Studies on the Coordination Behaviour of the Schiff-Bases Derived from Some Sulpha-Drugs and Substituted 2-Hydroxyacetophenones[+]

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Schiff-bases derived from sulphafurazole sulphamethoxy-pyridazine and sulpha-phenazole and 2-hydroxy-5-methylacetophenone and 2-hydroxy-5-chloroacetophenone were synthesized. The complexes of the Schiff-bases with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were prepared and characterised by elemental analysis, magnetic moment, infrared and electronic spectral studies. These studies suggest the square-planar structure for Cu(II) complexes and tetrahedral structure for rest of the metal ions complexes. The stepwise stability constants of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were also calculated by Irving and Rossotti's method in 25% (v/v) dioxane-water medium at an ionic strength $0.1M$ ($NaClO_4$) and $27 \pm 0.2°$. The order of stability constant of these metal ions is in agreement with the order given by Irving and William. Thermodynamic stabilization energy was also calculated by George McClure's method.

THE Schiff-bases derived from sulpha-drugs and salicylaldehyde have been successfully used for the bacteriostatic and complexation[1-6]. The survey of the literature reveals that no work has so far been done on the coordination behaviour of the Schiff-bases (A) formed from 5-methyl and 5-chloro substituted 2-hydroxy-acetophenone with sulpha-furazole (HSFHMA, HSFHCA), sulphamethoxypyridazine (HSMHMA, HSMHCA) and sulpha-phenazole (HSPHMA, HSPHCA). The present work embodies the preparation and characterisation (elemental analysis, magnetic moment, ir and electronic spectra) of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes. The stepwise stability constants were also calculated by Irving and Rossotti's[7] method in 25% (v/v) dioxane-water at an ionic strength $0.1M$ ($NaClO_4$) and $27 \pm 0.2°$.
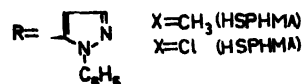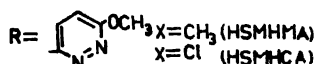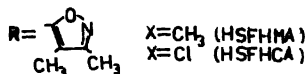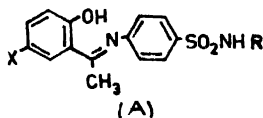
Experimental

Materials :

The sulpha drugs powder were precured from Ciba-Geigy of India Ltd., Bombay ; Roche Products Ltd., Bombay and Cyanamide India Ltd., Bulsar and were used without further purification. 2-Hydroxy-5-methylacetophenone and 2-hydroxy-5-chloroacetophenone were synthesized by usual methods[8]. All other chemicals used were of AnalaR grade and double distilled solvents were used throughout the work.

Measurements :

Electronic absorption spectra of the complexes in methanol were measured on Beckman DU-2 (manual) spectrophotometer. Infrared spectra were obtained from KBr pellets using Perkin-Elmer 337 spectrophotometer. Magnetic measurements were carried out at room temperature (27°) in powder form by Gouy's method using $Hg[Co(NCS)_4]$ as the calibrant. Systronic digital pH-meter type 335 was employed for pH measurements (sensitivity 0.01 unit) and calibrated for pH 4.05 and 9.18 using potassium hydrogen phthalate and borax buffer respectively.

Synthesis of the Ligands :

The Schiff-bases were synthesized by refluxing sulpha-drug and substituted 2-hydroxyacetophenone

in ethanol in 1 : 1 ratio in the presence of anhydrous sodium acetate and few drops of glacial acetic acid for 3-4 hrs. The reaction mixture was poured into water, the precipitate obtained, was crystallized from acetone.

Isolation of the Complex :

The complexes were synthesized by the following general method :

To a solution of metal ion (0.02 mole) in water was added in appropriate Schiff-base (0.04 mole) in acetone and the solution was refluxed ; precipitate of the complex began to appear in solution. After refluxing for 2-3 hrs, the precipitate was filtered and washed with 50% ethanol and then with diethyl ether and dried in a desiccator. These complexes are almost insoluble in water, ethanol, diethyl ether, n-hexane and carbon tetrachloride, but moderately soluble in N,N-dimethyl formamide, methanol, chloroform, acetone and benzene. Analytical data are shown in Table 1.

