

Synthesis, characterization and biological activity of (E₁, E₂) N¹,N²- bis[1-(3,4-dihydroxyphenyl)ethylidene]oxalohydrazide complexes: New method for ZrO²⁺ separation

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Abstract: The bond length, bond angle, HOMO, LUMO, dipole moment and charges on the atoms have been calculated to confirm the geometry of (E₁, E₂) N¹,N² - bis[1-(3,4-dihydroxyphenyl)ethylidene]oxalohydrazide, H₆DPOH. The metal complexes of Cr³⁺, VO²⁺, ZrO²⁺, HfO²⁺, UO₂²⁺ and MoO₂²⁺ with H₆DPOH have been prepared and characterized by partial elemental analysis, spectral studies (electronic; IR), thermal analysis and magnetic measurements. The data suggest the formation of [Cr(H₄DPOH)(H₂O)₃Cl]H₂O, [VO(H₄DPOH)(H₂O)₂], [Hf(H₄DPOH)(H₂O)]H₂O, [UO₂(H₄DPOH)(H₂O)₂]2H₂O [MoO₂(H₄DPOH)] and [(ZrO)₂(H₂DPOH)(C₂H₅OH)₂]. H₆DPOH behaves as a dibasic bidentate in all complexes except ZrO²⁺ which acts as a tetrabasic tetradentate for the two ZrO²⁺ ions. An octahedral geometry was proposed for the Cr³⁺, HfO²⁺, MoO₂²⁺ and UO₂²⁺ complexes and square pyramid for VO²⁺. The Cr(III) or VO²⁺ complexes are necessary to degrade the DNA of Eukaryotic subject completely; the other complexes have little effect. H₆DPOH was found applicable as a new reagent for the separation and preconcentration of ZrO²⁺ ions from different water samples using flotation technique with satisfactory results.

Keywords: (E₁, E₂) N¹,N² - bis[1-(3,4-dihydroxyphenyl)ethylidene]oxalohydrazide.

Introduction

Great interest has been focused on the synthesis and structural characterization of metal complexes of hydrazones in order to compare their coordinative behavior with their antimicrobial activities. Certain hydrazones and their Cu(II) complexes have antitumor activity (Ranford *et al.*, 1998). Diacetylmonoxime thiosemicarbazone is effective against vaccinia infections in mice by chelating some essential metal ions from the virus (Periin, 1976). Oximinohydrazones have antiparasitic, fungicidal and bactericidal properties (El-Asmy *et al.*, 2001). Compounds containing oxime and amino groups are used as analytical reagents for the microdetermination of some transition metal ions and as ion exchange resins (El-Asmy *et al.*, 1998). Previous papers (Mostafa *et al.*, 1983; Shallaby *et al.*, 1984; Huo *et al.*, 2004; El-Asmy *et al.*, 2000; Saracoglu *et al.*, 2004; Latha *et al.*, 2004; El-Asmy *et al.*, 2000) were reported on the synthesis and characterization of some oxime hydrazone complexes.

Up to date, no work was done on complexes containing Cr³⁺, VO²⁺, ZrO²⁺, HfO²⁺, UO₂²⁺ and MoO₂²⁺ ions with the investigated ligand, H₆DPOH.

Experimental

VOSO₄·2H₂O, CrCl₃·3H₂O, ZrCl₄, HfCl₄, UO₂(OAc)₂ and (NH₄)₂MoO₄, diethyl oxalate, hydrazine hydrate, 3,4-

dihydroxybenzaldehyde, ethanol, diethyl ether, DMF and DMSO were obtained from the BDH chemicals.

Synthesis of H₆DPOH

(E₁, E₂) N¹,N² bis[1-(3,4-dihydroxyphenyl)ethylidene]oxalohydrazide, Fig. 1, was prepared by heating a suspension (6 g, 0.05 mol) of oxalic acid dihydrazide (NH₂NHCOCONHNH₂) in 20 mL EtOH with 13.8 g (0.1 mol) of 3,4-dihydroxybenzaldehyde in 10 mL EtOH on a water bath for one day. Complete reaction is tested by TLC in petroleum ether-ethyl acetate (1:2) as eluent. It gives one spot with "R_f" = 0.34. The precipitate was filtered off, recrystallized from ethanol and dried; the yield is 79%. The ligand was characterized by spectral studies and elemental analysis. The ¹H NMR spectrum of the ligand gives different signals at δ = 12.05, 9.48, 7.41-6.85 and 2.32 ppm, corresponding to the protons of OH, NH, aromatic CH and aliphatic CH, respectively.

