



Design and synthesis of 2,6 organoheteroatom disubstituted pyridine organic donor species and their interactive behavior with UO_2^{2+} ion

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Abstract : The design and synthesis of novel 2,6-organoheteroatom disubstituted pyridine-based organic donor species have garnered significant interest due to their versatile coordination properties and potential applications in metal ion complexation. In this study, we report the synthesis of a series of 2,6-disubstituted pyridine derivatives bearing electron-donating heteroatoms (such as oxygen, sulfur, and nitrogen) and explore their interactive behavior with the uranyl ion (UO_2^{2+}). The co-ordinating species and their representative uranyl complexes have been characterized by physicochemical spectroscopy and X-ray crystallography method. The findings highlight the potential of these pyridine-based ligands in selective uranium ion recognition, which could have implications in nuclear waste remediation and environmental monitoring.

IndexTerms- 2,6-organoheteroatom disubstituted pyridine, UO_2^{2+} ions, X-ray structures

I.INTRODUCTION

The growing demand for nuclear energy worldwide has focused special interest on understanding the behavior of the UO_2^{2+} ion among the actinides.¹ Because of this, their existence in nature also raises significant environmental issues because they may encounter a wide range of chemical, geochemical, metabolic, and environmental activities.² It goes without saying that an understanding of the behavior of cationic UO_2^{2+} is necessary for accurate monitoring, speciation, and interactions during migration within terrestrial humic substances.³ In general, humic compounds have been looked at as potential remediation techniques for safe nuclear waste modification and nuclear fuel source reprocessing.⁴ By examining organic species with heteroatomic (O, N, X) (X = S, Se, or Te) donor combinations, our group also started this line of inquiry. These species showed a preference for UO_2^{2+} ions over a range of heavy and transition metal ions, such as alkali and alkaline-earth metal ions.⁵

Pyridine-based ligands have long been recognized as key structural motifs in coordination chemistry due to their tunable electronic properties, chelating abilities, and extensive applications in catalysis, material sciences, and metal ion recognition.⁶⁻⁷ Among these, 2,6-disubstituted pyridines, where electron-donating heteroatoms such as oxygen, sulfur, and nitrogen are introduced at the 2- and 6-positions, have gained particular attention for their ability to form stable metal-ligand complexes.⁸ The incorporation of these donor functionalities enhances the ligand's affinity toward actinide species, particularly the uranyl ion (UO_2^{2+}), due to the synergistic effects of electronic modulation and steric control.⁹

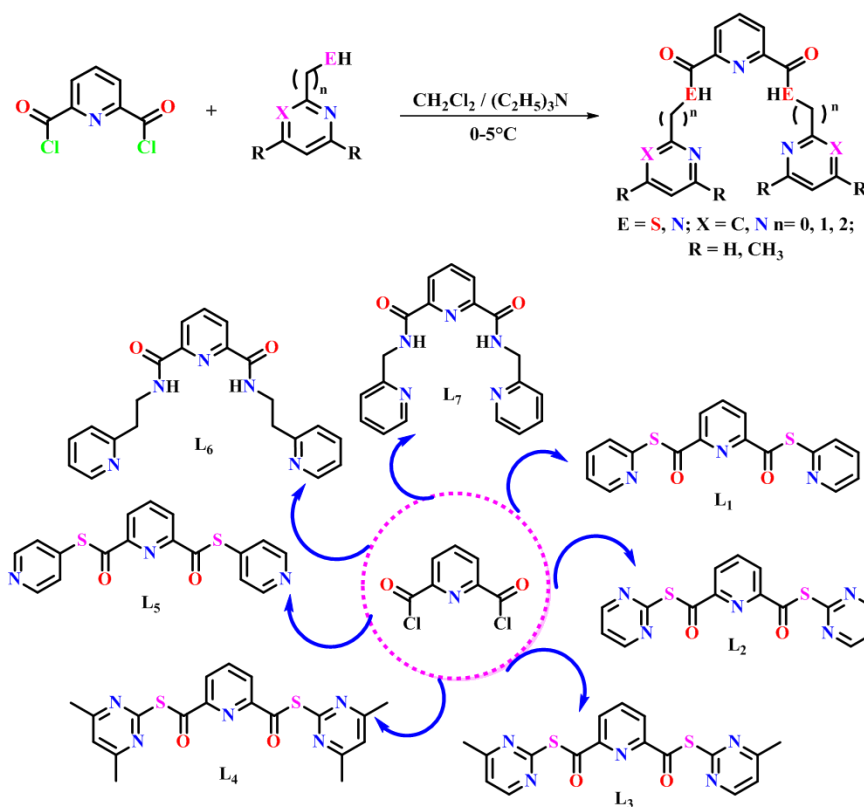
The uranyl ion (UO_2^{2+}) is one of the most stable and abundant uranium species in aqueous environments, primarily due to its linear dioxo structure and strong electrostatic interactions.¹⁰⁻¹¹ The development of selective ligands capable of strong yet reversible binding to UO_2^{2+} is crucial for nuclear waste remediation, uranium extraction, and environmental monitoring.¹²

