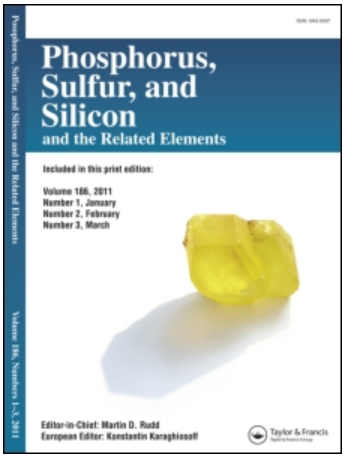

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Nasser M. Hosny[a]; Farid I. El-Dossoki[a]; Mohsen M. Mostafa[b]
[a] Chemistry Department, Faculty of Science, Suez-Canal University, Port-Said, Egypt [b] Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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SPECTRAL AND THERMAL STUDIES OF SOME NEW METAL COMPLEXES DERIVED FROM N-[(PHENYLAMINO)THIOXOMETHYL] HYDRAZINOCARBONYL METHYL PYRIDINIUM CHLORIDE (PTHMPC)

Nasser M. Hosny,[1] Farid I. El-Dossoki,[1] and Mohsen M. Mostafa[2]

[1]*Chemistry Department, Faculty of Science, Suez-Canal University, Port-Said, Egypt*

[2]*Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt*

New metal complexes derived from the reaction of N-[(phenylamino)thioxomethyl] hydrazino carbonyl methyl pyridinium chloride (H_2L; PTHMPC) with some metal salts of the general formula MX_2 [($X = Cl^-$ and/or CH_3COO^-; $M = Cd(II)$, $UO_2(II)$, $Mn(II)$ and $Zr(IV)$] were synthesized and characterized by elemental analyses, spectral analyses (IR, UV-vis., ^1H NMR), thermal analyses (TGA, DTG), and conductance and magnetic measurements. The results showed that the ligand exists in metal complexes either in the keto form or in the enol form. Moreover, the IR spectral data suggest that the acetate ion behaves in a monodentate manner. Semi-empirical calculations ZINDO/1, PM3, and AM1 have been used to study the molecular geometry and the harmonic vibrational spectra of the ligand and its metal complexes with the purpose of assisting the experimental assignment of the complexes. Generally, there is an agreement between the observed and the calculated spectra. Finally, the thermodynamic parameters (ΔE^*, ΔH, ΔG, and ΔS) have been calculated from the data of thermal analyses (TGA and DTG).

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Keywords Metal complexes; N-[(phenylamino)thioxomethyl] hydrazinocarbonyl methyl pyridinium chloride complexes; spectral studies; thermal studies

INTRODUCTION

Generally, the importance of the organic compounds or their metal complexes containing thiourea derivatives comes from not only their pharmacological applications[1–5] but also from their efficiency as recovery agents for precious and hazardous metals in hydrometallurgical and biometallurgical processing. The applicability of thiourea derivatives as leaching agents using these techniques comes from their ability to bind the metal ions and to

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Address correspondence to Nasser M. Hosny, Chemistry Department, Faculty of Science, Suez-Canal University, Port-Said, Egypt. E-mail: Nasserh56@yahoo.com

recover them by hydrothermal or biorecovery techniques.[6] N-[(phenylamino)thioxomethyl] hydrazinocarbonyl methyl pyridinium chloride (PTHMPC) possesses several possible modes of coordination sites. The modes of chelation of the analogue ligand, 1-acetyl-trimethylamonium chloride-4-phenyl-3-thiosemicarbazide, were reported earlier.[7] It was suggested that 1-acetyl-trimethylamonium chloride-4-phenyl-3-thiosemicarbazid coordinates via carbonyl oxygen or thione sulfur and the appropriate hydrazide nitrogen (NH^2). Also, it coordinates either in the keto or in the enol form according to the metal ion used.

