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Synthesis and Characterization of Erbium(3+) and Neodymium(3+) Cryptates

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Er^{3+} and Nd^{3+} cryptates with ligands 211 and 222BB have been prepared and characterized. Possible arrangements around the metal ions are proposed on the grounds of elemental analyses, IR, UV, and thermal analyses. Metal:ligand ratios of 1:2 were obtained for erbium cryptates, to our knowledge for the first time, when nitrate groups are the counterion and 1:1 for neodymium cryptates. It appears that the neodymium complexes are not of the inclusive type.

Introduction

Lanthanide cryptates, which have been studied in the last 10 years, are particularly useful as relaxation agents in NMR spectra because of their stability in water or in polar organic solvents and are also useful in electrochemistry,[1] synthesis,[2] and medicine.[3] For example the redox properties of the $Eu(222)^{3+}/Eu(222)^{2+}$ pair in several solvents allow them to be used as a redox potential reference.[4] The stability of lanthanide complexes has been studied by Gansow and co-workers[5] attaching a protein or enzyme to a bifunctional lanthanide cryptate.

Different kinds of cryptands have been synthesized recently.[6-11] A cryptand linked to a resin[12] can be used to separate and preconcentrate metal ions, such as lanthanides and other ions.

Recently,[13-15] important photophysical properties of lanthanides have been studied by cryptating them.

In this paper the synthesis and characterization of the following cryptates are presented: $Nd(222BB)(NO_3)_3\cdot H_2O$, $Nd(211)(NO_3)_3$, $Er(222BB)_2(NO_3)_3\cdot 2H_2O$, and $Er(211)_2(NO_3)_3$.

Experimental Section

Materials. The purchased reagents are the following: the ligands cryptofix(222BB) ≡ 5,6,14,15-dibenzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and cryptofix(211) ≡ 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane and 99% purity acetonitrile (0.78% water) from Merck; 99.9% purity $Nd(NO_3)_3\cdot 5H_2O$ and $Er(NO_3)_3\cdot 5H_2O$ from Alfa Products; anhydrous triethyl orthoformate and calcium hydride 4–40 mesh from Sigma Chemical Co.; and anhydrous ethyl ether from Monterrey, SA.

The hydrated metal nitrates were dehydrated in situ prior to their use.

Synthesis of the Cryptates. The cryptates were obtained by using a modified method by Gansow and Triplett.[16] A solution of 0.2 mmol of the hydrated metal nitrate, 2 mL of triethyl orthoformate, and 25 mL of previously dehydrated acetonitrile with calcium hydride was stirred and refluxed betwen 70 and 76 °C for 5 h. A solution of 0.2 mmol of the ligand in 5 mL of anhydrous acetonitrile was added to the dehydrated metal salt solution. This step took 4 and 25 h for the complexes of neodymium and erbium, respectively. The solutions were cooled and filtered, and anhydrous ethyl ether was added dropwise until cloudiness appeared. The mixtures were left overnight at 4 °C; from these solutions the cryptates were precipitated, and the crystals were filtered and dried for 5 h under vacuum at about 10^{-4} Torr.

Spectroscopic and Analytical Studies. Infrared spectra were recorded with a Nicolet M X-1 IR-FT spectrometer.

UV spectra were recorded with 0.05 mg/mL solutions of the complexes in acetonitrile and methanol; a Beckman 35 UV-visible spectrophotometer was utilized.

^1H NMR spectra were recorded on a Varian FT-80A spectrometer, and finally the thermogravimetric and thermodifferential analyses were done with use of a Shimadzu DT 30 instrument with a heating rate of 20 °C min^{-1}, under a nitrogen flow.

Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN; the results are shown in Table I.

Results

The four cryptates were microcrystalline powders with the characteristic colors of the lanthanide ions employed. They were stable in air, as well as in the solvent used. A 1:2 metal:ligand (M:L) ratio was found for the erbium complexes and 1:1 for those of neodymium. Other M:L ratios would lead to larger discrepancies between the calculated and experimental elemental analysis results.

