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Coordination Chemistry of f-Block Elements with Imine Acids. Part II. Studies on Dioxouranium(VI) Complexes of *N*-(Salicylidene)-L-valine and *N*-(Orthovanillidene)-L-valine

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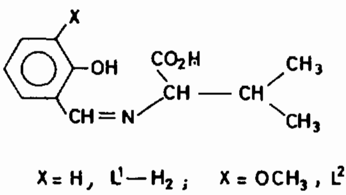
Abstract

N-(Salicylidene)-L-valine (L^1-H_2) and *N*-(orthovanillidene)-L-valine (L^2-H_2) have been used to synthesize new uranyl complexes including some mixed ligand ones. These chiral complexes, as well as some isolated earlier, have been thoroughly characterized through physico-chemical studies. Information pertaining to their conformation has been obtained from ^1H NMR and circular dichroism spectral studies and steric considerations.

Introduction

Imine acid complexes of several borderline Lewis acids (e.g., Cu^{2+}, Co^{2+}, etc.) have been the subject of considerable interest and prolonged research due to their importance in transamination and other related reactions [1]. The present work is part of our studies regarding coordination compounds of such ligands with hard acids like UO_2^{2+} and trivalent lanthanides (Ln^{3+}) as there is still a need to have a thorough understanding about structure and bonding in such cases, particularly the conformations of both the chelated ligands and the complex molecules [2, 3]. Preliminary results on the synthesis of some new coordination compounds of the UO_2^{2+} entity with L^1-H_2 using a phthalate buffer have been reported earlier [2]. Here we present spectroscopic studies on these UO_2^{2+} complexes as well as on several other new UO_2^{2+} complexes of both L^1-H_2 and L^2-H_2 prepared in this study. Although some circular dichroism (CD) spectral studies exist on both Cu^{II}–imine acid complexes and UO_2^{2+}–Schiff base complexes, subsequent development of the salicylidene-imine chirality rule helps in interpreting more significantly (especially the conformational aspect) the CD spectral curves of the present chiral UO_2^{2+} complexes [4–8]. Actually there have been considerable developments of chiroptical methods for determining absolute configurations of *in situ* transition metal complexes [9, 10].



X = H, L^1—H_2 ; X = OCH_3, L^2—H_2

Experimental

$NH_4[UO_2(CO_3)(OH)(H_2O)_3]$, $[UO_2(C_2O_4)(H_2O)_3]$, $[UO_2(SO_4)(H_2O)_3]$ and $[UO_2F_2(H_2O)_2]$ were obtained by a literature procedure [11]. $[(UO_2)_2(L^1)(L^1\text{-}H)(CH_3COO)(H_2O)_2]$, $[(UO_2)_2(C_2O_4)_2(L^1\text{-}H_2)(H_2O)_4]$, $[UO_2F_2(L^1\text{-}H_2)]\cdot 2H_2O$ and $[(UO_2)_2(L^1\text{-}H)_2(CO_3)]$ were prepared by a method using phthalate buffer (pH 5.5) described earlier by the authors [2].

After destruction of organic matter with concentrated H_2SO_4 followed by H_2O_2, uranium was analyzed titrimetrically in each sample [12]. Nitrogen was determined by the micro Dumas method.

Optical rotatory power measurements at the sodium D line were obtained using a visual polarimeter and a 0.5 dm microcell (Rudolph Instruments, U.S.A.) on ~0.2% (*w*/*v*) solutions of the complexes in methanol; for the ligands 0.5% solutions were prepared *in situ* in water–methanol (1:1 *v*:*v*) medium in the presence of one equivalent of NaOH.

Electronic spectra in methanol were recorded on a Shimadzu (UV-240) spectrophotometer. CD spectra (600–260 nm) were recorded on a Jobin Yvon dichrograph RJ Mark III. IR spectra (4000–600 cm^{-1}) were recorded on a Beckman IR-20 spectrophotometer in nujol mull. IR spectra in the CsI phase (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 577 IR spectrophotometer. ^1H NMR spectra (FT) of the complexes were recorded on a Varian

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XL-100 spectrometer. ^1H NMR spectra (CW) of the ligands prepared *in situ* (using one equivalent of NaOH) in D_2O–methanol medium were recorded on a Varian EM-360 60 MHz NMR spectrometer.

Preparation of the Complexes

$[UO_2(L^1)(H_2O)_2]$, $Na[(UO_2)_2(L^1\text{-}H)_3(SO_4)(H_2O)_2]$

$UO_2(NO_3)_2 \cdot 6H_2O$ or $[UO_2(SO_4)(H_2O)_3]$ was reacted with L-valine, salicylaldehyde and KOH/NaOH in a 1:2:2:2 molar ratio in water–methanol (1:1 *v*/*v*) medium at 60 °C with stirring. The solution was concentrated, cooled and the crystals were filtered, washed with water, methanol, ether and finally dried over concentrated H_2SO_4; pH was *ca.* 3.5; yield, 55–60%.

