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Physicochemical Studies of the Metal Complexes of N-(2-Hydroxy-1-Naphthalidene) anthranilic acid and N-(2-Hydroxy-1-Naphthalidene)-β-alanine (Schiff bases)

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N-(2-Hydroxy-1-Naphthalidene)anthranilic acid (H_2NA) and N-(2-Hydroxyl-1-Naphthalidene)-β-alanine ($H_2N\beta A$) Schiff bases form solid complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and UO_2(II). Elemental analysis, molecular weight, magnetic data and electronic absorption spectra conform to 1 : 1 metal-ligand stoichiometry of these compounds. Excepting Cu(II) complex which exists as a dimer, the remaining complexes exist as monomers in the solid state. The dimeric nature of the Cu(II) is explained by assigning a nonplanar bridged structure involving the two cupric ions at the opposite ends of an eight-membered ring so that superexchange is prevented between the copper atoms. The presence of nitrogen atom of the azomethine group in β-position to the carboxylic group is responsible for the behaviour of the two Schiff bases.

SIMILARITIES between salicylaldimine and naphthalidimine complexes are expected from the common O–N donor atom set of each ligand system and the presence of conjugated six-membered chelate ring in each group of complexes. Analogous to the salicylaldimine complexes of the structural type (I) there exist naphthalidimine complex (II) in which M, B and L represent metal ion, bridging group substituent and oxygen respectively.

It is reported[1],[2] that the general similarities in the magnetic behaviour of the complexes of type (I) are not dependent upon the presence or absence of the phenyl radical but it is mainly due to the presence of nitrogen atom of the azomethine group in the β-position to the carboxylic group. The present study have been undertaken to investigate whether similar situation exists for the naphthalidimine complexes (II) which are structurally similar to salicylaldimine complexes (I).

A survey of the literature[3] reveals that no systematic investigation has been carried out using anthranilic acid and β-alanine Schiff bases with 2-hydroxy-1-naphthaldehyde[4],[5]. Anthranilic acid and β-alanine possess a phenyl group and an open chain molecule respectively. Both form biprotic tridentate Schiff bases with 2-hydroxy-1-naphthaldehyde and these are structurally similar.

Experimental

Materials and Methods :

AnalaR (BDH) reagents of metal salts were used for the synthesis of the metal complexes. Anthranilic acid and β-alanine (L.R.) supplied by BDH were used without further purification. A.R. 2-hydroxy-1-naphthaldehyde (Flucka) was employed in the preparation of the Schiff bases.

Gallenkamp Semi-micro Ebulliometer was used to determine the molecular weights of the solid complexes employing benzene as the solvent. Hosli's electrical micro combustion furnace was used for combustion analysis. Magnetic susceptibility measurements were made on Guoy apparatus. The electronic absorption spectra were recorded using Uvispeck Hilger Spectrophotometer.

Preparation of the Schiff bases and their metal complexes :

The Schiff bases N-(2-hydroxy-1-naphthalidene)-anthranilic acid and N-(2-hydroxy-1-naphthalidene)-β-alanine, were synthesised by the method of Pfeiffer *et al.*[6] and their metal complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and UO_2(II) by the method of Yamada *et al.*[7],[8]. The pyridine solvates of these complexes were obtained by the method reported earlier[1]. However Cu(II) does not form a hydrated complex or its pyridine solvate with these ligands.

Results and Discussion

Elemental analyses, molecular weight, magnetic data and electronic absorption spectra of the complexes are given in Tables 1 to 3.

A perusal of the data summarized in Tables 2 and 3 suggest that the behaviours of N-(2-hydroxy-1-naphthalidene)-anthranilic acid and N-(2-hydroxy-1-naphthalidene)-β-alanine are similar. In general, their metal complexes display 1 : 1 metal-ligand stoichiometry. The molecular weight data given

TABLE 1—ELEMENTAL ANALYSIS AND MOLECULAR WEIGHTS OF THE METAL COMPLEXES OF N-(2-HYDROXY-1-NAPHTHALIDENE) ANTHRANILIC ACID AND N-(2-HYDROXY-1-NAPHTHALIDENE)-β-ALANINE.

