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Rare earth coordination compounds: from monodentate ligands via crown ether complexes to a variety of bidentate ligands

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Abstract

With a wide range of ionic radii, the rare-earth ions, M^{3+}, exhibit a large variety of coordination geometry. Coordination numbers vary from 6 (octahedron) to 12. Ligands may be monodentate like halide ions and water molecules, bidentate like acetate, proprionate, β-diketonates, tetra- to hexadentate as with crown ethers, hexadentate like tetraglyme. The coordination polyhedra might be monomers, di- or trimers or they may be incorporated into chains, layers, or even networks. Therefore, from a plethora of structures, complexes with special properties (optical, magnetic) might in principle be tailored.

Keywords: Rare earth complexes; Ligands; Crown ethers

1. From monodentate ligands (X^-)

The trivalent rare earths cations, M^{3+} (M=Sc, Y, La, Ce-Lu), cover a wide range of ionic radii, between 75 and 103 pm when scaled to coordination number six (CN 6) [1,2], the minimum CN for monodentate ligands such as the spherical halide anions, X^- (X=F,Cl,Br,I). With the larger rare-earth ions, especially from La^{3+} through Gd^{3+}, they usually exhibit larger CN of up to CN 11.

Examples to mention are: LaF_3 with CN 11 for La^{3+} (pentacapped trigonal prism) and CN 9 in $LaCl_3$ (tricapped trigonal prism, UCl_3 type of structure), CN. 8 for Tb^{3+} in $TbCl_3$ (bicapped trigonal prism) and, finally, the octahedron in many binary trihalides, e.g., YCl_3. For a detailed discussion see for example [2]. CN 7 has not been seen in trihalides, MX_3.

There is, however, a fair number of ternary halides exhibiting CN 7 for M^{3+}. Ba_2ErCl_7 was the first example with an *isolated* [MCl_7] polyhedron [3–6] meaning that in accord with the formula $Ba_2[EuCl_7]$ all seven chloride ligands are terminal. In K_2PrCl_5, Pr^{3+} also has CN 7 but the monocapped trigonal prisms are now connected via two trans edges forming a one-dimensional chain [7,8]. This is in accord with the large ionic radius of Pr^{3+} (99 pm) which could afford CN 9 as in $PrCl_3$ itself; however, Pr^{3+} competes with the much larger K^+ ions for the ligands of which there are only five for three cations. The [$PrCl_7$] polyhedra need to be connected to meet the formula's requirement of 5 Cl^- per Pr^{3+}. Trans edge-connection according to [$PrCl_{3/1}Cl_{4/2}$] is apparently the best choice to minimize the lattice energy of K_2PrCl_5. With the smaller Dy^{3+} we observe CN 6 and *cis*-corner connected octahedra according to [$DyCl_{4/1}Cl_{2/2}$] in Cs_2DyCl_5 [9].

In a different formula type, however, Dy^{3+} may also be seven-coordinate. This is the case in KDy_2Cl_7 where [$DyCl_7$] monocapped trigonal prisms share one common face and two edges with three equivalent polyhedra thereby forming a layer [10].

On the other hand, the rare-earth cation may afford a higher coordination number (8) as Gd^{3+} in $BaGdCl_5$ [11] when the anion to cation ratio is higher. Square antiprisms [$GdCl_8$] are connected via two common edges and corners each according to [$GdCl^{c}_{2/2}Cl^{e}_{4/2}Cl^{t}_{2/1}$] (c means corner, e edge sharing and t terminal). CN 8 is also achieved in the anti-scheelite type chlorides, e.g., $LiGdCl_4$ [12] whereas the analogous sodium chlorides $NaMCl_4$ have CN 8 for M^{3+} [13–16].

The apparently lowest coordination number for a trivalent rare-earth cation in halides, CN 6, is always seen when the counter cations are large and relatively numerous and/or the ionic radius of M^{3+} is sufficiently small. Note that even when there are enough chloride ligands available,

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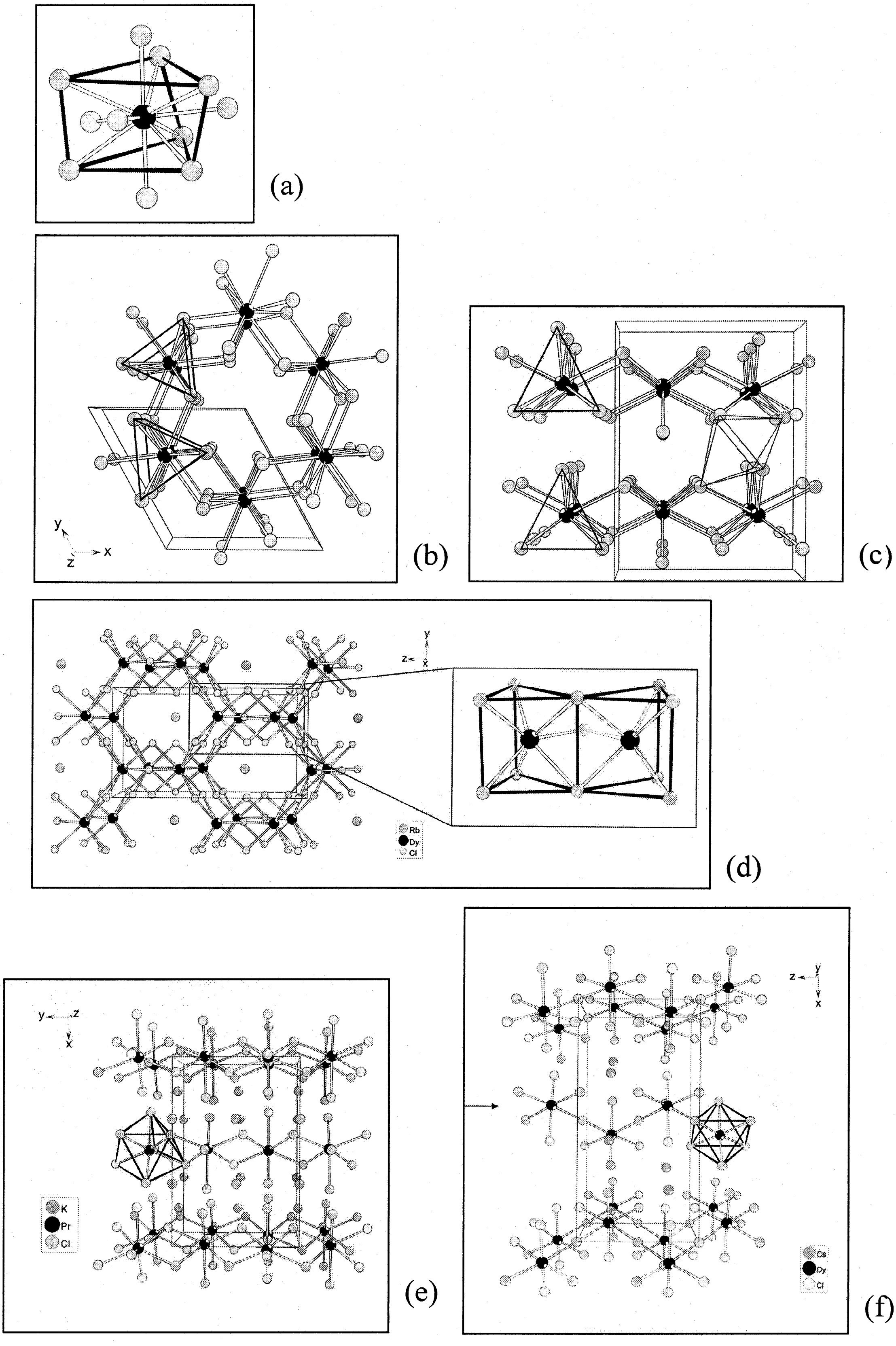


