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Metal Complexes of Tetrapodal Ligands: Synthesis, Spectroscopic and Thermal Studies, and X-ray Crystal Structure Studies of Na(I), Ca(II), Sr(II), and Ba(II) Complexes of Tetrapodal Ligands *N*,*N*,*N*′,*N*′-Tetrakis(2-hydroxypropyl)ethylenediamine and *N*,*N*,*N*′,*N*′-Tetrakis(2-hydroxyethyl)ethylenediamine

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Twelve complexes **1**–**12** of general category [M(ligand)(anion)$_x$(water)$_y$], where ligand = *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxypropyl/ethyl)ethylenediamine (HPEN/HEEN), anion = anions of picric acid (PIC), 3,5-dinitrobenzoic acid (DNB), 2,4-dinitrophenol (DNP), and *o*-nitrobenzoic acid (ONB), M = Ca^{2+}, Sr^{2+}, Ba^{2+}, or Na^+, $x = 1$ and 2, and $y = 0$–4, were synthesized. All of these complexes were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, and thermal studies. X-ray crystal studies of these complexes **1**–**12,** $[Ca(HPEN)(H_2O)_2](PIC)_2{\cdot}H_2O$ (**1**), [Ca(HEEN)(PIC)](PIC) (**2**), $Ba(HPEN)(PIC)_2$ (**3**), $[Na(HPEN)(PIC)]_2$ (**4**), $Ca(HPEN)(H_2O)_2](DNB)_2{\cdot}H_2O$ (**5**),$Ca(HEEN)(H_2O)](DNB)_2{\cdot}H_2O$ (**6**), $[Sr(HPEN)(H_2O)_3](DNB)_2$ (**7**), $[Ba(HPEN)(H_2O)_2](DNB)_2{\cdot}H_2O\}_2$ (**8**), $\{[Ba(HEEN)(H_2O)_2](ONB)_2\}_2$ (**9**), $\{[Sr(HPEN)(H_2O)_2](DNP)_2\}_2$ (**10**), $\{[Ba(HPEN)(H_2O)_2](DNP)_2\}_2$ (**11**), and [Ca(HEEN)(DNP)](DNP) (H_2O) (**12**), have been carried out at room temperature. Factors which influence the stability and the type of complex formed have been recognized as H-bonding interactions, presence/absence of solvent, nature of the anion, and nature of the cation. Both the ligands coordinate the metal ion through all the six available donor atoms. The complexes **1** and **5**–**11** have water molecules in the coordination sphere, and their crystal structures show that water is playing a dual character. It coordinates to the metal ion on one hand and strongly hydrogen bonds to the anion on the other. These strong hydrogen bonds stabilize the anion and decrease the cation–anion interactions by many times to an extent that the anions are completely excluded out of the coordination sphere and produce totally charge-separated complexes. In the absence of water molecules as in **2** and **3** the number of hydrogen bonds is reduced considerably. In both the complexes the anions case interact more strongly with the metal ion to give rise to a partially charge-separated **2** or tightly ion-paired **3** complex. High charge density Ca^{2+} forms only monomeric complexes. It has more affinity toward stronger nucleophiles such as DNP and PIC with which it gives partially charge-separated eight-coordinated complexes. But with relatively weaker nucleophile like DNB, water replaces the anion and produces a seven coordinated totally charge-separated complex. Sr^{2+} with lesser charge/radius ratio forms only charge-separated monomeric as well as dimeric complexes. Higher coordination number of Sr^{2+} is achieved with coordinated water molecules which may be bridging or nonbridging in nature. All charge-separated complexes of the largest Ba^{2+} are dimeric with bridging water molecules. Only one monomeric ion-paired complex was obtained with $Ba(PIC)_2$. Na^+ forms a unique dinuclear cryptand-like complex with HPEN behaving as a heptadentate chelating-cum-bridging ligand.

Introduction

Synthetic and natural macromolecules resemble each other in their preference for smaller cations over larger ones. This may be partly attributed to the enhanced site–site repulsions within the ligand molecule.[1,2] This is true for the bi- and tricyclic ligands. However, for the flexible macrocycles, the complexes of the small cations have been isolated only under

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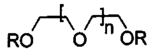
special conditions. This discrimination may be attributed primarily to the strong involvement of such cations.[3] The site−site repulsions may only help in the retreat of the macrocycle when it fails to encapsulate the cation. If the counteranion is stabilized in some way, during complexation of the cation, it is believed that high specificity for the small divalent (Ca and Mg) and monovalent (Na and Li) cations may be noted,[4] contrary to the earlier predictions.[2,5]

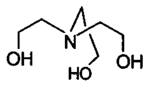
On the other hand, selectivity order of the neutral, synthetic, open chain, multidentate ligands (sensors/podands) for a cation is greatly determined by its own structural aspects and the solvent medium. Apparently the principles of complexation discovered for the metal−crown systems are not applicable to the understanding of the cation selectivities of the metal−podand systems. On the contrary, the results of the two systems appear dissimilar. Crown ethers are usually selective for low charge density cations (K^+, Rb^+, Cs^+) whereas most sensors select the medium charge density cations (Na^+, Ba^{2+}, Sr^{2+}, Ca^{2+}). The high charge density Mg^{2+} is not bound by any of the two under ordinary reaction employing organic and aqueous organic media. However, the simultaneous stabilization of the counteranion by the ligand carrying polarizable hydrogens affects the results in much the same way as in the case of the macrocyclic ligands.

With the aim of understanding the chemical principles and the intriguing interactive preferences of Na^+, K^+, Mg^{2+}, and Ca^{2+} atoms in the natural system,[6] a broad-based chemical and crystallographical investigations on the alkali and alkaline earth metal cations in general was undertaken and a series of the cations in comparable environments with regard to charge neutralizer and the ligand were investigated using cyclic multidentate ligands.[7,8] The work was later on extended to include double-action acyclic multidetate ligands[9,10,11] such as **I**−**III**. The charge neutralizers found to be the most suitable are corresponding anions of picric acid (PIC), 3,5-dinitrobenzoic acid (DNB), 2,4-dinitrophenol (DNP), and *o*-nitrobenzoic acid (ONB), etc. The double action ligands offer an advantage of stabilizing the anion in addition to coordinating with the countercation so that similar cations can be investigated under a diminished (or lifted) anion effect, especially the trio Ca^{2+}, Sr^{2+}, and Ba^{2+} for which the group discrimination is the most ticklish.

