Inorganica Chimica Acta, 29 (1978) 83–87

The Crystal and Molecular Structure of *Tetrakis*(diacetamide)calcium(II) Chlorate Monohydrate

P. S. GENTILE* and A. P. OCAMPO
Department of Chemistry, Fordham University, Bronx, New York, 10458 U.S.A.
Received October 22, 1977

The crystal structure of tetrakis(diacetamide)calcium(II) chlorate monohydrate, $[Ca(DA)_4](ClO_3)_2\cdot H_2O$, *has been determined from three-dimensional X-ray data. The complex has the cell parameters* a = *12.399(3)* Å, b = *7.900(2)* Å, c = *14.725(3)* Å, β = *98.35(2)°, Z = 2. The unit cell is monoclinic, space group P2/c. The structure was determined by direct methods and refined anisotropically by block-diagonal least squares to a conventional unweighted R of 0.11.*

The calcium ion is 8-coordinated and its coordination sphere can be described as a square antiprism formed by eight carbonyl oxygens from 4 diacetamide ligands; two ligands are related to the other two by a two-fold rotation axis. One of the amide nitrogens is hydrogen bonded to a chlorate oxygen. In addition, hydrogen bonding between an amide nitrogen and an uncoordinated water molecule results in the formation of infinite chains parallel to [100]. Calcium–oxygen distances fall within the range 2.41–2.44 Å.

Introduction

The crystal structures of a number of diacetamide complexes of the alkaline earth metals [1–3] have all proven to be interesting in that they led to high coordination numbers (9 for Sr^{++}, 10 for Ba^{++}), or as in the case of magnesium, one of the diacetamide molecules was held in the secondary coordination sphere, *via* hydrogen bonding, with a coordinated water. The crystal structure of $[Ca(DA)_4](ClO_3)_2\cdot H_2O$ (DA = diacetamide) was undertaken in order to complete the series and determine whether it is 9-coordinate and isostructural with $[Sr(DA)_4(H_2O)](ClO_4)_2$.

Experimental

Preparation

$[Ca(DA)_4](ClO_3)_2\cdot H_2O$ was prepared by solid–solid interaction using stoichiometric amounts of $Ca(ClO_3)_2\cdot 2H_2O$ and diacetamide. The materials were ground together and dried *in vacuo*. Crystals suitable for X-ray work were obtained by dissolving the powder in absolute methanol and allowing the solvent to evaporate slowly at room temperature.

X-ray Study

Since the crystals were highly hygroscopic, they were mounted inside quartz capillaries for all X-ray measurements. The cell parameters were initially determined from oscillation and Weissenberg photographs taken of crystals mounted on the *b* and *c* axes. The only systematic absence was *h0l, l* odd, showing the space group tp be either Pc (noncentrosymmetric) or P2/c (centrosymmetric).

The intensity data collection was done on an Enraf-Nonius CAD-4 diffractometer using CuK_α radiation using a crystal of approximate dimensions 0.10 X 0.16 X 0.22 mm. The auto-indexing option was employed and the lattice parameters determined were *a* = 12.399(3) Å, *b* = 7.900(2) Å, *c* = 14.725(3) Å and β = 98.35(2)°. Density measurements by flotation method showed there were 2 molecules per unit cell (d_{obs} = 1.48 g/cm^3, d_{calc} = 1.52 g/cm^3). The values obtained were in agreement with the parameters derived from film data.

All data were scaled to a single intensity control reflection which was measured after every twenty-five reflections. A total of 2898 reflections was collected of which 2392 were considered observed based on the criterion $I \geqslant 1.5\ \sigma_I$.

Solution and Refinement

The structure was solved by direct methods using computer programs obtained from the National Research Council of Canada [4]. Three origin defining reflections plus four additional reflections were needed to determine the entire set of phases consisting of 393 reflections with |E|'s > 1.5. The space group P2/c was considered more likely due to the statistical distribution of |E|'s. The choice of P2/c was subsequently found to be correct.

