

Thermodynamics of Solid Coordination Compounds of Co(II), Ni(II), Cu(II), Zn(II) & Cd(II)

G. C. BHATTACHARYA, H. C. DAS GUPTA & A. CHATTERJEE
University Department of Chemistry, Ranchi University, Ranchi 834008

Received 12 July 1976; revised 6 August 1977; accepted 17 August 1977

Preparation of coordination compounds of fluoborates and sulphates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with mono- and bi-functional ligands (α -, β -, γ -picolines and dioxane) is reported. The thermodynamic studies of the compounds cover pressure-composition isothermals, heats of dissociation, entropy and free energy changes. It has been found that in solid phase, the determination of free energy change is the only reliable and helpful parameter for ascertaining the order of stabilities of comparable complexes.

PREPARATION and thermodynamic studies in solid phase of coordination compounds of fluoborates and sulphates of Co(II), Ni(II), Zn(II) and Cd(II) with ligands like α -, β - and γ -picolines and dioxane have not been reported. It was, therefore, considered of interest to study their stabilities in solid state and other behaviour.

Materials and Methods

The fluoborates of Co(II), Ni(II), Zn(II) and Cd(II) were prepared by adding metal carbonates to a slight excess of fluoboric acid. It was necessary to keep the solution slightly acidic to avoid association of F^- ions. The crystals of metal fluoborates obtained had the composition $M(BF_4)_2 \cdot 6H_2O$ [$M = Co(II), Ni(II), Zn(II)$ and $Cd(II)$]. Metal sulphates were recrystallized before use. Picolines and dioxane were also purified.

The fluoborates were found to be insoluble in α -picoline and dioxane and soluble in β - and γ -picolines. Complexes with dioxane and α -picoline were prepared by adding dropwise saturated solutions of the fluoborates in absolute ethanol to the ligands with constant stirring. The solution was evaporated to induce crystallization.

BF_4^- was estimated as nitron¹ fluoborate, picolines² by steam distillation of the alkaline solution of the complexes into a known volume of standard H_2SO_4 . Metals were estimated by the standard methods³. The analytical data of the complexes are recorded in Tables 1 and 2.

Pressure-composition isothermals—The apparatus used for the measurements of dissociation pressures and pressure-composition isothermals was of the type described by Bhattacharya and Sinha⁴. It could be set at desired temperature with an accuracy of $\pm 0.05^\circ$ and by repeating the experiments on stepwise dissociation, the stable systems of a particular compound were isolated and chemically analysed to establish the nature and composition.

Dissociation pressures and heats of dissociation—The dissociation pressures of the complexes and their lower and lowest order of systems (isolated from the studies of the isothermals) were measured

TABLE 1—ANALYTICAL DATA OF THE PICOLINE COMPLEXES

Compound	Found (calc.), %		
	M	BF_4^-	Pico
Zn(BF_4) ₂ ·(α -pico) ₄	10.50 (10.70)	29.61 (28.42)	60.24 (60.88)
Cd(BF_4) ₂ ·(α -pico) ₄	17.17 (17.08)	26.08 (26.39)	56.79 (56.53)
Co(BF_4) ₂ ·(β -pico) ₄	9.71 (9.75)	28.80 (28.72)	60.90 (61.53)
Ni(BF_4) ₂ ·(β -pico) ₄	9.65 (9.71)	28.92 (28.74)	61.75 (61.55)
Zn(BF_4) ₂ ·(β -pico) ₄	10.65 (10.70)	28.50 (28.42)	61.33 (60.88)
Cd(BF_4) ₂ ·(β -pico) ₄	17.00 (17.08)	26.29 (26.30)	56.48 (56.53)
Co(BF_4) ₂ ·(γ -pico) ₄	9.70 (9.75)	28.30 (28.72)	60.70 (61.57)
Ni(BF_4) ₂ ·(γ -pico) ₄	9.66 (9.71)	28.80 (28.74)	60.80 (61.55)
Zn(BF_4) ₂ ·(γ -pico) ₄	10.65 (10.70)	28.50 (28.42)	60.72 (60.88)
Cd(BF_4) ₂ ·(γ -pico) ₄	17.07 (17.09)	26.25 (26.39)	56.48 (56.53)
CoSO ₄ ·(γ -pico) ₄	11.14 (11.18)	18.17 (18.22)	70.52 (70.60)
NiSO ₄ ·(γ -pico) ₄	11.13 (11.04)	18.15 (18.23)	70.50 (70.63)