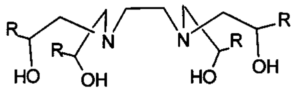


R = H **(I)**

R = CH_3 **(II)**



(III)



R=CH_3 **(a)**

R=H **(b)**

(IV)

With combination of our results with the literature,[12] it can be summarized that, in the complexes of acyclic ligands such as **II** which do not possess a polarizable hydrogen at the end group, the H-bonding interactions are lacking and the anion interacts strongly with the cation resulting in the formation of tight ion pairs.[9,13,14] The ligands carrying polarizable hydrogens (like dipodal ligands **I** and tripodal ligand **III**) play a dual role. They coordinate with the cation and also interact with the counteranion producing an extensive network of H-bonding. The latter leads to a decrease in the cation−anion interactions to the extent that the cation and anion no longer remain within a bonding

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distance of each other resulting in totally charge-separated complexes in most of the cases.[11a,b,g,f,15,16] A partial charge separation or a tight ion pair is seen only in the case of a metal ion of high charge density paired with a very strong nucleophile[10,11e,15b,17] or for a large-sized metal ion whose coordination sphere is not satisfied by coordinating to the ligands alone.[11c,d,18]

Working along the same lines, we have now included the tetrapodal ligands *N*,*N*,*N′*,*N′*-tetrakis(2-hydroxypropyl)ethylenediamine (**IVa**) (HPEN) and *N*,*N*,*N′*,*N′*-tetrakis(2-hydroxyethyl)ethylenediamine (**IVb**) (HEEN) in our studies. There is a big gap, as discovered during the literature survey, regarding the complexation properties and structures of their complexes. To the best of our knowledge only one X-ray crystallographic study[19] has been done so far, and that is a complex $Cu(HPEN)(ClO_4)_2 \cdot H_2O$. Presently we are reporting 12 new complexes of ligands **IV**. These complexes belong to the general type $M(anion)_x(ligand)(H_2O)_y$ in different stoichiometries. The main aim of this investigation is to study the coordination modes of the ligands, their behavior as double-action ligands, and the role played by water in deciding the cation−anion interactions.

Experimental Section

All the details regarding the instruments, chemicals and synthetic methods used, elemental, spectroscopic, thermal, and crystal data, and treatment of disordered structures are being included as Supporting Information.

X-ray Data Collection, Structure Determination, and Refinement. Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromatized Mo Kα ($\lambda = 0.710\,73$ Å) radiations. The data were corrected for Lorentz and polarization effects.[20] An absorption correction was applied using ψ scans.[21] The structures were refined by full-matrix least-squares refinement methods based on F^2, using SHELXTL-PC.[22] Complex neutral atom scattering factors were used for the calculations.[23]An anisotropic refinement of non-hydrogen atoms was done for all the complexes except for some disorderd atoms in a few cases (as given in the note on disordered structures). All the hydrogens were attached geometrically except for those bonded to hydroxyl oxygens and water molecules which were located from difference Fourier maps. None of these hydrogens were refined, and they were made to ride on their respective atoms. The hydrogens bonded to secondary and tertiary carbons were assigned an isotropic thermal parameter which was 1.2 times the U_{iso} value of their carrier atom, whereas hydrogens of primary carbons were given a U_{iso} value of 1.5 times that of their carrier. The hydrogens of hydroxyl groups were given a fixed U_{iso} value of 0.052. The dihedral angles, least-squares planes, hydrogen bonding, and torsion angles were measured using computer program PARST.[24]

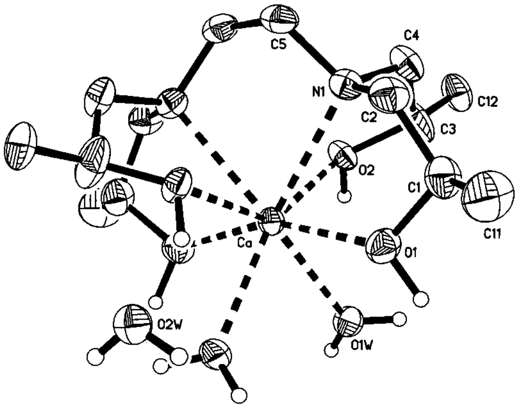

Figure 1. ORTEP drawing of complex **1**, showing the labeling scheme. The anion and the hydrogens attached to the carbons have been removed for clarity. **5** is isostructural with one extra lattice water molecule.

Results

Description of Structures. $[Ca(HPEN)(H_2O)_2](PIC)_2 \cdot H_2O]$ (1). The complex possesses a 2-fold axis of rotation passing through O2W and Ca^{2+} and midway bisecting the C5−C5A bond (where A = $-x + 1, y, -z + 1/2$). The Ca^{2+} ion is eight coordinated through all the four hydroxyl groups, both the amine nitrogens, and two water molecules (Figure 1). A lattice water O2W is also present in the complex. The two picrate anions do not directly interact with the metal ion but remain outside the coordination sphere. The complex is thus a charge-separated complex (type **Ib**, Chart 1). There are extensive intermolecular H-bonding interactions (Figure 2) involving the hydroxyl oxygens, water molecules, phenolic oxygen, and oxygens of the *o*-nitro groups of the picrate ion. The phenolic oxygen O5 is forming two H-bonds with the coordinated water O1W and lattice water O2W. These two water molecules are also H-bonded to the oxygens O10 and O7 of the *o*-nitro groups, through the same hydrogens, respectively. The second hydrogen of O1W also H-bonds to O7 of a symmetry-related PIC. Hydroxyl oxygen O1 is showing interctions with O6 and O10 of the *o*-nitro groups whereas the other hydroxyl oxygen O2 is donating a H-bond to the lattice water O2W. Thus, the coordinated water molecule is involved in three whereas the lattice water molecule forms as much as six H-bonding interactions.

[Ca(HEEN)(PIC)](PIC) (2). The eight-coordinated Ca^{2+} ion is bonded to hexadentate HEEN (Figure 3) with two remaining coordination sites being occupied by the phenolate oxygen O12 and *o*-nitro oxygen O13 of one of the picrate anions. The second picrate ion remains uncoordinated