---

*Author to whom correspondence should be addressed.

TABLE I. Fractional Atomic Coordinates and Isotropic Thermal Parameters.

Atom	x/a	y/b	z/c	*B*
Ca	0.5 (0)	0.3813 (2)	0.25 (0)	2.9
O_1	0.3903 (4)	0.1409 (6)	0.1944 (4)	3.6
O_2	0.3124 (4)	0.4609 (6)	0.1996 (4)	3.4
C_1	0.2962 (5)	0.0997 (8)	0.1974 (5)	3.0
C_2	0.2254 (5)	0.3905 (8)	0.1998 (5)	3.2
C_3	0.2566 (6)	−0.0793 (9)	0.1916 (6)	4.5
C_4	0.1189 (6)	0.4846 (10)	0.1901 (8)	4.6
N_1	0.2158 (4)	0.2178 (7)	0.2101 (4)	3.0
O_5	0.4911 (4)	0.6232 (6)	0.3472 (4)	3.8
O_6	0.4102 (4)	0.3144 (6)	0.3830 (4)	3.7
C_5	0.4260 (6)	0.6745 (8)	0.3932 (5)	3.5
C_6	0.3487 (6)	0.3969 (9)	0.4223 (5)	3.5
C_7	0.4198 (8)	0.8570 (10)	0.4217 (6)	4.8
C_8	0.2623 (8)	0.3175 (12)	0.4713 (7)	5.6
N_2	0.3510 (5)	0.5697 (8)	0.4281 (4)	3.6
O_7	0.1817 (9)	0.7296 (18)	0.5052 (7)	11.9
O_8	0.0835 (14)	0.7736 (28)	0.3646 (8)	19.9
O_9	0.1280 (16)	0.9559 (25)	0.4348 (19)	28.4
O_{10}	0.0 (0)	0.0892 (10)	0.25 (0)	4.8
Cl	0.0899 (2)	0.8140 (3)	0.4567 (2)	5.6
H_{10}	−0.0093	0.0835	0.2070	0.7
H_{20}	0.1703	0.2028	0.1798	6.1
H_{30}	0.3145	0.6139	0.4611	2.5
H_{11}	0.1937	−0.1052	0.1207	6.8
H_{12}	0.2473	−0.1193	0.2465	3.9
H_{13}	0.3301	−0.1551	0.2264	7.9
H_{21}	0.0474	0.4107	0.1469	4.6
H_{22}	0.1237	0.5640	0.2109	5.4
H_{23}	0.0917	0.5070	0.1001	13.3
H_{71}	0.4126	0.9206	0.3495	15.9
H_{72}	0.3876	0.8799	0.4679	7.8
H_{73}	0.4639	0.8499	0.4913	4.4
H_{81}	0.2900	0.3421	0.5489	3.9
H_{82}	0.1714	0.3435	0.4166	9.3
H_{83}	0.2581	0.2151	0.4726	3.3

Acceptable positions for the calcium and chlorine atoms were determined from an E-map. The calcium was found to lie on a two-fold rotation axis: 1/2, y, 1/4 where y = 0.3813. A three-dimensional Fourier map using calcium and chlorine as the phasing model revealed the positions of the other non-hydrogen atoms. The oxygen of the water was found in the special position: 0, y, 1/4 where y = 0.0833. Assignment of individual isotropic temperature factors followed by block-diagonal least squares refinement of the coordinates, thermal parameters and scale factor gave an R of 0.18.

The hydrogen atoms were located from a difference electron density map and their positions were refined isotropically giving a final R-factor of 0.11. The fractional coordinates and isotropic thermal parameters of all atoms are given in Table I. Anisotropic thermal parameters are given in Table II.

