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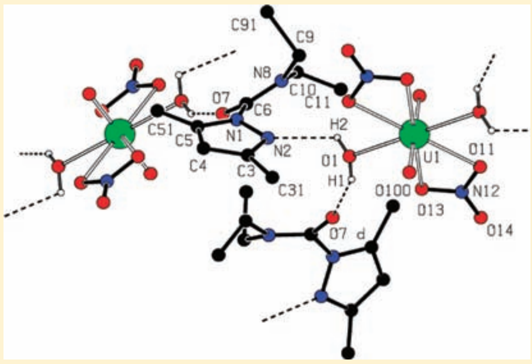
Steric Effects on Uranyl Complexation: Synthetic, Structural, and Theoretical Studies of Carbamoyl Pyrazole Compounds of the Uranyl(VI) Ion

Debasish Das,[†] Shanmugaperumal Kannan,*[,#] Dilip K. Maity,*[,‡] and Michael G. B. Drew[≠]

[†]Fuel Reprocessing Division, Bhabha Atomic Research Centre, Mumbai-400085, India
[#]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400085, India
[‡]Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai-400085, India
[≠]Department of Chemistry, University of Reading P.O. Box 224, Whiteknights, Reading, RG6 6AD, United Kingdom

Supporting Information



ABSTRACT: New bifunctional pyrazole based ligands of the type [$C_3HR_2N_2CONR'$] (where R = H or CH_3; R′ = CH_3, C_2H_5, or $^{i}C_3H_7$) were prepared and characterized. The coordination chemistry of these ligands with uranyl nitrate and uranyl bis(dibenzoyl methanate) was studied with infrared (IR), ^{1}H NMR, electrospray-mass spectrometry (ES-MS), elemental analysis, and single crystal X-ray diffraction methods. The structure of compound [$UO_2(NO_3)_2(C_3H_3N_2CON\{C_2H_5\}_2)$] (**2**) shows that the uranium(VI) ion is surrounded by one nitrogen atom and seven oxygen atoms in a hexagonal bipyramidal geometry with the ligand acting as a bidentate chelating ligand and bonds through both the carbamoyl oxygen and pyrazolyl nitrogen atoms. In the structure of [$UO_2(NO_3)_2(H_2O)_2(C_5H_7N_2CON\ \{C_2H_5\}_2)_2$], (**5**) the pyrazole ligand acts as a second sphere ligand and hydrogen bonds to the water molecules through carbamoyl oxygen and pyrazolyl nitrogen atoms. The structure of [$UO_2(DBM)_2C_3H_3N_2CON\{C_2H_5\}_2$] (**8**) (where DBM = $C_6H_5COCHCOC_6H_5$) shows that the pyrazole ligand acts as a monodentate ligand and bonds through the carbamoyl oxygen to the uranyl group. The ES-MS spectra of **2** and **8** show that the ligand is similarly bonded to the metal ion in solution. Ab initio quantum chemical studies show that the steric effect plays the key role in complexation behavior.

■ INTRODUCTION

The coordination chemistry of uranium is growing rapidly in recent years due to the presence of new synthetic methods available[1] and also the interesting properties such as selective ion-exchange, mixed valency, ionic conductivity, enhanced fluorescence, magnetic ordering, and nonlinear optical properties exhibited by its complexes.[2] The basic understanding of the coordination chemistry of the uranyl group is very important for the selective complexation and separation of this ion from the acid medium during reprocessing of irradiated advanced heavy water reactor (AHWR) nuclear fuel[3] and biological and environmental samples.[4,5] The coordination chemistry of uranyl ion is different from that of other spherical ions due to the presence of the linear uranyl (O═U═O) group. Hydroxy pyridinone based ligands show selectivity for uranyl ion from biological and environmental samples[4] whereas the iso-butyramide based ligands show selectivity from nitric acid medium.[6] In both cases, steric effects play an important role in the formation of the equatorial plane. It is also reported that steric effects play a more important role when the ligand forms a five membered metallocyclic ring with the metal center rather than a six or higher.[7] In continuation of our interest on the complex chemistry of uranyl ion with newly synthesized ligands,[8] we report herein the synthesis, characterization, and complex chemistry of two types of carbamoyl pyrazole based ligands (Figure 1a,b), which are expected to form a five membered ring with uranyl nitrate. We also compared the complex chemistry of these ligands with the analogous carbamoyl methyl pyrazole based ligands (Figure 1c,d), which form a six membered metallocyclic ring with uranyl nitrate.[8b] The steric effect on complexation of these ligands with uranyl ion is explained on the basis of first principle base quantum chemical calculations.

■ RESULTS AND DISCUSSION

Synthesis of Carbamoyl Pyrazole Ligands. The reaction of pyrazole or dimethyl pyrazole with the corresponding *N*,*N*′-dialkyl carbamoyl chloride yielded the carbamoyl pyrazole ligands **L**^{1}–**L**^{6} (Scheme 1). The infrared (IR) spectra of all ligands show the presence of carbamoyl groups in the synthesized ligands. The ^{1}H NMR of all ligands show the expected peak multiplicities and integrations. The CHN analyses support the expected stoichiometry for the newly prepared ligands.

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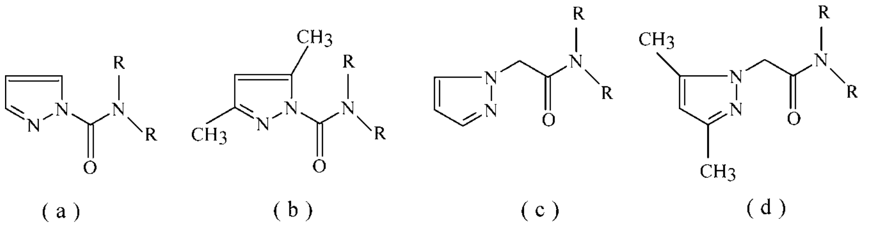
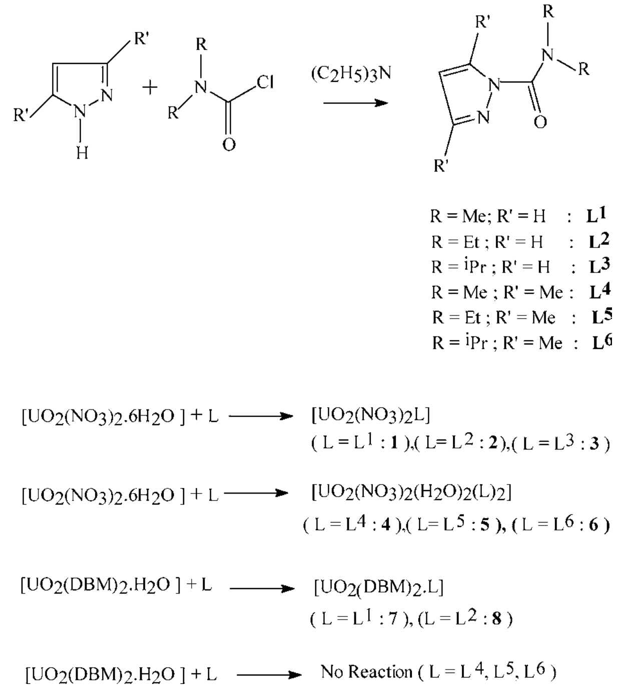


