Asian Journal of Chemistry Vol. 6, No. 4 (1994), 960–967

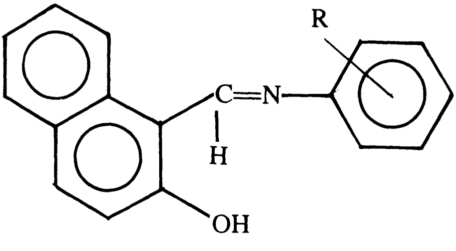
Magnetic Susceptibility and Molecular Structure; Study of Uranyl Complexes with Schiff Bases of 2-Hydroxy-1-Naphthaldehyde and Some Aryl Amines

S.S. DODWAD*
Physical Chemistry Division, The Institute of Science
15, Madam Cama Road, Fort, Bombay-400 032, India

Uranyl complexes of some Schiff bases obtained by condensing some aryl amines with 2-hydroxy-1-naphthaldehyde are synthesised and characterised by elemental analysis, spectral and conductivity data. All the complexes are orange-red to red in colour, microcrystalline in nature and form compounds of the type $[UO_2(LH)_2](CH_3COO)_2$ where (LH) is a Schiff base molecule. The bonding with the metal in the complexes takes place from hydroxyl oxygen and imine nitrogen of the ligand. It is observed that uranyl ion form 1 : 2 adducts with these Schiff bases. Conductivity measurements, analytical data and spectral study show that these complexes have co-ordination number eight with hexagonal bipyramid structure. All the complexes studied are spin paired, since they exhibit property of diamagnetism. Diamagnetism of complexes is discussed.

INTRODUCTION

Metal complexes with Schiff bases of 2-hydroxy-1-naphthaldehyde with various aromatic amines are known. In the present communication, the authors report the synthesis and physical properties of a few uranyl complexes with Schiff bases shown below:



Ligand (m.f.)	*R*	*Ligand (m.f.)*	*R*
$L_1(C_{17}H_{13}ON)$	H.	$L_6(C_{17}H_{12}ONCl)$	3-Cl
$L_2(C_{18}H_{15}ON)$	2-CH_3	$L_7(C_{17}H_{12}ONCl)$	4-Cl
$L_3(C_{18}H_{15}ON)$	3-CH_3	$L_8(C_{17}H_{12}O_3N_2)$	2-NO_2
$L_4(C_{18}H_{15}ON)$	4-CH_3	$L_9(C_{17}H_{12}O_3N_2)$	3-NO_2
$L_5(C_{17}H_{12}ONCl)$	2-Cl	$L_{10}(C_{17}H_{12}O_3N_2)$	4-NO_2

---

*Present address: Principal, S.I.W.S. (Smt) Thirumalai College of Science, Wadala, Bombay-400 031, India.

EXPERIMENTAL

Uranyl acetate used for preparing the complexes was of A.R. grade. 2-Hydroxy-1-naphthaldehyde used was of Fluka make. All the aromatic amines used were of L.R. grade, which were purified by conventional methods. The Schiff bases were prepared by refluxing calculated quantities of 2-hydroxy-1-naphthaldehyde and corresponding aromatic amines in alcoholic medium for 1–2 h. The compound solidified rapidly on cooling which was recrystallised in ethanol. All the Schiff bases crystallised as light yellow to orange yellow coloured crystals. They exhibit the property of thermochromism and photochromism. The complexes were prepared[1, 2] by refluxing 1 part of uranyl acetate and two parts of ligand in ethanolic medium for 1–2 h. On cooling the orange-red to red coloured complexes were separated. They were filtered, washed with alcohol and dried in vacuum over fused $CaCl_2$. The purity of the complexes was ascertained by elemental analysis. The results of elemental analysis are given in Table 1.