TABLE 2—ANALYTICAL DATA OF DIOXANE COMPLEXES

Compound	Found (calc.), %			
	M	BF_4^-	C	H
Co(BF_4) ₂ (dioxane) ₂	14.31 (14.41)	42.40 (42.49)	23.45 (23.50)	3.96 (3.94)
Ni(BF_4) ₂ (dioxane) ₂	14.43 (14.37)	42.47 (42.53)	23.50 (23.53)	3.82 (3.97)
Cu(BF_4) ₂ (dioxane) ₂	15.26 (15.37)	42.00 (42.00)	23.15 (23.25)	3.86 (3.90)
Zn(BF_4) ₂ (dioxane) ₂	15.68 (15.77)	41.88 (41.72)	23.20 (23.18)	3.83 (3.88)

at different temperatures, using the apparatus referred to above. The values of $\log_{10} p$ were plotted against $10^6/T$ and from the slope of the linear graphs, heat of dissociation, ΔH , for each system was calculated. The evaluated ΔH values fairly agreed with those calculated by the direct application of the readings to Claypeyron-Clarius equation with two adjacent temperatures. The values of ΔH evaluated as such are shown in Table 3.

Free energy changes of the compounds — ΔF values at different temperatures of dissociation were evaluated by the application of Vant Hoff's reaction isotherm for heterogeneous solid-gas phases (Eq. 1).

$$-\Delta F = RT \ln k_p - RT \sum \nu \ln p \quad \dots(1)$$

The reduced form of Eq. (1) is given by the expression $-\Delta F = RT \ln P_1/P_2$ where P_1 and P_2 are the vapour pressures of the ligands under consideration and equilibrium pressures of the complexes at temperature T respectively. It has been possible to calculate the ΔF values of all the compounds and their respective systems at different temperatures by the application of the reduced form of the

equation. Although work has been done at different temperatures, the results of only three temperatures are given in Table 3 for a discussion on the results.

Entropy changes of the compounds — The changes in entropy ΔS may be directly evaluated from the well-known thermodynamic expression $\Delta S = (\Delta H - \Delta F)/T$. The values of ΔS are listed in Table 3.

Results and Discussion

Previous workers paid much attention to the determination of ΔH values for assessing the order of stabilities in a given series of comparable complexes. Previous reports on ammonia complexes⁵⁻⁷ and some complexes with heterocyclic bases⁸ show that the heat of dissociation of a system containing highest number of ammonia molecules or any other base is the lowest. However, the present data reveal that this is not always true. Similar deviations have been noted earlier⁹⁻¹³. A comparatively wider coverage of the present work reveals (Table 3) that no generalization is possible from the determination of ΔH values of the comparable complexes.