Fig. 1. Some coordination features of rare-earth cations (M^{3+}) with monodentate ligands (X^-): CN 11 in LaF_3 (a), CN 9 in the UCl_3 type ($LaCl_3$-$GdCl_3$) (b), CN 8 in the $PuBr_3$ type ($TbCl_3$) (c), CN 7 in $RbDy_2Cl_7$ (d) and in K_2PrCl_5 (e), and CN 6 in Cs_2DyCl_5 (f).

small Sc^{3+} is only surrounded by six Cl^- as for example in $Ba_2ScCl_7 \equiv Ba_2Cl[ScCl_6]$ [17]. In all of the elpasolites, e.g., $Cs_2AgEuCl_6$ [18], cryolites, e.g. Na_3ErCl_6 [19], or in the stuffed derivatives of the $LiSbF_6$ type of structure, e.g. Na_3GdCl_6 [20], the rare-earth cation M^{3+} is octahedrally surrounded by six halide ligands, see also [21], Fig. 1.

2. Via crown ether complexes

Hints that $Ph_4P[ScCl_4]$ may contain an isolated tetrahedron as In^{3+} in $Et_4N[InCl_4]$ [22] have not been verified. Whenever larger rare-earth cations are chosen and crystallization is carried out from solution, CN 6 is easily achieved as the edge-connected dimeric anions in, e.g., $(Ph_4P)DyCl_4(CH_3CN) \equiv (Ph_4P)_2[Dy_2(\mu_2\text{-}Cl)_2(\mu_1\text{-}Cl)_6(CH_3CN)_2]$ [23] clearly show, Fig. 2.

The same anion is also seen in $[Dy_2Cl_4$(dibenzo-18-crown-6$)_2][Dy_2Cl_8(CH_3CN)_2]$ [24]. In the cation, Dy^{3+} has only CN 3 against Cl^-, two Y-shaped ‘triangles’ sharing a common edge. However, there is the crown ether Dibenzo-18-crown-6 that adds its six oxygen ligator atoms to the coordination sphere so that the coordination number may be given as CN=3+6.

CN 9 is not unusual in crown ether complexes as the examples of the monomeric complex $[SmI_3$(dibenzo-18-crown-6] [25] and the dimeric complexes $[La_2I_2(OH)_2$(dibenzo-18-crown-6$)_2]I(I_3)$ [26] and $[Ce_2I_2(OH)_2$(dibenzo-18-crown-6$)_2]I_2(H_2O)_{3.3}$ [27] clearly show. The latter two contain hydroxide bridged dimeric cations. In all three complexes the M^{3+} cations reside within the plane of the six oxygen ligator atoms of the crown ether, thus they are *in-cavity* complexes. *Out-of-cavity* complexes appear when the diameter of the cavity is too small to accomodate the rare-earth cation. Examples are the monomeric $[LaBr_3$(12-crown-4)(acetone)] [28] and $[NdCl_3$(15-crown-5)] [29] and the dimeric $[Y_2(OH)_2$(benzo-15-crown-5$)_2(CH_3CN)_2]I_4$ [30], again with hydroxide bridges. These three have only CN 8 which appears to be rather typical for out-of-cavity complexes. There are, however, *in-cavity* complexes with CN 8 as the example of the rather complicated complex with divalent europium shows: $(H_3O)_4Eu_2Br_4$(dibenzo-18-crown-6$)_6[EuBr_6](H_2O)_2$ [27]. This salt contains crown ether complexes of H_3O^+ and Eu^{2+} and $[EuBr_6]^{4-}$ octahedra. The H_3O^+ cation resides about 120 pm above the oxygen hexagon of the dibenzo-18-crown-6. The Eu^{2+} cation adds two bromide ligands to its coordination sphere to achieve CN 8, Fig. 3.

