

The Geometry of Calcium-Carboxylate Interactions in Crystalline Complexes

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Abstract

The geometries of some 170 examples of calcium-carboxylate interactions from crystal structures of calcium complexes are reviewed. Calcium-carboxylate interactions fall into three main categories: a unidentate mode in which the Ca ion binds to only one of the carboxylate O atoms; a bidentate mode in which the carboxylate ion uses both O atoms to chelate the Ca ion; and an additional chelation mode, the α mode, that is observed when a suitable ligand for the Ca ion is attached at the α position and in which chelation of the Ca ion is achieved by use of the α substituent together with one of the carboxylate O atoms. The three modes show distinct geometrical preferences, but in each there is a strong tendency for the Ca ion to lie near the plane of the carboxylate group. In general, there is little tendency for a Ca ion to be collinear with the C—O bond. The unidentate examples cluster on both sides of the C—O bond, with most Ca ions lying at Ca—O—C angles of about 150–170° on the side away from the second O atom of the carboxylate group, or 110–140° on the side toward the second O atom. The Ca ions bound in the bidentate mode are confined to a restricted region by interactions with both O atoms of the carboxylate groups; these Ca ions occur at Ca—O—C angles of about 90°. In the α -chelation mode, Ca ions are restricted to a narrow region with Ca—O—C angles of about 110–130°. There is an apparent correlation between Ca—O distance and Ca—O—C angle; examples with shorter Ca—O distances tend to be those with more nearly linear Ca—O—C angles.

Introduction

As part of a systematic study of the structural chemistry of the Ca ion, we have compiled crystallographic data on the interactions of this cation with certain specific types of ligands. From the distribution of observed calcium-ligand geometries, we have sought features of a general nature that might aid in understanding the stereochemistry of this cation. An analysis of calcium-water interactions has been published

(Einspahr & Bugg, 1980). We present here the results of a second study, an analysis of the interactions between Ca ions and carboxylate* groups as observed in a variety of crystal structure determinations. A preliminary report of this work has been published (Einspahr & Bugg, 1977).

Experimental

We have examined 54 crystal structures that display calcium-carboxylate interactions. The structures include 59 crystallographically independent Ca ions, which are coordinated to a total of 94 crystallographically independent carboxylate groups. Ca ions are usually found to bind several carboxylate groups. The most commonly observed number is three, and the carboxylate groups so bound may be crystallographically independent or symmetry-related. Carboxylate groups are likewise found to coordinate to more than one Ca ion; the most common number is two Ca ions. For the purpose of our analysis, we divide the calcium-carboxylate interactions into the three general categories depicted in Fig. 1. Those calcium interactions with only one O atom of a carboxylate group are classified as unidentate (Fig. 1*a*); there are 105 such examples. Those interactions involving chelation by the pair of O atoms from a single carboxylate group are classified as bidentate (Fig. 1*c*); there are 29 examples of this type. A third mode of interaction that we have analyzed involves those carboxylate derivatives that chelate Ca ions through a carboxylate O atom acting in concert with a suitable ligand (O or N) that is bonded to the atom in the α position of the derivative (Fig. 1*b*). We included 36 examples of this type of interaction, which we designate as the α mode.

* A report of the crystal structure of a calcium-mandelate-acetate complex containing acetic-acid solvate molecules has appeared (Cameron & Duffin, 1977). The positions of the H atoms in this structure are not fixed with certainty, and there are suggestions of disorder in the H-bonding scheme. Nevertheless, it appears clear that, whatever arrangement the H atoms assume, this structure must contain the only examples we find of binding of Ca ions by un-ionized carboxyl groups.

These crystal structures also include several examples of more complex patterns that involve one or more ligands in addition to a carboxylate group in the chelation of a Ca ion. We have assigned each of these more complex chelation examples to either the unidentate or the α categories (Fig. 1*a,b*). Most of these complex examples include a ligand atom attached to the α position and follow the general trend that is observed for the simple α chelates; these examples are included in the α category. The few remaining examples of complex chelation geometries appear indistinguishable from typical unidentate interactions, and they are included in the unidentate category. We find no examples of complex chelation patterns in which both O atoms of the carboxylate group are coordinated to the Ca ion (the bidentate mode).

In a few cases, it seemed difficult to distinguish between the unidentate and bidentate modes by simple inspection. In those cases, examples were assigned to the unidentate category if three criteria were satisfied: (1) one of the two Ca--O--C angles was greater than 100° , (2) the ratio of the two Ca--O distances to the two O atoms of the carboxylate group was outside the range 0.833–1.20, and (3) one of the Ca--O distances to the carboxylate group in question was significantly longer than all other Ca--O distances within the calcium coordination polyhedron. Otherwise the interaction was included in the bidentate category. In most cases, it was immediately clear whether a particular interaction was an example of the unidentate or the bidentate mode.

The 54 crystal structures from which we draw examples do not represent a complete tabulation. We may have overlooked a few structure determinations that belong in our survey. We have purposely excluded from the survey a small number of structure determinations that give evidence of insufficient accuracy.

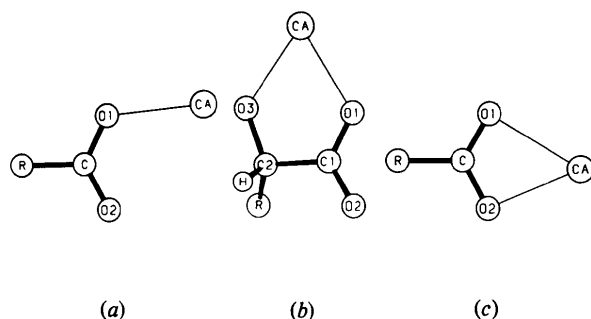


Fig. 1. The three most commonly observed modes of calcium-carboxylate interactions. (a) The unidentate mode in which the Ca ion interacts with only one of the two O atoms of the carboxylate group. (b) The α mode in which the Ca ion is chelated by a carboxylate O atom combined with a suitable ligand atom attached to the α position. (c) The bidentate mode in which the Ca ion is chelated by the pair of carboxylate O atoms. [These drawings, as well as those of Figs. 3 and 4, were prepared with the aid of the program ORTEP (Johnson, 1965).]

