Some New Complexes of Hydrazide Schiff bases with Uranium (VI)

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Abstract:

The synthesis of some new complexes was performed by the reaction of uranyl salts with three ligands of Schiff base. The ligands were obtained by the condensation of benzoin with benzoyl hydrazide (DBEH₂), salicyloyl hydrazide $(DSEH_2)$ and *p*-nitrobenzoylhydrazide $(DPEH_2)$. The complexes of the general formula $[UO_2(LH_2)_2]X_2$ and $[(UO_2)_2L_2]$ (where LH₂ and L=are neutral and dibasic form of the three ligands, X=NO₃ or CH₃COO ions) for those formed by the reaction of uranyl salts and the ligands in neutral and basic medium, respectively. All the complexes were characterized by using elemental microanalysis, molar conductances, infrared, electronic and ¹HNMR spectra. These studies revealed octacoordinate of uranium atom for complexes formed in neutral medium and dinuclear hexacoordinate complexes formed in basic medium.

Introduction:

The most characteristic respect in which compounds containing the C=N bond show basic properties is in the formation of complexes with metal ions⁽¹⁻³⁾. These complexes provide some very characteristic series of coordination compounds, and consequently large number of them have been prepared and their properties were examined and compared^(4,5). The coordination chemistry of acid hydrazides and their Schiff bases with aldehydes and ketones are of special interest because of the variety of ways in which these species could be bonded to the metal ions⁽⁶⁻⁸⁾. These N-N, N-O donor Schiff bases act as multidentate ligands and the formation of oxygenbridged bi-and tri-nuclear complexes have been reported^(9,10). Schiff bases derived from benzoin and substituated benzoylhydrazides have been shown to be biologically active^(11,12) and have interesting ligational properties^(13,14).

In the present work, new uranyliom (IV) complexes formed with Schiff base ligands derived from benzoin with 1,2-diphenyl-2-(benzoylhydraziono) ethanol (DBEH₂), 1,2-diphenyl-2-(salicyloylhydrazino) ethanol (DSEH₂) and 1,2-diphenyl-2-(*p*-nitrobenzoylhydrazino) ethanol (DPEH₂) have been synthesised and characterized by different chemical, physical and spectral methods.

Experimental:

Material and Methods:

All chemicals were of analytical grade used as supplied without further purification. The complexes were analysed microanalytically for C, H and N at the Department of Chemistry, College of Science, University of Mosul, Iraq using 1106CE microanalyzer. The molar conductances were measured for 10⁻³M solution of the complexes in dimethylformamide (DMF) using a LF-42 conductivity bridge.

Infrared absorption spectra of the Schiff bases and their complexes were recorded in the 400-4000cm⁻¹ range using Nujol mulls and KBr disc on a Pye-Unicam SP-1100 spectrophotometer. Shimadzu UV-VIS spectrophotometer UV-160 was used for electronic spectral measurements for 10⁻³M solution of the ligands and their complexes in DMF at 25°C using 1cm quartz cell. ¹HNMR spectra were recorded at room temperature with Perkin-Elmer (A-60) spectrometer using TMS as internal standard for ligands and complexes ¹HNMR.

ligand. The Schiff base 1. 2-diphenyl-2-(benzoylhydrazine) ethanol (DBEH2) was prepared by using the following procedure: Benzoin (0.01mol) in ethanol (15cm³) was mixed with benzoylhydrazine (0.01mol in 15cm³ ethanol) [prepared by the reaction of methylbenzoate and hydrazinehydrate]⁽¹⁰⁾ in 100cm³ round bottomed flask and the mixture was boiled under reflux for ca 3h. It was allowed to cool room temperature and on further cooling in ice bath, the resulting precipitate was removed by filteration, washed with cold ethanol and recry stallized from ethanol.

The same procedure was used to prepare te ligands $(DSEH_2)$ and $(DPEH_2)$.

Preparation of the complexes:

Two general procedures were used for the preparation of the complexes:

i. Neutral medium complexes: (0.01 mol) of uranyl salt dissolved in a minimum amount of ethanol (1:2 metal to ligand ratio). The mixture so obtained was refluxed on a water bath for about one hour, then cooled. The precipitated complexes were filtered off, washed with cold ethanol and dried.

ii. Basic medium complexes: A mixture of 1:1 metal to ligand molar ratio was prepared by adding an ethanolic solution containing (0.01 mol) of the ligand to an ethanolic solution of (0.01 mol) uranyl salt. To this mixture 1N ethanolic KOH solution was added until complete precipitation of the complexes which occurred at pH 8-9. The mixture was then digested on a water bath for about 10 minutes and cooled. The precipitated complexes were filtered off washed with ethanol and dried.