Preparation of complexes

The solid complexes were prepared by reacting the calculated amounts for 2:1 ratio [M:L] of metal salt and ligand in H₂O-EtOH (v/v) solution and the mixture was heated under reflux on a water bath for 6-8 h. In the preparation of VO²⁺ complex, 0.1g of sodium acetate was added. The precipitate thus formed was filtered off, washed with hot water, hot ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl₂.

Flotation method

A 3 ml aliquot containing 0.5x10⁻⁵ mol l⁻¹ ZrO²⁺ was mixed with H₆DPOH (1x10⁻⁴ mol l⁻¹) and 3 ml bidistilled water. The pH was adjusted at ~ 3. The solution was then transferred quantitatively to the flotation cell and completed to 10 ml with double distilled water. The cell was shaken well for few seconds to ensure complete complexation. To this solution, 3 ml of 1x10⁻⁵ mol l⁻¹ oleic acid (HOL) were added and the cell was then inverted upside down many times by hand. After complete separation, the scum containing ZrO²⁺ - H₆DPOH complex was separated, eluted with 4 ml of 4 mol l⁻¹ HCl, diluted to 10 ml in a volumetric flask and subjected to spectral determination.

Antibacterial and genotoxicity studies

The organic ligand and its metal complexes were screened for their antimicrobial activity using gram-positive (BT) and gram-negative bacteria (*E. coli*). The media prepared for bacteria were as reported earlier (Al-Gammal & El-Asmy, 2008). For a genotoxicity study, a solution of 2 mg of Calf thymus DNA was dissolved in 1 ml of sterile distilled water where the investigated ligand and its complexes were prepared by dissolving 2 mg/ml DMSO. An equal volume of each compound and DNA were mixed thoroughly and kept at room temperature for

2-3 h. The effect of the compounds on the DNA was analyzed by agarose gel electrophoresis. A 2 μ l of loading dye was added to 15 μ l of the DNA mixture before being loaded into the well of an agarose gel. The loaded mixtures were fractionated by electrophoresis, visualized by UV and photographed.

Equipment and analysis

Carbon, hydrogen and nitrogen contents of the ligand and its complexes were determined at the Microanalytical Unit of Cairo University, Egypt. The metal content was determined by gravimetric or complexometric methods (Vogel, 1994). The IR spectra were recorded as KBr disc on a Mattson 5000 FTIR Spectrophotometer. The UV-Vis. spectra of the complexes were recorded on UV₂ Unicam Spectrophotometer. The ¹H-NMR spectrum of the ligand was recorded in deuterated DMSO (DMSO-d₆), on a Bruker WP 200 SY spectrometer at room temperature using TMS as an external standard. The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. Thermogravimetry was measured (20-800 °C) on a Shimadzu TGA-50; the nitrogen flow and heating rate were 20 ml min⁻¹ and 10 °C min⁻¹, respectively. ESR spectra were obtained on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 KHz modulation frequency. The microwave power was set at 0.004. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

All molecular calculations were carried out by HyperChem 7.51 software package. The molecular geometry of the ligand and its ZrO²⁺ complex is first optimized at molecular mechanics (MM+) level. Semi empirical method PM3 is then used for optimizing the full geometry of the system using Polak-Ribiere (conjugate gradient) algorithm and Unrestricted Hartree-Fock (UHF) is employed keeping RMS gradient of 0.01 kcal/Å mol.

Results and discussion

The data of elemental analysis together with some physical properties of the complexes are summarized in Table 1. The results confirm the formulae [Cr(H₄DPOH)(H₂O)₃Cl]H₂O, [M(H₄DPOH)(H₂O)_n]mH₂O (M = VO, HfO, MoO₂ or UO₂) and [(ZrO)₂(H₂DPOH)(C₂H₅OH)₂]. The complexes are insoluble in most common organic solvents and partially soluble in DMF and DMSO. The partial solubility of the complexes in DMSO and/or DMF prevents the growing of crystals for X-ray crystallography and the measurement of their molar conductances and ¹H NMR spectra. The intense color may be due to a charge transfer or a defect of crystal during the preparation. HfO²⁺ complex has a more intense color than ZrO²⁺ complex which may be due to high polarizability; this observation is supported by the appearance of a band at 14680 cm⁻¹ in its electronic spectrum due to LMCT. The thermal analyses confirm a high stability for some complexes. This behavior may indicate a polymeric nature for these complexes.

Molecular modeling of the ligand

The molecular numbering of the ligand is shown in Fig. 1. Analysis of the data in Tables 1S and 2S calculated for both length and angle for each bond in the ligand molecule, one can conclude the following remarks:

- 1-All bond lengths of the O-H bonds are nearly similar.
- 2-All bond lengths of the C-O bonds are nearly similar, except C(16)-O(17) and C(13)-O(15) which are smaller than the rest due to the double bond character.
- 3-The two N-N bond lengths are typical due to the similarity of moieties on the two sides.
- 4-All bond angles predict sp³ and sp² hybridization.
- 5-The bond angles of C(21)-N(20)-N(18), O(17)-C(16)-C(13) and C(16)-C(13)-O(15) are 123.39, 123.35 and 124.87 while C(23)-C(21)-N(20) is 127.39 °. The larger the substituent moiety on N(20) the high stretching and the more bond angle.

