

SYNTHESIS OF SOME COMPLEXES OF DIOXOURANIUM(VI) WITH DI-HALOGENO-TETRA-METHYL SALEN LIGANDS

Aurel PUI,^a Doina HUMELNICU,^{a*} Ionel HUMELNICU^b and Cătălin TANASE^c

^a Faculty of Chemistry, “Al. I. Cuza” University, Department of Inorganic and Analytical Chemistry, Bvd. Carol I, No. 11, Iași 700506, Roumania,

^b Faculty of Chemistry, “Al. I. Cuza” University, Department of Theoretical and Physical Chemistry, Bvd. Carol I, No. 11, Iași 700506, Roumania,

^c Faculty of Biology, “Al. I. Cuza” University, Laboratory of Vegetal Biology, Bvd. Carol I, No. 20 A Iași 700505, Roumania.

Received December 8, 2006

This paper deals with the synthesis and characterization of some complex compounds of uranium (VI) with different symmetrical Schiff bases. These compounds have been characterized by elemental analysis, IR and UV-Visible spectroscopy and thermal analysis. The obtained results suggest the fact that the coordination number of uranium (VI) in these complexes is 7. The reaction of the ligands with a U(VI) salt leads to the formation of a monomeric complex compound with the formula $[\text{UO}_2\text{LEtOH}] \cdot n\text{H}_2\text{O}$ (where $n = 0.5 \div 1.5$). A possible structure for the complex has been proposed. The formation of the U(VI) complexes with such Schiff bases opens new ways for the extraction of uranium from ores or different solutions in order to use it as nuclear fuel.

INTRODUCTION

Uranium exists in various concentrations in all parts of the environment, in certain types of rocks *e.g.* some types of granites, and various mineral deposits. There are also some artificial contributions of uranium to the environment *e.g.* from mineral exploration, emissions from the nuclear industry, the combustion of coal and other fuels, and the use of phosphate fertilizers that contain uranium.¹

Natural uranium is one of the elements that can be transferred to the plants or accumulated under the influence of microbial processes including oxidation-reduction, production of complexing compounds, and biosorption. In this way, plants and fungi are directly involved in the absorption, accumulation of major and trace elements including radionuclides. In natural and also in disturbed environments, accumulation of uranium has been observed in plants, mushrooms and fungal mycelium.² The contents have been observed in mycelia by coupling the microscopic and spectrometric methods.

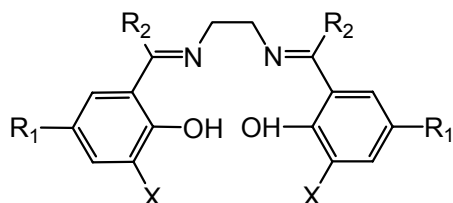
The complex compounds formed between uranyl ions and different complexing agents are of great interest due to their possibilities to be applied in extraction of metallic ions from ores, extraction of uranium from solutions of low concentration,

treatment of the radioactive waters and in environmental chemistry. It is known the fact that the uranyl ions have a big complexing capacity in the presence of different organic and inorganic compounds. Behavior of uranium in solution is very interesting. Usually, uranium is found in form of uranyl ions very stable in both solution and solid state. From the structural point of view, the uranyl ions has in its center the uranium atom with the oxidation state (VI), and the two atoms of oxygen form two double bonds $\text{O}=\text{U}=\text{O}$ with an angle of 180° between them (linear, stable structure), fact demonstrated by Duval³ and Frankuchen⁴ (in his studies over the uranyl and sodium acetate). The ligands coordinate equatorially to the uranium atom and in a perpendicular plane on the plane of the $\text{O}=\text{U}=\text{O}$ bonds, coordination numbers being between 4 and 7 depending on the chemical surrounding.⁵⁻⁷ The Schiff bases are chelating agents used to get different complexes with transitional metals. They form complexes compounds with different metallic ions in the 1/1 ratio form 3 very stable chelate cycles. Taking into account the high capacity of the Schiff bases to coordinate metallic ions, these are the intensively utilized as complexing agents to extract some

* Corresponding author: doinah@uaic.ro

metals from various media. The uranyl ions form complex compounds with numerous Schiff bases showing a strong affinity for ligands with oxygen- and nitrogen-bearing ligands, a series of such complexes being already studied.⁸⁻¹¹

Further on, we studied a new series of complex compounds of the uranyl ions with symmetrical Schiff bases.