Result and Discussion:

The reaction of the uranyl salts with the Schiff base ligands was carried out in neutral and basic media may be depicted as follows:

(where X=NO₃ or $\overline{CH_3COO}$, LH_2 represent any of three ligands, L=dibasic form of the ligands, and n=2 or 6). The molar ratio 1:2 and 1:1 metal to ligand was confirmed by elemental analysis (Table 1).

Table 1 : Analytical and some	physical data of complexes
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	Complex	Color	M.P. °C	$\Lambda_{\rm M}({\rm DMF})$		Analysi	is% found (calculated)			
	Complex		(Dec.)	(cm ² ohm ⁻¹ mol ⁻¹)	С		Н		Ν	
1	$[UO_2(DBEH_2)_2](NO_3)_2$	Pale yellow	222	126	47.96	(48.09)	3.81	(3.43)	8.16	(8.01)
2	[UO ₂ (DBEH ₂) ₂](CH ₃ COO) ₂	yellow	218	132	52.68	(52.37)	3.24	(3.98)	5.58	(5.31)
3	$[UO_2(DSEH_2)_2](NO_3)_2$	Pale orange	228	127	46.58	(46.40)	2.96	(3.31)	7.69	(7.73)
4	[UO ₂ (DSEH ₂) ₂](CH ₃ COO) ₂	Yellowish orange	210	130	52.09	(51.11)	3.54	(3.88)	5.26	(5.18)
5	$[UO_2(DPEH_2)_2](NO_3)_2$	Deep yellow	232	141	44.23	(44.05)	3.02	(2.97)	9.48	(9.79)
6	$[UO_2(DPEH_2)_2](CH_3COO)_2$	Deep yellow	217	138	48.72	(48.50)	3.30	(3.51)	7.44	(7.38)
7	$[(UO_2)_2(DBE)_2]^*$	Pale yellow	206	19	42.52	(42.14)	2.40	(2.67)	4.34	(4.68)
8	[(UO ₂) ₂ (DSE) ₂]*	Pale yellow	215	23	40.81	(41.04)	2.86	(2.60)	4.61	(4.56)
9	$[(UO_2)_2 (DPE)_2]^*$	yellow	221	16	39.48	(39.19)	2.21	(2.33)	6.07	(6.53)

* The same complex was obtained by using different uranyl salts. All the complexes are stable to air at room temperature but they are decompose with out melting above 200°C.

Their analytical data (Table 1) are in a good agreement with the given formulations as shown in above equations. They are insoluble in water, but moderately soluble in ethanol and dimethylformamide.

The molar conductivities in DMF for 10^{-3} M solutions at room temperature (Table 1) suggested 1:2 and non-

electrolytic nature for the mono-and dinuclear complexes, respectively.

The main infrared absorption bands (Table 2) characteristic for the active sites of the ligands are those located in the spectra of the free ligand molecules at 3350-3380, 3200-3220, 1685-1690, 1630-1635, 1280-1300 and 1010 cm⁻¹ which are due to v(OH), v(NH), v(C=O), v(C=N), δ (OH) and v(N-N), respectively.

Table 2: Infrared and UV-spectral data of the ligands and their complexes

Compound	IR(cm ⁻¹)								UV(nm)	
Compound	v(OH)	v(NH)	v(C=O)	v(C=N)	δ(OH)	v(N-N)	v(U-O)	ν(U-N)	v ₁	v ₂
DBEH ₂	3350	3200	1690	1630	1300	1010	-	-	290	340
DSEH ₂	3380	3220	1690	1635	1280	1010	-	-	280	330
DPEH ₂	3350	3200	1685	1630	1300	1010	-	-	285	330
$[UO_2(DBEH_2)_2](NO_3)_2$	3300	3200	1665	1605	1260	1040	445	490	280	360
[UO ₂ (DBEH ₂) ₂](CH ₃ COO) ₂	3310	3205	1670	1600	1255	1045	440	485	285	370
[UO ₂ (DSEH ₂) ₂](NO ₃) ₂	3330	3225	1660	1600	1250	1040	440	490	285	365
[UO ₂ (DSEH ₂) ₂](CH ₃ COO) ₂	3335	3220	1665	1605	1250	1035	450	480	290	370
$[UO_2(DPEH_2)_2](NO_3)_2$	3300	3205	1660	1600	1260	1040	445	480	285	370
$[UO_2(DPEH_2)_2](CH_3COO)_2$	3310	3200	1670	1605	1270	1040	440	485	280	360
$[(UO_2)_2(DBE)_2]^*$	-	-	-	1600	-	1040	440	495	290	370
$[(UO_2)_2(DSE)_2]^*$	-	-	-	1605	-	1045	450	480	280	360
$[(UO_2)_2(DPE)_2]^*$	-	-	-	1605	-	1045	445	490	285	365

* The same complex was obtained by using different uranyl salts.