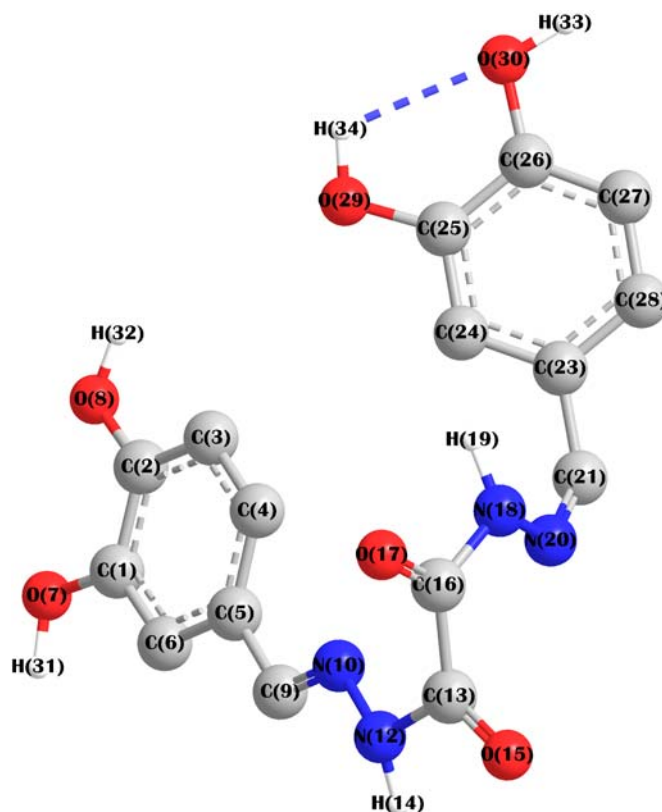


Fig. 1. Molecular modeling of H₆DPOH (vide cover page -colour)

The molecular parameters calculated by hyperchem program are found as: total energy = -1041311 kcal/mol; binding energy = -4295 kcal/mol; electronic energy = -740887 kcal/mol; heat of formation = -22 kcal/mol; dipole moment = 3.144 (Debyes); HOMO = -8.773392 eV and LUMO = -0.3302211 eV are calculated. Tables 1S and 2S gathered the values calculated for the bond lengths and bond angles.

IR Spectra

The IR spectrum of the ligand showed bands at 3486, 2363(w), 2338(w), 3374(w), 1653(vs), 1612(s), 1517(w) and 1366(s) due to the $\nu(\text{OH})_{\text{free}}$, $\nu(\text{OH})_{\text{bonded}}$, $\nu(\text{NH})$,

Table 1. Color, melting points and partial elemental analyses of H_6DPOH and its complexes

Compound	Color	M.P, °C	C	% Found (Calcd.)		
				H	N	M
H_6DPOH $C_{16}H_{14}N_4O_6$, 358.32	Pale yellow	295-96	53.2 (53.6)	5.5 (5.9)	14.9 (15.6)	-
$[VO(H_4DPOH)(H_2O)_2]$ $C_{16}H_{16}N_4O_7V$, 459.27	Brownish green	>300	42.2 (41.8)	3.7 (3.5)	13.0 (12.2)	11.4 (11.1)
$[Cr(H_4DPOH)(H_2O)_3Cl]H_2O$ $C_{16}H_{20}N_4O_{10}CrCl$, 516.73	Brown	>300	36.8 (37.2)	3.7 (3.9)	10.4 (10.8)	10.5 (10.1)
$[(ZrO)_2(H_2DPOH)(C_2H_5OH)_2]$ $C_{20}H_{22}N_4O_{10}Zr_2$, 660.83	Yellowish orange	>300	37.0 (36.4)	4.0 (3.6)	8.1 (8.5)	31.9 (32.4)
$[HfO(H_4DPOH)(H_2O)]H_2O$ $C_{16}H_{14}N_4O_8Hf$, 586.84	Brownish orange	>300	33.2 (32.7)	3.3 (2.7)	8.9 (9.5)	-
$[UO_2(H_4DPOH)(H_2O)_2]2H_2O$ $C_{16}H_{20}N_4O_{12}U$, 698.45	Brown	>300	26.9 (27.5)	3.3 (2.9)	-	34.5 (34.1)
$[MoO_2(H_4DPOH)]$ $C_{16}H_{12}N_4O_8$, 483.91	Brownish green	>300	39.3 (38.8)	3.8 (4.2)	11.8 (11.6)	-

