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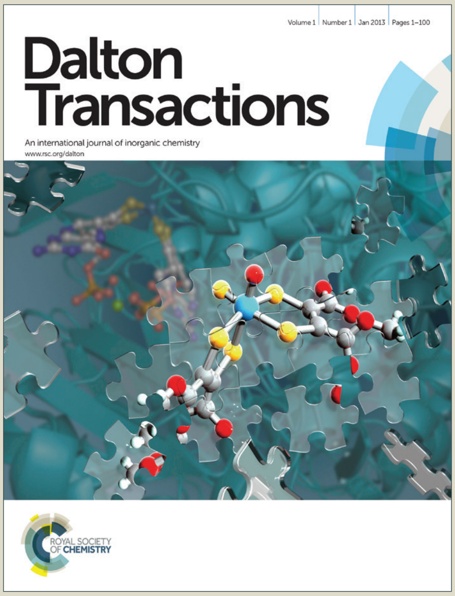

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ARTICLE TYPE

Complexation of Trivalent Americium and Lanthanides with Terdentate 'N' donor ligands: Role of Rigidity in Ligand Structure

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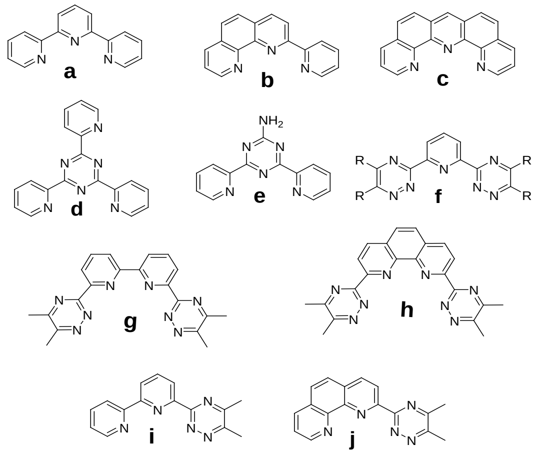
A systematic study on the Ln^{3+} complexation behaviour with two terdentate 'N' donor ligands of varying structural rigidity, viz. 5,6-dimethyl-(1,2,4)-triazinylbipyridine (Me_2TBipy) and 5,6-dimethyl-(1,2,4)-triazinylphenanthroline (Me_2TPhen), is performed in the present work using UV-Vis spectrophotometry and time resolved fluorescence spectroscopy (TRFS) and electrospray ionization mass spectrometric (ESI-MS) studies. These studies indicate the formation of 1:1 complex of La^{3+}, 1:2 complexes of Eu^{3+} and Er^{3+} with both the ligands. Density functional theoretical (DFT) study is carried out to determine the solution phase structure of Eu^{3+} complex considering the species (from UV-Vis spectrophotometry) and C_{2v} site symmetry around Eu^{3+} ion (from TRFS study). Me_2TPhen is found to be stronger complexing ligand as compared to Me_2TBipy irrespective of the Ln^{3+} ions. Solid state crystal structure of La^{3+} complex of Me_2TPhen is determined using single crystal X-ray diffraction (SCXRD) technique. The complexation of trivalent Am^{3+} ion is also studied with both these ligands using UV-Vis spectrophotometric titrations which show the formation of 1:2 complexes with higher complexation constant values as compared to all the Ln^{3+} ions studied indicating the selectivity of these ligands for the trivalent actinides over the lanthanides.

Introduction

Separation of trivalent actinides and lanthanides is an important and challenging task in the nuclear fuel cycle because of their similar charge to radius ratios.[1,2] The reagents proposed for actinide partitioning from high level radioactive wastes, viz. carbamoyl methylene phosphine oxide (CMPO), trialkyl phosphine oxide (TRPO), diamides and diglycolamides cannot distinguish between the trivalent '4f' and '5f' block elements.[3,4] It is, therefore, required to introduce a separate step for the mutual separation of these trivalent '4f' and '5f' block elements using soft ('N', 'S', 'Cl') donor ligands.[1,5] A large number of literature reports are available on the exploration and evaluation of various soft donor ligands for this purpose. 'S' donor ligands show very high selectivity.[6,7] Their application is, however, limited by their poor stability.[8] Subsequently, 'N' donor aromatic heteropolycyclic ligands are reported to be effective for the selective extraction of An^{3+} over Ln^{3+}.[9,10] A tridentate 'N' donor ligand, terpyridine (terpy) (Figure 1a) along with a long chain bromo carboxylic acid, was introduced in the SANEX-I process.[10] Selectivity was, however, found to be rather poor due to the presence of the hard donor carboxylic acid. Terdentate 'N' donor ligands similar to terpy with increasing structural rigidity, viz. MPP (Figure 1b) and DPP (Figure 1c) were also studied in the literature.[11-14] In these ligands, all the three 'N' donors are from the pyridine rings. In case of 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (TPTZ) (Figure 1d) and 4-amino-bis-(2,6)-(2-pyridyl)-1,3,5-triazine (ADPTZ) (Figure 1e) out of the thee donor rings, the two lateral rings are pyridine rings, whereas the central ring is the 1,3,5-triazine, showed higher selectivities for trivalent actinides over the lanthanides.[10] Kolarik et al.[9] have reported high selectivity using another class of 'N' donor ligands, bis(5,6-dialkyl-(1,2,4)triazinyl)pyridine (RBTP) derivatives (Figure 1f), where out of three 'N' donor rings two are 1,2,4-triazine rings and the central ring is the pyridine ring. Out of various tetradentate 'N' donor ligands, bis(1,2,4-triazinyl)bipyridine (BTBP) (Figure 1g) and its analoguous ligand with more structural rigidity, viz. BTPhen (Figure 1h) have been exhaustively studied in the literature and BTPhen derivatives were found to be superior over the BTBP derivatives for Ln/An separation.[15,16] Drew et al.[17] synthesized a ligand which structurally falls in between terpy and BTP, i.e. (1,2,4)-triazinylbipyridine (TBipy) (Figure 1i).