Table I. Elemental Analyses of Erbium and Neodymium Cryptates

	$Er(222BB)_2(NO_3)_3\cdot 2H_2O$			$Er(211)_2(NO_3)_3$	
	required, %	found, %		required, %	found, %
H	5.74	5.58	H	6.07	5.07
N	7.34	8.27	N	10.54	11.91
Er	12.53	11.44	Er	17.99	17.92
O	27.54	28.72	C	36.15	36.05
	$Nd(222BB)(NO_3)_3\cdot H_2O$			$Nd(211)(NO_3)_3$	
	required, %	found, %		required, %	found, %
H	4.67	5.24		4.56	4.26
N	8.53	8.20		11.32	12.23
C	38.00	38.29			
Nd	17.57	15.14		23.31	23.93

UV Spectroscopy. The cryptand 222BB exhibits intramolecular transitions that give rise to two absorptions, the most important one being from 274 to 276 nm; these absorptions are characteristic of the catechol ethers. Figure 1 shows the UV spectra of the free ligand 222BB and its cryptates of erbium and neodymium in methanol. A variation of the absorption intensities when the complexes are formed can be observed in this figure. The absorption at 275 nm splits when the complexes are formed, and a new absorption appears at longer wavelengths (~283 nm). This splitting has been observed in crown ether complexes[17] and in lanthanide cryptates.[18]

The molar extinction coefficients (ϵ) for the free ligand and its complexes have the following values: for 222BB, 9641 L/(mol·cm); for $Er(222BB)_2(NO_3)_3$, 12411 L/(mol·cm); and for $Nd(222BB)(NO_3)_3$, 7471 L/(mol·cm).

These spectra were run a second time after 45 days, and no

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Table II. IR Data (cm^{-1}) for Er^{3+} and Nd^{3+} Cryptates[a]

	ν_s(C—N—C)	ν_s(C—O—C)	ν_s(C—O—CH=) ν_s(C—N—C)	ν_b(H—C—H) ν(NC=CH)	NO$_3^-$ ionic	NO$_3^-$ coord
222BB	1209 s	1172 s	1046 s	979 s, 960 s 935 w, 749 s		
Nd(222BB)(NO$_3$)$_3$·H$_2$O	1217 s	1128 s	1054 s	942 s, 923 ms 882 w, 742 s		816 s 1328 s 1039 w
Er(222BB)$_2$(NO$_3$)$_3$·2H$_2$O	1217 s	1135 s	1061 s	942 s, 920 ms 883 ms, 742 s	1358 ms	816 s 1328 s 1031 s 1707 w
211	1246 mw	1179 mw 1122 s	1064 mw	934 s, 850 w 738 s		
Nd(211)(NO$_3$)$_3$	1261 w 1217 w	1143 s 1113 s	1091 ms	(957 s, 927 w) 861 w, 742 s		1321 s 1039 s
Er(211)$_2$(NO$_3$)$_3$	(1261 w, 1217 w)	1135 s 1113 s	1091 mw	(942 s, 927 w) 861 ws, 749 s	794 mw	823 s 1328 s 1039 ms 1766 w

[a] Values in parentheses indicate splitting.

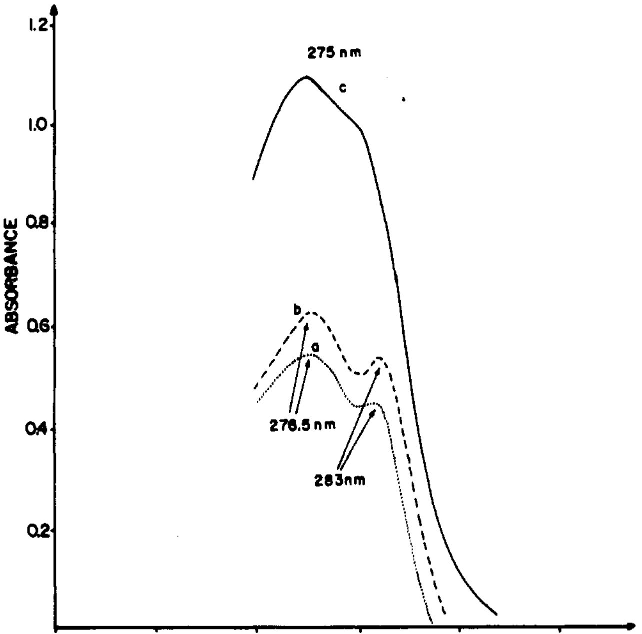

Figure 1. UV spectra of lanthanide cryptates with ligand 222BB in methanol: (a) erbium cryptate; (b) neodymium cryptate; (c) free ligand. Speed of the chart: 0.1 in./min.

changes were observed in them.