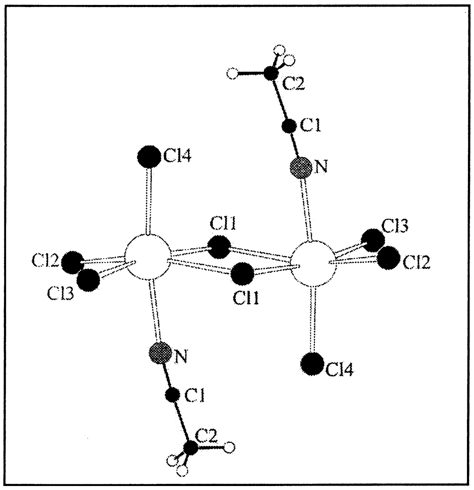


Fig. 2. The anion $[Dy_2Cl_8(CH_3CN)_2]^{2-}$ as observed in $(Ph_4P)DyCl_4(CH_3CN) \equiv (Ph_4P)_2[Dy_2(\mu_2\text{-}Cl)_2(\mu_1\text{-}Cl)_6(CH_3CN)_2]$ and in $[Dy_2Cl_4$(dibenzo-18-crown-6$)_2][Dy_2Cl_8(CH_3CN)_2]$.

An example for an even higher coordination number is found in $[NdCl(NO_3)_2$(tetraglyme)] [31]. Here the tetraethylene glycol dimethyl ether acts as a pentadentate ligand so that with chloride monodentate and the two bidentate nitrate ligands Nd^{3+} has now CN 10 in this heteroleptic complex, Fig. 4.

3. To a variety of bidentate ligands

The highest coordination numbers, however, are found with rather old-fashioned bidentate ligands such as nitrate. Already in the salt $(NH_4)_2[M(NO_3)_5(H_2O)_2](H_2O)_2$ that *Auer von Welsbach* used to separate the didymium twins by fractional crystallization (M=Pr, Nd) [32,33] contains twelve coordinate M^{3+} [34]. Five bidentate nitrate ligands and two water molecules surround M^{3+}. Nitrate ligands alone achieve CN 12 in the ternary ammonium nitrates $(NH_4)_3M_2(NO_3)_9$ (M=La-Gd) [35]. A complicated network structure is observed with nitrate ligands acting not only bidentately but also as tridentate-bridging ligands. An isolated anionic complex with only bidentate nitrate ligands is found in $(NH_4)_6[Nd(NO_3)_6](NO_3)_3$ with three lonesome nitrate groups in a sense that they are not coordinated to Nd^{3+} [36].

With the smaller rare-earth elements M=Tb-Lu,Y the coordination number is reduced von 10 in the nitrates $(NH_4)_2[M(NO_3)_5]$ [37]. Crystals of all of these ternary ammonium nitrates are rather easily obtained from ammonium nitrate melts at about 180–190°C where NH_4NO_3 sublimes and decomposes slowly (to N_2O and H_2O) so that the melt slowly concentrates.

An example for CN 9 is found in the heteroleptic molecular complex $Yb(NO_3)_3(H_2O)_3$, the trihydrate of ytterbium(III) nitrate [38], Fig. 5.

Another example of a potentially tridentate ligand is the carbonate ion, CO_3^{2-}. As for nitrate, there is no crystal structure of a binary carbonate yet available because crystal growth could not be achieved. However, ternary carbonates such as $CsPr(CO_3)_2$ [39] and a number of

