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Study of Diamagnetism in Uranyl Complexes of Some Schiff Bases

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Uranyl complexes of Schiff bases obtained by condensing 2-hydroxy-1-naphthaldehyde or salicylaldehyde with aromatic amines have been isolated and characterised. The complexes have the formula $[M(LH)_2(NO_3)_2]$ where $M = UO_2$ and LH = Schiff base. The magnetic susceptibilities of these complexes have been measured on Gouy balance. These values have been compared with the computed ones, obtained by adding the molar susceptibilities of the components, assuming strict additivity. The deviations between the observed and computed values of molar magnetic susceptibility have been discussed in the light of Van Vleck's equation for molar susceptibility of polyatomic molecules.

INTRODUCTION

A large number of metal complexes with Schiff base ligands derived from aromatic aldehydes with aromatic amines are known.[1] Solution stability constants of the complexes of Schiff bases with various metal ions have been extensively studied[2]. In the present communication we report synthesis and magnetic properties of some uranyl complexes of Schiff bases.

EXPERIMENTAL

Uranyl nitrate used was of AR grade and 2-hydroxy-1-napthaldehyde and salicylaldehyde were of E. Merck quality. Aniline, amino-acids and aminophenols were of LR grade. They were purified by conventional methods.

Preparation of Schiff Bases

The Schiff bases were prepared by refluxing calculated quantities of 2-hydroxy-1-napthaldehyde or salicylaldehyde and corresponding amine in ethanolic medium for 2 h. Solidification occurred on cooling. In some cases the reaction was instantaneous, but even then the mixture was refluxed for 2 h. The resulting compounds were purified by recrystalling from ethanol. The Schiff bases thus obtained were yellow or orange in colour. The skeleton structures of Schiff bases thus prepared are represented below.

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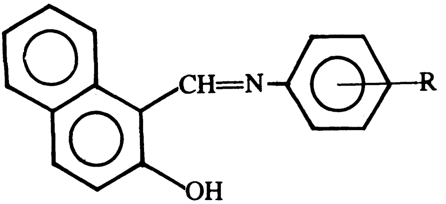

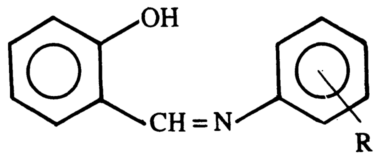

where R=H, 2–COOH, 3–COOH, 4–COOH, 2–OH, 3–OH and 4–OH.

Preparation of Complexes

The complexes were prepared by refluxing one part of metal salt and two parts of ligand in ethanolic medium. Some complexes were prepared by dissolving the ligands in dioxane and metal salts in ethanol and then refluxing for 3–4 h. The complexes obtained were yellow to orange in colour. These complexes were filtered and washed with ethanol and dioxane and dried under reduced pressure over fused $CaCl_2$. Uranium content in the complexes was estimated as U_3O_8 gravimetrically and nitrogen was estimated by conventional method. The elemental analysis values thus obtained are reported in Table 1.

The magnetic susceptibility of all the complexes were measured at room temperature (300 K) on a modified form of Gouy balance as described by Prasad *et al.*[3] The values of specific susceptibility (χ) and molar susceptibility (χ_m) of all complexes were determined. The molar magnetic susceptibilities of complexes were computed using Pascal additivity law and the value of susceptibility for uranyl ion required for this purpose was taken from literature. The results thus obtained are summarised in Table 1.

RESULTS AND DISCUSSION

It is evident from results that all complexes are diamagnetic. This indicates that all of them are spin paired complexes of hexavalent uranium. Assuming the Pascal's additivity law, molar magnetic susceptibilities of all the complexes were computed. Further the computed values of molar magnetic susceptibility were found to be higher than the experimental values. These deviations are beyond experimental error and therefore significant.

According to Van Vleck[4] the susceptibility of polyatomic molecule without a resultant spin is given by the equation $\chi_m = \chi_d + \chi_p$. where χ_d represents diamagnetic term and is a function of $\sum_{n} \overline{r}^2$ (the radius of all electronic orbits in the molecule) and χ_p represents the second order paramagnetism, independent of temperature arising on account of the mixing of the ground state and excited states of electrons in the molecule. If the metal-nitrogen (or ligand) bond in the complex is sufficiently strong, the associating units will come very close to metal atom thus decreasing the value of $\sum_{n} \overline{r}^2$ and hence that of diamagnetic susceptibility of the molecule.