Figure 1: Structures of various terdentate 'N' donor heteropolycyclic ligands evaluated for Ln^{3+}/An^{3+} separation; (a) terpy, (b) MPP, (c) DPP, (d) TPTZ, (e) ADPTZ, (f) RBTP (g) BTBP, (h) BTPhen, (i) Me_2TBipy, (j) Me_2TPhen



The extraction behaviour of this ligand was found to be closer to terpy than the BTP derivatives. In our earlier work, we introduced a ligand (1,2,4-triazinyl)phenanthroline (TPhen) (Figure 1j) which has similar coordinating sites as TBipy but the bipyridine moity in TBipy was replaced by the structurally rigid phenanthroline.[18] TPhen derivatives showed higher extraction and selectivity as compared to the TBipy derivatives. Solution phase complexation study of the ‘f’ block elements with these TBipy and TPhen derivatives is essential to understand the extraction behaviour in biphasic system and lacking in the literature. In the present work, the complexation of Ln^{3+} ions (La^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+}) is, therefore, studied using Me_2TBipy and Me_2TPhen in acetonitrile medium with the help of UV-Vis spectrophotometry and fluorescence spectroscopy. Acetontrile medium is chosen in order to minimize the effect of solvation and desolvation on the complexation due to its poor solvation efficiency as compared to the alcoholic solvents.[19] As a representative of trivalent actinides, the Am^{3+} complexation with both the ligands is studied by UV-Vis spectrophotometric titrations. The results show stronger complexation in case of Am^{3+} as compared to the Ln^{3+} ions, indicating the selectivity of these ligands for the trivalent actinides over the lanthanides. Solid state crystal structures of many of the Ln^{3+} complexes of Me_2TBipy are reported in the literature[17], whereas not a single structure of any of the Ln^{3+} complex of Me_2TPhen is reported. Single crystals of the La^{3+} complex of Me_2TPhen was, therefore, grown from acetonitrile medium and its structure was determined using single crystal XRD technique.

Experimental

Reagents and Chemicals

The ligands (Me_2TBipy and Me_2TPhen) were synthesized following the procedure described elsewhere[12] and characterized by CHN-elemental analysis, measuring their melting point and recording ^{1}H-NMR as well as ^{13}C-NMR spectra. High purity crystals (99.99%) of $Ln(NO_3)_3.nH_2O$ (n=5 or 6) from Sigma-Aldrich were used to prepare appropriate solutions in HPLC grade acetonitrile. Tetramethyl ammonium nitrate (TMAN) used to maintain the ionic strength was of Sigma-Aldrich make.

UV-Visible spectrophotometric titrations

Spectrophotometric titrations for the Ln^{3+} ions were carried out with a Jasco V-530 UV-Vis spectrophotometer by following the π-π* absorption bands of Me_2TBipy and Me_2TPhen in the wavelength range of 225 - 450 nm. The solution of Me_2TBipy and Me_2TPhen derivatives (1.0×10^{-4} M) in acetonitrile medium was titrated with Ln(III) solution (4.0×10^{-4}– 2.0×10^{-3}M) till the variation in the absorption spectra became negligible. Am^{3+} complexation was studied by titrating 2mL of ^{241}Am solution in acetonitrile (0.26 mM) with 0.005M of the ligand solution at a fixed ionic strength of 0.01M. The change in the Am^{3+} peak at 509 nm was followed. In all the UV-Vis spectrophotometric titrations, a fixed ionic strength of 0.01M was maintained using tetramethyl ammonium nitrate (TMAN). The stability constants for Ln(III)- Me_2TBipy/Me_2TPhen ($\log\beta_{xy}$) complexes were calculated from each set of UV-visible absorption spectra over the wavelength range of 225-450 nm using Hyperquad.[20,21] The absorbance, ($A^i(\lambda)$) at a particular wavelength (λ) for i^{th} injection can be expressed as (Lambert Beer’s law)

$$A^i(\lambda) = l \ \Sigma \ \varepsilon_j(\lambda) \ C_j^i \qquad (1)$$

Where $\varepsilon_j(\lambda)$ is the molar absorbance of the j^{th} species, C_j^i is the concentration of the j^{th} species at i^{th} injection. The equation in combination with mass balance equations (3, 4) were solved using Hyperquad to obtain the log β_{xy} as well as free equilibrium concentration of different species.