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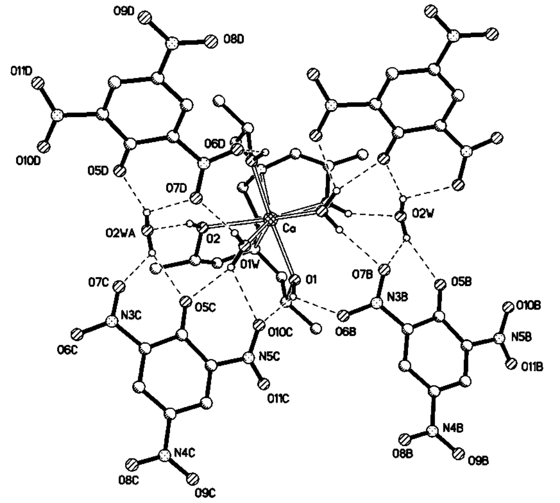
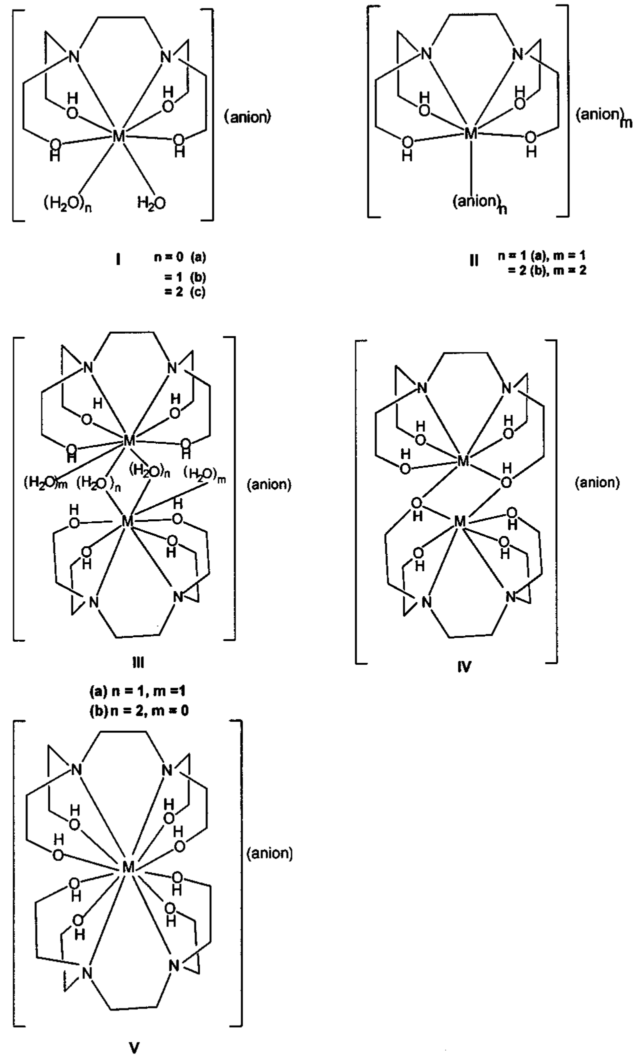


Figure 2. Hydrogen bonding in complex **1**. Hydrogens attached to carbon atoms have been removed.

Chart 1. Modes of Coordination of the Tetrapodands



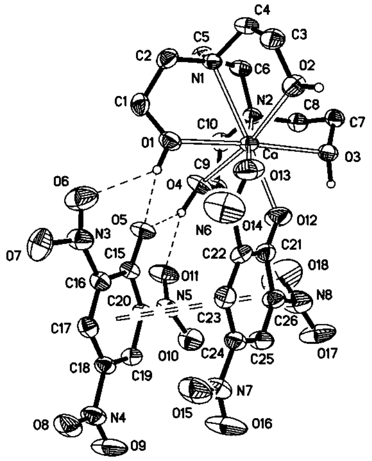


Figure 3. ORTEP drawing of complex **2**, showing the labeling scheme and $\pi\angle\pi$ interaction. Hydrogens attached to carbon atoms have been removed. **12** is isostructural with the anion being DNP instead of PIC.

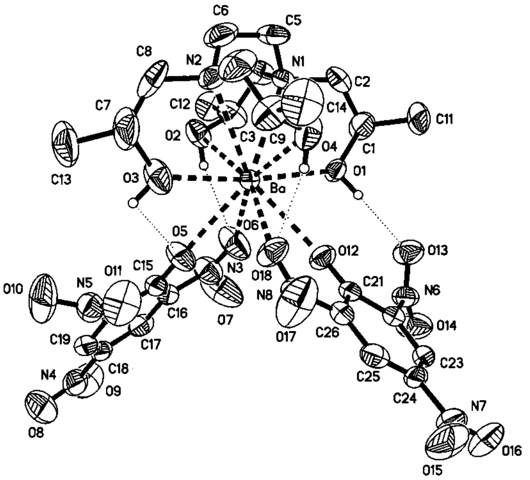


Figure 4. ORTEP drawing of complex **3**, showing the labeling scheme and H- bonding. Hydrogens attached to carbons have been omitted for clarity.

resulting in a partially charge-separated complex (type **IIa**). The picrate anion which is coordinated to the Ca^{2+} ion does not participate in any inter- or intramolecular H-bonding. The uncoordinated picrate anion is involved in intramolecular H-bonding interactions with the HEEN. The phenolic oxygen O5 forms two H-bonds with two hydroxyl groups O1 and O4. O6 and O11 belonging to the *o*-nitro groups of this PIC also form H-bonds to these hydroxyl groups. The other two hydroxyl groups O2 and O3 form intermolecular H-bonds with their symmetry-related counterparts. The uncoordinated PIC anion also has face to face $\pi\cdots\pi$ interactions (3.8 Å) with the coordinated anion. The H-bonding and these interactions probably prevent its interaction with the Ca^{2+} ion.

Ba(HPEN)(PIC)$_2$ (3). The complex has a 10-coordinated Ba^{2+} (Figure 4). Two picrate ions directly coordinate to Ba^{2+} ion through the phenolic oxygen and one oxygen of the *o*-nitro group to form an ion-paired complex (type **IIb**). The complex shows only intramolecular H-bonding between the four OH groups and phenolic oxygens and the oxygens of the *o*-nitro groups of both the picrates. The hydroxyl group O3 forms an H-bond to the phenolic O5, and O2 donates an H-bond to O6 of the *o*-nitro group of one of the PIC groups. The other two hydroxyl groups O1 and O4 H-bond with oxygens O13 and O18 of the *o*-nitro group of the second PIC. In this complex the ligand−anion interactions are less in number and the nucleophilicity of the PIC is not quenched and a tight ion-paired complex is formed.

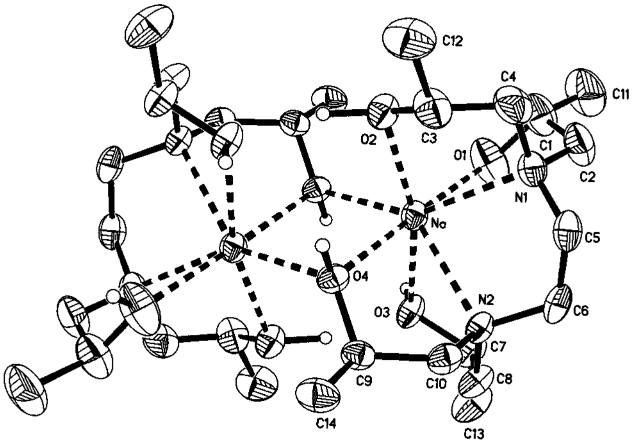


Figure 5. ORTEP drawing of complex **4**, showing the labeling scheme. Hydrogens attached to carbons have been removed for clarity.

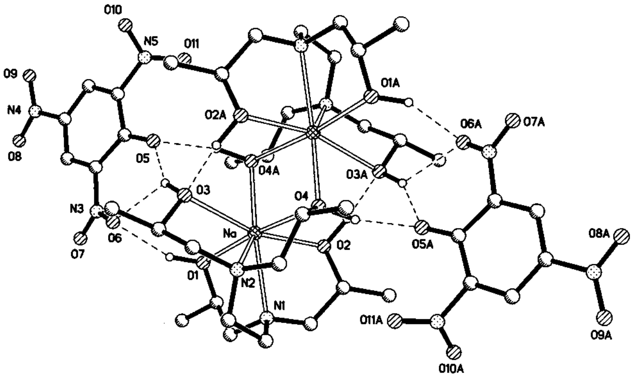


Figure 6. Showing hydrogen bonding in complex **4**. Hydrogens attached to carbons have been removed for clarity.