Metal Complex	Hydrated complexes								Pyridine complexes					
	Molecular weight		Metal (%)		Nitrogen (%)		Water (%)		Molecular weight		Metal (%)		Nitrogen (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	N-(2-Hydroxy-1-Naphthalidene)anthranilic acid													
$Fe(C_{18}H_{11}NO_3)X_3$	407	398.4	13.84	13.99	3.47	3.51	13.46	13.54	568	579.8	9.58	9.62	9.55	9.65
$Co(C_{18}H_{11}NO_3)X_3$	385	401.9	13.57	14.65	3.41	3.48	13.38	13.43	591	584.9	9.98	10.07	9.49	9.57
$Ni(C_{18}H_{11}NO_3)X_3$	391	401.7	13.54	14.61	3.40	3.48	13.54	13.61	594	584.7	9.96	10.04	9.46	9.58
$Cu_2(C_{18}H_{11}NO_3)_2$	695	705.0	17.97	18.01	3.86	3.97	—	—	—	—	—	—	—	—
$Zn(C_{18}H_{11}NO_3)$	360	372.4	17.47	17.56	3.65	2.75	4.76	4.83	430	433.4	15.00	15.09	6.39	6.46
$Pd(C_{18}H_{11}NO_3)X$	401	413.4	25.56	25.76	3.31	3.38	4.22	4.35	461	474.4	22.27	22.42	4.71	5.90
$Cd(C_{18}H_{11}NO_3)X$	427	419.4	26.71	26.80	3.26	3.33	4.20	4.29	483	480.4	23.26	23.39	5.69	5.82
$UO_2(C_{18}H_{11}NO_3)X$	569	577.0	41.19	41.24	2.36	2.42	3.01	3.11	616	638.0	37.24	37.31	4.22	4.38
	N-(2-Hydroxy-1-Naphthalidene)-β-alanine													
$Fe(C_{14}H_{10}NO_3)X_3$	365	350.8	15.88	15.91	3.89	3.99	15.27	15.39	544	533.8	10.32	10.45	10.37	10.49
$Co(C_{14}H_{10}NO_3)X_3$	370	353.9	16.58	16.64	3.91	3.96	15.21	15.26	527	536.9	10.82	10.97	10.32	10.43
$Ni(C_{14}H_{10}NO_3)X_3$	372	353.7	16.55	16.63	3.87	3.98	15.22	15.27	526	536.7	10.80	10.94	10.31	10.43
$Cu_2(C_{14}H_{10}NO_3)_2$	598	609.0	20.77	20.85	4.46	4.59	—	—	—	—	—	—	—	—
$Zn(C_{14}H_{10}NO_3)X$	340	324.4	20.03	20.16	4.12	4.32	5.48	5.54	390	385.7	16.81	16.96	7.14	7.26
$Pd(C_{14}H_{10}NO_3)X$	355	365.4	29.01	29.12	3.74	3.83	4.87	4.93	437	426.4	24.82	24.95	6.46	6.56
$Cd(C_{14}H_{10}NO_3)X$	383	371.4	30.07	30.26	3.64	3.77	4.73	4.84	441	432.4	25.84	25.99	6.39	6.46
$UO_2(C_{14}H_{10}NO_3)X$	539	529.0	44.89	44.99	2.52	2.64	3.32	3.40	600	590.0	40.12	40.34	4.67	4.75

X is either H_2O or Pyridine (abbr. Py)

TABLE 2—ELECTRONIC ABSORPTION SPECTRA AND MAGNETIC MOMENT DATA OF THE METAL COMPLEXES OF N-(2-HYDROXY- 1-NAPHTHALIDENE) ANTHRANILIC ACID