IR Spectroscopy. The IR bands that undergo significant changes upon complexation with the lanthanides are those shown in Table II. Upon complexation, band splitting was observed for the ligand 211 only.

For the 222BB complexes, the ν_s(C—O—C) band at about 1172 cm^{-1} in the free ligand is shifted about 44 and 37 cm^{-1} toward lower frequencies in the neodymium and erbium complexes, respectively. The ν_b(H—C—H) band at 979 cm^{-1} shows a strong shift toward lower frequencies of more than 37 cm^{-1}, and the band at 935 cm^{-1} due to the HC=CH vibration shifts 52 cm^{-1} toward lower frequencies in both complexes.

However, upon complexation with ligand 211, both cryptates show splitting: splittings of the bands at 1246 and 934 cm^{-1}, due to ν_s(C-N-C) and ν_b(H-C-H) vibrations, respectively. The ν_s(C-O-C) at 1064 cm^{-1} in the free ligand is shifted 27 cm^{-1} toward higher frequencies.

The IR bands exhibited by ionic and coordinated nitrate groups are also shown in Table II. The spectra of neodymium complexes suggest that all nitrate groups are coordinated to the metal ion; however, those of the erbium complexes suggest that both ionic and coordinated nitrate groups are simultaneously present.

No bands arising from coordinated water molecules to metal ion (400–450 cm^{-1}) were found. However some evidence of network-trapped H$_2$O molecules was observed in the 222BB complexes. Finally, no sign of solvation due to the solvents used in the synthesis of the cryptates was found in the spectra.

Preliminary results of Er^{3+} and Nd^{3+} complexes with ligand 222BB have been submitted for publication in *Revista de la Sociedad Quimica de Mêxico.*

NMR Spectroscopy. Proton NMR spectra of the free cryptand 222BB and its complexes with erbium and neodymium nitrates in CDCl$_3$ are shown in Figure 2. The free ligand presents complex multiplets centered at 2.8 (which integrates to 12 protons), 3.2 and 3.4 (8 protons), and 4.15 ppm (triplet) (8 protons), as well as a peak at 6.8 ppm (8 protons) and a small one at 7.4 ppm (this peak is due to a small amount of chloroform in the deuteriochloroform solvent). The N-CH_2 protons are located at 2.8 ppm whereas the O-CH_2 protons are found in the range between 3.2 and 3.4 ppm. The C$_6$H$_4$-OCH_2 protons are assigned to the multiplet at 4.15 ppm, while for the C$_6$$H_4$-OCH$_2$ protons the peak is found at 6.8 ppm (Figure 2a). The proton NMR spectrum of the cryptate Nd(222BB)(NO$_3$)$_3$·H$_2$O shows a shift with respect to the free cryptand. The N-CH_2, O-CH_2, and C$_6$H$_4$-OCH_2 protons are assigned to the peaks at 2.6 (which integrates to 2 protons), 3.2 (22 protons), and 4.2 ppm (4 protons), respectively. The changes in the intensities, as compared to the case of the free ligand, probably indicate that the M-L bond is mainly established by means both of the nitrogen bridges and of the oxygens in the bridges containing the benzene groups.[18] Finally the peak at approximately 7.0 ppm corresponds to the protons of the benzene groups (8 protons) (Figure 2b). The cryptate Er(222BB)$_2$(NO$_3$)$_3$·2H$_2$O shows peaks at 2.4 (6 protons), 3.2 (42 protons), 4.2 (9 protons), and 6.9 ppm (16 protons) assigned to the same protons as the last compound, although a widening of the peaks is observed (Figure 2c).

The free cryptand 211 presents two complex multiplets in the spectrum. When the solvent is D$_2$O, the multiplets are found at 2.6 (integrates to 12 protons) and 3.7 ppm (16 protons), which are assigned to N-CH_2 and O-CH_2 protons, respectively. At approximately 4.7 ppm (2 protons) a sharp peak is observed; this peak is due to H$_2$O present in the D$_2$O solvent (Figure 3a), but when the solvent is CDCl$_3$, the multiplets are found at 5.4 (12 protons) and 7.4 ppm (16 protons), which are assigned to the same protons as before (Figure 4a).