TABLE 1 —ANALYTICAL DATA OF THE LIGANDS AND THEIR METAL CHELATES

Compound	Found%			Calculated%			μ_{eff} (B.M.)
	N	Cl	M	N	Cl	M	
1	2	3	4	5	6	7	8
HSFHMA	10.63	—	—	10.53	—	—	—
Cu(SFHMA)₂	9.82	—	7.34	9.77	—	7.39	1.76
Ni(SFHMA)₂	9.90	—	6.90	9.83	—	6.87	3.36
Co(SFHMA)₂	9.78	—	6.83	9.82	—	6.89	4.34
Fe(SFHMA)₂	9.80	—	6.50	9.86	—	6.55	4.92
Mn(SFHMA)₂	9.80	—	6.28	9.87	—	6.45	5.50
HSFHCA	10.14	8.56	—	10.01	8.46	—	—
Cu(SFHCA)₂	9.40	7.94	6.92	9.32	7.88	7.05	1.77
Ni(SFHCA)₂	9.21	8.00	6.63	9.38	7.93	6.55	3.40
Co(SFHCA)₂	9.24	7.78	6.68	9.38	7.92	6.57	4.30
Fe(SFHCA)₂	9.33	7.80	6.39	9.41	7.95	6.25	4.92
Mn(SFHCA)₂	9.58	7.84	6.00	9.42	7.96	6.15	5.54
HSMHMA	13.65	—	—	13.59	—	—	—
Cu(SMHMA)₂	12.73	—	7.02	12.65	—	7.17	1.76
Ni(SMHMA)₂	12.80	—	6.60	12.72	—	6.66	3.33
Co(SMHMA)₂	12.58	—	6.83	12.71	—	6.69	4.28
Fe(SMHMA)₂	12.88	—	6.44	12.76	—	6.36	4.92
Mn(SMHMA)₂	12.94	—	6.41	12.77	—	6.26	5.55
HSMHCA	13.08	8.34	—	12.95	8.21	—	—
Cu(SMHCA)₂	12.26	7.73	7.00	12.09	7.66	6.85	1.80
Ni(SMHCA)₂	12.31	7.61	6.21	12.15	7.70	6.37	3.32
Co(SMHCA)₂	12.02	7.84	6.26	12.15	7.70	6.39	4.36
Fe(SMHCA)₂	12.08	7.88	6.24	12.19	7.73	6.07	4.90
Mn(SMHCA)₂	12.33	7.91	6.16	12.20	7.74	5.98	5.49
HSPHMA	12.68	—	—	12.56	—	—	—
Cu(SPHMA)₂	11.89	—	6.81	11.75	—	6.66	1.77
Ni(SPHMA)₂	11.73	—	6.32	11.80	—	6.19	3.41
Co(SPHMA)₂	11.92	—	6.00	11 80	—	6.21	4.41
Fe(SPHMA)₂	11.98	—	5.81	11.84	—	5.90	4.93
Mn(SPHMA)₂	11.70	—	5.93	11.85	—	5.81	5.50
HSPHCA	12.22	7.53	—	12.00	7.61	—	—
Cu(SPHCA)₂	11.11	7.00	6.49	11.26	7.14	6.38	1.79
Ni(SPHCA)₂	11.21	7.38	5.81	11.32	7.17	5.93	3.39
Co(SPHCA)₂	11.13	7.41	6.12	11.31	7.17	5.95	4.40
Fe(SPHCA)₂	11.49	7.00	5.41	11.35	7.19	5.65	4.94
Mn(SPHCA)₂	11.53	7.10	5.40	11.36	7.20	5.57	5.56

Potentiometric Titrations :

The stepwise stability constants were calculated by the Irving and Rossotti's method[7]. The following solutions were titrated against carbonate free 0.05M sodium hydroxide under nitrogen atmosphere.