TABLE 1
COLOUR, ELEMENTAL ANALYSIS, FORCE CONSTANT AND BOND LENGTH OF URANYL COMPLEXES

Complex No.	Complex/Colour	% Analysis Found (Calcd.)		Force constant F_{UO} in m dynes/Å	Bond length R_{UO} in Å
		U	N		
C_1	$[UO_2(C_{17}H_{13}ON)_2](CH_3COO)_2$ (Orange)	26.74 (26.98)	3.50 (3.17)	7.03	1.73
C_2	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (Orange)	26.03 (26.15)	3.60 (3.07)	7.03	1.73
C_3	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (Orange red)	25.90 (26.15)	3.30 (3.07)	7.18	1.73
C_4	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (Orange red)	26.10 (26.15)	2.20 (3.07)	6.88	1.74
C_5	$[UO_2(C_{17}H_{12}ONCl)_2](CH_3COO)_2$ (Orange red)	25.15 (25.02)	3.15 (2.94)	6.88	1.74
C_6	$[UO_2(C_{17}H_{12}ONCl)_2](CH_3COO)_2$ (Orange red)	24.86 (25.02)	2.70 (2.94)	7.18	1.73
C_7	$[UO_2(C_{17}H_{12}ONCl)_2](CH_3COO)_2$ (Orange red)	24.80 (25.02)	2.90 (2.94)	7.33	1.73
C_8	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (Orange red)	24.10 (24.48)	6.10 (5.76)	6.88	1.74
C_9	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (Orange red)	24.19 (24.48)	5.95 (5.76)	7.03	1.73
C_{10}	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (Red)	24.88 (24.48)	5.90 (5.76)	7.18	1.73

RESULTS AND DISCUSSION

The complexes obtained are orange red to red in colour, microcrystalline in nature and are insoluble in water and in common organic solvents. However they are freely soluble in DMF. This insolubility did not permit the determination of their molecular weights. The results of elemental analysis suggest that the complexes have 1 : 2 stoichiometry.

It is observed that the molar conductances in DMF at 10^{-3}M are in the range of 150–165 ohm^{-1} cm^2 $mole^{-1}$, indicating that the complexes behave as 1 : 2 electrolytes. This is in accordance with the observations of Geary[4]. It is clear from conductivity data that the complexes behave as strong electrolytes and that the DMF molecules replace the weakly coordinated acetate groups from the coordination sphere[5].

The infrared spectra of the Schiff bases and their complexes exhibit a weak band characteristic of aromatic C—H stretching vibration in the range of 3025–2900 cm^{-1}. The spectra of the ligands as well as their complexes show a strong, sharp or medium to high intensity band in the region 1605–1420 cm^{-1} which is assigned to C═C stretching vibration. In the complexes as well as the ligands a strong and sharp band in the regions 1370–1330 cm^{-1} and 1210–1180 cm^{-1} is attributed to the C—O stretching vibration. A characteristic frequency observed in the region 930–910 cm^{-1} in all the complexes is assigned to UO_2 ion and agrees well with the values reported in the literature[6–9]. Absence of measurable absorption in the infrared region characteristic of OH absorption (3650–3590 cm^{-1}) has been attributed to the existence of intramolecular hydrogen bonding. The formation of a bond between the oxygen of the OH group and the metal in all the complexes increases the electron density on the latter. Consequently, the frequency for C═C will shift towards higher wave number side due to increase in C—N bond order[11, 12]. This observable shift obtained in the C═N stretch after complexing confirms the formation of a coordinate bond from oxygen and imine nitrogen to the metal in the complexes. A strong band which is observed in all the complexes but not in the ligands, in the region 3390–3480 cm^{-1} may be attributed to acetate group. Further the bands observed at 1440 cm^{-1}, 926 cm^{-1} and 646 cm^{-1} substantiates[13–15] the coordinated acetate ion. Table 2 summarises all these IR frequencies.

On the basis of analytical data, conductivity measurements and infrared spectral data, it may be suggested that the complexes have coordination number eight with hexagonal bipyramid structure and is represented as

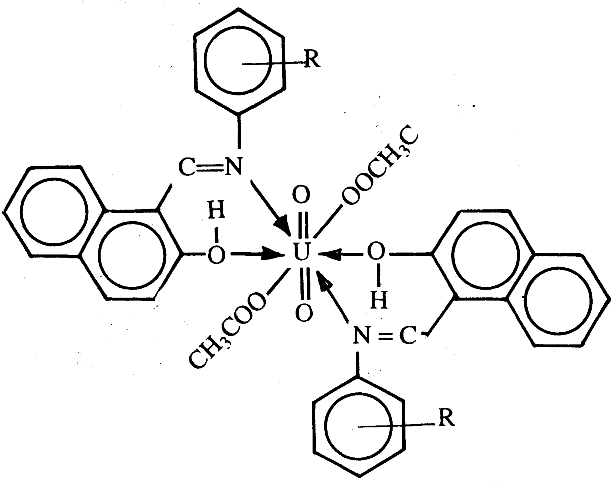


TABLE 2
SELECTED IR FREQUENCIES (cm^{-1}) OF SCHIFF BASES (L) AND THEIR URANYL COMPLEXES (C)