Figure 1. Different bifunctional carbamoyl pyrazole based ligands.

Scheme 1. Synthesis of Ligands and Their Uranyl Complexes



Carbamoyl Pyrazole Uranyl Nitarte Complexes. The reaction of ligands L^1–L^3 with $[UO_2(NO_3)_2{\cdot}6H_2O]$ yielded compounds **1**–**3** (Scheme 1). C, H, and N analyses revealed that the ratio of ligand to uranyl nitrate is 1:1 in all compounds. The IR spectra of **1**–**3** show that the water molecules from the starting compound $[UO_2(NO_3)_2{\cdot}6H_2O]$ are completely replaced by the ligand and that the ligand is bonded through the carbamoyl oxygen atom to the uranyl group. The observed frequency difference for a carbamoyl ($\Delta\nu_{CO}$ = 20–40 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO(\text{free ligand})} - \nu_{CO(\text{coordinated})}$) group is consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed in $[UO_2(NO_3)_2(N\text{-cyclohexyl,2-pyrrolidone})_2]$,[9a] $[UO_2(NO_3)_2(\text{1,3-dimethyl,2-imidazolidone})_2]$,[9b] $[UO_2(NO_3)_2\{{}^iC_3H_7CON({}^iC_4H_9)_2\}_2]$,[6a] $[UO_2(NO_3)_2({}^iC_3H_7)_2N\,COCH_2CON\,({}^iC_3H_7)_2]$,[10] and $[UO_2(NO_3)_2(C_{15}H_{27}N_3O)]$.[8b]

The ^{1}H NMR spectra of **1**–**3** show the expected peaks and integrations. The pyrazolyl protons are deshielded by ca. 1–1.8 ppm with respect to the free ligand indicating that the bonding between pyrazolyl nitrogen and uranyl group persists in solution.[8b] It is apparent from IR and NMR spectral results that the ligand acts as a bidentate chelating ligand and bonds through the carbamoyl and pyrazolyl nitrogen to uranyl group. The structure of **2** has been determined by single crystal X-ray diffraction methods and confirms the spectral and analysis results.

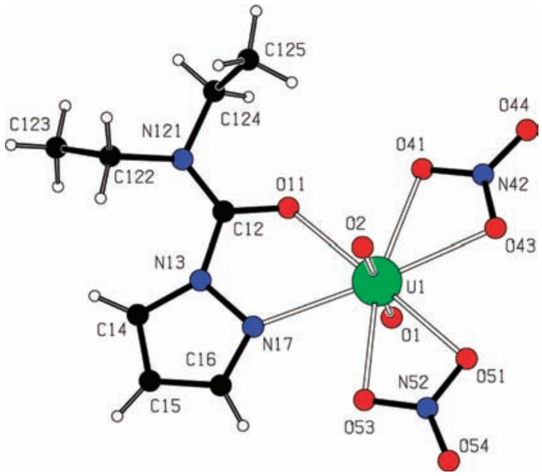


Figure 2. Structure of compound **2**.

Table 1. Important Bond Lengths (Å) and Angles (°) for 2, 5, and 8

	2		
U1−O2	1.775(9)	U1−O51	2.467(9)
U1−O2	1.778(9)	U1−O53	2.494(9)
U1−O11	2.392(8)	U1−O43	2.513(9)
U1−O41	2.466(8)	U1−N17	2.544(9)
O1−U1−O2	178.4(4)	O51−U1−O53	50.7(3)
O41−U1−O43	50.7(3)	O11−U1−N17	61.7(3)
O53−U1−N17	66.3(3)	C12−O11−U1	127.4(7)
	5		
U1−O100	1.711(7)	U1−O1	2.434(7)
U1−O11	2.484(7)	U1−O13	2.492(6)
O1−H1	0.838(10)	O1−H2	0.841(10)
O100−U1−O100	179.999(1)	O1−U1−O1	180.0
O1−U1−O13	63.7(2)	O11−U1−O13	128.9(2)
	8		
U1−O1	1.772(4)	U1−O2	1.774(4)
U1−O11	2.350(5)	U1−O15	2.318(5)
U1−O41	2.326(5)	U1−O45	2.358(5)
U1−O71	2.437(5)	C72−O71	1.221(8)
O1−U1−O2	179.6(2)	O15−U1−O41	77.07(16)
O15−U1−O11	69.88(16)	O41−U1−O45	70.72(16)
O45−U1−O71	71.93(16)	C72−O71−U1	177.8(5)

Structure of $[UO_2(NO_3)_2C_3H_3N_2CON\{C_2H_5\}_2]$ (2). The structure of **2** is shown in Figure 2, and selected bond distances and angles are given in Table 1. The structure of **2** shows that the uranium atom is surrounded by one nitrogen and seven oxygen atoms in a hexagonal bipyramidal geometry. Four oxygen atoms of the two bidentate nitrate groups, together with one oxygen and one nitrogen atom of bidentate carbamoyl pyrazole ligand, form the equatorial hexagonal plane. The UO_5N atoms in the equatorial plane show a root mean square (rms) deviation of 0.082 Å. The two uranyl oxygen atoms occupy the axial positions.

