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The important effect of the ligand architecture on the selectivity of metal ion recognition in An(III)/Ln(III) separation with N-donor extractants.

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The existence of a strong correlation between the ligand architecture and the metal ion binding selectivity is demonstrated through the large differences in the separation efficiencies found in the selective extraction of Am^{3+} from an acidic mixture of Am^{3+} and Eu^{3+} for three new tetrapodal hexadentate ligands containing four 2-pyrazinyl-methyl groups attached to three different diamino spacers.

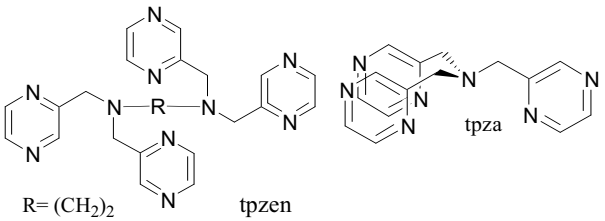
Ligand architecture is a key factor in the control of metal ion binding affinity in metal ion recognition[1] second only in importance to the choice of ligand donor atom type according to the hard and soft acid-base classification of Pearson[2]. Hay and Hancock have recently pointed out the crucial importance of the proper orientation of the donor atoms with respect to the metal ion.[3] This is an aspect of metal-ligand complementarity that is often overlooked in the optimisation of covalent or electrostatic metal-ligand interactions. Very recently Hay and coworkers reported an example where deliberate design of ligand architecture yielded an enhancement in metal ion binding affinity.[4]

Here we provide a rare example of how a small variation in the ligand architecture can lead to a strong enhancement in the selectivity of metal ion binding.

The design of selective extractants for the separation of trivalent actinides from trivalent lanthanides is one of the main problems in nuclear waste reprocessing.[5] Heterocyclic imines have been reported to complex actinides(III) more strongly than lanthanides(III), owing to a greater covalent contribution to the metal-nitrogen bonding. Tridentate ligands such as 2,2':6,2"-terpyridine, 2,4,6-tris(4-alkyl-2-pyridyl)-1,3,5-triazine,[6] 2 , 6 -bis(5-alkyl-1,2,4-triazol-3-yl)pyridine, 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine[7] and tetradentate tripodal oligoamines such as tris[(2-pyridyl)methyl]amine (tpa) and tris[(2-pyrazinyl)methyl]amine (tpza)[8] have been shown to selectively extract actinides in preference to the lanthanides from nitric acid solutions into an organic phase. The higher selectivity shown by the tpza ligand with respect to tpa has been explained by the softer character of the pyrazinyl group with respect to the pyridyl group, which is expected to give rise to a stronger interaction with the actinides. In spite of the large number of N-donor extractants studied, the relationship between the architecture linking the donor atoms of the extractant and its selectivity remains unexplored. In order to maximize the metal-pyrazine interaction and therefore the selectivity we have designed new ligands containing four 2-pyrazinylmethyl units connected through a more flexible spacer with respect to tpza.

Here we report the extraction properties of the three new neutral hexadentate N-donor ligands containing four 2-pyrazinyl-methyl groups *N,N,N',N'*-tetrakis(2-pyrazinylmethyl)ethylenediamine (tpzen), *N,N,N',N'*-tetrakis(2-pyrazinylmethyl)*trans*-1,2-cyclohexanediamine (tpzcn) and *N,N,N',N'*-tetrakis(2-pyrazinylmethyl)trimethylenediamine (tpztn) and the crystal structure of their lanthanum iodide complexes. These ligands can be seen as the flexible hexadentated tetrapodal analogs of the semirigid tetradentate tripodal ligand tpza.

Tpzen, tpzcn and tpztn have been prepared in 75% yield by reacting 2-chloromethylpyrazine with ethylenediamine, *trans*-1,2-cyclohexanediamine or trimethylenediamine in the presence of K_2CO_3 as base.†



R= $(CH_2)_2$ tpzen
R= $(CH_2)_3$ tpztn
R= *trans*-1,2-c-C_6H_{10} tpzcn

The iodide salts of the lanthanum complexes of tpzen, tpztn and tpzcn were isolated from anhydrous acetonitrile‡ and their crystal structure was determined in order to investigate how these ligands bind f elements. Two different crystal structures,

