or will decompose too rapidly. It may be possible to prepare a "$\text{MR}'_x\text{R}_y$" species by reduction of a M(V) complex (M = Mo or W; R′ is a bulky, relatively innocuous ligand (e.g. mesityl), and R is methyl) that approaches the balance that apparently is achieved in "$\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3$". We will continue to operate under the assumption that under the right circumstances alkyl ligands can provide an electronically favorable circumstance for dinitrogen to bind.

Acknowledgment. R.R.S. thanks the National Institutes of Health for support through Grant GM-31978 and the Division of University and Industry Programs, U.S. Department of Energy, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER 75292). We thank Andy Liu, Terry Nicholson, and John Dewan for discussions and help concerning the structure study, and Erin Byrne for helpful discussions.

Registry No. $\text{MoCl}_3(\text{THF})_3$, 31355-55-2; Mo(nor)_4, 115406-98-9; CO, 630-08-0; 1-norbornyllithium, 930-81-4; pyridine, 110-86-1; propylene oxide, 75-56-9; 3-hexyne, 928-49-4; 2,6-dimethylphenol, 576-26-1.

Supplementary Material Available: Experimental procedures, a table of crystallographic data, an ORTEP drawing, and listings of positional and anisotropic thermal parameters, general temperature factor expressions, bond distances for non-hydrogen atoms, and bond angles for non-hydrogen atoms (20 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Miami University, Oxford, Ohio 45056

Direct C–Cl···Ca^{2+} Binding: Crystal Structure of Calcium Chloroacetate Hydrate

Anastas Karipides* and Karen Peiffer

Received February 24, 1988

Although carbon-bound halogen atoms (X = F, Cl, Br, I) are generally considered to be poor donors toward metal ions, there have been a number of recent reports of C–X···M coordination encompassing a broad range of structural environments and bond motifs.[1-4] Both "convalent" and "ionic" C–X···M interactions have been observed. These weak C–X···M interactions, which carbon-bound hydrogen atoms cannot emulate, can be of utmost importance in influencing the structural features of metal–halo ligand coordination chemistry.

We have been particularly interested in the versatility of metal ion coordination by fluorine- and chlorine-substituted carboxylate ligands. In alkali-metal salts of fluoro and chloro carboxylic acids, there has been ample crystallographic evidence for the existence of significant C–X···M interactions.[1,2] However, there has been a paucity of reported crystallographic investigations of multivalent salts/complexes of halo carboxylic acids. In these latter systems, we may anticipate that binding of "hard" metal ions would be dominated by carboxylate (oxygen) coordination, although in some instances participation of the halogen atom in metal ion binding may be of great importance.

As part of a systematic study to investigate the structural coordination chemistry of the halocarbon environments in multivalent derivatives of halo carboxylic acids, we have determined the crystal structure of calcium chloroacetate hydrate, in which the chloroacetate moiety exhibits a direct C–Cl···Ca^{2+} mode of binding.

Table I. Fractional Coordinates and Equivalent Isotropic Displacement Parameters for Calcium Chloroacetate Hydrate[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2
Ca	0.08561 (9)	0.04037 (3)	0.75694 (8)	1.55
Cl(1)	−0.0702 (1)	0.18605 (5)	0.7497 (2)	3.98
Cl(2)	−0.3655 (2)	−0.18102 (5)	0.5818 (2)	5.50
Ow	0.3789 (4)	−0.0322 (1)	0.6986 (4)	3.00
O(1)	−0.2927 (4)	0.0635 (1)	0.7324 (3)	2.48
O(2)	−0.6030 (4)	0.0987 (1)	0.8432 (3)	2.76
O(3)	−0.0410 (4)	−0.0594 (1)	0.9017 (3)	2.18
O(4)	−0.0961 (4)	−0.0612 (1)	0.5809 (3)	2.14
C(1)	−0.4101 (5)	0.1048 (2)	0.8068 (4)	2.07
C(2)	−0.3138 (6)	0.1688 (2)	0.8668 (6)	3.33
C(3)	−0.1054 (5)	−0.0868 (1)	0.7456 (1)	1.75
C(4)	−0.1850 (7)	−0.1543 (2)	0.7687 (5)	3.13
H1(Ow)	0.378	−0.054	0.574	5.00
H2(Ow)	0.516	−0.011	0.721	5.00
H1(C2)	−0.279	0.168	1.023	5.00
H2(C2)	−0.431	0.206	0.834	5.00
H1(C4)	−0.264	−0.158	0.905	5.00
H2(C4)	−0.046	−0.186	0.774	5.00

[a] Estimated standard deviations in the least significant digits are given in parentheses here and in other tables.

