STRUCTURE OF RARE EARTH CARBOXYLATES IN DIMERIC AND POLYMERIC FORMS

A. OUCHI

Department of Chemistry, College of Arts and Sciences, University of Tokyo, Meguro, Tokyo 153 (Japan)

Y. SUZUKI, Y. OHKI and Y. KOIZUMI

Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Higashi-Mita, Tama, Kawasaki 214 (Japan)

(Received 28 April 1987)

CONTENTS

A. INTRODUCTION

Carboxylate ions are coordinated to metal atoms in many transition metal salts, and many structures have already been published [1].

Many types of rare earth carboxylate have also been obtained [2], but until recently there were few structure reports. From X-ray structure analyses, lanthanoid carboxylates were observed to exhibit diverse types of dimeric and polymeric forms bridged by carboxylate ions [3]. Even the same metal carboxylates were able to adopt several crystalline states including different numbers of water molecules. In some lanthanoid carboxylates, even when

the chemical composition is the same, their crystal system and/or space group are different.

Recently, we studied the structures of many lanthanoid complexes, including those of a series of lanthanoid carboxylates and compared their detailed data with each other. In this review, we report some general aspects about lanthanoid carboxylate structures.

To simplify the discussion, we consider only carboxylates without any other functional groups coordinated to the lanthanoid metal atom, as in the case of the ligands chosen by Mehrotra and Bohra [1].

B. GENERAL STRUCTURAL ASPECTS OF RARE EARTH(III) CARBOXYLATES

(i) Nature of the bonding in carboxylate rare earth complexes

In many $3d$-element carboxylato complexes the ligands are unidentate, although there are frequent exceptions, for example, in some copper(II) complexes two metal atoms are bridged by bidentate carboxylate ions [4]. In $3d$-metal carboxylates, the four-membered chelate ring is rarely found, and in such examples the ring is generally quite deformed [4].

In the case of lanthanoid, yttrium and scandium carboxylates, however, diverse coordination types are recognized. The respective coordinating forms of the carboxylate ions are schematically shown in Fig. 1. Although only typical forms are shown, some forms intermediate between the two types are also found. For example, a tridentate type, where the M–O$'$ distance is much longer than those of the M–O and M$'$-O$'$ bonds, is regarded as the intermediate of the tridentate and the Z,E-type bidentate [3].
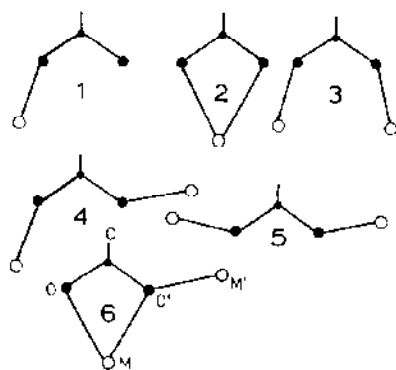

Fig. 1. Coordinating forms of the carboxylate ions: 1, unidentate; 2, chelating-type bidentate; 3, Z,Z-type bridging bidentate; 4, Z,E-type bridging bidentate; 5, E,E-type bridging bidentate; 6, bridging tridentate.

(ii) Coordination geometries around the metal atoms

Lanthanoids(III) are known to take high coordination numbers such as 7-10. The respective typical coordination geometries are shown in Fig. 2. Other than these typical forms, there are some intermediate forms: for example, a deformed dodecahedron-type complex which is also regarded as a deformed square-antiprism (SAP) one. In some complexes, several M O distances are found to be a little longer than the common distance, but they occupy the respective apices of the polyhedron geometry, and another appropriate geometry without them cannot be assumed. In some other complexes, such long-distance bonding atoms are at the additional positions, such as the cap of the original polyhedron. Although these bonds are weak, at least some of them are likely to be included in the coordination geometries [5,6]. The most popular coordination geometries of lanthanoid carboxylates are the octa-coordinate square-antiprism and ennea-coordinate tricapped trigonal-prism (TTP) geometries. The former geometry is generally found in the carboxylates where the ligands have some relatively large hydrophobic part such as a benzene or pyridine ring or trichloromethyl group. The latter orientation, however, is adopted in the carboxylates where the ligand is relatively small, but there are exceptions: for example, in the neodymium(III) or lanthanum(III) 1-hydroxy-2-naphthoates, the metal atoms are in the TTP geometry in spite of the large naphthalene ring of the ligand [7-9].
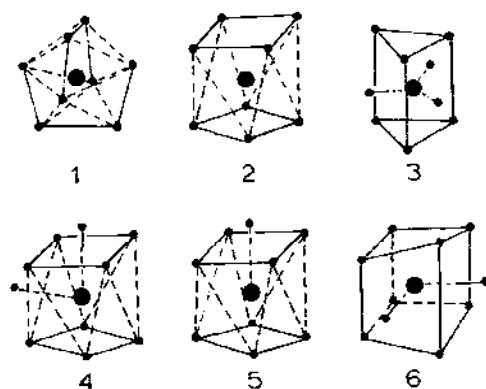