Table 2. Assignments of the IR spectral bands of H_6DPOH and its complexes

Compound	$\nu(OH)$	$\nu(NH)$	$\nu(C=O)$	$\nu(C=N)$	$[\delta(N-H)+\nu(C-N)]$	$\delta(OH)$	$\nu(M-O)$
H_6DPOH	3486, 2363, 2338	3374	1653	1612	1517	1367	-
$[VO(H_4DPOH)(H_2O)_2]$	3396, --	3242	1644	1593	1517	1366,	468
$[Cr(H_4DPOH)(H_2O)_3Cl]H_2O$	3343, --	3247	1653	1611	1517	1337* 1366	470
$[(ZrO)_2(H_2DPOH)(C_2H_5OH)_2]$	--	3247	1656	1614	1515	1365*	466
$[HfO(H_4DPOH)(H_2O)]H_2O$	3442, --	3247	1656	1614	1515	1338* 1359	464
$[UO_2(H_4DPOH)(H_2O)_2]2H_2O$	3344, --	3247	1653	1607	1516	1369	467
$[MoO_2(H_4DPOH)]$	3419, --	3180	1679	1589	1530	1372	521

* $\delta(OH)$ of the coordinated water

$\nu(C=O)$, $\nu(C=N)$, amide II $[\delta(N-H)+\nu(C=N)]$ and $\delta(OH)$ vibrations, respectively. The bands at 2363 and 2338 cm^{-1} are due to the O-H...O hydrogen bonding (El-Metwally *et al.*, 2006).

The absence of the bands due to the free and bonded OH groups (Table 2) in the spectra of all complexes indicates the destruction of the hydrogen bond during complexation. Another band appears at 3396-3442 cm^{-1} in the spectra of all complexes, except for the ZrO^{2+} complex, indicating the involvement of only two OH's in chelation; the other two are still protonated with weak hydrogen bond. In ZrO^{2+} complex, no band in this region confirming the involvement of the four OH's in coordination. Another support for the OH coordination is the appearance of $\delta(OH)$ band at 1366 cm^{-1} with low intensity as well as another one at 1338 cm^{-1} . The new band may be due to $\delta(OH)$ of the coordinated water. Ethanol bonding in zirconyl complex is supported by the appearance of $\delta(OH)$ strong. The $\nu(NH)$, $\nu(C=O)$ and $\nu(C=N)$ bands appeared more or less at the same position as in the spectrum of H_6DPOH indicating no chelation through these groups; these groups exist opposite to

each other (from molecular calculation). Also, the IR spectra of the metal chelates showed new band at 464-521 cm^{-1} due to $\nu(M-O)$ (El-Asmy *et al.*, 2008). In addition, the vanadyl complex showed a broad band at 970 cm^{-1} attributed to $\nu(V=O)$ which is a former evidence for the square-pyramidal configuration of the VO^{2+} complex (El-Metwally & El-Asmy, 2006).

The IR spectrum of $[UO_2(H_4DPOH)(H_2O)_2]2H_2O$ displayed bands at 929 and 873 assigned to ν_3 and ν_1 of the dioxouranium ion (El-Sonbati *et al.*, 1998). The ν_3 value is used to calculate the force constant (F) of the U=O bond (McGlynn & Smith,

1961) by: $(\nu_3)^2 = (1307)^2(F_{U-O})/14.103$

The force constant was then substituted into the Jones relation (Jones, 1958): $R_{U-O} = 1.08 (F_{U-O})^{-1/3} + 1.17$

The calculated F_{U-O} and R_{U-O} were 7.125 mdynes $\text{\AA}^{-1}$ and 1.73 $\text{\AA}$, respectively, falling within the usual range for the uranyl complexes (El-Sonbati *et al.*, 1998).

Analogous to the UO_2 complex, the spectrum of MoO_2^{2+} complex showed bands at 904 and 850 cm^{-1} . Using the same equations, F_{Mo-O} and R_{Mo-O} are calculated to be 6.75 mdynes $\text{\AA}^{-1}$ and 1.74 $\text{\AA}$, respectively. The radius of Mo-O is approximately similar to U-O.

The broad bands at 3361, 890 and 540 cm^{-1} in the spectra of $[VO(H_4DPOH)(H_2O)_2]$, $[Cr(H_4DPOH)(H_2O)_3Cl]H_2O$ and $[UO_2(H_4DPOH)(H_2O)_2]2H_2O$ are attributed to $\nu(OH)$, $\rho_r(H_2O)$ and $\rho_w(H_2O)$, respectively, confirming water coordination (El-Asmy *et al.*, 1994); these bands were absent in the other complexes.

