

Infrared and Raman Studies of  $[\text{UO}_2(\text{salen})(\text{L})]$  ( $\text{L} = \text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ )

E. M. NOUR\*, A. A. TAHA and I. S. ALNAIMI

Department of Chemistry, Qatar University, Doha 2713, Qatar (Arabian Gulf)

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## Abstract

The infrared and Raman spectra of  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  ( $\text{salen} = N,N'$ -ethylenebis(salicylideneimine)) have been recorded. Assignments for the fundamental vibrations are proposed on the basis of  $C_{2v}$  symmetry for the former species and  $C_s$  for the latter. The calculated values of the stretching force constant of the uranyl group,  $F_{\text{UO}}$ , are 6.87 and 6.63  $\text{mdyn \AA}^{-1}$  for  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ , respectively. The corresponding values of the U=O bond lengths calculated as 1.738 and 1.745  $\text{\AA}$ .

## Introduction

Since the preparation of Co(II)–Schiff base complexes in 1933 by Pfeiffer [1] and the discovery of their oxygen carrying properties [2], this class of Schiff base complexes (particularly of the tetradentate bases such as  $N,N'$ -ethylenebis(salicylideneimine), known as salen) have been extensively studied [3–8]. Most of these studies are focused on the complexes of the d-block elements and little attention has been given to the Schiff base complexes of the f-block elements. Detailed vibrational studies for this class of compounds appears to be limited in the literature [9–10] and in most cases the assignments are mainly focused on the ligand C=N and C–O vibrations.

In a previous communication [3], both the infrared and Raman spectra of Co(salen), together with the spectra of its dioxygen complexes, are discussed. In this work we report the preparation of the species  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$ . The Raman and infrared spectra of this compound, together with those of  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  prepared by Bandoli *et al.* [8], are recorded. Assignments for most of the fundamental vibrations are proposed in view of the compound structures.

\*Author to whom correspondence should be addressed.

## Experimental

## Preparation of compounds

All chemicals were analytical reagent grade. The Schiff base salen was prepared from the condensation of ethylenediamine with salicylaldehyde, according to the known method [1]. The Schiff base was characterized through its infrared and  $^1\text{H}$  NMR spectra. Singlets are observed at 3.96, 8.35 and 9.88 ppm and are assigned to the  $-\text{CH}_2-$ ,  $-\text{CH}=\text{}$  and  $-\text{OH}$  groups, respectively. A multiplet is shown in the region 6.72–7.65 ppm related to the phenyl groups. The uranyl complex  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  was obtained from the addition of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.004 g, 2 mmol) in acetone to a stoichiometric amount of the Schiff base (0.536 g, 2 mmol) in acetone. The yellowish brown mixture was stirred at room temperature for a few minutes. The orange–red crystals precipitated and were filtered off, washed with acetone and dried under vacuum to yield the compound  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$ . Preparation in dioxane instead of acetone gives the same compound as shown by the elemental analysis, UV–Vis and infrared spectra. The red–yellow complex  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  was prepared in a similar way using  $\text{CH}_3\text{OH}$  as a solvent. The same compound can also be obtained according to the method reported by Bandoli *et al.* [8] from the reaction of ethylenediamine, salicylaldehyde and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{CH}_3\text{OH}$ . The high yield in each case infers that the  $\text{UO}_2^{2+}$ –salen reaction may go to completion with a 1:1 ratio. This was also confirmed by the fact that the yields are almost the same under a higher salen ratio. The  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  complexes were characterized by their elemental analyses as well as their infrared and Raman spectra. *Anal.*  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$ : C, 33.82 (34.66); H, 3.05 (2.80); N, 5.25% (5.05%);  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ : C, 35.70 (35.90); H, 3.55 (3.20); N, 5.02% (4.93%) (the calculated values are shown in parentheses). Infrared bands with medium intensities due to the coordinated water are shown at 3567 and 3645  $\text{cm}^{-1}$  in the spectrum of  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$ . These bands do not exist in the spectrum of  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ ; instead a weak broad band at 3590  $\text{cm}^{-1}$  related to  $\nu(\text{O}-\text{H})$  as well

as weak bands at 2930, 2867 and 2847  $\text{cm}^{-1}$  due to  $\nu(\text{CH}_3)$  of the coordinated methanol are observed.  $^1\text{H}$  NMR measurements for the above two uranyl complexes were found to be impossible due to the very low solubilities of the complexes in most common solvents.