Compd. No.	Aromatic CH stretching vibrations	C═N stretching vibrations	Aromatic C═C stretching vibrations	C—O stretching vibrations	OH bending vibrations	ν(O═U═O)
L_1	—	1620 (s)	1590 (m) 1545 (m) 1535 (sh)	1350 (sh) 1210 (s)	1320 (sh)	—
L_2	2930 (w)	1620 (sh)	1605 (sh) 1585 (sh) 1560 (sh) 1485 (sh)	1605 (sh) 1200 (s)	1275 (sh)	—
L_3	2920 (w)	1615 (sh)	1580 (sh) 1500 (sh)	1325 (sh) 1200 (sh)	1300 (s)	—
L_4	2900 (w)	1610 (sh)	1575 (m) 1500 (m)	1340 (m) 1210 (m)	1300 (sh)	—
L_5	—	1615 (s)	1600 (sh) 1560 (sh) 1470 (m)	1330 (sh) 1190 (sh)	1270 (m)	—
L_6	—	1615 (sh)	1600 (m) 1565 (sh) 1465 (m)	1330 (m) 1180 (m)	1270 (m)	—
L_7	—	1615 (sh)	1600 (sh) 1485 (s)	1330 (m) 1210 (m)	1295 (m)	—
L_8	—	1620 (sh)	1595 (m) 1565 (m) 1505 (sh)	1335 (sh) 1210 (m)	1269 (m)	—
L_9	3000 (w)	1615 (sh)	1600 sh 1515 (s) 1570 (m)	1350 (s) 1210 (m)	1300 (sh)	—
L_{10}	—	1610 (sh)	1570 (sh) 1495 (sh) 1540 (m)	1330 (s)	1285 (sh)	—
Uranyl Complex of $L_1(C_1)$	3025 (w)	1630 (s)	1585 (s) 1520 (s) 1485 (sh) 1465 (sh)	1360 (sh) 1155 (sh)	1310 (s)	920s
Uranyl Complex of $L_2(C_2)$	—	1630 (s)	1580 (sh) 1520 (m) 1465 (s)	1365 (sh) 1160 (sh)	1320 (s)	920s
Uranyl Complex of $L_3(C_3)$	2900 (w)	1600 (s)	1580 (sh) 1530 (sh) 1475 (m) 1450 (m)	1360 (sh) 1180 (sh)	1310 (s)	930s
Uranyl Complex of $L_4(C_4)$	2925 (w)	1630 (s)	1540 (m) 1520 (sh) 1485 (sh) 1465 (m)	1370 (sh) 1150 (sh)	1320 (s)	910s

Compd. No.	Aromatic CH stretching vibrations	C=N stretching vibrations	Aromatic C=C stretching vibrations	C—O stretching vibrations	OH bending vibrations	ν(O=U=O)
Uranyl Complex of $L_5(C_5)$	—	1610 (s)	1565 (s) 1540 (w) 1510 (sh) 1460 (sh)	1355 (sh) 1150 (sh)	1310 (s)	910s
Uranyl Complex of $L_6(C_6)$	—	1625 (s)	1590 (s) 1540 (w) 1510 (s) 1460 (s)	1360 (s) 1150 (s)	1310 (s)	930s
Uranyl Complex of $L_7(C_7)$	—	1630 (s)	1580 (s) 1520 (m) 1480 (s) 1460 (m)	1370 (s) 1150 (s)	1310 (s)	940s
Uranyl Complex of $L_8(C_8)$	2980 (w)	1610 (s)	1540 (s) 1460 (s) 1420 (m)	1350 (s) 1170 (s)	1310 (s)	910s
Uranyl Complex of $L_9(C_9)$	—	1610 (s)	1580 (m) 1520 (s) 1480 (m)	1350 (s) 1160 (s)	1310 (s)	920s
Uranyl Complex of $L_{10}(C_{10})$	3020 (w)	1615 (s)	1520 (s) 1480 (m) 1450 (s)	1330 (m) 1160 (s)	1300 (s)	930s