Electronic and magnetic studies

The magnetic moment values measured for VO^{2+} and Cr^{3+} complexes are 1.74 and 3.57 BM, respectively, consistent with the presence of one and three unpaired

Table 3. Magnetic moments and electronic spectral bands of the compounds

Compound	μ_{eff} (BM)	State	Intraligand and charge transfer (cm ⁻¹)	d-d transition (cm ⁻¹)
H ₆ DPOH	--	DMF	35740;33000; 32050;27900; 26455	--
[(ZrO) ₂ (H ₂ DPOH)(C ₂ H ₅ OH) ₂]	0.00	DMF	36765;32680; 29410; 27470	--
[Cr(H ₄ DPOH)(H ₂ O) ₃ Cl]H ₂ O	3.69	DMF	35970; 32895	22830;21830; 18050; 16450
[UO ₂ (H ₄ DPOH)(H ₂ O) ₂]2H ₂ O	0.00	DMSO	35710;33110;27860; 24340	--
[MoO ₂ (H ₄ DPOH)]	0.00	Nujol DMF	34720;31650;27625;26040x 33110;28250;24040;19840	--
[VO(H ₄ DPOH)(H ₂ O) ₂]	1.74	Nujol	33110;28250; 23920	19840
[HfO(H ₄ DPOH)(H ₂ O)]H ₂ O	0.00	Nujol	24330;22330; 21190; 14640	--

Table 4. Effect of some foreign ions on the flotation of 5×10^{-5} mol L⁻¹ ZrO₂²⁺ using 1×10^{-4} mol L⁻¹ H₆DPOH and 1×10^{-3} mol L⁻¹ HOL at pH ~3

Cation	Foreign/ ZrO ₂ ²⁺	F (%)	Anion	Foreign/ ZrO ₂ ²⁺	F (%)
Na ⁺	200	99.2	Cl ⁻	200	99.4
K ⁺	200	98.4	SO ₄ ²⁻	20	92.2
Ca ²⁺	200	98.5	Citrate	20	80.0
Co ²⁺	20	99.5	HPO ₄ ⁻	20	86.7
Ni ²⁺	20	98.5	CH ₃ COO ⁻	20	99.2
Cu ²⁺	20	8.5			
Zn ²⁺	20	75.8			
Cd ²⁺	20	99.5			
NH ₄ ⁺	100	98.4			
Al ³⁺	20	74.2			

electrons. The other complexes have a diamagnetic nature in accordance with the d⁰ or d¹⁰ configuration.

The electronic spectrum of the ligand showed $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands in the region 35740 - 26455 cm⁻¹. Changes are observed on the spectra of its complexes (Table 3). The band at 24340 cm⁻¹ in the spectrum of the UO₂²⁺ complex may be due to LMCT.

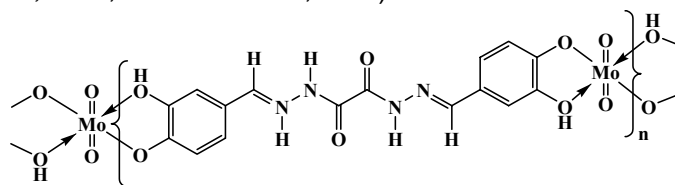
The electronic spectrum of [Cr(H₄DPOH)(H₂O)₃Cl]H₂O showed two strong absorption bands at 18050 and 22831 cm⁻¹ attributed to the ⁴A_{2g} (F) → ⁴T_{2g} (P) (ν₁) and ⁴A_{2g} (F) → ⁴T_{1g} (F) (ν₂) transitions, in an octahedral geometry. An additional broad band centered at 24210 cm⁻¹ is due to a charge transfer. The ligand field parameters (Dq = 1805 cm⁻¹, B = 429.8 cm⁻¹ and β = 0.46) are further support for the proposed geometry. The lower value of β is indication of more covalency.

The presence of two bands at 23920 and 19840 cm⁻¹ in [VO(H₄DPOH)(H₂O)₂] is assigned to the d_{xz} → d_{xy} transition (El-Metwally *et al.*, 2005), in a square-pyramidal geometry. The color and IR band support the proposed structure.

The u.v. spectrum of [UO₂(H₄DPOH)(H₂O)₂]2H₂O showed a band at 24340 cm⁻¹ assigned to $\sum g \rightarrow {}^3\pi_4$ similar to the O=U=O symmetric stretching frequency for the first excited state (McGlynn *et al.*, 1961).