For the complex Nd(211)(NO$_3$)$_3$ in D$_2$O, a multiplet of 3.7 ppm (which integrates to 12 protons) assigned to N-CH_2 protons

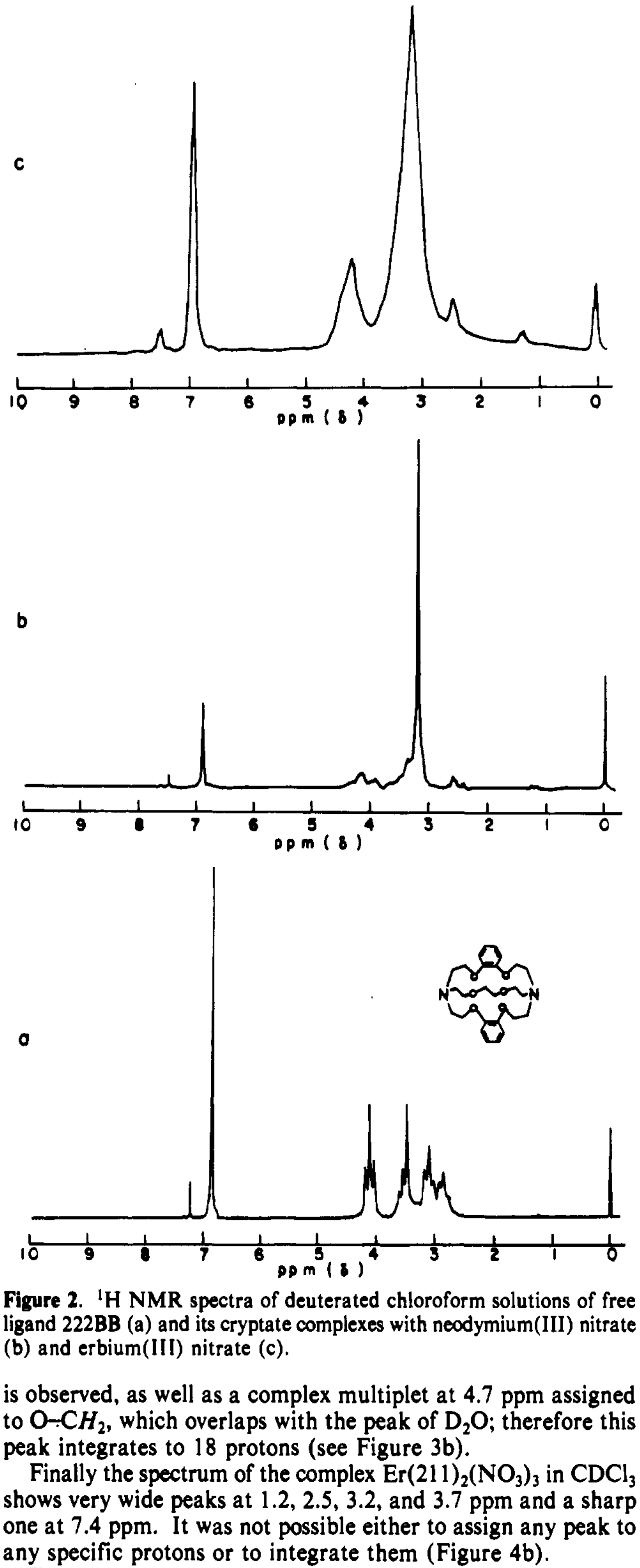

Figure 2. ^1H NMR spectra of deuterated chloroform solutions of free ligand 222BB (a) and its cryptate complexes with neodymium(III) nitrate (b) and erbium(III) nitrate (c).

is observed, as well as a complex multiplet at 4.7 ppm assigned to O–CH_2, which overlaps with the peak of D_2O; therefore this peak integrates to 18 protons (see Figure 3b).