Metal Complex	Hydrated complexes					Pyridine complexes				
	$\chi_s \times 10^6$ at 303°K	$\chi_m \times 10^6$	Magnetic moment B.M.	No. of unpaired electrons	ν_{max} (cm^{-1})	$\chi_s \times 10^6$ at 303°K	$\chi_m \times 10^6$	Magnetic moment B.M.	No. of unpaired electrons	ν_{max} (cm^{-1})
$Fe(C_{18}H_{11}NO_3)X_3$	27.8770	11322.10	5.20	4	—	19.3932	11450.70	5.29	4	—
$Co(C_{18}H_{11}NO_3)X_3$	24.5942	10064.16	4.96	3	13330, 21740	17.8934	10601.20	5.09	3	14200, 21600
$Ni(C_{18}H_{11}NO_3)X_3$	8.0570	3415.14	2.89	2	17540, 24390	6.1399	3731.94	3.02	2	16900, 24500
$Cu_2(C_{18}H_{11}NO_3)_2$	1.7182	1461.65	1.89*	1	14080	—	—	—	1	23810, 11900

Zn(II), Pd(II), Cd(II) and UO_2(II) complexes were found to be diamagnetic, as expected.

* The magnetic moment for each Cu(II) ion in the complex is 1.89 B.M

TABLE 3—ELECTRONIC ABSORPTION SPECTRA AND MAGNETIC MOMENT DATA OF THE METAL COMPLEXES OF N-(2-HYDROXY-1-NAPHTHALIDENE)-β-ANALANINE

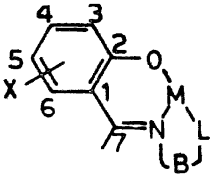
Metal Complexes	Hydrated Complexes					Pyridine Complexes				
	$\chi_s \times 10^6$ at 300°K	$\chi_m \times 10^6$	Magnetic moment B.M.	No. of unpaired electrons	ν_{max} (cm^{-1})	$\chi_s \times 10^6$ at 303°K	$\chi_m \times 10^6$	Magnetic moment B.M.	No. of unpaired electrons	ν_{max} (cm^{-1})
$Fe(C_{14}H_{10}NO_3)X_3$	31.9469	11364.30	5.27	4	—	22.1670	11931.90	5.40	4	—
$Co(C_{14}H_{10}NO_3)X_3$	28.9636	10406.44	5.04	3	13510, 27030	19.7597	10726.50	5.12	3	13000, 27450
$Ni(C_{14}H_{10}NO_3)X_3$	8.8691	3300.33	2.86	2	13160, 25000	7.2478	3806.45	3.05	2	13000, 25100
$Cu_2(C_{14}H_{10}NO_3)_2$	1.8610	1446.23	1.88*	1	13360, 26670	—	—	—	1	12660, 25640

Zn(II), Pd(II), Cd(II) and UO_2(II) are found diamagnetic as expected.

* The magnetic moment for each Cu(II) ion in the complex is 1.88 B.M.

in Table 1 indicate that Fe(II), Co(II) and Ni(II) complex possess the composition [MLX_3], where M = Fe(II), Co(II) or Ni(II): X = H_2O or Py and LH_2 = [$C_{18}H_{13}NO_3$] or [$C_{14}H_{13}NO_3$]. Their magnetic moments indicate the presence of 4, 3 and 2 unpaired electrons in the Fe(II), Co(II) and Ni(II) complexes respectively. The high magnetic moments of Co(II) complexes seem to be due to spin-orbit coupling. The electronic absorption spectra of Co(II) and Ni(II) complexes in dioxan and pyridine were recorded and their frequency maxima are summarized in Tables 2 and 3. These frequencies correspond to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions for the Co(II) complexes and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ for the Ni(II) complexes. These data support a near octahedral structure for Co(II) and Ni(II) complexes.

The spectral studies supported by elemental analysis and molecular weight data (Table 1) suggest an octahedral structure for Co(II) and Ni(II) complexes.