$R_1 = R_2 = X = H$ - bis (salicylaldehyd)ethylendiammin, Salen;
 $R_1 = R_2 = CH_3, X = H$ - tetramethyl salen, (tMeSalen);
 $R_1 = H, R_2 = CH_3, X = H$ - dimethyl salen, (dMeSalen);
 $R_1 = R_2 = CH_3, X = Cl$ - di -chloro-tetramethylsalen, (dCltMeSalen);
 $R_1 = R_2 = CH_3, X = Br$ - di-bromo-tetramethylsalen, (dBrMeSalen);
 $R_1 = R_2 = CH_3, X = I$ - di-iodo-tetramethylsalen, (dItMeSalen);

Fig. 1 – General formula of the used Schiff bases.

RESULTS AND DISCUSSION

The tetradentate Schiff bases, with the structure presented in Fig.1, are very good chelating agents. These ligands coordinate to a metallic cations and form 3 very stable chelate cycles.

The results of elemental analysis summarized in Table 1, prove formation of some complexes in a

molar ratio of 1/1 along with different number of water molecules.

Table 1

Analytical and physical data of the complexes

Compound	Formula	Color	Yield, %	Formula weight	Anal. Found (calc.) %			
					C	H	N	U
1	$[UO_2(salen)EtOH] \cdot H_2O$	Orange	72.5	582.39	37.12 (37.34)	3.46 (3.5)	4.81 (4.78)	40.87 (40.75)
2	$[UO_2(tMesalen)EtOH] \cdot H_2O$	Orange	70	638.5	41.38 (41.25)	4.42 (4.5)	4.39 (4.35)	37.28 (37.30)
3	$[UO_2(dMesalen)EtOH] \cdot 0.5H_2O$	Orange	75	610.44	39.35 (39.30)	3.96 (3.95)	4.59 (4.60)	38.99 (38.95)
4	$[UO_2(dCltMesalen)EtOH] \cdot 1.5H_2O$	Yellow	80	707.39	37.35 (37.40)	3.70 (3.65)	3.96 (3.93)	11.31 (11.25)
5	$[UO_2(dBrtMesalen)EtOH] \cdot H_2O$	Yellow	76	794.07	33.18 (33.20)	3.29 (3.30)	3.52 (3.50)	10.05 (10.16)
6	$[UO_2(dItMesalen)EtOH] \cdot H_2O$	Red-orange	74	890.04	29.68 (29.65)	2.94 (2.90)	3.15 (3.20)	26.74 (26.80)

IR spectra

The free ligands exhibit IR spectral bands in the region $3400-3600\text{ cm}^{-1}$, characteristic of OH groups; the band at ca. 1600 cm^{-1} correspond to the azomethynic groups, $\nu_{C=N}$. The stretching frequency due to δ_{C-OH} of the ligand occurs at about 1250 cm^{-1} , Table 2. Between $1600-1400\text{ cm}^{-1}$ occur the vibration bands of aromatic nuclei, and at about 1170 and 1060 cm^{-1} occur the stretching frequencies corresponding to the C-O and C-N bonds.¹⁸

The IR spectra of that complex compounds that contain the UO_2^{2+} ion present a series of modifications, as a result of complexation of the uranyl ions with respective ligands (Fig. 2).

Thus, the stretching frequencies $\nu_{C=N}$ in the spectra of ligands is shifted as a result of involving the nitrogen atoms in coordination. Also, the deformation bands, δ_{Ar-OH} from the ligands spectra are modified in the spectra of complexes, as a result of involving of the oxygen atom in coordination with the uranyl ion. The stretching frequencies ν_{C-O} and ν_{C-N} in the spectra of ligands also undergo modifications due to involvement of the oxygen and nitrogen atoms in coordination. In the spectra of complexes, an intense band occurs at about 910 cm^{-1} corresponding to stretching frequency of $\nu_{U=O}$ in the $O=U=O$ group. Also, in the $400-600\text{ cm}^{-1}$ region occur a series of bands assignable to the new U-O and U-N bonds,¹⁹ Table 2.