Finally the spectrum of the complex $Er(211)_2(NO_3)_3$ in $CDCl_3$ shows very wide peaks at 1.2, 2.5, 3.2, and 3.7 ppm and a sharp one at 7.4 ppm. It was not possible either to assign any peak to any specific protons or to integrate them (Figure 4b).

Thermal Analyses. Thermal decomposition studies were done on the complexes. The results are discussed as follows.

(a) **Ligand 222BB.** The decomposition of this ligand begins at 340 °C and takes place in only one step. At 780 °C, a residue consisting of 13.8% of the ligand remains. A complete decomposition was expected because of the organic nature of the compound.

(b) **$Er(222BB)_2(NO_3)_3·2H_2O$.** Thermogravimetric analysis (TGA) of this cryptate exhibits three decomposition steps. The first one is due to the release of one of the ligands at 295 °C. The second is the consequence of a slow elimination of the other ligand; this step ends at 460 °C. The $Er(NO_3)_3$ thus formed at 460 °C decomposes immediately, to give Er_2O_3 as a final residue. Water is eliminated between 80 and 100 °C.

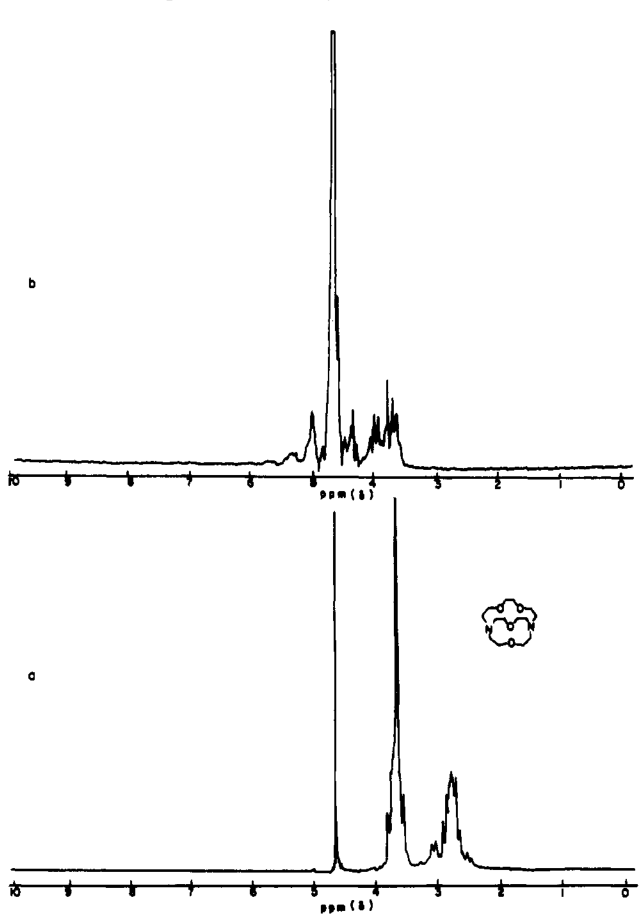

Figure 3. ^1H NMR spectra of deuterated water of free ligand 211 (a) and its cryptate complex with neodymium(III) nitrate (b).

These results suggest the following decomposition mechanism:

$$Er(222BB)_2(NO_3)_3·2H_2O \xrightarrow{I} Er(222BB)(NO_3)_3 + 222BB + 2H_2O$$

$$Er(222BB)(NO_3)_3 \xrightarrow{II} Er(NO_3)_3 + 222BB$$

$$2Er(NO_3)_3 \xrightarrow{III} Er_2O_3 + 3N_2O_5$$

(c) **$Nd(222BB)(NO_3)_3·H_2O$.** The thermal decomposition of this compound is rather complex. At 260 °C, where the decomposition of the cryptate begins no clear sign of Nd_2O_3 formation is observed, as no plateu is ever reached; even above 900 °C, weight continues to be lost. Such behavior has been observed for 1:1 lanthanide crown ether complexes,[19] where the residue $LnONO_3·Ln_2O_3$ has been proposed. Water is eliminated between 80 and 100 °C.

(d) **$Er(211)_2(NO_3)_3$.** The decomposition process occurs in two steps. The two ligands are lost simultaneously at 210 °C in a strongly endothermic process, which suggests the same arrangement for the two ligands around the cation. The erbium nitrate thus formed is decomposed at 340 °C to Er_2O_3 in an endothermic process.