The mean atomic scattering factors had been corrected for real and imaginary dispersion effects [5]. Absorption corrections were not applied. The function minimized in the least squares calculation was $R = \Sigma w(|F_o| - k|F_c|)^2$. All observed reflections were given unit weight and unobserved reflections were not included in the summation. A table of observed and calculated structure factors is available from the Editor.

Results and Discussion

A number of 8- and 9-coordinate complexes have appeared in the literature [6] with the majority composed of monodentate ligands such as CN^-. Some Group II metals with oxygen donors have also been reported [7]. However, data are limited where multidentate ligands are involved. The coordination number varies from one metal to another in the Group II-A series. A coordination number of 10 was

TABLE II. Anisotropic Thermal Parameters ($\times 10^3$) as Mean Square Amplitude[a].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	39 (3)	38 (4)	39 (4)	0	6 (1)	0
O_1	34 (2)	31 (3)	87 (4)	−12 (3)	16 (3)	−2 (2)
O_2	34 (2)	28 (3)	82 (4)	5 (3)	13 (3)	−2 (1)
C_1	37 (4)	30 (3)	56 (4)	−2 (3)	8 (3)	−2 (3)
C_2	36 (4)	31 (3)	65 (4)	3 (3)	14 (3)	3 (3)
C_3	58 (5)	30 (4)	92 (7)	−7 (4)	14 (5)	−5 (4)
C_4	36 (4)	43 (5)	143 (9)	5 (5)	24 (5)	10 (4)
N_1	31 (3)	31 (3)	67 (4)	−2 (3)	13 (3)	−2 (2)
O_5	48 (3)	34 (3)	87 (4)	−13 (3)	24 (3)	−6 (2)
O_6	62 (3)	30 (3)	67 (4)	3 (3)	22 (3)	2 (2)
C_5	43 (4)	27 (3)	71 (4)	−10 (3)	−7 (3)	1 (3)
C_6	55 (4)	42 (3)	55 (4)	1 (4)	14 (3)	−4 (4)
C_7	95 (6)	65 (4)	93 (7)	−4 (4)	51 (5)	20 (4)
C_8	85 (8)	32 (6)	82 (8)	−19 (4)	12 (2)	4 (2)
N_2	51 (4)	41 (3)	62 (4)	−8 (3)	22 (5)	4 (3)
O_7	207 (14)	311 (16)	124 (7)	98 (10)	106 (9)	195 (12)
O_8	282 (16)	458 (9)	110 (8)	−58 (13)	−28 (9)	23 (19)
O_9	224 (23)	196 (22)	758 (41)	25 (8)	83 (15)	−37 (19)
O_{10}	62 (2)	60 (3)	62 (1)	0	9 (3)	0
Cl	66 (1)	85 (2)	92 (2)	9 (1)	15 (1)	11 (1)

[a] The form of the anisotropic thermal parameter is $\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)\}$.

TABLE III. Bond distances and Bond Angles.