Fig. 2. Schematic presentation of the coordination geometries around the metal atom: 1, dodecahedral octa-coordination; 2, SAP octa-coordination; 3, TTP ennea-coordination; 4, *cis*-bicapped SAP deca-coordination; 5, monocapped SAP ennea-coordination; 6, *cis*-bicapped cube deca-coordination.

There are some carboxylato complexes in the other geometries; dodeca-hedral octa-coordination, *cis*-bicapped cubic deca-coordination, mono-capped and bicapped square-antiprism-type ennea- or deca-coordination geometries are examples.

From the reported X-ray structure analytical data [10–12], the yttrium(III) carboxylates are generally isomorphous with the heavy lanthanoid(III) salts of the same ligand: the former structure especially resembles that of the dysprosium through erbium carboxylates. However, scandium(III) carboxy-lates are mostly hexa-coordinate, being in an octahedral geometry, and the structure is different from those of the yttrium(III) or of the lanthanoid(III) salts of the same acid [10,13].

(iii) Bridge between the unit complexes

There are few monomeric lanthanoid(III) carboxylates: structural data are available for the neodymium(III) 1-hydroxy-2-naphthoate heptahydrate and octahydrate (the latter is isomorphous with the lanthanum salt) (see Fig. 10) [8,9]. Almost all carboxylates are in the dimeric or in the linear polymeric forms, where the unit complexes are bridged by carboxylate ions, although some formates exceptionally adopt two-dimensional polymeric form [11,14,15]. There are many types of intermetal atomic bridges, and in some complexes, several types of bridge appear alternately in the polymer chain.

The simplest bridge, where each pair of unit complexes is bridged by only one bidentate carboxylate, is found in some salts [16 18]. However, in many cases, respective pairs of the metal atoms are bridged by two, four or three (in scandium(III) salts) Z,Z-type bidentates, by two tridentates, or by several numbers of both types of carboxylate ions. The example of a linear

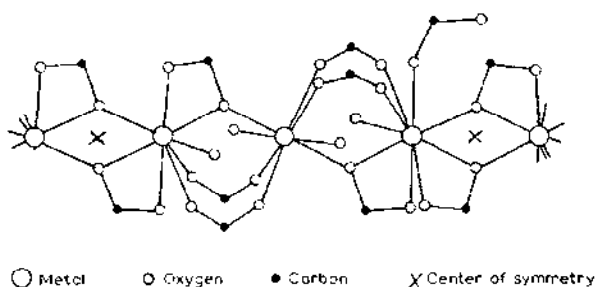

○ Metal   ○ Oxygen   ● Carbon   ✗ Center of symmetry

Fig. 3. Schematic presentation of the bridging ligands between metal atoms in the linear polymeric heavy lanthanoid chloroacetates $[M_2L_6(H_2O)_3]_n$ (M = Gd–Yb; HL = chloroacetic acid).

polymeric complex where the respective pairs of metal atoms are bridged by such types of ligand is shown schematically in Fig. 3 [19].

Commonly, the M · · · M interatomic distance in such a chain is shorter when more ligands are bridging. The tridentate type is likely to be more effective than the bidentate in shortening the distance; however, there are some exceptions to the relation between the bridging modes and M · · · M distances; an exact quantitative rule has not yet been obtained [19,20,32].

