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Synergistic Effect of Nitrogen Neutral Bases in the Solvent Extraction of Zinc(II) and Cadmium(II) Diphenylcarbazonates

Etsu YAMADA,* Eiichiro NAKAYAMA,† Tooru KUWAMOTO, and Taitiro FUJINAGA
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606
†*Research Center for Instrumental Analysis, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606*

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The extraction behavior of zinc and cadmium with diphenylcarbazone(DPC) into benzene and chloroform were studied in both the absence and presence of neutral bases(S). In the case of chloroform, all of the neutral bases gave rise to adduct complexes with the formula of $M(DPC)_2S$. On the other hand, in the case of benzene, the adduct complexes can be represented as $M(DPC)_2S$ for all neutral bases except for 1,10-phenanthroline(phen), in which the adduct complexes can be expressed as $M(DPC)_2(phen)_2$. The stability of the adduct complexes is related not only to the basicity of the bases, but also to the steric effect attributable to substitution. Furthermore, the adduct-formation constant increase in the following order against the normalized values of basicity: pyridine bases<2,2′-bipyridyl <1,10-phenanthroline derivatives. This order agrees with the increasing order of the coordinated ability as ligands. The basicity of the bases has a larger effect on the adduct-formation constants for Cd than on those for Zn. This may be attributed to the fact that Zn chelates have greater stability than the Cd chelates, as a result, the "residual Lewis acidity" of Zn is smaller than that of Cd, and therefore zinc chelates form less stable adducts.

In a previous paper by the present authors it has been shown that the cadmium complex of diphenylcarbazone is quantitatively extracted in the presence of 1,10-phenanthroline and that an extract has a higher molar absorptivity than that of diphenylthiocarbazone (dithizone).[1)]

Several factors, such as the basicity of the bases and steric considerations, controlling the stability of the adduct complexes, have been investigated by a number of workers in connection with phosphorylated donors or pyridine bases.[2–5)] In attempt to establish the relative importance of steric hindrance and other factors in the adduct formation, the present authors decided to study the effects of pyridine bases, and 2,2′-bipyridyl and 1,10-phenanthroline derivatives on the extraction of zinc and cadmium with DPC.

In addition, we investigated the extraction behavior of zinc and cadmium with mixtures of DPC and a neutral base in both solvents, benzene and chloroform, in order to check the solvent effect in this extraction system, which has lately been noted as an interesting problem.[6–8)]

Experimental

Apparatus and Reagents. The apparatus and chemicals, such as cadmium, diphenylcarbazone, and 1,10-phenanthroline, used in the extraction have been previously described.[1)]

The stock solution of zinc(II) [10^{-2} M (1 M=1 mol dm^{-3})] was prepared by dissolving weighed amounts of zinc chloride in dilute hydrochloric acid and then diluted with distilled water as required. The pyridine was purified by distillation under reduced pressure. All the other neutral bases, such as 2,2-bipyridyl, 2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline, were of an analytical-reagent grade and were used without further purification. All the other chemicals were also of an analytical-reagent grade.

Extraction Procedure. A 20 ml portion of a buffered cadmium or zinc solution (10^{-5} M) and a 20 ml portion of the reagent solution in chloroform or benzene were equilibrated at 25 °C by vigorously shaking for 30 min, a period which was adequate for equilibrium to be attained. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value. After phase separation, the aqueous phase was immediately analyzed with the atomic-absorption spectrophotometer, whereas the organic phase was analyzed after back-extracting into a 0.2 M nitric acid solution.

Isolation of Cd/DPC/Phen Synergistic Complexes. Synergistic complexes were synthesized according to Healy's method.[9)] A 250 ml portion of a buffered aqueous solution ($Na_2B_4O_7$–HCl) of 2.5×10^{-3} M cadmium chloride was added to a 250 ml of a chloroform solution of 5×10^{-3} M DPC and 2.5×10^{-3} M 1,10-phenanthroline. The mixture was shaken vigorously for about 20 min, the aqueous phase was removed, and the chloroform solution was dried by the use of anhydrous sodium sulfate and then evaporated with a rotary evaporator. After almost all the chloroform had been evaporated, a red-violet complex was precipitated by the addition of hexane. Further purification was brought about by recrystallization from chloroform. In the case of benzene, a 250 ml portion of a buffered aqueous solution of 2.5×10^{-3} M cadmium chloride was added to a 250 ml portion of a benzene solution of 5×10^{-3} M DPC and 5×10^{-3} M 1,10-phenanthroline. The procedure was also essentially the same as in the case of chloroform. These complexes were dried *in vacuo* at room temperature.

