

Titanyl(IV), Zirconyl(IV), Hafnyl(IV) and Uranyl(VI) Complexes of Terdentate Benzoyl Hydrazones

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
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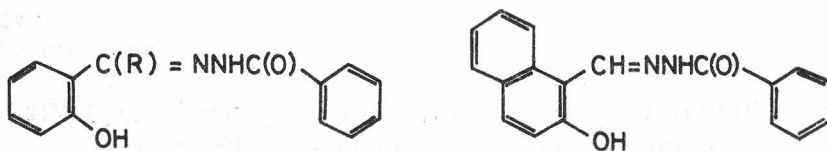
Titanyl(IV), zirconyl(IV), hafnyl(IV) and uranyl(VI) complexes of benzoyl hydrazones derived from benzoyl hydrazine and salicylaldehyde (BSH), *o*-hydroxy acetophenone (BAH), *o*-hydroxy propiophenone (BPH) and 2-hydroxy-1-naphthaldehyde (BNH) are described. These complexes were characterised on the basis of elemental analyses, electrical conductance and spectral (IR, UV and visible) data. The titanyl(IV) complexes having the formula $[TiL(OH)(H_2O)_2]_2O$ appear to have a seven-coordinate geometry, the zirconyl and hafnyl complexes, $[ML(OH)_2(H_2O)_4]_4$ ($M = Zr$ or Hf) appear to possess tetrameric structure in which each metal atom is eight-coordinated as in the original salt, $MOCl_2 \cdot 8H_2O$ ($M = Zr$ or Hf); whereas uranyl complexes $[UO_2L(H_2O)_2]_2$ are dimeric having phenoxide bridges,

as revealed by the  ring vibrations in the IR spectra at ca. 845 cm^{-1} , with each metal atom having an eight-coordinated structure. In all these complexes the benzoyl hydrazones act as dibasic terdentate (N, O^-, O^-) chelating agents.

INTRODUCTION

In recent years, a large number of high-coordination number (> 6) complexes of IV group elements with nitrogen and oxygen containing ligands have been studied.¹⁻⁴ However, little is known about the coordination chemistry of the oxycations of titanium, zirconium and hafnium.⁵⁻⁷ A lively controversy has been raging regarding the existence of oxycations of these elements with discrete $M = 0$ units.^{7,8} These studies were initiated with a view to study the behaviour of these oxycations in aqueous media. This paper describes the syntheses and some of the properties of titanyl(IV), zirconyl(IV) and hafnyl(IV) complexes with benzoyl hydrazones derived from benzoyl hydrazine and *o*-hydroxy arylaldehydes and ketones.

Some new uranyl(VI) complexes of these ligands were also been included to make the study more comprehensive. These benzoyl hydrazones, whose structures are depicted below, have been found to act as mono- and di-basic terdentate ligands with many bi- and trivalent metal ions of the first transition series.⁹⁻¹²



R = H(BSH), Me(BAH), Et(BPH)

(BNH)

EXPERIMENTAL

Benzoyl hydrazones were prepared following the method of Struve.¹³

Syntheses of complexes

(i) *Zirconyl and hafnyl complexes.* — On mixing equimolar solutions (1:1) of the metal chloride ($\text{MOCl}_2 \cdot 8\text{H}_2\text{O}$) in methanol and the ligand in acetone, a yellow solution was obtained. The colour of the solution deepened on raising its pH to ca. 5.0 by addition of 1% ethanolic KOH. The contents were gently heated for about 15 min. On slow evaporation yellow to deep yellow crystals were obtained. These were thoroughly washed with acetone and ether and dried under vacuo. Yield ca. 50%.

The zirconyl complexes are soluble in dimethylformamide, dimethylsulphoxide, and chloroform, partially soluble in acetone and ethanol; the hafnyl complexes are soluble only in dimethylformamide and dimethylsulphoxide and partially soluble in chloroform, acetone and ethanol.

(ii) *Uranyl complexes.* — An intense red colour developed on mixing equal volumes of equimolar solutions of uranyl nitrate in ethanol and the ligand in acetone. The pH of the solution was raised to ca. 5.5 by addition of 1% ethanolic KOH, when a reddish orange complex separated out. The contents were gently heated for a few minutes, cooled, filtered and the complexes obtained were recrystallised from acetone and dried under vacuo. Yield ca. 70%.

