

Thermodynamics of Chromium and Manganese Complexes

P. S. Relan and P. K. Bhattacharya*

The formations of Cr (III) and Mn (II) complexes with pyridine and substituted pyridines have been studied by pH method. Stepwise formation constants of the complexes have been determined by McCreynold Carlson method¹ and free energies were calculated. The stability constants have been interpreted.

Complex formation of Cr(III)² and Mn(II)³ with different ligands have been studied. In case of Mn (II) the sub-shell d is half-filled while there are three electrons in case of Cr (III). An attempt has been made in the present investigation to work out the formation constants in the reaction of pyridine and substituted pyridines with Cr (III) and Mn (II) to study the effect of $d_{\pi}-p_{\pi}$ M-L bonding and the Hund stabilization of d^5 state in Mn⁺⁺.

EXPERIMENTAL

The inorganic compounds were all BDH (A.R.) quality and ligands were either German or BDH pure quality. The compounds were purified by usual method and purity tested. The pH was recorded by polymetron CL41 pH meter which reads up to an accuracy of ± 0.05 . The thermostat was controlled at $\pm 0.1^{\circ}$.

Solutions : The stability constants were determined by Bjerrum's method using McCreynold Carlson technique. The solutions were prepared as follows : Manganese chloride 2.5 ml. of 0.4 *M*, Hydrochloric acid 0.25 ml. of 8.75 *M*, Potassium chloride 10 ml. of 1.25 *M*. Total volume 25 ml.

Chromium chloride 5 ml. of 0.4 *M*, Hydrochloric acid 10 ml. of 0.5 *M*, Potassium chloride 20 ml. of 1.25 *M*. Total volume 50 ml.

The solutions were titrated in each case with 5*M* ligand and pH was noted after the addition of each fraction (the burette had an accuracy of ± 0.01). The values of $\bar{n}A$, \bar{n} and pL were calculated. Log K_1 and log K_2 were obtained from the formation curve. The log K_1 and log K_2 values have an accuracy of ± 0.05 .

* Present address :—Chemistry Department, Faculty of Science, M.S. University of Baroda, Baroda-2. (Gujarat).

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TABLE I

Formation constants of Mn (II) complexes at 35°

	log K ₁	log K ₂	−ΔF ₁	−ΔF ₂
			K.cals.	
Pyridine	0.98	0.65	1.38	0.91
α-Picoline	1.30	0.85	1.83	1.19
β-Picoline	1.28	0.82	1.80	1.15
γ-Picoline	1.32	1.17	1.86	1.64
2-Aminopyridine	1.92	1.36	2.70	1.91
2 : 4-Lutidine	1.81	1.43	2.55	2.01
2 : 6-Lutidine	1.74	1.22	2.45	1.72
2 : 4 : 6-Collidine	1.94	1.51	2.73	2.12

TABLE 2

Formation constants of Cr (III) complexes at 35°

	log K ₁	log K ₂	−ΔF ₁	−ΔF ₂
			K.Cals.	
Pyridine	2.86	2.02	4.03	2.84
α-Picoline	3.60	2.54	5.07	3.58
β-Picoline	3.08	2.21	4.34	3.11
γ-Picoline	3.60	2.82	5.07	3.97
2-Aminopyridine	4.37	—	6.16	—
2 : 4-Lutidine	3.82	—	5.38	—
2 : 6-Lutidine	3.63	—	5.11	—
2 : 4 : 6-Collidine	3.88	—	5.46	—

DISCUSSION OF THE RESULT

The tertiary amines pyridine and their substituted derivatives are less basic than the primary amines and hence their complexes with Cr (III) and Mn (II) are not as stable as of ammonia or primary amine complexes. The free energy changes involved are also not high as seen in the table. There is, however, an increase in ΔF values and the stabilities as we go from pyridine to 2 : 4 : 6-collidine. This is in accordance with the basicity of the ligands.

The plots of log K₁ of complexes against pK_a of the corresponding ligands in the case of Mn (II) and Cr (III) complexes show an almost linear relationship⁴. The deviations from the linear relationship may be ascribed to the changes in entropy and enthalpy and also some π-interaction between the metal and the ligand.

4. A. E. Martell and M. Calvin, 'Chemistry of Chelate Compounds', Prentice-Hall, 1952, p. 153.

Though chromium and manganese are members of the same transition series the complexes formed with Cr (III) are more stable than Mn (II) complexes. This may be due to higher charge on the chromium ion. Since the difference is significant there could be contribution from the M-L π interaction. Pyridine and its derivatives have appreciable tendency to accept electrons from the metal ion because of the following resonating structure.



In the Cr (III) complexes, therefore, there is M-L $d\pi-p\pi$ interaction. The synergic effect stabilizes the M-L bonds and yields relatively stable chromium complexes. The π interaction is probably not enough to bring in the required crystal field splitting to overcome the high pairing energy in the half filled d shell of Mn (II). This results in spin free manganese complexes and accounts for their lower stability.

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Department of Chemistry,
Vikram University,
Ujjain, M.P.

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