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Structural characterization of [Ln$(TFA)_3(HMPA)_3$] (Ln=La, Nd, Er) complexes

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Abstract

The X-ray data on La, Nd, Er complexes ([Ln$(TFA)_3(HMPA)_3$]) show that they crystallize in different forms depending on the solvent content. Er is six and seven coordinated in the two complex cations coexisting in the crystal cell: $[Er(TFA)_2(HMPA)_4]^+$ and $[Er(TFA)_2(HMPA)_2(H_2O)_3]^+$. The trifluoroacetate anions are monodentate in both coordination polyhedra. In the $[Nd(TFA)_2(HMPA)_4]^+$ cations, Nd is eight coordinated with bidentate trifluoroacetate ligands.

Keywords: Lanthanides; Trifluoroacetate; Hexamethylphosphoramide; Structures

1. Introduction

The interest for the study of the hexamethylphosphoramide (HMPA) lanthanide complexes containing trifluoroacetates (TFA) as counter ions is related to the possibility for the latter to act as monodentate or bidentate or bridging different metal ions with the formation of polynuclear species. Previous studies on lanthanide complexes with halides and HMPA, have shown the possibility to obtain 1:3 complexes of the type $LnCl_3L_3$ [1] or 1:4 complexes of the type $LnBr_3L_4(H_2O)_3$ [2]. Isomeric forms with relative different positions of the anionic and the oxygen donor neutral ligands can be obtained for the 1:3 derivative: three chlorines and three oxygens (from HMPA) *cis* to each other or with *trans* positions for two chlorines and two oxygens. This latter isomer is preferred in the crystals owing to the steric demands of the ligands [1]. The use of the more steric demanding trifluoroacetates anions expands the type of possible derivatives that can be obtained, as beside the possible isomeric forms, different stechiometries can be postulated.

Spectroscopic studies on the series of complexes $Ln(TFA)_3(HMPA)_3$ (Ln=La, Nd, Eu, Gd, Dy, Ho and Er) did not allow a clear identification of the coordination mode for the trifluoroacetate anion along the series of compound [3]. Here we present some results obtained by X-ray single crystal analysis on the complexes of possible composition $Ln(TFA)_3(HMPA)_3$ (Ln=La, Nd, Er).

2. Experimental

The synthesis of La, Nd and Er derivatives has been made by dissolving the hydrate salts in absolute ethanol with HMPA (in acetone) in a 1:3 molar ratio [3]. They were recrystallized from ethanol in the form of white prismatic crystals La and Er, pale violet prisms Nd.

2.1. Crystal data

For erbium derivative a crystal of approximate dimensions 0.10×0.15×0.22 mm was mounted on a Nonius Kappa CCD with graphite-monochromated MoKα radiation, and the complete set of data was collected. The intensities were corrected for Lorentz-Polarization effects and for absorption, (Blessing's empirical method [4]). Computing cell, refinement and data reduction were done by DENZO-SMN [5]. In Table 1 are reported the crystal data.

The structure was solved by standard heavy atom

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Table 1
Crystal data

Compound	$[Er(TFA)_2(HMPA)_4][Er(TFA)_2(HMPA)_2(H_2O)_3]\cdot 2(TFA)\cdot H_2O$
Chemical formula	$Er_2P_6N_{18}C_{48}O_{22}F_{18}H_{116}$
Formula weight	2159.90
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.548(2)
b/Å	14.900(2)
c/Å	41.604(9)
β/°	92.73(2)
V (Å^3)	9627(3)
Z	4
T, °C	293(2)
D_{calc}, g cm^{-3}	1.49
F(000)	4376
μ(MoKα) cm^{-1}	19.31
No. reflections collected	15 928
No. observed [$I \geq 3\sigma(I)$]	10 849
Weight	$1/[\sigma^2(Fo^2) + 0.0994\ P)^2 + 65.64\ P^*]$
R (Fo)[a]	0.069
R_w (Fo^2)[b]	0.193
Goodness of fit	1.19

[a] $R(Fo) = \Sigma|Fo| - |Fc|/\Sigma|Fo|$.
[b] $R_w\ (Fo^2) = \Sigma(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.
* $P = \max(Fo^2 - Fc^2)^2/3$.

method. Refinement was carried out by full-matrix least-squares; the function minimized was $\Sigma w(Fo^2 - Fc^2)^2$, with weighting scheme $w = 1/[(2(Fo^2) + 6.54\ P]$, where $P = \max(Fo^2 + 2Fc^2)/3$. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 Uequiv of the parent carbon atom).

SHELXL-93 [6] program was used for structure refinement and final geometrical calculations, drawings were produced using ORTEP II [7]. Selected geometric parameters are reported in Table 2.