#### Spectroscopic Measurements

The Raman spectra of the uranyl complexes were measured with a Carry Model 82 spectrometer equipped with a Coherent Radiation Innova 12 argon ion laser. To prevent decomposition by the laser beam, each sample (as a pressed disc, 20–25% by weight in KBr) was examined in a rotating solid disc of conventional design. The laser excitation line 514.5 nm was used in the measurements. The infrared spectra were recorded from potassium bromide discs on a Pye Unicam SP 2000 spectrometer. The  $^1\text{H}$  NMR spectrum of the Schiff base salen was obtained from deuteriochloroform solution using a Varian T-60A 60 MHz spectrometer. Chloroform was utilized as the internal standard.

#### Results and Discussion

The infrared spectra of  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  are shown in Fig. 1; their Raman spectra recorded using the 514.5 nm excitation line are shown in Fig. 2. The vibrational assign-

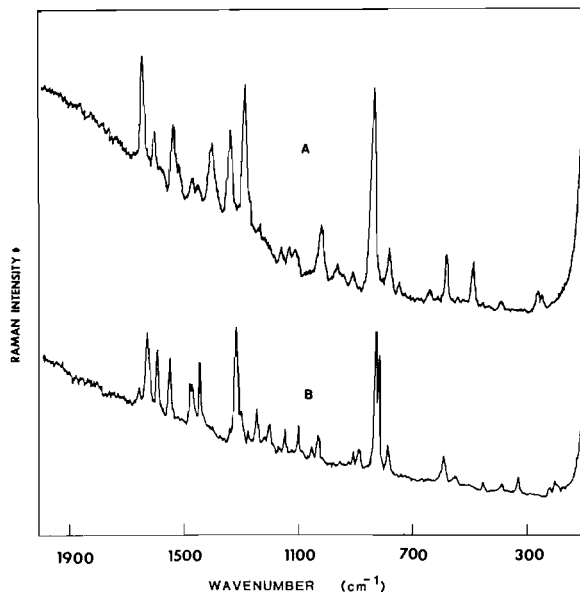


Fig. 2. Raman spectra of: (A)  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and (B)  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ .

ments for the observed bands are given in Table I. Before explaining such assignments, the structures of the two complexes must first be discussed. Bandoli *et al.* [8] reported the crystal structure of  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$  and indicated that the four donor atoms (2 nitrogens and 2 oxygens) of the Schiff base

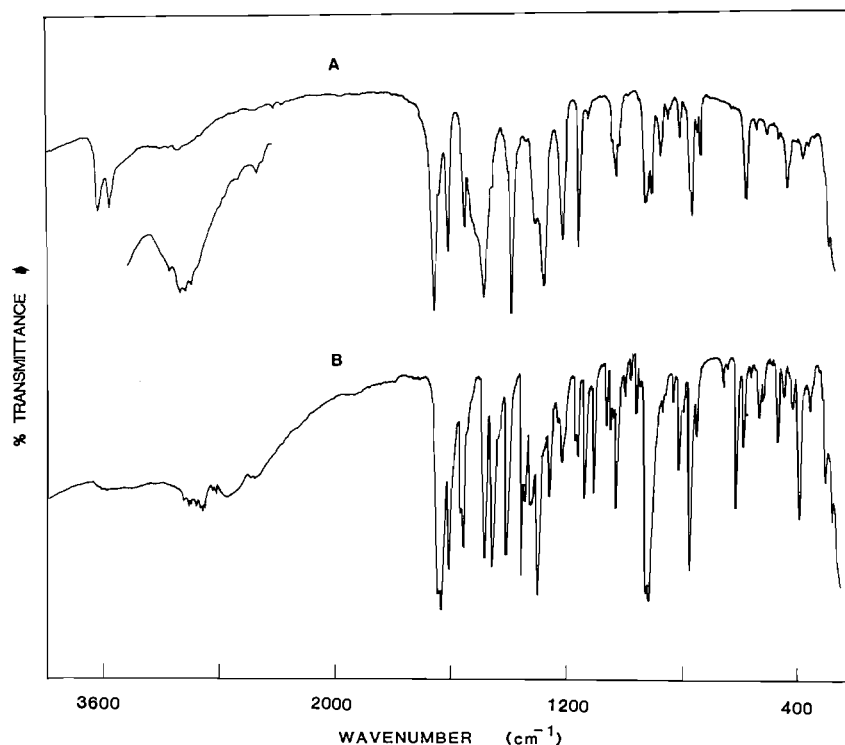


Fig. 1. Infrared spectra of: (A)  $[\text{UO}_2(\text{salen})(\text{H}_2\text{O})]$  and (B)  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ .

TABLE I. Infrared and Raman Frequencies<sup>a</sup> (cm<sup>-1</sup>) and Assignments for [UO<sub>2</sub>(salen)(L)] (L = H<sub>2</sub>O and CH<sub>3</sub>OH)

Infrared		Raman		Assignments
L = H <sub>2</sub> O	L = CH <sub>3</sub> OH	L = H <sub>2</sub> O	L = CH <sub>3</sub> OH	
3645ms				$\nu_{as}(\text{O}-\text{H})$ ; coord. H <sub>2</sub> O
	3590wb			$\nu(\text{O}-\text{H})$ ; coord. CH <sub>3</sub> OH
3567m				$\nu_s(\text{O}-\text{H})$ ; coord. H <sub>2</sub> O
3152w				
3080w	3073w			} $\nu(\text{C}-\text{H})$ ; phenyl
	3065vw			
3048w	3037w			} $\nu(\text{C}-\text{H})$ ; =CH-
	3020vw			
3000w	3000w			} $\nu(\text{C}-\text{H})$ ; -(CH <sub>2</sub> ) <sub>2</sub> -
2960w	2955w			
2940w	2942w			} $\nu(\text{C}-\text{H})$ ; CH <sub>3</sub> -
	2930w			
	2867w			
	2847w			
1659s	1650vs			$\nu_{as}(\text{C}=\text{N})$
1648sh	1642s	1647s	1640sm	$\nu_s(\text{C}=\text{N})$
1640sh				
1612s	1608s	1607m	1597ms	} phenyl breathing modes (quadrant and semicircular vibrations)
1571sh	1570s	1580w		
1554m	1560s	1543m	1553ms	
1520sh		1520m		
1484s	1483s	1477wm	1483m	} CH deformations;
			1475m	
1458sh	1458s	1455w	1447ms	} CH <sub>3</sub> - and -(CH <sub>2</sub> ) <sub>2</sub> -
	1447sh			} phenyl breathing modes (sextant vibrations)
1406sh	1408s	1408ms		
1391s				
1345w	1349s	1343ms	1345w	} $\nu(\text{C}-\text{C})$ ; phenyl and azo carbons
	1342m			
1315m	1318m		1323s	} $\nu(\text{C}-\text{C})$ , $\nu(\text{C}-\text{O})$ , and $\nu(\text{C}-\text{N})$
1288s	1293vs	1291s	1275w	
	1252m		1250m	
			1240w	
1225s	1225wm	1230w		} $\nu(\text{C}-\text{C})$ , $\nu(\text{C}-\text{O})$ , and $\nu(\text{C}-\text{N})$
	1211m		1210m	
1160s	1163m	1165w		} CH bend; -(CH <sub>2</sub> ) <sub>2</sub> -
	1155m		1153wm	
1132w	1132ms	1130w		} CH bend; -(CH <sub>2</sub> ) <sub>2</sub> -
	1100ms		1103m	
	1055m		1055w	
	1042m			
1034m	1035mw		1035wm	
			1029wm	
1024sh	1022ms	1021m		} CH, bend; phenyl
	993mw			
	975mw			
954vw	955m	960mw		
	943w			
927ms	921vs	910w		$\nu_{as}(\text{U}=\text{O})$
912ms	913vs			
			895wm	
880m			889wm	$\nu_s(\text{U}=\text{O})$
	827mw	843s	833s	
			823s	

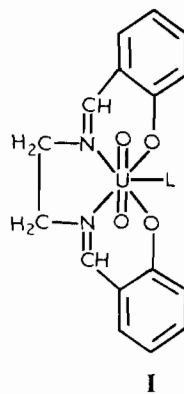
(continued)

TABLE I. (continued)

