#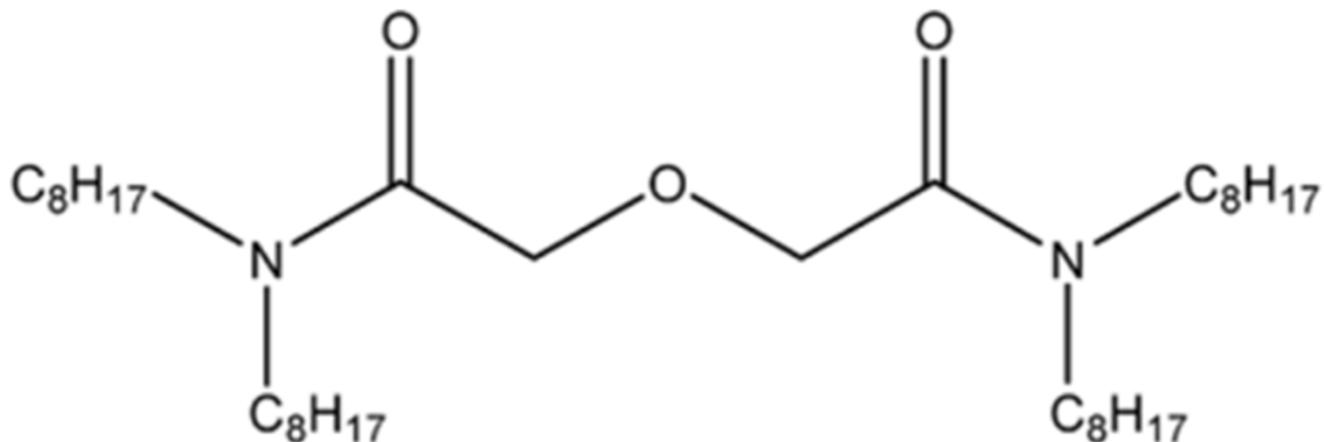 Are diglycolamide ligands hard or soft Lewis bases? Implications on their complexation and solvent extraction separation of lanthanides and actinides

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TODGA, *N,N,N′,N′*-tetraoctyl-diglycolamid, very efficient, but non-selective extractant of Ln i An(III) from aqueous HNO$_3$ solutions

Conclusions and hypotheses presented in this lecture are based on the analysis of the quantum-mechanical calculations by A. Wodyński, presented in:

Narbutt J., Wodyński A., Pecul M.: „On the selectivity of diglycolamide (TODGA) and bis-triazine-bipyridine (BTBP) ligands in actinide/lanthanide complexation and solvent extraction separation – a theoretical approach", *Dalton Transactions*, 2015, **44**, 515-521

Aim of the theoretical studies

1. To understand why TODGA ligand is a non-selective extractant of An^{3+} i Ln^{3+}

2. To compare the selectivity of complexation of An^{3+} i Ln^{3+} with the **soft** N-donor ligand CyMe$_4$-BTBP, selective for Am^{3+}, and with the **hard** (**as expected**) O-donor TODGA.
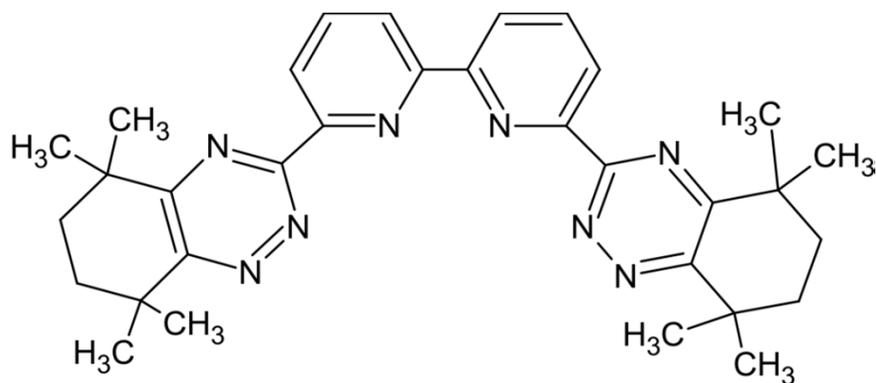
CyMe$_4$-BTBP
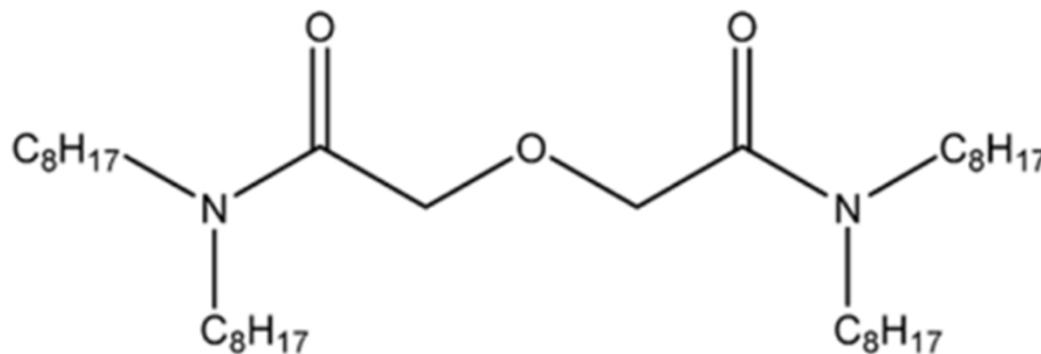
TODGA