The electronic spectrum of [MoO₂(H₄DPOH)] in Nujol (DMF) shows bands at 34720 (33110), 31650, 27625 (28250) and 26040 (24040) cm⁻¹ due to intraligand transitions similar to those in the ligand spectrum. The band at 24040 cm⁻¹ is similar to that in the UO₂ spectrum indicating O=Mo=O moiety. The shoulder at 19840 cm⁻¹ in DMF spectrum arose from O pseudo-sigma combinations to the singly occupied Mo 4d orbital in the xy

plane suggesting a considerable covalency in the ground-state electronic structure of [MoO₂(H₄DPOH)]_n (Fig. 2). There is no evidence of any d-d transition and the data supported the six coordination of the complex (Syamal *et al.*, 1986; McMaster *et al.*, 2001).


Fig. 2. Formulae of [MoO₂(H₄DPOH)]_n

Thermal analysis

The thermogravimetric curves (25 - 800°C) of some complexes were recorded to give an insight into the thermal stability of the complexes studied. In Cr³⁺ and HfO²⁺, the first decomposition step is due to loss of water of crystallization in the temperature range 40-150°C. In the other complexes, the first decomposition step begins at 205, 207 and 268°C.

The TG curve of [VO(H₄DPOH)(H₂O)₂] displayed a thermal stability till 205 °C, after which five degradation steps were observed at 205 - 285, 286 - 353, 355 - 434, 435 - 515 and 516 - 730°C. The first decomposition step is due to the removal of the two coordinated water molecules with 8.0 (Calcd. 7.8%) weight losses. C₇H₄NO₂VO still exists in the last step by 40.7 (Calcd. 40.9 %) revealing a high stability of the final species at the final decomposition temperature (730°C).

In [(ZrO)₂(H₂DPOH)(C₂H₅OH)₂], the decomposition begins at 268 °C indicating a high stability of the complex. The first step at 269 - 362 °C is due to the removal of 2C₂H₅OH + C₄H₂O₂. The final step ending at 800 °C corresponds to Zr₂O₃ as a residual part.

ESR spectral studies

The ESR spectrum of the vanadyl complex (Fig. 3) provides information about hyperfine and superhyperfine structures which are important in studying the metal ion in the complexes. Generally, the mononuclear VO²⁺ ion (S = 1/2, I = 7/2) has a characteristic octet ESR spectrum showing the hyperfine coupling to the ⁵¹V nuclear magnetic moment. Upon the existence of two vanadyl

ions, the two electron spins may combine to a non-magnetic spin singlet ($S = 0$) or a paramagnetic spin triplet state ($S = 1$); only the latter is ESR detectable. The superexchange interaction between the two vanadium ions lead to a configuration in which the two electron spins have an antiferromagnetic character, i.e. the singlet state is energetically favored (Thaker *et al.*, 1994). Therefore, the ESR spectrum of strongly coupled pairs has the form of a single broad line with inhomogeneous broadening.

Vanadium(IV) complexes generally have g-values less than the g-value " g_e " of the free electron 2.0023 (admixture of empty MO's).

The room temperature (300 K) ESR spectrum of $[VO(H_4DPOH)(H_2O)_2]$ gave a typical eight-line pattern (Fig. 3) similar to those reported for mononuclear vanadium molecule (Khasaa *et al.*, 2003). In the powdered mono vanadium complexes, the spectra showed

the parallel and the perpendicular features which indicate axially symmetric anisotropy with well resolved sixteen-lines hyperfine splitting characteristic for the interaction between the electron and the vanadium nuclear spin ($I = 7/2$) (Raman *et al.*, 2003). The spin Hamiltonian parameters are calculated to be $g_{\parallel}$ (1.93), $g_{\perp}$ (1.97), $A_{\parallel}$ ($190 \times 10^{-4} \text{ cm}^{-1}$) and $A_{\perp}$ (60). The calculated ESR parameters indicate that the unpaired electron (d^1) is present in the d_{xy} -orbital with square-pyramidal or octahedral geometry. The values obtained agree well with the g-tensor parameters reported for square pyramidal geometry (Kivervson & Lee, 1964).

The molecular orbital coefficients α^2 and β^2 for $[VO(H_4DPOH)(H_2O)_2]$ were calculated by the well-known equations and found to be 0.93 and 0.77, respectively. The lower value of β^2 compared to α^2 indicates that the in-plane σ -bonding is less covalent and are well consistent with other reported data (Warad *et al.*, 2000). Solving the equations to obtain α^2 and β^2 , where the dipolar interaction constant "P" between magnetic moment of the electron and vanadium nucleus can be calculated from the following equation (Gangadharmath *et al.*, 2001) $p = 7/6(A_{\parallel}/A_{\perp})$. The spin-orbit coupling coefficient, λ , is

Table 5. Recovery (R %) of ZrO^{2+} ions added to 10 ml of some water samples using $1 \times 10^{-4} \text{ mol L}^{-1}$ H_6DPOH and $1 \times 10^{-3} \text{ mol L}^{-1}$ HOL at pH ~ 3