Results and Discussion

Relation of Stability Constants of Base Adducts to the Basicity of Neutral Bases. The equation of the extracted equilibrium of zinc and cadmium with DPC can be represented as follows.

$$M^{2+} + x\mathrm{HDPC}_{(0)} \overset{K_{\mathrm{ex},x}}{\rightleftharpoons} \mathrm{M(DPC)}_{x(0)} + x\mathrm{H}^+, \tag{1}$$

where;

$$K_{\mathrm{ex},x} = \frac{[\mathrm{M(DPC)_x}]_0[\mathrm{H}^+]^x}{[\mathrm{M}^{2+}][\mathrm{HDPC}]_0^x} = \frac{\mathrm{D}_0[\mathrm{H}^+]^x}{[\mathrm{HDPC}]_0^x}. \tag{2}$$

When neutral bases(S) are present, the extraction equation can be written as:

$$\mathrm{M}^{2+} + x\mathrm{HDPC}_{(0)} + y\mathrm{S}_{(0)} \overset{K_{\mathrm{ex},xy}}{\rightleftharpoons} \mathrm{M(DPC)}_x\mathrm{S}_{y(0)} + x\mathrm{H}^+. \tag{3}$$

The extraction constant, $K_{\mathrm{ex},xy}$ is given by:

$$K_{\mathrm{ex},xy} = \frac{[\mathrm{M(DPC)}_x\mathrm{S}_y]_0[\mathrm{H}^+]^x}{[\mathrm{M}^{2+}][\mathrm{HDPC}]_x^0[\mathrm{S}]_0^y} = \frac{\mathrm{D}[\mathrm{H}^+]^x}{[\mathrm{HDPC}]_0^x[\mathrm{S}]_0^y}. \tag{4}$$

The reaction of primary interest involves adduct formation in the organic phase. By the proper manipulation of the above equilibria, the expression for the adduct formation can be obtained as follows:

$$\mathrm{M(DPC)}_{x(0)} + y\mathrm{S}_{(0)} \overset{\beta_y}{\rightleftarrows} \mathrm{M(DPC)}_x\mathrm{S}_{y(0)}, \tag{5}$$

where β_y is the adduct-formation constant. By introducing Eqs. 2 and 4 into Eq. 6, it can be shown that:

$$\beta_y = \frac{[\mathrm{M(DPC)}_x\mathrm{S}_y]_0}{[\mathrm{M(DCP)}_x]_0[\mathrm{S}]_0^y} = K_{\mathrm{ex},xy}/K_{\mathrm{ex},x}. \tag{6}$$

The extraction behavior of zinc and cadmium by DPC into benzene was studied in both the absence and presence of nitrogen neutral bases. The plots of log *D* *vs.* such variables as the pH of the aqueous phase and the logarithms of the concentrations of DPC and of neutral bases were obtained in order to determine the stoichiometry and equilibrium constants of the extraction.

In the absence of neutral bases, the slopes of log *D* *vs.* pH are 2; those of log *D* *vs.* log $[\mathrm{DPC}]_0$ are also 2 for Zn and Cd. These results suggest that the extracted species are $\mathrm{Zn(DPC)_2}$ and $\mathrm{Cd(DPC)_2}$, which is in agreement with Balt's report.[10]

Extraction in the presence of neutral bases was also evaluated by slope analysis. The slopes of log *D* *vs.* pH are 2; those of log *D* *vs.* log $[\mathrm{DPC}]_0$ are also 2. The plots of log *D* *vs.* log $[\mathrm{S}]_0$ in the presence of pyridine bases, such as pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine, exhibit a linear range of unit slopes. These results suggest that one pyridine base adducts to $\mathrm{Zn(DPC)_2}$ or $\mathrm{Cd(DPC)_2}$. In the presence of 1,10-phenanthroline, the plots of log *D* *vs.* log $[\mathrm{phen}]_0$ are as shown in Fig. 1. The slope of log *D* *vs.* log $[\mathrm{phen}]_0$ was 2, so it is suggested that two 1,10-phenanthroline adduct to $\mathrm{Cd(DPC)_2}$, while a greater quantity of an additive causes the slope of the line to decrease gradually, become horizontal, and finally turn down in a negative slope, −2. The extraction behavior of zinc with DPC in the presence of 1,10-phenanthroline is similar to that of cadmium. Furthermore, extraction in the presence of 1,10-phenanthroline derivatives, such as 4,7-diphenyl-1,10-phenanthroline, 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline, was also examined. The slopes of log *D* *vs.* log $[\mathrm{S}]_0$ are very close to unity. These results suggest that one 1,10-phenanthroline derivative adducts to $\mathrm{Zn(DPC)_2}$ or $\mathrm{Cd(DPC)_2}$.