$$xM + yL == M_XL_Y \qquad \log\beta_{xy} \qquad (2)$$

$$C_M^T = [M] + \sum x\beta_{xy}[M]^x[L]^y \qquad (3)$$

$$C_L^T = [L] + \sum y\beta_{xy}[M]^x[L]^y \qquad (4)$$

Where C_L^T and C_M^T are total concentration of ligand and metal ion respectively, and [L] and [M] are the respective equilibrium concentrations. Several chemically possible species (M_xL_y) (x =1-2 and y = 1-3) were submitted as input to Hyperquad. However the software program consistently converged (lowest χ^2)with the specific set of metal complex species only.

Luminescence Studies

The luminescence studies were performed using an Edinburgh FLS 900 unit provided with CD-920 controller and micro sec (Xe) flash lap. The data acquisition and analysis were done by the F-900 software provided by Edinburgh Analytical Instruments, UK. The fluorescence decay curves for all the samples were recorded on 8 ms scale and fitted via an iterative method.

ESI-MS Study

ESI-MS studies of Ln^{3+} (La^{3+}, Eu^{3+} and Er^{3+}) complexes of Me_2TBipy and Me_2TPhen in acetonitrile were carried out using a Varian (USA) make instrument of model no. 410 Prostar Binary LC with 500 MS IT PDA Detectors. Direct infusion masses with soft ionization technique like ESI (Electrospray Ionization) ionization were collected in positive mode using an ion trap.

Computational Studies

Gas phase geometries of the Eu(III) complexes of Me_2TBipy with mono and bidentate coordination of nitrate ions are optimized at the GGA level of density functional theory (DFT) by using Becke’s exchange functional [22] in conjunction with Perdew’s correlation functional [23] (BP86) with generalized gradient approximation (GGA) where 28 electron core pseudopotentials (ECPs) along with the corresponding def-SV(P) basis set were selected for the Eu(III) ion and all other lighter atoms were treated at the all electron (AE) level. Single point calculations on solvent effects were carried out with the gas phase optimized geometries of the complexes using the COSMO approach [24] with the TURBOMOLE program package [25,26] at DFT level using the hybrid exchange correlation functional (B3LYP) [22,27] where 28 electron core pseudo potentials (ECPs) along with the corresponding TZVP basis set were selected for the Eu(III) ion. The dielectric constants (ε's) of acetonitrile were considered as 37.5. For the cavity generation, the atomic radius of Eu was considered to be 1.82 Å [28], whereas for the other elements the optimized radii as implemented in TURBOMOLE were used in COSMO calculations. The charge distribution in the complexes in the presence of solvent was calculated by natural population analysis in TURBOMOLE.

Single crystal XRD Studies

Suitable X-ray quality crystals of La^{3+} complex of Me_2TPhen were grown in acetonitrile and X-ray diffraction study was undertaken. X-ray crystallographic data were collected from single-crystal sample at 150(2) K that were mounted on a OXFORD DIFFRACTION XCALIBUR-S CCD system equipped with graphite-monochromated Mo-K_α radiation (0.71073 Å). The data were collected by using a ω-2θ scan mode, and the absorption correction was applied using multi-Scan. The structure was solved by direct methods in SHELX-97 and refined by full-matrix least-squares against F2 using SHELX-97 [29] software. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model. A summary of crystal data and structure refinement parameters are listed in Table 1 and .cif files are provided as Supporting Information.

Table 1. Summary of crystallographic data collection and refinement for the La^{3+} complex of Me_2TPhen

Complex	**La^{3+}-Me_2TPhen Complex**
Formula	$La(Me_2TPhen)(NO_3)_3(H_2O)_2$
Empirical formula	$La\ C_{17}\ H_{17}\ N_8\ O_{11}$
Formula weight	648.30
T (K)	150(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a =9.5804(4) Å b = 9.7438(4) Å c = 13.7155(5) Å α = 97.264(3)° β = 92.617(3)° γ = 115.428(4)°
Volume	1139.86(8) $Å^3$
Z	5
Density (calculated)	1.88876 g/cm^3
Abs coefficient (mm^{-1})	15.189
F(000)	640
Reflections collected	4385
Goodness-of-fit on F2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0614
R indices (all data)	0.0228

Results and Discussion

UV-Visible spectrophotometric titrations

UV-Vis spectrophotometric titrations were carried out to identify the complexed species and to calculate the formation constants of the Ln^{3+} (La^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+}) and Am^{3+} complexes with Me_2TBipy and Me_2TPhen, which are listed in Table 2.