Pyridine-based organic donor species, particularly those functionalized with heteroatoms at strategic positions, offer promising avenues for selective uranyl recognition through electrostatic and coordination-driven interactions. In this study, we report the

design and synthesis of a series of 2,6-organoheteroatom disubstituted pyridine donor species and investigate their binding behavior with the UO_2^{2+} ion. The findings contribute to the development of new functionalized pyridine-based ligands for uranium ion sequestration and related applications

II. Synthesis of organic donor species (L_1 – L_7)

The acyclic species (L_1 – L_7) bearing O, N and S heteroatom donor functionalities were prepared by the reaction of 2,6-bis(chlorocarbonyl) pyridine and substituted pyrimidine thiol /pyridine alkyl amine and triethylamine. The thiol derivative dissolved in dichloromethane was added dropwise over 10 min to a stirred solution of 2,6-bis(chlorocarbonyl)-pyridine in dichloromethane at 0°C . The reaction appeared to be completed with few hours as the insoluble white triethylamine hydrochloride salt was precipitated out. the reaction mixture was filtered and filtrate was concentrated under reduced pressure.



Scheme 1.1: Experimental route for the synthesis of donor species (L_1 – L_7).

The resultant filtrate was taken to dryness under reduced pressure to yield a crude solid (L_1 – L_7) and product was then recrystallized from hot dichloromethane and crystallized from pentane and dried to constant weight under high vacuum to afford desired species, in ~85–90% yield [Scheme 1.1]. The isolated species were found analytically pure based on physicochemical analysis and stable enough to atmospheric air in ambient laboratory conditions.

III. Results and Discussion

1. UV–Vis. Spectroscopic Studies

The interactive behavior of the UO_2^{2+} ion with selected organic donor species were examined by UV–Vis. titration experiments. In the experiment, solution of a species (L_7) in two different concentrations (1×10^{-4} M, 1×10^{-5} M) were monitored by UV-Visible spectroscopy. The UV-Visible spectrum exhibited absorption maxima at λ_{max} . 226, 260 nm (for concentration, 1×10^{-4} M) in CH_3CN solution were correspondingly due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Decisively, concentration of (1×10^{-4} M solution) were chosen to monitor UV–Visible titration changes in the presence of uranyl ions.