These results suggest the following decomposition mechanism:

$$Er(211)_2(NO_3)_3 \rightarrow Er(NO_3)_3 + 2(211)$$

$$2Er(NO_3)_3 \rightarrow Er_2O_3 + 3N_2O_5$$

(e) **$Nd(211)(NO_3)_3$.** The decomposition of this compound is as complicated as the neodymium cryptate with the ligand 222BB. The ligand is easily eliminated at 310 °C. However the neodymium nitrate decomposes continuously, with no plateau indicating the formation of Nd_2O_3, giving way above 700 °C to $NdONO_3·Nd_2O_3$.

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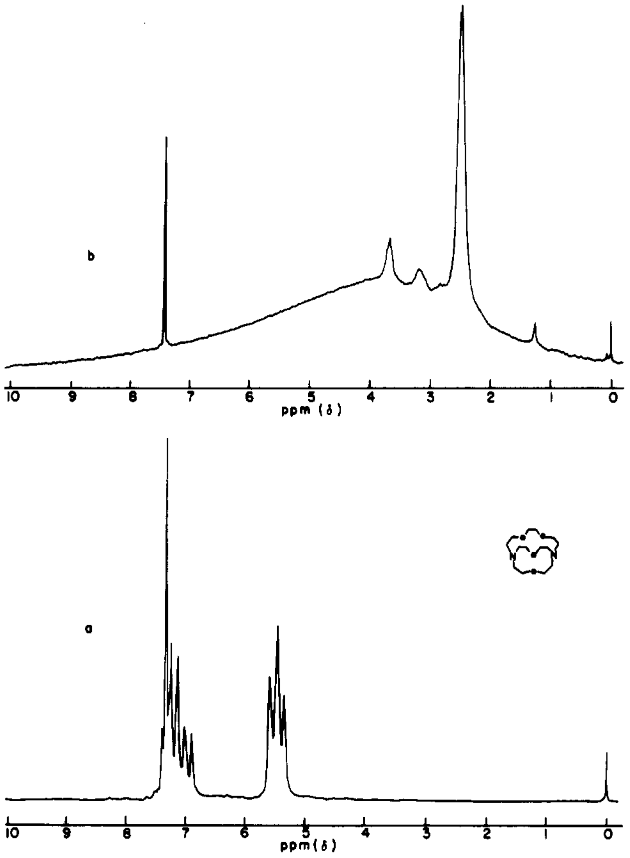

Figure 4. ^{1}H NMR spectra of deuterated chloroform of free ligand 211 (a) and its cryptate complex with erbium(III) nitrate (b).

Discussion

The elemental analysis results show, in some cases, abnormally high differences between the calculated and the experimental values. The formation during the elemental analysis procedure of final combustion products differing from the expected Ln_2O_3 might explain some of these discrepancies.

Metal:ligand (M:L) ratios of 1:2 and 1:1 were found for the erbium and neodymium complexes, respectively, when only the latter ratio was expected.[20] To our knowledge, lanthanide cryptates with a M:L ratio of 1:2 have not been reported previously. However, some crown ether complexes with the 1:2 ratio are known.[21,22]

Beginning with the erbium cryptates, we first calculate the ratio metal ion diameter:cryptand cavity diameter (MID:CcD), obtaining 0.8 and 1.1 for the complexes with the cryptands 222BB and 211, respectively. If the metal:ligand molar ratio is 1:1, the high coordination nature of the counterion NO_3^- should prevent the 1:2 ratio. If MID:CcD is between 0.5 and 0.7 or larger than 1.4, the M:L = 1:2 ratio should be obtained.[23] However the 1:2 ratio has been found in spite of a MID:CcD ratio of 0.8–1.1 for some complexes.[24] According to this, it is possible to obtain the 1:2 ratio for the erbium complexes in spite of the high coordination power of the nitrate groups. The small rigid size of the cryptand 211, the rigidity due to the benzene rings of the cryptand 222BB, and the small size of the erbium ion can favor this ratio.