Table 2: Species observed and complexation constants of Am^{3+} and Ln^{3+} complexes with Me_2TBipy, Me_2TPhen and MeBTP in acetonitrile medium in presence of 0.01M TMAN calculated from UV-Vis Spectrophotometric titrations ([a]: present work, [b]: Ref 32)

Ln^{3+}	Me_2TBipy [a]	Me_2TPhen [a]	MeBTP [b]
La^{3+}	ML $\log \beta_{11} = 3.77 \pm 0.01$	ML $\log \beta_{11} = 4.44 \pm 0.09$	ML $\log \beta_{11} = 4.11 \pm 0.01$
Nd^{3+}	ML $\log \beta_{11} = 4.10 \pm 0.01$	ML_2 $\log \beta_{12} = 8.91 \pm 0.03$	ML, ML_2 $\log \beta_{11} = 4.86 \pm 0.01$ $\log \beta_{12} = 7.51 \pm 0.01$
Eu^{3+}	ML_2 $\log \beta_{12} = 7.43 \pm 0.01$	ML_2 $\log \beta_{12} = 9.94 \pm 0.02$	ML, ML_2 $\log \beta_{11} = 4.47 \pm 0.01$ $\log \beta_{12} = 8.58 \pm 0.03$
Er^{3+}	ML_2 $\log \beta_{12} = 7.96 \pm 0.01$	ML_2 $\log \beta_{12} = 9.69 \pm 0.03$	ML, ML_2 $\log \beta_{11} = 4.20 \pm 0.02$ $\log \beta_{12} = 8.92 \pm 0.01$
Am^{3+}	ML_2 $\log \beta_{12} = 8.46 \pm 0.11$	ML_2 $\log \beta_{12} = 10.25 \pm 0.21$	ML_2 $\log \beta_{12} = 9.96 \pm 0.20$

The change in absorption spectra of Me_2TBipy or Me_2TPhen during the titration with Eu^{3+} ion and molar absorbances of free Me_2TBipy and Me_2TPhen and their Eu^{3+} complexes, obtained from Hyperquad, are shown in Figure 2. The change in Am^{3+} spectra with increasing the addition of Me_2TPhen is shown in figure 3a and the molar absorbances of Am^{3+} and its Me_2TPhen complex obtained by fitting the titration data using Hyperquad are shown in figure 3b.The results show similar complexation behaviour of Me_2TBipy and Me_2TPhen with the Ln^{3+} ions except for Nd^{3+}. Both these ligands form only 1:1 complexes with lighter lanthanides, viz. La^{3+} and 1:2 complexes with heavier lanthanides (Eu^{3+} and Er^{3+}) and Am^{3+}. The complexation constant is, however, higher in the case of Me_2TPhen as compared to Me_2TBipy in case of all the trivalent 'f' elements studied due to the preorganized rigid structure of Me_2TPhen as compared to Me_2TBipy.

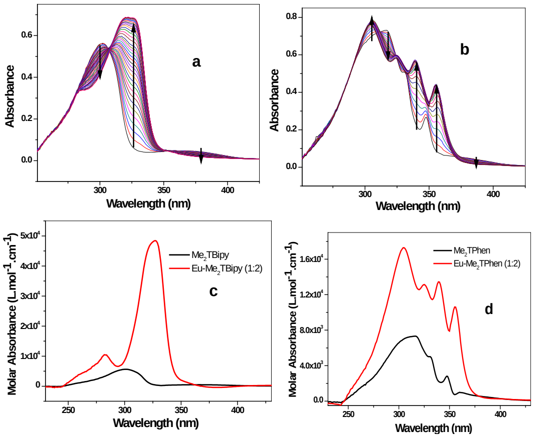
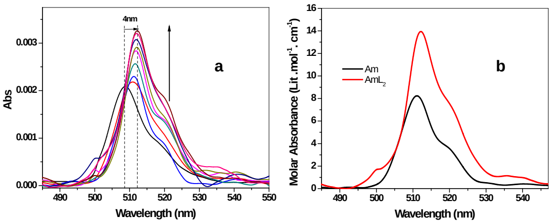


Figure 2: Change in ligand absorbance spectra due to the formation of the Eu(III) complex and molar absorbances of free ligands and their Eu(III) complex; Change in absorbance of (a) Me_2TBipy and (b) Me_2TPhen during addition of Eu^{3+}; Molar absorbances of (c)Me_2TBipy and its Eu(III) complex, (d) Me_2TPhen and its Eu(III) complex;

