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# CALORIMETRIC STUDY OF THE REACTION OF BIS(*N*-BENZOYL-*N′*,*N′*-DIPHENYLTHIOUREATE) M(II) (M = Zn, Cd) WITH SOME NITROGEN BASES

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## ABSTRACT

The stability constants, $K$, and the molar enthalpy changes, $\Delta H$, for the formation of the bis(*N*-benzoyl-*N′*,*N′*-diphenylthioureate) M(II) (M = Zn, Cd) adducts with pyridine (I), $\beta$-picoline (II), $\gamma$-picoline (III) and piperidine (IV) in toluene were determined.

The following values were found for $K$ (l mol$^{-1}$) and $H$ (kJ mol$^{-1}$). (i) Zn(II) adducts: (I) $K = 25.97 \pm 0.47$, $\Delta H = -21.80 \pm 0.34$; (II) $K = 32.86 \pm 0.74$, $\Delta H = -29.65 \pm 0.40$; (III) $K = 42.76 \pm 0.66$, $\Delta H = -26.87 \pm 0.27$; (IV) $K = 538 \pm 13$, $\Delta H = -31.7 \pm 0.14$. (ii) Cd(II) adducts: (I) $K = 0.78 \pm 0.17 \times 10^3$, $\Delta H = -27.67 \pm 0.12$; (II) $K = 2.36 \pm 0.14 \times 10^3$, $\Delta H = -26.59 \pm 0.19$; (III) $K = 2.91 \pm 0.07 \times 10^3$, $\Delta H = -25.63 \pm 0.07$; (IV) $K = 2.71 \pm 0.57 \times 10^3$, $\Delta H = -40.76 \pm 0.22$.

The observed order of the stability constants, relative to those of the Ni(II) adduct previously reported, is Cd(II) $\gg$ Zn(II) > Ni(II).

## INTRODUCTION

Thiourea ligands of the general formula $R_1R_2N{-}CS{-}NH{-}CO{-}Ph$ can form chelates with various metals where the central metal atom is bonded with the ligand through the S and O atoms [1]. Some of these chelates behave as Lewis acids and can therefore react with neutral bases and form addition compounds [2–4].

The coordination ability of the $MO_2S_2$ skeleton of the Ni(II) bis adduct has been investigated and the stability constants and the enthalpy changes for the formation of adducts with nitrogen bases have been determined [3,4]. Zn(II) and Cd(II) chelates were found to form only the mono adducts with nitrogen bases and were more stable than those of the Ni(II) adducts [5].

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In this work, we report the results of the calorimetric titrations of $M(dpbt)_2$ (where $M = Zn$, Cd; dpbt = *N*-dibenzoyl-*N*′,*N*′-diphenylthioureate) with pyridine, β-picoline, γ-picoline and piperidine in toluene. The main interest was to compare the stability constants of the adduct formation with the stabilities of the chelate formation which have been reported previously and shown to follow the order $Ni \gtrsim Zn > Cd$ [6].

## EXPERIMENTAL

$Zn(dpbt)H_2$ and $Cd(dpbt)_2$ were prepared and recrystallized as previously described [5]. Pyridine, β-picoline, γ-picoline and piperidine were purified and distilled before using, and stored with a molecular sieve (4 Å Merck). Toluene was purified by distillation and also stored with a molecular sieve (4 Å Merck).

Incremental calorimetric titrations were carried out using toluene as the solvent. A solution of the chelate ($5.0 \times 10^{-3}$ M) in a calorimetric vessel, at a temperature of $298.15 \pm 0.02$ K, was titrated with the base solution (concentration range 0.12–0.15 M) (Fig. 1, curve A). The enthalphy change corresponding to the dilution of the base was determined by titrating pure toluene with base solution (curve B), and the enthalpy change corresponding to the chelate dilution was determined by titrating the chelate solution with pure toluene (curve C). The corrected enthalpy change (curve D) was then determined for each point by the summation $Q_D \equiv Q_{obs} = Q_A - Q_B - Q_C$ [7].

The equipment used was the precision calorimetric system LKB-8700. All the calorimetric titrations were carried out at least in duplicate, in an atmosphere protected against atmospheric moisture.

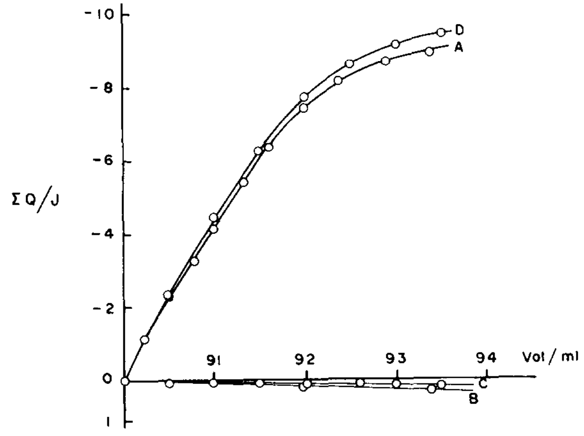

Fig. 1. Calorimetric titration of $Cd(dpbt)_2$ with γ-picoline.