This type of coordination is similar to that observed in the compounds of the bifunctional ligands, malonamide, carbamoyl methyl phosphonate, carbamoyl methyl phosphine oxide, and carbamoyl methyl pyrazole with uranyl nitrate, such as $[UO_2(NO_3)_2(\{^iC_3H_7)_2NCO\}_2]$,[10] $[UO_2(NO_3)_2(^iC_3H_7O)_2PO\text{-}CH_2CONEt_2]$,[11a] $[UO_2(NO_3)_2(C_6H_5)_2POCH_2CONEt_2]$,[11b] $[UO_2(NO_3)_2.C_6H_5SOCH_2CONBu_2]$,[8a] and $[UO_2(NO_3)_2\text{-}(C_{15}H_{27}N_3O)]$.[8b] The U−O(amide) distance (2.392(8) Å) in **2** is comparable in magnitude with those of earlier reported uranyl nitrate-amide compounds, such as $[UO_2(NO_3)_2$(*N*,*N*-dimethylformamide)$_2]$ (2.397(6) Å),[13] $[UO_2(NO_3)_2$(tetrabutylglutaramide)$_2]$ (2.378(6)Å,[12] $[UO_2(NO_3)_2$(dibutyldecanamide)$_2]$ (2.37(2) Å),[14] and $[UO_2(NO_3)_2(C_{15}H_{27}N_3O)]$ (2.364(7) Å).[8b] The U−N(pyrazole) distance (2.544(9) Å) is very close to the values observed in $[UO_2(NO_3)_2(C_{15}H_{27}N_3O)]$ (2.554(9)Å),[8b] $[UO_2(NO_3)_2$(phenanthroline)] (2.556(2)Å),[15] and $[UO_2$(terpyridine)](OTf)$_2$ ((2.567(6), 2.592(6) Å).[16] The observed average U−O(NO_3) bond distance 2.485(9) Å is normal.[8−14] The angles subtended at the metal atom show that the uranium atom has a slightly distorted hexagonal bipyramidal geometry.

Carbamoyl 3,5-Dimethyl Pyrazole Uranyl Nitrate Complexes. The reaction of ligands L^4−L^6 with $[UO_2\text{-}(NO_3)_2{\cdot}6H_2O]$ yielded the compounds **4**−**6** (Scheme 1). The C, H, and N analysis revealed that the ratio of ligand to uranyl nitrate is 2:1 in all compounds. The IR spectra of **4**−**6** show that the water molecules from the starting compound $[UO_2\text{-}(NO_3)_2{\cdot}6H_2O]$ have not been completely replaced by the ligand and that the ligand is uncoordinated in the complex.[18] The ^1H NMR of **4**−**6** shows the expected peaks and multiplicities for the ligand. They show further that the peaks are broadened and their positions are very similar to those of free ligands. This shows clearly that there is no bonding between ligand and metal in solution. In order to find out the nature of bonding between the carbamoyl 3,5-dimethy pyrazole ligand and uranyl nitrate in solid state, the structure of **5** has been determined by single crystal X-ray diffraction methods.

Structure of $[UO_2(NO_3)_2(H_2O)_2(C_5H_7N_2CON\{C_2H_5\}_2)_2]$ (5). The structure of **5** is shown in Figure 3, and selected bond distances and angles are given in Table 1. The structure consists of centrosymmetric $[UO_2(NO_3)_2{\cdot}2H_2O]$ groups, bridged by carbamoyl, dimethyl pyrazole ligand via O−H···O and O−H···N hydrogen bonds. The structure shows that there is no direct bonding between ligand and that the uranyl ion and the uranium(VI) ion are surrounded by eight oxygen atoms to give hexagonal bipyramidal geometry. The ligand forms a second sphere coordination[17] compound with $[UO_2(NO_3)_2{\cdot}2H_2O]$. Such types of second sphere compounds with uranyl nitrate are known previously for the weak donor ligands, such as crown ethers[18] or alcohols[19a] but not with a strong donor ligand amide. However, some compounds of phosphine oxide with the transition metal ions show second sphere coordination.[19b,c] The average distances for U−O$_{uranyl}$ (1.711(7) Å),[8−16] U−O$_{H2O}$ (2.434(7)Å),[18,19]and U−O$_{NO3}$ (2.488(7)Å)[8−14] agree well with the values reported earlier. The hydrogen bonding O$_{water}$···O$_{carbonyl}$ and O$_{water}$···N distances and angles are within the accepted values. Thus, O(1)−H(1)···O(7) ($x - 1, y, z$) has dimensions O···O, 2.760(9) Å, O−H···O, 155°, and H···O, 1.98 Å while O(1)−H(2)···N (2) ($0.5 - x, y + 0.5, 0.5 - z$) has dimensions O···N, 2.691(10) Å, O−H··N, 152°, and H···N, 1.92 Å.

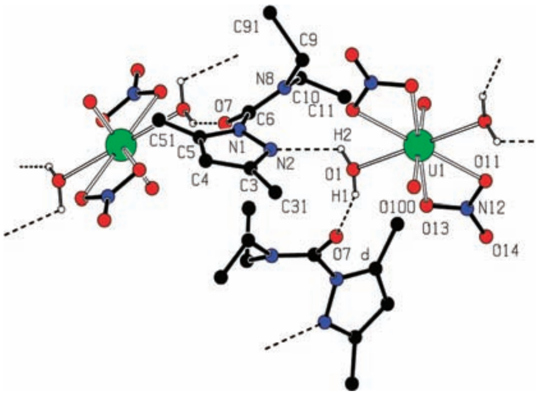


Figure 3. Structure of **5** (hydrogen atoms of the ligand are removed for clarity). Hydrogen bonds are shown as dotted lines. The metal atoms occupy center of symmetry.