Bond Distances (Å)		Bond Angles (°)	
$\mathrm{Ca{-}O_1}$	2.405(5)	$\mathrm{O_1{-}Ca{-}O_2}$	68.6(2)
$\mathrm{Ca{-}O_2}$	2.407(5)	$\mathrm{O_5{-}Ca{-}O_6}$	68.2(2)
$\mathrm{Ca{-}O_5}$	2.402(5)	$\mathrm{O_1{-}Ca{-}O_5}$	139.4(2)
$\mathrm{Ca{-}O_6}$	2.449(5)	$\mathrm{O_2{-}Ca{-}O_6}$	110.0(2)
$\mathrm{N_1{-}C_1}$	1.395(8)	$\mathrm{N_1{-}C_1{-}O_1}$	122.0(6)
$\mathrm{N_1{-}C_2}$	1.381(8)	$\mathrm{O_1{-}C_1{-}C_3}$	123.9(6)
$\mathrm{C_1{-}C_3}$	1.495(10)	$\mathrm{N_1{-}C_1{-}C_3}$	114.0(6)
$\mathrm{C_2{-}C_4}$	1.498(10)	$\mathrm{C_1{-}N_1{-}C_2}$	124.9(6)
$\mathrm{N_2{-}C_5}$	1.393(9)	$\mathrm{O_2{-}C_2{-}N_1}$	123.1(6)
$\mathrm{N_2{-}C_6}$	1.368(9)	$\mathrm{N_1{-}C_2{-}C_4}$	114.4(6)
$\mathrm{C_5{-}C_7}$	1.505(10)	$\mathrm{O_5{-}C_5{-}N_2}$	123.0(7)
$\mathrm{C_6{-}C_8}$	1.511(13)	$\mathrm{O_5{-}C_5{-}C_7}$	123.0(9)
$\mathrm{C_1{-}O_1}$	1.214(8)	$\mathrm{N_2{-}C_5{-}C_7}$	114.7(6)
$\mathrm{C_2{-}O_2}$	1.210(8)	$\mathrm{C_5{-}N_2{-}C_6}$	125.4(6)
$\mathrm{C_5{-}O_5}$	1.203(9)	$\mathrm{N_2{-}C_6{-}C_8}$	113.2(7)
$\mathrm{C_6{-}O_6}$	1.212(9)	$\mathrm{O_6{-}C_6{-}N_2}$	123.9(7)
$\mathrm{Cl{-}O_7}$	1.412(11)	$\mathrm{O_7{-}Cl{-}O_8}$	108.1(9)
$\mathrm{Cl{-}O_8}$	1.384(18)	$\mathrm{O_7{-}Cl{-}O_9}$	104.3(11)
$\mathrm{Cl{-}O_9}$	1.275(21)	$\mathrm{O_8{-}Cl{-}O_9}$	106.3(9)
$\mathrm{N_1{-}O_{10}}$	2.990(6)		
$\mathrm{N_2{-}O_7}$	2.822(13)		
$\mathrm{Ca{-}N_1}$	3.701(5)		
$\mathrm{Ca{-}N_2}$	3.741(6)		
$\mathrm{O_1{-}O_2}$	2.712(6)		
$\mathrm{O_5{-}O_6}$	2.719(7)		
$\mathrm{C_3{-}H_{11}}$	1.2		
$\mathrm{C_3{-}H_{12}}$	0.9		
$\mathrm{C_3{-}H_{13}}$	1.1		
$\mathrm{C_4{-}H_{21}}$	1.2		
$\mathrm{C_4{-}H_{22}}$	0.7		
$\mathrm{C_4{-}H_{23}}$	1.2		
$\mathrm{C_7{-}H_{71}}$	1.2		
$\mathrm{C_7{-}H_{72}}$	0.8		
$\mathrm{C_7{-}H_{73}}$	1.1		
$\mathrm{C_8{-}H_{81}}$	1.2		
$\mathrm{C_8{-}H_{82}}$	1.2		
$\mathrm{C_8{-}H_{83}}$	0.8		
$\mathrm{O_{10}{-}H_{10}}$	0.6		
$\mathrm{N_1{-}H_{20}}$	0.7		
$\mathrm{N_2{-}H_{30}}$	0.8		

found for $[Ba(DA)_5](ClO_4)_2$ [2] but its Ca counterpart [8] exhibited a coordination number of 8.

Tetrakis(diacetamide)monoaquostrontium(II) perchlorate, $[Sr(DA)_4(H_2O)](ClO_4)_2$, is 9-coordinate with 8 of the coordinated oxygens contributed by the four bidentate diacetamide ligands and the ninth oxygen contributed by the water to form to vertices of a monocapped square antiprism. However, $[Ca(DA)_4](ClO_3)_2 \cdot H_2O$ is not isostructural but instead forms a slightly distorted 8-coordinate square antiprism. There are only two non-equivalent diacetamide ligands in the complex, the other two being related to the former by a two-fold rotation axis.