b = broad, m = medium, s = strong, sh = sharp, w = weak
L_1 = 2-hydroxy-1-naphthalidene-anil,
L_2 = 2′-methyl-2-hydroxy-1-naphthalidene-anil,
L_3 = 3′-methyl-2-hydroxy-1-naphthalidene-anil,
L_4 = 4′-methyl-2-hydroxy-1-naphthalidene-anil,
L_5 = 2′-chloro-2-hydroxy-1-naphthalidene-anil,
L_6 = 3′-chloro-2-hydroxy-1-naphthalidene-anil,
L_7 = 4′-chloro-2-hydroxy-1-naphthalidene-anil,
L_8 = 2′-nitro-2-hydroxy-1-naphthalidene-anil,
L_9 = 3′-nitro-2-hydroxy-1-naphthalidene-anil,
L_{10} = 4′-nitro-2-hydroxy-1-naphthalidene-anil,

Magnetic susceptibilities of uranyl complexes were measured on Gouy balance at room temperature as described by Prasad *et al.*[16] The values of specific susceptibility (χ) and molar susceptibility (χ_m) of uranyl complexes were determined. The molar magnetic susceptibilities were than computed using Pascal's additivity law. The computed values were found to be higher than the experimental values. This deviation from Pascal's law is regarded as measure of ligand field strength in terms of χ_p values: χ_{specific} χ_m the molar susceptibility, and χ'_m the computed susceptibility as reported in Table 3. Also the calculated percentage deviation values are reported in Table 3. 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 these complexes were computed. The computed values were found to be higher than the experimental values (Table 3). These deviations are beyond experimental error and therefore significant.

TABLE 3
MAGNETIC SUSCEPTIBILITY DATA OF URANYL COMPLEXES

Complex No.	The complex (M. wt.)	χ	χ_m (Observed)	χ'_m (Computed)	$\Delta\chi_m = \chi_p = \chi_m - \chi'_m$	% $\Delta\chi_m$
			-1×10^{-6} cgs units			
C_1	$[UO_2(C_{17}H_{13}ON)_2](CH_3COO)_2$ (882)	0.3811	336.13	406.02	69.89	–20.80
C_2	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (910)	0.3901	354.90	429.74	74.75	–21.00
C_3	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (910)	0.3925	357.17	426.54	69.37	–19.00
C_4	$[UO_2(C_{18}H_{15}ON)_2](CH_3COO)_2$ (910)	0.3808	346.52	428.20	81.68	–23.00
C_5	$[UO_2(C_{17}H_1ONCl)_2](CH_3COO)_2$ (951)	0.3885	369.46	434.16	64.70	–17.00
C_6	$[UO_2(C_{17}H_{12}ONCl)_2](CH_3COO)_2$ (951)	0.3892	370.12	432.16	62.04	–16.00
C_7	$[UO_2(C_{17}H_{12}ONCl)_2](CH_3COO)_2$ (951)	0.3950	375.64	434.70	69.06	–18.00
C_8	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (972)	0.3888	377.91	446.90	68.99	–18.00
C_9	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (972)	0.3852	374.41	444.25	69.84	–17.00
C_{10}	$[UO_2(C_{17}H_{12}O_3N_2)_2](CH_3COO)_2$ (972)	0.3982	387.05	445.90	58.85	–15.00

According to Van Vleck[17], 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 $\sum_n \bar{r}^2$ (the radius of all electronic orbits in the molecule), 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 bond in the complex is sufficiently strong, the associating units will come very close to metal atom thus decreasing the value of $\sum_n \bar{r}^2$ and hence that of diamagnetic susceptibility of the molecule.

Freed and Kasper[18] and Lawrence[19] have observed that χ_p term is definitely present in uranyl complexes. Van Vleck attributed this paramagnetism to the matrix elements of the magnetic moment operator $\beta(L + 2S)$ between the ground state and higher states. The contribution from the spin magnetic moment is zero since all spins are paired off in the ground state. As the largest orbital contribution comes from the $5f^6$ bonding elecrons, Einstein and Pryce[20] have assumed that $5f^6$ electrons are responsible for the magnetism of the uranyl ion. Belford and Belford[21, 22] have shown from orbital overlap integral calculations that the

$5f^6$ orbitals do not overlap much with the oxygen orbitals as the 6d orbitals do, and that considerable π-bonding also must be involved.