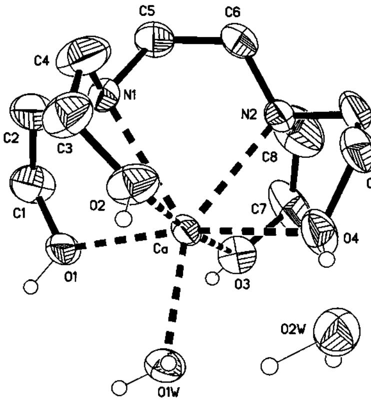


Figure 7. ORTEP drawing of complex **6**, showing the labeling scheme. Hydrogens attached to carbons and anions have been removed for clarity.

[Na(HPEN)]$_2$(PIC)$_2$ (4). The complex is a charge-separated seven-coordinated centrosymmetric dimer (Figure 5). Each HPEN ligand shows heptadentate coordination to Na$^+$ ion by bridging between two Na$^+$ ions through one of its hydroxyl oxygens O4 (type **IV**). An average M−O distance is 2.476(3) Å, and an average M−N distance is 2.560(4) Å. Thus, Na$^+$ ion is encapsulated in an almost spherical crptand-like cavity. The Na−O4 distance is greater (2.629(3) Å) than the other three M−O(hydroxyl) distances (2.412(3), 2.393(3), 2.505(3) Å) and also greater than the Na−O4^I distance (2.443(3) Å) (I = $-x$, $-y + 1$, $-z + 1$). Therefore, O4 is further away from Na$^+$ than the rest of the oxygens but is closer to the centrosymmetrically related Na$^+$. This type of unsymmetrical bridging where the bridging atom of one molecule is closer to the metal ion of second molecule in the dimer is a unique feature in this complex. The overall structure is, however, similar to that found in case of [Na(TEA)(ClO$_4$)$_2$] and [Na(TEA)I]$_2$, where two hydroxyl oxygens of TEA are bridging between Na$^+$ ions forming chains or parallel sheets in the crystals.[17b,25] The crystal structure shows H-bonding involving hydroxyl oxygens, a phenolic oxygen, and one of the oxygens of the *o*-nitro group of picrate (Figure 6). The hydroxyl oxygen O3 is forming two intramolecular H-bonds to the phenolic oxygen O5 and oxygen of the *o*-nitro group O6. It accepts an H-bond from hydroxyl oxygen O2 of the symmetry-related HPEN ligand. O5 also shows an intermolecular H-bonding interaction with O4 whereas O6 accepts another bond from the hydroxyl oxygen O1. Thus, both O5 and O6 act as double H-bond acceptors and a total of five H-bonding interactions are observed in the crystal lattice.

[Ca(HPEN)(H$_2$O)$_2$](DNB)$_2$·2H$_2$O (5). Ca^{2+} is located at 2-fold axis of rotation which passes midway through the C5 and C5^I bond (I = $-x + 1$, y, $-z + 1/2$). It is eight coordinated by a hexadentate HPEN and two water molecules. Both DNB anions are lying outside the coordination sphere resulting in a totally charge-separated complex (type **Ib**). Two lattice water molecules O2W and O2WI are also present. Its structure is similar to **1**. The complex exhibits extensive intra-and intermolecular hydrogen-bonding interactions. The polar hydroxyl groups of the ligand HPEN, coordinated and lattice water molecules, and DNB anions participate in hydrogen bonding. The carboxyl oxygen O5 is H-bonded to the coordinated water O1W, and the second oxygen O6 is triply H-bonded to the hydroxyl oxygen O1 and the lattice water molecule O2W. The second hydroxyl oxygen O2 donates an H-bond to the lattice water molecule. O1W also forms an H-bond with its symmetry-related counterpart. Thus, both the coordinated and lattice water molecules act as donors as well as acceptors and in the process the anion is being held away by them.

[Ca(HEEN)(H$_2$O)](DNB)$_2$·H$_2$O (6). Ca^{2+} is 7-fold coordinated by hexadentate ligand (HEEN) and a water molecule O1W (Figure 7). The charge neutralizer DNB groups are excluded from the coordination sphere (type **Ia**) of the metal ion but are hydrogen bonded with the hydroxyl groups of the ligand HEEN. The complex has extensive intra- and intermolecular hydrogen-bonding interactions.The hydroxyl O1 forms an intramolecular H-bond with carboxyl oxygen O5 whereas O2 and O3 form intra and intermolecular bonds with carboxyl O11 of the DNB. Other two carboxyl oxygens O6 and O12 form two intramolecular H-bonds with coordinated water O1W and lattice water O2W, respectively. O1W is also donating an H-bond to hydroxyl O2, and O2W, to O4. Thus, coordinated water molecule O1W is only donating hydrogen bonds but the lattice water molecule acts as donor as well as acceptor of hydrogen bonds.

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(25) Naiini, A. A.; Pinkas, J.; Plass, W.; Young, V. G., Jr.; Verkade, J. G. *Inorg. Chem.* **1994**, *33*, 2137.

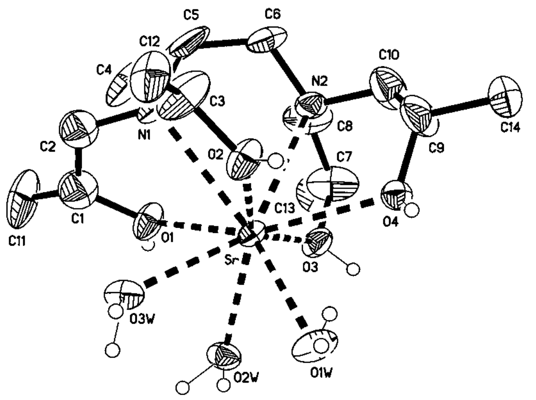


Figure 8. ORTEP drawing of complex **7**, showing the labeling scheme. Hydrogens attached to carbons and anions have been removed for clarity.

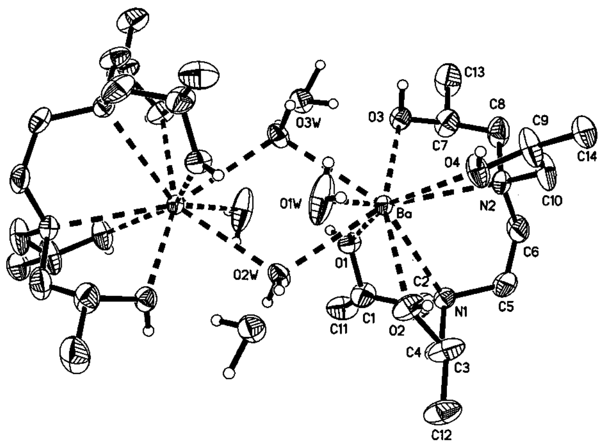


Figure 9. ORTEP drawing of complex **8**, showing the labeling scheme. The anions and the hydrogens attached to the carbons have been removed for clarity. **10** is isostructural except for the fact that it lacks lattice water molecules.