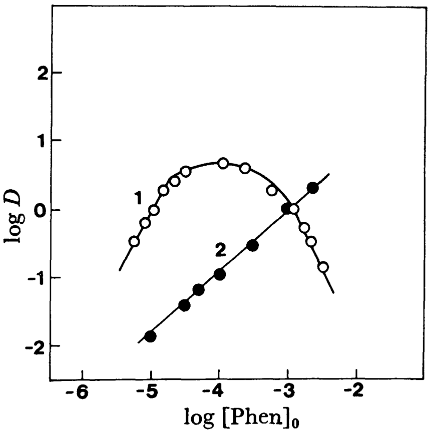

Fig. 1. Extraction of cadmium with mixtures of DPC and 1,10-phenanthroline into benzene and chloroform as a function of the phenanthroline concentration. $[\mathrm{DPC}]_0 = 5\times10^{-4}$ M, pH 7.1. 1: Benzene, 2: chlofoform.

From these results, the adduct-formation constants were calculated. These values of Cd are listed in Table 1. In the case of pyridine bases, the adduct formation constants increase in the following order: 2-methylpyridine < pyridine < 3-methylpyridine < 4-methylpyridine. The increasing order of the adduct-formation constants corresponds with the increaseing basicity (K_{HB})[11,12] of the bases, except for 2-methylpyridine. The higher stability of 4-methylpyridine as compared with that of pyridine also reflects the increased donor power of the nitrogen atom due to the introduction of a methyl group. The much lower stability of 2-methylpyridine may be attributed to the steric interference of the 2-position methyl group. In the case of 1,10-phenanthroline derivatives, the adduct-formation constants increase in the following order: 2,9-dimethyl-1,10-phenanthroline < 4, 7 - diphenyl - 2, 9 - dimethyl - 1, 10 - phenanthroline < 4, 7 -diphenyl - 1, 10 - phenanthroline < 1,10-phenanthroline. The increasing order of the adduct-formation constants corresponds with the increasing basicity of the bases, except for 2,9-dimethyl-1,10-phenanthroline and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline. The much lower stabilities of 2,9-dimethyl-1,10-phenanthroline and 4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline may also be caused by the steric interference of 2,9-position methyl substituents.

TABLE 1. THE EFFECT OF NITROGEN BASES ON THE SYNERGISTIC EXTRACTION OF CADMIUM AND ZINC DIPHENYLCARBAZONATES INTO BENZENE

No.	Base	Cd			Zn			log K_{HB}
		log $K_{\mathrm{ex},x}$	log $K_{\mathrm{ex},xy}$	log β_y	log $K_{\mathrm{ex},x}$	log $K_{\mathrm{ex},xy}$	log β_y	
1	Pyridine	−10.43	−7.12	3.31	−8.36	−4.09	4.27	5.23
2	2-Methylpyridine	−10.43	−7.55	2.88	−8.36	−4.51	3.85	5.97
3	3-Methylpyridine	−10.43	−5.94	4.49	−8.36	—	—	5.68
4	4-Methylpyridne	−10.43	−5.61	4.82	−8.36	−3.56	4.80	6.02
5	2,2′-Bipyridyl	−10.43	−5.45	4.98	−8.36	—	—	4.33
6	1,10-Phenanthroline	−10.43	2.45	12.88	−8.36	1.60	9.96	4.92
7	4,7-Diphenyl-phen	−10.43	−0.58	9.85	−8.36	1.28	9.64	4.30
8	2,9-Dimethyl-phen	−10.43	−2.52	7.91	−8.36	−2.74	5.62	6.15
9	4,7-Diphenyl-2,9-dimethyl-phen	−10.43	−2.09	8.34	—	—	—	—

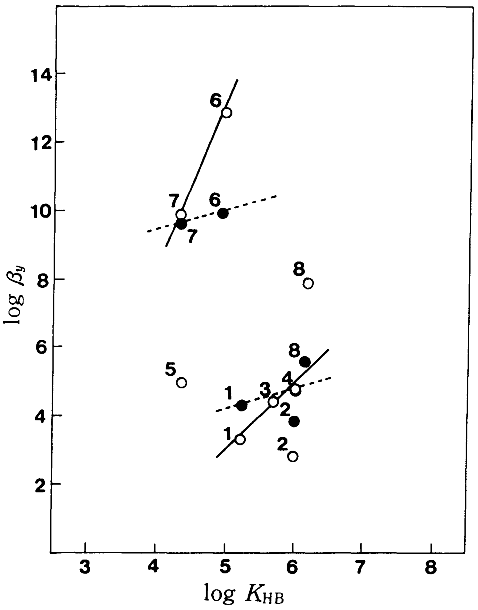

Fig. 2. Relationship of log β_y and log K_{HB} in the synergistic extraction of cadmium and zinc.
1: Pyridine, 2: 2-methylpyridine, 3: 3-methylpyridine, 4: 4-methylpyridine, 5: 2,2′-bipyridyl, 6: 1,10-phenanthroline, 7: 4,7-diphenyl-1,10-phenanthroline, 8: 2,9-dimethyl-1,10-phenanthroline, ○: cadmium, ●: zinc.