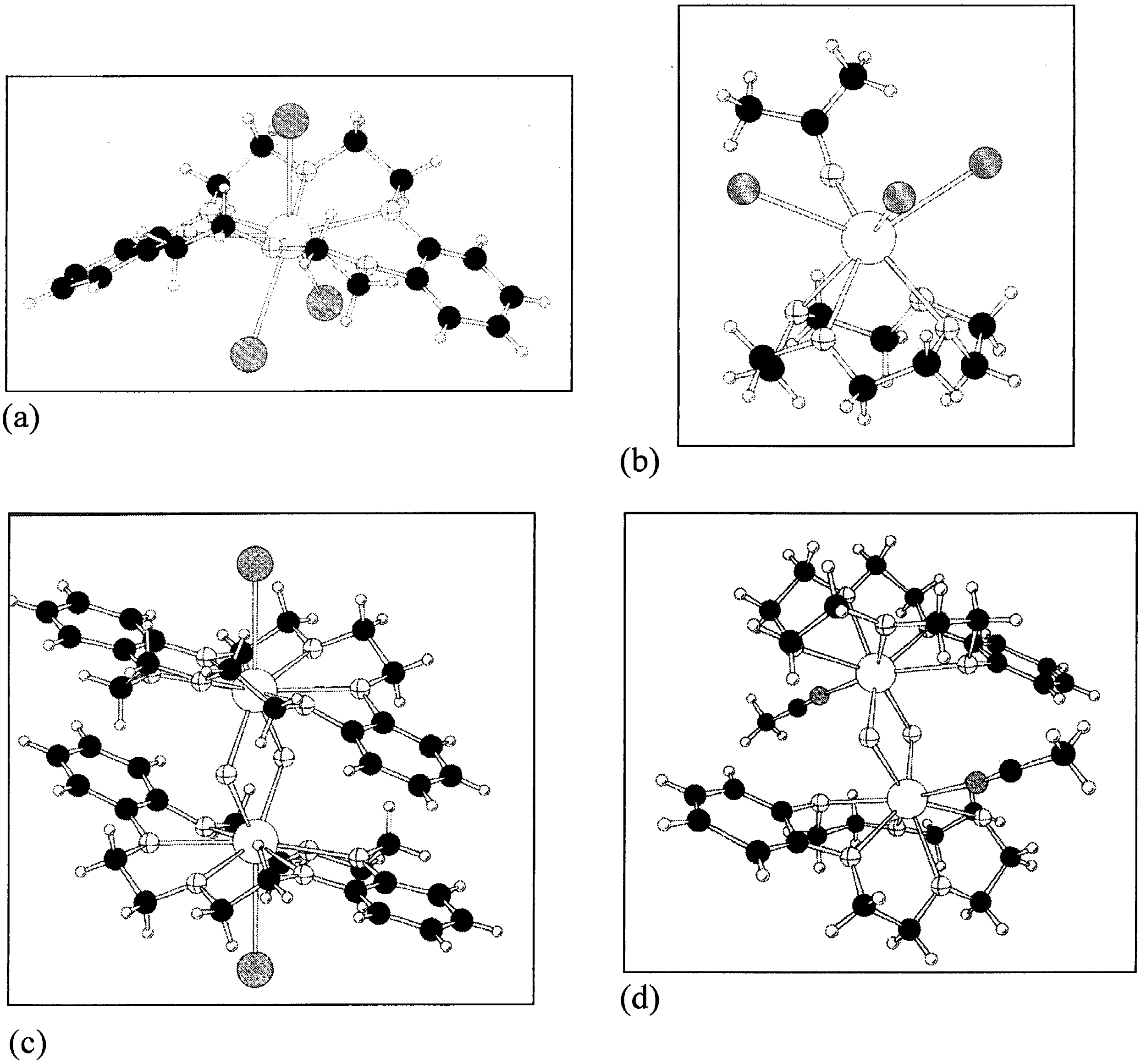


Fig. 3. Crown ether complexes: Monomeric and dimeric *in-cavity-* and *out-of-cavity* complexes as observed in [SmI_3(dibenzo-18-crown-6] (a), [$LaBr_3$(12-crown-4)(acetone)] (b), [$La_2I_2(OH)_2$(dibenzo-18-crown-6$)_2$]$I(I_3)$ (c), and [$Y_2(OH)_2$(benzo-15-crown-5$)_2(CH_3CN)_2$]I_4 (d), respectively.

potassium and rubidium analogues, $KM(CO_3)_2$ (M=La-Nd) [40] and $Rb(Sm(CO_3)_2$ [41] are now structurally well known. Additionally, single crystals of basic carbonates such as $Dy_2(CO_3)O_2$ and $Dy(CO_3)(OH)$ could be grown hydrothermally and the crystal structures were determined [42]. Coordination numbers for Dy^{3+} in these compounds are usually 8 or 7, for Pr^{3+} in $CsPr(CO_3)_2$ 8 and 9, respectively, Fig. 6.

Whereas single crystals of binary carbonates and nitrates have not yet been obtained, almost the complete series of anhydrous binary acetates is now known. In $Sc(CH_3COO)_3$ [43], Sc^{3+} has CN 6, three bidentate-bridging acetate ligands lead to a chain. Moving on to larger M^{3+} cations like Lu^{3+}, the coordination number is enhanced to 7 and further to 8 ($Ho(CH_3COO)_3$) [44]. In $Pr(CH_3COO)_3$ we find a network-type structure with CN of 9 and 10 for Pr^{3+} [45] and, finally, with the largest rare-earth cation, La^{3+}, CN 10 is achieved in $La(CH_3COO)_3$ [46].

Coordination numbers of 9 are also found in a number of heteroleptic complexes. In the 2:1:3 and 1:2:7 type acetate-chloride-hydrates $M(CH_3COO)_2Cl(H_2O)_3$ and $M(CH_3COO)Cl_2(H_2O)_7$, respectively, chloride is, as the weaker ligand, in the outer coordination sphere [47–51]. In

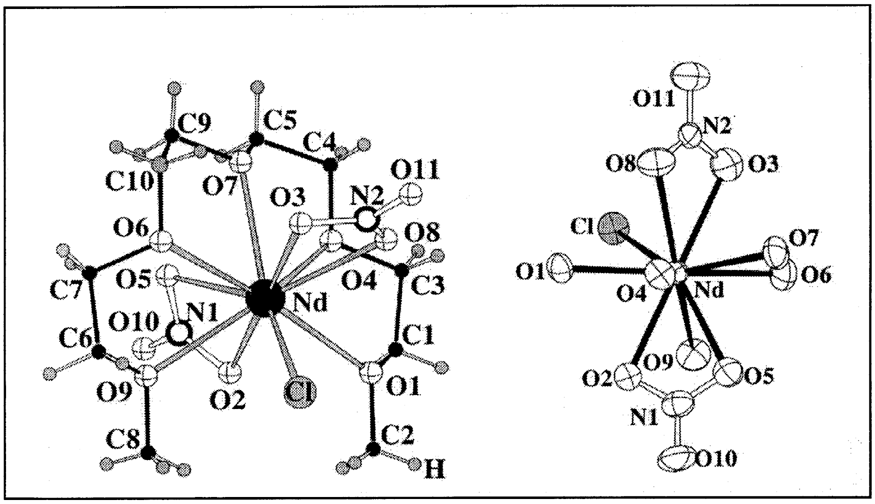
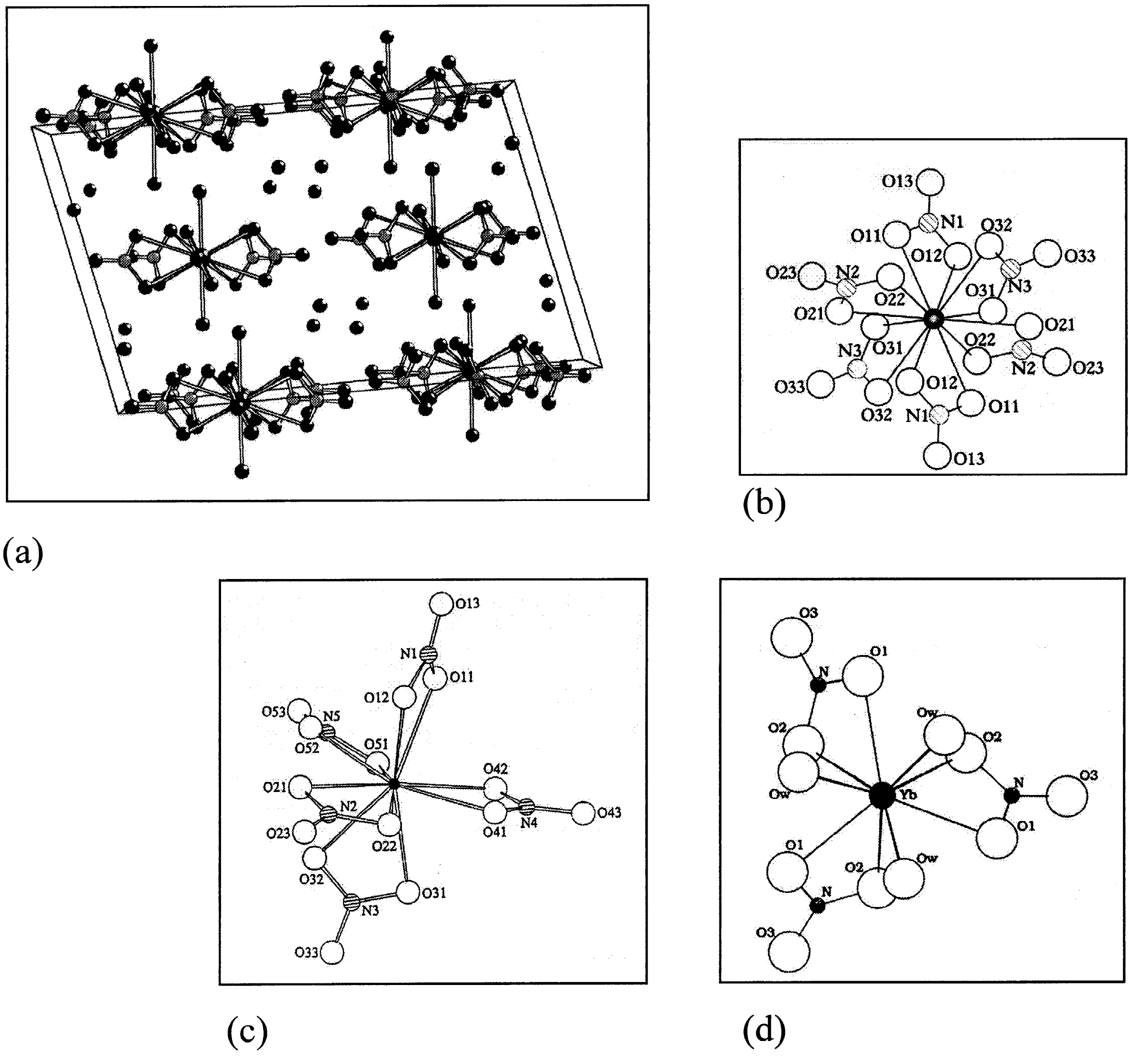