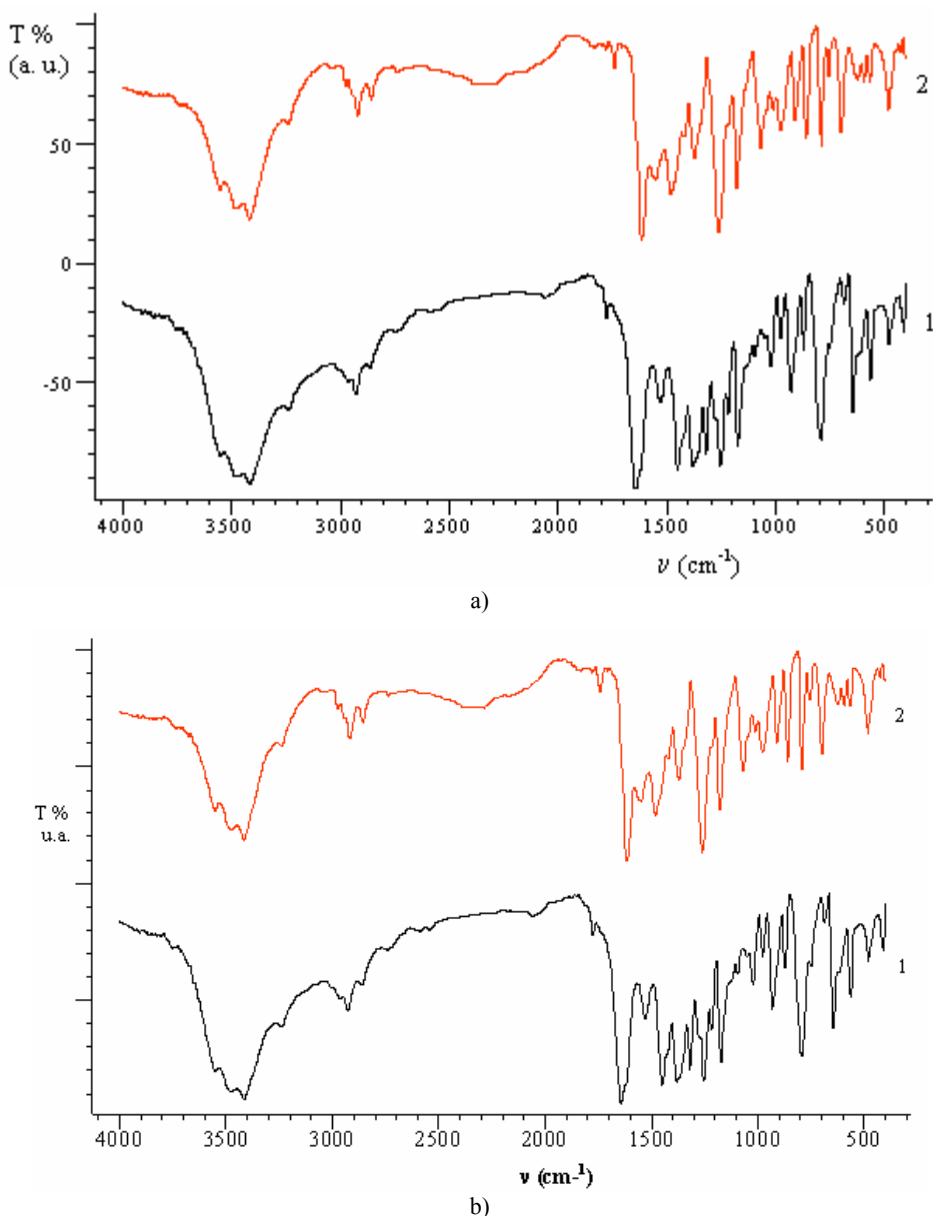


Fig. 2 – IR spectra of the complex compounds and ligands.
 a) 1 – complex compound 4; 2 – ligand: dCltMeSalen;
 b) 1 – complex compound 5; 2 – ligand: dBrtMeSalen.