C. OCTA-COORDINATE LANTHANOID(III) CARBOXYLATES

(i) Parallel square-antiprism (SAP) units

This group of complexes is schematically shown in Fig. 4 [21–28], together with examples to explain the abbreviated presentations in the
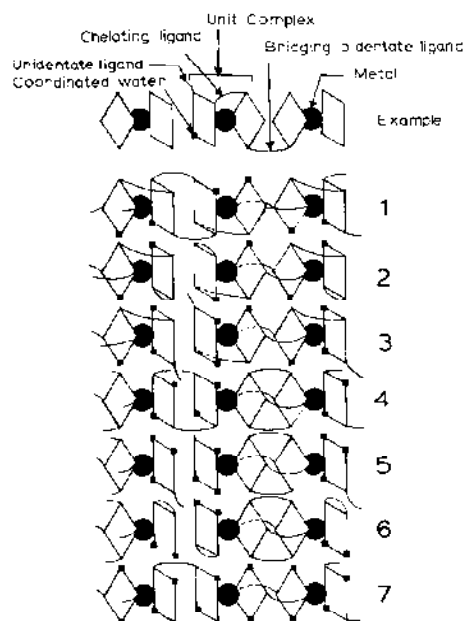

Fig. 4. Schematic presentation of linear polymeric and dimeric parallel SAP unit-type complexes (1, 4 and 7 are in the linear polymeric form, and the others are in the dimeric form): 1, La–Nd m-hydroxybenzoates, $[ML_3(H_2O)_2] \cdot (HL) \cdot 2H_2O$ [27] and erbium iso-nicotinate, $[ML_3(H_2O)_2]$ [25]; 2, dysprosium p-aminobenzoate, $[ML_3(H_2O)_2]_2 \cdot 2H_2O$ [26]; 3, Sm–Yb m-hydroxybenzoates, $[ML_3(H_2O)_3]_2$ [27]; 4, lanthanum isonicotinate, $[ML_3(H_2O)_2]$ [23], and holmium nicotinate complex, $[Cr(NCS)_6][M(HL)_3(H_2O)_3] \cdot 2H_2O$ [23]; 5, Pr–Eu trifluoroacetates, $[ML_3(H_2O)_3]$ [28]; 6, La–Tm nicotinates, $[ML_3(H_2O)_2]_2$ [21,22]; 7, europium isonicotinate, $[ML_3(H_2O)_4](NO_3)$ [24]. (HL in each formula means the acid.)

scheme. Although there are many kinds of this type of complex, the main structural differences between them are only the positions of the carboxylato bridge and of the coordinated water oxygen atoms.

In most complexes (but not all) of this type, the side-by-side square planes of two dimeric complexes are nearly parallel: they are bridged by carboxylato ions, or there may be some hydrogen bonds between them. Even the dimer complex of this type is stacked almost linearly in the crystal.

(ii) Non-parallel square-antiprism units

The following types of structures have been reported.

In the erbium(III) trichloroacetate dihydrate [29], there are two kinds of crystallographically independent metal atoms; both of them have a geometry almost identical to the SAP geometry of the type of dimers described in Section C (i). Each pair of these dimers is bridged by two Z,Z-type bidentate carboxylate ions as well as by one water oxygen atom. As a result, the square planes of both kinds of dimers are not parallel. the dimers having the square planes in two directions appearing alternately in the chain.

In the heavy lanthanoid(III) chloroacetates [19], there are dimers of the SAP-type complexes in which a couple of the side-by-side unit complexes commonly share two apices. There are two crystallographically independent dimers, and pairs of dimers are connected with a capped square-antiprism type to the other unit complex, forming a chain structure.

In the dysprosium(III) benzoate [18], each pair of the SAP complexes is bridged by a Z,E-type carboxylate ion, forming a linear polymer. Because the squares of the adjacent complexes are not parallel, complexes where the square planes are in two directions appear alternately.

In the yttrium(III), holmium(III) and erbium(III) formates, which are isomorphous with each other, the unit SAP-type complexes are bridged to four other units; to two units by only one bidentate carboxylate ion and to the other two units by a couple of this type of ion, respectively, forming a two-dimensional polymeric form [11,14,15].
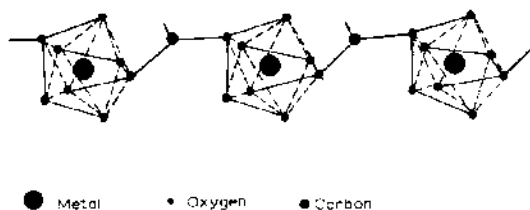

● Metal   • Oxygen   ● Carbon

Fig. 5. Schematic presentation of linear polymeric complexes in the dodecahedral geometry; the units are bridged by an E,E-type bidentate ligand.