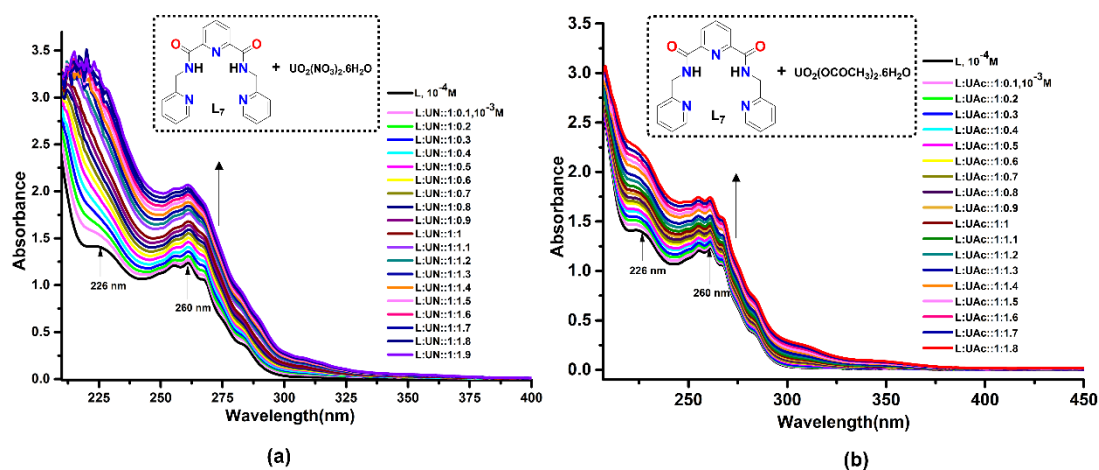


Figure 1.9: Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes upon titrating H_2L_4 (1×10^{-4} M) with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , and (b) spectroscopic changes upon titrating H_2L_4 (1×10^{-4} M) with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN .

In UV–Vis. titration experiments, on gradual addition of a solution of UO_2^{2+} ion (as either uranyl acetate or nitrate) to a solution of L_7 in acetonitrile has shown remarkable spectroscopic changes with the formation of uranyl species with donor species L_7 formed in solution through the interaction presumably single one and enough stable (**Figure 6.9**). The appearance of two absorption bands at λ , 226 and 260 nm for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ in UV–Vis spectra as a function of the added UO_2^{2+} ion and were found consistent and reproducible upon repeated experimentation. These results reveal an identical solution behavior regardless to anion associated with uranyl ion.

IV. Fluorescence Studies

The interactive behavior of UO_2^{2+} ion with donor species in solution were also further studied by fluorescence spectroscopy and changes in emission intensity or shift in the emission band were taken as interactive measure for donor species and UO_2^{2+} ion. The fluorescence titration experiments of species (L_7) were recorded with the addition of an aliquot of uranyl ion solution up to a molar ratio of ($\text{UO}_2^{2+} : \text{L}_7$) (5:1) and depicted as in Figure 6.10.

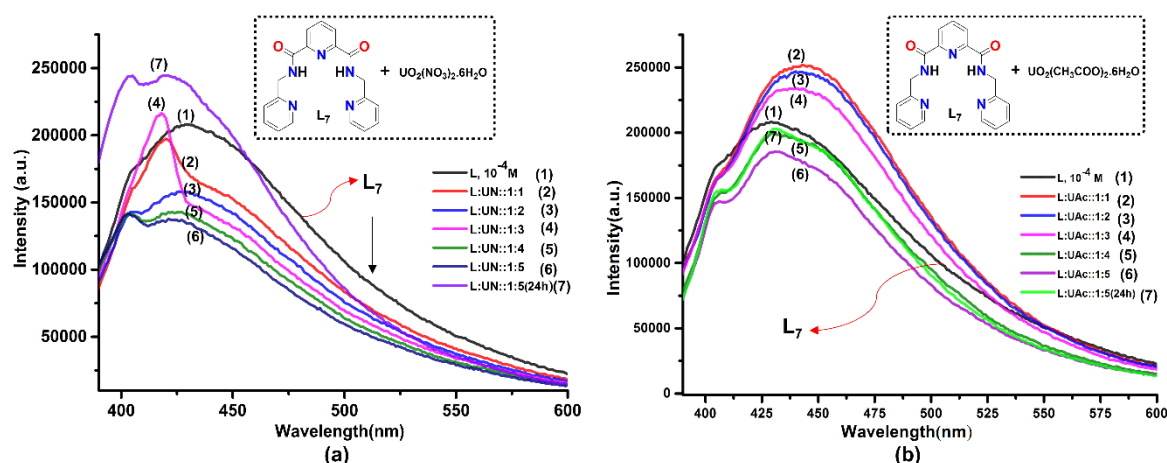


Figure 1.10: Changes observed in the emission spectra of species L_7 (1×10^{-4} M) solution upon successive addition of a solution of (a) $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, (1×10^{-3} M) ($\lambda_{\text{Ex.}} = 360$ nm, $\lambda_{\text{Em.}} = 380$ nm), (b) $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 360$ nm, $\lambda_{\text{Em.}} = 380$ nm) in CH_3CN , starting from a molar concentration of ($\text{UO}_2^{2+} : \text{L}_7$) (1:1) up to (5:1).