Fig. 4. Molecular structure of [NdCl$(NO_3)_2$(tetraglyme)] and the coordination sphere around Nd^{3+} (right).



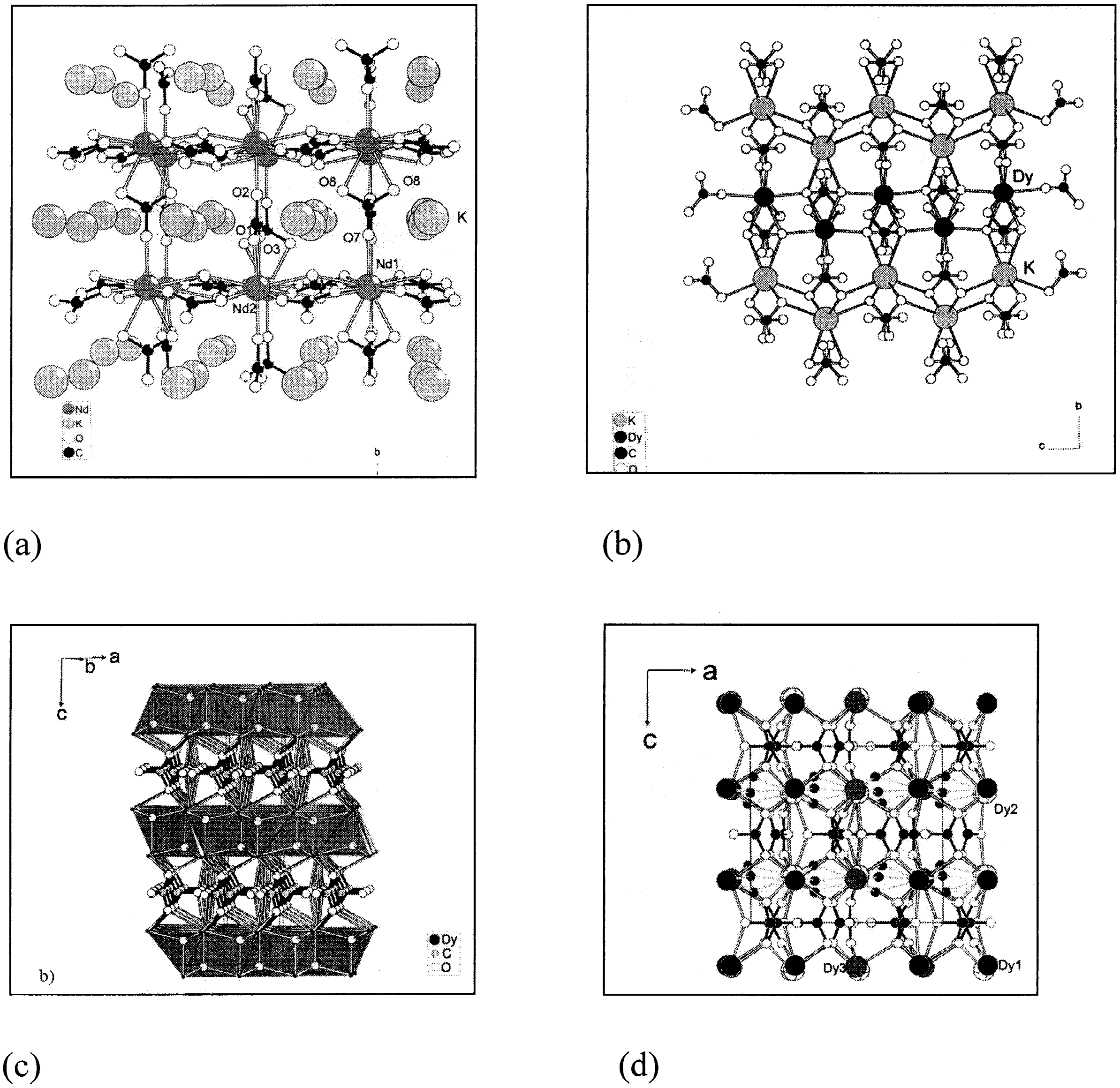
(a)