So as to minimize the subjective aspects of this culling, each rejected structure was required to demonstrate evidence of both (1) poor data and/or poor refinement as judged by the usual indices (for example, all but one of the rejected structures have R indices greater than 0.1), and (2) improbable distortions of molecular geometry, especially multiple aberrations in the carboxylate geometry. Culled from the survey by application of these criteria are all structure determinations based only on projection data and all structure determinations with R indices greater than 0.15. Also eliminated are all examples in which the carboxylate group has a C—O bond longer than 1.4 Å, or in which the sum of the three angles about the carboxylate C atom is less than 359° . References to the structure reports that contribute examples to this study are shown in Table 1.

Geometry of the carboxylate group

The distribution of carboxylate geometries was examined in order to assess the quality of the accumulated set of calcium-carboxylate examples. Histograms showing the observed distributions of C—O and C—C bond distances, and C—C—O and O—C—O bond angles are shown in Fig. 2(*a,b,c,d*). Fig. 2(*e*) shows the distribution of a parameter Δ , which is the absolute value of the deviation from 360° of the sum of the three bond angles about the carboxylate C atom. We have selected Δ as a measure of carboxylate planarity. The Δ distribution and the distributions of C—C bond distances and C—C—O bond angles include only those carboxylate examples that have a C atom in the α position. The average carboxylate group included in this survey has C—O distances of 1.25 Å, a C—C distance of 1.52 Å, C—C—O angles of 118° , an O—C—O angle of 124° , and is within 0.1° of planarity as judged by the parameter Δ . As may be seen in Fig. 2, the observed carboxylate distances and angles appear to form normal distributions with estimated standard deviations of 0.02 Å and 2° , respectively. The sample contains only 10 examples with Δ values greater than 0.1° , but the range of Δ extends to 0.6° .

For the most part, the carboxylate groups in these calcium complexes display bond lengths and angles that are typical of those found in other crystal structures of carboxylate derivatives (see, for example, Borthwick, 1980). For calcium-carboxylate interactions of the bidentate mode, however, calcium binding appears to produce some small distortions of the carboxylate bond angles. These effects can be seen from Fig. 2(*c*) and (*d*), in which the contributions from bidentate examples are indicated by shaded portions of the histograms. The C—C—O and the O—C—O bond-angle distributions of the bidentate examples differ slightly from those of the rest of the calcium-carboxylate examples. The average O—C—O angle for

Table 1. *References to crystal structure reports from which calcium-carboxylate examples are drawn*