On successive addition of solution of UO_2^{2+} ion [as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M)] to a solution of species L_7 in CH_3CN revealed in continued reduction in of the emission intensity up to a molar ratio of ($\text{UO}_2^{2+} : \text{L}_7$) (5:1) as a ‘turnoff’ of fluorescence behaviour at wavelength 430 nm, [Figure 1.10 (a)]. The after 24h and found unchanged.

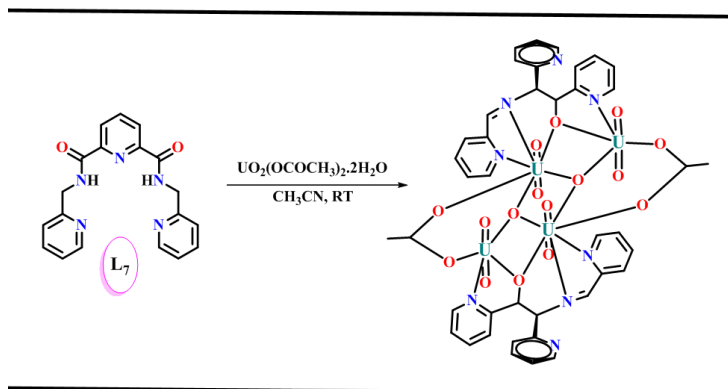
On the other hand, the titration experiment of species **L₇** with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN revealed significant changes on interactions. The changes in emission intensity showing a 'turn on' behavior on gradual addition of a solution of uranyl acetate dihydrate to a solution of species **L₇**. The fluorescence intensity got decreased during titration up to $(\text{UO}_2^{2+} : \text{L}_7)$ (5:1), but the same (5:1) ratio solution after about 24h, exhibited a considerable increase in the newly developed emission band further indicating structural complexity. To further examine the interactive behavior in solid state, complexation of donor species and UO_2^{2+} ion was carried out.

V. Complexation Studies

Synthesis of Uranyl Complex (**C₁**)

Several attempts were made to isolate uranyl complex from donor species (**L₁**-**L₇**). The spectroscopy and physicochemical data were found insufficient to provide a correct information about the structure and geometry of uranyl complexes in the solid. Therefore, only complex species where crystals were obtained is explained herein.

The complex **C₁** was prepared in a conventional coordination way by mixing and stirring a solution of donor species (**L₇**) in acetonitrile and UO_2^{2+} (VI) in solution $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ in (1:1) molar ratio at room temperature and structural information based on X-ray analysis is depicted in (Scheme 1.2).



Scheme 1.2: Complexation reactions of donor species **L₇** and $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ at room temperature and structures shown on the basis of their X-ray analysis.

The physicochemical studies of the complex (**C₁**) could not provide any direct evidence to its formation as expected.

VI. Mass Spectrometry Studies of Complexes (**C₁**)

The representative complex species (**C₁**) was examined by mass spectrometry. ESI-MS of the complex species showed several peaks (m/z) of the cations and some of which were identified as depicted in **Figure 1.11**. For the complex (**C₁**) derived from donor species **L₇** exhibited a peak with highest intensity at m/z 717.2609 assigned. In addition, fragments for $[(\text{UO}_2)\text{L}_7]\text{C}_2\text{H}_5\text{O}_3\text{K}^+$, $[(\text{UO}_2)(\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2)\text{K}]^+$ and $[(\text{UO}_2)_2(\text{C}_{19}\text{H}_{17}\text{N}_5\text{O}_3)]^+$ were correspondingly observed at m/z 733.2254, 540.1045 and 903.2144 respectively for **C₁**. Nevertheless, the crystal structure obtained for this species could not be confirmed via fragmentation pattern of complex species **C₁** by ES-MSI spectrum.