The adduct-formation constants of Zn are also listed in Table 1. The order is related not only to the basicity of the bases, but also to the steric effect due to substitution, in the same manner as in the case of Cd.

The relationship of log β_y and log K_{HB} in the synergistic extraction of Cd and Zn is shown in Fig. 2. A comparison of the adduct-formation constants of these bases against the normalized values of basicity shows that their values increase in the following order : pyridine bases<2,2′-bipyridyl<1,10-phenanthroline derivatives. This fact suggests that the stability of the adducts is related not only to the basicity of the bases, but also to the coordinated ability to act as ligands. The basicity of the bases has a larger effect on the adduct-formation constants of Cd than those of Zn. This may be attributed to the fact that zinc chelates have a greater stability than the cadmium chelates: as a result, the "residual Lewis acidity"[3] of Zn is smaller than that of Cd, and therefore zinc chelates form less stable adducts.

Effect of Organic Solvents. The behavior of the extraction of cadmium and zinc chelates into chloroform is similar to that into benzene, except for the case of 1,10-phenanthroline. In the absence of neutral bases, the extracted species are $Cd(DPC)_2$ and $Zn(DPC)_2$; the log *D* *vs.* pH plots and the log *D* *vs.* log $[DPC]_0$ plots, give the same slopes as in the case of benzene: the plots of log *D* *vs.* pH give a slope of 2, and the plots of log *D* *vs.* log $[DPC]_0$ give a slope 2, for both metals. In the presence of neutral bases, the plots of log *D* *vs.* pH exhibit a slope of 2, and the plots of log *D* *vs.* log $[DPC]_0$ exhibit a slope of 2, for both metals. In the case of Cd, the plots of log *D* *vs.* log $[S]_0$ all exhibit a linear range of unit slopes for pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline. These results suggest that the extracted species are $Cd(DPC)_2S$. In the case of Zn, the plots of log *D* *vs.* log $[S]_0$ indicate a linear range of unit slopes for pyridine and 1,10-phenanthroline. These results suggest that the extracted species are $Zn(DPC)_2S$.

In the case of benzene, the extracted species of both metals are $M(DPC)_2S$ in all the neutral bases except 1,10-phenanthroline. In the presence of 1,10-phenanthroline, the extracted species of both metals are $M(DPC)_2(phen)_2$, different from those in chloroform. Furthermore, we carried out elementary analyses of the synthesized Cd–DPC–phen chelates and compared the results with those obtained from slope analysis. As is shown in Table 2, the results obtained from elementary analysis fit those obtained from slope analysis. Hence, the extracted species into chloroform can be expressed as $Cd(DPC)_2\cdot phen$, and that into benzene, as $Cd(DPC)_2(phen)_2$.

Consequently, in the case of chloroform, one neutral base adducts to cadmium chelate and zinc chelate for all neutral bases, so the extraction can be expressed as:

$$M^{2+} + 2HDPC_{(o)} + S_{(o)} \rightleftharpoons M(DPC)_2S_{(o)} + 2H^+. \quad (7)$$

On the other hand, in the case of benzene, the extraction can be represented as Eq. 7 for all neutral bases except for 1,10-phenanthroline. In the presence of 1,10-phenanthroline, the extraction stoichiometry can be expressed as:

$$M^{2+} + 2HDPC_{(o)} + 2phen_{(o)} \rightleftharpoons M(DPC)_2(phen)_{2(o)} + 2H^+. \quad (8)$$

From these results, it would appear that the adduct stability is enhanced by an increase in the basicity of the adducting base, by an increase in the coordinated ability, and by an increase in the residual Lewis acidity of the metal atom, *i.e.*, after chelation. Furthermore, the composition of the extracted zinc and cadmium chelates with the mixtures of DPC and 1,10-phenanthroline is different depending on the solvent used in extraction.

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Table 2. Analytical data of Cd–DPC–phen complexes

Complex	Found (%)			Calcd (%)		
	C	H	N	C	H	N
$Cd(DPC)_2(phen)$ (from chloroform)	60.95	4.18	18.32	59.04	4.17	18.12
$Cd(DPC)_2(phen)_2$ (from benzene)	62.00	4.23	17.97	62.99	4.23	17.63

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