(b)

(c)

(d)

Fig. 5. Nitrates: Coordination numbers of 12 in the anions of $(NH_4)_2[M(NO_3)_5(H_2O)_2](H_2O)_2$ (a) and $(NH_4)_6[Nd(NO_3)_6](NO_3)_3$ (b), CN 10 in $(NH_4)_2[M(NO_3)_5]$ (c) and CN 9 in the molecule $Yb(NO_3)_3(H_2O)_3$ (d).



(a) (b) (c) (d)

Fig. 6. Carbonates: Crystal structures of the ternary carbonates $KNd(CO_3)_2$ (a) and $KDy(CO_3)_2$ (b) and of the basic carbonates $Dy_2(CO_3)O_2$ (c) and $Dy(CO_3)(OH)$ (d).

the first one, $[M(CH_3COO)_2(H_2O)_3]Cl$ with M=Ce-Lu, Y, we observe infinite chains of nine-coordinate M^{3+} where four bidentate-bridging acetate ligands act as bidentate and monodentate ligands twice each. Three water molecules molecules fill up the coordination sphere. In the latter one, $[M(CH_3COO)(H_2O)_6]Cl_2(H_2O)$ with M=La-Sm, dimers are formed through two bidentate-bridging acetate ligands and the coordination sphere is completed by six water molecules. The only example that we could find for an inner-sphere chloride ligand is $[La_2(CH_3COO)_2(H_2O)_7Cl_3]Cl$ [52]. Both symmetrically independent La^{3+} have CN 9, however with 2 Cl+7 O and 1 Cl+8 O ligator atoms, respectively, Fig. 7.

With regard to acetates, initial investigations have also been carried into proprionates, of which $Pr(CH_3CH_2COO)_3(H_2O)_3$ [53] exhibits in principle the same schemes as do acetates. It has a chain structure with Pr^{3+} CN 9 and 10, respectively.

Additionally, after the above-mentioned heteroleptic chloride-acetates, we have started to look into chloro-acetates. $Pr_2(Cl_2HCCOO)_6 \cdot Cl_2HCCOOH \cdot 5H_2O$ and $Sm_2(Cl_2HCCOO)_6 \cdot 4H_2O$ are first examples [54], Fig. 8.

In pursuit of new β-diketonato complexes of the rare earths, especially europium for its optical properties, two new salts were obtained: $(CH_3NH_2)[Eu(C_6H_5COCH_2COCF_3)_4]$ and the naphthyl analogue $(CH_3NH_2)[Eu(C_{10}H_{17}COCH_2COCF_3)_4]$ [27]. In both, Eu^{3+} has CN 8 (Fig. 9).