For the complexes formed in neutral medium. The v(NH) and v(OH) (phenolic) bands remain almost without change in positions indicating that there is no coordination through these groups. The aliphatic v(OH) and δ (OH) bands were shifted to lower frequency by about 40-50 and 30-45cm⁻¹ compared to the free Schiff bases indicating coordination of the alcholic oxygen atom.

Further support for this coordination is the splitting of v(C-O) into two peaks, suggesting coordination of the alcohol with out deprotonation. On the other hand, negative shifts of about 15-30 and 25-35cm⁻¹ were observed in C=O and C=N stretching frequency, respectively, while a positive shift of about 25-35cm⁻¹ was observed for N-N stretching band. These pretubation in the infrared bands suggested coordination of the ligands through alcoholic oxygen atoms and azomethine nitrogen and carbonyl oxygen atoms^(15, 16).

For the dinuclear complexes formed in basic medium, the v(OH), δ (OH), v(C=O) and v(NH) bands disappeared due to deprotonation of the alcoholic and enolic form of the ligands. Instead, new bands at 1625-1635 and 1580cm⁻¹ are present, which we assign to [v(O-C=N) + v(C=O)] combination and v(C=N-N=C] (azine chromophor) repsectively^(7, 17).

The presence of these bands is strong evidence for enolization and deprotonation in basic medium. In addition C=N stretching was also shifted to lower

frequency by 25-30cm⁻¹, suggesting involvement of the azomethine nitrogen in coordination. Further support for this coordination was indicated by the positive shift of N-N band of about 30-35cm⁻¹.

In addition to the preturbation of ligand bands, new bands (not observed in ligand spectra) located at 440-450 and 480-495 cm⁻¹ assigned to U-N and U-O stretching vibrations, respectively⁽¹⁸⁾.

Furthermore, the infrared absorption due to UO_2 group were observed at 820cm⁻¹ as weak band and at 920cm⁻¹ as a sharp strong band corresponding to symmetric and asymmetric U-O stretching vibration respectively^(19, 20). For neutral medium complexes, the C=O stretching vibration of the acetate ion was observed at 1720 cm⁻¹, while for uranyl nitrate complexes bands were observed at 1370 and 820cm⁻¹ indicating noncoordinating acetate and nitrate groups respectively⁽²¹⁾. This observation was in accord with the 1:2 electrolytic nature found from conductivity measurements for these complexes.

The above mentioned observations were confirmed by measuring the proton NMR spectra of the ligands and their complexes. In addition to the aromatic complex signals which remained almost at the same position (7.0-7.9ppm) in complexes spectra, showed another important signals due to; CH, C-OH and NH. These bands are located in the free ligands at 4.8, 4.0-4.2 and 6.4ppm respectively. The ¹HNMR spectra for the complexes formed in neutral medium showed perturbation in the

signals of the above mentioned groups. The C-OH and NH signals located at 4.3-4.6 and 6.6-6.8ppm, respectively. The down field shift in these bands confirm the previous suggestion of coordination derived from the infrared absorption spectra for these complexes. On the other hand, in the ¹HNMR spectra for complexes formed in basic medium, the signals due to NH and C-OH protons disappeared as a result of deprotonation of the ligand, while phenyl protons and CH aliphatic proton showed similar perturbation to that observed for the complexes formed in neutral solution.

The UV-VIS spectra of the ligands and their complexes in dimethylformamide solution have been recorded. The maximum at about 260-268nm in the case of the ligands are due to the $\pi \rightarrow \pi^*$ (benzenoid) electronic transition⁽¹⁶⁾. This band is almost unchanged in the complexes. Moreover, the spectra of the ligands show broad band at about 325-335nm which is due to $n \rightarrow \pi^*$ within the C=N chromophore. On transitions complexation, a blue shift is observed due to the polarization in the C=N band caused by the metal ligand electron interaction during the chelation⁽¹⁶⁾. This shift is due to the donation of nitrogen lone pair of the azomethine group to uranium atom⁽²²⁾. However, in the visible region at about 440nm, a band observed which can be related to a charge transfer absorption from ligand orbital to metal orbital. This ligand to metal charge transfer band is possibly the responsible for the colours of these complexes⁽²³⁾.

From the above considerations and the various physicochemical, spectral and analytical studies, it was concluded that the ligands act in neutral medium as neutral tridentate forming mononuclear complexes, and as dibasic tridentate in basic medium forming oxygen bridged binuclear complexes. Thus cationic and neutral octacoordinated complexes were suggested and might have square antiprism or dodecahedron structure, Fig. 1.



