATION

VIII.* PYRIDINE ADDUCTS OF ZINC(II) β-DIKETONATES

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Abstract

Equilibrium constants and enthalpies in benzene solution are reported for the formation of 1 : 1-adducts of pyridine with four zinc(II) complexes of β-diketones, determined by calorimetric titration. Adduct formation constants at 30°C fall in the range 300–2000 and enthalpies of formation lie between −15 and −34 kJ mol⁻¹. Though the enthalpies of formation differ little from those of corresponding copper(II) complexes, the adducts are about a hundred times more stable. The pyridine adduct of bis(2,2,6,6-tetramethylheptane-3,5-dionato)zinc(II) is entropy-stabilized relative to those of other complexes. No evidence was obtained for the addition of a second molecule of pyridine under the experimental conditions used.

Introduction

Zinc(II) complexes of β-diketones have been shown to be monomeric in solution in non-donor solvents.[1] The complex bis(2,2,6,6-tetramethylheptane-3,5-dionato)-zinc(II) is also monomeric and tetrahedral in the solid state,[2] but bis(acetylacetonato)-zinc(II) is trimeric in the solid state, one of the zinc atoms being six-coordinate and the other two five-coordinate.[3] This tendency to increase the coordination number above four is also shown by the formation of the five-coordinate hydrate[4] of bis(acetyl-acetonato)zinc(II) and of adducts with one or two molecules of nitrogenous bases;[1] molecular weights of these adducts suggest that although the six-coordinate bis-adducts are very unstable in solution, the five-coordinate 1 : 1-adducts are only slightly dissociated. Despite the obvious interest of comparison with corresponding copper(II) complexes no measurements of the stability of these adducts have been made, largely because of the lack of suitable analytical methods, though such measurements have been reported for base adducts of zinc complexes with dimethyldithio-carbamic acid[5] and some dialkyldithiophosphoric acids.[6]

Equilibrium constants and enthalpies of formation in benzene solution are now reported for 1 : 1-adducts of pyridine with four zinc(II) β-diketone complexes, determined by the method of calorimetric titration.

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Results and Discussion

Thermodynamic data have been obtained for addition of one molecule of pyridine to zinc(II) complexes of acetylacetone (acacH), benzoylacetone (bzacH), dibenzoylmethane (bzbzH), and 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane, dpmH) in benzene solution at 30°C. Under the experimental conditions no evidence was found for the addition of a second molecule of base, though adducts with two molecules of base have been isolated from solutions in pure base.[1] The results obtained by calorimetric titration are summarized in Table 1; details of individual titrations at different concentrations of complex are shown in the Experimental part, Table 3.

TABLE 1

AVERAGE VALUES OF THERMODYNAMIC PARAMETERS FOR THE REACTION $ZnL_2 + py = ZnL_2(py)$
(LH = β-diketone) IN BENZENE SOLUTION AT 30°C

L	$10^3[M]$ (mol l^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
acac	9·9–18·3	$-14·8 \pm 0·3$	$-33·8 \pm 3·4$	-63 ± 12
bzac	2·9–14·3	$-17·5 \pm 0·3$	$-31·9 \pm 3·2$	-48 ± 10
bzbz	2·8–12·3	$-19·1 \pm 0·3$	$-37·8 \pm 3·8$	-55 ± 11
dpm	10·7–18·9	$-15·7 \pm 0·3$	$-15·4 \pm 3·6$	$+1 \pm 13$

Small increases in the free energy of formation of the adducts in the order $Zn(acac)_2(py) < Zn(bzbz)_2(py)$ probably reflect the inductive effect of replacing methyl by phenyl in the ligand; the difference in enthalpy of formation of $Zn(acac)_2(py)$ and $Zn(bzac)_2(py)$ is not significant.

The adduct $Zn(dpm)_2(py)$ is of similar stability to the others, despite a much less negative enthalpy of formation; it is thus entropy-stabilized relative to the other adducts, a result the reverse of what might be expected on simple steric grounds. Perhaps the most likely explanation of the unexpectedly low entropy resistance to the formation of $Zn(dpm)_2(py)$ is that the pyridine and t-butyl groups, while not interfering with one another, have the combined effect of squeezing out solvent molecules, so that this adduct is less extensively solvated than the others.