(A) : 2.0 ml HClO₄ (0.05M)

(B) : (A)+10.0 ml Schiff-base (0.01M)

(C) : (B)+2.5 ml metal ion (0.008M)

The total volume was kept 40.0 ml of the solution keeping 25% (v/v) dioxane-water medium at ionic strength 0.1M (NaClO₄) and temperature 27±0.2°. The correction in pH-meter reading in dioxane-water medium was also made as described in literature[9,10].

Results and Discussion

For the calculation of stepwise stability constants it was assumed that factors like hydrolysis of metal ions and presence of polynuclear complexes were absent, because the following conditions were observed during the experimental work :

(i) The solutions used in the titrations were very dilute, hence the probability of polynuclear species was not expected.

(ii) The metal-ligand curves were much lower from the ligand curve at the pH value of hydrolysis of the metal ions.

The ligands being monoprotonic, it neutralizes one equivalent of base to give one buffer region in its titration curve. Values of formation functions $\bar{n}_H$ (the average number of protons attached per ligand molecule), $\bar{n}$ (the average number of ligand ions attached per metal ion) and pL (free ligand exponent) were calculated using the Irving and Rossotti's equations[7]. The protonation constant of the ligands (log K_1^H) and stepwise stability constant of metal-ligand, log K_1 and log K_2, were calculated using the half-integral method, least-square method and pointwise-calculation method. The values are in good agreement with each other and average values are reported in Table 2.

It has been found that log $K_1 >$ log K_2 in all the cases under study. This may be attributed to a larger steric hindrance offered by the Schiff-bases as compared with coordinated water molecule. The order of stability constant is found to be Cu(II)>Zn(II)>Ni(II)>Co(II)>Mn(II), which is in agreement with Irving and Williams[11] order of stability of bivalent metal complexes. The complexes of Cu(II) are found to be relatively more stable than those of Ni(II) and Zn(II). This might be due to the difference in the configuration of

TABLE 2—PROTONATION CONSTANT AND STEPWISE STABILITY CONSTANTS OF SCHIFF-BASES AND THEIR METAL CHELATES IN 25%(v/v) DIOXANE, $\mu=0.1M$ (NaClO$_4$) and $27\pm0.2°$

CONSTANT 1	HSFHMA 2	HSFHCA 3	HSMHMA 4	HSMHCA 5	HSPHMA 6	HSPHCA 7
H(I)						
log K_1^H	8.74	7.68	8.53	7.42	9.03	8.10
$-\Delta G$	12.02	10.56	11.73	10.20	12.41	11.14
Cu(II)						
log K_1	7.53	7.28	7.41	7.20	7.71	7.50
log K_2	5.11	5.02	5.03	4.81	5.18	5.14
log β_2	12.64	12.30	12.44	12.01	12.89	12.64
$-\Delta G$	17.38	16.91	17.10	16.51	17.72	17.38
δH	26.10	26.02	26.12	26.19	26.10	26.19
Zn(II)						
log K_1	7.41	7.22	7.30	7.00	7.63	7.35
log K_2	5.07	4.93	5.02	4.54	5.15	5.00
log β_2	12.48	12.15	12.32	11.54	12.78	12.35
$-\Delta G$	17.16	16.70	16.94	15.87	17.57	16.98
Ni(II)						
log K_1	7.28	7.00	7.12	7.02	7.40	7.22
log K_2	4.66	4.62	4.54	4.50	4.82	4.71
log β_2	11.94	11.62	11.66	11.52	12.22	11.93
$-\Delta G$	16.42	15.98	16.03	15.84	16.80	16.00
δH	34.81	34.59	34.69	34.85	34.66	34.80
Co(II)						
log K_1	6.55	6.41	6.41	6.24	6.71	6.53
log K_2	4.30	4.03	4.23	3.88	4.40	4.18
log β_2	10.85	10.44	10.64	10.12	11.11	10.71
$-\Delta G$	14.92	14.35	14.63	13.91	15.27	14.72
δH	24.65	24.72	24.68	24.69	24.69	24.83
Mn(II)						
log K_1	5.42	5.24	5.23	5.14	5.50	5.22
log K_2	3.04	2.93	2.81	2.78	3.12	3.00
log β_2	8.46	8.17	8.04	7.92	8.62	8.22
$-\Delta G$	11.63	11.23	11.05	10.89	11.85	11.30