It is noteworthy that the analogous pyrazole ligands L^1−L^3 form inner sphere complexes with uranyl nitrate and directly bond to the metal center in the bidentate fashion via the carbamoyl oxygen and pyrazolyl nitrogen atoms. However, such type of bonding is not seen with the ligands L^4−L^6. It is interesting to note further that the analogous carbamoyl methyl pyrazole and carbamoyl methyl, 3,5-dimethyl pyrazole (Figure 1c,d) ligands form an inner sphere complex with the uranyl nitrate[8b] and also act as bidentate chelating ligands. These observations could be explained purely on the basis of a steric effect due to the interaction between the methyl groups at the 3 and 5 positions of the pyrazole group with the carbamoyl oxygen and pyrazolyl nitrogen atoms of the ligands (see the theoretical work below for detail) during metal ligand bond formation. However, the analogous carbamoyl methyl pyrazole (Figure 1c,d) type of ligands form a six member metallocyclic ring with the uranyl ion,[8a] and here, the methyl groups at the 3 and 5 positions are positioned well away from the donor groups. These differences are consistent with the earlier reports that the steric effects play an important role during complex formation when ligands form a five member metallocyclic ring.[7]

Carbamoyl Pyrazole Uranyl Bis(Dibenzoyl Methanate) Complexes. The reaction of L^1−L^2 with $[UO_2(C_6H_5COCH\text{-}COC_6H_5)_2{\cdot}2H_2O]$ yielded the compounds **7** and **8** (Scheme 1). C, H, and N analyses revealed that the ratio of ligand to uranyl bis(dibenzoyl methanate) is 1:1 in both compounds. The IR spectra of **7** and **8** show that the water molecules from the starting compound $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ are completely replaced by the ligand, and furthermore, the observed frequency difference for a carbamoyl ($\Delta\nu_{CO}$ = 35 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO\ (\text{free ligand})} - \nu_{CO(\text{coordinated})}$) group is consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed in $[UO_2(DBM)_2\{^iC_3H_7CON\text{-}(^iC_3H_7)_2\}_2]$ (where DBM = $C_6H_5COCHCOC_6H_5$),[6a] $[UO_2\text{-}(NO_3)_2$(*N*-cyclohexyl,2-pyrrolidone)$_2]$,[9a] $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone)$_2]$,[9b] $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON\ (^iC_3H_7)_2]$,[10] and $[UO_2(NO_3)_2(C_{15}H_{27}N_3O)]$[13b].

The ^1H NMR spectra of **7**−**8** show the expected peaks and integrations. The pyrazolyl protons are deshielded by ca. 0.5 ppm with respect to the free ligand indicating that the bonding between ligand and uranyl group persists in solution.[8a] The structure of **8** has been determined by single crystal X-ray diffraction methods and confirms the spectral and analysis results.

Structure of $[UO_2(C_6H_5COCHCOC_6H_5)_2C_3H_3N_2CON\{C_2H_5\}_2]$ (8). The structure of **8** is shown in Figure 4 together with the numbering scheme, and selected bond distances and angles are given in Table 2. The structure shows that the uranyl group is bonded to two $C_6H_5COCHCOC_6H_5$ groups and a carbamoyl pyrazole ligand to give a coordination number of seven. The pyrazole ligand acts as a monodentate ligand and is bonded through the carbamoyl oxygen atom to the uranyl group. Four oxygens from two bidentate $C_6H_5COCHCOC_6H_5$ groups and one oxygen from the carbamoyl pyrazole ligand form the equatorial plane, and together with two oxygen atoms of the uranyl group form a pentagonal bipyramidal geometry around the uranium(VI) ion.

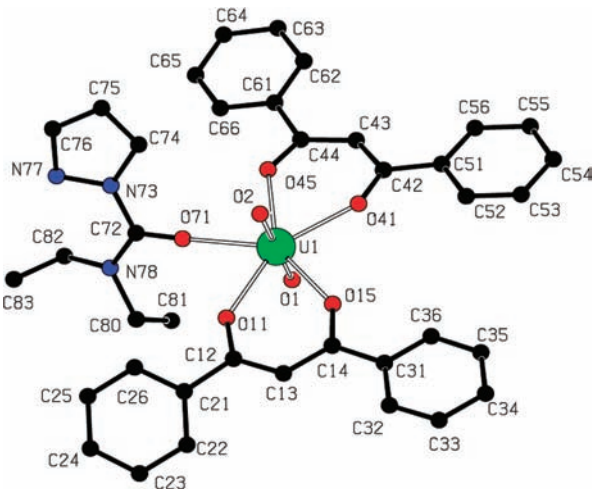


Figure 4. Structure of **8**.

Table 2. Crystal Data Refinement of Compounds 2, 5, and 8[a]

	2	5	8
empirical formula	$C_8H_{13}N_5O_9U$	$C_{20}H_{38}N_8O_{12}U$	$C_{38}H_{35}N_3O_7U$
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	8.3229(6)	10.207(2)	10.2750(5)
b (Å)	18.0208(11)	8.5355(17)	21.6295(10)
c (Å)	10.6066(8)	18.095(4)	15.8792(7)
β (°)	100.902(8)	95.74(2)	100.913(4)
V (cm^3)	1562.12(19)	1568.6(6)	3465.2(3)
Z	4	2	4
ρ_{calcd} [g cm^{-3}]	2.386	1.737	1.694
μ [mm^{-1}]	10.445	5.240	4.738
reflections collected/ unique	9807/4518	9787/4376	17433/9611
data/restrains/ parameters	4518/0/210	4376/31/202	9611/0/444
goodness of fit on F^2	1.038	1.010	1.073
final R_1 indices [$I > 2\sigma(I)$]	0.0755	0.0658	0.0639
wR_2 indices (all data)	0.1855	0.1496	0.1133

[a] $w = 1/[\sigma^2(Fo^2) + (0.1166P)^2 + 0.000P]$ for **2**, $w = 1/[\sigma^2(Fo^2) + (0.0667P)^2 + 0.000P]$ for **5** and $w = 1/[\sigma^2(Fo^2) + (0.0378P)^2 + 3.2432P]$ for **8**, where $P = (Fo^2 + 2Fc^2)/3$.