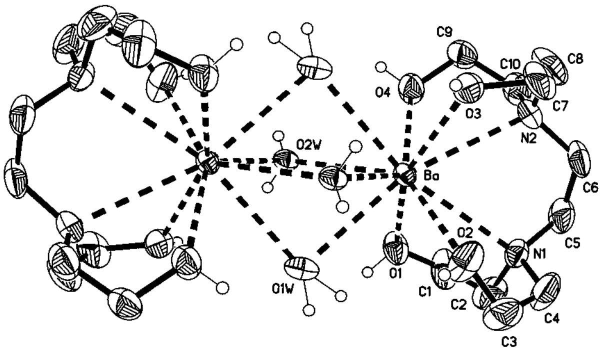


Figure 10. ORTEP drawing of complex **9**, showing the labeling scheme. The anions and the hydrogens attached to the carbons have been removed for clarity. **11** is isostructural.

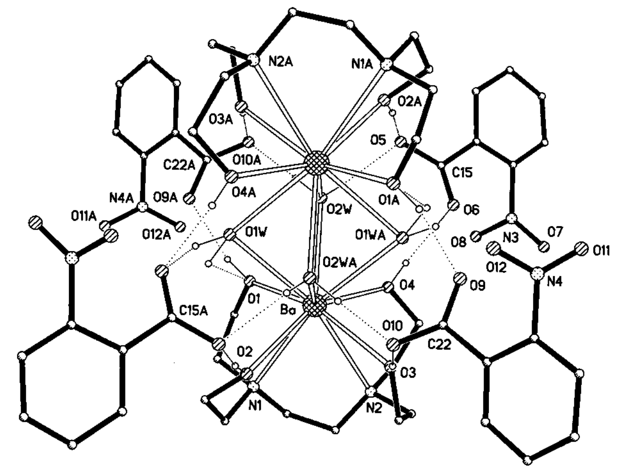


Figure 11. Hydrogen bonding in complex **9**. Hydrogens attached to carbons have been removed for clarity.

[Sr(HPEN)(H_2O)$_3$](DNB)$_2$ (7). **7** is a charge-separated (type **Ic**) complex where Sr^{2+} is nine coordinated to the ligand and three water molecules (Figure 8). Both inter- and intramolecular hydrogen-bonding interactions have been observed in the title complex. The polar hydroxyl groups of HPEN, water molecules, and carboxyl oxygens of DNB extensively participate in hydrogen-bonding interactions. The carboxyl oxygens O5 and O6 of one DNB are forming intramolecular H-bonds to hydroxyl oxygens O4 and O2, respectively. The O11 and O12 of the second carboxyl group are intermolecularly H-bonded to hydroxyl group O3 and water molecule O3W, respectively. O12 also forms two intermolecular H-bonds with O2W and one more intramolecular H-bonds with O3W. Thus, this carboxyl group is involved in five H-bonds. Water molecule O1W acts as an H-bond donor toward hydroxyl oxygens O4 and O2.

[Ba(HPEN)(H_2O)$_2$]$_2$(DNB)$_4$·2H_2O [8]. This charge-separated (type **IIIa**) complex is a centrosymmetric dimer (Figure 9). Each Ba^{2+} ion is nine coordinated to the ligand and one terminally bonded and another bridging water molecule. There are also present two lattice water O3W molecules in the dimer. The complex is extensively involved in inter- as well as intramolecular hydrogen-bonding interactions. Two of the four hydroxyl groups O4 and O3 of the ligand are donating hydrogen bonds to the carboxyl oxygens O6 and O12, respectively. The remaining two O1 and O2 are H-bonded to the terminally coordinated water O1W and lattice water O3W, respectively. Other two carboxyl oxygens O5 and O11 are also H-bonded to the water molecules. The water molecules O1W and O3W are accepting as well as donating hydrogen bonds while O2W is only acting as a donor. The coordinated terminal water molecule O1W and the lattice water molecules are connecting one dimeric unit with another in the crystal structure.

[Ba(HEEN)(H_2O)$_2$]$_2$(ONB)$_4$ (9). The complex is a charge-separated centrosymmetric dimer (Figure 10). Each Ba^{2+} ion in the dimer is coordinated to one hexadentate HEEN and four bridging water molecules (type **IIIb**). The complex is involved extensively in inter- and intramolecular hydrogen-bonding interactions. Two of the carboxyl oxygens O6 and O10 are forming intramolecular H-bonds with the hydroxyl oxygens O4 and O3, respectively (Figure 11). The remaining two carboxyl oxygens O5 and O9 are intermolecularly bonded to the hydroxyl groups O2 and O1. O5, O6, and O10 are also accepting H-bonds from water molecules O1W and O2W and behaving as double H-bond acceptors. Hydroxyl oxygen O1 accepts an intramolecular H-bond from O1W. Thus, it behaves as a donor as well as acceptor.

[Sr(HPEN)(H_2O)$_2$]$_2$(DNP)$_4$ (10). The complex is a centrosymmetric dimer. With the coordination number around each Sr^{2+} ion being 9, the structure of the complex (type

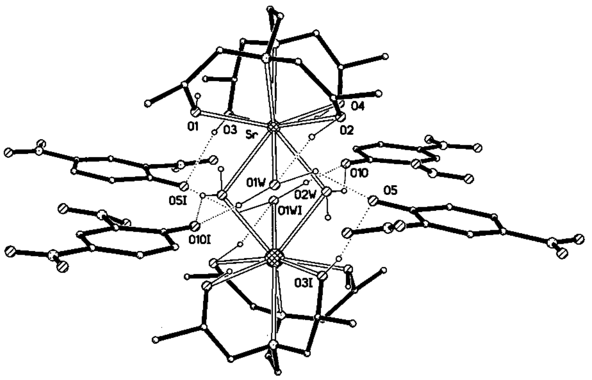


Figure 12. Hydrogen bonding in complex **10**. Hydrogens attached to carbons have been removed for clarity.

IIIa) is similar to that of **8**. The phenolic oxygen O5 of one of the DNP anions is hydrogen bonded to the hydroxyl group O3 and water molecule O1W (Figure 12). The second phenolic oxygen O10 is doubly H-bonded to both the water molecules O1W and O2W. O1W is also H-bonded to hydroxyl oxygen O2. Nitro groups of the anions are not involved in any H-bonding interactions.