## RESULTS AND DISCUSSION

$Zn(dpbt)_2$ and $Cd(dpbt)_2$ react with pyridine, β-picoline, γ-picoline and piperidine to form 1 : 1 adducts,

$$M(dpbt)_2(sln) + L(sln) = M(dpbt)_2L(sln);\ K,\ \Delta H,$$

where $K = |M(dpbt)_2L|/|M(dpbt)_2|\ |L|$. The calculated enthalpy change, $Q_{calc}$, was obtained using the equation

$$Q_{calc}(i) = n(i)\ \Delta H \qquad (1)$$

where $n(i)$ is the number of moles of adduct in the experimental point $(i)$ and $\Delta H$ is the molar enthalpy change for the reaction.

The initial values of $K$ and $\Delta H$ were estimated by using the graphical method of Bolles–Drago [8]. These values were further refined by minimization of the error square sum function, $U(K, \Delta H)$, over all data points for the corrected enthalpy, $Q_{obs}(i)$, and calculated enthalpy, $Q_{calc}(i)$.

$$U(K, \Delta H) = \sum_{i=i}^{n} W(i)(Q_{obs}(i) - Q_{calc}(i))^2 \qquad (2)$$

$W(i)$ is the weight of each experimental datum and was assumed to be

$$W(i) = 1/Q_{obs}(i) \qquad (3)$$

The standard deviation $D(U)$ for $K$ and $\Delta H$ were calculated as by Sillen [9], using the equation

$$D(U) = (U_0/(N-2))^{1/2} \qquad (4)$$

where $N$ is the number of experimental points and $U_0$ is the minimum value of $U$.

Using the procedure of Mullens et al. [10], the best values of $K$ and $\Delta H$ were found by mapping the function $AU(K, \Delta H)$, where

$$AU = (U - U_0)/U \qquad (5)$$

Figure 2 shows the contour map for the calorimetric titration of Cd(dpbt) with γ-picoline. The mapping was carried out by a programme developed for a microcomputer [11] and the figure was generated by sweeping $K$ (l $mol^{-1}$) from 2750 to 3110 in increments of $\Delta K = 4$, and $\Delta H$ (J $mol^{-1}$) from −25450 to −25800 in increments of $\Delta(\Delta H) = 7$. The best values of $K$ and $\Delta H$ are located at the center of the contour map and the deviations are shown by the boundaries 1, 2, 3, etc. In Fig. 2, the boundaries 1, 2 and 3 correspond to a standard deviation of 0.008, 0.05 and 0.1, respectively. The results of the calculations are listed in Table 1.

The results show that the enthalpy changes for the adduct formation in solution are not appreciably different, with the same base, for the Zn(II) and Cd(II) complexes. The values of the stability constants are, however, considerably larger for the Cd(II) complexes. Comparing the stability constants

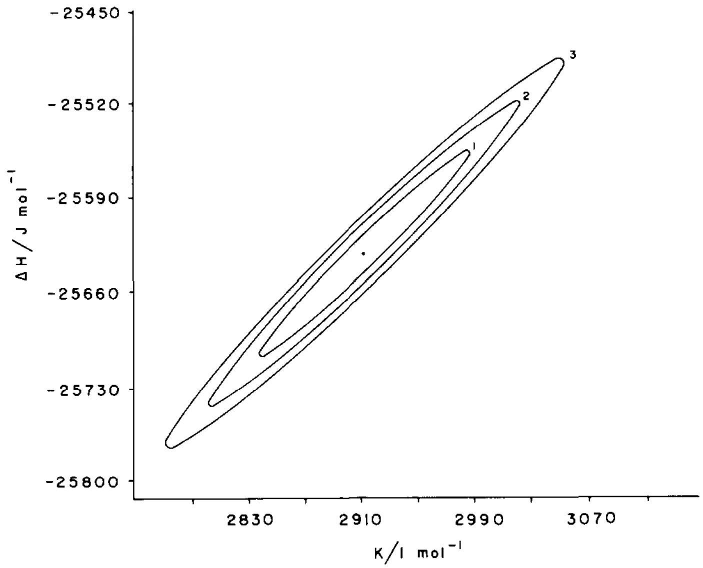

Fig. 2. Contour map for the calorimetric titration of the $Cd(dpbt)_2$ with γ-picoline.

with those of Ni(II) adducts, the observed sequence Cd(II) ≫ Zn(II) > Ni(II) is in the reverse order of the chelate stability constants (i.e., Ni(II) ≳ Zn(II) > Cd(II)) [6].