(iii) *Titanyl complexes.* — Potassium titanyl oxalate (0.01 M) was dissolved in distilled water (100 ml) and the ligand (0.01 M) dissolved in acetone was added to it. A reddish precipitate immediately separated out and it increased in volume on raising the pH of the solution to ca. 4.5 by addition of 1% aqueous KOH. The contents were digested for 0.5 hr at ca. 70 °C, cooled, filtered, washed successively with acetone and ether and dried under vacuo. Yield ca. 80%.

The complexes are soluble in dimethylformamide, dimethylsulphoxide and partially soluble in acetone and chloroform.

The zirconyl, hafnyl and titanyl complexes were also synthesized by taking different metal-ligand molar ratios; however, only one type of the complexes was isolated in each case as reported herein.

The molecular weights of the complexes were determined by Rast's Camphor method and are given in Table I.

TABLE I
Molecular Weights and Analytical Data of the Complexes ($M = \text{Ti, Zr, Hf, U}$).

| Compound | Found/% | | | | Calculated/% | | | | Molecular Weight | |
|---|---------|-------|------|------|--------------|-------|------|------|------------------|-------|
| | M | C | H | N | M | C | H | N | Calcd. | Found |
| [Ti(C ₁₄ H ₁₀ N ₂ O ₂)(OH)(H ₂ O)] ₂ O | 14.75 | 50.52 | 3.91 | 8.40 | 14.55 | 51.09 | 3.98 | 8.51 | 658 | 641 |
| [Ti(C ₁₃ H ₁₂ N ₂ O ₂)(OH)(H ₂ O)] ₂ O | 14.10 | 52.99 | 4.44 | 8.10 | 13.96 | 52.50 | 4.40 | 8.16 | 686 | 666 |
| [Ti(C ₁₆ H ₁₄ N ₂ O ₂)(OH)(H ₂ O)] ₂ O | 13.50 | 54.32 | 4.90 | 7.96 | 13.42 | 53.79 | 4.79 | 7.84 | 714 | 700 |
| [Ti(C ₁₈ H ₁₂ N ₂ O ₂)(OH)(H ₂ O)] ₂ O | 12.52 | 56.72 | 4.05 | 7.42 | 12.63 | 57.01 | 3.98 | 7.38 | 758 | 780 |
| [Zr(C ₁₄ H ₁₀ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 24.07 | 43.78 | 3.62 | 7.45 | 23.91 | 44.07 | 3.70 | 7.34 | 1526 | 1551 |
| [Zr(C ₁₅ H ₁₂ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 23.33 | 45.80 | 3.99 | 6.98 | 23.07 | 45.54 | 4.08 | 7.08 | 1582 | 1618 |
| [Zr(C ₁₆ H ₁₄ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 22.01 | 47.23 | 4.50 | 7.01 | 22.28 | 46.91 | 4.43 | 6.84 | 1638 | 1599 |
| [Zr(C ₁₈ H ₁₂ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 21.33 | 49.90 | 3.79 | 6.42 | 21.13 | 50.10 | 3.74 | 6.49 | 1726 | 1695 |
| [Hf(C ₁₄ H ₁₀ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 38.20 | 35.70 | 2.95 | 6.03 | 37.81 | 36.01 | 3.02 | 6.00 | 1867 | 1850 |
| [Hf(C ₁₅ H ₁₂ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 37.02 | 37.20 | 3.41 | 5.91 | 36.71 | 37.46 | 3.35 | 5.83 | 1923 | 1953 |
| [Hf(C ₁₆ H ₁₄ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 35.92 | 39.11 | 3.72 | 5.75 | 35.67 | 38.83 | 3.66 | 5.66 | 1979 | 1961 |
| [Hf(C ₁₈ H ₁₂ N ₂ O ₂)(OH) ₂ (H ₂ O)] ₄ | 33.90 | 41.70 | 3.20 | 5.51 | 34.15 | 41.84 | 3.12 | 5.42 | 2067 | 2040 |
| [UO ₂ (C ₁₄ H ₁₀ N ₂ O ₂)(H ₂ O)] ₂ ·2 | 44.09 | 31.22 | 2.55 | 5.09 | 43.73 | 30.89 | 2.59 | 5.14 | 1088 | 1100 |
| [UO ₂ (C ₁₅ H ₁₂ N ₂ O ₂)(H ₂ O)] ₂ ·2 | 43.00 | 32.66 | 3.00 | 4.90 | 42.62 | 32.26 | 2.89 | 5.02 | 1116 | 1098 |
| [UO ₂ (C ₁₆ H ₁₄ N ₂ O ₂)(H ₂ O)] ₂ ·2 | 41.31 | 31.90 | 3.10 | 4.97 | 41.59 | 33.57 | 3.17 | 4.89 | 1144 | 1123 |
| [UO ₂ (C ₁₈ H ₁₂ N ₂ O ₂)(H ₂ O)] ₂ ·2 | 39.50 | 36.21 | 2.66 | 4.81 | 40.05 | 36.39 | 2.71 | 4.71 | 1188 | 1180 |