Ligands with **oxygen donor atoms,** also from alkylamide groups (e.g. TODGA), are **commonly** (see the list below) **considered hard Lewis bases** (according to Pearson's HSAB concept).

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Our results

Optimization of the structures of cationic complexes (1:3) of Am^{3+} an Eu^{3+} with TEDGA ligand (homologue of TODGA)

M–L	d (Å)	angle	deg
Am–O_{am}	2.46	O_{am}-Am-O_{eth}	59.8
Am–O_{eth}	**2.65**	O_{am}-Am-O_{am}'	119.8
Eu–O_{am}	2.42	O_{am}-Eu-O_{eth}	60.6
Eu–O_{eth}	**2.62**	O_{am}-Eu-O_{am}'	120.7
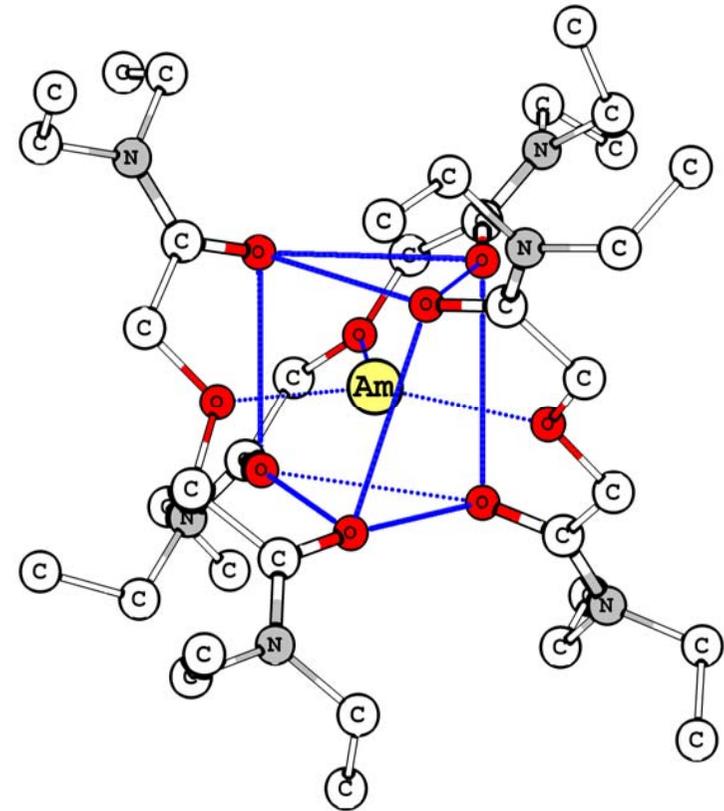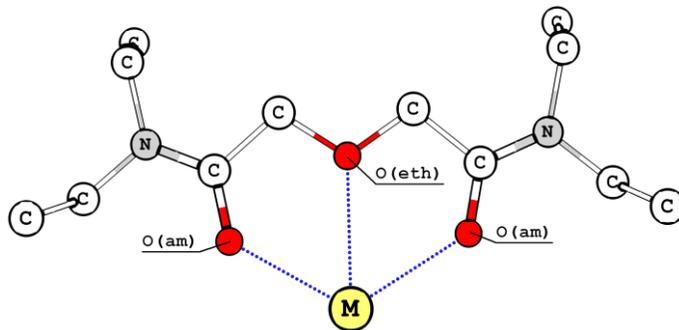
$$d(Am–O_{amide}) << d(Am–O_{ether}) \text{ i } d(Eu–O_{amide}) << d(Am–O_{ether})$$
$$\text{oraz } d(Am–O) > d(Eu–O)$$

Pearson's concept of Hard/Soft Acids/Bases (HSAB) in coordination chemistry – recapitulation

Chemical hardness/softness of ligand molecules (L) can be considered in terms of the amount of electron density donated by the ligand (Lewis base) to the central metal ion (Lewis acid) in the complex.