(iii) Dodecahedral structures

Ytterbium(III) formate [16] and ytterbium(III) (methylthio)acetate [17] form dodecahedral structures. Each pair of unit complexes is bridged by only one E,E-type carboxylate bridge, as shown schematically in Fig. 5, to give a linear polymeric form. Each intermetallic distance in this type of chain is long.

D. STRUCTURES OF ENNEA-COORDINATE LANTHANOID(III) COMPLEXES

In many complexes of this type, a pair of adjacent TTP-type complexes share a common bottom triangle edge, and the triangles are almost coplanar. (Sometimes, but not always, the center of symmetry is at the midpoint of the common edge.) The neodymium(III) 1-hydroxy-2-naphthoate ethanol adduct [7] is in a dimeric form of this type, while cerium(III) acetate [30] and m-hydroxybenzoate [31] are, as shown schematically in Fig. 6, in this type of linear polymeric form. In the light lanthanoid(III) chloroacetates, pairs of the two crystallographically independent dimers of this type are connected
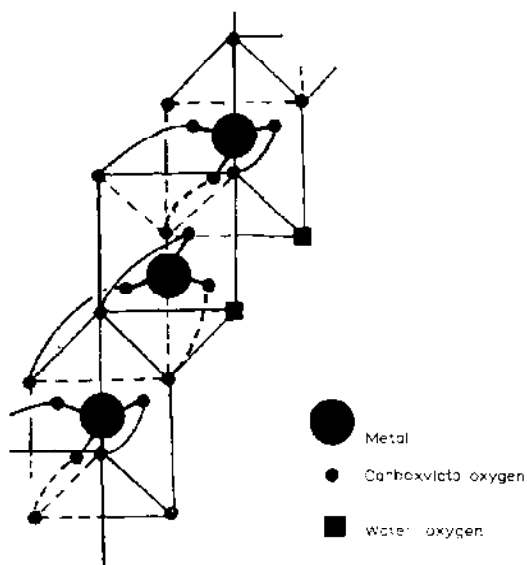

● Metal

● Carboxylato oxygen

■ Water oxygen

Fig. 6. Schematic presentation of the bridges between the unit TTP-type complexes of cerium m-hydroxybenzoate, $[CeL_3(H_2O)]_n$.
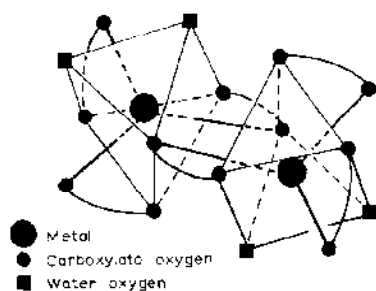
Fig. 7. Schematic presentation of the bridges in the heavy lanthanoid (Gd Yb) acetate tetrahydrate dimer.

by another unit complex of bicapped SAP geometry forming a linear chain (see Section E (i)) [31].

However, as shown schematically in Fig. 7, some complexes consisting of dimeric TTP units, where the center of symmetry is at the midpoint between two metal atoms, are bound by bridges where one apex of one complex is used as a cap of the other complex. For example, in the heavy lanthanoid(III) and yttrium(III) acetate tetrahydrates [12,33–35], two TTP-type units are bridged by two tridentate-type carboxylate ions in this way. In the (methylthio)acetate of neodymium(III) [20], there are two crystallographic types of neodymium atom, and one of them is in this type of dimeric form; pairs of the dimer are bridged by another type of unit complex forming a linear polymeric chain (see Section E (i)).