In this investigation, we synthesized new metal complexes derived from PTHMPC with some heavy metal salts, i.e., Cd(II), Mn(II), UO_2(II), and Zr(IV) salts. The isolated solid complexes have been characterized by elemental analyses, molar conductivities, spectral (IR, UV-vis., and ^{1}H NMR) and magnetic measurements. Semi-empirical calculations AM1, PM3, and ZINDO/1 have been used to simulate the IR spectra of the ligand and its metal complexes. Moreover, the thermodynamic parameters of the metal complexes under investigation have been studied using the data of thermal analyses (TGA, DTG).

RESULTS AND DISCUSSION

The analytical data of the isolated solid complexes together with some physical properties are shown in Table I. The low values of the melting points for the solid complexes (220–278°C) suggest that the ligand is weakly coordinated to the metal ions and proceeds through simple coordination. The results indicate that the metal complexes are quite stable in air and easily soluble in H_2O, DMF, and DMSO but insoluble in most common organic solvents, indicating their electrolytic nature. The molar conductance values of the metal complexes in DMF at 25°C fall in the 23–128 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ range are taken as additional evidence for the electrolytic nature of these complexes.[8] This suggests that at least one chloride ion of the ligand exists outside the coordination sphere.

IR Spectra

The most important observed and calculated IR spectral bands of the ligand and its metal complexes are collected in Table II. The results suggest that the ligand (PTHMPC) is represented by two tautomeric forms (keto and enol) as shown in Figure 1 (A and B). The IR spectrum of the free ligand in KBr shows three strong bands at 3286, 3210, and 3021 cm^{-1} assigned to νNH^1, νNH^2, and νNH^4 vibrations, respectively. Also, the bands observed at

Table I Analytical data and physical properties of the complexes

Compound	Color	Mp (°C)	Found (Calcd) (%) C	H	M	Cl	Λ^a in DMF
[Cd H_2L (Ac)$_2$]Cl	White	245	39.3 (39.1)	3.9 (3.6)	20.0 (20.1)	6.4 (6.6)	23.0
[UO_2H_2L (Ac)$_2$]Cl·1/2H_2O	Brown	220	30.7 (30.1)	3.4 (2.9)	33.6 (33.1)	5.2 (4.9)	25.0
[Mn_2 H_2L (H_2O)$_8$]Cl_5·H_2O	Pink	278	22.5 (22.8)	4.6 (4.4)	15.4 (14.9)	25.0 (24.1)	128.0
[ZrHL(OH)$_3H_2O$]Cl_2·8H_2O	Yellowish white	225	25.7 (25.4)	5.1 (5.3)	14.0 (13.9)	11.0 (10.7)	46.0

[a] $\Omega^{-1}\cdot cm^2\cdot mole^{-1}$.

Table II Observed and calculated wave numbers (cm^{-1}) of the ligand H_2L and its metal complexes

Compound	ν (NH)	ν (C=O)	ν (CONH)	ν (C=N)py	ν (C=C)	ν (C=N*)	ν (CS)	ν (N−N)
H_2L	3286, 3210, 3021	1700	1635	1595	1535	—	1197, 746	950
AM1	3392, 3381, 3114	1704	1653	1610	1573	—	1208, 806	942
PM3	3355, 3290, 3120	1778	1762	1618	1590	—	1220, 849	943
ZINDO/1	4338, 4173, 3950	1754	1646	1627	1582	—	1223, 738	966
Cd Exp	3255, 3019	—	—	1595	1531	1563	1216, 753	965
PM3	3408, 3353	—	—	1596	1513	1529	1221, 762	976
ZINDO/1	5284, 4950	—	—	1616	1528	1585	1206, 750	1030
Mn Exp	3276, 3232, 3043	1685	1666	1614	1543	—	1220, 756	968
PM3	3415, 3340, 3242	1726	1682	1624	1480	—	1231, 740	948
ZINDO/1	3303, 3240, 3177	1677	1625	1597	1524	—	1210, 668	941
Zr Exp	3241, 3197, 3014	1707	1660	1604	1520	—	1196, 742	969
PM3	3349, 3335, 3084	1663	1650	1592	1513	—	1227, 952	952
ZINDO/1	3773, 3704, 3487	1796	1667	1637	1541	—	1173, 750	973
U Exp	3259, 3230, 2025	1713	1633	1595	1544	—	1189, 765	966

1700 and 1635 cm^{-1} are assigned to ν(C=O) and ν(CONH) vibrations, respectively.[9] Moreover, the bands observed at (1197 and 746), 1535, and 950 cm^{-1} are assigned to ν(C=S), ν(C=C), and ν(N−N) vibrations, respectively.[10] Finally, the band located at 1595 cm^{-1} is assigned to $\nu(C{=}C{+}C{=}N)_{py}$ vibration. The last band remains in the spectra of all the metal complexes unaltered, indicating that the heterocyclic nitrogen is not involved in coordination.