Hard ligands donate little electron density, and interact with the metal ion mainly *via* electrostatic attraction, forming the M–L bonds of mainly ionic character.

Soft ligands donate much more electron density, and interact with the metal ion forming the M–L bonds with a significant covalent contribution.

The results of our QM calculations will be analyzed in terms of the above recapitulation.

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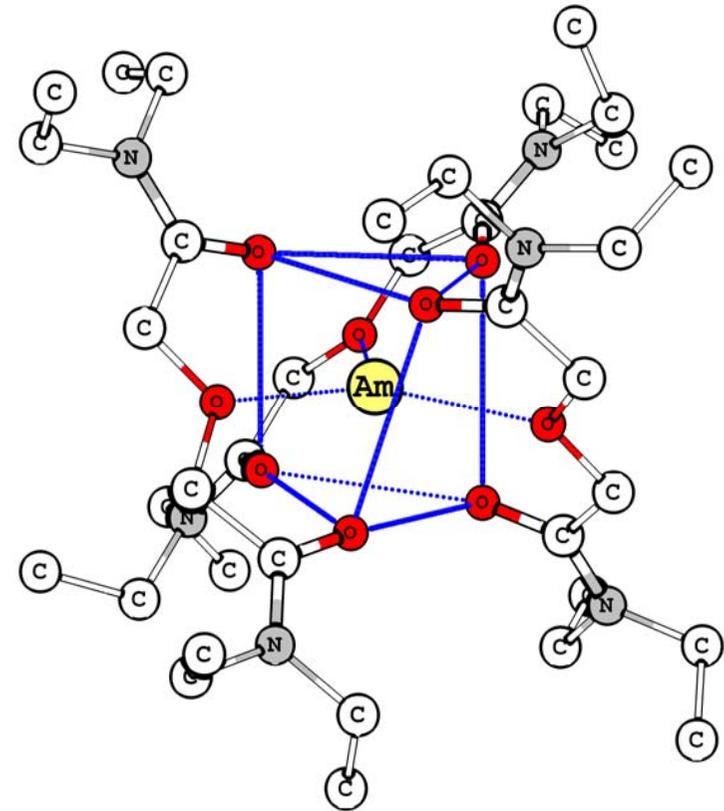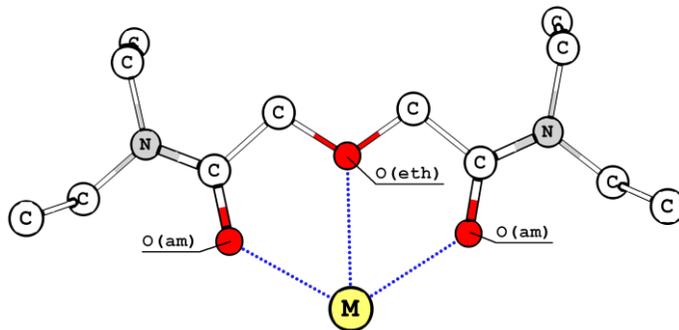
$d(Am–O_{amide}) << d(Am–O_{ether})$ i $d(Eu–O_{amide}) << d(Am–O_{ether})$

oraz $d(Am–O) > d(Eu–O)$

Natural Population Analysis: Total shifts of electron density on the central metal ion from the fragments of TEDGA ligand: amide and etheral groups
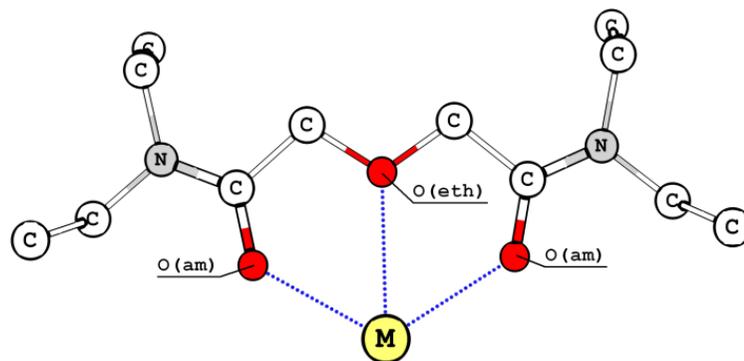
Average parial charges on the atoms and the amide and etheral groups in TEDGA ligands; free (L) and in the $[ML_3]^{3+}$ complexes, calculated with the use of Mulliken method. Shifts of electron density, Δq, from each group on the metal ions in the complexes

species	M	O_{am}	O_{eth}	amid	ether	Δq_{amid}	Δq_{eth}
$[AmL_3]^{3+}$	1.98	−0.64	−0.58	0.149	0.045	0.14	0.07
$[EuL_3]^{3+}$	2.03	−0.65	−0.58	0.147	0.031	0.14	0.05
L	-	−0.55	−0.48	0.010	−0.022	-	-

$$\Delta q(amid) > \Delta q(eth)$$

(but not in all the calculation methods used)