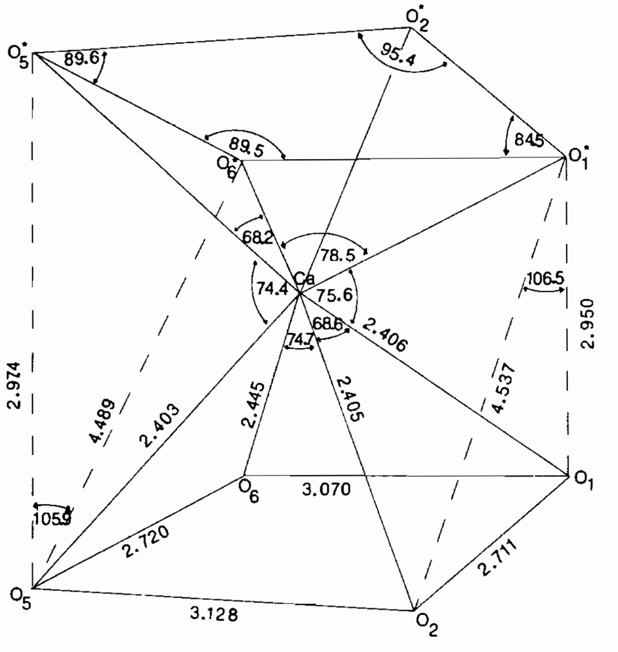

Figure 1. Schematic diagram of the square antiprismatic coordination sphere around Ca ion. Starred atoms are related to equivalent atoms by a two-fold rotation axis.

The opposite faces of the antiprism, although slightly distorted squares, are planar (rms deviation = 0.1 Å, dihedral angle = 2.98°). All calcium–oxygen distances are in the range 2.41–2.44 Å, roughly equivalent to the sum of the atomic radii of calcium and oxygen [9]. A perspective view of the coordination sphere is given in Figure 1.

The diacetamides are in the *anti–anti* conformation and the distortion that exists is manifested as a fold along the Ca–N axes. The dihedral angle between planes O_1–C_1–N_1 and O_2–C_2–N_1 is 10.46° and that between planes O_5–C_5–N_2 and O_6–C_6–N_2 is 5.84°. The bite of the ligands (2.71, 2.72 Å) is similar to those found for $[Sr(DA)_4(H_2O)](ClO_4)_2$, $[Ba(DA)_5](ClO_4)_2$ and $[Mg(DA)_2(H_2O)_2](DA)_2(ClO_4)_2$ [1–3].

The oxygen in the water molecule is hydrogen bonded (distance 2.99 Å) to two equivalent amide nitrogens (N_1) forming an intermolecular bridge across adjacent unit cell resulting in infinite chains parallel to [100] (Figure 2). Intramolecular hydrogen bonding (2.81 Å) occurs between a chlorate oxygen (O_7) and the other amide nitrogen (N_2) in the complex, accounting for the low thermal parameter for O_7. For both types of hydrogen bonds, the H---O