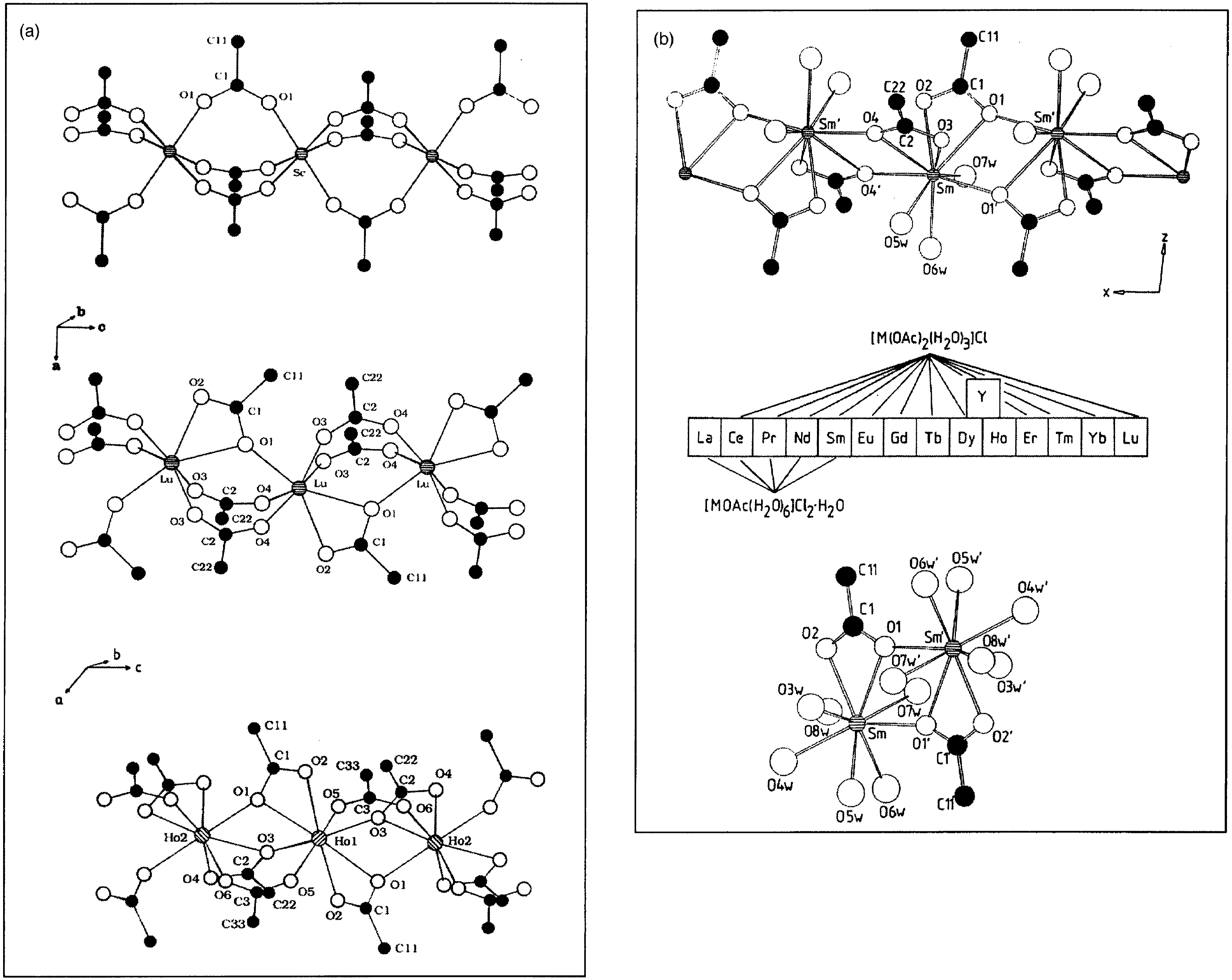
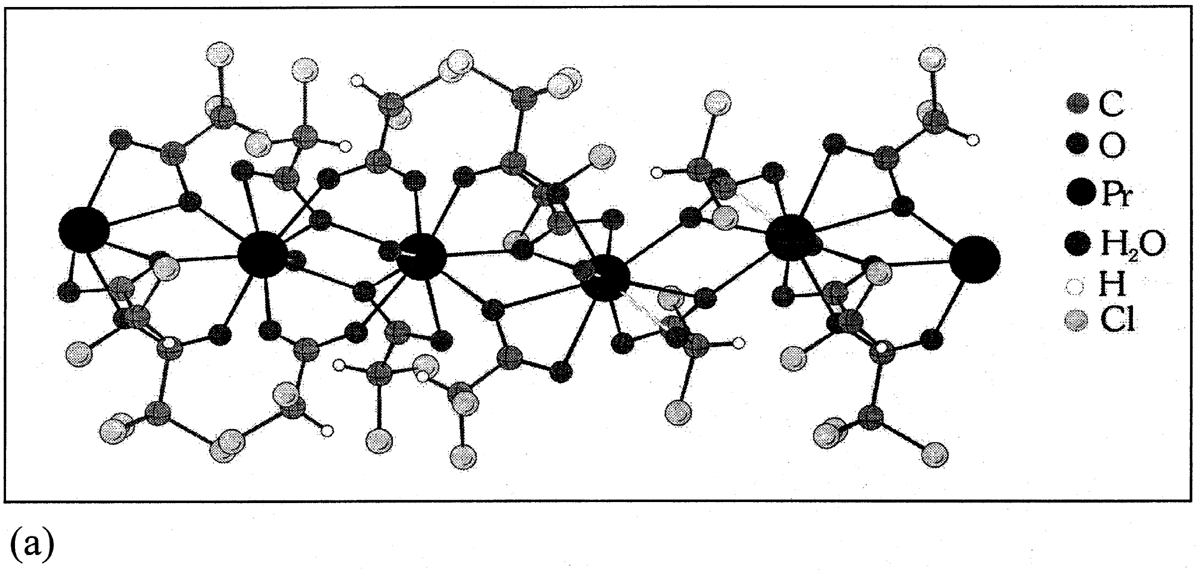


Fig. 7. Acetates and acetate-chlorides: (a) One-dimensional chains in the anhydrous acetates $Sc(CH_3COO)_3$ (CN 6), $Lu(CH_3COO)_3$ (CN 7), and $Ho(CH_3COO)_3$ (CN 8); (b) chains and dimers in the crystal structures of $[Sm(CH_3COO)_2(H_2O)_3]Cl$ and $[Sm(CH_3COO)(H_2O)_6]Cl_2(H_2O)$, respectively.