The conclusion on the greater covalency of M–O$_{amid}$ than M–O$_{ether}$ bonds results as well from quantum-mechanical bond analysis in the [M(TEDGA)$_3$]$^{3+}$ complexes: e.g. from Wiberg bond indices; from QTAIM parameters of the M–O bonds (e.g. electron densities, ρ_b, in the Bond Central Point) etc.; cf. the original paper in Dalton Trans. 2015.

This conclusion is also in line with the calculated bond lenghts: d(M–O$_{ether}$) > d(M–O$_{amid}$) by ~0.2 Å.
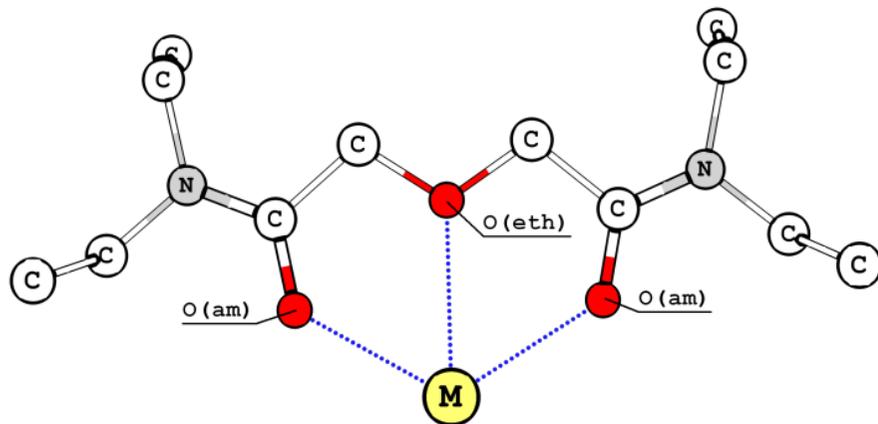
In general, all the M–O bonds are mainly of ionic character with some covalent contribution.

According to the concept of different „local hardness" of molecules (see e.g. M. Torrent-Sucarrat, F. De Proft, P. W. Ayers, P. Geerlings, *Phys. Chem. Chem. Phys.*, 2010, 12, 1072), we could distinguish in the TODGA ligand one 'hard' donor atom, O(ether), and two relatively 'soft' O(amide) atoms. To check this unexpected hypothesis we calculated the hardness (η) of both ligands: C2-BTBP and TEDGA:

$$\eta = \tfrac{1}{2}(IP - EA)$$

where IP - ionization energy, and EA - electron affinity of the molecule.

The ionization energies, IP, electron affinities, EA,
and chemical hardness, η, [eV], of some ligands

species	TEDGA	C2-BTBP	H_2O	H_2O	ether[x]	ketone[y]	amide[z]
source	Our calculations			Literature data			
IP	7.92	7.27	12.7	12.6	10.0	9.7	-
EA	–0.94	0.56	–1.49	–6.4	–6.0	–1.5	-
η	4.43	3.36	7.1	9.5	8.0	5.6	2.7

[x] CH_3-O-CH_3; [y] CH_3-(C=O)-CH_3; [z] CH_3(C=O)N(CH_3)$_2$

The calculations show that in spite of the common opinion the diglycolamide ligands, e.g. TODGA, are relatively soft, which is probably due to the presence of the two donor oxygen atoms od the amide groups.

What can be the effect of this idea?