(ΔG and δH in K cal mole^{-1})

Cu(II) complex from those of Ni(II) and Zn(II). It is probable that the Cu(II) forms square-planar complex using inner dsp^2 orbitals, while Ni(II) and Zn(II) form tetrahedral or preferably octahedral complexes.

The value of overall change in free energy ($-\Delta G$ Kcal mole^{-1}) was calculated by usual expression. Thermodynamic stabilization energy (δH Kcal mole^{-1}) was calculated by George and McClure's method[12]. The values are reported in Table 2, which are of the same order as for other nitrogen and oxygen donor ligands. The fact is further supported by the slight shift to higher atomic number in the curve ΔH_L (heat of complexation) as compared to the ΔH_H (heat of hydration of metal ions) against atomic number. A straight line joining Mn(II) and Zn(II) represents the situation in the absence of crystal field stabilization.

The ir discussion is confined to important bands of the ligands and their complexes. The broad bands at ~ 3350 cm^{-1} and ~ 2750 cm^{-1} in the ligands are assigned to νOH intramolecularly hydrogen bonded[13,14] and these bands disappeared in the complexes indicating the M$-$O bond formation. The value of νC$-$O band (ligands ~ 1265 cm^{-1}) shift to higher region by ~ 60 cm^{-1} in the complexes further support M$-$O bonding. A considerable fall in the intensity and frequency in νC$=$N band (ligands ~ 1650 cm^{-1} and complexes ~ 1625 cm^{-1}) indicate the M$-$N bonding[15,16]. In the ligands a strong band at ~ 3110 cm^{-1} is assigned to SO$_3-$NH$-$ group. The bands at ~ 1325 cm^{-1} (band I), ~ 1165 cm^{-1} (band II) and ~ 890 cm^{-1} are assigned to SO$_3-$N (band I and II) and S$-$N str. vibration respectively[17]. These bands remain almost on same place in the complexes and indicate that these groups are not taking part in bond formation with the metal ions. The assignments between 650-400 cm^{-1} are difficult owing to the conjugation between the M$-$O, O$-$C and C$-$C bonds. The bands in the region 560-540 cm^{-1} and 520-500 cm^{-1} may be attributed to νM$-$O and νM$-$N respectively

which may also be coupled with the ligand bands[16,18]

Electronic spectra of the metal complexes were recorded and found that the complexes, of one metal ions with different Schiff-bases, show the almost same value of d—d transition, hence approximate values are shown here for different transitions and ligand field parameters.

The magnetic moment value of Cu(II) complexes is very close to spin-only value for one unpaired electron (1.73 B.M.) which indicate that the orbital contribution is almost quenched by the crystalline field. The electronic spectra of the complexes show only three bands ~15000 cm^{-1} ($^2B_g{\rightarrow}^2A_{1g}$), ~20000 cm^{-1} ($^2B_g{\rightarrow}^2E_g$) and ~22000 cm^{-1} (charge transfer). Tetrahedral Cu(II) complexes are expected to give single broad band in the near ir region and no absorption between 10000 cm^{-1} and 200000 cm^{-1}. The d—d bands for Cu(II) complexes for which a planar structure has been proposed[19-21] to occur in the range 14000—18000 cm^{-1}. Hence the above information are consistent with an essentially planar structure.