This leads to the higher extraction ability of Me_2TPhen as compared to Me_2TBipy.[18] Nd^{3+} forms 1:1 complex with Me_2TBipy and 1:2 complex with Me_2TPhen, indicating more tendencies to form higher stoichiometric complexes with Me_2TPhen as compared to Me_2TBipy. The trends in complexation constant values along the Ln^{3+} series in case of both the ligands agrees well with the Ln^{3+} complexation of terpy and analogous ligands with increasing rigidity, viz. MPP (Figure 1b), DPA (Figure 1c)[11-14] and 2,9-Di(pyrid-2-yl)-1,10-phenanthroline (DPP)[30], where the Ln^{3+} complexation increases monotonically along the series in case of terpy, whereas in case of structurally rigid ligands (MPP, DPA and DPP), the complexation increases from La^{3+} to Sm^{3+} and successively decreases to Lu^{3+} resulting in peaking near Sm^{3+}, which is explained based on the strain energy during the formation of the complexes obtained from the molecular mechanics (MM) calculation. In the present work also, the Ln^{3+} complexation increases monotonically from La^{3+} to Er^{3+} in case of Me_2TBipy, whereas in case of structurally rigid Me_2TPhen, the complexation increases from La^{3+} to Eu^{3+} (next to Sm^{3+}) and then decreases to Er^{3+}. Formation of higher stoichiometric (1:2) complexes in the case of heavier Ln^{3+} ions could be explained on the basis of the more pronounced positive cooperative effect which favours the approach of second ligand molecule in presence of the first ligand molecule in the metal complex.[31,32] Such observations were also reported for the Ln^{3+} complexation with bis-(1,2,4)-triazinylpyridine (RBTP) derivatives and this effect was more pronounced for the larger alkyl (R) groups of the RBTP molecules.[32] It is interesting to note here that the complexation ability of Me_2TBipy is less as compared to MeBTP, whereas that of Me_2TPhen is higher as compared to MeBTP. Mixed complexed species (both 1:1 and 1:2) were observed in case of MeBTP with many of the Ln^{3+} ions, except La^{3+}.[32] Both Me_2TBipy and Me_2TPhen, however, form distinct complexed species (either 1:1 or 1:2) with all the Ln^{3+} ions studied. Similar to MeBTP, both the ligands form only 1:2 complexes with Am^{3+} with higher formation constants as compared to any of the four Ln^{3+} ions studied in the present work. This clearly indicates the selectivity of these ligands for the trivalent actinides over the lanthanides.

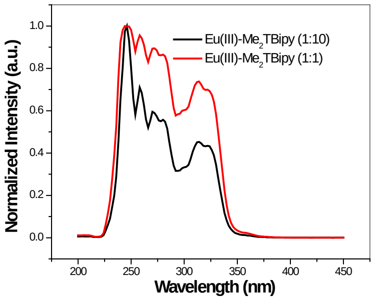
Figure 3: (a)The change in Am^{3+} spectra with increasing the addition of Me_2TPhen (b) Molar absorbances of Am^{3+} and its complex with Me_2TPhen;



Luminescence Studies

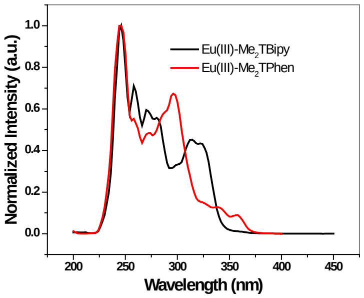
Time resolved fluorescence studies were carried out for the detailed understanding of Eu^{3+}complexation with Me_2TBipy and Me_2TPhen. The excitation spectra of Eu^{3+}-Me_2TBipy complex with 616 nm emission were found to be similar when the M:L ratio was varied from 1:10 to 1:1 (Figure 4), which indicated no change in species by varying the M:L ratio as also observed from the UV-Vis spectrophotometric titrations.

Figure 4: Excitation spectra of Eu(III) complex of Me_2TBipy with M:L = 1:10 and 1:1 in acetonitrile (λ_{em} = 616 nm)



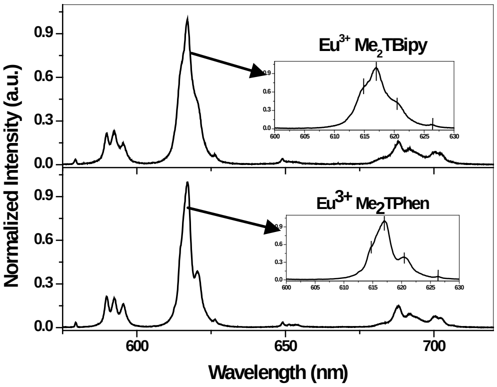
The excitation spectra of the Eu^{3+} complexes of Me_2TBipy and Me_2TPhen with 616 nm emission are shown in Figure 5.

Figure 5: Excitation spectra of Eu(III) complexes of Me_2TBipy and Me_2TPhen (M:L = 1:10) in acetonitrile (λ_{em} = 616 nm)