The hypothesis on the relative softness of the ligands with „soft" donor oxygen atoms of the amide or even carbonyl groups allows us to explain the results of numerous experimental and theoretical studies on the rational way. In my opinion, it is a more plausible interpretation of QM calculations indicating a greater covalency of the Am–O than Eu–O bonds in 2,9-dicarboxyl-1,10-phenantroline complexes than that given by Manna and Ghanty (*Phys. Chem. Chem. Phys.*, 2012, 14, 11060): *"the presence of softer nitrogen atoms in the Phen moiety ... has a profound influence in changing the soft nature of the actinide ion, which in turn binds with the hard oxygen atoms in a stronger way"*.
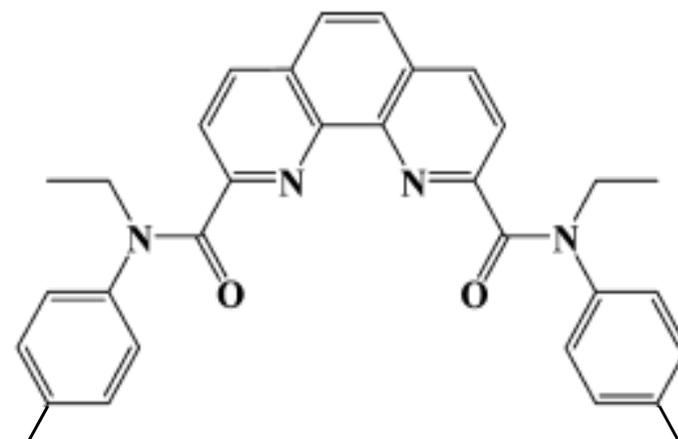
Recently, Mariani et al. (*Dalton Trans*., 2013, <u>42</u>, 16930) reported the stronger coordination affinity to Am^{III} and Eu^{III} ions of the amide oxygen atoms in 2,9-diamide-1,10-phenantroline than that of the ketone oxygen atoms in 2,9-diketone-1,10-phenantroline. Also, this difference can be interpreted in terms of the greater softness of amides than of ketones (see the Table above).

New hypothesis have been formulated and theoretically tested, on the effect of substituents, R, in the amide groups, $O=C-NR_2$, in the ligands (extractants), that would hopefully allow to control the shift of electron density on the central metal ion from the ligands, i.e. to control the Hardness / softness of the ligands.

Appendix

The comparison of C2-BTBP and TEDGA complexes
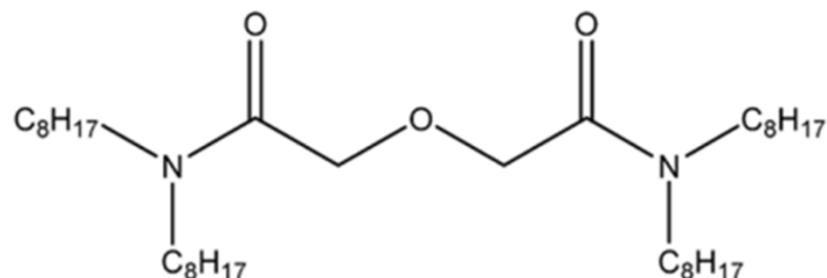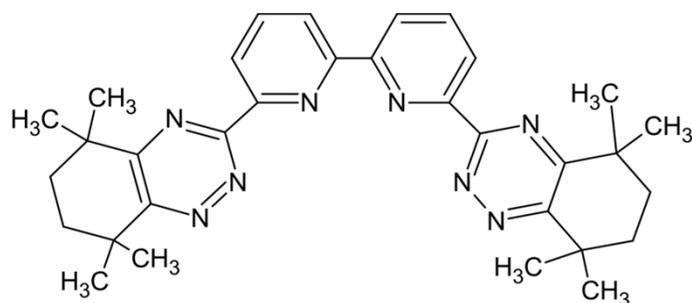
NPA analysis of atomic orbitals

Electron density distribution on the sub-shells of Am^{3+} and Eu^{3+} ions in kationic complexes with C2-BTBP and TEDGA ligands.

complex	M = Am	M = Eu
[M(BTBP)$_2$]$^{3+}$	[core] 7s(0.16) 5f(6.14) **6d(0.71)**	[core] 6s(0.14) 4f(6.12) **5d(0.58)**
[M(TEDGA)$_3$]$^{3+}$	[core] 7s(0.14) 5f(6.13) **6d(0.71)**	[core] 6s(0.13) 4f(6.07) **5d(0.61)**

Unexpectedly, similar shifts of electron density from two ligands on the central metal ions have been calculated, both from the seemingly hard TEDGA and from the soft BTBP; in fact, greater from BTBP, but the difference is not so big.

Total shifts of electron density from the ligands are greater on the Am^{III} than on $Eu^{III} \rightarrow$ the Am–N and Am–O bonds are more covalent than Eu–N and Eu–O ones.

The energy and Gibbs free energy of formation of the $[M(TEDGA)_3]^{3+}$ complexes are less negative than the respective values of the $[M(BTBP)_2]^{3+}$ complexes, but the differences are not so big, less than 10 kJ/mol.

Thank you for your attention