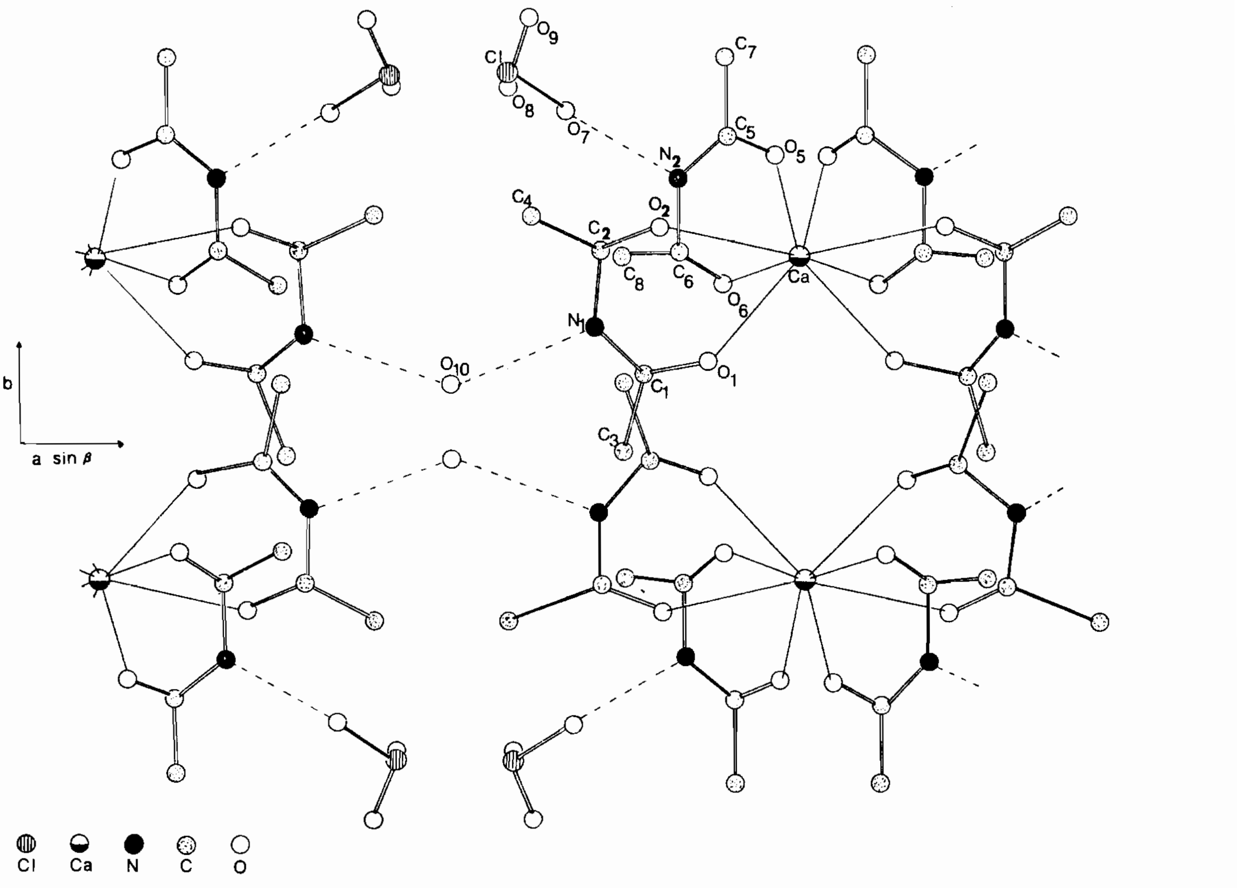

Figure 2. Packing diagram along [001] projection.

distances are within the range of the van der Waals radii of hydrogen and oxygen. Interatomic distances and bond angles are given in Table III.

References

1 P. S. Gentile, M. P. Dinstein and J. G. White, *Inorg. Chim. Acta, 19,* 67 (1976).
2 P. S. Gentile, J. G. White and S. Haddad, *Inorg. Chim. Acta, 13,* 149 (1975).
3 P. S. Gentile, J. G. White, M. P. Dinstein and D. D. Bray, *Inorg. Chim. Acta, 21,* 141 (1976).
4 F. R. Ahmed, M. E. Pippy and S. R. Hall, "NRC Crystallographic Programs", National Research Council of Canada (1968).
5 "International Tables for X-ray Crystallography", Kynoch Press, Birmingham (1968) Vol. III.
6 N. V. Sidgwick, "The Chemical Elements and Their Compounds", Oxford University Press (1950).
7 R. Cotton, R. D. Peacock and G. Wilkinson, *Nature, 182,* 393 (1958).
8 J. P. Roux and G. J. Kruger, *Acta Crystallogr., B32,* 1171 (1976).
9 J. C. Slater, *J. Chem. Phys., 41,* 3199 (1964).