Ca(Malonate)-2H ₂ O, Gel-grown phase Albertsson, J., Oskarsson, A. & Svensson, C. (1978) Acta Cryst. B34 , 2737-2743.	CaBr(Pantothenate) DeLucas, L., Einspahr, H. & Bugg, C. E. (1979) Acta Cryst. B35 , 2724-2726.	Ca(2-Keto-Gluconate) ₂ -3H ₂ O Mazid, M. A., Palmer, R. A. & Balchin, A. A. (1976) Acta Cryst. B32 , 885-890.
Ca(Tartrate)-4H ₂ O Ambady, G. K. (1968) Acta Cryst. B24 , 1543-1557.	Ca(Sn(Acetate)) ₂ Dewan, J. C., Silver, J., Donaldson, J. D. & Thomas, M. J. K. (1977) J. Chem. Soc. Dalton, 2319-2322.	Ca(Glycerate) ₂ -2H ₂ O Meehan, E. J. Jr., Einspahr, H. & Bugg, C. E. (1979) Acta Cryst. B35 , 828-832.
Ca(Ethylenedioxydiacetate)-3H ₂ O Ancillotti, F., Boschi, G., Perego, G. & Zazzetta, A. (1977) J. Chem. Soc. Dalton, 901-905.	Ca(Glutamate)-3H ₂ O Einspahr, H. & Bugg, C. E. (1974) Acta Cryst. B30 , 1037-1043.	CaCl ₂ (Glycylglycine) ₂ Meulemans, R., Piret, P. & Van Meerassche, M. (1971) Bull. Soc. Chim. Belges 80 , 73-81.
CaCl ₂ (Sarcosine) ₂ Ashida, T., Bando, S. & Kakuda, M. (1972) Acta Cryst. B28 , 1560-1565.	Ca(Glutamate) ₂ -4H ₂ O Einspahr, H. & Bugg, C. E. (1979) Acta Cryst. B35 , 316-321.	CaI ₂ (Glycine) ₃ -H ₂ O Natarajan, S. & Mohana Rao, J. K. (1977) Curr. Sci. 46 , 595.
Ca(5-Keto-Gluconate) ₂ -2H ₂ O Balchin, A. A. & Carlisle, C. H. (1965) Acta Cryst. 19 , 103-111.	Ca(Aspartate)(Ascorbate)-H ₂ O Einspahr, H. & Bugg, C. E. (1980) In Preparation.	Ca ₂ (Co(Aspartate) ₂) ₄ -15H ₂ O Oonishi, I., Saito, S. & Saito, Y. (1975) Acta Cryst. B31 , 1318-1324.
Ca ₂ (Ethylenediaminetetraacetate)-7H ₂ O Barnett, B. L. & Uchtman, V. A. (1979) Inorg. Chem. 18 , 2674-2679.	CaCl(Glutamate)-H ₂ O Einspahr, H., Gartland, G. L. & Bugg, C. E. (1977) Acta Cryst. B33 , 3385-3390.	Ca(Co(Aspartate)) ₂ -10H ₂ O Oonishi, I., Shibata, M., Marumo, F. & Saito, Y. (1973) Acta Cryst. B29 , 2448-2455.
CaNa(Nitrilotriacetate) Barnett, B. L. & Uchtman, V. A. (1979) Inorg. Chem. 18 , 2674-2678.	Ca(Cycloheptanecarboxylate) ₂ -5H ₂ O Flapper, W. M. J., Verschoor, G. C., Rutten, E. W. M. & Romers, C. (1977) Acta Cryst. B33 , 5-10.	Ca(Gamma-Carboxyglutamate)-3H ₂ O Satyshur, K. & Rao, S. T. (1977) Private Communication.
Ca(Acetate)(Thioacetate)-3H ₂ O Borel, M. M. & Ledesert, M. (1975) J. Inorg. Nucl. Chem. 27 , 2334-2335.	CaCl(Acetate)-5H ₂ O, Monoclinic Giuseppetti, G., Tadini, C. & Ungaretti, L. (1970) Period. Mineral. 39 , 145-158.	Ca(Phthalate)-H ₂ O Schuckmann, W., Fuess, H. & Bats, J. W. (1978) Acta Cryst. B34 , 3754-3756.
Ca(Hydrazinecarboxylate) ₂ -H ₂ O Braibanti, A., Manotti Lanfredi, A. M., Pellinghelli, M. A. & Tiripicchio, A. (1971) Acta Cryst. B27 , 2261-2268.	CaCl(Acetate)-5H ₂ O, Triclinic Giuseppetti, G., Tadini, C. & Ungaretti, L. (1972) Period. Mineral. 41 , 9-21.	Ca(Hydrogen Citrate)-3H ₂ O Sheldrick, B. (1974) Acta Cryst. B30 , 2056-2057.
Ca(Hydrazinecarboxylate) ₂ Braibanti, A., Manotti Lanfredi, A. M., Pellinghelli, M. A. & Tiripicchio, A. (1971) Acta Cryst. B27 , 2448-2452.	Ca(Garcinate)-4H ₂ O Glusker, J. P., Minkin, J. A. & Casciato, C. A. (1971) Acta Cryst. B27 , 1284-1293.	Ca(Serinate) ₂ -2H ₂ O Sicignano, A., Gandhi, S. & Eriks, K. (1977) Private Communication.
Ca(Malate)-2H ₂ O Brändén, C.-I. & Söderberg, B.-O. (1966) Acta Chem. Scand. 20 , 730-738.	Ca(Hibiscusate)-4H ₂ O Glusker, J. P., Minkin, J. A. & Soule, F. B. (1972) Acta Cryst. B28 , 2499-2505.	Ca(Oxalate)-2H ₂ O Sterling, C. (1965) Acta Cryst. 18 , 917-921.
Ca(Malonate)-2H ₂ O Briggman, B. & Oskarsson, A. (1977) Acta Cryst. B33 , 1900-1906.	Ca(Hydrogen Homophthalate) ₂ -5H ₂ O Gupta, M. P. & Prasad, N. (1976) Acta Cryst. B32 , 3257-3261.	Ca(Dipicolinate)-3H ₂ O Strahs, C. & Dickerson, R. E. (1968) Acta Cryst. B24 , 571-579.
Ca(Formate) ₂ , Alpha Phase Burger, N., Fuess, H. & Mason, S. A. (1977) Acta Cryst. B33 , 1968-1970.	Ca(Fumarate)-3H ₂ O Gupta, M. P., Prasad, S. M., Sahu, R. G. & Sahu, B. N. (1972) Acta Cryst. B28 , 135-139.	Ca(Gluconate)-4H ₂ O Taga, T. & Osaki, K. (1976) Bull. Chem. Soc. Japan 49 , 1517-1520.
Ca(Trans-1,2-Diaminocyclohexane-N, N'-Tetraacetatoaquoferrate(III)) ₂ -8H ₂ O Cohen, G. H. & Hoard, J. L. (1966) J. Amer. Chem. Soc. 88 , 3229-3234.	Ca(5-Ethylidenehydroorotate) ₂ -3H ₂ O Hingerty, B., Kulikowska, E., Saenger, W. & Shugar, D. (1976) Z. Naturforsch. 31c , 518-523.	CaNa(Galacturonate) ₃ -6H ₂ O Thanomkul, S., Hjortas, J. A. & Sorum, H. (1976) Acta Cryst. B32 , 920-922.
CaBr(Lactobionate)-4H ₂ O Cook, W. J. & Bugg, C. E. (1973) Acta Cryst. B29 , 215-222.	Ca(Hydrogen Maleate) ₂ -5H ₂ O Hsu, B. & Schlemper, E. O. (1978) Acta Cryst. B34 , 930-932.	Ca ₂ (Dihydrogen Mellitate)-9H ₂ O Uchtman, V. A. & Jandacek, R. J. (1980) Inorg. Chem. 19 , 350-355.
Ca(Benzo-15-Crown-5) ₂ (3,5-Dinitrobenzoate) ₂ -3H ₂ O Cradwick, P. D. & Poonia, N. S. (1977) Acta Cryst. B33 , 197-199.	CaCd(Acetate) ₄ -6H ₂ O Langs, D. A. & Hare, C. R. (1967) Chem. Comm., 890-891.	Ca(Oxydiacetate)-6H ₂ O Uchtman, V. A. & Oertel, R. P. (1973) J. Amer. Chem. Soc. 95 , 1802-1811.
CaBr(Gluconate)-3H ₂ O DeLucas, L., Bugg, C. E., Terzis, A. & Rivest, R. (1975) Carbohydr. Res. 41 , 19-29.	CaCu(Acetate) ₄ -6H ₂ O Langs, D. A. & Hare, C. R. (1967) Chem. Comm., 890-891.	CaCl ₂ (Glycylglycylglycine)-3H ₂ O van der Helm, D. & Willoughby, T. V. (1969) Acta Cryst. B25 , 2317-2326.
	Ca(Terephthalate)-3H ₂ O Matsuzaki, T. & Iitaka, Y. (1972) Acta Cryst. B28 , 1977-1981.	Ca(Nitrilotriacetate)-2H ₂ O Whitlow, S. H. (1972) Acta Cryst. B28 , 1914-1919.

bidentate examples is about 122°, some 2°, or one standard deviation, smaller than the overall average. Similarly, the average C-C-O angle for the bidentate mode of 119° is about 1° larger than the overall average value. Thus it appears that interactions of Ca ions with carboxylate groups in the bidentate mode tend to result in smaller O-C-O bond angles.