For La the bad quality of the crystals and their easy decomposition under X-ray did not allow the crystal structure determination and only crystal cell parameters have been determined, while for Nd a partial structure determination (due also in this case to the poor quality of the diffraction data) has been possible.

$[Nd(TFA)_2(HMPA)_4]\cdot(TFA)\cdot x(H_2O)\cdot(EtOH)$, monoclinic (space group $P2_1/a$), $a = 27.814(4)$, $b = 17.548(3)$, $c = 39.148(6)$ Å, $\beta = 90.00(5)°$, $V = 19140$ Å^3, $Z = 12$.

$[La(TFA)_3(HMPA)_3\cdot n(H_2O)]$, tetragonal (not well identified space group) $a = 32.467(8)$, $c = 29.365(7)$ Å.

Crystallographic data (excluding structure factors) for the erbium structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC.149447. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 2
Selected bond distances (Å) and angles (°) in the two coordination polyhedra for $[Er(TFA)_2(HMPA)_4][Er(TFA)_2(HMPA)_2(H_2O)_3]\cdot 2(TFA)\cdot H_2O$

Octahedral		Pentagonal bipyramidal	
Er(1)–O(1)$_{HMPA}$	2.221(7)	Er(2)–O(21)$_{HMPA}$	2.218(8)
Er(1)–O(2)$_{HMPA}$	2.202(9)	Er(2)–O(22)$_{HMPA}$	2.222(9)
Er(1)–O(3)$_{HMPA}$	2.219(7)	Er(2)–O(24)$_{TFA}$	2.27(1)
Er(1)–O(4)$_{HMPA}$	2.22(1)	Er(2)–O(26)$_{TFA}$	2.29(1)
Er(1)–O(5)$_{TFA}$	2.207(8)	Er(2)–O(23)$_{water}$	2.32(1)
Er(1)–O(6)$_{TFA}$	2.214(8)	Er(2)–O(25)$_{water}$	2.350(9)
		Er(2)–O(27)$_{water}$	2.35(1)
O(5)–Er(1)–O(6)	176.0(3)	O(21)–Er(2)–O(22)	173.9(3)
O(2)–Er(1)–O(4)	175.9(3)	O(24)–Er(2)–O(26)	71.5(4)
O(1)–Er(1)–O(3)	176.7(2)	O(24)–Er(2)–O(27)	72.4(3)
		O(23)–Er(2)–O(25)	72.8(4)
		O(23)–Er(2)–O(27)	72.8(4)
		O(25)–Er(2)–O(26)	72.8(3)

3. Results and discussion

On the basis of the X-ray analysis on Er, Nd, La derivatives they are not isomorphous, as shown from the different crystal cells observed (see Crystal data Section).

The Er derivative for which a complete crystallographic analysis has been possible, consists of two monopositive coordination entities associated with two ionic trifluoroacetates (see Fig. 1) The Er(1) cation is linked to four O-donor atoms of the uncharged HMPA ligand lying approximately in a square plane and to two monodentate trifluoroacetates situated on opposite sides of the plane with an octahedral geometry. The Er(2) complex cation has in the pentagonal plane, two monodentate TFA units and three water molecules, while in the axial positions of

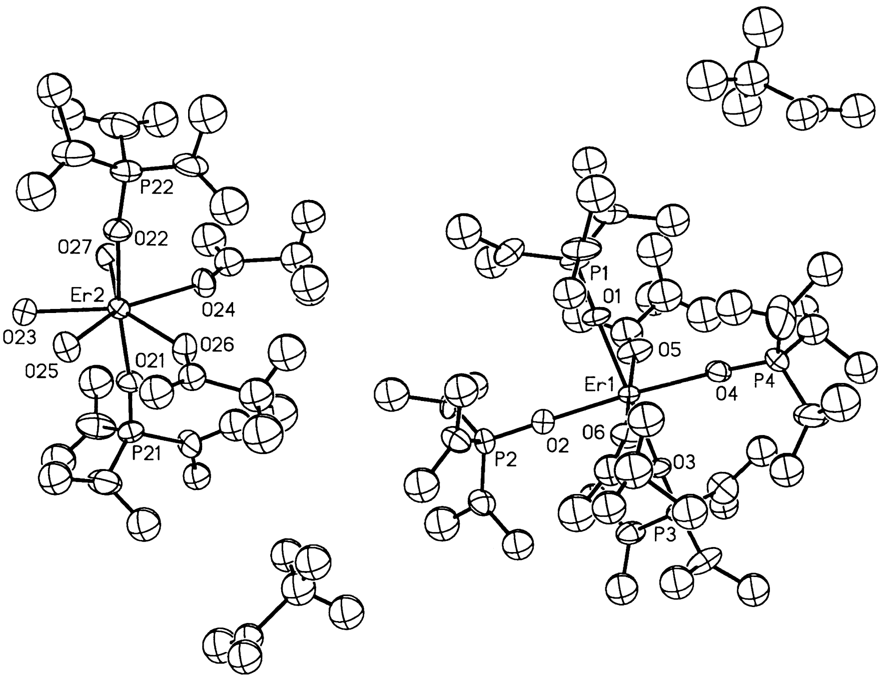

Fig. 1. ORTEP view of $[Er(TFA)_2(HMPA)_4][Er(TFA)_2(HMPA)_2(H_2O)_3]\cdot 2(TFA)$, hydrogen atoms are omitted for clarity.

