PREPARATION AND CRYSTAL STRUCTURE OF $CaCl_2 \cdot [OC(NH_2)_2]_4$

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Abstract

Calcium dichloride tetra urea was prepared by the reaction of calcium chloride with urea in aqueous solution. The crystals are monoclinic, a= 7.633, b= 12.451, c= 8.118 Å, β = 113.17, Z = 4, space group P 2_1/a. The crystal structure was determined by single crystal X-ray methods and refined to R= 0.041. The calcium atoms are coordinated to four oxygen atoms of urea and to two chloride ions. The coordination polyhedra are distorted octahedra.

Introduction

The coordination of calcium in azide compound with urea was the subject of several investigations. Recently, it was shown that the urea molecules can also be incorporated into calcium azide: $[OC(NH_2)_2]_4 \cdot Ca(N_3)_2$ form crystal structures, whose calcium atoms are coordinated to four oxygen atoms of urea and to two nitrogen atoms of azide groups [1]. The present communication describes experiments to obtain compounds of calcium chloride with urea and to determine their crystal structure.

Experimental Section

Slow cooling of a saturated aqueous solution of calcium chloride and half saturated solution of urea from 70°C to 20°C yields small, colourless crystals, usually of octahedral shape. According to the chemical analysis, the molar ratio of $CaCl_2$: $OC(NH_2)_2$ is 1:4. Crystals are shock insensitive and they are not stable at ambient conditions for several days. The crystals were sealed in a glass capillary.

Structure Determination

Relevant experimental parameters and crystal data are collected in Table 1. A freshly prepared and carefully

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Table 1. Experimental Parameters and Data

Chemical formula	$CaCl_2 [OC(NH_2)_2]_4$
Formula weight	351
Cell constants	a= 7.633 (3) Å b= 12.451 (5) Å c= 8.118 (4) Å β= 113.17 (3)° V= 709.3 Å
Space group	P 21/a
Z	4
Calculated density	1.64 $Mg.m^{-3}$
Instrument	STOE four circle diffractometer
Crystal dimensions	0.40 x 0.28 x 0.20 mm^3
Temperature	26+ 2 °C
Data collection limits	$0° \leq 2 \leq \Theta \leq 65$ $-11 \leq h \leq 11$, $0 \leq k \leq 18$, $0 \leq 1 \leq 12$
scan mode	ω scan, Δω= 1.4
Number/frequency of standard reflections	3/100
Independent reflections	2918
$F_0^* \geq 4\sigma(F_*)$	1618
Atomic scattering factors	International tables (1974)
Least squares parameters	121
R_1: $\sum(\lvert F_o \rvert - \lvert F_c \rvert) / \sum \lvert F_o \rvert$	0.041
R_2: $\lvert \sqrt{\omega} (\lvert F_o \rvert \lvert F_c \rvert / \sum \sqrt{\omega} F_o$	0.045

dried crystal was used for all experiments.

The structure was solved with Patterson techniques and difference fourier syntheses [2]. The hydrogen-atom positions were obtained from difference fourier-syntheses. Non-hydrogen atoms were refined with anisotropic, hydrogen atoms with isotropic temperature coefficients. Atomic coordinates and atomic displacement coefficients are summarized in Tables 2 and 3.

All calculations were carried out on a Vax computer. The computer Programs molen [3] were used. Further details on the structure analysis can be obtained from the author and the literature reference.

Table 2. Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
CA	0.500	0.000	1.000	1.93 (1)
CL	0.22367 (8)	0.07337 (5)	0.68649 (8)	3.05 (1)
O1	0.7248 (2)	0.1020 (1)	0.9507 (2)	2.71 (3)
O2	0.4475 (2)	0.1447 (1)	1.1512 (2)	2.77 (4)
N11	0.8472 (3)	0.0112 (2)	0.7827 (3)	2.96 (4)
N12	0.9466 (3)	0.1788 (2)	0.8760 (3)	3.39 (5)
N21	0.6090 (4)	0.1516 (2)	1.4474 (3)	5.30 (7)
N22	0.4534 (3)	0.2967 (2)	1.2968 (3)	3.69 (5)
C1	0.8364 (3)	0.0968 (2)	0.8729 (3)	2.23 (4)
C2	0.5025 (3)	0.1959 (2)	1.2946 (3)	2.51 (5)
H12	0.915 (3)	0.007 (2)	0.738 (3)	3.2 (6)*
H14	0.935 (3)	0.231 (2)	0.920 (4)	5.3 (8)*
H13	1.021 (3)	0.170 (2)	0.831 (3)	4.4 (7)*
H24	0.644 (4)	0.094 (2)	1.450 (4)	5.5 (8)*
H23	0.650 (4)	0.196 (2)	1.544 (4)	6.0 (8)*
H21	0.376 (4)	0.322 (2)	1.200 (4)	5.0(7)*
H22	0.497 (3)	0.323 (2)	1.397 (4)	4.8(7)*
H11	0.777 (3)	-0.044 (2)	0.781 (4)	5.2 (7)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2* B (1,1) + b2* B (2,2) + c2* B (3,3) + ab (cos gamma) *B (1,2) + ac (cos beta) *B (1,3) + bc (cos alpha) *B (2,3)]