Parameters describing the geometry of calcium-carboxylate interactions

The calcium-carboxylate interactions in these crystal structures are described according to the coordinate

system depicted in Fig. 3. The pertinent features of this reference system are: (1) the ligand O atom of the carboxylate group is at the origin of a Cartesian coordinate system, (2) the carboxylate plane is coincident with the *xz* plane, (3) the C-O bond that joins the carboxylate C atom and the ligand O atom lies along the *z* axis, and (4) the second O atom of the carboxylate group is situated in the +*x*, -*z* quadrant of the *xz* plane. The calcium-carboxylate geometries can then be conveniently expressed in terms of spherical coordinates in the following manner: (1) the radial coordinate is the distance between the Ca ion and the ligand O atom; (2) θ is the acute angle between the

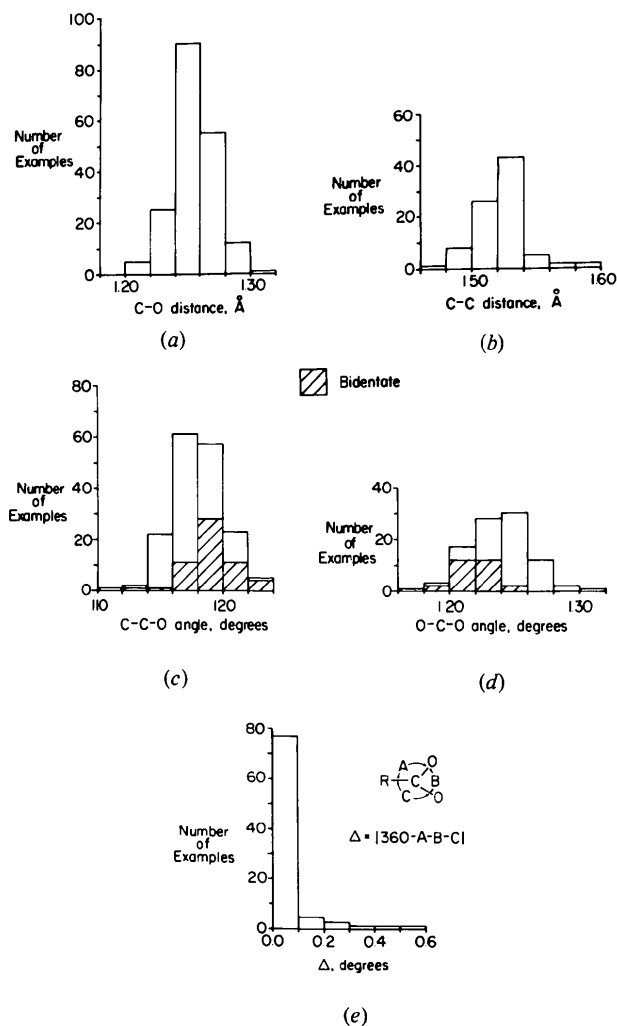


Fig. 2. Histograms describing the distribution of carboxylate geometries. (a) C—O distances. (b) C—C distances. (c) C—C—O angles. (d) O—C—O angles. (e) Δ , the angular deviation from planarity calculated as the positive difference between the sum of the three carboxylate angles (the O—C—O and two C—C—O angles) and 360° .

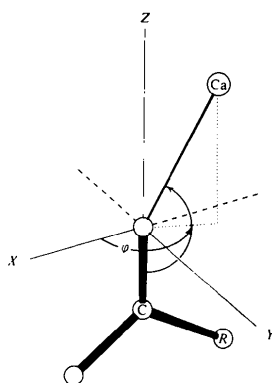


Fig. 3. Spherical and Cartesian coordinate systems for the description of calcium-carboxylate geometries.

Ca—O vector and the z axis; and (3) ϕ is the angle, measured in the counterclockwise direction about z, between the x axis and the projection of the Ca—O vector onto the xy plane.

The angle θ is a measure of the deviation of the Ca ion from collinearity with the C—O bond. Throughout our description of calcium-carboxylate interactions, we discuss the Ca—O—C angles, which are equal to $180^\circ - \theta$. The angle ϕ is useful in evaluating the position of the Ca ion relative to the two O atoms of the carboxylate group, and in monitoring orientations of Ca ions relative to the carboxylate plane.

In applying the parameters as we have defined them above, each unidentate and α example represents a single calcium-carboxylate geometry. Such is not the case for the bidentate examples. For these, each C—O bond of the carboxylate group may serve as the reference vector for calculation of the geometrical parameters, and two geometrical descriptions result. Both geometries for a bidentate example are included in the following analyses; but, where convenient, each is given half weight so as not to distort the overall distribution.

We expected that the distribution of calcium-carboxylate geometries might reflect the influence of a number of environmental factors, and we therefore monitored several parameters that are measures of calcium-carboxylate environments. One of these parameters is the calcium coordination number, which we take as the number of ligand atoms in the nearest-neighbor sphere about a Ca ion. In most cases, calcium coordination numbers could be assigned by inspection. In those structures where the coordination numbers were not obvious, they were assigned according to the criterion proposed by Brunner (1977). In addition to calcium coordination numbers, we also kept accountings of the numbers of H bonds and coordination bonds to each of the carboxylate O atoms.