the pentagonal bipyramidal polyhedron are two HMPA ligands. The formula of the compound can be described as two complex cations: $[Er(HMPA)_4(TFA)_2]^+$, and $[Er(HMPA)_2(TFA)_2(H_2O)_3]^+$, the two uncoordinated TFA anions provide for the neutrality of the complex. In the octahedral coordination polyhedron around Er(1) the square plane formed by the oxygens of HMPA moiety is distorted in tetrahedral direction with O(1) and O(3) about $-0.060(8)$ Å out of the plane and by converse O(2) and O(4) are respectively 0.060(8) and 0.076(8) Å in the opposite direction. The apical O(5) and O(6) are respectively at $-2.206(8)$ and 2.211(8) Å. The O(5)–Er(1)–O(6) angle is 176.0(3)°. The Er–O_{HMPA} bond distances average 2.22(1) Å and are comparable to the Er–O_{TFA} $2.21(1)_{av}$. Å. In the bipyramidal polyhedron around Er(2) the pentagonal plane is rather puckered with deviations of the atoms in the range $-0.28(1)$ (O(25)) to 0.22(1) Å (O(26)).

The presence of three water molecules in the basal plane causes the large deviations from planarity, due to possible hydrogen bonds either intramolecular with the non-bonded TFA oxygens in the coordination plane (O(27)···O(241) 2.62(2) Å, O(25)···O(261) 2.69(2) Å) or intermolecular with the oxygens of the two uncoordinated TFA anions (O(25)···O(71)′ 2.65(2) (′$1-x$, $1-y$, $-z$), (O(27)···O(80)″ 2.65(2) (″ x, $0.5-y$, $z-0.5$) and (O(23)···O(70)′ 2.65(2), (O(23)···O(81)″ 2.71(2) Å. While the Er(2)–O_{HMPA} bond distances in apical position have distance comparable to the corresponding of Er(1), being unaffected by the increased coordination number, the Er(2)–O_{TFA} bond distances in the crowded equatorial plane are significantly larger of about 0.05(1)Å than those with Er(1). The Er(2)–O_{water} bond distances range from 2.32(1) to 2.35(1) Å.

The presence of four additional water molecules chlatrated in the crystal structure contributes to the crystal packing with formation of hydrogen bonds with the ‘free’ TFA anions.

For the Nd derivative the results of an approximate structure determination have shown clearly the presence in the crystal cell of three independent $[Nd(TFA)_2(HMPA)_4]+$ units. In Fig. 2 one of the three

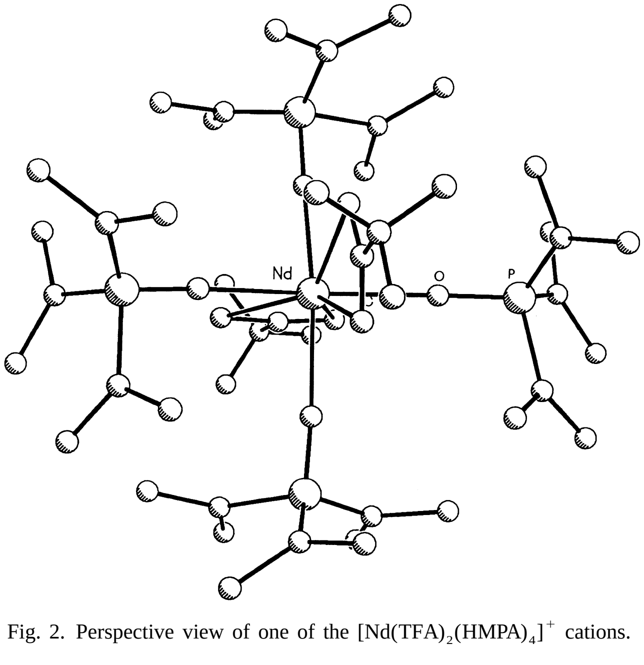

Fig. 2. Perspective view of one of the $[Nd(TFA)_2(HMPA)_4]^+$ cations.