The five oxygen atoms in the equatorial plane show an rms deviation of 0.062 Å. Similar structures are also observed in the compounds of phosphine oxides, sulfoxides, ketones, N-oxides, and amides with the uranyl bis(β-diketoantes), viz, $[UO_2(DBM)_2(OPPh_3)]$,[20a] $[UO_2(DBM)_2(C_6H_5SOCH_3)]$,[20b] $[UO_2(TTA)_2(C_5H_5NO)]$,[20c] $[UO_2(DBM)_2(camphor]$,[20d] $[UO_2(DBM)_2({}^iC_3H_7CON\{{}^iC_3H_7\}_2)]$,[8] and $[UO_2(DBM)_2(C_4H_9CON\{C_4H_9\}_2)]$.[20e] The observed U−O amide bond distance (2.437(5)Å) is much longer in length compared to any of the amide−uranyl bond distances reported, and the U−O−C angle is very close to linear (177.8(5)°). These dimensions are unusual in metal amide chemistry[21] with U−O(amide) distance being longer and the U−O−C angle being larger than usual. The inverse relation between the M−O bond distance and M−O−C bond angle is reported in the literature[22] and could be explained on the basis of π donation of electron from the filled p orbitals of oxygen to the vacant f/d orbitals of metal center thereby shortening of M−O bond distance with the opening in M−O−C bond angle.[6a,22b,c] However, the observed dimensions in **8** could be explained purely on the basis of steric effects caused by the interaction between the pyrazole group and the bulky phenyl groups of the diketonate units, which may lead to the formation of a longer M−O bond with larger M−O−C bond angle.

Reaction Between $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ and L^4−L^5. The reaction between $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ and $\mathbf{L^4}$−$\mathbf{L^5}$ yielded back the unreacted starting compound $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ and free ligand revealed by the IR and NMR spectral studied. This observation could also be explained purely on the basis of steric effects caused between the methyl groups of the dimethyl pyrazole group and the carbamoyl group which do not allow the ligand to approach the metal center during complexation.

Electrospray-Mass Spectrometry Study. Electrospray-mass spectrometry (ES-MS) study for two of the pyrazole based uranyl compounds **2** and **8** was carried out to see the nature of species in solution and also to see whether the ligand retains bonding with metal ion in solution or not. It is known in many compounds of uranyl ion with the bifunctional ligands, like carbamoylmethyl phosphoshine oxides,[11] malonamides,[10] carbamoylmethyl sulfoxids,[8a] and carbamoyl methyl pyrazole,[8b] that the ligands form 1:1 species in the solid state whereas they form 2:1 species in solution.[8a,b,23] Electrospray ionization mass spectrometric detection of positive ions for **2** in CH_2Cl_2 shows three intense peaks at the m/z values of 499.1 (61%), 517.15 (63%), and 666.24 (100%). These peaks are assigned to the species $[UO_2(NO_3)L]^+$ (69%), $[UO_2(NO_3)(H_2O)L]^+$ (71%), and $[UO_2(NO_3)L_2]^+$ (100%) (where L = $C_3H_3N_2CON(C_2H_5)_2$), respectively. This study shows clearly that the ligand retains its bonding with the metal ion in solution and also that the compound undergoes disproportionation to give a mixture of 1:1 and 1:2 complexes.[8a] The ES-MS spectrum of **8** in CH_2Cl_2 shows peaks at the m/z values of 660.2 (100%), 678.2 (24%), and 849(18%). The peaks at 660.2 and 678.2 could be assigned to the species $[UO_2(DBM)L]^+$ and $[UO_2(DBM)L(H_2O)]^+$, respectively, thus showing clearly that the ligand retains bonding with the metal ion in solution.

■ THEORETICAL STUDY

Full geometry optimization of *N,N*-dimethyl analog of the ligands (Figure 1a−d) has been carried out applying a correlated nonlocal hybrid density functional, namely, B3LYP. SARC-ZORA basis sets for U and Gaussian type atomic basis

Table 3. Selected Geometrical and Other Parameters of the Complex Calculated Applying B3LYP/6-31+G(d) Level of Theory[a]

	Mulliken atomic charge density in the corresponding ligand (au)		selected bond distances (Å) in the complex				
complex	N1	O1	U−N1	U−N2	U−O1	δ(N1−O1−U−O(NO2)) (degree)	binding energy (kcal/mol)[b]
A	−0.13	−0.24	2.91	3.75	2.77	1.7	27.8 (17.0)
B	−0.20	−0.28	3.06	3.80	2.75	14.1	24.7 (14.6)
C	−0.19	−0.30	2.92	3.84	2.69	7.6	28.8 (18.0)
D	−0.20	−0.29	2.93	3.81	2.73	9.4	28.5 (17.6)
E					2.75	0.6	27.6 (16.9)

[a] For U atom, SARC-ZORA basis function has been considered. [b] Binding energy has been calculated in gas phase as well as in water medium applying a macroscopic solvent model, namely, PCM. Binding energy has been calculated by moving away the ligand from U ion to a distance of 2.5 times of the equilibrium distance of U−N2 as shown in Figure 5 or U−O1 (in case of complex E). The values in parentheses show the calculated binding energy including solvent effect (water).

functions 6-31+G(d) for H, C, N, and O atoms are applied for all the calculations. Table 3 displays the calculated atomic charge density over N1 and O1 atoms of the corresponding ligands and O atoms of H_2O molecule. It is clearly observed that charge density increases over N1 and O1 atoms (see Figure 5) on putting −CH_3 groups as expected. This indicates the formation of coordinated complexes to be facilitated in case of methylated ligands. Geometry of the complexes A−D (Figure 5) has been optimized, adopting the same level of theory, and selected geometrical parameters are listed in the same Table 3. It is observed that, in case of complex B, the distance between U and N1 is longer than that in other cases by ~0.15 Å. The calculated distance suggests that due to steric factor N1 atom fails to approach U ion close in comparison to other complexes making the binding of this ligand weak to make the complex. This is reflected in the calculated binding energy (BE) of the complexes as displayed in Table 3. Binding energy has been calculated from the theoretical BE curve as shown in Figure 6. This curve has been generated by calculating the total energy of the complex, keeping the ligand at different distances from the central ion of the complex until it goes to dissociation limit. The calculated binding energy has been refined, considering PCM macroscopic solvent model, and the results do show a similar trend as reflected in the table. To form a stable complex, a suitable geometry and proper orbital orientation of the central ion and chelating sites of the ligand is essential. In the present case, the chelating atoms of the ligand and the central ion should be in a plane to have a good orbital overlap to result in a stable complex. Calculated angle between N1−O1−U and O1−U−O(NO2) planes are also listed in Table 3. It suggests that, in case of complex B, chelating site of the ligand N1 is out of plane from the remaining atoms by ~14°. This configuration may not allow good overlap between N1 and U ion orbitals. As a result, this complex is expected to be weaker compared to the other complexes. In fact, X-ray crystallography data suggests that two H_2O molecules stay in the first solvation layer and this ligand stays in the second solvation layer. This should make the complex more stable due to additional four H-bonding between four H atoms of two H_2O molecules and the ligands as shown in Figure 3. Binding energy curve of the complex E with two H_2O molecules in place of the ligand (complex B) is depicted in Figure 7, which suggests complex E to be more stable than complex B by 1.9 kcal/mol.