[Ba(HPEN)(H_2O)$_2$]$_2$(DNP)$_4$ (11). The complex is a charge-separated, centrosymmetric dimer (type **IIIb**) with a structure similar to that of **9**. The complex shows extensive hydrogen-bonding interactions. The phenolic oxygen O5 forms three H-bonds with the hydroxyl groups O1 and O4 and water molecule O2W. The second phenolic oxygen O10 is also having two H-bond interactions with hydroxyl oxygen O3 and water molecule O1W. The oxygen of the nitro group O14 is forming one intramolecular H-bond with hydroxyl oxygen O2 whereas O6 and O11 are H-bonded with the water molecules.

[Ca(HEEN)(DNP)](DNP)(H_2O) (12). **12** is a partially charge-separated (type **IIa**) complex with Ca^{2+} ion coordinated by a hexadentate ligand and one DNP anion. DNP is coordinating through its phenolic oxygen and one of the oxygens of the *o*-nitro groups. The structure of the complex is similar to that found for **2**. Unlike **2** there is one lattice water molecule O1W in the complex. The coordinated DNP is not forming any H-bond with the ligand or the lattice water. The second DNP is not coordinating to the metal but is only involved in H-bonding interactions. Its phenolic oxygen O10 is accepting two intra- and one intermolecular H-bonds from three hydroxyl groups O1, O4, and O2, respectively. The fourth hydroxyl group O3 is donating a H-bond to the lattice water molecule.

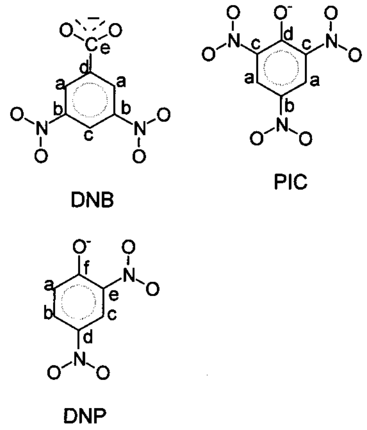
Discussion

Spectral Studies. In the solution state, these complexes (1) can retain the geometries as observed in the solid state, (2) can attain new geometries, and (3) can completely dissociate to give mixtures of metal salts and ligands. In case 3 the NMR spectra of the complexes should be quite similar to the ones observed for their separate components, but in cases 1 and 2 the coordination shifts can be helpful in defining the coordination behavior of ligands and the counteranions in the solution phase.The counteranion and ligand compete for their coordination toward metal ions, and so their ^1H and ^{13}C NMR spectra should be affected with any change in their coordination. In ^1H NMR since the coordination shifts are small and are also affected by the extent of water present in DMSO-d_6, it was not possible to measure the coordination shifts. However in the case of ^{13}C NMR spectra, the coordination shifts are appreciable so these have been calculated and analyzed (for HEEN complexes), to comment on the effect of metal ions on their complexation toward ligands and counteranions (Table 1). These changes are consistent with the complexation of HEEN to the cation (0.10−1.42 ppm upfield for ^{13}C NMR).

Table 1. ^{13}C NMR Chemical Shifts (ppm) of Complexes of HEEN

Complex	$-OCH_2$	$-NCH_2$	$-NCH_2$
[Ca(HEEN)(PIC)](PIC) (**2**)	−0.03	−0.10	+0.19
[Ca(HEEN)(H_2O)](DNB)$_2$·H_2O (**6**)	−1.03	−0.90	−0.52
[Ca(HEEN)(DNP)](DNP)·H_2O (**12**)	−0.50	−1.13	−0.84

Chart 2



A comparison of various HEEN complexes was made to their corresponding salts (Chart 2). A downfield shift for all the aromatic carbons in **2** and **12** (Table 2) shows that the anion not only remains coordinated to the metal ion as in Ca(PIC)$_2$ salt but is also involved in H-bonding interactions. An upfield shift for all the aromatic carbons and carboxylate carbon in **6** indicates that the anion is set free on complexation of HEEN to the metal and a charge-separated complex of Ca(DNB)$_2$ is formed. On this basis, **12** could be predicted to form an ion paired/partially charge-separated complex, and it has been found to be so in its crystal structure also. Thus, phenolates seem to have more affinity for Ca^{2+} than benzoates.

The ^1H NMR spectrum of HPEN exhibits multiple signals for all protons. Similarly, its ^{13}C NMR spectrum shows six signals each for NCH_2 and OCH carbons. This is due to the presence of four chiral centers in HPEN which results in a mixture of diastereomers. So it was not possible to make a comparison of the chemical shifts of the ligand to that of its complexes. A comparison of various complexes was made with their corresponding salts. Unlike HEEN complexes, the HPEN complexes do not show a simple relationship of the change in chemical shift on complexation to the type of structure in the solution phase. The ^1H and ^{13}C NMR spectra in the case of **8**, are however remarkable. The ^1H NMR of

Table 2. Change in Chemical Shifts (ppm) of Anions in Different Complexes

complex	a	b	c	d	e	f
$[Ca(HPEN)(H_2O)_2](PIC)_2 \cdot H_2O$ (**1**)	−0.35	−0.50	−0.24	−0.33		
$Ca(HEEN)(PIC)](PIC)$ (**2**)	+0.45	+0.34	+0.57	+0.51		
$Ba(HPEN)(PIC)_2$ (**3**)	−0.04	−0.22	+0.13	−0.10		
$[Na(HPEN)]_2(PIC)]_2$ (**4**)	+0.44	+0.51	+0.65	+0.66		
$[Ca(HPEN)(H_2O)_2](DNB)_2 \cdot 2H_2O$ (**5**)	−0.95	−0.20	−1.33	−1.26	−1.48	
$[Ca(HEEN)(H_2O)](DNB)_2 \cdot H_2O$ (**6**)	−1.95	−2.37	−2.22	−2.18	−1.35	
$[Sr(HPEN)(H_2O)_3](DNB)_2$ (**7**)	−0.62	−0.06	−0.35	0.0	+0.32	
$[Ba(HPEN)(H_2O)_2]_2(DNB)_4 \cdot 2H_2O$ (**8**)	+1.62	+1.49	+3.68	−8.23	+0.30	
$[Sr(HPEN)(H_2O)_2]_2(DNP)_2$ (**10**)	−0.71	−0.73	−0.72	−0.77	−0.61	−0.74
$[Ba(HPEN)(H_2O)_2](DNP)_2$ (**11**)	−0.02	−0.04	−0.05	−0.15	+0.42	−0.01
$[Ca(HEEN)(DNP)](DNP) \cdot H_2O$ (**12**)	+0.36	+0.17	+0.28	+0.29	+0.09	+0.65