E. THE COMPLEX UNITS OF OTHER COORDINATION NUMBERS

(i) Capped polyhedrons

In the linear chain complexes of the light lanthanoid(III) chloroacetates [32] and the neodymium(III) (methylthio)acetate [20], a capped SAP-type unit complex connects each pair of dimers of the TTP-type units. In the former case, especially in its lanthanum(III) complex, another oxygen atom also approaches the side cap-position of this type of unit, which is considered to be deca-coordinate. In the guanidinium tetraacetatolanthanoidate(III) hydrates (M = La through Sm), as shown in Fig. 8, the coordination geometry around the central metal atom is regarded as a *cis*-bicapped cube, though deformed [3,36]: the distances between the longest M O of an apex of the cube are a little too long especially in the complexes of the higher atomic number metals. In the dimer, a couple of the unit complexes are bridged, where an apex and a cap atom of a unit complex are used as the cap and the
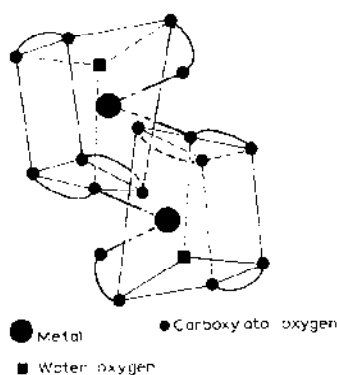
Fig. 8. Schematic presentation of the bridges in the guanidinium tetraacetatoaqualanthanoidate(III) dimer (La–Sm).

apex of the other complex respectively, and the center of symmetry is at the midpoint between the metal atoms.

(ii) Scandium(III) carboxylates

Scandium(III) chloroacetate is in an octahedral configuration, and pairs of metal atoms are bridged by three Z,Z-type carboxylate ions respectively, forming a linear polymer, as shown in Fig. 9; the three oxygen atoms of the three ligands bridging to one side metal atom are in the *fac* configuration [10].

Scandium(III) formate is also octahedral, with three pairs of Z,Z-type carboxylate ions bridging to three other metal atoms respectively; the complex has a two-dimensional polymeric form [13].
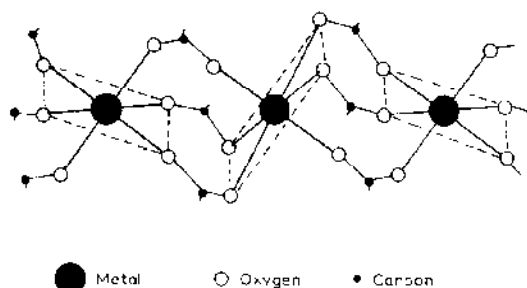

Fig. 9. Schematic presentation of the triple bridges between the unit octahedral complexes of the linear polymeric scandium(III) chloroacetate, $[ScL_3]_n$.

F. A SERIES OF RARE EARTH COMPLEXES OF THE SAME CARBOXYLATE LIGAND

During the synthetic process, if non-aqueous solvent–water mixtures with different compositions are used as the mother liquor to obtain crystals, the number of hydrated water molecules in the respective crystals is expected to change. In such a case, either the central metal complex core is changed, or only the number of non-coordinated water molecules is changed.

As an example, three kinds of neodymium(III) 1-hydroxy-2-naphthoate were synthesized, and all their structures were elucidated; their metal-complex cores are shown schematically in Fig. 10 [7–9]. The coordinating types of ligand are different from each other.

In addition, two kinds of yttrium(III) formate with different structures were also reported [11,14,37].

However, even when almost the same synthetic conditions are applied to obtain the lanthanoid(III) complexes of the same carboxylate, two series of isomorphous salts, of light and heavy lanthanoids were obtained respectively. The borderline element is not always gadolinium, which is at the center of the series, though in some cases this is true. The lanthanoid chloroacetates in the crystalline state are divided into two isomorphous groups: lanthanum through europium, and gadolinium through ytterbium as well as yttrium [19,32].

With guanidinium tetraacetatolanthanoidate(III) monohydrates, only the lanthanum through samarium salts were obtained by the common synthetic method. If the method is applied to the heavier lanthanoids, only their acetate (tetrahydrate) crystals were deposited [3]. However, the SAP-type
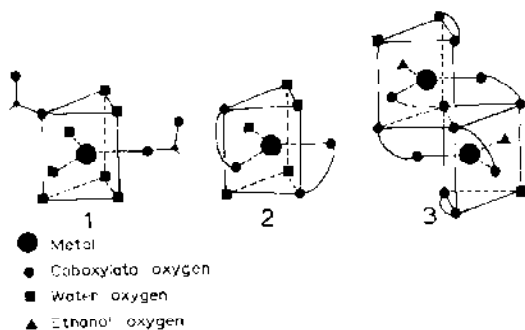