Table 2

The main IR spectral data of UO_2^{2+} complexes

Compounds	$\nu_{\text{C=N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{O=U=O}}$	New bands	
					$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
Salen	1633	1198	1041			
dMeSalen	1610	1158	1065	-	-	-
tMeSalen	1614	1185	1078	-	-	-
dCltMeSalen	1611	1174	1067	-	-	-
dBrtMeSalen	1608	1176	1085	-	-	-
dItMeSalen	1610	1165	1071	-	-	-
1	1627	1207	1054	915	605	462
2	1619	1205	1034	922	633	460
3	1620	1178	1031	921	617	459
4	1640	1165	1092	927	641	471
5	1609	1171	1087	889	646	502
6	1603	1184	1086	888	617	501

The presence of the methylenic group bounded to the atom of azomethinic carbon (C=N) produces an increase of the electronic density of the nitrogen atom (donor) which has influence also over the coordination uranium atom. This effect leads to a shift towards smaller wavelengths of valence vibration $\nu_{C=N}$ in both free ligand and complex compound. In exchange, the $\nu_{O=U=O}$ vibration from the complexes **2**, **3**, **4** shifts to larger wavelengths comparably to the complex **1**.

Appearance of the second methylenic group in *para* position in relation with the donor oxygen produces lesser modifications over stretching frequency of the azomethinic groups. The presence of a halogen in *ortho* position in relation with oxygen, with effect of electron attracting leads to a decrease (compensation) of the electronic density on the uranium atom and a shift towards longer wavelengths of the $\nu_{C=N}$ stretching frequency. The presence of bromine or iodine, with electronegativity much less than that of chlorine, in the *ortho* position in relation with donor oxygen leads to a shift the azomethinic $\nu_{C=N}$ stretching frequency towards less wavelengths ($888\text{-}889\text{ cm}^{-1}$).²⁰

On the basis of these results, it can be concluded that the uranyl ion coordinates to the

ligands through two oxygen and two nitrogen atoms of the ligands.

The magnetic measurements point out a diamagnetic behaviour of these complex compounds. This fact shows that all electrons of uranium ions are paired.

Electronic spectral studies

The UV-VIS spectra of the free ligands and complexes were recorded in DMF. The spectra of ligands exhibit two absorption peaks at 330 and 359 nm in the 300 - 370 nm region that can be assigned due to the intra-ligand bands (ligand's own ones) corresponding to an $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively. The intra-ligand bands is slightly shifted in complex at 350, and 410 nm, respectively, with a reduction of the molar extinction coefficient (from $\epsilon = 530\text{ L/mol}\cdot\text{cm}$ at $\epsilon = 330\text{ L/mol}\cdot\text{cm}$, and from $\epsilon = 520\text{ L/mol}\cdot\text{cm}$ at $\epsilon = 490\text{ L/mol}\cdot\text{cm}$, respectively) in the complex compounds spectrum because the non-participating electron of nitrogen are employed in the coordination of uranyl ions. In addition, all these complexes display a strong band in the 400-450 nm region assignable to the metal band (LMCT).^{9,18}