Results

Stereoscopic representations of calcium-carboxylate interactions

The distribution of the calcium-carboxylate geometries can be seen from the stereoscopic drawings in Fig. 4, each of which shows a composite of calcium positions around a carboxylate group. Each individual calcium interaction with a carboxylate O atom is represented by a calcium position in these plots. The calcium position is plotted relative to the carboxylate O atom with which it interacts; this reference O atom is shown at the end of the vertical C—O bond in Fig. 4(a) and eclipses the C atom in Fig. 4(b). Unidentate examples are shown as filled circles. Examples of α chelation, shown as open circles, cluster on the left side

in each view in a region that is approximately equidistant from the carboxylate O atom and the second ligand atom (not shown), which is attached to the atom in the α position of the carboxylate derivative. Bidentate examples, which are also shown as open circles, cluster on the right side in each view in a region that is nearly equidistant from the two O atoms of the carboxylate group. In these stereoplots, each Ca ion bound in the bidentate mode is represented by two positions, which depict the locations of the Ca ion when each of the two carboxylate O atoms is used as the reference O atom.

Examination of Fig. 4 reveals a number of interesting features about the geometry of calcium-carboxylate interactions in these crystal structures:

(1) Ca ions generally lie near the planes of the carboxylate groups.

(2) Examples in the bidentate mode are confined to a restricted range by interactions with both O atoms of the carboxylate group. These interactions result in Ca--O--C angles that are near 90° .

(3) The α examples also show a restricted range of geometries, but the range is on the side of the C--O bond opposite that of the bidentate mode and Ca--O--C angles are somewhat greater than 90° .

(4) The unidentate examples occur in two different regions, one on either side of the C--O bond. Most of these examples have Ca--O--C angles of 110 – 170° . There are relatively few examples of Ca ions that are nearly collinear with the C--O bond.

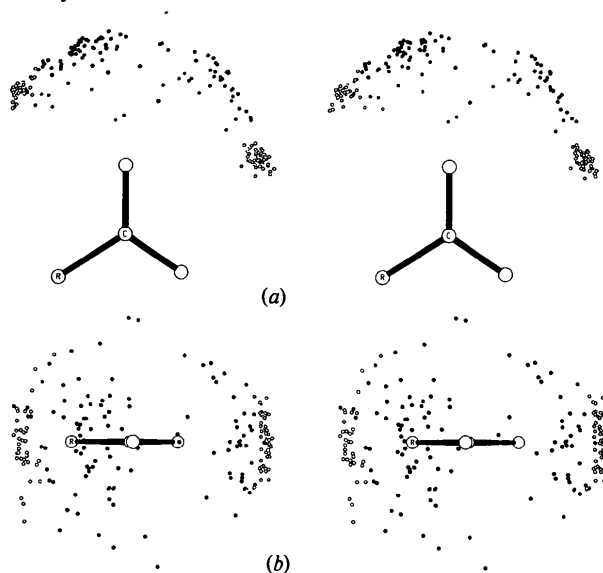


Fig. 4. Stereoplots of the distribution of observed calcium-carboxylate configurations. All calcium positions are plotted relative to one of the C--O bonds of the carboxylate group; the reference C--O bond is vertical in view (a) and is perpendicular to the page in view (b). Unidentate examples are shown as filled circles; examples of α and bidentate chelation are shown as open circles. Each bidentate example is represented by two open circles corresponding to the position of the Ca ion relative to each C--O bond.

Angular distributions

An outstanding feature of these interactions is the tendency for Ca ions to lie near the planes of carboxylate groups. According to the spherical coordinate system defined in Fig. 3, Ca ions that are coplanar with the carboxylate group would have φ values of 0 or 180° . Fig. 5 shows the distribution of φ values that are observed in these crystal structures. As suggested by the stereoplots in Fig. 4, the majority of the examples are clustered near φ values of 0 and 180° . The bidentate examples exhibit φ values near 0° ; the α examples exhibit φ values near 180° . The unidentate examples display a much broader distribution of φ values, but there is a clear tendency for these examples to assume values near $\varphi = 0^\circ$ or $\varphi = 180^\circ$. Fig. 6 is a histogram that describes the deviations of Ca ions from the carboxylate planes. All Ca ions in bidentate examples lie within 1 \AA of carboxylate planes. The majority of the α examples show deviations of less than 0.6 \AA from carboxylate planes, although deviations up to 1.6 \AA are found. The unidentate examples display deviations as great as 2.4 \AA ; but the median deviation for these examples is between 0.4 and 0.6 \AA , and the average deviation is 0.6 (5) \AA .

Fig. 7 depicts the distribution of Ca--O--C angles. All of the bidentate examples display Ca--O--C angles between 80 and 100° . The Ca--O--C angles of α examples lie in the range 110 – 140° . The bimodal distribution of unidentate examples is clear from Fig. 7. Most of the unidentate examples with Ca--O--C angles in the 110 – 140° range have φ values near 0° ; most of

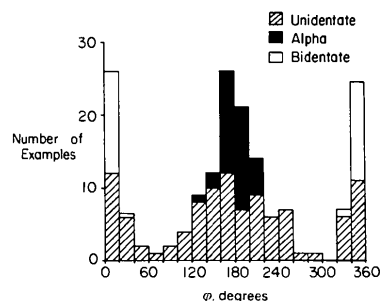


Fig. 5. Histogram showing numbers of examples as a function of φ , the dihedral angle between the Ca--O--C plane and the carboxylate O--C--O plane.

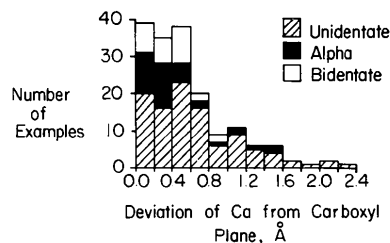


Fig. 6. Histogram showing numbers of examples as a function of the deviation of the Ca ion from the carboxylate plane.

the subset with Ca--O--C angles in the 150–170° range have φ values near 180°. There is little overlap in the distributions of Ca--O--C angles for the unidentate, bidentate and α modes. The only apparent region of overlap involves the α examples and the subset of unidentate examples with Ca--O--C angles of 110–140°; but, because the α examples occur near $\varphi = 180^\circ$ while the subset of unidentate examples with Ca--O--C angles of 110–140° is confined almost exclusively to the region near $\varphi = 0^\circ$, the apparent overlap is an artifact. As may be seen in Fig. 4, the actual region of overlap between α and unidentate modes, at Ca--O--C angles of about 130° and φ near 180°, involves fewer than about 15 examples.