● Metal
● Carboxylate oxygen
■ Water oxygen
▲ Ethanol oxygen

Fig. 10. The metal cores of the three types of neodymium(III) 1-hydroxy-2-naphthoate crystals: 1, $[ML_2(H_2O)_7](HL) \cdot H_2O$; 2, $[ML_2(H_2O)_6](HL) \cdot 2H_2O$; 3, $[\{ML_3(H_2O)(C_2H_5OH)\}_2] \cdot 2H_2O \cdot 2C_2H_5OH$.

m-hydroxybenzoate tetrahydrates were obtained with samarium through ytterbium, and the same synthetic method gave only their acid adducts $[ML_3(H_2O)_2] \cdot HL \cdot 2H_2O$ (HL = *m*-hydroxybenzoic acid) with lanthanum through neodymium [27].

There are some carboxylates which have three (or more) types of isomorphous series observed through the lanthanoid elements, as discussed below.

In the case of acetates, although the boundaries are not yet clarified, the lanthanum [38], cerium [30] and heavy lanthanoid salts [3,33–35] exhibit different structures from each other. In the case of (methylthio)acetates, obtained by the same synthetic method, the lanthanum salt includes 4.5,

TABLE 1

The typical variation of the M–O interatomic distances of the corresponding tridentate-type ligand in a series of isomorphous lanthanoid(III) carboxylates

(i) Guanidinium tetraacetatoaqualanthanoidates(III) ($[(NH_2)_3C]_2[M_2L_8(H_2O)_2]$)

M	M–O′ [a]	M–O [a]	M′–O′ [a]	M–O (calc) [b]	
				$N = 10$ [c]	$N = 9$ [c]
La	2.860	2.601	2.529	2.62	2.57
Ce	2.880	2.571	2.505	2.60	2.55
Pr	2.891	2.547	2.483	2.58 [d]	2.53
Nd	2.919	2.529	2.465	2.56 [d]	2.48
Sm	3.074	2.475	2.401	2.53 [d]	2.48

(ii) Lanthanoid(III) nicotinates ($[ML_3(H_2O)_2]$)

M	M–O′ [a]	M–O [a]	M′–O′ [a]	M–O (calc) [b]	
				$N = 8$ [c]	$N = 7$ [c]
La	2.918	2.536	2.513	2.51	2.45
Sm	3.223	2.411	2.363	2.43	2.37
Tm	3.487	2.306	2.260	2.40	2.35 [d]

(iii) Lanthanoid(III) chloroacetates ($[M_3L_9(H_2O)_5]_n$)

M	M–O′ [a]	M–O [a]	M′–O′ [a]	M–O (calc) [b]	
				$N = 9$ [c]	$N = 10$ [c]
Gd	2.802	2.472	2.350	2.46	2.40
Er	2.853	2.385	2.287	2.41	2.35
Yb	2.897	2.368	2.250	2.39	2.34

[a] The positions of M, M′, O and O′ in the table are the same as those in Figs. 1–6.
[b] Sums of the respective Shannon's ionic radii, where M is tervalent, and O is divalent (coordination number is 2, 1.35 Å). See R.D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751. [c] The coordination number (N) of the metal atom. [d] As the ionic radii of these ions with this coordination number were not given by Shannon, values of 0.5 Å longer than those of the ennea-coordinate ions are tentatively adopted.

cerium through europium salts 1.5. and dysprosium and ytterbium salts two water molecules per metal atom respectively [17.20]. Although the dihydrate crystals of yttrium, holmium and erbium formates are orthorhombic, that of ytterbium is triclinic [11,14–16]. In the case of the nicotinates, however, the lanthanum through gadolinium salts are found to be isomorphous [21], and recently, it was reported that even the thulium salt has the same crystal structure [22]. Therefore this salt has only one type of structure among almost all the lanthanoids.