$[UO_2(L^1)(bipy)]$, $[UO_2(L^1)(phen)(H_2O)]$

To a solution of L-valine (1 mmol) in a mixture of 2 ml of phthalate buffer (pH 5.5) and 2 ml of water were added salicylaldehyde (1 mmol) in 6 ml of methanol, 2,2′-bipyridyl or 1,10-phenanthroline (0.5 mmol) in 6 ml of methanol and $UO_2(NO_3)_2 \cdot 6H_2O$ (0.5 mmol) in 3 ml of water, with stirring at 60 °C. The mixture was slightly concentrated, cooled and the precipitate was worked up as before; final pH was *ca.* 4.5–5; yield, 45–50%.

$[UO_2(L^2)(H_2O)_2]$, $Na[UO_2(L^2\text{-}H)(SO_4)] \cdot H_2O$

$UO_2(NO_3)_2 \cdot 6H_2O$ was reacted with L-valine and orthovanillin in a 1:2:2 molar ratio in water–methanol (2.5:1 *v*/*v*) medium at 60 °C with stirring (1 h) and the precipitate was recovered as before; final pH was below 4; yield, 55–60%. The product was recrystallized from water–methanol (1:1 *v*/*v*) medium. $[UO_2(L^2)(H_2O)_2]$ may also be obtained by using other starting materials like $UO_2(ClO_4)_2$, $[UO_2(CH_3COO)_2(H_2O)_2]$ and $[UO_2(C_2O_4)(H_2O)_3]$.

$Na[UO_2(L^2\text{-}H)(SO_4)] \cdot H_2O$ was obtained from $[UO_2(SO_4)(H_2O)_3]$ (1 mmol) by a similar procedure using NaOH (1 mmol) as an additional reagent.

No pure product could be isolated for $[UO_2F_2(H_2O)_2]$ in the solid state from the reaction mixture.

$[(UO_2)_2(L^2\text{-}H_2)_3(CO_3)_2]$

To the ligand solution prepared *in situ* from L-valine (0.23 g, 2 mmol) in 10 ml of water and orthovanillin (0.3 g, 2 mmol) in 15 ml of methanol, finely powdered $NH_4[UO_2(CO_3)(OH)(H_2O)_3]$ (0.42 g, 1 mmol) was added with stirring (1 h) at 60 °C. The mixture was filtered and the filtrate was concentrated to crystallization; final pH was *ca.* 4.5; yield, 45%.

$[UO_2(L^2)(bipy)(H_2O)]$, $[UO_2(L^2)(phen)]$

$UO_2(NO_3)_2 \cdot 6H_2O$ was reacted with L-valine, orthovanillin, NaOH and 2,2′-bipyridyl or 1,10-phenanthroline in a 1:1:1:1 molar ratio in water–methanol (1:1 *v*/*v*) medium with stirring at 60 °C; final pH was *ca.* 4; yield, 50–55%.

Results and Discussion

The characterization data for these two series of complexes ($L^1\text{-}H_2$ and $L^2\text{-}H_2$) are given in Tables I and II, respectively; different types of mixed ligand

TABLE I. Characterization Data for the Dioxouranium(VI) Complexes of *N*-(Salicylidene)-L-valine

Complex	$[\alpha]_D$	λ_{max} (nm) (log ϵ) in methanol[a]	ν_3 (cm^{-1}), F_{UO} (mdyne/Å) and R_{UO} (Å) of the UO_2^{2+} entity	pK_a Values of unneutralised protons
$[(UO_2)_2(L^1)(L^1\text{-}H)(CH_3COO)(H_2O)_2]$	−886	218sh(4.71); 230(4.76); 262sh(4.35); 340(3.93); 470sh(2.96)	915, 905; 6.88; 1.74	7.1
$[(UO_2)_2(C_2O_4)_2(L^1\text{-}H_2)(H_2O)_4]$	b	b	950, 940; 7.42; 1.72	b
$[UO_2F_2(L^1\text{-}H_2)] \cdot 2H_2O$	−463	218(4.51); 232sh(4.43); 258sh(4.21); 275sh(4.04); 335(3.72); 470(2.45)	955; 7.58; 1.72	6.00 7.69
$[(UO_2)_2(L^1\text{-}H)_2(CO_3)]$	−1422	218sh(4.69); 230(4.74); 262sh(4.33); 340(3.91); 470sh(2.94)	910, 895; 6.77; 1.74	8.12 7.05

[a] Electronic spectral data for $L^1\text{-}H_2$ in water–methanol (1:1 *v*/*v*) medium in the presence of one equivalent of NaOH. 255(4.09); 270sh(3.3); 320(3.54). [b] Insoluble. sh = shoulder. $[\alpha]_D$ for $L^1\text{-}H_2$ in the above mentioned medium: −416. (L^1) is the anion ($C_{12}H_{13}NO_3^{2-}$) of $L^1\text{-}H_2$.