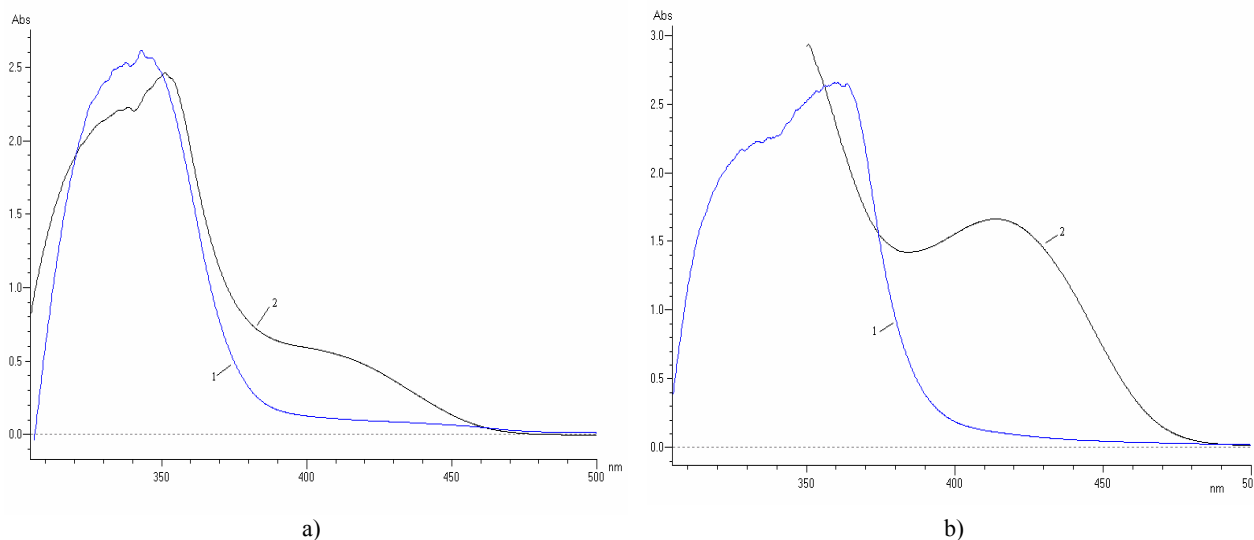


Fig. 3 – The UV-VIS spectra for the **2** (a) and **5**(b) complexes: 1- ligand; 2- complex.

Thermal studies

The TG and DTG studies were carried out for the complex **5** in the temperature range of 35° - 740°C. The representative TG and DTG curves are recorded in Fig. 4. The thermograms of the complexes showed a loss of 1.11 mg (2.21 %) in the range of 125 – 160 °C corresponding to one

molecule of water. In the range of 160-250 °C takes place a mass loss of 2.09 mg (4.19 %), corresponding to one molecule of EtOH. In the range of 250-290 °C takes place a loss of 9.85 mg (19.7 %) corresponding to a loss of 2 atoms of bromine. Up to 615 °C takes place a continue decomposition of the complex, at this temperature remained UO_3 . Over this temperature, up to 740 °C,

the formed uranium oxide decomposes, with a light loss of oxygen, remaining at the end, 17.28 mg

residue (34.56 %) corresponding to a mixt oxide, U_3O_8 .¹⁹

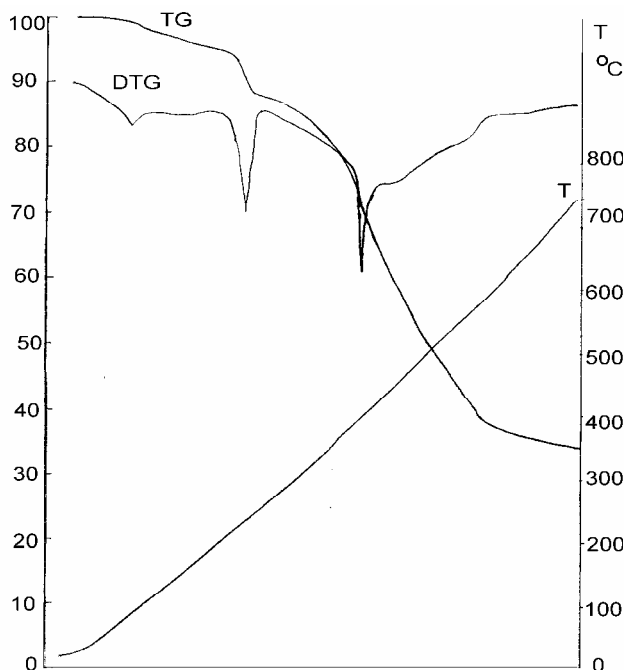


Fig. 4 – DTG, TG and T curves for the complex 5.