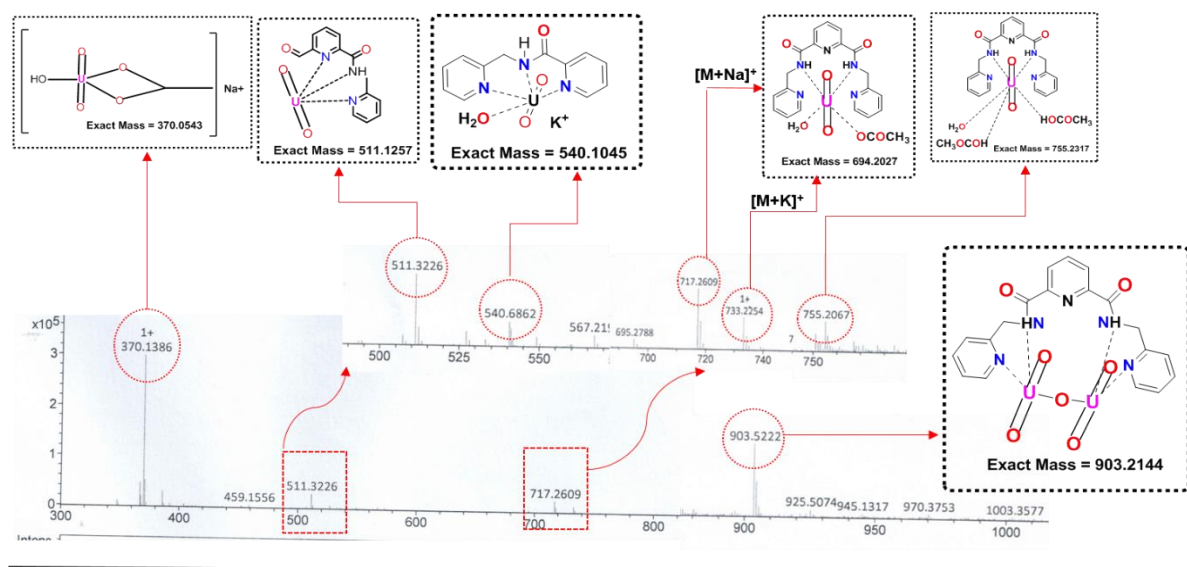


Figure 1.11: ESI-MS spectrum of the complexation reaction of donor species **L7** and uranyl acetate in acetonitrile.

VII. IR Studies

For a representative donor species **L7**, the IR absorptions at 1697 or 1640 cm^{-1} were assigned due to the vibration of the amide (HNC=O) functionality for the free and donor species. Nevertheless, the interaction between the carbonyl atoms of amide group (HNC=O) group and the UO_2^{2+} ion resulted different spectral pattern in addition to involvement of UO_2^{2+} in coordination. Further, in comparison $\nu(\text{N-H})$ of the amidic group, that observed at 3563 cm^{-1} in free donor species **L7**, showed extended broadening on complexation. The broadening of $\nu(\text{N-H})$ peaks may be suggestive of participation of amidic proton to uranyl ion in their protonated form on complexation. Further, the (U=O) stretching frequency of linear (O=U=O) were observed at 915 cm^{-1} in the complex. The combined IR spectral information may only be suggestive of participation of amide ($-\text{NH}$) group on coordination with uranyl ion.

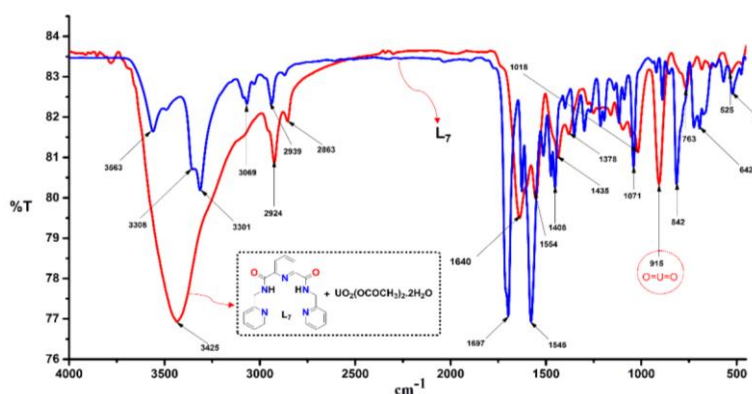


Figure 1.12: Overlap of the IR spectra of (**L7**) (Blue) and its complex with $\text{UO}_2(\text{OCOCH}_3)_2$ (red) exhibiting $(\text{UO}_2^{2+} : \text{L}_7)$ interactive behavior.