Analyses and apparatus. — The conductivity of the complexes was measured on a Toshniwal conductivity bridge (CL 01/01) using a diptype cell. The electronic spectra were recorded in dimethylformamide on Cary-14, IR on Perkin-Elmer-621 (in KBr pellets) and far-IR on Beckman IR-12 spectrophotometers (in nujol mull). The metal content in the complexes was determined as the respective oxides.

RESULTS AND DISCUSSION

Elemental analyses (Table I) reveal 1:1 metalligand ratio in all these complexes. The complexes behave as non-electrolytes in dimethylformamide and dimethylsulphoxide ($\Lambda_M = 15-20 \text{ S cm}^2 \text{ mol}^{-1}$). The molecular weights (Table I) of the complexes reveal that uranyl complexes are dimeric whereas hafnium and zirconium complexes are tetrameric in nature. Accordingly, the complexes can be represented by the formulae $[\text{ML}(\text{OH})_2(\text{H}_2\text{O})]_4$, where $\text{M} = \text{Zr}$ or Hf ; $[\text{TiL}(\text{OH})(\text{H}_2\text{O})]_2\text{O}$ and $[\text{UO}_2\text{L}(\text{H}_2\text{O})_2]_2$, L stands for any of the benzoyl hydrazones. The presence of water molecules in these complexes is also indicated by thermal and infrared spectral studies. All the complexes are resistant to aerial oxidation and have high melting points ($>250^\circ\text{C}$). The coordination number and tentative structures of these complexes were inferred on the basis of their infrared and electronic spectra.

Infrared spectra. — The important infrared spectral bands of the ligands and their complexes are given in Table II. The strong bands at ca. 3200—3250 and 2700—2775 cm^{-1} in the spectra of the ligands are assigned to $\nu(\text{OH})$ vibrations involving hydrogen bonding.¹⁴ The bands in the 1600—1675, 1515, 1250, 650 and 495—505 cm^{-1} regions appear to have their origin in different amide group vibrations^{11,15,16} and may be attributed to amide-I ($\nu\text{C} = \text{O}$), amide-II ($\nu\text{CN} + \delta\text{NH}$), amide-III (δNH), amide-IV (in-plane $\text{C} = \text{O}$ deformation) and amide-VI (out-of-plane $\text{C} = \text{O}$ deformation) vibrations, respectively. The appearance of these bands suggests that the ligands exist in the amido form. The bands appearing in the 1610—1625 cm^{-1} region are assigned to $\nu(\text{C} = \text{N})$ of the azomethine linkage.

The spectra of the complexes exhibit no band characteristic of the amide group; instead a new strong band, similar to the one shown by azines, is observed at ca. 1600 cm^{-1} and it can be assigned to the stretching mode of the $>\text{C}=\text{N}-\text{N}=\text{C}<$ group.¹⁷ This suggests that the amide group of these hydrazones undergoes enolization and its oxygen makes a bond with the metal atom through deprotonation.¹⁸ The enolization of the ligands during complexation is also supported by the appearance of a new band in the 1550—1570 cm^{-1} region attributed to $\nu(\text{NCO})$ vibrations.¹⁵ The new bands appearing in the 390—440 cm^{-1} region can tentatively be assigned to enolic $\nu(\text{M}-\text{O})$ vibrations.¹⁴ It is worth mentioning that the enolization of the hydrazones, among other factors, also depends upon the pH of the reaction medium. The uranyl complexes prepared at lower pH have these ligands coordinated in the amido form.¹⁹ The $\nu(\text{C}=\text{N})$ band shows a downward shift of ca. 15 cm^{-1} indicating that the nitrogen atom of the azomethine group is coordinated to the metal atom. The new bands appearing in the 460—485 cm^{-1} region may be assigned to $\nu(\text{M}-\text{N})$ vibrations.²⁰

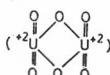
The disappearance of bands at ca. 3200—3275 and 2700—2775 cm^{-1} due to $\nu(\text{OH})$ indicates the involvement of phenolic oxygen in coordination