TABLE II. Characterization Data for the Dioxouranium(VI) Complexes of *N*-(orthovanillidene)-L-valine and *N*-(Salicylidene)-L-valine

Complex	Colour $[\alpha]_D$	Analysis, found (Calc.) (%) U	C	H	N	TGA Total mass loss, found (calc.) (%)	λ_{max} (nm) (log ε) in methanol[b]	ν_3 (cm^{-1}), F_{UO} (mdyne/Å) and R_{UO}(Å) of UO_2^{2+} entity	pK_a Values of unneutralised protons
$[UO_2(L^2)(H_2O)_2]$	dark red −916	42.72 (42.88)	28.0 (28.1)	3.54 (3.42)	2.72 (2.52)	51.08 (51.35)	231(4.56); 268sh (4.13); 340(3.68); 400(3.27); 480sh (2.80)	935; 7.27; 1.73	7.9 11.24
$[(UO_2)_2(L^2\text{-}H_2)_3(CO_3)_2]$	dark red −1399	34.76 (33.68)	34.85 (34.82)	4.9 (3.61)	3.36 (2.97)	61.45 (61.78)	228(4.95); 265sh (4.59); 340(4.10); 400(3.70)	935, 920; 7.15; 1.73	8.35 8.35 8.07
$[UO_2(L^2)(bipy)(H_2O)]$	dark red −2068	33.18 (34.34)	40.3 (39.82)	4.0 (3.32)	6.29 (6.06)	61.46 (61.03)	232(4.64); 276 (4.40); 340(3.61); 400(3.25); 480sh (2.73)	915, 925; 7.04; 1.73	7.65
$[UO_2(L^2)(phen)]$	dark red −1127	36.17 (34.04)	43.0 (42.91)	4.16 (3.29)	5.82 (6.00)	61.41 (61.37)	228(4.65); 263 (4.40); 340(3.40); 480sh(2.69)	915, 925; 7.04; 1.73	
$Na[UO_2(L^2\text{-}H)(SO_4)]\cdot H_2O$[a]	dark red −1157	37.96 (36.22)	24.3 (23.7)	2.88 (2.74)	2.26 (2.13)	54.43 (55.4)	223(4.57); 260sh (4.17); 330(3.72); 390(3.34); 480 (2.78)	935; 7.27; 1.73	7.2
$[UO_2(L^1)(bipy)]$	orange red −1096	35.53 (36.84)	40.7 (40.93)	2.96 (3.25)	5.88 (6.51)	58.0 (58.14)	215sh(4.45); 232 (4.55); 275(4.33); 340(3.6); 472(2.6)	918; 7.0; 1.73	
$[UO_2(L^1)(phen)(H_2O)]$	dark red −2061	35.05 (34.64)	43.0 (41.92)	2.71 (3.64)	7.26 (6.11)	57.15 (60.69)	228(4.86); 262 (4.62); 340(3.65); 472br(2.60)	892; 6.62; 1.74	7.87
$Na[(UO_2)_2(L^1\text{-}H)_3(SO_4)(H_2O)_2]$[a]	orange red −1253	35.83 (35.12)	33.0 (31.88)	3.94 (3.39)	2.97 (3.10)	56.6 (58.45)	218(4.82); 232sh (4.80); 258sh (4.53); 335(4.53); 470(2.99)	925; 7.11; 1.73	8.07 7.65 8.21
$[UO_2(L^1)(H_2O)_2]$	red −911	46.03 (45.33)	28.85 (27.43)	3.3 (3.24)	2.70 (2.66)	50.62 (48.57)	235sh(4.22); 260sh (4.05); 280sh (3.83); 330br (3.63); 400sh (3.23)	920, 900; 688; 1.74	7.78 10.95

[a] Satisfactory Na analyses have been found by atomic absorption spectrometry. [b] Electronic spectral data for $L^2\text{-}H_2$ in water–methanol (1:1 *v*/*v*) medium: −217(4.69); 240sh (4.46); 265(4.4); 293(4.36); 345sh(3.78); 415br(3.95). $[\alpha]_D$ for $L^2\text{-}H_2$ in the above mentioned medium: −91. (L^2) is the anion ($C_{13}H_{15}NO_4^{2-}$) of $L^2\text{-}H_2$, bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline.

complexes are known for the UO_2^{2+} entity [11]. Although most of these complexes are only slightly soluble in methanol or ethanol, they have a higher solubility in DMSO and DMF.

Usually during interaction between the UO_2^{2+} entity and imine acids, some alkali or buffer solution (e.g., a phthalate buffer, pH 5.5) should be added to ensure complex formation and to shift the equilibrium over to the right; however, an interesting point is that in the UO_2^{2+}–orthovanillin–valine system, no alkali is usually required during complex formation and the pertinent uranyl complexes crystallize out of the reaction medium at pH 4.5–5.