Table II. Selected Bond Lengths (Å) and Angles (deg) for Calcium Chloroacetate Hydrate[a]

Ca–Cl(1)	3.206 (1)	C(1)–O(1)	1.254 (4)
Ca–Ow	2.418 (2)	C(1)–O(2)	1.237 (4)
Ca–O(1)	2.388 (2)	C(1)–C(2)	1.518 (5)
Ca–O(2^d)	2.331 (2)	C(2)–Cl(1)	1.778 (4)
Ca–O(3)	2.461 (2)	C(3)–O(3)	1.254 (3)
Ca–O(4)	2.665 (2)	C(3)–O(4)	1.247 (3)
Ca–O(3^b)	2.387 (2)	C(3)–C(4)	1.511 (4)
Ca–O(4^c)	2.344 (2)	C(4)–Cl(2)	1.741 (4)
O(1)–C(1)–O(2)	126.4 (3)	O(3)–Ca–O(4)	50.44 (7)
O(1)–C(1)–C(2)	119.5 (3)	O(3)–Ca–O(3^b)	72.42 (8)
O(2)–C(1)–C(2)	114.0 (3)	O(4)–Ca–O(4^c)	74.99 (8)
Cl(1)–C(2)–C(1)	112.9 (2)	Cl(1)–Ca–O(1)	60.79 (6)
O(3)–C(3)–O(4)	122.4 (3)	Cl(1)–Ca–O(2^d)	75.35 (6)
O(3)–C(3)–C(4)	115.6 (3)	Cl(1)–Ca–O(3^b)	78.75 (6)
O(4)–C(3)–C(4)	121.9 (3)	Cl(1)–Ca–O(4^c)	80.27 (6)
Cl(2)–C(4)–C(3)	115.2 (2)	Cl(1)–Ca–Ow	145.71 (7)
C(1)–Cl(1)–Ca	93.4 (1)	Cl(1)–Ca–O(3)	135.78 (6)
Ca–O(3)–Ca^b	107.58 (8)	Cl(1)–Ca–O(4)	129.54 (6)
Ca–O(4)–Ca^c	105.01 (8)		

[a] Superscripts are defined in Figure 1.

Experimental Section

Colorless prismatic crystals of the title compound were readily grown from an aqueous solution of the salt by slow evaporation. The crystals cleave easily, are quite hygroscopic, and must be handled carefully to prevent fracturing. A well-formed single crystal of approximate dimensions 0.28 × 0.28 × 0.22 mm, which gave sharp optical extinction along three mutually perpendicular directions under crossed polarizers, was sealed in a thin-walled glass capillary tube. Unit cell constants were determined from a least-squares refinement of the setting angles of 25 reflections in the range $18° < 2\theta < 37°$ measured with Mo Kα radiation on a CAD4 computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromater.

Crystal Data: $\text{Ca(CH}_2\text{ClCOO)}_2(\text{H}_2\text{O})$, fw 245.08, monoclinic, space group $P2_1/c$, $a = 6.186\ (1)$ Å, $b = 20.992\ (2)$ Å, $c = 6.804\ (1)$ Å, $\beta = 92.990\ (9)°$, $Z = 4$, $V = 882.34$ Å^3, $\rho_{\text{calcd}} = 1.84$ g/cm^3, $\rho_{\text{measd}} = 1.83$ g/cm^3, $\mu(\text{Mo K}\alpha) = 12.6$ cm^{-1}, $T = 292$ K.

Integrated three-dimensional intensity data in quadrants $h,k,\pm l$ in the range $1° \leq 2\theta \leq 53°$ were collected on the aforementioned diffractometer by using the ω–θ scan techniques. Absorption and secondary extinction corrections were not applied. After data reduction a total of 1670 independent reflections had $F_o \geq 0.50\sigma(F_o)$ and were used in subsequent calculations.[5]

The structure was solved by using a combination of direct and heavy-atom methods and refined by a full-matrix least-squares procedure.

---

(1) Murray-Rust, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 3206.

(2) Karipides, A.; Miller, C. *J. Am. Chem. Soc.* **1984**, *106*, 1494.