The extensive π delocalization in the $MO_2S_2$ coordination environment appears to be responsible for the decrease in the metal orbital available for interaction with bases [12]. Evidence for an increase of the electron delocalization is given by the $^{13}C$ NMR of these chelates, as shown in Table 2. While the average chemical shifts of the C(O) and C(S) resonances remain

TABLE 1

Thermochemical data of the formation of the adduct $M(dpbt)_2L$ in toluene solution at 298.15 K

| L | $K$ (l $mol^{-1}$) | $-\Delta H$ (kJ $mol^{-1}$) | $-\Delta G$ (kJ $mol^{-1}$) | $-\Delta S$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| *$Zn(dpbt)_2L$* | | | | |
| py | 25.97 ± 0.47 | 21.80 ± 0.34 | 8.07 ± 0.05 | 60.0 ± 1.7 |
| β-pic | 32.86 ± 0.74 | 29.65 ± 0.40 | 8.66 ± 0.06 | 70.4 ± 1.5 |
| γ-pic | 42.76 ± 0.66 | 26.87 ± 0.27 | 9.31 ± 0.04 | 58.9 ± 1.0 |
| pip | 538 ± 13 | 31.70 ± 0.14 | 15.59 ± 0.06 | 54.0 ± 0.7 |
| *$Cd(dpbt)_2L$* | | | | |
| py | $(0.78 \pm 0.17) \times 10^3$ | 27.67 ± 0.12 | 16.50 ± 0.05 | 37.5 ± 0.6 |
| β-pic | $(2.36 \pm 0.14) \times 10^3$ | 26.59 ± 0.19 | 19.24 ± 0.15 | 24.6 ± 1.1 |
| γ-pip | $(2.91 \pm 0.07) \times 10^3$ | 25.63 ± 0.07 | 19.78 ± 0.06 | 19.6 ± 0.4 |
| pip | $(2.71 \pm 0.57) \times 10^3$ | 40.76 ± 0.22 | 19.54 ± 0.53 | 71.2 ± 2.5 |

TABLE 2

Chemical shift of $^{13}C$ NMR of the ligand and chelates (in ppm)

| | $\delta C(O)$ | $\delta C(S)$ | $\delta C(S) - \delta C(O)$ |
|---|---|---|---|
| Hdpbt | 162.2 | 182.2 | 20.0 |
| $Ni(debt)_2$[a] | 172.5 | 172.2 | −0.3 |
| $Zn(dpbt)_2$ | 174.5 | 178.9 | 4.4 |
| $Cd(dpbt)_2$ | 167.1 | 180.7 | 13.6 |

[a] debt = *N*-benzoyl-*N′*,*N′*-diethylthiourea [13].

relatively unchanged on complex formation, the separation of the peaks reflects the same relative order as the chelate stability constants.

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## REFERENCES

1 L. Beyer, E. Hoyer, J. Liebscher and H. Hartmann, Z. Chem., 21 (1981) 81.
2 L. Beyer, E. Hoyer, H. Henning, R. Kirmse, H. Hartmann and J. Liebscher, J. Prakt. Chem., 317 (1975) 829.
3 J. Lerchner, L. Beyer and E. Hoyer, Z. Anorg. Allg. Chem., 445 (1978) 13.
4 C.M.M. Costa and Y. Gushikem Inorg. Chim. Acta, 90 (1984) 133.
5 C.M.M. Costa and Y. Gushikem, 37th Natl. Congr. SBPC, Supl. Ciênc. Cult., 384 (1985).
6 E. Uhlemann, H. Bukowsky, L. Beyer, F. Dietze and E. Hoyer, Z. Anorg. Allg. Chem., 470 (1980) 177.
7 Y. Gushikem, R. Giesse and P.L.O. Volpe, Thermochim. Acta, 68 (1983) 83.
8 T.F. Bolles and R.S. Drago, J. Am. Chem. Soc., 87 (1965) 5015.
9 L.G. Sillen, Acta Chem. Scand., 16 (1962) 11.
10 J. Mullens, Y. Yperman, J.P. François and L.C. Van Poucke, J. Phys. Chem., 89 (1985) 2937.
11 Y. Gushikem, A.P. Chagas and C.M.M. Costa, Quím. Nova, submitted.
12 T.N. Lockyer and R.L. Martin, Prog. Inorg. Chem., 27 (1980) 223.
13 E. Kleimpeter, S. Behrendt and L. Beyer, Z. Anorg. Allg. Chem., 495 (1982) 105.