Molar electroconductance values Λ_M (ohm^{-1} cm^2 mol^{-1}) for the complexes of the L^1-H_2 series in methanol (Philips conductivity bridge, model 9500) at concentrations of $2–4.5 \times 10^{-4}$ M vary in the range 9–18 (except for $Na[(UO_2)_2(L^1\text{-}H)_3(SO)_4)(H_2O)_2]$ which is slightly higher); for the L^2-H_2 series Λ_M values are in the range 4–17 at concentrations of $3–9 \times 10^{-4}$ M ($Na[UO_2(L^2\text{-}H)(SO_4)] \cdot H_2O$ shows a higher Λ_M value) [13].

In order to have some idea about the acidity of the protons present in some of these complexes containing partly deprotonated ligands, their acid dissociation constants were measured (EC digital pH meter, model 5651) in water–methanol (2:3 v/v) medium at constant ionic strength (0.1 M $NaClO_4$) at 30 °C by Bjerum's method (using the equation $\bar{n}_H = nA - P - [H^+] + [OH]/A$) applying the Kelvin–Wilson titration technique; pK_a values were obtained by the least-squares method from the $\bar{n}_H - B$ values [14–17]. Although there is a possibility of calculating the pK_a values up to the third or later stages of dissociation in several cases, this could not be done in all of them due to the formatin of $Na_2U_2O_7$ after a certain stage of titration. The pK_a values for $[UO_2(L^1)(phen)(H_2O)]$, $[UO_2(L^1)(H_2O)_2]$, $[UO_2(L^2)(H_2O)_2]$ and $[UO_2(L^2)(bipy)(H_2O)]$ refer to their aqua groups.

TGA data (Table II; ~7 °C/min; air) of the complexes of the L^1-H_2 series show that major portions of their weights are lost over the region 280–530 °C. For the L^2-H_2 series main breaks in the TGA curves appear over the range 290–500 °C. The coordinated water molecules of the pertinent complexes are usually lost over the region 120–190 °C; the weight loss data (for aqua groups) are supported by IR experiments as well [11, 18]. For $[UO_2(L^1)(phen)(H_2O)]$ and $[UO_2(L^2)(bipy)(H_2O)]$ the IR spectral bands (νOH modes) in the range 3600–2800 cm^{-1} are completely eliminated (except the νCH modes) by heating these complexes to *ca.* 190 °C, thereby indicating the intraspheric nature of the water molecules as well as the complete deprotonation of the ligand residues in these cases. For these two ligands (L^1-H_2 and L^2-H_2) the νOH modes of the dissociable protons (–CO_2H and phenolic –OH) appear in the range 3600–2600 cm^{-1}. For most of the other complexes mentioned here no such complete elimination (of νOH modes) on heating (190 °C) is observed, indicating the presence of unneutralised ligand protons.

Electronic spectral data in methanol are shown in Tables I and II. Apart from the intraligand charge-transfer bands in the region 210–350 nm, the electronic spectral curves of these complexes are quite similar because they result from electronic transitions mainly localized on the ligand moiety bonded to the uranyl entity. The apical oxygen → f transition within the uranyl entity, centered at about 390–450 nm, has been covered by the aforesaid strong charge-transfer absorption occurring in the range 350–550 nm from the equatorial ligand pπ orbital to the 5f and/or 6d orbital of the uranium atom [5, 19–22].

For L-valine, δ_{as} and δ_s modes of the $\overset{+}{N}H_3$ group appear at 1615 and 1500 cm^{-1}, whereas the ν_{as} and ν_s vibrations of the CO_2' group are observed at 1580 and 1400 cm^{-1}, respectively. Although for L^1-H_2 obtained *in situ* (using NaOH) a good IR spectrum could not be obtained, some prominent bands could be identified: the ν(OH) mode together with the ν(CH) modes appear around 3600–2650 cm^{-1} (broad); the ν_{as} and ν_s modes of the CO_2' group are observed at 1595 and 1395 cm^{-1}, respectively; the ν(C=N) mode of the azomethine group and the OH bending vibration of the phenolic OH group appear at 1640 and 1405 cm^{-1}, respectively [23–26].

For $[UO_2(L^1)(bipy)]$ the absence of any ν(OH) mode indicates complete deprotonation of the ligand residue; the ν(C=N) mode appears as two prominent bands at 1670 and 1620 cm^{-1} respectively (the phenomenon of splitting of the ν(C=N) mode on coordination has been discussed earlier by other authors) [27–29]. The ν_{as} and ν_s modes of the CO_2' group appear at 1610 and 1395 cm^{-1}, respectively, the $\Delta\nu$ value (215 cm^{-1}) being consistent with unidentate carboxylate coordination [30, 31]; the C–O (phenoxide) stretching vibration appears at 1205 cm^{-1}. Thus the ligand is acting as a tridentate one here using the CH=N, CO_2' and phenoxide groups [32]. In the case of $[UO_2(L^1)(phen)(H_2O)]$ and $[UO_2(L^1)(H_2O)_2]$ similar types of IR data are observed for the three coordinating groups mentioned above, thereby indicating a similar type of coordination of the ligand unit in these two cases as well; IR band assignments have also been checked on oven-dried samples. For other complexes of the L^1-H_2 series, the appearance of several broad bands covering the region 1630–1200 cm^{-1} (up to 1690 cm^{-1} in several cases) interfers with the proper identification of vibrational modes for the CH=N and CO_2' groups; various modes of phenolic OH group (e.g., OH bending and C–O stretching) appear at around 1400 and 1220 cm^{-1}, respectively (the C–O mode being somewhat broadened possibly due to coordination) [15].