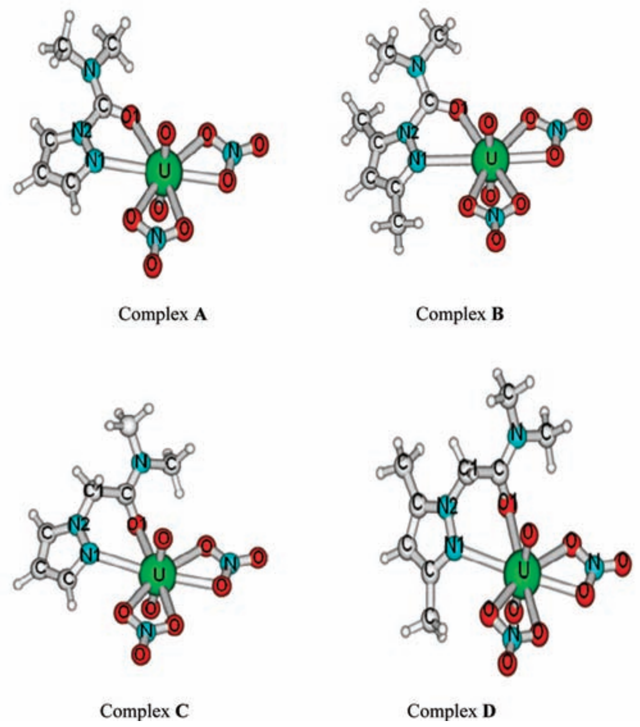


Figure 5. Fully optimized minimum energy structure for the $[UO_2(NO_3)_2]$ complex with the *N,N*-dimethyl analog of the ligands (A−D).

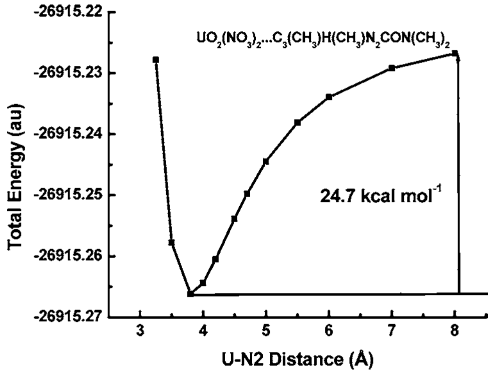


Figure 6. Binding energy curve for the complex B.

■ EXPERIMETAL SECTION

General Consideration. All reagents and solvents were of analytical grade and used as received. IR spectra were recorded as nujol mulls using a JASCO-610 FITR spectrometer. ^1H NMR spectra were

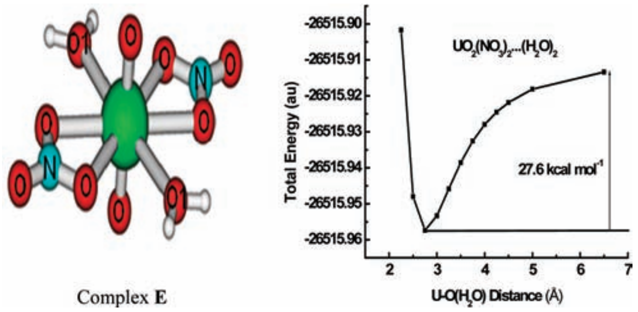


Figure 7. Minimum energy structure and binding energy curve for $[UO_2(NO_3)_2{\cdot}2H_2O]$.

recorded using a Bruker AMX-300 or 500 spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in hertz. Electrospray ionization mass spectrometric detection of positive ions in CH_2Cl_2 was recorded using a MicrOTOF Q-II instrument. The samples were introduced into the source with the syringe pump. Nitrogen was employed as both the drying and spraying gas with a source temperature of 180 °C. The cone voltage was set to 45 V; the voltage applied on the capillary was 1162 kV, and the sample solution flow rate was 5 μL min^{-1}. Spectra were recorded from m/z of 100 to 1000.

Synthesis of L^1. A solution of pyrazole (10 g, 0.14 mol) and triethyl amine (17.5 g, 0.17 mol) in benzene (50 mL) was added slowly to a solution of *N,N*-dimethyl carbamoyl chloride (15.8 g, 0.14 mol) in benzene (50 mL) with stirring. The reaction mixture was refluxed for 6 h and treated with 100 mL of 5% HCl solution. The organic layer was separated, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent in vacuum yielded a colorless solution of **L**^{1} in 59% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 3.23 [s, 6H, NCH_3], 6.35 [q, 1H, pz], 7.64 [d, 1H, pz], 8.12 [q, 1H, pz]. IR (cm^{-1}): ν = 1693 (C═O). Analysis Calcd for $C_6H_9N_3O$: C, 51.8; H, 6.5; N, 30.2. Found: C, 51.1; H, 6.1; N, 29.7.

Synthesis of L^2. This was prepared similarly as for **L**^{1} by taking *N,N*-diethyl carbamoyl chloride (20 g, 0.14 mol) and pyrazole (10 g, 0.14 mol) in 73% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 1.27 [t, 6H, CH_3], 3.61 [br, 4H, NCH_2], 6.34 [q, 1H, pz], 7.62 [d, 1H, pz], 8.13 [q, 1H, pz]. IR (cm^{-1}): ν = 1687(C═O). Analysis Calcd for $C_8H_{13}N_3O$: C, 57.5; H, 7.8; N, 25.1. Found: C, 56.9; H, 7.4; N, 24.7.

Synthesis of L^3. This was prepared similarly to **L**^{1} by taking *N,N*-di-isopropyl carbamoyl chloride (25 g, 0.15 mol) and pyrazole (10 g, 0.14 mol) in 90% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 1.38 [d, 12H, CH_3], 4.09 [m, 2H, CH, ^{i}Pr], 6.33 [q, 1H, pz], 7.60 [d, 1H, pz], 8.03 [q, 1H, pz]. IR (cm^{-1}): ν = 1687(C═O). Analysis Calcd for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.7; N, 21.5. Found: C, 61.2; H, 8.4; N, 21.1.