Type of Water (location)	ZrO^{2+} added (mg L^{-1})	R %
Tap water (Home lab.)	5.36	98.9
	10.71	98.2
Nile water (Mansoura City)	5.36	98.8
	10.71	98.5
Sea water (Gamasa)	5.36	98.2
	10.71	97.5
Underground water (Belkas city)	5.36	99.0
	10.71	98.5
Lake water (El-Manzala lake)	5.36	99.6
	10.71	97.5

Table 1S. Bond length of H_6DPOH

O(30)-H(33)	0.9487	C(13)-O(15)	1.2140
O(29)-H(34)	0.9486	N(12)-H(14)	0.9998
N(20)-C(21)	1.2954	N(12)-C(13)	1.4407
N(18)-N(20)	1.3893	N(10)-N(12)	1.3893
N(18)-H(19)	1.0026	C(9)-N(10)	1.3060
C(16)-N(18)	1.4346	O(8)-H(32)	0.9500
C(16)-O(17)	1.2161	O(7)-H(31)	0.9494
C(13)-C(16)	1.5213		

Table 2S. Bond angles of H_6DPOH

H(33)-O(30)-C(26)	107.7006	O(17)-C(16)-C(13)	123.3534
H(34)-O(29)-C(25)	108.6656	C(16)-C(13)-O(15)	124.8748
C(23)-C(21)-N(20)	127.3905	C(16)-C(13)-N(12)	117.3339
C(21)-N(20)-N(18)	123.3914	O(15)-C(13)-N(12)	117.5478
H(19)-N(18)-N(20)	115.7852	H(14)-N(12)-C(13)	116.6089
H(19)-N(18)-C(16)	115.9519	H(14)-N(12)-N(10)	116.0826
N(20)-N(18)-C(16)	117.1674	C(13)-N(12)-N(10)	114.7887
N(18)-C(16)-O(17)	116.6323	N(12)-N(10)-C(9)	121.8820
N(18)-C(16)-C(13)	119.9555	N(10)-C(9)-C(5)	119.3663
H(31)-O(7)-C(1)	107.3883	H(32)-O(8)-C(2)	107.5004

Separation of ZrO^{2+} using H_6DPOH

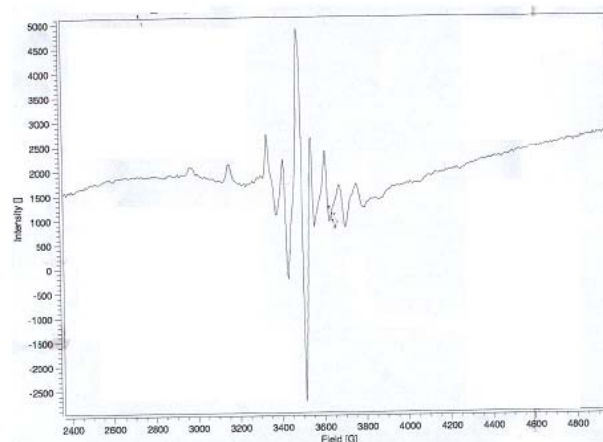
Different factors affecting the flotation of ZrO^{2+} using H_6DPOH have been studied to maximize its separation efficiency. The most important are:

pH: A series of experiments were carried out to show the effect of HCl and/or NaOH on the separation of 0.5×10^{-4}

assumed to be 170 cm^{-1} for VO^{2+} ion and E is the electronic transition energy of ${}^2B_2 \rightarrow {}^2E$ and k is the Fermi contact term which is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus.

Eukaryotic DNA degradation test
Examining the DNA degradation assay for H_6DPOH and its metal complexes revealed variability on their immediate damage on the calf thymus (CT) DNA. The complexes have a higher effect on the calf thymus DNA than the ligand itself, with the VO^{2+} and ZrO^{2+} complexes degrading the CT DNA completely (Fig. 4). The results suggest that direct contact of VO^{2+} and ZrO^{2+} is necessary to degrade the DNA of Eukaryotic subject. The ligand and its metal complexes were tested against gram-positive (BT) and gram negative bacteria (E. coli). All compounds have small inhibitory effects on bacteria.

Fig. 3. ESR spectrum of $[VO(H_4DPOH)(H_2O)_2]$



mol l⁻¹ ZrO²⁺, in the presence of 1×10⁻⁵ mol l⁻¹ oleic acid (HOL) and 1×10⁻⁴ mol l⁻¹ H₆DPOH. The results show that the floatability of ZrO²⁺- H₆DPOH increases with increasing the pH, reaching a maximum at 2.5-3.5. Therefore, all work experiments were carried out at pH ~ 3.