Infrared		Raman		Assignments
L = H <sub>2</sub> O	L = CH <sub>3</sub> OH	L = H <sub>2</sub> O	L = CH <sub>3</sub> OH	
813m	809m			} CH bend; phenyl
	790s	781m	789m	
773ms	770s			
755wm		750w		
743m	745m			
710vw				} CH in-plane quadrant bends
	655m			
638vw	640wm	642w		
	609sm			
583ms	583m	585m	598m	
552w	560w		556w	} CH out-of-plane quadrant bends
	528m			
516wm	515wm			
		493m		
475w	465m		458w	
443m	443m			} $\nu_{as}(U-O)$ $\nu_s(U-O)$
	413m			
390mw	389sm	395w	395vw	
368w				
	348m		337wm	
	293m			} $\nu(U-O)$ ; oxygen of CH <sub>3</sub> OH $\nu_{as}(U-N)$ $\nu_s(U-N)$ $\delta(UO_2)$
269m	270m			
		265w		
		245w	223w	
			205w	

<sup>a</sup>m, medium; s, strong; w, weak; b, broad; sh, shoulder.

and the oxygen of the methanol are coordinated to U(VI) in a plane forming a slightly irregular pentagon, with the uranyl group perpendicular to this plane. The U–O–C angle (oxygen and carbon of CH<sub>3</sub>OH) is  $\sim 122^\circ$ . Under this structure, the complex has no symmetry elements except for a plane of symmetry. Accordingly, the species may belong to the  $C_s$  symmetry. In such a case the 123 vibrations of [UO<sub>2</sub>(salen)(CH<sub>3</sub>OH)] are distributed between motions of the type A' and A''; all are monodegenerate and infrared and Raman active. The four vibrational motions of the UO<sub>2</sub> unit in this compound are 3A' + A''. The O=U=O stretches are associated with 2A' while the two UO<sub>2</sub> bends are related to A' and A''. In the case of the aqua complex [UO<sub>2</sub>(salen)(H<sub>2</sub>O)] which was obtained from either acetone or dioxane solutions using the hexahydrated uranyl salt, the H<sub>2</sub>O molecule is coordinated to U(VI) in a way similar to that in the case of CH<sub>3</sub>OH, as shown in I. This conclusion was supported by the two infrared bands with medium intensities observed at 3567 and 3645 cm<sup>-1</sup>, characteristic of coordinated water. However, the water molecule may be oriented to be in the plane of the Schiff base due to the expected hydrogen bonding with the two oxygens of the ligand rather than with the two uranyl oxygens. In the



latter case, the distances between the UO<sub>2</sub> oxygens and the H<sub>2</sub>O hydrogens are expected to be too long. This conclusion is in agreement with that found in [UO<sub>2</sub>(salen)(CH<sub>3</sub>OH)] where the hydrogen bonding from the methanol is reported [8] to take place with the Schiff base oxygen. Under these conditions, the species may belong to the  $C_{2v}$  symmetry. Such symmetry is supported by the infrared activity of the two stretches,  $\nu(O-H)$ , of the coordinated water (Table I). Under  $C_{2v}$  symmetry, [UO<sub>2</sub>(salen)(H<sub>2</sub>O)] is expected to display 114 fundamentals which all

are monodegenerate. These are distributed between the  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  modes; all are infrared and Raman active, except for the  $A_2$  modes which are only Raman active. Four of the above modes,  $2A_1 + B_1 + B_2$ , are related to the  $UO_2$  unit. The two  $O=U=O$  stretches belong to  $A_1 + B_1$ , while the  $UO_2$  bends are associated with the two modes  $A_1 + B_2$ . The  $U-OH_2$  unit should display six modes and these are  $3A_1 + B_1 + 2B_2$  corresponding to:  $\nu_s(O-H)$ ,  $A_1$ ;  $\nu_s(U-O)$ ,  $A_1$ ;  $\nu_{as}(O-H)$ ,  $B_2$ ;  $\delta_s(H_2O)$ ,  $A_1$ ; in-plane  $\delta_{as}(H_2O)$ ,  $B_2$ ; and out-of-plane  $\delta_{as}(H_2O)$ ,  $B_1$ .