The enthalpies of formation of $Zn(acac)_2(py)$ and $Zn(bzac)_2(py)$ are about 5 kJ mol^{-1} more negative than those of the corresponding copper(II) complexes,[7] but their free energies are about 12 kJ mol^{-1} more negative so that there is a significant entropy contribution to the higher stability of the adducts of the zinc complexes. This is particularly well shown by the isoequilibrium temperatures of about 600 K, compared with about 370 K for the copper(II) complexes.

The larger entropy resistance to adduct formation by the copper(II) complexes probably arises from the need to preserve almost unchanged the planar CuL_2 unit in the adducts;[8,9] the five-coordinate zinc complexes are more flexible, aquabis(acetylacetonato)zinc(II) for example being intermediate stereochemically between square-pyramidal and trigonal-bipyramidal.[4]

[7] Graddon, D. P., and Heng, K. B., *Aust. J. Chem.*, 1971, **24**, 1781.

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[9] Duckworth, V. F., Graddon, D. P., Mockler, G. M., and Stephenson, N. C., *Inorg. nucl. Chem. Lett.*, 1967, **3**, 471.

Experimental

Anhydrous zinc(II) β-diketonates were prepared and purified according to methods in the literature[1,10] and their purity confirmed by carbon and hydrogen analyses,* shown in Table 2.

TABLE 2

CARBON AND HYDROGEN ANALYSES OF COMPLEXES

Complex	Formula	Calc. (%)		Found (%)	
		C	H	C	H
Zn(acac)$_2$	C$_{10}$H$_{14}$O$_4$Zn	45·6	5·4	45·6	5·3
Zn(bzac)$_2$	C$_{20}$H$_{18}$O$_4$Zn	62·0	4·7	61·9	4·8
Zn(bzbz)$_2$	C$_{30}$H$_{22}$O$_4$Zn	70·4	4·3	70·4	4·4
Zn(dpm)$_2$	C$_{22}$H$_{38}$O$_4$Zn	61·2	8·9	61·1	8·7

Calorimetric titrations were carried out on a LKB 8700-2 titration calorimeter. The method of preparing solutions, drying solvent and pyridine, carrying out the titration and calculating the results has been described previously;[7] results for each titration are given in Table 3, in which are included

TABLE 3

THERMODYNAMIC DATA FROM INDIVIDUAL TITRATIONS IN BENZENE SOLUTION AT 30°C

Concentration in mol l^{-1}; K in l. mol^{-1}; $\Delta G°$, $\Delta H°$ in kJ mol^{-1}; $\Delta S°$ in J K^{-1} mol^{-1}

L	10^3[ZnL$_2$]	K	$\Delta G°$	$\Delta H°$	$\Delta S°$	L	10^3[ZnL$_2$]	K	$\Delta G°$	$\Delta H°$	$\Delta S°$
acac	9·86	330	−14·7	−33·0	−60	bzbz	2·80	1930	−19·2	−37·0	−59
	9·86	340	−14·8	−34·0	−64		5·80	1760	−19·0	−40·0	−69
	13·3	340	−14·8	−33·0	−60		12·3	1860	−19·1	−36·5	−58
	18·3	340	−14·8	−35·0	−66	dpm	10·7	480	−15·7	−14·5	−4
bzac	2·90	920	−17·3	−30·0	−42		11·1	500	−15·8	−16·2	+1
	4·73	920	−17·3	−33·5	−53		14·0	480	−15·7	−12·0	−12
	11·1	1000	−17·5	−31·0	−45		18·9	495	−15·7	−19·0	+11
	14·3	1100	−17·8	−33·0	−50						

uncertainties of $\pm 10\%$ in K and ΔH, together with derived uncertainties in ΔG and ΔS, except for a rather larger uncertainty in ΔH for Zn(dpm)$_2$, for which an unusually large range of individual values of ΔH was obtained, though even in this case the reproducibility is still quite good.

* Analyses were performed by Dr E. Challen, University of New South Wales microanalytical laboratory.

[10] Hammond, G. S., Nonhebel, D. C., and Chin-hua, S. Wu, *Inorg. Chem.*, 1963, **2**, 73.