It has been shown that the ligand 222B has a behavior similar to that of the ligand 221, so it can be expected that the ligand 222BB behaves similarly to the ligand 211. With rigid cryptands such as these, it is quite difficult to obtain a M:L ratio larger than 1; for a small ion like erbium,[25] the ratio should be 1 or lower. Another factor, perhaps the most important, could be our reaction temperature for the synthesis between 70 and 76 °C. Relatively high temperatures such as these might give rise to the M:L = 1:2 ratio observed for the erbium cryptates and to a temperature-dependent exclusive–inclusive complex equilibrium,[26,27] where the exo–exo or exo–endo conformations of ligands could be favored and thus complexes of the exclusive type, according to the following mechanism, where cryptand stands for the ligand 211 or 222BB:

$$Er^{3+} + \text{cryptand} \rightarrow Er \cup \text{cryptand}$$

$$Er \cup \text{cryptand} \rightarrow Er \subset \text{cryptand}$$

$$Er \subset \text{cryptand} \rightarrow Er \cup \text{cryptand}$$

$$Er \cup \text{cryptand} + \text{cryptand} \rightarrow Er \cup (\text{cryptand})_2$$

where $\cup$ means exclusive and $\subset$ inclusive types, respectively. Complexes of the exclusive type have been found for cesium cryptates[26] with the ligands 211, 221, and 222B.[27]

For our erbium cryptates it is not known how the two ligands are attached and if they are caught simultaneously, or not, by the Er^{3+} ion. If the first ligand attached to the erbium gives way to an inclusive complex, the metal ion should be strongly and completely coordinated to that ligand and it would not accept another ligand. If the complex is of the exclusive form, then due to its small size it could bind another ligand, thus being trapped between them.

TGA showed that the ligands 222BB and 211 do not interact with the erbium ion in the same way. The two 211 ligand molecules were eliminated at the same temperature, while the two 222BB ligand molecules were eliminated at different temperatures, but the residues of both molecules were similar: Er_2O_3. These results would suggest an equal coordination of the two ligands 211 to the metal ion and an unequal coordination of the two ligands 222BB in this latter case due probably to steric effects and to the greater cavity size of this ligand.

On the other hand, in comparison to those of the free ligands, the infrared spectra of the complexes obtained show important differences. IR spectra also suggest that the coordination of the metal ions with the ligand 211 is stronger than with the ligand 222BB.

The IR spectrum of the $Er(211)_2(NO_3)_3$ complex shows important shifts of –C–O–C and splittings of C–N–C and C–H vibrations due to the strong coordination of the metal ion to the ligands. It also shows similar changes of the symmetry in the two 211 cryptates.

An endo–endo conformation of the erbium cryptates is not probable, first because it is not a 1:1 inclusive complex and second because the NMR spectra do not present strong paramagnetic shifts with respect to the free ligand. A strong paramagnetic shift was to be expected in the case of a true inclusive complex.[18]

The M–L interaction in the $Er(222BB)_2(NO_3)_3 \cdot 2H_2O$ is weaker, and no apparent symmetry changes were observed; this may be explained by the fact that the ligand has a larger cavity size and lower selectivity (due to the benzene rings) than the ligand 211. The IR and NMR spectra support this deduction. The presence of a water lattice was confirmed by the elemental analysis.

Both erbium complexes are 1:2 sandwichlike compounds and possess ionic and coordinated nitrate groups. Passing now to the (1:1) neodymium complexes, one of the main questions concerns the encryptation of the metal. The MID:CcD ratio is 1.3 with 211 and 0.9 with 222BB. These M:L ratios support the hypothesis of a formation of inclusive complexes. However there are some parameters that do not support this. According to our results the IR spectra of these cryptates are similar to those of the Er complexes. The reaction temperature (70–76 °C) can give way to

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the formation of not inclusive complexes. The only important difference with respect to erbium complexes in the IR spectra is that all the nitrate groups in the Nd complexes are coordinated and those in the erbium complexes are ionic and coordinated, as is shown in Table II.