Ligand concentration: The efficiency does not exceed 35% on floating the ZrO²⁺ ions alone with oleic acid. H₆DPOH was found to be the reagent added to give good results. The floatability of a series of solutions containing 0.5×10⁻⁴ mol l⁻¹ ZrO²⁺, 1×10⁻⁵ mol l⁻¹ HOL and various amounts of H₆DPOH at pH ~3 was performed. The results show a maximum efficiency (98.4 %) at 1: 2 (ZrO: H₆DPOH) ratio. Excess ligand has no effect, so the procedure find application for real samples containing ZrO²⁺. A concentration of H₆DPOH equals two-folds of ZrO²⁺ or more was used.

Surfactant concentration: ZrO²⁺ ions were separated using various concentrations of HOL; the results show maximum floatability at 1×10⁻⁵ - 3.36×10⁻² mol l⁻¹ of HOL, above which the flotation decreases. Accordingly, 1×10⁻⁵ mol l⁻¹ HOL was the desired concentration.

ZrO²⁺ concentration: Various amounts of ZrO²⁺ were floated in the presence of 1×10⁻⁴ mol l⁻¹ H₆DPOH using 1×10⁻⁵ mol l⁻¹ HOL at pH ~3. The floatability reaches 98.2% at 0.5×10⁻⁴ mol l⁻¹ of ZrO²⁺ corresponding to 1 : 2 (ZrO: H₆DPOH). At higher concentration of ZrO²⁺, the efficiency decreases and needs excess H₆DPOH.

Temperature: Solutions of ZrO²⁺, H₆DPOH and HOL were either heated or cooled; HOL was quickly poured into the mixture and introduced into the flotation cell. No change in the floatability % in the temperature range 0-70°C. Since the industrial waste waters are usually hot, the introduced procedure finds successful application in the direct analysis of ZrO²⁺ ions. The subsequent measurements were carried out at room temperature ~ 30 °C.

Foreign ions: Separation of ZrO²⁺ (0.5×10⁻⁴ mol l⁻¹) using H₆DPOH (1×10⁻⁴ mol l⁻¹) and oleic acid (1×10⁻⁵ mol/L) was carried out at higher concentrations of various cations and anions usually found in some water samples (Table 4). Tolerable amount (presented as ion: ZrO ratio) gave a maximum error of ± 2% in the flotation efficiency. All the investigated ions did not interfere except Mn²⁺, Zn²⁺ Cu²⁺, Al³⁺, HPO₄⁻ and citrate ions. The interference is diminished by adding excess H₆DPOH. Thus, the introduced procedure is fairly selective and can be safely employed for the separation and determination of ZrO²⁺ in various materials.

Ionic strength: The effect of some salts on the flotation efficiency of 0.5×10⁻⁴ mol l⁻¹ ZrO²⁺ is studied. The salts used were similar to those in natural water samples. The ionic strength of the medium has no effect on the flotation process.

Application To apply the recommended procedure for separation and determination of ZrO²⁺ in water samples taken from different locations, 5.36 or 10.71 ppm of ZrO²⁺ was added to 10 ml of clear water and the pH was adjusted to ~ 3 at 30 °C. After flotation, the concentration of ZrO²⁺ was determined spectrophotometrically using xylene orange at 535 nm in the mother liquor. From the data obtained (Table 5), ZrO²⁺ ions can be determined with satisfactory results.

Conclusion

A new chelating agent has been prepared and characterized for chelation with VO²⁺, ZrO²⁺, HfO²⁺, MoO₂²⁺ and UO₂²⁺ as well as Cr(III). It chelates as mononegative bidentate and forms mononuclear complexes with all metal ions except ZrO²⁺ which forms binuclear complex. The complexes seem to be polymeric in nature due to their insolubility and high melting points. [Cr(H₄DPOH)(H₂O)₃Cl]

H₂O, [HfO(H₄DPOH)(H₂O)]H₂O, [MoO₂(H₄DPOH)] and [UO₂(H₄DPOH)(H₂O)₂]2H₂O have been proposed to be octahedral; [(ZrO)₂(H₂DPOH)(C₂H₅OH)₂] is four coordination, where [VO(H₄DPOH)(H₂O)₂] is square based pyramid. VO²⁺ and Cr(III) complexes degrade the DNA of Eukaryotic subject completely. The flotation technique was found applicable for the separation of 0.5×10⁻⁴ mol l⁻¹ ZrO²⁺ ions using 1×10⁻⁴ mol l⁻¹ H₆DPOH and 1×10⁻⁵ mol l⁻¹ oleic acid at pH 3.

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Fig. 4. Biological effect of the ligand and its complexes on the Calf Thymus DNA



Lanes arranged as: C- control DNA, 1- ligand, 2- VO²⁺ 3- Cr 4- ZrO²⁺ 5- MoO₂²⁺

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