#### Band Assignments

The observed bands of the two uranyl complexes were assigned (Table I) based on the spectra intensities and symmetry considerations outlined above, as well as by comparison with the literature data for related compounds. It should be mentioned here that the spectra of the  $[UO_2(salen)(CH_3OH)]$  complex is more complicated than that of the corresponding  $[UO_2(salen)(H_2O)]$ . This is in agreement with the conclusion drawn above that the  $CH_3OH$  complex belongs to lower symmetry ( $C_s$ ) than that of the aqua complex ( $C_{2v}$ ) and this will lead to the observation of more bands for the former species. The  $\nu_s(U=O)$ ,  $A_1$  and  $\nu_{as}(U=O)$ ,  $B_1$  stretching frequencies of the uranyl group in  $[UO_2(salen)(H_2O)]$  are assigned to the strong Raman band at  $843\text{ cm}^{-1}$  and to the strong infrared doublet at  $927$  and  $912\text{ cm}^{-1}$ , respectively. The corresponding vibrations in  $[UO_2(salen)(CH_3OH)]$  are assigned to the strong Raman doublet at  $833$  and  $823\text{ cm}^{-1}$ ,  $\nu_s(U=O)$ ,  $A'$ ; and the strong infrared doublet at  $921$  and  $913\text{ cm}^{-1}$ ,  $\nu_{as}(U=O)$ ,  $A'$ . The doublet structures of  $\nu(U=O)$  are a result of the solid-solid interactions. These assignments for the uranyl stretches are in agreement with our previous work on  $(UO_2X_4)^{2-}$  ion complexes [11] as well as with other reported values for dioxouranium(VI) species [5]. Moreover, both the above  $\nu_s$  and  $\nu_{as}$  values satisfy the proposed equation by McGlynn *et al.* [12]:

$$\nu_s = (1 + 2M_O/M_U)^{-1/2} \nu_{as}$$

for the linear  $UO_2$  moiety ( $M_O$  and  $M_U$  are the atomic masses of oxygen and uranium, respectively). Comparison between the values of both  $\nu_s$  and  $\nu_{as}$  for the uranyl unit in the complexes under study,  $[UO_2(salen)(H_2O)]$  and  $[UO_2(salen)(CH_3OH)]$ , with those for the same unit ( $UO_2^{2+}$ ) in simple salts, indicates the shift of these frequencies in our case to lower values. One way of explaining this is due to the weakening of the  $U=O$  bonds resulting from the increase in electron density on  $U(VI)$  by the Schiff base. This will lead to an increase in electron repulsion between those of the uranyl oxygens and the metal ion. However, structural studies on  $[UO_2(salen)(CH_3OH)]$  indicate [8] that the equatorial ligand has little effect upon the  $U=O$  bond length,

and other studies [13] have shown that the uranyl  $U-O$  distance varies as a function of the bond strength. Accordingly, the decrease of  $\nu(U=O)$  upon complexation is more likely to be associated in part with the expected increase in the  $U(VI)$  mass upon coordination.

The force constant  $F_{UO}$  for the  $U=O$  bond has been calculated for each complex according to the published method [12]; values of  $6.87$  and  $6.63\text{ mdyn \AA}^{-1}$  are obtained for the aqua and methanol complexes, respectively. These values are close to those obtained for the uranyl unit at  $6.71$  and  $6.83\text{ mdyn \AA}^{-1}$  in our previous study [11] based on full normal coordinate analysis for  $(UO_2Cl_4)^{2-}$  and  $(UO_2Br_4)^{2-}$  ion complexes, respectively. The  $F_{UO}$  value in each case was used to calculate the  $U=O$  bond length, using the formula developed by Jones [14] for the  $UO_2^{2+}$  species. It gives values of  $1.738$  and  $1.745\text{ \AA}$  for  $[UO_2(salen)(H_2O)]$  and  $[UO_2(salen)(CH_3OH)]$ , respectively. These values are in good agreement with the average value ( $1.765\text{ \AA}$ ) reported for the methanol complex based on a crystal structure study [8].

The bands of the coordinated water in  $[UO_2(salen)(H_2O)]$  occur at  $3645$ ,  $3567$  and  $1640\text{ cm}^{-1}$ . The first two bands are assigned to  $\nu_{as}(O-H)$  and  $\nu_s(O-H)$ , respectively, while the  $1640\text{ cm}^{-1}$  band is due to  $\delta(H_2O)$ . The above three bands do not exist in the infrared spectrum of the methanol complex. The  $\nu(O-H)$  of the coordinated methanol occurs at  $3590\text{ cm}^{-1}$ . This band is weak and broad due to the hydrogen bonding shown in the crystal structure [8]. In the  $\nu(C-H)$  region, six bands are observed as weak features in the infrared spectrum of  $[UO_2(salen)(H_2O)]$  at  $3152$ ,  $3080$ ,  $3048$ ,  $3000$ ,  $2960$  and  $2941\text{ cm}^{-1}$ . These were assigned (Table I) to the phenyl,  $=CH-$  and  $-(CH_2)_2-$  groups [15]. Interestingly, more weak bands were observed in the spectrum of  $[UO_2(salen)(CH_3OH)]$ , particularly for the  $\nu(CH_3)$  of  $CH_3OH$  at  $2930$ ,  $2867$  and  $2847\text{ cm}^{-1}$ .