The structure of the ligand and of the complex obtained was simulated with the Hyper - Chem programs,²⁰ and structures' optimization was made by the PM3 semi-empirical method²¹⁻²³, with the

Polak-Ribiere algorithm and the condition of convergence, RMS gradient of 0.001kcal/Å.mol.

The probable structure proposed by us, based on these studies, is represented in Fig. 5.

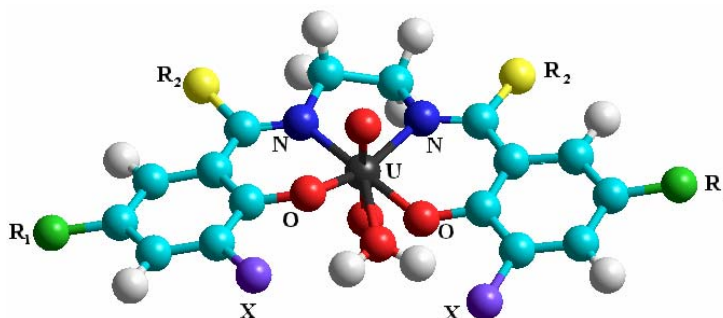


Fig. 5 – The probable structure proposed for the complex compounds of uranium with the investigated Schiff bases.

EXPERIMENTAL PART

All reagents used were of analytical grade.

1. Preparation of ligands. The Schiff bases utilized as ligands were prepared according to the methods available in literature¹², by condensation of the 2-hydroxyacetophenone derivative with ethylenediammine, in a molar ratio of 2/1 (e.g., 1 g of 2-hydroxy-5-methylacetophenone in *EtOH* condenses with 0.23 g ethylenediamine in *EtOH*, under stirring for 2 h. After 12 hours, the precipitate is filtered, washed with cool *EtOH* and dried. A quantity of 0.97 g precipitate was obtained ($\eta = 93.5\%$ with 98 % purity). The other ligands were prepared similarly. Synthesis of the 2-halogeno-5-methyl-2-hydroxy acetophenols was carried out as follows: 2-hydroxy-

3-Cl-5-Me-acetophenone was obtained by a Friedel Crafts condensation of 2-Cl-4-methylphenol with CH_3COCl in the presence of $AlCl_3$ at 180 °C for 30 minutes.¹³ It recrystallizes from MeOH, $\eta = 65\%$.

2-Hydroxy-3-Br-5-Me-acetophenone was obtained by bromination of 2-HO-5-Me-acetophenone with pyridinium bromchromate (PBC).¹⁴ Its recrystallization was performed from EtOH with $\eta = 74.8\%$.

2-Hydroxy-3-I-5-Me-acetophenone was prepared by iodination of 2-HO-5-Me-acetophenone with iodine in the presence of HgO ($\eta = 64\%$).

All ligands were characterized by ¹H NMR, elemental analysis, UV-VIS and IR spectroscopy.¹³

2. Synthesis of the complex. Synthesis of the complex was carried out according to the methods available in literature.¹⁶

The Schiff base (0.2 mmol) was dissolved in 10 mL warm ethanol to which was added the uranyl nitrate (0.2 mmol) dissolved in doubly distilled water. The mixture was stirred at 40-50 °C for one hour for precipitate separation. The precipitate was separated by filtration, washed with water, water-ethanol solution (1/1v) and ethanol and dried in air ($\eta = 70-80\%$).

3. Physical measurements. The elemental analysis was carried out with a Perkin-Elmer analyzer, Model 2400. The uranium content was determined gravimetrically as U_3O_8 after decomposing the uranium (VI) complex with concentrated nitric acid followed by igniting the residue.¹⁵

The IR spectra of ligands and uranium complex compounds prepared were recorded on the JASCO FTIR 600 plus spectrometer, using KBr pellets. The electronic spectra were obtained in DMF with a CINTRA 10 spectrophotometer. The magnetic susceptibilities of the complexes were measured by the Gouy's method at room temperature, using a Gouy D 104 balance.

The thermogravimetric measurements were carried out in air on a MOM Budapest derivatograph, at heating rate of 10 °C/min., using samples as big as 50 mg.