If inclusive complexes had been formed, larger shifts of –C–O–C, C–N–C, H–C–H, and –C=C vibrations would be expected; important paramagnetic shifts in the NMR spectra that are characteristic of inclusive complexes were not observed for the neodymium cryptates, but neodymium does not give rise to important paramagnetic shifts of protons, as has been reported by Gansow[28] and Horrocks.[29]

Concerning our 222BB complexes, it is important to state that the molar extinction coefficient of the free ligand 222BB is somewhat modified upon complexation and the new peak at 283 nm shows that the metal ion perturbs slightly the degenerate $\pi-\pi^*$ transition of the benzene rings in the metal complexes, resulting in a slight change in the degeneracy of the transition.

Conclusions

The experimental conditions are very important for the M:L ratio. According to our results, the 1:2 ratio is also possible for the lanthanide cryptates.

The M:L = 1:1 ratio in the Nd complexes is supported by the larger size of Nd^{3+} and therefore the probable major coordination number or its better arrangements to coordinate than Er^{3+}; however it is still not clear if they are inclusive cryptates or not. The metal–ligand interaction suggests a not complete encryptation of the metal ions by the ligands. The IR, UV, and NMR spectra afford evidence of complexation of the neodymium and erbium nitrates with the cryptands 222BB and 211. The IR spectra are too complex to allow a distinction between monodentate and bidentate nitrate groups.

IR and NMR spectra of the erbium complexes show a medium-strength metal–ligand interaction, enough to keep the metal between the two ligands with a sandwich configuration.

Registry No. 222BB, 40471-97-4; 211, 31250-06-3.

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New Orthocyclophane Cyclotetraphosphazanes: $[C_6H_4N_2(PR)_2]_2$ (R = Ph, Me) and $[C_6H_4N_2(PPh)(PhPS)]_2$

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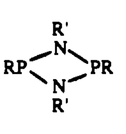
The orthocyclophane cyclotetraphosphazanes $[C_6H_4N_2(PR)_2]_2$ (R = Ph (**4**), Me (**5**)) have been obtained from $RPCl_2$/1,2-$(NH_2)_2C_6H_4$/Et_3N reactions. S_8 oxidation of **4** yields $[C_6H_4N_2(PhP)(PhPS)]_2$ (**6**) and $[C_6H_4N_2]_2(PhPS)_3(PhP)$ (**7**). **4**–**7** are characterized by spectral (MS, IR, ^1H and ^{31}P NMR) data. **4** and **6** are further characterized by X-ray single-crystal analyses. **4**: monoclinic, $C2/c$, a = 18.629 (4) Å, b = 9.108 (3) Å, c = 18.874 (3) Å, β = 104.17 (2)°, V = 3105 Å^3, Z = 4, d_{calc} = 1.37 g cm^{-3}. **6**: triclinic, $P\bar{1}$, a = 10.8724 (12) Å, b = 11.1319 (16) Å, c = 14.219 (2) Å, α = 99.812 (11)°, β = 93.707 (10)°, γ = 91.460 (10)°, V = 1691 Å^3, Z = 2, d_{calc} = 1.384 g cm^{-3}. **4**–**7** contain eight-membered P_4N_4 rings, of alternating phosphorus and nitrogen atoms, made up of two diazaphosphole ring units bonded by bridging PhP groups. The two bridging PhP phosphorus atoms and four nitrogen atoms of **4** and **6** are coplanar. The P_4N_4 ring is in a boat conformation. The *o*-phenylene (C_6H_4) and bridging PhP phenyl rings are mutually cis oriented above and below the P_4N_4 ring. The bridging PhP phenyl rings create a molecular cleft into which the diazaphosphole phosphorus(III) atom electron pairs are directed. Formation of **4** and **5**, regioselectivity in reactions of **4** with sulfur, and the potential of **4**–**6** for novel donor coordination are discussed.

Introduction

Cyclophosphazanes consisting of four- (**1**),[2-5] six- (**2**),[4,5,6-8] and eight-membered (**3**)[4,5,9-14] rings of alternating phosphorus and nitrogen atoms are known and, in several cases, have been the



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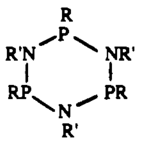

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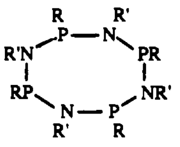

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object of detailed structural, reactivity, and mechanistic studies. Cyclodiphosphazanes (diazadiphosphetidines; **1**) have been examined in considerable detail with respect to their structural,[2-5]

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