The magnitude of diamagnetic unsusceptibility is directly proportional to the square of the effective radius of ion. Other parameters being identical any

TABLE 1
ANALYTICAL AND MAGNETIC SUSCEPTIBILITY DATA OF URANYL COMPLEXES

Compound (C) (Complexing ligand)	Analysis % Found (Calcd.)		Mol. Wt.	$\chi_{(Specific)}$ $\times 10^{-6}$ c.g.s	$\chi_{m\ (obs)}$	χ'_m (Comptd)	$\Delta\chi_m = \chi_p$ $= (\chi_m - \chi'_m)$	% $\Delta\chi_m$
	N	U						
$[UO_2(C_{13}H_{11}ON)_2]\ (NO_3)_2\ (C_1)$ (salicylidene-anil)	6.60 (7.11)	30.56 (30.18)	788.54	0.2400	189.12	210.18	−21.06	−11.13
$[UO_2(C_{14}H_{11}O_3N)_2](NO_3)_2(C_2)$ (2′-carboxylic acid-salicylidene-anil)	5.93 (6.39)	27.06 (27.16)	876.57	0.2298	201.43	241.15	−39.71	−19.71
$[UO_2(C_{14}H_{11}O_3N)_2](NO_3)_2(C_3)$ (3′-carboxylic acid-salicylidene-anil)	6.01 (6.39)	27.36 (27.16)	876.57	0.1929	169.13	241.15	−72.02	−42.58
$[UO_2(C_{14}H_{11}O_3N)_2](NO_3)_2(C_4)$ (4′-carboxylic acid-salicylidene-anil)	5.62 (6.39)	26.28 (27.16)	876.57	0.2211	193.81	241.15	−47.34	−24.42
$[UO_2C_{13}H_{11}O_2N]_2(NO_3)_2(C_5)$ (2′-hydroxy-salicylidene--anil)	6.28 (6.83)	28.56 (29.01)	822.55	0.2501	205.22	222.78	−17.56	−8.55
$[UO_2(C_{13}H_{11}O_2N)_2](NO_3)_2(C_6)$ (3′-hydroxy-salicylidene-anil)	6.50 (6.83)	28.62 (29.01)	822.55	0.2362	193.81	222.78	−28.97	−14.94
$[UO_2(C_{13}H_{11}O_2N)_2](NO_3)_2(C_7)$ (4′-hydroxy-salicylidene-anil)	6.10 (6.83)	29.38 (29.01)	822.55	0.2559	209.98	222.78	−12.8	−6.09
$[UO_2(C_{17}H_{13}NO)_2](NO_3)_2(C_8)$ (2-hydroxy-1-naphthalidene-anil)	6.02 (6.30)	27.06 (26.80)	888	0.3191	283.36	328.72	−45.36	−16.00
$[UO_2(C_{18}H_{13}O_3N)_2](NO_3)_2(C_9)$ (2′-carboxylic acid-2-hydroxy-1-naphthalidene-anil)	4.92 (5.76)	24.86 (24.37)	976.72	0.3280	320.36	360.34	−39.98	−12.47

$[UO_2(C_{18}H_{13}O_3N)_2](NO_3)_2(C_{10})$ (3′-carboxylic acid-2-hydroxy-1-naphthalidene-anil)	5.06 (5.76)	24.86 (24.37)	976.72	0.3111	303.85	360.34	–56.49	–18.58
$[UO_2(C_{18}H_{13}O_3N)_2](NO_3)_2(C_{11})$ 4′-carboxylic acid-2-hydroxy-1-naphthalidene-anil	4.98 (5.76)	23.74 (24.37)	876.72	0.3016	294.58	360.34	–65.76	–22.32
$[UO_2(C_{17}H_{13}O_2N)_2](NO_3)_2(C_{12})$ 2′-hydroxy-2-hydroxy-1-naphthalidene-anil	5.77 (6.09)	25.44 (25.85)	920.66	0.3101	285.49	341.62	–56.12	–19.65
$[UO_2(C_{17}H_{13}O_2N)_2](NO_3)_2(C_{13})$ 3′-hydroxy-2-hydroxy-1-naphthalidene-anil	5.97 (6.09)	24.66 (25.85)	920.66	0.3080	283.56	341.62	–58.06	–20.47
$[UO_2(C_{17}H_{13}O_2N)_2](NO_3)_2(C_{14})$ 4′-hydroxy-2-hydroxy-1-naphthalidene-anil	5.48 (6.09)	25.18 (25.85)	920.66	0.2967	273.15	341.62	–68.47	–25.06

distortion that causes deviation from close packing results in the increase of effective radius of ion. Thus distortion in general, gives rise to a large diamagnetic susceptibility.