There are only a few reports concerning the crystal structure comparison of a series of isomorphous lanthanoid carboxylates. From the series of structural data for the guanidinium tetraacetatolanthanoidates [3], lanthanoid monochloroacetates [19,32] and their m-hydroxybenzoates [27], the unit cell volume (and accordingly also each axis length) generally decreases with atomic number of the central metal. In each series, the average M–O bond lengths also decrease in the same order, though not all the bonds are shortened equally. Generally, some relatively long M–O bonds in the early member metal complexes are not shortened so much as the others in the later member complexes; sometimes they are elongated to give ligating space to other oxygen atoms. Depending on such unequal changes in the bond lengths, the relative positions of some atoms are also changed slightly to accomplish the closest possible packing of the ligating atoms around the metal atom. However, these changes are not sufficient to rule them out from the isomorphous group. The geometries of the respective carboxylate ions in the isomorphous series are also kept about the same. The most apparent
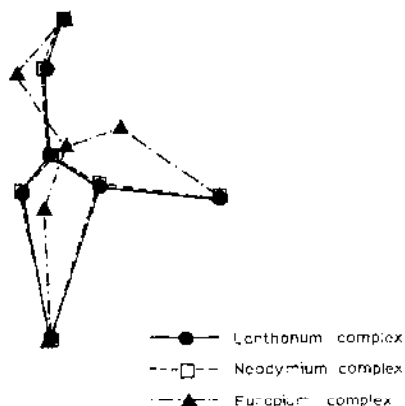

—●— Lanthanum complex

---□--- Neodymium complex

·—▲—· Europium complex

Fig. 11. The projection of a tridentate-type ligand and the bonding metal atoms of the light lanthanoid chloroacetates, $[M_3L_9(H_2O)_5]_n$; a common origin of the unit cell and the common scaling lengths are taken (HL = chloroacetic acid).

ligand deformations are found in the tridentate ligands. In the typical tridentate carboxylate ions, the M–O, M′–O′ and M–O′ bonds should be equal, but in many cases the M–O′ bond is weaker than the other two bonds. In such cases, the M–O′ bond is elongated with the atomic number of the metal atom. The examples found in some series of salts are shown in Table 1 [3,19,21,22]. If the deformation is extreme, the ligand is expected to be regarded as a Z,E-type bidentate; the directions of the C O and M′ O′ bonds are kept on the opposite side of the C–O′ bond from each other. However, such extreme cases are rarely found; at most, it only turns into an intermediate of both types. In the case of a light lanthanoid chloroacetate [32], the form of one tridentate carboxylate ion in the complex in the lanthanum through neodymium salts shows the above-mentioned typical change. However, in the europium salt, it suddenly turns into a Z,Z-type bidentate bridge of approximately standard interatomic distances and angles. The superposed projection of the ligands in the lanthanum, neodymium and europium complexes are shown in Fig. 11 [32]. Such a sudden complete change of ligand form is exceptional and rarely found.

G. CONCLUSION

From the structural data mentioned above, we suspect that in the lanthanoid carboxylates the bonds around each metal atom are likely to be the intermediate between the ionic and coordinate bonds. Of course, respective anionic ligands are approximately localized around each metal complex core, forming a complex molecule such as that of the $3d$ metals: the anions are not distributed in the crystal as in typical ionic salts, but the bridging carboxylate ions between two metal atoms are regarded as belonging to the two metal atoms. As there are many bridging anions, they are expected to some extent to engender delocalization. Moreover, the apparent coordination number of the metal atoms of these complexes is very high; to attain such a coordination number, the ligating atoms accomplish the closest possible packing around each metal atom. Therefore, locally, non-directional interatomic forces between the metal and the ligating atoms, as well as between ligating atoms are likely to be the main factors in selecting the respective coordination geometry. The hybridization orbital concept, which is useful with the $3d$-metal complexes, is not thought to be appropriate for the lanthanoid carboxylates. Of course, the mutual steric hindrance of the ligand molecules should be considered as well.