The azomethine stretches  $\nu(C=N)$  are observed at  $1659$  and  $1647\text{ cm}^{-1}$  in  $[UO_2(salen)(H_2O)]$ . The first, which is strong in the infrared spectrum, should be assigned to the antisymmetric  $C=N$  stretch of the type  $B_2$ , and the other band which occurs as a weak shoulder in the infrared spectrum and strong in the Raman spectrum should be related to the symmetric  $C=N$  stretch ( $A_1$ ). The corresponding  $\nu(C=N)$  values in  $[UO_2(salen)(CH_3OH)]$  occur at  $1650$  and  $1642\text{ cm}^{-1}$ , respectively. It should be mentioned that the corresponding values for the free ligand salen are observed at  $1642$  and  $1634\text{ cm}^{-1}$ . The shift of  $\nu(C=N)$  in the complexes to higher frequency values may indicate that the bond order of the carbon-nitrogen link is increased upon coordination to  $U(VI)$ . This may suggest that the salen ligand coordinates to  $U(VI)$  through both  $\sigma$ - and  $\pi$ -donation. The  $\pi$ -donation is expected to come mainly from the  $\pi^*$  of the

C=N to the empty  $t_{2g}$  orbitals of U(VI). This will decrease the  $\pi^*$ -electron density of the C=N group and hence increases both its bond order and vibrational frequency.

In the assignments of the breathing vibrations of the phenyl groups, the expression developed by Colthup *et al.* [16] and used by Datta *et al.* [9] in their work on Ni(II)-Schiff base complexes is used. The infrared and Raman bands occur in the region 1610–1570  $\text{cm}^{-1}$  (see Table I) and should be assigned to the phenyl quadrant stretching vibrations, while the phenyl semicircular stretches are assigned to the bands in the region 1550–1475  $\text{cm}^{-1}$ . The phenyl sextant stretching vibrations are associated with the group of bands occurring in the region 1406–1391  $\text{cm}^{-1}$ . The bands in the region around 1450  $\text{cm}^{-1}$  are assigned as expected to the CH deformations of the  $-(\text{CH}_2)_2$  and  $\text{CH}_3$  groups. The group of bands in the region 1345–1100  $\text{cm}^{-1}$  are related to C–O, C–C and C–N stretches of the chelate ring, as well as those of the  $=\text{N}-(\text{CH}_2)_2-\text{N}=\text{C}$  and  $\text{CH}_3-\text{OH}$ . The phenyl CH bending vibrations occur in the region 990–710  $\text{cm}^{-1}$  (Table I) and the in-plane CH quadrant bends are associated with the bands around 650–550  $\text{cm}^{-1}$ . The phenyl out-of-plane CH quadrant deformations are assigned in the region 470–337  $\text{cm}^{-1}$ .

Finally, the  $\nu_{\text{as}}(\text{U}-\text{O})$  stretch (oxygen of salen) is assigned in both complexes to the infrared band around 515  $\text{cm}^{-1}$ , while the corresponding  $\nu_{\text{s}}(\text{U}-\text{O})$  is assigned to the Raman band at 493  $\text{cm}^{-1}$ . The  $\nu(\text{U}-\text{O})$ , oxygen of  $\text{CH}_3\text{OH}$ , is related to the infrared band at 293  $\text{cm}^{-1}$ , while  $\nu_{\text{as}}(\text{U}-\text{N})$  and  $\nu_{\text{s}}(\text{U}-\text{N})$  are assigned to the medium infrared band at 270  $\text{cm}^{-1}$  and the weak Raman band at 265  $\text{cm}^{-1}$ , respectively. The assignments of these metal–ligand stretches are made on the basis of their activities as well as the relative bond strengths shown from the crystal structure data known [8] for  $[\text{UO}_2(\text{salen})(\text{CH}_3\text{OH})]$ , and also that the assigned bands do not exist in the free ligand spectra. However, the  $\nu(\text{U}-\text{N})$  stretches

were assigned at relatively low frequency values compared to other U–ligand vibrations. This is in agreement with the bond length values, which indicate that the U–N bond is the weakest with a value of 2.56 Å.

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