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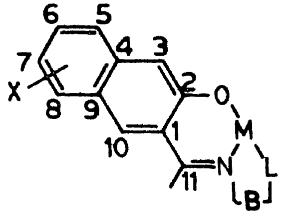

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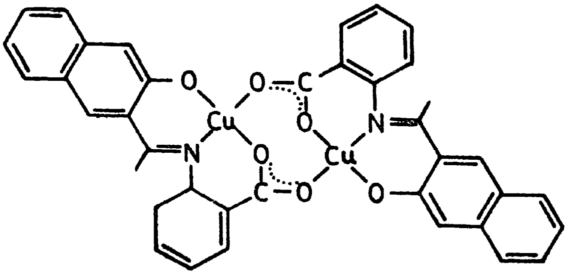

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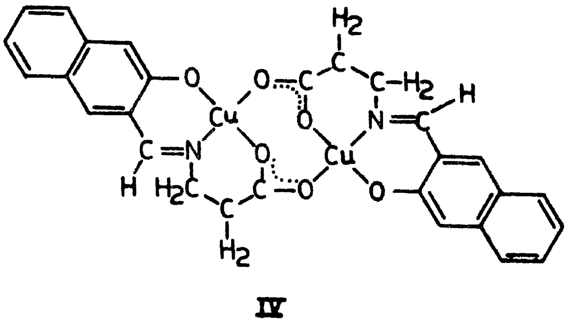

IV

However, Cu(II) displays an anomalous behaviour. It does not form solvated complexes as is evident from the elemental analysis and molecular weight data (Tables 1 to 3) which also suggest the existence of these Cu(II) complexes as dimers in the solid state. I.R. data of the Cu(II) complex in carbonyl region indicate the presence of anti-symmetric COO^- stretching vibrations (1580–1595 cm^{-1}) and the absence of bands around 3650 cm^{-1} due to –OH group and 3250 cm^{-1} due to coordinated water molecule. These results confirm that the Cu(II) complexes are not hydrated ones. The electronic absorption spectra of the Cu(II) complexes in dioxan and pyridine were recorceded and are given in Tables 2 and 3. The band at 14,080 cm^{-1} or 13,360 cm^{-1} may be due to the electronic transition $^2E \rightarrow {}^2T_2$ of the Cu(II) and the other at 23,810 cm^{-1} or 26,670 cm^{-1} is due to an intra-ligand charge transfer band (redox spectra). Cu(II) complexes of H_2NA and $H_2N\beta A$ display normal magnetic moments of 1·89 and 1·88 B.M. at 303°K (Table 2) respectively for each Cu^{2+} ion in the complexes.

Based on the analogy with the copper(II) complexes of N-salicylaldine anthranilic acid[9] and N-salicylalidene-β-alanine[1], it is suggested that the Cu(II) complexes under study, shuld also possess non-planar dimeric bridged structures (III and IV) involving delocalized carboxylic group and in which the two cupric ions are assumed to be too far apart for direct spin-exchange and are located at the opposite ends of an eight-membered ring thereby effectively preventing super-exchange via the intermediate atoms. Thus these structures find some support from the experimental data (Tables 1-3). However, the confirmation of these structures need further investigation.

The Zn(II), Pd(II), Cd(II) and UO_2(II) complexes of the Schiff bases under study also exhibit 1 : 1 metal-ligand stoichiometry and their composition can be represented by [MLX], where M stands for the metal ion, $LH_2 = [C_{18}H_{13}NO_3]$ or $[C_{14}H_{13}NO_3]$ and X = H_2O or Py. The hydrated complexes and their pyridine solvates have been experimentally found diamagnetic, as expected. These data can be explained by assigning a tetrahedral structure for Zn(II) and Cd(II) complexes, a square-planar structure for Pd(II) complexes and an octahedral structure for UO_2(II) complexes.

The results so far obtained conclusively prove that the complexes of the general type II derived from these Schiff bases are not dependent upon the presence or absence of the phenyl group and the general similarly is due to the presence of the nitrogen atom of the azomethine group in β-position to the carboxylic group. This result is also in agreement with earlier findings[1,10].

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