Among the secondary anions of these two series of complexes only the ν_{as} (O–C–O) mode of the $C_2O_4^{2-}$ group of $[(UO_2)_2(C_2O_4)_2(L^1\text{-}H_2)(H_2O)_4]$ could be identified at 1675 cm^{-1} [18].

As in the case of L^1-H_2, for L^2-H_2 (obtained *in situ* using NaOH) only a few IR bands could be identified; the ν(OH) mode appears around 3600–2800 cm^{-1}; the $\nu_{(C=N)}$ mode is located around 1640 cm^{-1}, the ν_{as} and ν_s modes of CO_2' group are observed at 1590 and 1395 cm^{-1}, respectively.

In the case of $[UO_2(L^2)(phen)]$ no ν(OH) band (for $-CO_2H$ and phenolic OH groups) is present, as expected; the ν(C=N) mode is split into two components, as for the base adducts of L^1-H_2, which appear at 1670 and 1620 cm^{-1}, respectively; the ν_{as} and ν_s modes of the CO_2' group appear at 1605 and 1390 cm^{-1}, the $\Delta\nu$ value (215 cm^{-1}) indicates unidentate carboxylate coordination also for this complex; the C–O (phenoxide) stretching vibration appears at 1185 cm^{-1}. These data are consistent with tridentate ligand coordination involving the CH=N, CO_2' and phenoxide groups [32]. $[UO_2(L^2)(bipy)(H_2O)]$ and $[UO_2(L^2)(H_2O)_2]$, as well as their oven-dried (190 °C) species, exhibit similar types of IR data for the three abovementioned coordinating groups, thereby indicating tridentate ligand coordination for these complexes also.

For the other two complexes of the L^2-H_2 series, the appearance of several broad bands over the region 1650–1250 cm^{-1} prevents unambiguous IR band assignments for most of the pertinent coordinating groups; various modes of the phenolic OH group, e.g., OH bending and C–O stretching vibrations coupled with the OH bending mode, appear around 1400 and 1220 cm^{-1}, respectively (somewhat broadened as compared to that in the free ligand) [15].

For these uranyl complexes the ν_3 of the UO_2^{2+} entity appears around 955–892 cm^{-1} (Tables I and II). From these ν_3 values (average taken when this band is split) F_{UO} (mdyne/Å) and R_{UO} (Å) values for the UO_2^{2+} entity have been calculated; the R_{UO} (Å) values fall within the range found from crystallographic measurements on uranyl complexes [33, 34].

In the low frequency IR spectra of these complexes, the ν_2 of the UO_2^{2+} entity appears as a strong band (usually split) in the range 270–245 cm^{-1} [35, 36]. A prominent band appears at 370–365 cm^{-1} for the complexes of the L^1-H_2 series except for $[UO_2(L^1)(bipy)]$, $[UO_2(L^1)(phen)(H_2O)]$ and $[UO_2(L^1)(H_2O)_2]$, it may be assigned to a metal–OH (unneutralised phenolic) bond stretching mode ($\nu HO \rightarrow U$) and it should be absent for complexes with completely deprotonated ligands, which is actually the case [15]. For the L^2-H_2 series this $\nu_{HO\rightarrow U}$ (unneutralised phenolic OH) mode appears at 385–380 cm^{-1} and it is absent in the case of $[UO_2(L^2)(phen)]$, $[UO_2(L^2)(bipy)(H_2O)]$ and $[UO_2(L^2)(H_2O)_2]$ [15].

^1H NMR spectral data for the ligands (L^1-H_2) and (L^2-H_2) obtained *in situ* and those of the corresponding uranyl complexes are given in Table III. The low solubility (0.1-0.2% *w/v*) of these complexes in the solvents used for recording the ^1H NMR spectra prevents identification of the multiplicities of the hydrogen signals in some cases. The hydrogen on the chiral carbon atom of L-valine could not be located with certainty due to the presence of residual solvent peaks (e.g., for CD_3OD at 4.85 and 3.35δ ppm and for D_2O at 4.7–4.6 δ ppm).

For $[UO_2(L^1)(H_2O)_2]$ the azomethine (CH=N) hydrogen is deshielded from its position in the free ligand due to its coordination to the UO_2^{2+} entity; however, both upfield and downfield shifts of δ (ppm) values may be due to several factors other than only coordination to the UO_2^{2+} entity, e.g., magnetic anisotropy of the UO_2^{2+} entity, proximity of ligands in a rigid chelate structure, etc. [21, 25, 26, 37]. The signals for the two methyl groups appear as two distinct doublets, indicating their nonequivalence in this complex (Fig. 1). Similar types of data are obtained for $[UO_2(L^1)(bipy)]$ where, in addition to the usual hydrogen signals, some peaks corresponding to the 2,2'-bipyridyl ring hydrogens are present. For $[UO_2F_2(L^1\text{-}H_2)]\cdot 2H_2O$ the multiplicities of the methyl hydrogen (6H) signals are different from those of the two other complexes mentioned above and appear as a doublet (2H) and a quintuplet (4H), respectively; possibly a different mode of ligand (L^1-H_2) coordination (and/or conformation is responsible for this change in multiplicity [25, 37].