Lengths of calcium-carboxylate coordination bonds

Fig. 8 shows a series of histograms that describe the distribution of coordination distances between Ca ions and the O atoms of carboxylate groups. The histogram on the left in Fig. 8 shows the overall distribution of Ca--O distances for the 170 unique calcium-carboxylate examples that we accumulated; the four histograms on the right subdivide the overall distribution according to calcium coordination number. In each histogram, a breakdown in terms of the three modes of calcium binding is provided. As was found in the calcium-water study (Einspahr & Bugg, 1980), the

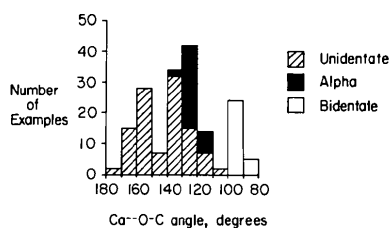


Fig. 7. Histogram showing numbers of examples as a function of the Ca--O--C angle.

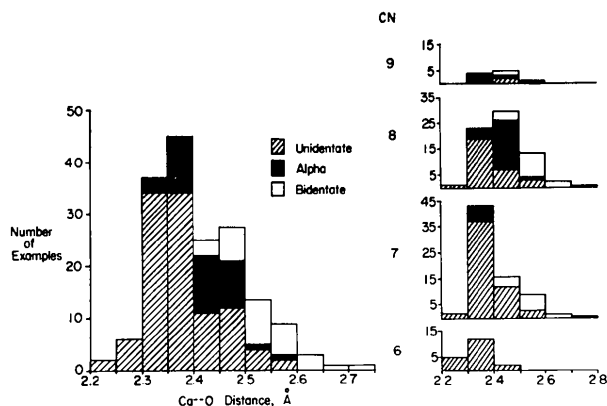


Fig. 8. Histograms showing numbers of examples as a function of the Ca--O distance. The four histograms on the right show a breakdown of the overall distribution according to calcium coordination number.

majority of the Ca--O distances lie between 2.3 and 2.5 Å. Although Ca--O distances range out to almost 2.75 Å, few examples occur beyond 2.6 Å. In the calcium-water study, no credible examples were found with Ca--O distances less than 2.3 Å. In this study, we find eight examples of calcium-carboxylate interactions with Ca--O distances between 2.2 and 2.3 Å, but no credible examples with Ca--O distances less than 2.2 Å. These eight examples apparently represent unusually strong calcium-carboxylate interactions, and all are found to occur in the unidentate mode.

The three modes show overlapping Ca--O distance distributions that differ (though not significantly in the statistical sense) in mean values. Averages for the unidentate, α , and bidentate modes are 2.38 (7), 2.42 (6) and 2.53 (7) Å, respectively. The tendency for unidentate examples to show shorter Ca--O distances, and bidentate examples longer distances, is also reflected in the series of histograms on the right in Fig. 8, in which the distribution of Ca--O distances is subdivided according to calcium coordination number. As expected, the higher coordination numbers correspond to longer average Ca--O distances. The proportion of unidentate examples decreases with increasing calcium coordination number, while the proportion of bidentate examples increases. The proportion of α examples also increases with increasing calcium coordination number, but in each histogram the peak in the distribution of α examples occurs at a shorter Ca--O distance than that of the bidentate examples. No α or bidentate examples were found in sixfold coordination polyhedra. As was found in the calcium-water study, the most commonly occurring calcium coordination numbers are seven and eight.

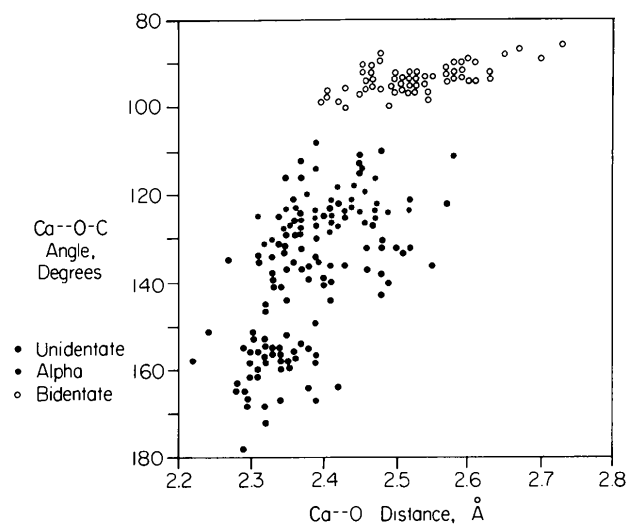


Fig. 9. A plot of paired values of Ca--O--C angle and Ca--O distance, one for each example. Bidentate examples are represented by two open circles corresponding to the position of the Ca ion relative to each C--O bond.

Fig. 9 shows the relationship between Ca--O distances and Ca--O--C angles. There appears to be a general tendency for Ca--O distances to decrease as the Ca--O--C angle approaches 180°, and this tendency is seen both in the overall distribution and in the distribution of the unidentate examples only. The longest Ca--O distances correspond to bidentate examples, which have Ca--O--C angles below 100°. All of the Ca--O distances below 2.3 Å correspond to unidentate examples that display Ca--O--C angles in the range 130–180°.