molecules is reported. Differently from the Er derivative, two TFA anions are chelating the metal ion (Nd–Oaverage 2.60(2) Å) on the opposite sides of the square where the four HMPA ligands are O-bonded, with Nd–O_{HMPA} bond distance (average value) of 2.32(2) Å. The coordination geometry can be described as octahedral if we consider a chelating TFA as one coordination position. Disordered TFA anions, one for each Nd unit, water and ethanol molecules complete the crystal cell. The chelation of TFA ligand is rather uncommon for lanthanides as in general the monodentate mode of coordination is preferred as in the Er derivative previously described and in $[Eu(CF_3CO_2)_2(H_2O)_6][CF_3CO_2]\cdot(18\text{-crown-}6)$ [8]. An example of TFA chelating mode is shown by the structure of tetra(μ-trifluoroacetato)-bis(trifluoroacetato)tetrakis(tetramethylenesulfoxide) dineodimium(III) [9] where in any case the bridging mode is prevalent, probably due to the steric hindrance of the trifluoro groups.

In the lanthanides HMPA derivatives with different anions a great variety of structures are present: monomeric of the type $LnCl_3(HMPA)_3$ octahedral, *trans* isomers with Dy [1], Yb [10] and Pr [11], $La(NO_3)_3(HMPA)_3$ [12] octahedral *trans* isomer, while with NCS either seven coordinate species having bipyramidal pentagonal coordination geometry as in $Nd(NCS)_3(HMPA)_4$ [13] and $La(NCS)_3(HMPA)_4$ [14] or mixed octahedral and pentagonal bipyramidal species as $Nd(NCS)_3(HMPA)_3\cdot Nd(NCS)_3(HMPA)_4$ [15] detected in the same crystal. In the latter the less hindering anion stabilizes the *cis* octahedral coordination geometry. The cationic complex $Yb(H_2O)_5(HMPA)_2$ [10] with five water molecules in the pentagonal plane and two HMPA in axial position, is an interesting example of the different behaviour of HMPA ligand which behaves as bonding and non-bonding ligand. In fact a third HMPA molecule, three chlorines and a water molecule are outside the coordination sphere probably connected by a net-work of hydrogen bonds to the coordinated water molecule. The observed flexibility in the considered ligands, produces rather different stoichiometries with changes in the ligand ratio and the presence in the same crystal of different forms for the same molecule or even different coordination polyhedra confirms once again the mainly electrostatic nature of the bonds to the metal ion, for which small energetic difference or hydrogen bond interactions with consequent different crystal packing effects, are sufficient to address the ligands towards different coordination polyhedra with the formation either of neutral or complex cationic species.

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References

[1] X.W. Zhang, X.F. Li, F. Benetollo, G. Bombieri, Inorg. Chim. Acta 139 (1987) 103.

[2] G.V. Tsintsadze, V.V. Skopenko, K.B. Kereselidze, T.M. Kublashivili, Ukr. Chim. Zh. 43 (1977) 907.

[3] V. Silva Oliveira, D.M. Araújo Melo, Z. Rocha da Silva, L.B. Zinner, K. Zinner, J. Alloys Comp. 303 (2000) 157.

[4] R.H. Blessing, Acta Cryst. A51 (1995) 33.

[5] Z. Otwinoswski, W. Minor, DENSO-SMN, in: C.W. Carter Jr., R.M. Sweet (Eds.), Macromolecular Crystallography Part A, Methods in Enzymology, Vol. 276, Academic Press, 1997, pp. 307–326.

[6] G.M. Sheldrick, SHELXL-93, in: University of Göttingen, Germany, 1993, Program for the Refinement of Crystal Structures.

[7] J.K. Johnson, ORTEP, in: Report Ornl-5138, Oak Ridge National Laboratory, Tennessee, 1976.

[8] J.W. Steed, B.J. McCool, P.C. Junk, J. Chem. Soc., Dalton Trans. (1998) 3417.

[9] E.E. Castellano, G. Oliva, L.B. Zinner, G. Vicentini, Inorg. Chim. Acta 110 (1985) 77.

[10] Z. Hou, K. Kobayashi, H. Yamazaki, Chem. Lett. (1991) 265.

[11] J.T. Donoghue, D.A. Peters, J. Inorg. Nucl. Chem. 31 (1969) 467.

[12] G.V. Tsintsadze, Z.O. Dzhavakhishvili, G.G. Aleksandrov, Yu.T. Struchkov, Koord. Khim. 8 (1982) 367.

[13] Z.O. Ozhavakhishvili, G.V. Tsintadze, G.G. Aleksandrov, Y.T. Struchkov, Soob Akad. Nauk. Gruz SSR 104 (1981) 637.

[14] D. Barr, A.T. Brooker, M.J. Doyle, S.R. Brake, P.R. Raithby, R. Siraith, D.S. Wright, Angew. Chem. Int. Ed. English 29 (1990) 285.

[15] C.A. de Simone, E.E. Castellano, C.A. Fantin, L.B. Zinner, G. Vicentini, Lanth. Actin. Res. 2 (1987) 127.