42

REFERENCES

1　R.C. Mehrotra and R. Bohra, Metal Carboxylates, Academic Press, New York, 1983, p. 1.
2　E.R. Birnbaum, Gmelin Handbook of Inorganic Chemistry, 8th edn., System No. 39, Part D5. Springer, Berlin, 1984, p. 1.
3　H. Sawase, Y. Koizumi, Y. Suzuki, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 57 (1984) 2730.
4　A. Ouchi, Y. Sato, Y. Yukawa and T. Takeuchi, Bull. Chem. Soc. Jpn., 56 (1983) 2241.
5　J.F. Sawyer and R.J. Gillespie, Prog. Inorg. Chem., 34 (1986) 65.
6　N.W. Alcock, Adv. Inorg. Chem. Radiochem., 15 (1972) 1.
7　Y. Ohki, Y. Suzuki, T. Takeuchi, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 59 (1986) 1015.
8　Y. Ohki, Y. Suzuki, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 551.
9　Y. Ohki, Y. Suzuki and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 1543.
10　Y. Sugita, Y. Ohki, Y. Suzuki and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 3441.
11　A.S. Antsyshkina, M.A. Porai-Koshits, I.V. Arkhangel'ski and L.A. Butman, Koord. Khim., 2 (1976) 565.
12　A.S. Antsyshkina, M.A. Porai-Koshits, I.V. Arkhangel'ski, V.N. Ostrikova and A.Z. Amanov, Izv. Akad. Nauk Az. SSR, 34 (1978) 22.
13　M.K. Gusejnova, A.S. Antsyshkina and M.A. Porai-Koshits, Zh. Strukt. Khim., 9 (1968) 1040.
14　H.R. Wenk, Z. Kristallogr., 154 (1976) 137.
15　N.G. Furmanova, L.V. Sobolova, N.V. Belov and L.M. Belyaev, Krystallografiya, 26 (1981) 1315.
16　N.G. Formunova, L.V. Sovolova, L.I. Khapaeva and N.V. Belov, Kristallografiya, 28 (1983) 62.
17　A. Ouchi, M. Shimoi and S. Kondo, Bull. Chem. Soc. Jpn., 58 (1985) 1053.
18　M.S. Khiyalov, I.R. Amiraslanov, F.N. Musaev and Kh.S. Mamedov, Koord. Khim., 8 (1982) 548.
19　Y. Sugita and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 171.
20　S. Kondo, M. Shimoi, A. Ouchi and T. Takeuchi, Bull. Chem. Soc. Jpn., 55 (1982) 2840.
21　J.W. Moore, M.D. Glick and W.A. Baker, Jr., J. Am. Chem. Soc., 94 (1972) 1858.
22　K. Prout, J.M. Martin, C.A. Hutchinson, Jr., Acta Crystallogr., Sect. C, 41 (1985) 201.
23　J. Kay, J.W. Moore and M.D. Glick, Inorg. Chem., 11 (1972) 2818.
24　L.A. Aslanov, I.D. Kiekbaev, I.K. Abdul'minev and M.A. Porai-Koshits, Kristallografiya, 19 (1974) 170.
25　I.K. Abdul'minev, L.A. Aslanov, M.A. Porai-Koshits and R.A. Chupakhina, Zh. Strukt. Khim., 14 (1973) 383.
26　M.S. Khiyalov, I.R. Amiraslanov, Kh.S. Mamedov, F.M. Movsumov, Koord. Khim., 7 (1981) 445.
27　Y. Koizumi, H. Sawase, Y. Suzuki, T. Takeuchi, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 57 (1984) 1809.
28　S.P. Bone, D.B. Sowerby, R.D. Verma, J. Chem. Soc., Dalton Trans., (1978) 1544.
29　T. Imai and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 408.
30　G.G. Sadikov, G.A. Kukina and M.A. Porai-Koshits, Zh. Strukt. Khim., 8 (1967) 551.
31　Y. Koizumi, H. Sawase, Y. Suzuki, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 57 (1984) 1677.
32　T. Imai, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 60 (1987) 159.
33　M.C. Favas, D.L. Kepert, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1980) 454.

34 J.W. Bats, R. Kalus and H. Fuess, Acta Crystallogr., 35 (1979) 1255.
35 L.A. Aslanov, I.K. Abdul'minev, M.A. Porai-Koshits and V.I. Ivanov, Dokl. Akad. Nauk SSSR, 205 (1972) 343.
36 G.G. Sadikov, G.A. Kukina and M.A. Porai-Koshits, Zh. Strukt. Khim., 12 (1971) 859.
37 N.G. Furmanova, Z.P. Razmanova, L.V. Sobolova, I.A. Maslyanitsin, G. Sigert, V.D. Shigorin and G.P. Shipulo, Kristallografiya, 29 (1984) 476.
38 A.S. Antsyshkina, M.A. Porai-Koshits, I.V. Arkhangel'ski, V.N. Ostrikova and A.Z. Amanov, Dokl. Akad. Nauk Az. SSR, 36 (1980) 47.