Estimates of the influence of the calcium-carboxylate environment

The 94 unique carboxylate groups that we examined are embedded in a wide variety of crystallographic environments. Each carboxylate O atom in this survey forms from one to three H bonds and/or coordination bonds. All, some or none of these bonds may be to Ca ions or to other metal ions, and each interaction with a metal ion may be of the unidentate, α or bidentate type. About 70% of the carboxylate O atoms that are coordinated to Ca ions form one additional interaction (an H bond or a coordination bond). We encountered no examples of carboxylate O atoms that form no interactions, or that form more than three interactions. About 85% of the carboxylate O atoms are coordinated to at least one metal ion.

Clearly, there are many different patterns in which calcium-carboxylate interactions can occur. For example, we encountered 30 carboxylate groups that form only unidentate interactions with Ca ions. These include 10 examples in which only one O atom of the carboxylate group is coordinated to a Ca ion, 15 examples in which each O atom binds a Ca ion, and five examples in which one of the O atoms binds two Ca ions. In four of these latter examples, the other O atom binds another Ca ion; in one it does not. Of the 29 carboxylate groups that bind Ca ions in the bidentate mode, about a third are not coordinated to any additional Ca ions, and about half bind an additional Ca ion with each of the carboxylate O atoms in a unidentate fashion. About a third of the carboxylate groups that bind Ca ions in the α mode bind no additional Ca ions; apart from three examples that bind an additional Ca ion in the bidentate mode, the remainder occur in several patterns that are combinations of α and unidentate modes. If this variety of patterns is taken as a measure of the diversity of environments in which calcium-carboxylate interactions occur, then it may be concluded that, while certain types of environments are found more frequently than others, no particular environments seem to dominate as influences of calcium-carboxylate geometries. On the contrary, it appears that the observed geometrical features of calcium-carboxylate inter-

actions persist despite a variety of quite different crystallographic environments.

Discussion

The most prominent feature of the distribution of calcium-carboxylate geometries is the clustering of Ca ions in rather restricted regions around the carboxylate groups. Ca ions generally lie near the planes of carboxylate groups, and they are largely confined to two regions that are located to the sides of the coordinating C—O bonds. The geometries are somewhat different for the unidentate, bidentate and α modes of interaction. However, in general, Ca ions are found at Ca--O--C angles in the range of 80–140° in the region between the two carboxylate O atoms, and in the range of 110–170° in the region on the other side of the coordinating C—O bond.

About one third of the carboxylate groups that bind Ca ions do so in the bidentate mode of chelation. The Ca ions bound in the bidentate mode cluster in a restricted region that is approximately equidistant from the carboxylate O atoms, at Ca--O--C angles in the range 80–100°, and close to the carboxylate plane. These geometrical features clearly distinguish the bidentate examples from the other modes of calcium-carboxylate interactions. Such a distinct separation between the bidentate examples and those unidentate examples that lie between the two O atoms of the carboxylate group was not anticipated. The discontinuity between the unidentate and bidentate modes can be seen in Figs. 4 and 9. The distinction is also obvious from the Ca--O distances: the longest Ca--O distance in the bidentate mode is 2.74 Å, which is considerably shorter than 2.97 Å, the lower limit found in unidentate examples for the distance between a Ca ion and the second O atom of the carboxylate group.

The Ca ions in examples of the α mode are all found within a rather narrow range of Ca--O--C angles between about 110 and 140°. However, in contrast to the bidentate mode, many of the α examples show considerable deviations from the carboxylate planes. The observed clustering within a narrow range of Ca--O--C angles is a consequence of the fact that the Ca ions bound in the α mode tend to occupy positions about equidistant from the two ligand atoms, the α substituent and the carboxylate O atom. The distribution of Ca ions relative to the carboxylate plane appears to be correlated with the orientation of the α substituent. While the α substituent usually lies near the plane of the carboxylate group (Dunitz & Strickler, 1968), there is considerable variation in the conformation about the bond between the carboxylate C atom and the atom in the α position. In some examples, α substituents deviate markedly from coplanarity with carboxylate groups, and the Ca ions in these examples

are displaced significantly from the carboxylate planes. Although the α examples tend to cluster in the region near the carboxylate plane, deviations up to 1.25 Å are observed, and φ values cover the range between 120 and 220°. The α -chelation pattern appears to be a particularly favorable configuration for binding Ca ions (Meehan, Einspahr & Bugg, 1979). We encountered 50 examples of carboxylate groups that possess an O or N atom attached to the atom in the α position. All of these examples display calcium binding in the α mode, except for one that binds a Ca ion in the bidentate mode (see Table 1: Glusker, Minkin & Soule, 1972) and three that do not bind a Ca ion at all (Table 1: Glusker, Minkin & Casciato, 1971; Mazid, Palmer & Balchin, 1976; Taga & Osaki, 1976).

The unidentate mode is the most common calcium-binding pattern that we encountered in these crystal structures. As expected, the geometry of the unidentate examples shows much more variability than that found in the bidentate or α modes. Nevertheless, there is a clear tendency for unidentate examples to cluster in rather well defined regions about the carboxylate groups. The unidentate examples show some significant deviations from the carboxylate planes (as great as 2.2 Å), but the majority of these examples lie within 0.6 Å of the carboxylate planes. There are also a few unidentate examples that display Ca--O--C angles that are atypical of the general distribution. However, it is noteworthy that the unidentate calcium-carboxylate interactions show restricted geometries, despite the absence of the constraints of chelation that encourage the clustering of Ca ions in particular regions.