For $[UO_2(L^2)(H_2O)_2]$ the azomethine signal appears at 9.27 δ ppm as compared to that for L^2-H_2 at 8.5 δ ppm, as a result of coordination; the two methyl groups are also non-equivalent here, as indicated by the appearance of two distinct doublets instead of the six methyl quartet for the free ligand. ^1H NMR data also indicate a similar

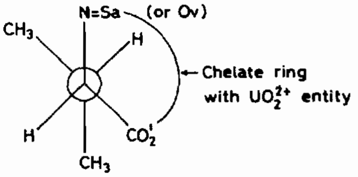

Fig. 1. Proposed Newman projection for $[UO_2(L^1)(H_2O)_2]$ or $[UO_2(L^2)(H_2O)_2]$; Sa = salicylidene, Ov = orthovanillidene moiety.

type of ligand coordination in the case of $UO_2(L^2)$-(bipy)(H_2O)]. For [$(UO_2)_2(L^2$-$H_2)_3(CO_3)_2$], although the azomethine signal appears at 9.39 δ ppm as before, the multiplicities of the methyl signals are different as compared to that of the other two complexes of the L^2-H_2 series, indicating a different

TABLE III. ^{1}H-NMR Spectral Data (δ (ppm) *vs.* TMS or DSS) of the Ligands and the Corresponding UO_2^{2+} Complexes

L^1-H_2[a]	CH=N (8.5, 1H, singlet); aromatic hydrogens (8–6.6, 4H, several multiplets); tertiary hydrogen (2.45, 1H, d); methyl hydrogens (1.2, 6H, quartet, *J* = 4.2 Hz)
[$UO_2(L^1)(H_2O)_2$][b]	CH=N (9.28, 1H, singlet); aromatic hydrogens (7.57, 2H, multiplet; 7.11, 1H, doublet; 6.79, 1H, sextet); tertiary hydrogen (2.45, 1H, octet); methyl hydrogens (1.23, 3H, doublet, *J* = 7.01 Hz; 1.01, 3H, doublet, *J* = 7.11 Hz)
[$UO_2(L^1)$(bipy)][b]	CH=N (9.24, 1H, singlet); 2,2′-bipyridyl ring hydrogens (8.66, 2H, doublet; 8.36, 2H, triplet; 7.96, 2H, triplet; 7.45, 2H, triplet); aromatic hydrogens (7.66, 2H, multiplet; 7.1, 1H, doublet; 6.78, 1H, multiplet); tertiary hydrogen (2.43, 1H,d); methyl hydrogens (1.23, 3H, doublet, *J* = 6.01 Hz; 1.0, 3H, doublet, *J* = 7.01 Hz)
[$UO_2F_2(L^1$-$H_2)$]·$2H_2O$[c]	CH=N (9.38, 1H, singlet); aromatic hydrogens (7.77, 2H, quartet; 7.09, 1H, doublet; 6.94, 1H, triplet); tertiary hydrogen (2.42, 1H, octet); methyl hydrogens (1.2, 2H, doublet, *J* = 7.01 Hz; 1.01, 4H, quintuplet, *J* = 3 Hz, 4 Hz)
L^2-H_2[a]	CH=N (8.5, 1H, singlet); aromatic hydrogens (7.68–6.5, 3H, d); methoxy hydrogens (4.2, 3H, singlet); tertiary hydrogen (2.38, 1H, d); methyl hydrogens (1.25, 6H, quartet, *J* = 3.1 Hz)
[$UO_2(L^2)(H_2O)_2$][b]	CH=N (9.27, 1H, singlet); aromatic hydrogens (7.31, 2H, sextet; 6.76, 1H, triplet); methoxy hydrogens (4.07, 3H, singlet); tertiary hydrogen (2.44, 1H, d); methyl hydrogens (1.23, 3H, doublet, *J* = 6.11 Hz; 1.01, 3H, doublet, *J* = 6.71)
[$UO_2(L^2)$(bipy)(H_2O)][b]	CH=N (9.24, 1H, singlet); 2,2′-bipyridyl ring hydrogens (8.66, 2H, doublet; 8.32, 2H, triplet; 7.96, 2H, multiplet; 7.45, 2H, d); aromatic hydrogens (7.28, 2H, d; 6.76, 1H, d); methoxy hydrogens (4.06, 3H, singlet); tertiary hydrogen (2.42, 1H, d); methyl hydrogens (1.21, 3H, doublet, *J* = 6.81 Hz; 0.99, 3H, doublet, *J* = 7.01 Hz)
[$(UO_2)_2(L^2$-$H_2)_3(CO_3)_2$][c]	CH=N (9.39, 3H, singlet); aromatic hydrogens (7.42, 6H, sextet; 6.88, 3H, quartet); methoxy hydrogens (4.12, 9H, singlet); tertiary hydrogen (2.4, 3H, d); methyl hydrogens (1.21, 6H, doublet, *J* = 6.31 Hz; 1.02, 12H, quartet, *J* = 5 Hz, 2.2 Hz)

[a] In D_2O–methanol (1:1 *v*/*v*) medium in the presence of one equivalent of NaOH with TMS as external reference. [b] In CD_3OD. [c] In D_2O. [d] Unresolved multiplet.