8 exhibits only one doublet at δ 1.03 ppm (for the $-CH_3$ group), and its ^{13}C NMR shows only one signal due to each of the chemically equivalent CH_3, NCH_2CH_2 , NCH_2CH, and CH carbons. These results indicate that during formation of the $Ba(DNB)_2$ complex, only one of the diasteromer separates out. On using a 1:1 equiv ratio of HPEN−$Ba(DNB)_2$, 11−12% of **8** was obtained, and on increasing the concentration of HPEN to 2−4 equiv, the amount of the complex increased to 20−45%. Their results indicate that $Ba(DNB)_2$ preferably complexes with only one of the diastereomer of HPEN and other diastereomers remain in solution. In the case of **5** and **7**, both ^1H and ^{13}C NMR spectra have multiple signals attributed to complex formation by more than one diastereomer. A comparison of the ^{13}C NMR of $Ba(DNB)_2$ to **8** shows that on complexation all the a−e signals are shifted downfield except “d”, which is shifted upfield by δ −8.23 ppm. As the aromatic ring cannot undergo any conformational change during complexation, these changes in chemical shifts can be due to the variation of electron density only. The signal d shows electron gain and points toward the presence of an electron-rich group at “e” whereas all other carbons feel the effect of electron withdrawal. An upfield shift of this carbon can be explained by the formation of free DNB carboxylate ion during complexation of Ba^{2+} with HPEN, decreasing electrostatic interactions between carboxylate and Ba^{2+}, in complex **8**. It causes formation of CO_2^- and shifts the signal d upfield. The downfield shift of a−c reflects involvement of nitro groups in H-bonding. These results are in consonance with the X-ray structure of **8**. The Ca^{2+} complex retains its charge-separated structure in the solution form also as is obvious from an upfield shift of all of the aromatic carbons of DNB. There is almost no change in the chemical shift values of “b” and “d” carbons in **7** so it is impossible to make a comment on it. Most probably it dissociates in solution phase into its salt. In the solid state also this was observed to be a rather unstable complex dissociating very easily within 2−3 days. The $Ba(PIC)_2$ complex of HPEN (**3**) in solution phase does not follow any consistent trend and seems to have a different structure in solution than that observed in the solid. **1**, **10**, and **11** retain their solid-state charge-separated structures in the solution. **4** has downfield shifting suggesting removal of ligand from the metal ion in solution.

Bonding Modes of HPEN and HEEN. Both HPEN and HEEN have six potential donor atoms and may adopt different modes of coordination to the metal ion (Chart 1). The 1:1 metal ligand complexes may adopt any of the first four types of coordination depending on the size of metal ion, type of anion, and availability of the solvent. In types **I**−**III** and **V,** ligands behave as hexadentate chelating ligands whereas type **IV** has a heptadentate chelating-cum-bridging mode of coordination. Formation of a 1:2 complex (type **V**) like TEA[11a,b,d,g,f,16a,c,18,25] would only be possible for a metal ion with larger size and higher coordination number. The largest metal ion Ba^{2+} in our report is known to have a coordination number of 9−10 so none of the reported complexes have a 1:2 metal ligand ratio. The **Ia** type of complexation is quite rare in the case of neutral tripodand TEA ligand and has been found[11g] only in the case of Li^+. In the present case, this is expected to be a much preferred type of coordination for Ca^{2+} in the absence of strongly binding anions and in the presence of a solvent capable of H-bonding. A type **Ib** structure given by **1** and **5** is ideal for Ca^{2+} in coordination number 8 in the presence of water molecules, but type **IIa** is found in **2** and **12** when there is no water molecule present or a strongly binding anion is present in the complex. The Sr^{2+} complex **10** has a Sr−Sr nonbonding distance of 4.346(2) Å, which is comparable to 4.402 and 4.565 Å found in dimeric $[Sr(EO4)(H_2O)(DNB)_2]_2$ and $[Sr(EO3)(DNB)_2] \cdot 2H_2O$ complexes.[10a,c] Complex **8** has one terminal bonded water and one bridging water (type **IIIa**), whereas **9** and **11** have two bridging waters and no terminal water (type **IIIb**). The Ba−Ba nonbonding distance in these complexes varies as 4.832(1), 4.291(1), and 4.196(1) Å, respectively, showing an increase in the dimeric association with increasing number of bridging water molecules. Complex **3** adopts a **IIIb** type of coordination forming an ion-paired monomeric complex. Out of the four anions, picrate seems to have the highest affinity for Ba^{2+} so that it replaces the water molecules completely from the complex. The type **IV** mode of coordination is shown by only Na^+ in complex **4**, where HPEN is behaving as a chelating-cum-bridging ligand. The structure is similar to that found in the case of $[Na(TEA)I]_2$ and $[Na(TEA)(ClO_4)_2]$. TEA, however, forms an ion paired complex, but **4** is a totally charge-separated complex. Due to wrapping by larger HPEN which does not leave space for an anion to enter into the coordination sphere, one hydroxyl group undergoes bridging to satisfy the coordination of Na^+. The tendency of bridging by hydroxyl groups is much less in comparison to TEA where polymeric sheets or chains are formed due to bridging. Nevertheless, the nonbonding Na−Na distance of 3.430(3) Å in **4** is much shorter than 3.979(1) and 3.722(2) Å found in $[Na(TEA)(ClO_4)_2]$ and $[Na(TEA)I]_2$ complexes.

Role of Solvent and Hydrogen Bonding. Except for the three complexes of picrates **2**−**4**, the remaining nine complexes have water molecules in the coordination sphere, as lattice water or both. From the crystal structure data for **1** and **5**−**11**, involvement of water molecules in producing extensive hydrogen-bonding interactions is quite evident (Figures 2, 6, 11, and 12). Water here is displaying a dual role; it is coordinating to the metal ion on one side and is H-bonding to the anion on the other hand. As the ligands are offering a pseudocryptand-like cavity and are wrapping around the metal ion in three dimensions, only a small surface of metal ion is exposed to additional donor atoms from outside. This exposed portion can be conveniently occupied by smaller water molecules which push relatively bigger anions outside the coordination sphere; thus, water molecules are relatively preferred by the metal ion in comparison to the anions. Ligands HPEN and HEEN also have a dual character as they contain four polarizable hydroxyl hydrogens. So apart from grabbing the metal ion, they also H-bond to the anions and water molecules. A combination of (1) polarizable hydroxyl oxygens available for H-bond donation, (2) water molecules which are capable of H-bond donation/acceptance, and (3) H-bond-accepting phenolic, carboxyl, or nitro oxygens gives rise to an extensive H-bonding network in of these complexes. This stabilization of the anion, via H-bonding by water, excludes them from coordination to the metal ion producing a total charge separation in all of these eight complexes (**1**, **5**−**11**).

The Ba(PIC)$_2$ complex of HPEN (**3**) has no water molecules in its structure. There are only four intramolecular H-bonding interactions between hydroxyl oxygens and the anion. Lack of extensive H-bonding in the crystal results in a lesser decrease of the nucleophilicity of the anion and leads to an increase in cation−anion interactions. This gives rise to a tight ion-paired complex. Similarly complex **2** which lacks water also gives rise to a partially charge-separated complex. The picrate anion which is directly coordinated to the metal ion is not involved in any H-bonding, but the uncoordinated one is forming four intramolecular H-bonds with hydroxyl oxygens of HEEN and is also being stabilized by a face to face $\pi\cdots\pi$ interaction (3.8 Å). The same is true in the complex **12**. Only the uncoordinated DNP is involved in a strong H-bonding interaction with the ligand and the water molecule. This further endorses the observation that simultaneous stabilization of the counteranion decreases its nucleophilicity. [Na(HPEN)]$_2$(PIC)$_2$ is the only complex which does not have water molecules in it but is still giving a charge-separated complex. Although the ionic radii of Na$^+$ and Ca^{2+} are comparable, the charge/radius ratio of Ca^{2+} is more than Na$^+$. At the same time, due to −CH$_3$ groups of the HPEN ligand, there is steric crowding around the Na$^+$ ion which discourages coordination by the anion. Therefore, in the absence of water molecules, Na$^+$ satisfies its coordination sphere by sharing one hydroxyl oxygen between two metal ions, resulting in a charge-separated complex.