TABLE II
 Important Infrared Spectral Bands (cm^{-1}) of the Ligands and Their Complexes ($M = \text{Ti, Zr, Hf}$ or U).

| Compound | $\nu(\text{C}=\text{N})$ ($>\text{C}=\text{N}-\text{N}=\text{C}<$) $\nu(\text{NCO})$ | $\text{O}=\text{U}=\text{O}$ | | $\text{Ti}-\text{O}-\text{Ti}$ | $\nu(\text{M}-\text{O})$ Phenolic | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{O})$ Enolic |
|--|--|------------------------------|---------|--------------------------------|-----------------------------------|--------------------------|---------------------------------|
| | | ν_1 | ν_3 | | | | |
| [BSH] | 1625s | — | — | — | — | — | — |
| [BAH] | 1620s | — | — | — | — | — | — |
| [BPH] | 1620s | — | — | — | — | — | — |
| [BNH] | 1625s | — | — | — | — | — | — |
| [TiBSH(OH)(H ₂ O)] ₂ O | 1605s | — | — | 750s | 540m | 460m | 390w |
| [TiBAH(OH)(H ₂ O)] ₂ O | 1610s | 1600s | — | 760s | 515w | 455m | 390w |
| [TiBPH(OH)(H ₂ O)] ₂ O | 1605s | 1600s | — | 755s | 535m | 455m | 400w |
| [TiBNH(OH)(H ₂ O)] ₂ O | 1615s | 1595s | — | 760s | 530m | 470m | 395m |
| [ZrBSH(OH) ₂ (H ₂ O)] ₄ | 1610s | 1595s | — | — | 510m | 485m | 415m |
| [ZrBAH(OH) ₂ (H ₂ O)] ₄ | 1610s | 1560s | — | — | 510m | 470w | 415m |
| [ZrBPH(OH) ₂ (H ₂ O)] ₄ | 1610s | 1600s | — | — | 530m | 460m | 425m |
| [ZrBNH(OH) ₂ (H ₂ O)] ₄ | 1605s | 1595s | — | — | 525m | 480w | 435m |
| [HfBSH(OH) ₂ (H ₂ O)] ₄ | 1615s | 1605s | — | — | 535m | 480w | 430m |
| [HfBAH(OH) ₂ (H ₂ O)] ₄ | 1605s | — | — | — | 520m | 480w | 420m |
| [HfBPH(OH) ₂ (H ₂ O)] ₄ | 1610s | 1600s | — | — | 530m | 475m | 445m |
| [HfBNH(OH) ₂ (H ₂ O)] ₄ | 1610s | — | — | — | 510w | 460w | 415w |
| [UO ₂ BSH(H ₂ O)] ₂ | 1610s | 1600s | 900s | 845m | 525m | 470m | 435m |
| [UO ₂ BAH(H ₂ O)] ₂ | 1605s | 1560s | 900s | 840m | 540m | 460m | 420w |
| [UO ₂ BPH(H ₂ O)] ₂ | 1610s | 1595s | 910s | 840m | 540m | 485m | 435w |
| [UO ₂ BNH(H ₂ O)] ₂ | 1610s | — | 900s | 850m | 530m | 470m | 430w |



through deprotonation.¹⁰ The bands occurring in the region 510—540 cm^{-1} may be assigned to phenolic $\nu(\text{M—O})$ vibrations.²⁰ The bands observed in the ligand at ca. 1520 and 1280 cm^{-1} assignable¹⁴ to $\nu(\text{C—O})$ and $\delta(\text{C—O})$ vibrations, respectively, shift to higher frequencies (15—25 cm^{-1}) in the spectra of uranyl complexes only, thereby indicating the presence of phenoxide bridges. An increase in the frequencies of these two bands has been taken as a reliable criterion of the bi- or polymeric nature of the complexes involving phenoxide bridges.²² The appearance of a medium intensity band at 845 cm^{-1} also supports the presence of four-membered