All these observations suggest that the ligand mainly exists in the keto form, as shown in Figure 1A.

When the IR spectral data of the free ligand are compared with its metal complexes, it is observed that the ligand binds to the metal ion in different modes according to the metal ion used, the anion attached to the metal ion, and the conditions during the synthesis of the metal complexes.

The free ligand behaves as a neutral bidentate ligand coordinating to the metal ion in the enol form without participation or displacement of the hydrogen atom from the OH produced by enolization as in case of the Cd(II) complex. Consequently the ligand coordinates through the azomethine nitrogen (C=N) produced by the enolization of the carbonyl oxygen and the thione sulfur (C=S) groups forming a five-membered ring around the Cd(II) ion. This suggestion is mainly supported by the following evidence: (i) The shift of the bands assigned to ν(CS) to lower wave-number, suggesting the participation of this group in bonding, and (ii) the disappearance of the bands at 1700, 3286, and 1635 cm^{-1} assigned to ν(CO), ν(NH), and ν(CONH) vibrations, respectively, together with the appearance of a new band at 1563 cm^{-1} assigned to the azomethine group. This behavior suggests that the ligand coordinates to the cadmium ion in the enol form without

(A) (B)

Figure 1 Tautomeric structures (A, B) of the ligand (PTHMPC; H_2L).

displacement of the hydrogen atom (see Figure S1, available online in the Supplemental Materials). Also, the presence of a new band at 3444 cm^{-1} assigned to the enolized OH group supports our view. This band is obscured in the IR spectrum of the free ligand as well as the other metal complexes. (iii) The shift of the band assigned to ν(N—N) to higher wave-number suggests the participation of the azomethine nitrogen group in bonding. Any bands obscured in the 2500–2900 cm^{-1} region is taken as strong evidence for the absence of any type of hydrogen bonding[9] and/or the existence of a SH group producing from the the enolzation of the CS group. Moreover, the spectrum shows two new bands at 1496 and 1315 cm^{-1}assigned to $\nu_{as}(CH_3COO^-)$ and $\nu_s(CH_3COO^-)$ vibrations, respectively. The correlation between the positions of the antisymmetric and symmetric stretching vibrations of the acetate group and the type of coordination of this group was studied earlier.[10] The frequency difference between the stretching vibrations of the carboxylate ions ($\sim$181 cm^{-1}) indicates that the acetate group is monodentate in nature.[10] Finally, the new weak bands observed at 459 and 432 cm^{-1} are mainly assigned to the ν(M-N) and ν(M-S) vibrations, respectively.[9]

The IR spectrum of the UO_2(II) complex, $[UO_2H_2L(Ac)_2]Cl{\cdot}1/2H_2O$, shows that the ligand behaves in a neutral bidentate fashion coordinating via the NH^1 and thione sulfur (C=S) groups forming a five-membered ring around the UO_2(II) ion (see Figure S2, Supplemental Materials). This behavior is suggested on the basis of the following evidences: (i) The shift of the bands assigned to ν(CS) group to lower wave-numbers, and (ii) the shift of the band assigned to ν(N—N) to higher wave-number is taken as an evidence for the participation of NH^1 in bonding. The existence of the bands assigned to ν(C=O), ν(CONH), and $\nu(C{=}C{+}C{=}N)_{py}$ vibrations more or less as those observed in the free ligand is taken as a strong evidences for the inertness of these groups towards coordination. Also, the spectrum shows two new bands at 1494 and 1307 cm^{-1} assigned to $\nu_{as}(CH_3COO^-)$ and $\nu_s(CH_3COO^-)$ vibrations, respectively. The difference between these two bands (187 cm^{-1}) is taken as an evidence for the monodentate bonding of this group.[9,10] The υ_3 and υ_1 vibration bands due to UO_2 group are observed as sharp bands at 895 and 820 cm^{-1}, [11] respectively. The force constant (F) for the U=O vibration was calculated by the method of McGlynn and Smith[12] and with the help of the following equation:

$$R_{U-O} = 1.08\ F^{-1/3} + 1.17 \quad (1)$$

The force constant (F) and the U—O bond distance were found to be 6.612 mdynes/Å and 1.745 Å, respectively. The U-O bond distance calculated from the above relation is 1.745 Å, while the theoretically calculated value from molecular techniques is 1.90 Å, which falls in the usual range (1.60–1.92 Å)[13] observed for the majority of UO_2 (II) complexes.

The results of the IR spectrum of the binuclear Mn(II) complex, $[Mn_2(H_2L)(H_2O)_8]Cl_5{\cdot}H_2O$, suggests that the free ligand coordinates to two manganese ions forming a binuclear metal complex (see Figure S3, in the Supplemental Materials). The first manganese ion is bonded through the carbonyl oxygen and the nitrogen of the NH^2 groups, while the second manganese ion is coordinated *via* the thione sulfur (CS) and the nitrogen of the NH^1 group. The ligand forms two five-membered rings around the two manganese ions. This suggestion is supported by the following evidence: (i) The shift of the bands assigned to carbonyl group and amide II band (CONH) to lower wave-numbers, indicating the participation of carbonyl group in bonding; (ii) the shift of the bands assigned to the thione group to lower wave-number is taken as evidence of participation of thione sulfur in bonding;

(iii) the shift of the band assigned to N—N to higher wave-number is taken as an evidence of the participation of this group in bonding; and (iv) the appearance of new weak bands at 497 and 440 cm^{-1} assigned to ν(M—O) and ν(M—N) vibrations, respectively.[9] The high molar conductance value of this complex in DMF (128 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) suggests the electrolytic nature of this complex, as well as the existence of five chloride ions outside the coordination sphere.

The IR spectrum of the Zr(IV) complex, $[Zr(H_2L)(OH)_3H_2O]Cl_2\cdot 7H_2O$, suggests that the ligand acts as a neutral bidentate ligand coordinating via the nitrogen of the NH^1 and the carbonyl oxygen groups forming a five-membered ring around the Zr ion (see Figure S4, in the Supplemental Materials). This behavior is supported by the following evidence: (i) The shift of the bands assigned to carbonyl and NH^2 is taken as an evidence for the participation of the carbonyl oxygen in bonding and the presence of the ligand in the keto form; (ii) the shifts of the bands assigned to ν(NH) and ν(N—N) vibrations are taken as an evidence of the participation of NH^2 group in bonding; (iii) the bands assigned to the ν(CS) vibrations remain in the spectrum of the complex as those observed in the free ligand, indicating the inertness of this group towards coordination; and (iv) the presence of two new bands at 1313 and 1383 cm^{-1} assigned to δ(OH), which are obscured in the IR spectra of the free ligand and the other metal complexes. Also, the spectrum shows new bands at 497 and 472 cm^{-1} assigning to ν(M—O) ν(M—N) vibrations, respectively.[9]

The cause of the differences between the calculated and experimental values may result from the fact that the experimental data are obtained in the solid state, whereas the calculated frequencies are estimated in the gas phase.

Thermal Analyses

The thermal analyses (TGA and DTG) curves of the complexes were carried out within a temperature range from room temperature up to 800°C. The estimated mass losses were computed based on the TG results, and the calculated mass losses are computed using the results of microanalyses (Table I). The determined temperature range, descriptions, and the percent losses in mass are given in Table S1 (available online in the Supplemental Materials).