Further, the (U=O) stretching frequency of linear (O=U=O) were observed at 915 cm^{-1} in the complex.

VIII. Single Crystal X-ray Diffraction Studies

The crystal of the complex designated as (**C1**), was obtained by slow evaporation of a filtered solution of the complex species dissolved in acetonitrile at room temperature. The crystalline process took longer period (nearly three month) and was found suitable for X-ray structure determination. The formation of the uranyl complex as seen in X-ray is shown in **Scheme 1.2** and its perspective view depicted in **Figure 1.13**. The details regarding data collection, crystallography data and refinement parameter of the complex (**C1**) are summarized in **Table 1.1**. The selected bond lengths and bond angles for the complex species is listed in **Table 1.2**. The important structural parameters for the complex (**C1**) are briefly discussed herein.

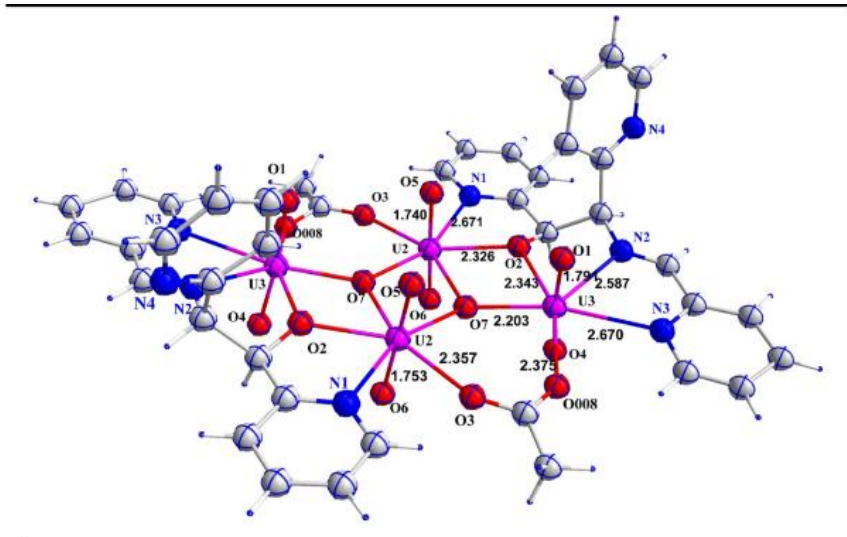


Figure 6.13: Perspective view of complex (C_1) with bonded acetate ions and atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

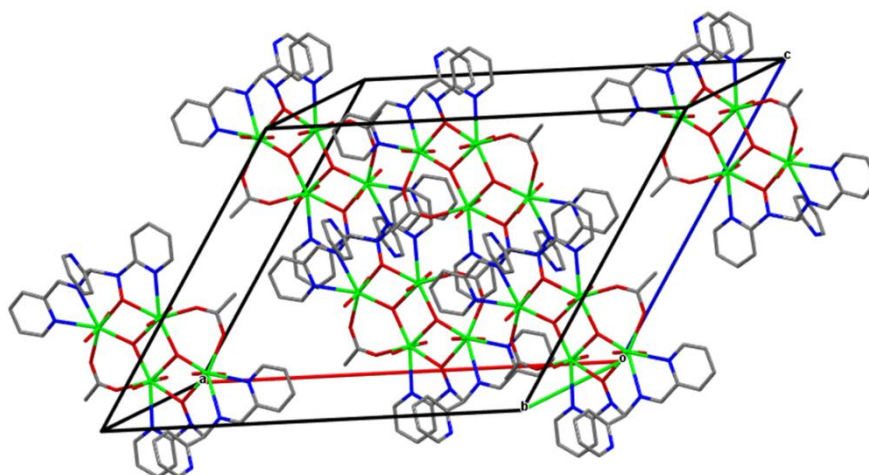


Figure 1.16: Perspective view of complex species (C_1) in unit cell along the cell axes 'b'. Color code: C = grey, N = blue, O = red, U = green

The complex species C_1 crystallized in *monoclinic* form space ' C_2/c ' with four molecules per unit cell. A perspective view of C_1 with its atomic numbering as shown in **Figure 1.13**. The crystal structure of the complex revealed that the species was obtained as hydrolysed done during complexation with UO_2^{2+} ion. In present structure, the donor species binds with four U(VI) ions resulting in a tetranuclear structure having pentagonal geometry around uranyl ion.