TABLE IV. Circular Dichroism (CD) Data for the Ligands and the Corresponding Dioxouranium(VI) Complexes

Compound	λ_{max} (nm), molar ellipticity (θ)
L^1-H_2[a]	263sh, −220; 268sh, −170; 290sh, +43.8; 310, +87.6; 330sh, +43.8; 350sh, +87.6; 390, +203; 420sh, +43.5; 440, −14.5
[$UO_2(L^1)(H_2O)_2$][b]	275, −24231; 320, +12873; 393br, −8802; 520br, +852
[$UO_2(L^1)$(phen)(H_2O)][b]	277, −23000; 300sh, −11000; 325, +2100; 355sh, −2900; 400br, −6700; 416sh, −5000; 445sh, −1700; 485sh, −650; 530, +324
[$UO_2F_2(L^1$-$H_2)$]·$2H_2O$	273, −10750; 300sh, −3250; 320, +4540; 400br, −3380; 530br, +200
[$(UO_2)_2(L^1)(L^1$-H)(CH_3COO)$(H_2O)_2$]	280, −30100; 320, +14500; 350sh, −1225; 400br, −11300; 530br, +540
L^2-H_2[c]	262sh, −14530; 266, −20342; 268, +11624; 275, −31966; 320br, +5812; 350br, −2906; 410br, +5812; 450br, +8718
[$UO_2(L^2)(H_2O)_2$][b]	275, −32781; 330, +12534; 410br, −5383; 530br, +1848
[$UO_2(L^2)$(bipy)(H_2O)][b]	280, −22259; 330, +6585; 410br, −3781; 530br, +793
[$(UO_2)_2(L^2$-$H_2)_3(CO_3)_2$][b]	280, −69290; 330, +37148; 380sh, −5037; 420br, −10074; 530br, +2203
Na[$UO_2(L^2$-H)(SO_4)]·H_2O	280, −34130; 330, +13338; 410br, −5589; 520br, +1765

[a] In H_2O–methanol (1:1 *v*/*v*) medium in the presence of one equivalent of NaOH. [b] In methanol. [c] In H_2O–methanol (3:1 *v*/*v*) medium; sh = shoulder, br = broad.

type of ligand coordination (and/or conformation) in this case. However, for both $[UO_2F_2(L^1\text{-}H_2O)] \cdot 2H_2O$ and $[(UO_2)_2(L^2\text{-}H_2)_3(CO_3)_2]$ no methyl signal corresponding to those of the free ligands (L^1-H_2 and L^2-H_2) could be observed, *i.e.*, no ligand dissociation takes place in solution for these complexes (containing ligands with unneutralised protons [37].

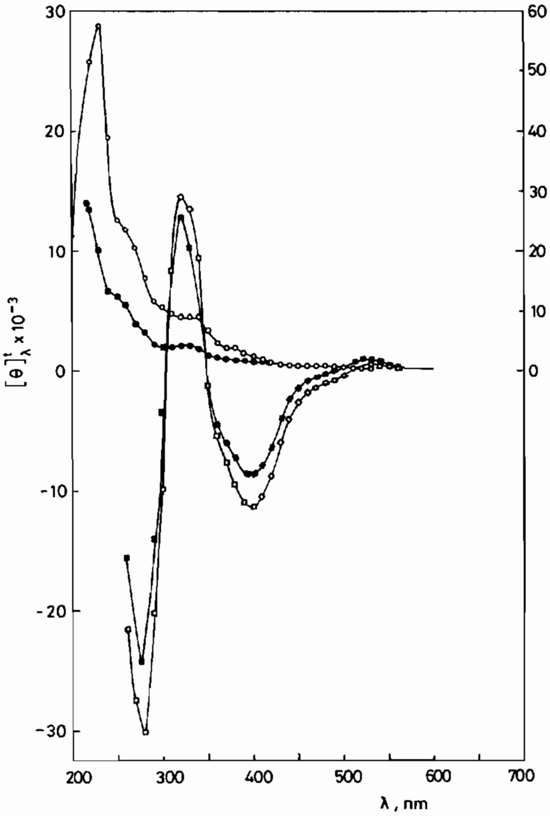

Fig. 2. Electronic and CD spectral curves of UO_2^{2+} complexes of L^1-H_2; (•–•–•/▪–▪–▪) $[UO_2(L^1)(H_2O)_2]$; (o–o–o/□–□–□) $[(UO_2)_2(L^1)(L^1\text{-}H)(CH_3COO)(H_2O)_2]$.