Synthesis of L^4. This was prepared similarly to **L**^{1} by taking *N,N*-dimethyl carbamoyl chloride (12 g, 0.11 mol) and dimethyl pyrazole (10 g, 0.11 mol) in 80% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 2.23 [s, 3H, CH_3, dmpz], 2.39 [s, 3H, CH_3, dmpz], 3.09 [s, 6H, NCH_3], 5.89 [s, 1H, dmpz]. IR (cm^{-1}): ν = 1697(C═O). Analysis Calcd for $C_8H_{13}N_3O$: C, 57.5; H, 7.8; N, 25.1. Found: C, 57.1; H, 7.2; N, 24.8.

Synthesis of L^5. This was prepared similarly to **L**^{1} by taking *N,N*-diethyl carbamoyl chloride (15 g, 0.11 mol) and dimethyl pyrazole (10 g, 0.11 mol) in 84% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 1.23 [t, 6H, CH_3, C_2H_5], 2.21 [s, 3H, CH_3, dmpz], 2.37 [s, 3H, CH_3, dmpz], 3.45 [s, 4H, NCH_2], 5.87 [s, 1H, dmpz]. IR (cm^{-1}): ν = 1691 (C═O). Analysis Calcd for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.7; N, 21.5. Found: C, 60.9; H, 8.5; N, 21.0.

Synthesis of L^6. This was prepared similarly to **L**^{1} by taking *N,N*-di-isopropyl carbamoyl chloride (17 g, 0.11 mol) and dimethyl pyrazole (10 g, 0.11 mol) in 86% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 1.31 [d, 12H, CH_3, ^{i}Pr], 2.16 [2, 3H, CH_3, dmpz], 2.28 [s, 3H, CH_3, dmpz], 3.66 [m, 2H, CH, ^{i}Pr], 5.81 [s, 1H, dmpz]. IR (cm^{-1}): ν = 1693 (C═O). Analysis Calcd for $C_{12}H_{21}N_3O$: C, 64.6; H, 9.4; N, 18.8. Found: C, 64.3; H, 9.1; N, 18.5.

Synthesis of 1. To a solution of **L**^{1} (200 mg, 1.44 mmol) in CH_2Cl_2 (20 mL), solid $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) was added and stirred for few minutes until all $[UO_2(NO_3)_2{\cdot}6H_2O]$ dissolved to give a clear solution. This solution was filtered and layered with iso-octane. The solution on slow evaporation yielded yellow crystalline solid, which was filtered, washed with hexane, and dried. Yield 85%. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 3.82 [br, 3H, NCH_3], 3.98 [br, 3H, NCH_3], 7.22 [br, 1H, pz], 9.26 [br, 2H, pz]. IR (cm^{-1}): ν = 1653(C═O), 935(U═O). Analysis Calcd for $C_6H_9N_5O_9U$: C, 13.5; H, 1.7; N, 13.5. Found: C, 13.4; H, 1.6; N, 13.2.

Synthesis of 2. This was prepared similarly to **1** by taking **L**^{2} (220 mg, 1.37 mmol) and $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) in % yield. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 1.56 [br, 6H, CH_3], 4.15 [br, 4H, NCH_2], 7.4 [s, 1H, pz], 8.98 [s, 1H, pz], 9.24 [s, 2H, pz]. ^{1}H NMR (25 °C, $CDCl_3$): δ 1.25 [br, 6H, CH_3], 4.06 [br, 4H, NCH_2], 7.12 [s, 1H, pz], 8.44 [s, 1H, pz], 9.4 [s, 2H, pz]. IR (cm^{-1}): ν = 1654 (C═O), 941 (U═O) 941. ES-MS (CH_2Cl_2): m/z = 666 $[UO_2(NO_3)(L^2)_2]^+$, 517 $[UO_2(NO_3)(L^2)H_2O]^+$, 499 $[UO_2(NO_3)(L^2)]^+$. Analysis Calcd for $C_8H_{13}N_5O_9U$: C, 17.1; H, 2.3; N, 12.5. Found: C, 17.0; H, 2.3; N, 12.4.

Synthesis of 3. This was prepared similarly to **1** by taking **L**^{3} (250 mg, 1.28 mmol) and $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) in 86% yield. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 1.35 [s, 3H, CH_3], 1.80 [s, 3H, CH_3], 4.42 [m, 2H, CH, ^{i}Pr], 7.21 [s, 1H, pz], 8.95 [s, 1H, pz], 9.2 [s, 2H, pz]. ^{1}H NMR (25 °C, $CDCl_3$): δ 1.25 [br, 6H, CH_3], 4.06 [br, 4H, NCH_2], 7.12 [br 1H, pz], 8.44 [br, 1H, pz], 9.4 [br, 2H, pz]. IR (cm^{-1}): ν = 1643(C═O), 939 (U═O). Analysis Calcd for $C_{10}H_{17}N_5O_9U$: C, 20.4; H, 2.9; N, 11.9. Found: C, 20.2; H, 2.7; N, 11.8.

Synthesis of 4. This was prepared similarly to **1** by taking **L**^{4} (220 mg, 1.37 mmol) and $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) in acetone. The acetone solution on slow evaporation yielded yellow crystalline solid, which was filtered, washed with ether, and dried. Yield 96%. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 2.14 [s, 3H, CH_3, dmpz], 2.31 [s, 3H, CH_3, dmpz], 3.05 [s, 6H, NCH_3], 5.94 [s, 1H, dmpz]. IR (cm^{-1}): ν = 3400−3200(H_2O), 1690 (C═O), 935 (U═O). Analysis Calcd for $C_{16}H_{30}N_8O_{12}U$: C, 25.1; H, 3.9; N, 14.6. Found: C, 25.0; H, 3.7; N, 14

Synthesis of 5. This was prepared similarly to **4** by taking **L**^{5} (250 mg, 1.28 mmol) and $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) in 92% yield. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 1.17 (t, 6H, CH_3, C_2H_5], 2.13 [s, 3H, CH_3, dmpz], 2.30 [s, 3H, CH_3, dmpz], 3.41 [s, 4H, NCH_2], 5.92 [s, 1H, dmpz]. IR (cm^{-1}): ν = 3500−3200(H_2O), 1691 (C═O), 941 (U═O). Analysis Calcd for $C_{20}H_{38}N_8O_{12}U$: C, 29.3; H, 4.6; N, 13.6. Found: C, 29.1; H, 4.5; N, 13.3.