(3) (a) Kulawiec, R. J.; Holt, E. M.; Lavin, M.; Crabtree, R. H. *Inorg. Chem.* **1987**, *26*, 2559. (b) Burk, M. J.; Crabtree, R. H.; Holt, E. M. *Organometallics* **1984**, *3*, 638.

(4) (a) Cotton, F. A.; Laherta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526. (b) Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482.

(5) Data reduction, structure solution and refinement were carried out on IBM 4381 or VAX 8250 computers using the Enraf-Nonius SDP software package as well as other programs.[6]

(6) Karipides, A. *Inorg. Chem.* **1979**, *18*, 3034.

0020-1669/88/1327-3255$01.50/0 © 1988 American Chemical Society

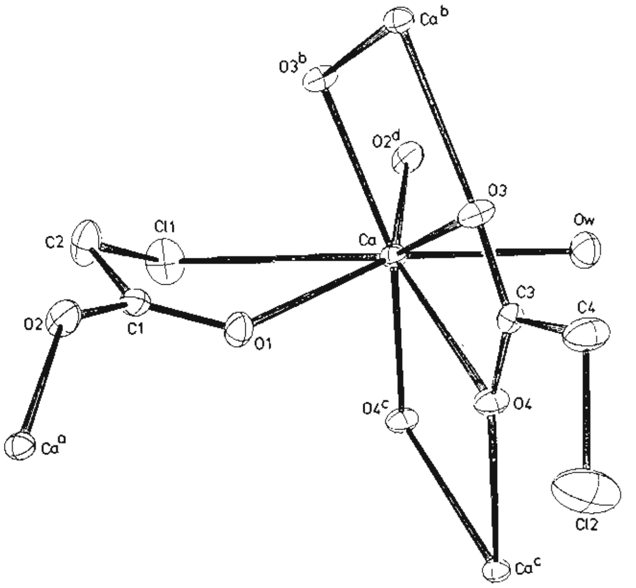

Figure 1. A portion of the crystalline structure showing the mode of chloroacetate-Ca^{2+} binding and the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Chloroacetate (A) is specified by atoms O(1), O(2), C(1), C(2), Cl(1) and chloroacetate (B) by atoms O(3), O(4), C(3), C(4), Cl(2). The superscripts specify the symmetry-related positions of the atoms given in Table I: (a) $x - 1, y, z$; (b) $-x, -y, 2 - z$; (c) $-x, -y, 1 - z$; (d) $x + 1, y, z$.

Hydrogen atom parameters were not refined. The function minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma(F_o))^2 + (0.02F_o)^2]^{-1}$. Anisotropic refinement (on F) of all non-hydrogen atoms (109 variable parameters; 15.3 data/parameter) converged to a conventional R factor (R) of 0.046, a weighted R factor (R_w) of 0.055, and an error in an observation of unit weight of 1.62. In the final cycle of refinement the largest ratio of shifts to estimated standard deviations was 0.01. Final fractional coordinates and equivalent isotropic thermal parameters are given in Table I.

Results and Discussion

There are no symmetry conditions imposed on the crystalline structure by the space group, and the asymmetric unit consists of one Ca^{2+}, two independent chloroacetate ions (designated A and B), and one water molecule. A view of the structure is shown in Figure 1. Bond distances and angles are given in Table II.

The most significant feature revealed in this structural investigation is the direct participation of a carbon-bound chlorine atom in Ca^{2+} binding. The two chloroacetate ligands differ in the manner in which they coordinate Ca^{2+} ions. Chloroacetate (A) chelates a Ca^{2+} ion through its chlorine atom, Cl(1), and carboxylate oxygen, O(1), forming a buckled five-membered chelate ring. In addition, a second Ca^{2+} ion is coordinated to carboxylate (A) oxygen, O(2), via a unidentate bridging interaction. Chloroacetate (B) binds three different Ca^{2+} ions through its carboxylate group—one through a reasonably symmetric, planar four-membered chelate ring and two others through unidentate bridging bonds, which lead to the formation of planar Ca–O–Ca–O four-membered rings. These bridging interactions are common features[7] in calcium carboxylates and form the basis for the polymeric nature of the crystalline structure.