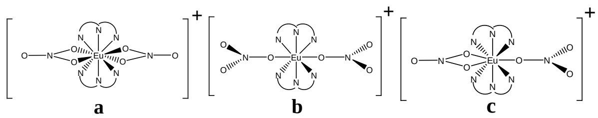
These two spectra are similar, except the fact that the Eu(III)-Me_2TBipy complex possesses a broad peak at ~325 nm, whereas Eu(III)-Me_2TPhen complex shows a peak at ~300 nm, which are the peaks for the $\pi \rightarrow \pi^*$ transitions of the ligands in the complex as observed from the UV-Vis spectrophotometric absorption studies (Figure 2c and 2d). This suggests the ligand sensitized fluorescence of the Eu^{3+} ion in these complexes. The emission spectra of the Eu^{3+} complexes of these two ligands with 247 nm excitation are shown in figure 6, which indicates the formation of similar complexes with Me_2TBipy and Me_2TPhen. It is to be noted here that the free ligand does not show any emission peak in the wavelength range scanned for their Eu^{3+} complexes. Both the excitation and emission spectra are, therefore, solely due to the Eu^{3+} complexes of Me_2TBipy and Me_2TPhen and no interference from the free ligand is observed. Splitting of various emission peaks of Eu^{3+} can be of help to elucidate the site symmetry around the Eu^{3+} ion in its complexes.[33] The appearance of the singlet for the transition $^5D_0 \rightarrow {}^7F_0$ at 580 nm suggests the site symmetry around the Eu^{3+} ion is not of the type D_n or D_{nd} but of lower symmetry (C_n or C_{nv}). The peak corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition, because of the degeneracies of the upper and lower levels can result in splitting into three lines in the spectral range 590-600 nm at lower symmetry around the Eu^{3+} ion.

Figure 6: Emission spectra of Eu(III) complexes of Me_2TBipy and Me_2TPhen (M:L = 1:10) in acetonitrile (λ_{ex} = 247 nm)



The experimentally observed spectra also show three lines due to the $^5D_0 \rightarrow {}^7F_1$ transition in case of both the ligands. Four lines were observed due to the $^5D_0 \rightarrow {}^7F_2$ transition at 610-630 nm in case of both the Eu^{3+} complexes. Considering the splitting patterns of these three transitions ($^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$) the site symmetry around the Eu^{3+} ion is predicted to be C_{2v}.[33] Results from UV-Vis spectrophotometric studies indicated the presence of two terdentate ‘N’ donor ligands (Me_2TBipy or Me_2TPhen) in the inner sphere of the complexes and using this clue, probable geometries around the Eu^{3+} ion considering the C_{2v} symmetry in these complexes are shown in figure 7, where both mono and bidentate coordination of nitrate ions are considered.

Figure 7: Probable geometries around Eu^{3+} in the Eu^{3+} complexes of Me_2TBipy and Me_2TPhen considering the C_{2v} site symmetry from their emission spectra



In the geometries, where both the nitrate ions are bidentate (Figure 7a) or monodentate (Figure 7b), the principal C_2 axis goes through the Eu^{3+} ion and two tridentate 'N' donor ligands. On the other hand in the Eu^{3+} complex, where one nitrate ion is monodentate and the other one is bidentate (Figure 7c), the principal C_2 axis goes through the Eu^{3+} ion and two nitrate ions. Fluorescence life time studies for the Eu^{3+} complexes were carried out with $\lambda_{ex} = 247$ nm and $\lambda_{em} = 616$ nm (ESI-1). The lifetime value ($\tau = 1.57$ ms) of the Eu^{3+} complex of Me_2TBipy is very close to that of the ML_2 type of Eu^{3+} complex of MeBTP ($\tau = 1.62$ ms) and EtBTP ($\tau = 1.74$ ms) [32], which further confirms the formation of ML_2 type of species. The higher lifetime of the Eu^{3+} complex of Me_2TPhen ($\tau = 2.16$ ms) as compared to that of Me_2TBipy ($\tau = 1.57$ ms) is due to more structural rigidity of Me_2TPhen. These results, therefore, nicely corroborate with the observed species from UV-Vis spectrophotometric studies, which show the formation of 1:2 Eu^{3+} complex with both the terdentate 'N' donor ligands, Me_2TBipy and Me_2TPhen.