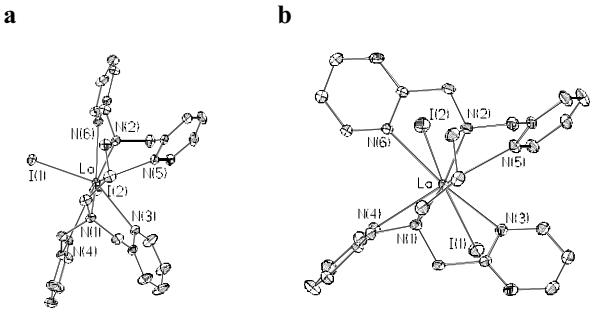


Fig.1 a)Crystal structure of the cation $[La(tpztn)I_2]^+$ in **1a,** with thermal ellipsoids at 30 % probability. Selected bond lengths (Å): La-N(1) 2.787(3), La-N(2) 2.753(3), La-N(3) 2.680(3), La-N(4) 2.794(3), La-N(5) 2.731(3), La-N(6) 2.759(3), La-I(1) 3.1014(4), La-I(2) 3.1786(4). b) Crystal structure of the cation $[La(tpztn)I_2]^+$ in **1b,** with thermal ellipsoids at 30 % probability. Selected bond lengths (Å): La-N(1) 2.705(2), La-N(2) 2.731(2), La-N(3) 2.705(2), La-N(4) 2.670(3), La-N(5) 2.637(2), La-N(6) 2.670(2), La-I(1) 3.1645(3), La-I(2) 3.2089(2).

1a and **1b**, were determined by X-ray crystallography for the complex $[La(tpztn)I_2]I$, **1**.§ In both structures, the lanthanum ion is eight-coordinated by the six nitrogens of tpztn and by two iodides, but the conformation of the tetrapodal ligand is different and results in a different coordination geometry of the La ion (a distorted dodecahedron in **1a** and a distorted square antiprism in **1b**). This difference in the orientation of the methylpyrazinyl arms leads to significant differences in the values of the metal-

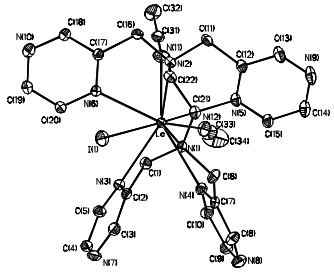


Fig.2 Crystal structure of the cation $[La(tpzen)(MeCN)_2I]^+$ in **2**, with thermal ellipsoids at 30 % probability. Selected bond lengths (Å): La-N(1) 2.734(3), La-N(2) 2.698(3), La-N(3) 2.748(3), La-N(4) 2.661(4), La-N(5) 2.704(4), La-N(6) 2.703(4), La-N(11) 2.650(4), La-N(12) 2.666(4), La-I(1) 3.2379(5).

nitrogen distances (mean value of La-Npyrazine = 2.74(5)Å for **1a** and =2.67(3) Å for **1b**) confirming the important effect of the metal-ligand orientation on the strength of the metal-ligand interaction. The structure of the lanthanum complex of tpzcn shows a eigth-coordinated La with the same orientation of the methylpyrazinyl groups as observed in **1b**.¶ The crystallographic determination of the structure of the lanthanum complex of tpzen, $[La(tpzen)(MeCN)_2I]I_2$, **2**,§ reveals the presence of a La(III) ion nine-coordinated by six nitrogens of the tpzen ligand, one iodide and two acetonitrile nitrogens. The orientation of the methylpyrazinyl groups is different from those observed for **1a** and **1b**. It is likely that a different ligand conformation is favored by the tpzen structure with respect to that of tpztn or tpzcn, leading to a change in the coordination environment of the metal ion.

Table 1 Distribution ratios and separation factors of tpza, tpzen, tpztn, tpzc

Ligand	[L] (mol/l)	$[HNO_3]$ini	$^{a}D_{Am(III)}$	$D_{Eu(III)}$	$^{b}SF_{Am/Eu}$
tpza	0.02 [8a]	0.06	0.004	0.0004	10
	0.1	0.06	0.2	0.008	23
tpzen	0.02	0.06	0.02	0.0005	35
	0.1	0.06	0.5	0.007	66
	0.1	0.03	45	0.6	70
tpztn	0.08	0.06	0.2	0.1	2.3
	0.08	0.04	1.1	0.5	2.2
	0.2	0.06	79	54	1.5
tpzcn	0.02	0.04	0.004	0.002	2
	0.05	0.02	0.04	0.02	2

[a] The distribution ratio D_M for a metallic cation M is defined as the ratio of the concentration of the metallic species in the organic phase in the presence of α-bromodecanoic acid as cationic exchanger (1mol/L in TPH) over its concentration in the aqueous phase.
[b] The separation factor $SF_{M1/M2}$ for two metallic cations M_1 and M_2 is defined as the ratio of their distribution ratios.