Kinetic Studies from TGA and DTG

The activation energy (E*; $kJmol^{-1}$) of the decomposition process of the complexes was evaluated graphically by employing the Coats–Redfern method (CR),[14] where they derived the following relation:

$$\mathrm{Log}[\log\{W_f/(W_f - W)\}/T^2] = \log[(AR/\theta E^*)\{1 - (2RT/E^*)\}] - (E^*/2.303RT) \quad (2)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T, A is the Arrhenius constant (S^{-1}), R is the gas constant ($JK^{-1}mol^{-1}$), and θ is the rate of heating (°C/Sec.). From the graphical application of this relation for the different stages of decomposition, the activation energy of the decomposition process and the Arrhenius constant of the investigated complexes were calculated. The linearity of the graphical relation with a higher correlation coefficient $R^2 \sim 0.9736$ indicates that these reactions are first order.

The entropy change of decomposition reactions ΔS (in $JK^{-1}mol^{-1}$) can be calculated by applying the following equation[15]:

$$\Delta S = R \ln(Ah/K_b T_s) \quad (3)$$

where (K_b) is the Boltzmann constant and (h) is the Plank constant. The enthalpy change, ΔH, and the Gibbs free energy change, ΔG, of decomposition process was also calculated by applying the following relations:

$$\Delta H = E^* - RT_s \quad (4)$$

$$\Delta G = \Delta H - T_s \Delta S \quad (5)$$

The calculated kinetic thermodynamic parameters are listed in Table S2 (in the Supplemental Materials). It was noted that the total activation energy of the decomposition increased as the ionic radius of the used cations decreased in the following order: Cd(II) (ionic radius, r = 0.97 Å) ($E^* = 360.958$ kJ mol^{-1}) > Mn(II) (r = 0.80 Å) ($E^* = 363.636$ kJ mol^{-1}) > Zr(IV) (r = 0.79 Å) ($E^* = 377.437$ kJ mol^{-1}). This can be explained where the smaller size of the ions permits a closer approach of the ligand and so more stability of the complex.[16–18]

Magnetic Moment and Electronic Spectra

The comparatively low value of the magnetic moment (5.3 B.M.) of the Mn(II) complex, $[Mn_2(H_2L)(H_2O)_8]Cl_5 \cdot H_2O$, indicates the presence of metal–metal interaction. It is well established that the type and magnitude of magnetic exchange interactions in binuclear complexes depend on bridge identity, the distance between metal ions, the bond angles at the bridging atom, and the dihedral angle between the planes containing the Mn(II) ions.[19]

The electronic spectrum of Mn(II) complex, $[Mn_2(H_2L)(H_2O)_8]Cl_5 \cdot H_2O$, shows several bands at 14500, 17240, 23700, 27000, and 31700 cm^{-1} assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^4T_{2g}$ (G), $^4A_{1g}$, $^4T_{2g}$ (D), and ^4E_g (D) transitions,[20] respectively. All these foundations, together with the value of magnetic moment as well as the pale pink of the complex, suggest an octahedral geometry around the two Mn(II) ions.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of the uranyl complex, $[UO_2(H_2L)(Ac)_2]Cl \cdot 1/2H_2O$, (Figure S5, Supplementary Materials) in d_6-DMSO shows three singlet signals at 11.33, 10.69, and 9.61 ppm, downfield with respect to TMS, assignable to the protons of NH^1 (attached to CO group), NH^4 (attached to Ph group), and NH^2 (attached to CS group), respectively. The presence of these signals indicates that the ligand exists mainly in the keto form. Also, the negative shifts of the second and third signals compared to the spectrum of the free ligand[21] suggest that the coordination proceeds through the NH^2 and CS groups. The singlet signal at 4.48 ppm is attributed to the protons of CH_2 ($N-CH_2$) group. The multiple signals in the 7.01–9.07 ppm region are assignable to the pyridyl and phenyl groups. Also, the spectrum shows two singlet signals at 2.52 and 2.68 ppm assigned to the protons of CH_3 of the two acetate groups (Figure S5, Supplemental Materials).

Geometrical Parameters

Selected bond lengths and angles of the optimized complexes are collected in Table S3 (Supplemental Materials).