The magnetic moment of rest of the metal complexes (Table 1) indicate the tetrahedral structure[22]. The electronic spectra of the Ni(II) complexes show two bands at ~8800 cm^{-1} [$^3T_1(F){\rightarrow}^3A_2(F)$], ~17500 cm^{-1} [$^3\Gamma_1(F){\rightarrow}^3T_1(P)$] transition. The values of ligand field parameters 10 Dq, B and β are calculated according to Figgis[23] and found to be ~4700 cm^{-1}, ~950 cm^{-1} and ~0.9 respectively. The electronic spectra of Co(II) complexes show two bands at ~7300 cm^{-1} [$^4A_2(F){\rightarrow}^4T_1(F)$] and ~16000 cm^{-1} [$^4A_2(F){\rightarrow}^4T_1(P)$]. The values of 10 Dq, B and β are found ~4000 cm^{-1}, ~920 cm^{-1} and 0.91 respectively. A broad band in the near ir region ~4400 cm^{-1} is assigned to $^5E{\rightarrow}^5T_2$ transition for Fe(II) complexes[24]. Two bands at ~20500 cm^{-1} and ~21500 cm^{-1} are observed for $^6A_1{\rightarrow}^4E(G)$ and $^6A_1{\rightarrow}^4A_1(G)$ respectively for Mn(II) complexes under study.

Acknowledgement

References

1. T. Tsukamato and K. Yuhi, Chem. Abs., 1958, 52, 1892b.

2. T. Tsukamato, Chem. Abs., 1961, 55, 5879f.

3. R. R. Gupta and R. Kaushal, J. Indian Chem. Soc., 1976, 53, 552.

4. P. Jain and K. K. Chaturvedi, J. Inorg. Nuclear Chem., 1977, 39, 901 ; 1976, 38, 799 ; J. Indian Chem. Soc., 1975, 52, 805, 1220.

5. S. V. Tatwadi, U. S. Katiyar and K. K. Narang, Curr. Sci., 1979, 48, 386.

6. K. Lal, Acta Chim. Acad. Sci., Hung., 1979, 99, 281 ; J. Indian Chem. Soc., 1979, 56, 749.

7. H. Irving and H. S. Rossotti, J. Chem. Soc. 1953, 3397 ; 1954, 2904.

8. A. I. Vogel, "A Text Book of Practical Organic Chemistry", Longman Group Ltd., London, Third Edition, 1956.

9. L. G. Van Uitert and C. G Haas, J. Amer. Chem. Soc., 1953, 75, 451.

10. K. Lal, Talanta, 1979, 26, 1171 , Indian J. Chem., 1979, 17A, 313.

11. H. Irving and R. J. P. Williams, J. Chem. Soc., 1953, 3192.

12. P. George and D. S. McClure, "Progress in Inorganic Chemistry" (Ed. F. A. Cotton), Interscience, New York, 1959, Vol. 1, p. 428.

13. K. Nakamoto. "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, 1963.

14. L. W. Lane and L. T. Taylor, J. Coord. Chem., 1973, 2, 295.

15. J. Csaszar and L. Kiss, Acta Chim. Acad. Sci., Hung., 1973, 78, 17.

16. K. Ueno and A. E. Martell, J. Phys. Chem., 1955, 59, 998 ; 1956, 60, 1270.

17. J. Brandmueller and M. Wahl, Spectrochim. Acta, 1967, 23A, 2465.

18. B. Hutchinson, D. Eversdyk and S. Albricht, Spectrochim. Acta, 1974, 30A, 1605.

19. J. P. Fackler, F. A. Cotton and D. W. Barnum, Inorg. Chem., 1963, 2, 97.

20. L. Sacconi and M. Ciampoline, J. Chem. Soc., 1964, 276.

21. U. Doraswamy and P. K. Bhattacharya, J. Inorg. Nuclear Chem., 1975, 37, 1665.

22. B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry" (Ed. F. A. Cotton). Interscience, New York, 1964, Vol. 6.

23. B. N. Figgis, "Introduction to Ligand Field", Wiley Eastern Ltd., New Delhi, 1966.

24. P. Day and C. K. Jorgenson, J. Chem. Soc., 1964, 6226.