The synergistic extraction of trace amounts of americium(III) and europium(III) from a nitric acid solution using α-bromodecanoic acid as cationic exchanger in the presence of these tetrapodal ligands has been studied. Distribution coefficients of americium(III) and europium(III) for the ligands tpza, tpzen, tpzcn and tpztn at different ligand concentration are given in Table 1. The tetrapodal ligand tpzen leads to an enhanced Am(III)/Eu(III) separation and to an improved extraction efficiency with respect to tripodal tpza. A large difference in selectivity is observed between the tetrapodal ligand tpzen, which is found to have one of the largest separation efficiencies so far reported for aza-aromatic extractants, and the ligands tpztn and tpzcn which have no selectivity at all. The increase in selectivity observed for tpzen with respect to tpza can be attributed to the presence of an additional soft pyrazinyl group associated with an improved metal–ligand interaction due to the higher flexibility of tpzen. The drastic difference in selectivity observed between tpzen and tpztn or tpzcn cannot be explained by sterical interactions or chelate effect. Indeed although tpztn forms 6-ring chelates and is expected to yield a decrease in stability with respect to tpzen which forms 5-ring chelates, tpzcn forms 5-rings chelate like tpzen and is preorganized into the skew form required for complex formation and should then lead to increased complex stability compared to tpzen. *Only a difference in the conformations preferred by the three ligands due to the different ligand architecture can then account for the different separation efficiencies.* The conformation adopted by tpzen probably allows a maximized Am(III)-Npyrazine covalent interaction and therefore leads to a better selectivity.

In summary we have demonstrated the existence of a relation between the ligand architecture and selectivity in the preferential extraction of Am(III) with respect to Eu(III). This results highlight a new parameter to be considered in the deliberate design of selective extractants. Further investigations of the relation between selectivity and ligand architecture including the elaboration of different ligand architectures are currently under way and will be described, together with the details of the synthesis and the solution coordination properties of ligands tpzen, tpzcn and tpztn, in a forthcoming report.

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Notes and References

† ^{1}H NMR is given in the supplementary information.
‡ *Synthesis*: Complexes **1** and **2** were prepared in (60-90%) yield by reacting $LaI_3(thf)_4$ with tpztn or tpzen in anhydrous acetonitrile.
^{1}H NMR (CD_3CN, 400 MHz, 298 K), δ (ppm): for **1**:8.73 (H3, d, 4H), 8.98 (H6, dd, 4H), 8.64 (H5, d, 4H), 4.20, 4.73 (quartet AB, 8H, Ha, Hb), 3.22 (t, 4H, -N-*CH*$_2$-CH$_2$-*CH*$_2$-N), 2.00 (q, 2H, -N-CH$_2$-*CH*$_2$-CH$_2$-N). For **2**: 8.74 (H3, d, 4H), 9.04 (H6, dd, 4H), 8.64 (H5, d, 4H), 4.36, 4.52 (quartetAB, 8H, Ha, Hb), 3.11 (s, 4H, -N-CH$_2$-CH$_2$-N).
§ *Crystal data*: for complex **1a**, $[La(tpztn)I_2]I$, $C_{23}H_{26}I_3N_{10}La$: M= 962.15, monoclinic, P2(1)/n, a = 17.635(1), b = 9.9451(6), c = 17.981(1) Å, β = 110.997(1)°, V = 2944.2(3) Å^3, Z = 4, D_c = 2.171 g cm^{-3}, μ = 4.628 mm^{-1}. 7003 independent reflections ($2\theta_{max}$ = 57.8) were collected at 223(2) K. $R_1[F> 4\sigma(F)]$ = 0.0404, wR2 = 0.0925. Maximum/minimum residual electron density: 2.000 and -1.910 e.Å^{-3}.
For complex **1b** $[La(tpztn)I_2]I.1.17$ MeCN , $C_{25.33}H_{29.50}I_3N_{11.17}La$: M= 1109.16, rhombohedral, R3c, a = 33.4373(13), c = 15.1099(8) Å, V = 14630.3(11) Å^3, Z = 18, D_c = 2.266 g cm^{-3}, μ = 7.876 mm^{-1}. 7890 independent reflections ($2\theta_{max}$ = 57.8) were collected at 223(2) K. $R_1[F> 4\sigma(F)]$ = 0.0306, wR2 = 0.0705. Maximum/minimum residual electron density: 2.737 and -1.570 e.Å^{-3}.
Crystal data for complex **2**, $[La(tpzen)I(CH_3CN)_2]I_2.2MeCN$, $C_{30}H_{36}I_3N_{14}La$: M= 1112.34, monoclinic, P2(1)/n, a = 11.4266(16), b = 14.839(2), c = 22.916(3) Å, β = 93.065(3)°, V = 3880.1(10) Å^3, Z = 4, D_c = 1.904 g cm^{-3}, μ = 3.529 mm^{-1}. 9297 independent reflections ($2\theta_{max}$ = 57.9) were collected at 293(2) K. $R_1[F> 4\sigma(F)]$ = 0.0336, wR2 = 0.0889. Maximum/minimum residual electron density: 2.061 and -1.805 e.Å^{-3}.
¶ Unpublished results.

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X

Fig./Scheme XX Caption.

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