IX. Conclusion

The species describe herein are 2,6-disubstituted pyridyl based donors with limited flexibility have been examined for their reactivity with uranyl ions. In natural environment, the mobility of UO_2^{2+} ion is controlled/ uncontrolled manners is much influence with the presence of water. The reaction outcome suggests that the UO_2^{2+} ion and their interaction with humic substances (being considered and proposed as remedial substrate for nuclear waste disposal) may be not so straight forward with amide functionalities associated with humic substances. Nevertheless, formation of tetranuclear species with the time is indicative of reduced geochemical migration of uranyl with increased nuclearity. On the hand, the sulfur substituted derivative proved to be the release of thiospecies as disulfides.

X. Experimental Section

Caution! Uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and uranyl acetate $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ principally containing the isotope (^{238}U) are reportedly radioactive materials and must be handled in dedicated fume hoods or glove boxes with a proper facility for their disposal. Any solid waste (such as gloves) can be disposed of as ordinary waste, unless heavily contaminated

XI. Synthesis of donor species (L_1 – L_7)

A mixture of substituted pyridine thiol/pyridine alkyl amine (19.6 mmol) and triethylamine (1.98 g, 19.6 mmol) dissolved in dichloromethane (50 mL) was added dropwise over 10 min to a solution of 2,6-bis(chlorocarbonyl)–pyridine (2.0 g, 9.8 mmol) in dichloromethane (50 mL) kept on stirring in an ice bath. The reaction was rapid and halted after 20 min. The insoluble white hydrochloride salt of triethylamine was removed via gravity filtration. The resultant filtrate was taken to dryness under reduced pressure to yield a crude solid (L_1 – L_7) and characterized by physicochemical and spectroscopic measurements. These species were found enough pure to be used in further reactions.

$\text{C}_{19}\text{H}_{17}\text{N}_5\text{O}_2$ (L_7)

White solid; Yield: ~88%; m.p. 152°C ; IR (KBr pellet) ν (in cm^{-1}): 3553, 3303, 3054, 2922, 1665, 1593, 1544, 1478, 1438, 1416, 1316, 1314, 1260, 1174, 1155, 1076, 1155, 999, 845, 776, 647, 678, 520, 472; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.43 (s, 1H,); 8.33 (s, 1H); 8.31 (t, 1H, $J = 4$ Hz); 7.98 (t, 1H, $J = 8$ Hz); 7.65 (t, 1H, $J = 4$ Hz); 7.37 (t, 1H, $J = 8$ Hz); 7.17 (d, 1H, $J = 4$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 163.63, 157.09, 149.18, 148.61, 138.7, 137.17, 125.05, 122.58, 122.58, 122.53, 44.51; ESI–MS: 370.1288 $[\text{M}+\text{Na}]^+$; Anal. calcd.: C, 65.69; H, 4.96; N, 20.16; Found: C, 64.97; H, 4.67; N, 19.89.

XII. Synthesis of $\text{UO}_2(\text{VI})$ complex (C_1)

To a solution of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.042 g, 0.50 mmol) in acetonitrile (2 mL) was added a solution of L_7 (0.0347g, 0.50 mmol) in acetonitrile (5 mL). An instant colour change was observed during mixing from colorless to light yellow precipitate. The reaction mixture was stirred overnight at room temperature and then concentrated under reduced pressure. The resulting viscous mass was washed with diethyl ether. The precipitate thus obtained was dried and dissolved in acetonitrile and kept for crystallization which afforded red-colored crystals after about three months which were found suitable for X-ray analysis. Yield ~67%; m.p.: $>200^\circ\text{C}$, For $\text{C}_{40}\text{H}_{38}\text{N}_8\text{O}_{16}\text{S}_2\text{U}_4$; Anal. Calcd.: C, 26.13; H, 2.08; N, 6.09; Found: C, 26.13; H, 2.05; N, 5.97; IR (KBr pellet): ν (in cm^{-1}) 3425, 2924, 2863, 1697, 1545, 1435, 1408, 1071, 915, 763.

XIII. ACKNOWLEDGMENT

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