CD spectral data for L^1-H_2, L^2-H_2 and their UO_2^{2+} complexes are given in Table IV; two CD spectral curves along with their electronic spectra are shown in Fig. 2. For L^1-H_2 the electronic spectral bands at 255 nm and 320 nm are assigned to transitions of the intramolecularly hydrogen bonded salicylideneimino chromophore; the shoulder at 270 nm may be attributed to the presence of a quinoid tautomer and another band around 400 nm, which is sometimes present in various *N*-salicylidene derivatives, could not be located here. In the case of L^2-H_2 also the observed electronic spectral bands are consistent with the data noted by other authors for comparable systems [7, 8].

Of the four Cotton effects observed in the CD spectra of L^1-H_2, the positive one at 310 nm (at 320 nm for L^2-H_2), corresponding to the electronic spectral band around 320–345 nm, is taken as the diagnostic one for assigning the preferred conformation of the ligand; for the UO_2^{2+} complexes of L^1-H_2 and L^2-H_2, apart from the two bands (corresponding to those of the ligands) around 273–280 nm and 320–330 nm, respectively, two other Cotton effects are observed at 400 nm (negative as compared to a positive one for the ligands around 390–410 nm) and at 530 nm (new one, not present in the ligand), respectively.

To correlate the sign of the Cotton effect with the absolute configuration of *N*-salicylidene derivatives, the salicylideneimino chirality rule has been developed using the coupled oscillator model (out of the three important mechanisms which account for the generation of Cotton effects [7, 8]) which is based on a knowledge of the transition moment vectors. For the *N*-salicylidene derivatives of aliphatic α-amino acids (e.g., L-alanine, L-valine, L-leucine, etc., with the (*S*)-absolute configuration [38]) the preferred conformation **3a** for the absolute configuration represented by **3** gives positive chirality (since the chirality of the relevant transition moment is positive) for the Cotton effect at 315 nm (Fig. 3). Now the positive Cotton effects in the range 310–320 nm for L^1-H_2, L^2-H_2, and around 320–330 nm for the corresponding UO_2^{2+} complexes, indicate the presence of conformer **3a** as the dominant one for dichroic absorption in these cases as well; so these chiral imino acids display stereospecificity in the formation of UO_2^{2+} complexes. This is in agreement with the empirical planar sector rule which predicts a positive Cotton effect at 315 nm when the larger group, *i.e.*, CO_2' (with higher rotatory perturbation),

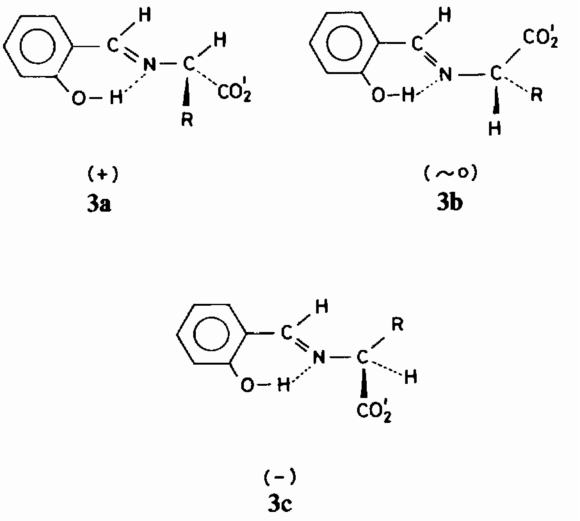

Fig. 3. Different conformers of L^1-H_2; R = $CH(CH_3)_2$.

is behind the plane of the salicylideneimino chromophore [6].

All the UO_2^{2+} complexes exhibit a positive Cotton effect at 520–530 nm assignable to a uranyl charge-transfer transition, dipole moment nearly forbidden, which couples with some uranyl vibrational frequency; an electron transfer of this type, from a π-oxygen orbital to an f-orbital of the uranium atom, is magnetically allowed. The molar extinction coefficient of the absorption band related to this Cotton effect is very low, and it is nearly impossible to detect the corresponding band in the electronic spectra [5].

A negative Cotton effect observed in these complexes around 393–420 nm, where charge transfer from equatorial ligand pπ orbital to 5f and/or 6d orbital of the uranium atom takes place, may be related to the conformation and distortion of the chelated *N*-(salicylidene)-L-valinato ring system [5, 21].

As the presence of both a chromophoric group and an optically active centre is essential in a molecule to produce a Cotton effect, it is likely that the existence of the asymmetric carbon atom induces the metal atom to be itself asymmetric and an asymmetric carbon atom of the same configuration in such compounds should cause the configuration of the UO_2^{2+} entity to be the same throughout. So the Cotton effect (around 320–330 nm) should be nearly identical for the complexes having the same configuration about the α-carbon atom of the ligand, which is actually experimentally observed here.

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