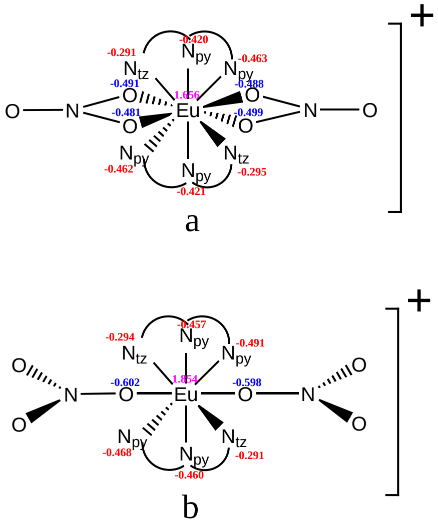
ESI-MS Study

In order to confirm the Ln^{3+} complexed species in the solution phase, ESI-MS studies were carried out in acetonitrile medium. Various peaks at different m/z values identified for different Ln^{3+} complex species are listed in ESI-2. In case of La^{3+} (ESI-3), only ML type of species was observed at m/z value 705.0 in case of Me_2TBipy complex $[LaL(NO_3)_2(S)_3(W)_3]^+$ and at m/z value of 690.8 in case of Me_2TPhen complex $[LaL(NO_3)_2(S)_3(W)]^+$, where L = Me_2TBipy or Me_2TPhen, S = acetonitrile and W = water. In order to confirm the species, the MS-MS study was carried out for the peak of m/z=705.0 of the La^{3+}-Me_2TBipy complex (ESI-4). A peak at m/z=644.5 due to the loss of an acetonitrile and a water molecule and another peak at m/z=579.2 due to the loss of three acetonitrile molecule from the species of m/z=705.0. The identified species of the MS-MS spectra, therefore, confirm the suggested species for the parent peak at m/z=705.0. In the cases of Eu^{3+} and Er^{3+} complexes of Me_2TBipy (ESI-5 and ESI-7), the peak at m/z = 821.4 and m/z = 853.8 were attributed to the ML_2 type of species $[EuL_2(NO_3)_2(W)]^+$ and $[ErL_2(NO_3)_2(W)_2]^+$, respectively. Eu^{3+} forms another ML_2 type of species, $[EuL_2(NO_3)_2(S)_2(W)_3]^+$, with Me_2TBipy at m/z = 938.8 (ESI-5). Two ML_2 type of species, on the other hand, were observed in the case of Eu^{3+} complexes of Me_2TPhen, viz. $[EuL_2(NO_3)_2]^+$ and $[EuL_2(NO_3)]^{2+}$ at m/z values of 851.5, and 395.1, respectively (ESI-6). In case of Er^{3+} complex of Me_2TPhen (ESI-8), the peak at m/z = 865.8 was attributed to the ML_2 type of species, $[ErL_2(NO_3)_2]^+$. Appearance of the peaks at m/z values of 803.3 and 579.1 in MS-MS spectra (ESI-9) of the species (of m/z = 865.8) due to the loss of one HNO_3 molecule and one ligand molecule, respectively, confirms the suggested species $[ErL_2(NO_3)_2]^+$ for the parent peak. The results obtained from the ESI-MS studies are, therefore, consistent with the observations of UV-Vis spectrophotometric studies indicating the formation of 1:1 complex in case of La^{3+} and 1:2 complexes in the cases Eu^{3+} and Er^{3+} with both the 'N' donor ligands, Me_2TBipy and Me_2TPhen.

Computational Study

Combining the results from all the experimental techniques, the Eu^{3+} complex is determined as $[EuL_2(NO_3)_2]^+$, which has C_{2v} site symmetry around the Eu^{3+} ion. DFT study was carried out on the Eu^{3+} complex of Me_2TBipy in order to determine the most stable geometry with C_{2v} site symmetry around the Eu^{3+} ion as predicted for the Eu^{3+} complex from TRFS study (Figure 7). The result shows that the structures with bi and mono dentate coordination from both the nitrate ions are very close in energy (ESI-10). The structure with bidentate nitrate ions (ESI-10a) is only 0.60 eV and 0.72 eV lower in energy in gas phase and acetonitrile medium, respectively, as compared to the complex with mono dentate nitrates (ESI-10b). Dobler et al.[34] extensively studied the nitrate complexation with the Ln^{3+} ions in absence and presence of water using DFT calculations. They observed that in case of the complexes without inner sphere water molecule, bidentate coordination of nitrate ions is much more favoured, whereas in presence of inner sphere water molecules both bi and mono dentate coordinations of nitrate ions are energetically comparable. The extra stability in the bidentate nitrate coordination is counter balanced by the extra steric burden in the complexes with high Ln^{3+} ion coordination number in presence of inner sphere water molecules. In case of the Eu^{3+} complexes in the present work, the coordination number of Eu^{3+} ion increase from 8 to 10, when both the monodentate nitrate ions became bidentate. The higher stability with bidentate nitrate coordination is, therefore, almost compensated by the extra steric burden in the complex due to increase in coordination number. The natural charges on the Eu and its neighboring 'N' and 'O' atoms in these two complexes are shown in figure 8. The charge on Eu reduced to 1.854 a.u. in the Eu^{3+} complex with monodentate nitrate coordination, whereas it reduced to 1.656 a.u. in the Eu^{3+} complex with bidentate nitrate coordination due to higher charge transfer from nitrate ion to Eu^{3+} when nitrate ions coordinate in bidentate fashion. The geometry with two nitrates of mono and bidentate coordination (with Eu^{3+} site symmetry as shown in figure 7C) was highly unstable and faced convergence problem due to coplanar arrangement of the two Me_2TBipy moieties. This geometry is, therefore, not considered in the present work as a model of the Eu^{3+} complex.