Synthesis of 6. This was prepared similarly to **4** by taking **L**^{6} (280 mg, 1.25 mmol) and $[UO_2(NO_3)_2{\cdot}6H_2O]$ (300 mg, 0.59 mmol) in 93% yield. ^{1}H NMR (25 °C, CD_3COCD_3): δ = 1.31 [d, 12H, CH_3, ^{i}Pr], 2.12 [2, 3H, CH_3, dmpz], 2.27 [s, 3H, CH_3, dmpz], 3.74 [m, 2H, CH, ^{i}Pr], 5.91 [s, 1H, dmpz]. IR (cm^{-1}): ν = 3500−3200(H_2O), 1687 (C═O), 941 (U═O). Analysis Calcd for $C_{24}H_{46}N_8O_{12}U$: C, 32.9; H, 5.3; N, 12.8. Found: C, 32.7; H, 5.2; N, 12.7.

Synthesis of 7. To a hot chloroform (30 mL) solution of **L**^{1} (70 mg, 0.5 mmol), solid $[UO_2(C_6H_5COCHCOC_6H_5)_2{\cdot}2H_2O]$ (350 mg, 0.47 mmol) was added and refluxed for 2 h. The clear solution was filtered and layered with iso-octane. The solution on slow evaporation yielded an orange colored product in 86% yield. ^{1}H NMR (25 °C, $CDCl_3$): δ = 4.24 [s, 6H, NCH_3], 6.91 [s, 1H, pz], 7.37 [s, 2H, DBM], 7.53 (t, 1H, pz), 7.61 [m, 12H, C_6H_5, DBM], 8.0 [d, 1H, pz], 8.46 [m, 8H, C_6H_5, DBM]. IR (cm^{-1}): ν = 1656 (C═O) (**L**^{1}), 1591 (C═O) (DBM), 904 (U═O) . Analysis Calcd for $C_{36}H_{31}N_3O_7U$: C, 50.5; H, 3.6; N, 4.9. Found: C, 49.7; H, 3.4; N, 4.7.

Synthesis of 8. This was prepared similarly to **7** by taking **L**^{2} (80 mg, 0.48 mmol) and $[UO_2(C_6H_5COCHCOC_6H_5)_2H_2O]$ (350 mg, 0.47 mmol) in 90% yield. ^{1}H NMR (25 °C, CD_3CO CD_3): δ = 1.18 [t, 6H, CH_3], 3.55 [m, 4H, NCH_2], 6.37 [s, 1H, pz], 7.40 [s, 2H, DBM], 7.65 [m, 13H, C_6H_5 + pz]. 8.6 [m, 8H, C_6H_5]. IR (cm^{-1}): ν = 1650 (C═O) (**L**^{2}), 1591 (C═O) (DBM), 902 (U═O). ES-MS (CH_2Cl_2): m/z = 678 $[UO_2(DBM)(L^2)(H_2O)]^+$, 660 $[UO_2(DBM)(L^2)]^+$. Analysis Calcd for $C_{38}H_{35}N_3O_7U$: C, 51.6; H, 3.9; N, 4.8. Found: C, 51.0; H, 3.7; N, 4.5.

Theoretical Calculations. Full geometry optimization for the *N*,*N*-dimethyl analog of the ligands a−d and complexes (A−D) has been carried out applying a popular nonlocal correlated hybrid density functional, namely, B3LYP. Gaussian type atomic basis functions, 6-31+G(d), are adopted for H, C, N, and O atoms, and for U atom, a very recently suggested basis set, SARC-ZORA,[24a] is used for all the calculations. SARC-ZORA basis sets are segmented all-electron scalar relativistic basis sets in which the coefficients of contracted GTOs have been optimized for use with the ZORA scalar relativistic Hamiltonian. These particular basis sets for U are obtained from Extensible Computational Chemistry Environment Basis Set Database, Pacific Northwest National Laboratory.[24b] The quasi-Newton−Raphson based algorithm has been applied to carry out geometry optimization to locate the minimum energy structure in each case. Hessian calculations have also been carried out to check the nature of the equilibrium geometry. Macroscopic solvation effect of solvent water has been incorporated in energy calculation through polarizable continuum model (PCM). All these calculations have been carried out applying GAMESS suit of ab initio program on a LINUX cluster platform.[24c]

Crystal Structure Determinations. Crystal data for **2**, **5**, and **8** were measured on a Oxford Diffraction X-Calibur CCD System at 150(2)K with the Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analysis was carried out with the CrysAlis program.[25a] The structures were solved using direct methods with the Shelxs97 program.[25b] All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they attached. Empirical absorption corrections were carried out using the ABSPACK program.[25c] The structures were refined to convergence on F^2 using Shelxl97.[25b] One of the CH_3 group of ethyl groups in compound **5** was shown to be disordered over two positions and was refined in split positions with occupancies of x and $1 - x$, x refining to 0.61(2). Selected crystallographic data for **2**, **5**, and **8** are summarized in Table 2.

■ CONCLUSIONS

In conclusion, the coordination chemistry of the bifunctional ligand, carbamoyl pyrazole with uranyl nitrate, shows that it acts as a bidentate chelating ligand bonding through both the carbamoyl oxygen and pyrazolyl nitrogen atoms. However, the analogous carbamoyl 3,5-dimethyl pyrazole ligand forms a second sphere complex with the uranyl nitrate. The complex chemistry of carbamoyl pyrazole ligands could be explained on the basis of steric effect, and this effect controls the complexation reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The IR, ^{1}H NMR spectra for L^2, L^5, **2**, and **5**, ESMS for **2** and **8**, (Figures S1−S10) and the crystallographic data for **2**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: skannan@barc.gov.in (S.K.); dkmaity@barc.gov.in (D.K.M.).

Notes

The authors declare no competing financial interest.

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