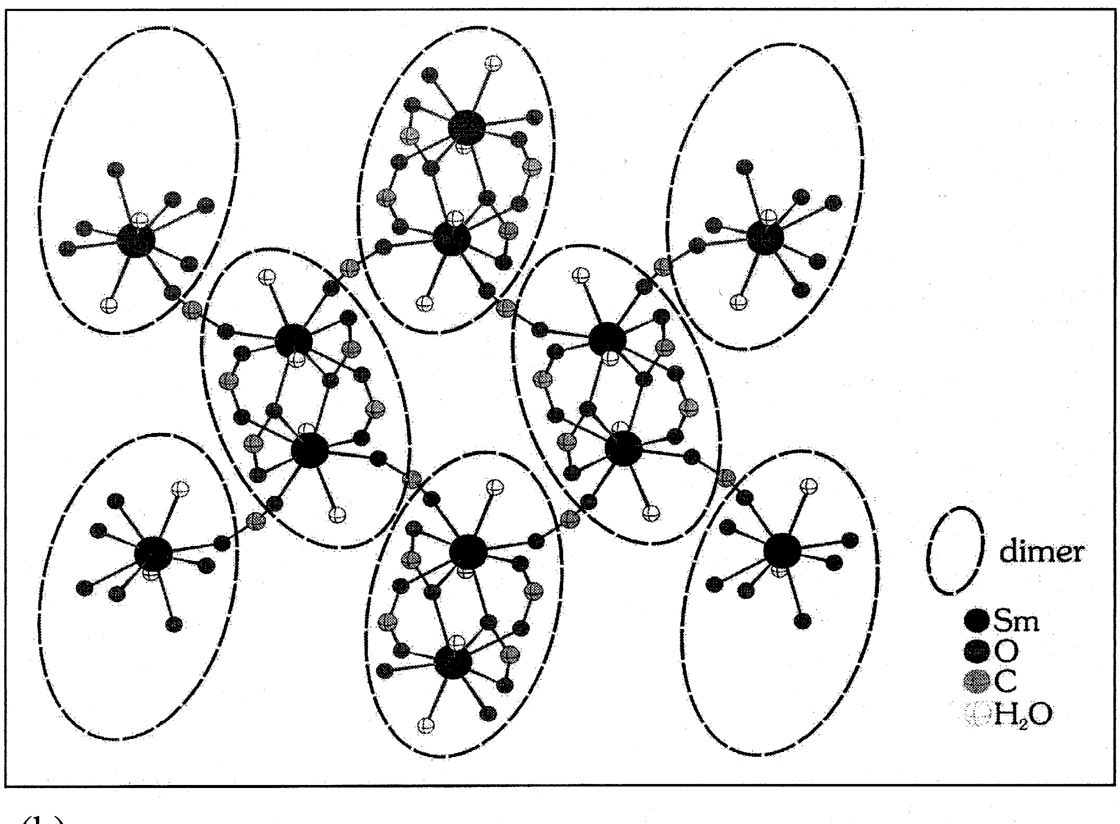


Fig. 8. Dichloroacetates: Chain of the composition $[Pr_2(Cl_2HCCOO)_6(H_2O)_3]$ in $Pr_2(Cl_2HCCOO)_6 \cdot Cl_2HCCOOH \cdot 5H_2O$ (a) and the layer built up from dimers in $Sm_2(Cl_2HCCOO)_6 \cdot 4H_2O$ (b).

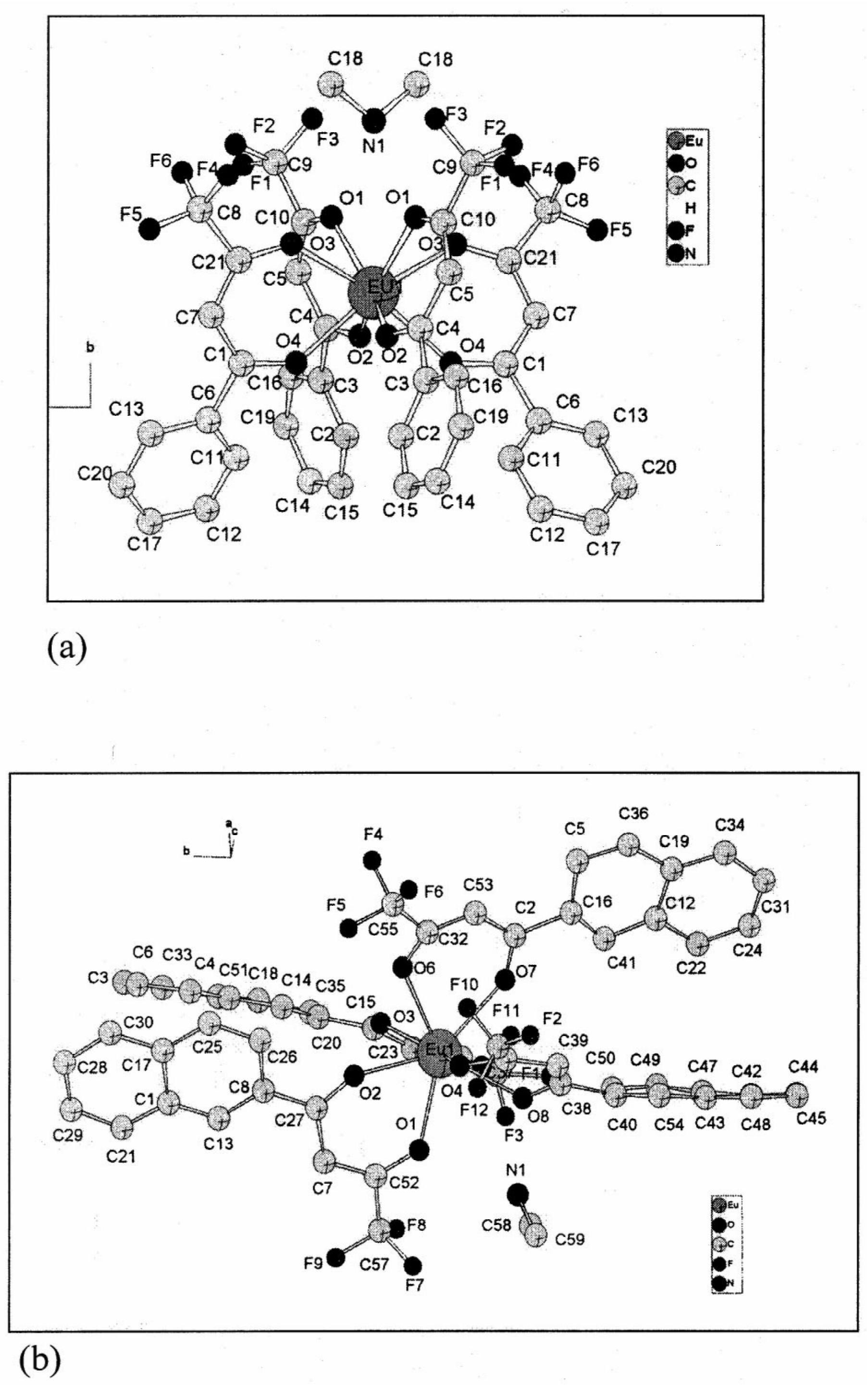


Fig. 9. β-Diketonato complexes: The anions $[Eu(C_6H_5COCH_2COCF_3)_4]^-$ (a) and $[Eu(C_{10}H_{17}COCH_2COCF_3)_4]^-$ (b) in the crystal structures of $(CH_3NH_2)[Eu(C_6H_5COCH_2COCF_3)_4]$ and $(CH_3NH_2)[Eu(C_{10}H_{17}COCH_2COCF_3)_4]$, respectively.

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