Cavity Shape and Size. Both the ligands offer a pseudocryptand type of cavity on complexation. The M−O(ligand) distance in each complex is shorter than its corresponding M−N distance by ∼0.2 Å. The longer M−N distance indicates that the metal is relatively far away from nitrogen and is closer to oxygens. So the pseudocavities being offered in each case are elliptical in shape (except **4**). In **4** Na$^+$ is totally encapsulated in an almost spheroidal cavity offered by heptadentate bridging-cum-chelating ligand HPEN. To cover the metal ion completely, the bridging O4 moves a little away from Na and comes closer to the centrosymmetrically related Na$^+$ in the dimer. There is no preformed cavity in podands, and they fold during complexation to provide a pseudocavity; therefore, this cavity size may vary depending on the metal ion in question. The nitrogens N1 and N2 of these ligands remain at the top of the pyramid, and four hydroxyl oxygens converge together to form the complex. The cavity sizes were calculated by measuring O$\cdots$O nonbonding distances between those two pairs of oxygens which are trans to each other (O−M−O angles close to 180°). These O$\cdots$O distances range 4.566−4.894 Å for Ca^{2+}, 4.992−5.069 Å for Sr^{2+}, and 5.049−5.498 Å for Ba^{2+} complexes. Thus, in the order from Ca^{2+} to Ba^{2+}, the ligands gradually open up to accommodate the ions of increasing radii. Mean plane calculations indicate that smaller Na$^+$ and Ca^{2+} are more in toward the pseudocryptand cavity with the larger Ba^{2+} ions out of the cavity and medium-sized Sr^{2+} is lying between these extremes.

Role of Anions. In this report only PIC and DNP have been seen to coordinate to the metal ion in **2**, **3**, and **12**, respectively. The ONB and DNB anions have not given any ion-paired complex and are extensively involved in H-bonding interactions. The Ca(DNB)$_2$ complexes with HPEN and HEEN (**5** and **6**) are both charge separated. Ca(PIC)$_2$ gives a charge-separated **1** complex with HPEN and partially charge-separated **2** complex with HEEN, and Ca(DNP)$_2$ gives a partially charge-separated **12**. A similar situation is found in Ca^{2+} complexes with TEA. Both Ca(TEA)$_2$(DNB)$_2$ and Ca(TEA)$_2$(PIC)$_2$ are charge separated,[11a,f] but Ca(TEA)$_2$(DNP)$_2$ is an ion-paired complex.[11e] From these results, it may be concluded that a high charge density cation like Ca^{2+} has the strongest affinity for DNP and PIC and a lesser affinity for weaker nucleophiles such as benzoates. The Ca^{2+}−anion interaction thus decreases along the series DNP > PIC >DNB. Sr(DNB)$_2$ and Sr(DNP)$_2$ complexes of HPEN (**7** and **10**) are both charge separated. Also Sr(TEA)$_2$(DNP)$_2$, Sr(TEA)$_2$(PIC)$_2$, Sr(TEA)$_2$(N$_3$)$_2$, Sr(TEA)$_2$(NO$_3$)$_2$, and Sr(TEA)$_2$Cl$_2$ are all charge-separated complexes.[11b,f,16a,c,d] Sr^{2+} has lesser charge density than Ca^{2+}, and its interactions are thus weakened with the anions which get easily displaced by a pseudocryptate ligand TEA or even by water in the case of tetrapodands.

Ba^{2+} has a larger size and hence has a lesser charge density than even Sr^{2+} so is expected to form only charge-separated complexes. The situation in Ba^{2+} complexes is not that simple as because of its size it prefers a higher coordination number than its predecessors. Tetrapodands by forming 1:1 metal ligand complexes are not able to fully encapsulate the metal ion and satisfy its coordination number. In the absence of competing solvent molecules it picks up the anion to form an ion-paired complex. Even a weaker anion would find its way to the metal producing partially charge-separated or ion-paired complexes although the interaction would be a weaker one. This is well illustrated in TEA complexes of Ba^{2+}. $Ba(TEA)_2(acetate)_2$ is a partially charge-separated complex,[18] and $Ba(TEA)_2(ClO_4)_2$ and $Ba(TEA)_2(PIC)_2$ are both loose ion pairs.[11c,25] These three anions form weak ninth and tenth interactions with Ba^{2+}. Only a strong nucleophile like DNP gives a strong ninth bond with Ba^{2+} in the case of $Ba(TEA)_2(DNP)_2$ in the absence of a competing solvent.[11d] In the presence of an H-bonding solvent like water, even DNP is displaced by it to give a charge-separated complex in **11**, where the coordination number 10 is achieved by two bridging water molecules. Similarly **8** and **9** are totally charge-separated complexes of Ba^{2+} due to the presence of dual character water molecules. Only the $Ba(HPEN)_2(PIC)_2$ (**3**) complex is a true ion pair in the absence of any water molecule. This could also be related to a dominant ionic (lesser covalency of Fajan's type) and hence chemically inert nature of lower charge density Ba^{2+} paired with low charge density picrate as is known for water-inert $K^+\cdots PIC^-$ compared to water-reactive $Na^+\cdots PIC^-$.[26]

Conclusions

The hydrogen bonding among ligand −OH groups, coordinated water molecules, and the anion is a very important interaction. In all charge-separated complexes the negatively charged end of the anion is involved in extensive hydrogen bonding with −OH groups and coordinated water molecules. This results in decreasing the nucleophilicity of the anion, and charge-separated complexes are likely to form. The ion-paired or partially charge-separated complexes are formed when the H-bonding interactions are diminished or absent due to (1) the nonavailability/lesser number of solvent molecules, (2) the presence of only intramolecular H-bonding, (3) the stronger affinity of the anion for the metal ion, (4) the stabilization of the anion moiety due to other interactions such as $\pi\cdots\pi$ interactions, and (5) the disfavorable orientation of the anion with respect to the polarizable H of the ligand.

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Supporting Information Available: Text giving complete experimental procedures and analytical data, tables of X-ray data, and X-ray data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] *Vogel's Text Book Of Quantitative Inorganic Analysis*, 4th ed.; Bassett, J., Denney, R. C., Jeffery, G. H., Mendhan, J., Eds.; Longman Press: Essex, England, 1978; p 849.