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 has been established:

(I) 2-Hydroxy-1-naphthalidene-anil > 2′-methyl-2-hydroxy-1-naphthalidene-anil > 3′-methyl-2-hydroxy-1-naphthalidene-anil > 4′-methyl-2-hydroxy-1-naphthalidene-anil

(II) 2-Hydroxy-1-naphthalidene-anil > 2′-chloro-2-hydroxy-1-naphthalidene-anil > 3′-chloro-2-hydroxy-1-naphthalidene-anil > 4′-chloro-2-hydroxy-1-naphthalidene-anil

(III) 2-Hydroxy-1-naphthalidene-anil > 2′-nitro-2-hydroxy-1-naphthalidene-anil > 3′-nitro-2-hydroxy-1-naphthalidene-anil > 4′-nitro-2-hydroxy-1-naphthalidene-anil

The effect of substituents at different isomeric positions in terms of χ_p values shows a very systematic trend, *viz.*, *para*, *meta*, *ortho* as expected in case of all the three substituents.

Percentage deviation and symmetry of the molecule

In the Schiff base complexes studied, coordination occurs through nitrogen[8, 11] and the bonds involved are of coordinate covalent type. These bonds are likely to cause contraction of the electron orbits whereby values of $\sum_n \bar{r}^2$ of the molecule are decreased. Since diamagnetic susceptibility is a radial function, the decrease in the value of $\sum_n \bar{r}^2$ 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 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 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 complex formed may be entirely different from that of the constituent molecule, the change in the χ_p term would obviously be more significant.

It appears that χ_p term is more significant in bringing about a change in the molar suceptibility of the complex. This term is dependent on the symmetry of the molecule and hence, greater the symmetry of the molecule, the smaller will be its contribution to χ_m in Van Vleck's equation. It is therefore expected that greater the symmetry of molecule, smaller will be the deviation from additivity[23, 24] and vice-versa. Hence all the complexes reported in this investigation appear to be distorted.

REFERENCES

1. C.P. Sengupta and C.R. Bera, *J. Indian Chem. Soc.*, **57**, 546, 558 (1980).
2. P.S. Prabhu and S.S. Dodwad, Presented at the Symposium on "Fundamental and Applied Electrochemistry" in March 1982.
3. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th Edn., Longman, p. 483 (1978).
4. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
5. S.S. Krishnamurthy and S. Soundarajan, *J. Inorg. Nucl. Chem.*, **28**, 689 (1966).
6. S.A. Zaveri and M.G. Datar, *Ind. J. Chem.*, **3**, 11 (1965).
7. P. Harve, M.G. Datar and D.D. Khanolkar, *J. Indian Chem. Soc.*, **41**, 769 (1964).
8. P.S. Prabhu and S.S. Dodwad, *J. Indian Chem. Soc.*, **60**, 546 (1983).
9. N. S. Biradar and V.H. Kulkarni, *J. Less Common Metals*, **26**, 365 (1972).
10. S.B. Hendricks, D.R. Wulf, G.F. Gilbert and U. Liddel, *J. Am. Chem. Soc.*, **53**, 1991 (1936).
11. N.S. Biradar and (Miss) A.L. Locker, *Indian J. Chem.*, **11**, 833 (1973).
12. S. Preed and C. Kasper, *J. Am. Chem. Soc.*, **52**, 4671 (1930).
13. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Inter-Science, 2nd Edn. (1970).
14. J.D. Donaldson, J.F. Fnifton and S.D. Ross, *Spectrochim. Acta*, **21**, 275 (1965).
15. F. Vratny, C.N. Rao and M.D. Illing, *Anal. Chem.*, **33**, 1455 (1961).
16. M. Prasad, S.S. Dharmatti and S.V. Gokhale, *Proc. Indian Acad. Sci.*, Sect. A, **20**, 224 (1944).
17. J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, Oxford (1932).
18. S. Freed and C. Kasper, *J. Am. Chem. Soc.*, **52**, 4671 (1930).
19. R.W. Lawrence, *J. Am. Chem. Soc.*, **56**, 776 (1834).
20. J.C. Einstein and M.H.L. Pryce, *R. Soc. Ser. QA*, **229**, 20 (1955).
21. R.L. Belford, *J. Chem. Phys.*, **34**, 318 (1961).
22. R.L. Belford and Belford, *J. Chem. Phys.*, **34**, 1330 (1961).
23. J.V. Narangule and M.G. Datar, *J. Univ. Bombay* (1970).
24. P.S. Prabhu and S.S. Dodwad, *J. Indian Chem. Soc.*, **63**, 610 (1986).

(*Received*: 12 October 1993; *Accepted*: 29 January 1994) AJC-778