CONCLUSIONS

Five Schiff bases were prepared by condensation of 2-hydroxyacetophenone derivatives with ethylenediamine in molar ratio 2/1, with good yields. The symmetrical Schiff bases are very good chelating agents for the uranyl ions. The elemental analysis, IR and UV-VIS spectra, and thermal analysis proved the structure of both Schiff bases and their complex compounds with uranium (VI), obtained by means of uranyl ions. The spectral properties pointed out that dioxouranium (VI) complex have 7 coordination number. The complex compounds investigated can be utilized for uranium extraction from ores or from different solutions in order to use it as nuclear fuel.

REFERENCES

1. C. Munier-Lamy, *Berthelin J.*, **2006**, 18th World Congress of Soil Science, July 9-15, 2006 - Philadelphia, Pennsylvania, USA.
2. J. Dighton, T. Tugay, N. Zhdanova and V. Zheltonozhsky, **2006**, 18th World Congress of Soil Science, July 9-15, 2006 - Philadelphia, Pennsylvania, USA.
3. A. E. Vaughn, D. B. Bassil, C. L. Barnus, S. A. Tucker and P. B. Duval, *J. Am. Chem. Soc.*, **2006**, *128*, 10656.
2. I. Frankuchen, *Z Kristallogr.*, **1935** *91*, 473.
3. F. Yuhua, B. Caifeng, L. Jinying, *J. Radioanal. and Nucl. Chem.*, **2002**, *254*, 641.
4. L. Gagliardi, I. Grenthe and B. O. Roos, *Inorg. Chem.*, **2001**, *40*, 2976.
5. W. J. Oldham, S. M. Oldham, B. L. Scott, S. K. D. Abnez, W. H. Smith and D.A. Costa, *J. Chem. Soc. Chem. Commun.*, **2001**, 1348.
6. A. M. El-Hendawy, A. E. El-Kourashy and M. H. Shanab, *Polyhedron*, **1992**, *11*, 523.
7. M. R. Maurya and R. C. Maurya, *Rev. Inorg. Chem.*, **1995**, *15*, 1.
8. M. T. H. Tarafder and A. R. Khan, *Polyhedron*, **1991**, *10*, 973.
9. L. Salmon, P. Thiery and M. Ephritikhine, *Polyhedron*, **2003**, *22*, 2683.
10. R. Dreos, G. Nardin, L. Randaccio, P. Siega, G. Tauzher and V. Vrdoljak, *Inorg. Chim. Acta*, **2003**, *349*, 239.
11. J. N. Kim and E. K. Ryu, *Synth. Commun.*, **1996**, 967.
12. S. B. Patwari, M. A. Baseer, Y. B. Vibhute and S. R. Bhusare, *Tetrahedron Lett.*, **2003**, *44*, 4893.
13. A. Pui, *J. Chem. Coord.*, **2006**, *7*, in press.
14. A. Syamal, M. M. Singh and D. Kumar, *React. & Funct. Polym.*, **1999**, *39*, 27.
15. R. Chandra, *Synth. React. Inorg. Met.-Org. Chem.*, **1993**, *23*, 257.
16. B. Erk and, N. Gündüz, *Inorg. Chim. Acta*, **1990**, *167*, 91.
17. A. Ramachandraiah, P. Nageswara Rao and M. Ramaiah, *Indian J. Chem.*, **1989**, *28*, 309.
18. S. M. E. Khalil, *Chem. Papers*, **2000**, *54*, 12.
19. H. Mahanta and K. C. Dash, *J. Inorg. and Nucl. Chem.*, **1977**, *39*, 1345.
20. HyperChem 5.02, Molecular Visualization and Simulation Program Package, Hypercube, Inc., Gainesville, Florida 32601.
21. J. J. P. Stewart, *J. Comput. Chem.*, **1989**, *10*, 209.
22. J. J. P. Stewart, *J. Comput. Chem.*, **1989**, *10*, 221.
23. I. Humelnicu, I. Cretescu, C. Ghirvu and M. Macoveanu, *An. St. Univ. "Al.I. Cuza" Iasi, s. Chimie*, **1998**, *VI*, 65.