The shortening of the bond lengths ^{2}N—Mn, ^{1}N—Mn, S—Mn, ^{2}N—Zr, and ^{3}O—Zr with respect to corresponding structures[22–24] reflects the strong electrostatic interactions between the central cations and these active sites. The S—Cd bond length is of the same order as those reported in corresponding crystal structures.[25] The bond lengths of ^{3}O—Mn and ^{1}N—Cd are longer than the average values in the corresponding crystal structure,[22,26] which may be explained on the basis of the depletion of electrons on these active sites. The angles of S—Cd—N^{1} and CN^{1}N^{2}C are 52.3 and 44.5°, respectively. The low values of the angles suggest a highly distorted tetrahedral structure around the Cd ion.

The net charges on the active sites of the free ligand and its complexes are summarized in Table S4 (Supplemental Materials). All the central ions are negatively charged, indicating the transfer of electrons from the ligand to the central ions. In comparison with the charge on the S atom of the free ligand, the negative charge increases in the case of Mn and Cd complexes, indicating the flow of electrons from the adjacent system to this atom.

CONCLUSION

In general, it is concluded that the observed and calculated vibrational spectra are agreed. AM1 is the most suitable method of calculation in case of the ligand. PM3 agrees well in case of Cd and Zr complexes, while PM3 and ZINDO/1 agree to the same extent in case of Mn complex. The ^{1}H NMR spectrum of the uranyl complex indicates that the ligand coordinates in the keto form. The ligand coordinates also in the keto form in the case of Mn and Zr complexes, while it exists in the enol form in the case of the Cd complex. The results showed that the ligand forms a binuclear complex only with Mn(II) chloride, while mononuclear complexes were obtained for the rest of the other metal ions. Also, the results of IR showed that the ligand coordinates to the metal ions either in a bidentate manner with different modes of chelation via the carbonyl oxygen (C=O) and NH^{1}, the thione sulfur (C=S) and NH^{2} and azomethine (C=N) and thione (C=S) groups, or in a tetradentate manner towards two Mn(II) ion *via* the carbonyl oxygen (C=O), NH^{1}, thione (C=S), and NH^{2} groups as in case of the Mn(II) complex. Moreover, the IR spectral data suggest that the acetate ions behave in a monodentate manner. Thermal analyses indicate that these complexes are thermally stable up to ca. 200°C.

EXPERIMENTAL

All the chemicals were of analytical grade and were used without further purifications. Carbon and hydrogen contents were performed at the Microanalytical Unit of Mansoura University. The metal contents were determined by a complexometric technique.[27] The uranium content was determined gravimetrically as U_3O_8.[27] Molar conductance measurements of the metal complexes in DMSO and/or water (10^{-3} M) were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration of the frequency reading was made with polystyrene film at Mansoura University. Electronic spectra of the solid complexes in DMF were recorded on UV2 Unicam UV/vis. spectrometer at Mansoura University. Magnetic measurements were carried out at room temperature (25°C) on a Sherwood magnetic

balance at Mansoura University. Thermal analysis measurements (TGA and DTG) were recorded on a Schimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 cm^3/min and 10°C/min, respectively. The ^1H NMR spectrum of the UO_2(II) complex was recorded in d_6-DMSO on a Gemini-200 spectrometer at Cairo University.

Synthesis of the Ligand

The ligand under investigation (PTHMP; H_2L) was prepared as described earlier by us.[20]

Synthesis of the Metal Complexes

The metal complexes were prepared by adding equimolar amounts (0.01 mol) of the hydrated metal salts (chloride and/or acetate) in absolute ethanol (10 mL) to an ethanolic solution (25 mL) of the ligand (PTHMPC) with constant stirring. The reaction mixture was then refluxed on a hot plate for 1 h and then left to cool at room temperature (25°C). The resulting solid complexes were filtered off and washed successively with EtOH and diethyl ether. Finally, the isolated solid complexes were kept in a desiccator over fused calcium chloride.

Computational Details

Molecular geometries of all forms of metal complexes were optimized using molecular mechanics and the semi-empirical ZINDO/1, PM3, and AM1 methods using the Hyperchem series of programs.[28] The molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures of the metal complexes. The low lying conformers obtained from this search were then optimized at AM1, ZINDO/1, and PM3, (Polak-Ribiere) RMS 0.01 kcal.

The uranyl complex is optimized by MM+ only since there is no data available for the metal in the program.

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