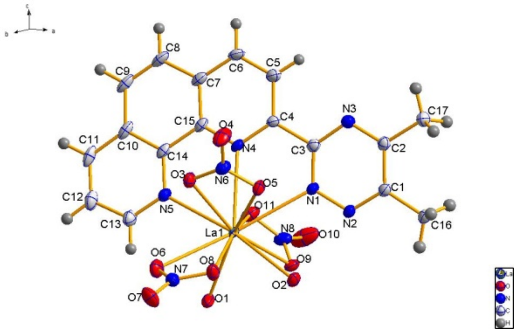
Figure 8: Natural charges on Eu^{3+} and its neighboring atoms in the Eu^{3+} complex of Me_2TBipy with (a)monodentate nitrate ions and (b) bidentate nitrate ions



Single crystal XRD Study

Solid state crystal structures of number of Ln^{3+} complexes of Me_2TBipy are reported in literature.[11] On the other hand none of the structure of Ln^{3+} complex of Me_2TPhen is reported in solid state. Crystals of La^{3+} complex of Me_2TPhen is, therefore, prepared in acetonitrile medium and the structure is determined (Figure 9). Unlike the dimeric La^{3+} complex of Me_2TBipy, monomeric La^{3+} complex of Me_2TPhen is isolated. The coordination number (eleven) of La^{3+} is, however, found to be similar as the dimmeric La^{3+} complex of Me_2TBipy. In the La^{3+}-Me_2TPhen complex, La^{3+} is bonded to three 'N' atoms of the terdentate ligand, Me_2TPhen, six 'O' atoms of three bidentate nitrate ions and two water molecules. Similar structure of La^{3+} complex was also reported with ADPTZ.[35]

Figure 9: Structure of La(III) complex of Me_2TPhen ($La(Me_2TPhen)(NO_3)_3(H_2O)_2$) as obtained from the SCXRD study, where the 'H' atoms of water molecules are not shown



In the dimeric La^{3+}-Me_2TBipy complex, reported by Hudson et al. [17], out of the two non-bridging nitrate ions, one acts as bidentate, whereas the other one is bordering on being monodentate rather than bidentate. In the monomeric La^{3+}-Me_2TPhen complex, however, all the three nitrate ions acts purely as bidentate ligands, with the differences in the 'La-O' bond lengths for the two coordinating 'O' atoms of each nitrate ion are 0.064, 0.08 and 0.131 Å only. There may be 'H' bond present between the nitrogen of the triazine ring (N(2)) and the coordinating water molecule (O2) with 'O---N' distance of 2.798 Å. There is another 'H' bond between O6 of the nitrate ion with the 'H' atom of another coordinating water molecule (O1) with O1---O6 distance of 2.832 Å. There is also a possibility of weak 'H' bonding between C13-H and O6 of the nitrate ion with H---O distance of 2.529 Å and C-H---O angle of 112°.

Conclusions

Solution phase Am^{3+} and Ln^{3+} complexation studies with two terdentate 'N' donor ligands of varying structural rigidity, viz. Me_2TBipy and Me_2TPhen were carried out using UV-Vis spectrophotometric titrations, fluorescence spectroscopy and ESI-MS techniques. Results suggest the formation of 1:1 complex in case of lighter lanthanide, La^{3+} and 1:2 complexes in the cases of heavier lanthanides (Eu^{3+} and Er^{3+}) and Am^{3+} with both the ligands. Nd^{3+}, on the other hand shows intermediate behaviour forming 1:1 complex with Me_2TBipy and 1:2 complex with Me_2TPhen. Higher complexation constant values in case of Am^{3+} as compared to any of the Ln^{3+} ions explains the efficiency of these ligands for the separation of trivalent actinides from the lanthanides. Probable geometries around the Eu^{3+} ion in these complexes were also depicted from the splitting pattern of the emission spectra of the Eu^{3+} complexes. DFT study indicated the possibility of bidentate as well as monodentate coordination from both the nitrate ions. Higher complexation constant value in case of Me_2TPhen as compared to that of Me_2TBipy is responsible for higher extraction efficiency of the former. Solid state structure of La^{3+} complex of Me_2TPhen were determined by SCXRD technique which is different from the species observed in the solution phase and also from the solid state structure of the La^{3+} complex of Me_2TBipy reported in the literature.

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Notes and references

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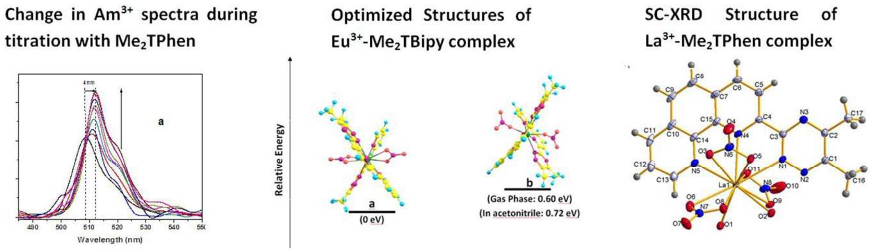
Change in Am^{3+} spectra during titration with Me_2TPhen

Optimized Structures of Eu^{3+}-Me_2TBipy complex

SC-XRD Structure of La^{3+}-Me_2TPhen complex

Americium and Lanthanide complexation with Me_2TBipy and Me_2TPhen is studied using UV-Vis Spectrophotometry, Time resolved luminescence spectroscopy, Single crystal XRD and DFT calculations

392x143mm (96 x 96 DPI)