X = H or o-OH or p-NO₂ Neutral medium monorud ear complexes



X = H or o-OH or p-NO Basic medium Diraclear cos

Fig. (1) The suggested structure for DBEH2, DSEH2 and DPEH2 complex

References:

- 1. N.S. Biradar and Y.H. Rulkarni, Inorg. Chim. Acta, 7, 267, (1973).
- 2. A. Chiesi-Villa and C. Guastini, Inorg. Chem., 25, 4518, (1986).
- 3. I.J. Sallomi and A.J. Al-Shaheen, Polyhedron, 6, 1, (1997).
- 4. S. Goel and K. Lat, Asian J. Chem., 2, 271, (1990).
- 5. S. Padhye and G.B. Kauffeman, Coord. Chem. Rev., 44, 635, (1985).
- 6. T.H. Mahmood, J. Edu. Sci., 39, 29, (1999).
- I.J. Sallomi and A.J. Al-Shaheen, Trans. Met. Chem., 19, 275, (1994).
- D.K. Rastogi, S.K. Dua, V.B. Rana and S.K. Sahir, J. Coord. Chem., 8, 97, (1979); J. Inorg. Nucl. Chem., 18, 56, (1978); Bull Chem. Soc. Japan, 52, 3088, (1979).
- 9. G. A. Wilkinson, R. D. Gillard and J. A. McCleverty, "Comprehensive Coordination Chemistry", Pergamaon Press, Oxford, England, 1 st edn., vol. 2, p. 716, (1987).
- I.J. Sallomi and M.A.Al-Ta'yy, Sci., J. Tikrit Univ. Engg. Sci., 8, 119, (2001).
- 11. J.L. Wang, F. Ding, J-Zh.Huo and Y.H. Qiang, Polish J. Chem., 78, 303, (2004).
- 12. I.J. Sallomi and M.A. Al-Ta'yy, J. Educ. Sci., vol. (34), (1999).
- 13. E.M. Hodnett and W.J. Dunn, J. Med. Chem., 13, 768, (1970).
- 14. M. Katyal and Y. Dutt, Talanta, 22, 151, (1975).
- 15. Y. Kumar and S.P. Tolani, Teor. Chim. Acta., 62, 73, (1989).
- N. Kanoongo, R.N. Singh and J.P. Tandon, Synth. React. Inorg. Met-Org. Chem., 17, 837, (1987).
- 17. N.S. Biradar and N.H. Kulkari, Inorg. Nucl. Chem., 33, 2451, (1971).
- K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 5 th edn., Wiley Interscience, New York, (1998).
- 19. L. Cattalini, U. Croatto, S. Degetto and E. Tondello, Inorg. Chim. Acta., 5, 519, (1971).
- 20. K. Srivastava, S. Sharma and R.K. Agarwal, J. Inorg. Chim. Acta, 235, 61, (1982).
- 21. C.C. Addison and B.M.G. Atehouse, J. Chem. Soc., 613, (1960).
- 22. N. Kanoongo, R. Singh and J.P. Tandon, Trans. Met. Chem., 12, 271, (1978).
- 23. K.M. Daud, Z.F. Dawood and M.M. Mohammed, J. Indian Chem. Soc., 71, 263, (1994).

بعض المعقدات الجديدة لهيدرازيدات قواعد شيف مع اليورانيوم (VI)

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الملخص:

مع ثلاثة ليكاندات من نوع قواعد شيف والتي تم الحصول عليها من مفاعلة التوصيل الكهربائي وأطياف الأشعة تحت الحمراء والأطياف الالكترونية البنزوين مع بعض الهيدرازيدات الحامضية وهي البنزويل هيدرازيد وأطياف الرنين النووي المغناطيسي. وقد دلت هذه الدراسات أن الليكاندات والساليسيلويل هيدرازيد وبارا-نايتروبنزويل هيدرازيد. حضرت جميع المعقدات تعمل بشكل متعادل ثلاثي السن في الوسط المتعادل وثلاثية السن ثنائية في كل من الوسطين المتعادل والقاعدي حيث تم الحصول على معقدات القاعدية في الوسط القاعدي وقد نتج عن ذلك معقدات ثمانية التناسق في

يتضمن البحث تحضير عدد من المعقدات الجديدة لأيون اليورانيل السداسي شخصت الليكاندات والمعقدات الناتجة بالتحليل الدقيق للعناصير وقياس أيونية موجبة في الوسط المتعادل ومعقدات متعادلة في الوسط القاعدي. الوسط المتعادل ومعقدات ثنائية النواة سداسية التناسق في الوسط القاعدي.