TABLE 3 — HEATS OF DISSOCIATION, FREE ENERGY CHANGES AND ENTROPIES OF COMPLEXES AT DIFFERENT TEMPERATURES

Compound	+ ΔH (kcal/mole)	- ΔF (kcal/mole) at			+ ΔS (e.u./mole) at		
		60°	70°	80°	60°	70°	80°
Zn(BF ₄) ₂ .4/3 (α -pico)	11.02	1.18	1.14	1.12	36.62	35.42	34.40
Zn(BF ₄) ₂ .3/2 (α -pico)	11.19	1.81	1.79	1.78	39.06	37.80	36.80
Zn(BF ₄) ₂ .2 (α -pico)	12.35	3.20	2.92	2.81	46.70	44.50	42.95
Cd(BF ₄) ₂ .4/3 (α -pico)	23.85	1.84	1.44	1.04	72.20	73.65	70.55
Cd(BF ₄) ₂ .3/2 (α -pico)	16.80	2.04	1.86	1.67	56.50	54.45	52.50
Cd(BF ₄) ₂ .2 (α -pico)	14.88	2.56	2.44	2.33	52.40	50.55	48.80
Co(BF ₄) ₂ .4/3 (β -pico)	16.70	1.26	1.14	1.00	53.80	52.00	50.15
Co(BF ₄) ₂ .3/2 (β -pico)	14.46	1.68	1.57	1.45	48.50	46.65	45.15
Co(BF ₄) ₂ .2 (β -pico)	14.64	2.26	2.09	1.98	50.80	48.80	47.10
Ni(BF ₄) ₂ .4/3 (β -pico)	14.81	1.84	1.76	1.71	50.00	48.25	46.80
Ni(BF ₄) ₂ .3/2 (β -pico)	14.76	—	2.8	2.78	—	51.20	49.70
Zn(BF ₄) ₂ .4/3 (β -pico)	12.28	1.08	1.08	1.07	40.20	38.95	37.80
Zn(BF ₄) ₂ .3/2 (β -pico)	12.34	1.59	1.57	1.55	41.80	40.55	39.35
Zn(BF ₄) ₂ .2 (β -pico)	14.33	2.70	2.64	2.53	51.20	49.50	47.75
Cd(BF ₄) ₂ .4/3 (β -pico)	15.94	1.43	1.20	0.92	52.15	50.00	47.75
Cd(BF ₄) ₂ .3/2 (β -pico)	20.16	2.10	1.92	1.67	66.80	63.45	61.95
Cd(BF ₄) ₂ .2 (β -pico)	16.83	2.34	2.21	2.07	57.50	55.55	53.55
Co(BF ₄) ₂ .4/3 (γ -pico)	16.04	1.88	1.78	1.64	53.80	51.95	50.00
Co(BF ₄) ₂ .3/2 (γ -pico)	14.78	2.17	2.11	2.03	50.90	49.50	47.55
Co(BF ₄) ₂ .2 (γ -pico)	15.53	—	2.59	2.48	—	52.80	51.00
Ni(BF ₄) ₂ .4/3 (γ -pico)	14.41	1.82	1.77	1.69	48.70	47.20	45.65
Ni(BF ₄) ₂ .3/2 (γ -pico)	17.49	2.25	2.11	1.95	59.25	57.10	54.50
Ni(BF ₄) ₂ .2 (γ -pico)	16.04	—	2.45	2.32	—	53.85	52.00
Zn(BF ₄) ₂ .4/3 (γ -pico)	13.05	1.23	1.20	1.14	42.80	41.50	40.2
Zn(BF ₄) ₂ .3/2 (γ -pico)	16.30	2.22	2.13	2.01	55.55	53.70	51.95
Zn(BF ₄) ₂ .2 (γ -pico)	15.90	3.10	3.00	2.92	57.10	55.15	53.30
Cd(BF ₄) ₂ .4/3 (γ -pico)	18.45	1.58	1.45	1.18	60.25	58.00	55.55
Cd(BF ₄) ₂ .3/2 (γ -pico)	18.95	2.14	1.99	1.72	63.30	61.15	58.55
Cd(BF ₄) ₂ .2 (γ -pico)	15.33	2.79	2.78	2.77	54.45	52.75	51.25
CoSO ₄ .4/3 (γ -pico)	11.91	1.30	1.24	1.19	39.60	38.30	37.15
CoSO ₄ .3/2 (γ -pico)	14.75	2.65	2.55	2.44	52.25	50.45	48.30
CoSO ₄ .2 (γ -pico)	14.30	3.10	3.02	2.95	52.25	50.50	48.50
NiSO ₄ .4/3 (γ -pico)	28.57	—	3.04	2.55	—	92.10	88.00
Co(BF ₄) ₂ .2 (dioxane)*	16.50	1.43	1.33	1.19	57.30	56.10	54.70
Co(BF ₄) ₂ (dioxane)*	18.34	1.67	1.54	1.37	63.95	61.10	61.00
Ni(BF ₄) ₂ .2 (dioxane)*	15.02	1.10	1.02	0.89	51.45	50.40	49.20
Ni(BF ₄) ₂ (dioxane)*	23.37	1.45	1.37	1.11	79.35	7.70	74.50
Cu(BF ₄) ₂ .2 (dioxane)*	11.92	1.21	1.17	1.10	42.00	41.715	40.35
Cu(BF ₄) ₂ (dioxane)*	14.07	1.41	1.34	1.24	49.45	48.45	47.40
Zn(BF ₄) ₂ .2 (dioxane)*	13.77	1.76	1.70	1.62	49.55	48.55	47.60
Zn(BF ₄) ₂ (dioxane)*	12.53	1.91	1.88	1.80	46.15	45.35	44.45

* ΔF and ΔS values at 40°, 45° and 50°.