This C–Cl···Ca^{2+} binding is to the best of our knowledge the first example of direct Ca^{2+}–halocarbon binding. An example of indirect Ca^{2+}–fluorocarbon binding mediated through a coordinated water molecule has been recently described.[2] The Ca^{2+}–Cl(1) distance is 3.206 (1) Å, which is in the range expected for a weak ion–dipole C–Cl···Ca^{2+} interaction. Essentially full ionic Ca^{2+}···Cl^- separations (2.741 Å in $CaCl_2 \cdot 4H_2O$)[8] are, of course, considerably shorter. Although there are no other reported direct chlorocarbon–Ca^{2+} linkages, the observed distance is shorter than the comparable C–Cl···K^+ separations (range 3.243–3.462 Å) found in potassium hydrogen chloromaleate,[9] potassium hydrogen trichloroacetate,[10] potassium hydrogen dichloroacetate,[11] and potassium bis(chloroacetato)stannate(II).[12]

The intramolecular bond lengths and angles of the two independent chloroacetate groups (Table I) are similar to the dimensions reported in other structures containing chloroacetate.[12-17] The dihedral angles between the carboxylate plane and the corresponding C–C–Cl plane are 18.8 and 25.4° for chloroacetate (A) and chloroacetate (B), respectively.

The CaO_7Cl polyhedron deviates extensively from idealized eight-coordinate geometries, and selection of an appropriate stereochemical description for eight-coordinate polyhedra is often difficult.[18] An analysis of shape parameters suggests the CaO_7Cl polyhedron lies along the reaction pathway connecting a dodecahedron and bicapped trigonal prism.[19]

Calcium chloroacetate monohydrate is easily crystallized from aqueous solution, and in view of the high affinity of Ca^{2+} for oxygen donor groups, it appears remarkable that the carbon-bound chlorine effectively competes with carboxylate oxygens and water molecules for Ca^{2+} binding. Because chloroacetate is well-known to bind metal ions only through its carboxylate group, the C–Cl···Ca^{2+} interaction does not arise because of any inherent geometrical constraint imposed by the ligand or complex. Thus, although weak, the observed C–Cl···Ca^{2+} binding represents a genuine attractive interaction that is undoubtedly largely Coulombic in origin. Although direct evidence is lacking, this C–Cl···Ca^{2+} binding may probably even occur in solution (albeit fleeting) inasmuch as this interaction survives in the crystal.

Acknowledgment. We are grateful to the National Science Foundation for a grant (CHE-8418897) (A.K.) used to purchase the CAD4 X-ray diffractometer system.

Registry No. $Ca(CH_2ClCOO)_2(H_2O)$, 72134-84-0.

Supplementary Material Available: Tables S1 and S2, listing anisotropic displacement parameters and hydrogen-bonding parameters (2 pages); table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

---

(7) Einspahr, H.; Bugg, C. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1044.
(8) Leclair, A.; Borel, M. M.; Monier, J. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2757.
(9) Ellison, R. D.; Levy, H. A. *Acta Crystallogr.* **1965**, *19*, 260.
(10) Golic, L.; Lazarini, F.; *Cryst. Struct. Commun.* **1974**, *3*, 645.
(11) Hadzi, D.; Leban, I.; Orel, B.; Iwata, M.; Williams, J. M. *J. Cryst. Mol. Struct.* **1979**, *9*, 117.
(12) Clark, S. J.; Donaldson, J. D.; Dewar, J. C.; Silver, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2550.
(13) Solans, X.; Miravitlles, C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1407.
(14) Dewan, J. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1935.
(15) Faggiani, R.; Johnson, J. P.; Brown, I. D.; Birchall, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3742.
(16) Ichikawa, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B28*, 755.
(17) (a) Davey, G.; Stephens, F. S. *J. Chem. Soc. A* **1971**, 1917. (b) Davey, G.; Stephens, F. S. *J. Chem. Soc. A* **1970**, 2803.
(18) Burdett, J. K.; Hoffman, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.
(19) (a) Mutterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (b) Kouba, J. K.; Wreford, S. S. *Inorg. Chem.* **1976**, *15*, 1463.

Contribution from the Rosenstiel School of Marine
and Atmospheric Science, University of Miami,
4600 Rickenbacker Causeway, Miami, Florida 33149

Determining the Stability Constant of Copper(I) Halide Complexes from Kinetic Measurements

Virender K. Sharma and Frank J. Millero*

Received March 15, 1988

Copper in oxidation state I seems to be the only first-row transition element showing typical class B behavior, characterized by the halide affinity sequence $F^- \ll Cl^- < Br^- < I^-$ in aqueous solution.[1,2] The complex formation of an acceptor in such a unique

0020-1669/88/1327-3256$01.50/0 © 1988 American Chemical Society