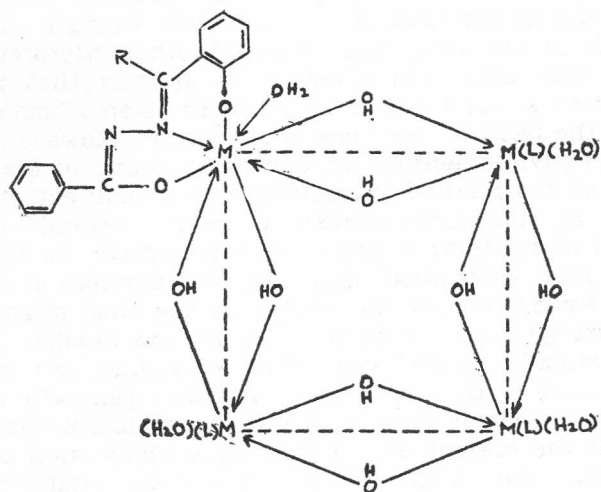
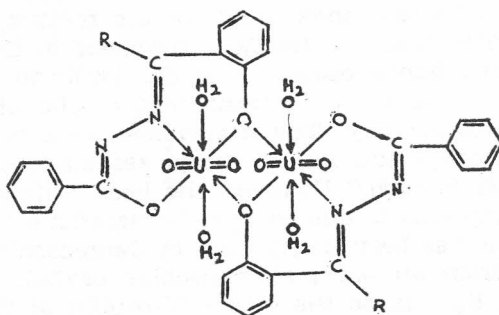
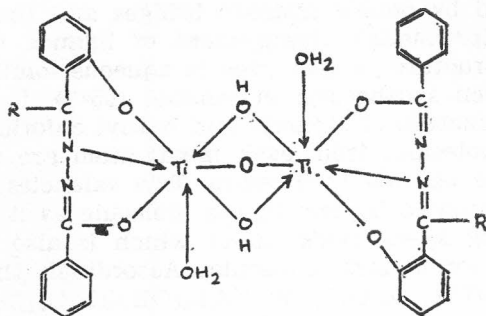
ring  however, it may be pointed out that the $\nu_s(\text{O=U=O})$

also absorbs around the same frequency.²³ Thus, their assignment is purely tentative. No such increase in the $\nu(\text{C—O})$ and $\delta(\text{C—O})$ bands has been observed for titanyl, zirconyl and hafnyl complexes, thus ruling out the presence of enolic or phenolic bridges in these complexes. Similar observations have also been made for the chromium complexes of several benzoyl hydrazones.¹⁰ The infrared spectra of the complexes show bands in the region 3400—3500 and 820—830 cm^{-1} assignable to $\nu(\text{OH})$ and $\rho\omega(\text{H}_2\text{O})$ vibrations of a coordinated water molecule, as in cobalt(III) complexes of these ligands.^{9a,14} The presence of coordinated water has also been confirmed by thermogravimetric studies which indicate loss of water molecules in the range 115—125 °C. Some of these complexes show medium intensity bands at ca. 560 cm^{-1} which can tentatively be assigned to $\nu(\text{M—O})$ (H_2O) vibrations.

The uranyl complexes show two additional bands at ca. 900—910 and 230—240 cm^{-1} assignable²³ to $\nu_{as}(\text{UO}_2)$ (ν_3) and $\delta(\text{UO}_2)$ (ν_1) vibrations, respectively. However, the existence of a discrete M=O ($\text{M}=\text{Ti}$, Zr or Hf) moiety in titanyl, zirconyl and hafnyl complexes has not been confirmed by X-ray diffraction methods, although several contentions have been made for their occurrence on the basis of infrared spectral data.^{6—8,24} A number of workers^{7,25} have assigned a discrete $\nu(\text{Ti=O})$ vibration in the titanyl complexes in the region 900—1100 cm^{-1} , but the presence of such a moiety has been contradicted on the basis of X-ray studies on some titanyl complexes.³ There is evidence from vibrational spectroscopy which shows that $\text{K}_2\text{TiO}(\text{OX})_2 \cdot 2\text{H}_2\text{O}$ contains $-\text{Ti—O—Ti}-$ chains;²⁶ such chains are associated with very strong and broad absorption near 750 cm^{-1} in the infrared. The present complexes of titanium also show a strong band at ca. 750—760 cm^{-1} which can be assigned to $(-\text{Ti—O—Ti}-)$ vibrations. Similarly, a large number of zirconyl and hafnyl complexes have been studied both in aqueous and non-aqueous media and spectral evidence has been presented for the existence of Zr=O and Hf=O moieties. Such an evidence does not appear convincing in view of the X-ray structure determination of $\text{MOCl}_2 \cdot 8\text{H}_2\text{O}$ ($\text{M}=\text{Zr}$ or Hf) which clearly indicates the absence of a M=O moiety in these molecules. On the contrary, X-ray analysis data indicated²⁷ that zirconyl and hafnyl chloride molecules are in fact tetrameric $[\text{M}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{+8}$ with the square-arrangement of