Freed and Kasper[5] and Lawrence[6] have observed that χ_p term is definitely present in uranyl complexes. Van Vleck attributed this paramagnetism to the matrix elements of the magnetic operator $\beta(L + 2S)$ between the ground state and higher state. The contribution from spin magnetic moment is zero since all spins are paired off in the ground state. As the largest orbital contribution comes from $5f_6$ bonding electrons, Eisenstein and Pryce[7] have assumed that f-electrons are responsible for the magnetism of uranyl ion. Belford and Belford[8,9] have shown from orbital overlap integral calculations, that $5f_6$ uranium orbitals do not overlap much with the oxygen orbitals as the 6d-orbitals do and that considerable π-bonding also might be involved. An attempt has been made to examine the magnetic susceptibility values of isomeric substituted complexes. A glance at the values of χ_m suggests that introduction of substituents in amine ring of Schiff base at various positions causes an increase in the diamagnetic susceptibility value. Langevin's theory postulates that a decrease in effective positive charge will result in an increase in the diamagnetic susceptibility. Since the nature of various ligands complexing with uranyl ion are similar in structure, it is concluded that comparison of χ_p values will be possible. Examination of results shows that χ_p value varies with the nature of the ligands. Considering the temperature independent paramagnetism χ_p term as a measure of ligand field strength, the following order of ligand field strength is established:

I. Salicylidene-anil > 2′-carboxylic acid-salicylidene-anil > 4′-carboxylic acid-salicylidene-anil > 3′-carboxylic acid-salicylidene-anil

II. 4′-Hydroxy salicylidene-anil > 2′-hydroxy-salicylidene-anil > salicylidene -anil > 3′-hydroxy salicylidene-anil

III. 2′-Carboxylic acid-2-hydroxy-1-naphthalidene-anil > 2-hydroxy-1-naphthalidene-anil > 3′-carboxylic acid-2-hydroxy-1-naphthalidene-anil > 4′-carboxylic acid-2-hydroxy-1-naphthalidene-anil.

IV. 2-Hydroxy-1-naphthalidene-anil > 2′-hydroxy-2-hydroxy-1-naphthalidene -anil > 3′-hydroxy 2-hydroxy-1-naphthalidene-anil > 4′-hydroxy-2-hydroxy-1-naphthalidene-anil.

According to French[10], if the substituent is *ortho & para* directing, the *ortho* compound should have higher susceptibility than either *meta* or *para* compound, while when the substituent is *meta* directing, the compound has higher susceptibility values than the other substituent. This difference is attributed to the presence of higher electron density at the *ortho* position in compounds containing two electron repelling groups *ortho* to each other and in *meta* compound to a higher electron density at *meta* position when two groups are at *meta* position to each other. The above order indicates that authors' findings are in partial agreement with the above view.

Percentage Deviation and Symmetry of the Molecule

In the Schiff base complexes studied co-ordination occurs through nitrogen[11-14] and that the bonds involved are of co-ordinate covalent type. These bonds are likely to cause contraction of the electronic orbits whereby values of $\Sigma_n \bar{r}^2$ of the molecule is decreased. Since diamagnetic susceptibility is a radial function, the decrease in the value of $\Sigma_n \bar{r}^2$ would lower the diamagnetic susceptibility of complex molecule. The view is supported by negative deviation observed by the authors.

It is thus clear that the observed deviation from additivity may be due to change in χ_d term of Van Vleck's equation. Further, since the bond between component molecule is strong, it is likely to bring about a change in symmetry of the component molecule. χ_p term, which is also dependent on symmetry of the molecule, is likely to be affected due to this type of bonding. Thus the observed deviation from additivity may be on account of the changes in the term χ_d and χ_p both. The deviation is therefore the net result of the two opposing effects χ_d and χ_p having opposite signs. Since symmetry of the complex formed may be entirely different from that of the constituent molecule, the change in χ_p term would obviously be more significant.

It appears that χ_p term is more significant in bringing about change in molar susceptibility of the complex. This term is dependent upon the symmetry of the molecule and hence greater the symmetry of the molecule smaller will be its contribution to χ_p in Van Vleck's equation. It is therefore expected that greater the symmetry of the molecule smaller will be the deviation[15,16] from additivity and vice-versa. Hence all the complexes reported in this investigation appear to be distorted.

The molar susceptibility values of the complexes were plotted against total number of electrons Σ_z. From the plot it appears that only few points lie on the straight line and most of them lie close to the straight line. It has been assumed that the line should pass through the origin. When the total number of electrons in the complex is zero χ_m should also be zero and the straight line should pass through origin. This observation is in conformity with the one made by Prasad and Mulay[17]. As the points do not lie exactly on the straight line, it shows that during formation of complex the components have undergone deformation, which is responsible for significant deviations from additivity of magnetic susceptibility.

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