It is not clear what factors might account for the observed bilobal distribution of unidentate examples. However, the distribution appears to be somewhat similar to that expected for the distribution of lone pairs of electrons on the carboxylate O atoms. Qualitative models for the electronic configuration of carboxylate O atoms describe the two unshared pairs of electrons on the O atoms in terms of sp^2 hybrid orbitals, which define diffuse lobes of electron density that have maxima in the carboxylate plane along directions of about 120° from the C—O bonds; residual electron density distributions resembling that expected for sp^2 hybridization have been observed in a variety of crystalline systems (Coppens, 1977). Assuming that Ca ions tend to interact with carboxylate O atoms along directions of maximum lone-pair electron density, one might expect to find calcium arrangements that display three general features: (1) Ca ions should show a preference for positions near the carboxylate plane, (2) there should be little tendency for Ca ions to lie at Ca--C—O angles near 180°, and (3) the Ca ions should cluster at Ca--C—O angles near 120° on both sides of the C—O bonds. These first two features are clearly apparent in the observed distributions. However, although the Ca ions in unidentate examples form

two clusters on the sides of the C—O bonds, the preferred Ca--C—O angles seem to deviate somewhat from 120°.

Regardless of the specific forces that account for calcium-carboxylate interactions, one might reasonably expect that these interactions would be sensitive to environmental and steric factors. Steric factors may be partially responsible for the observed distribution of unidentate examples. Most of the unidentate examples that are situated between the carboxylate O atoms display Ca--O—C angles in the 110–140° range, which is similar to the range that would be expected for trigonal binding to a carboxylate O atom. However, the unidentate examples that lie on the side of the C—O bond away from the second carboxylate O atom display much larger Ca--O—C angles, primarily in the range of 150–170°. Large deviations from trigonal configurations might be attributed to steric interactions between Ca ions and substituents that are attached to the atoms in the α positions of the carboxylate derivatives. A substituent at this position will tend to be nearly coplanar with the carboxylate group. If the ligand is a suitable calcium ligand, α chelation is found almost without exception. However, if the substituent is unsuitable as a calcium ligand, repulsion between this substituent and the Ca ion would be expected. Such repulsions should result in Ca--O—C angles that are considerably larger than those found for the α mode. It is noteworthy that the distribution of α examples and the neighboring subdistribution of unidentate examples are almost nonintersecting; the few examples that lie in the overlap region represent unusual carboxylate derivatives, such as those that have only H atoms as the atoms in the α position (calcium formate; Burger, Fuess & Mason, 1977, Table 1).

The observed correlation between Ca--O distances and Ca--O—C angles (Fig. 9) is somewhat surprising, considering the other evidence that Ca ions show little tendency to be collinear with the C—O bonds. On the face of it, one might expect that shorter Ca--O distances represent stronger and, therefore, more favorable calcium-carboxylate interactions. If this were so, the distribution of Ca--O—C angles, at least in the unidentate case, should show a significant number of examples near 180°, the region that corresponds to the shorter Ca--O distances. An alternative interpretation of our findings might be proposed on the basis of the hypothesis that atoms in crystals have non-spherical effective shapes (Nyburg, 1979). If the carboxylate O atoms have oblate shapes, flattened along the direction of the C—O bond, then the shorter distances at Ca--O—C angles near 180° may not be indicative of stronger Ca--O interactions.

It is clear that, in the crystalline state, stereochemical factors influence the geometries of calcium-carboxylate interactions. However, considering the wide variety of crystalline environments that are

sampled in our survey, we feel that the dominant geometrical features may have significance beyond the solid state. We would expect, for example, that the geometries of the bidentate and α modes would be relatively insensitive to environmental factors. The possibility remains that the observed distribution of the unidentate calcium-carboxylate geometries might be a consequence of crystallographic factors. Examination of nearest-neighbor interactions involving the carboxylate groups has not revealed any obvious crystallographic effects that might explain the restricted unidentate geometries, but a number of environmental factors that may be of significance have not been analyzed. Nevertheless, it appears likely that the unidentate distribution is also indicative of the calcium-carboxylate geometries that might be expected in other, noncrystalline environments.

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References*

- BORTHWICK, P. W. (1980). *Acta Cryst.* B36, 628–632.
 BRUNNER, G. O. (1977). *Acta Cryst.* A33, 226–227.
 CAMERON, T. S. & DUFFIN, M. (1977). *Cryst. Struct. Commun.* 6, 453–456.
 COPPENS, P. (1977). *Angew. Chem. Int. Ed. Engl.* 16, 32–40.
 DUNITZ, J. D. & STRICKLER, P. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 595–602. San Francisco: Freeman.
 EINSPAHR, H. & BUGG, C. E. (1977). *Calcium Binding Proteins and Calcium Function*, edited by R. H. WASSERMAN *et al.*, pp. 13–20. New York: Elsevier/North-Holland.
 EINSPAHR, H. & BUGG, C. E. (1980). *Acta Cryst.* B36, 264–271.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 MEEHAN, E. J. JR, EINSPAHR, H. & BUGG, C. E. (1979). *Acta Cryst.* B35, 828–832.
 NYBURG, S. C. (1979). *Acta Cryst.* A35, 641–645.

* See also Table 1.

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The Structure of Tricarbonyl(η^5 -cyclopentadienyl)rhenium(I)

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Abstract

[Re(C₅H₅)(CO)₃], CpRe(CO)₃ (Cp = η^5 -C₅H₅) crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.872$ (3), $b = 7.215$ (1), $c = 11.053$ (1) Å, $\beta = 116.46$ (2)°, $Z = 4$, $d_c = 2.626$ Mg m⁻³. The intensity data were obtained by the conventional θ - 2θ scan technique and the structure has been refined to $R_F = 0.0206$ and $R_w(F) = 0.0190$ for 1284 observed reflections [$I \geq 2\sigma(I)$]. The Re(CO)₃ moiety has C_{3v} symmetry; the average Re–C(O) distance is

1.894 (4) Å (*i.e.* very close to the predicted double-bond value of 1.94 Å) and the Re–C–O angle is 177.7 (4)°. The cyclopentadienyl ring is almost perfectly planar (largest deviation, 0.003 Å). The variation of C–C bond lengths within the ring indicates some tendency for localized bonding, which is quite unexpected for molecules of this type which possess effective cylindrical symmetry. This observation, however, may account for the anomalous vibrational spectroscopic results reported for this molecule, as well as for the deviation from D_{5h} symmetry of the Cp ring itself as

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