Zn(BF₄)₂.2(α-pico) showed the maximum values for Δ*H* whereas Cd(BF₄)₂.2(α-pico) exhibited the minimum value. β-Picoline series (Table 3) of Zn(II) compounds obeyed the expected order of increasing stability with the decreasing number of ligands, but Co(II), Ni(II) and Cd(II) compounds show altogether a different behaviour. In γ-picoline series, the deviation could be observed for Cd(II) and Co(II) compounds whereas Ni(II) and Zn(II) series partly exhibited the order as stated above. Values for CoSO₄.4(γ-pico) more or less agree with the expected order. The work with a bifunctional ligand, dioxane, similarly exhibited deviation in Zn(BF₄)₂ series.

Assessing the stability of the complexes on the basis of Δ*S* values has also not been successful in view of many anomalies observed (Table 3).

Attempts have also been made to assess the stability on the basis of the thermodynamic function Δ*F*. This has been used earlier by many workers¹³⁻¹⁵ in solution phase but there is no record for its application in solid phase studies. The basis of interpretation is to note the shift in the negative values of Δ*F*, an increase in the negative values of Δ*F* is expected with decrease in number of ligand molecules in a system. A reference to Δ*F* values (Table 3) reveals that Δ*F* values increase progressively with decreasing number of ligand molecules, indicating increase in the order of stability. The observation that the decreasing number of ligand molecules will result in increasing order of stability with the increase in the negative values of Δ*F* finds support from the work of N. Bjerrum¹⁶ in solution phases. Bjerrum for the first time, purely on statistical grounds, pointed out that the first ligand to be taken up would be bound somewhat more strongly than the succeeding one. It is interesting to note that while the interpretation of the order of stabilities on the basis of

Δ*H* and Δ*S* values, has not succeeded¹³⁻¹⁶, the same data could be successfully interpreted on the basis of Δ*F* values calculated from the values of heats of dissociation. It was observed, without any deviation, that the lowest system has got the maximum negative values of Δ*F*.

In the present investigation, the applicability of Δ*F* function vis-à-vis other two thermodynamic functions Δ*H* and Δ*S*, as a very dependable and useful parameter for predicting the order of stability of comparable coordination compounds in the solid state, has been brought out for the first time.

References

1. BHATTACHARYA, G. C. & DAS GUPTA, H. C., *J. Indian chem. Soc.*, **41** (1964), 655.
2. LANGE, B., *Ber. dt. chem. Ges.*, **21** (1889), 579.
3. VOGEL, A. I., *A textbook of quantitative analysis* (Longmans, Green, London), 1964.
4. BHATTACHARYA, G. C. & SINHA, P. C., *J. Indian chem. Soc.*, **32** (1955), 414.
5. BILTZ, W. & HUTTING, G. F., *Z. anorg. allg. Chem.*, **109** (1919), 89.
6. BILTZ, W. & FISCHER, W., *Z. anorg. Chem.*, **129** (1923), 1.
7. BILTZ, W. & MESSERKNECHT, C., *Z. anorg. Chem.*, **129** (1923), 14.
8. SINHA, P. C. & RAY, P. C., *Trans. Faraday Soc.*, **44** (1948), 790.
9. BHATTACHARYA, G. C. & SINHA, P. C., *J. Indian chem. Soc.*, **32** (1955), 415.
10. BHATTACHARYA, G. C. & DAS GUPTA, H. C., *Indian J. Chem.*, **1** (1963), 152.
11. DAVIS, T. L. & BETCHELDER, H. R., *J. Am. chem. Soc.*, **52** (1930), 4069.
12. DAVIS, T. L. & OU, C. W., *J. Am. chem. Soc.*, **96** (1934), 106.
13. BJERRUM, J., *Metal ammine formation in aqueous solution* (Hasse & Sons, Copenhagen), 1941.
14. ROSSETTI, F. J. C., *Modern coordination chemistry*, edited by J. Lewis & R. G. Wilkens (Interscience, New York), 1960.
15. CALVIN, M. & BALES, R., *J. Am. chem. Soc.*, **68** (1946), 953.
16. BJERRUM, N., *Chem. Rev.*, **46** (1950), 331.