metal atoms joined by double hydroxo bridges and the eight-coordinate (Archimedaen antiprismatic) arrangement of ligands (H_2O) around the metal atom. The structure persists even in aqueous solution. Since present complexes have been synthesised in ethanol (95%), it appears that the basic tetrameric structure of zirconyl and hafnyl chlorides remains intact and three water molecules from each metal atom are replaced by three donor atoms of the benzoyl hydrazones. Two valencies of each of these metal atoms are satisfied by one ligand molecule as it acts as a dibasic terdentate chelating agent (vide infra) which is also indicated by the absence of chloride ion in these molecules. Accordingly the complexes have the formulae $[\text{ML}(\text{OH})_2(\text{H}_2\text{O})]_4$ or $[\text{M}_4\text{L}_4(\text{OH})_8(\text{H}_2\text{O})_4]$.^{20,28,29} Similar observations have also been made by Kharitonova et al.³⁰ during their extensive studies on zirconyl and hafnyl complexes of several amino acids.

Electronic spectra. — Electronic spectra of the complexes were recorded in nujol and dimethylformamide in the range 50000—40000 cm^{-1} . The spectra of all the complexes show bands in the regions 40000, 36000 and 24000—22000 cm^{-1} . The first two bands also appear in the spectra of the ligands and thus the bands occurring at ca. 40000 and 36000 cm^{-1} may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the phenolic and azomethine group,^{9,11} respectively. The occurrence of a band at ca. 22000 cm^{-1} in titanyl, zirconyl and hafnyl complexes may be attributed to a charge-transfer phenomenon.²⁵ However, the band appearing at ca. 24200 cm^{-1} in uranyl complexes is due to the characteristic absorption of the uranyl cation and it has been interpreted by Jørgensen³¹ as being due to electron transfer from an occupied molecular orbital, localized mainly on the two oxygen ligands, to the empty 5f-orbital of the central atom. This band is of low intensity as compared to those observed for intraligand transitions. The low intensity of this band has been explained as being due to the extraordinarily low oscillator strength of $\pi_u \rightarrow 5f$ in a linear molecule of symmetry d_{coh} ,³¹ although other interpretations of this phenomenon have also been given.^{32,33} It appears that no systematic attempt has been so far made to establish the stereochemistry of uranyl complexes on the basis of their electronic spectra. However, the principal effect of ligand environment on the electronic spectra of uranyl complexes appears to be on the relative intensity and to a small extent on the energies of series of vibrational peaks.³⁴ There are several³⁵ empirical and semi-empirical correlations of uranyl complex spectra to their stereochemistries. One such correlation suggested by Vdovenko et al.³⁶ and later supported by Ryan,³⁴ relates the energy of the first intense vibrational band in the uranyl spectrum to the coordination number. It states that the eight-coordinated uranyl complexes (including two uranyl oxygen atoms contributing to the coordination number) generally do not absorb above 20000 cm^{-1} whereas those with a six-coordination number do. Thus, it appears that the present uranyl complexes which show only one band at ca. 24200 cm^{-1} due to the UO_2 moiety are also eight-coordinated, as also established by other studies. It may, however, be pointed out that this correlation is very tentative and requires further elaborate studies before being generalised.



$M = Zr \text{ or } Hf$

On the basis of the above discussion, the following structures can be suggested for the titanyl(IV), zirconyl(IV), hafnyl(IV) and uranyl(VI) complexes. (See Scheme).

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SAŽETAK

Titanil(IV)-, cirkonil(IV)-, hafnil(IV)- i uranil(VI)-kompleksi terdentatnih benzoilhidrazona

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Opisani su kompleksi TiO^{2+} , ZrO^{2+} , HfO^{2+} i UO_2^{2+} s benzoilhidrazonima (L) izvedenim iz benzoilhidrazina i salicilaldehida, *o*-hidroksiacetofenona, *o*-hidroksipropiofenona ili 2-hidroksi-1-naftilaldehida. Kompleksi su karakterizirani elementnom analizom, električkom vodljivošću te IR i UV/VIS spektrima na temelju čega su predložene njihove strukture. Kompleks $[TiL(OH)(H_2O)]_2O$ vjerojatno ima koordinaciju 7, dok su kompleksi $[ML(OH)_2(H_2O)]_4$ (M = Zr, Hf) tetramerne građe, s koordinacijom 8. Uranil-kompleksi, $[UO_2L(H_2O)_2]$ dimeri su s fenoksidnim mostovima. U svim kompleksima benzoilhidrazoni djeluju kao dvobazni terdentatni (N, O, O) ligandi.