Table 3. Table of General Displacement Parameter Expressions - U's

Name	U (1,1)	U (2,2)	U (3,3)	U (1,2)	U (1,3)	U (2,3)
CA	0.0237 (2)	0.0211 (2)	0.0278 (2)	-0.0012 (2)	0.0096 (2)	-0.0015 (3)
CL	0.0363 (2)	0.0432 (3)	0.0323 (2)	0.0077 (3)	0.0092 (2)	0.0052 (3)
O1	0.0324 (6)	0.0328 (8)	0.0424 (7)	-0.0070 (6)	0.0197 (5)	-0.0037 (7)
O2	0.0399 (8)	0.0272 (8)	0.0339 (7)	0.0030 (7)	0.0100 (6)	-0.0073 (7)
N11	0.0394 (9)	0.030 (1)	0.0454 (9)	-0.0009 (8)	0.0197 (7)	-0.0052 (9)
N12	0.0490 (9)	0.030 (1)	0.063 (1)	-0.0076 (8)	0.0355 (7)	-0.003 (1)
N21	0.101 (2)	0.057 (1)	0.033 (1)	0.033 (1)	0.015 (1)	0.007 (1)
N22	0.068 (1)	0.030 (1)	0.033 (1)	0.009 (1)	0.0092 (9)	-0.0075 (9)
C1	0.0261 (9)	0.026 (1)	0.0286 (9)	0.0010 (8)	0.0061 (7)	0.0049 (9)
C2	0.0346 (9)	0.031 (1)	0.0299 (9)	0.0014 (9)	0.0132 (7)	-0.0006 (9)

The form of the anisotropic displacement parameter is:
exp [-2PI2 {h2a2U (1,1) + k2b2U (2,2) + 12c2U (3,3) + 2hkabU (1,2) + 2hlacU (1,3) + 2k1bcU (2,3)}]
where a,b, and c are reciprocal lattice constants.

Description and Discussion of the Structure

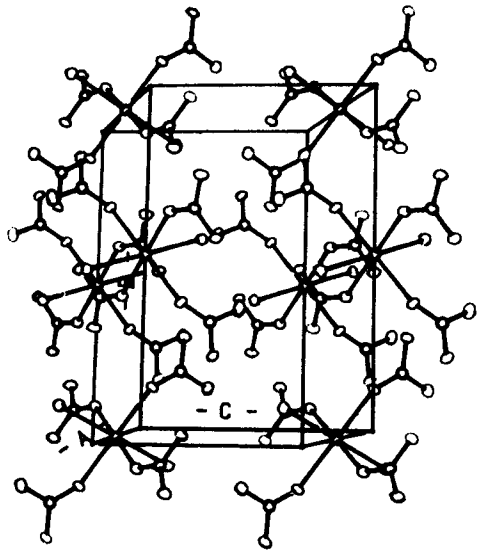
A stereoscopic ORTEP representation is shown in Figure 1; Tables 4 and 5 list relevant interatomic distances and angles.

Four urea oxygen atoms and two chloride atoms surround each calcium atom in a distorted-octahedral coordination. None of the chloride ions or urea molecules are bonded to more than one calcium atom.

Both crystallographically independent urea molecules have their oxygen atom coordinated to calcium. Their molecular geometries correspond to that of crystallized urea [4], with an approximately planar molecular skeleton. The hydrogen atoms show significant deviations from the mean molecular plane.

The quantities given in Tables 4 and 5 also suggest hydrogen bonds between the urea carbonyl oxygen and adjacent amide protons.

The present crystal structure is the same as the structure of calcium azide Tetrakis-urea, described in the Introduction.



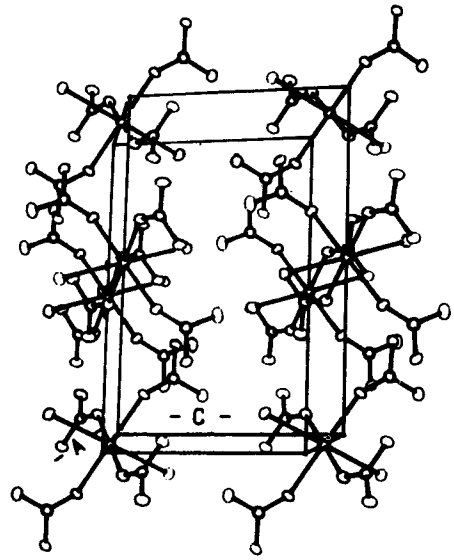


Table 4. Table of Bond Distances in Angstroms

Atom 1	Atom2	Distance	Atom1	Atom 2	Distance
CA	CL	2.7453 (5)	N12	H14	0.76 (3)
CA	O1	2.293 (2)	N12	H13	0.79 (3)
CA	O2	2.302 (2)	N21	C2	1.308 (3)
O1	C1	1.246 (3)	N21	H24	0.76 (3)
O2	C2	1.246 (3)	N21	H23	0.91 (3)
N11	C1	1.314 (3)	N22	C2	1.312 (3)
N11	H12	0.74 (3)	N22	H21	0.84 (2)
N11	H11	0.87 (3)	N22	H22	0.82 (3)
N12	C1	1.317 (3)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom1	Atom2	Atom 3	Angle
CL	CA	O1	90.49 (4)	C2	N21	H23	116. (2)
CL	CA	O2	90.14 (4)	H24	N21	H23	124. (3)
O1	CA	O2	87.63 (6)	C2	N22	H21	116. (2)
CA	O1	C1	140.2 (1)	C2	N22	H22	113. (2)
CA	O2	C2	146.4 (1)	H21	N22	H22	130. (3)
C1	N11	H12	122. (2)	O1	C1	N11	122.0 (2)
C1	N11	H11	119. (2)	O1	C1	N12	120.6 (2)
H12	N11	H11	119. (3)	N11	C1	N12	117.4 (2)
C1	N12	H14	119. (2)	O2	C2	N21	121.7 (2)
C1	N12	H13	117. (2)	O2	C2	N22	120.6 (2)
H14	N12	H13	124. (3)	N21	C2	N22	117.7 (2)
C2	N21	H24	120. (2)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

References

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