The Crystal Structure of Calcium 1,1-Dicyanoethylene-2,2-dithiolate Pentahydrate†

Christian Wolf and Hans-U. Hummel*
Institut fur Anorganische Chemie I der Universität Erlangen-Nurnberg, Egerlandstrasse 1, D-8520 Erlangen, W. Germany

The title compound, $Ca[S_2CC(CN)_2]·5H_2O$, has been synthesized and characterized by *X*-ray structural analysis. Calcium has a distorted bicapped trigonal-prismatic co-ordination of six O and two N atoms. Two O atoms are co-ordinated to two different Ca^{2+} ions forming dimeric units, $(CaO_4O_2N_2)_2$. Each $S_2CC(CN)_2$ ligand bridges different dimeric units *via* its N atoms. The S atoms of the ligand are not included in the co-ordination sphere of Ca^{2+} but they are involved in several O–H ⋯ S hydrogen bonds with O–H ⋯ S distances in the range 321—337 pm.

Little is known about the geometry of the dianionic ligand 1,1-dicyanoethylene-2,2-dithiolate (isomaleonitriledithiolate, i-mnt) in the solid state. In the series $M(S_2C_4N_2)·nH_2O$ with M = Ca, Sr, or Ba, the influence of the metal on the polydentate i-mnt is expected to be small. Therefore it should be possible to obtain information about the dianion with respect to various packing arrangements. A barium salt (M = Ba, n = 3) was first synthesized by Soderback.[1] The ligand is expected to be planar with a delocalized π-electron system. This has been confirmed by structural analysis of $[Cu_8(\text{i-mnt})_6]^{4-}$ by McCandlish *et al.*[2] and of $K_2(\text{i-mnt})·H_2O$ by Hummel.[3]

Experimental

By a similar method to that of Soderback[1] for the barium salt, calcium 1,1-dicyanoethylene-2,2-dithiolate pentahydrate was prepared by addition of $Ca(SCN)_2·4H_2O$ in absolute ethanol to $Na_2(\text{i-mnt})$‡ (Found: C, 17.8; H, 3.3; Ca, 13.7; N, 10.0. $C_4H_{10}CaN_2O_5S_2$ requires C, 17.8; H, 3.7; Ca, 14.8; N, 10.4%). The substance is nearly insoluble in the solvent used and can be recrystallized by dissolving in water and evaporation at *ca.* 293 K yielding yellow crystals.

X-Ray Structure Determination.—Weissenberg and precession photographs were carried out with systematic extinctions: $h0l, l = 2n + 1; 0k0, k = 2n + 1$.

Crystal data. $C_4CaN_2S_2·5H_2O$, $M = 267.7$, monoclinic, $a = 889.4(2)$, $b = 987.9(6)$, $c = 1\,419.9(5)$ pm, $\beta = 121.2(2)°$, $U = 1\,066.9 \times 10^6$ pm^3 (based on 25 high-indexed diffractometer measured intensities, $\lambda = 55.87$ pm), space group $P2_1/c$, D_m (pycnometric) = 1.8 g cm^{-3}, $Z = 4$, $D_c = 1.7$ g cm^{-3}, $F(000) = 552$. Yellow prismatic crystals with $d = 0.1$ mm (parallel to [010]), $\mu(\text{Ag-}K_\alpha) = 0.554$ mm^{-1}.

Data collection and processing. PW 1100 diffractometer, ω-scan (width 1.00 + 0.20 tanθ°), graphite-monochromated Ag-K_α radiation; 5 984 reflections measured ($3 \leqslant \theta \leqslant 20°$; $-8 \leqslant h \leqslant 8$, $-10 \leqslant k \leqslant 10$, $-12 \leqslant l \leqslant 12$), 1 654 symmetry independent reflections after merging and correction for Lorentz, polarization, and geometrical effects; $R_{int} = 0.0342$.

Structure analysis and refinement. Direct methods (MULTAN[5]) and Fourier procedures, 1 247 observed reflections with $F_o \geqslant 6\sigma(F)$ ($\sin\theta_{max.}/\lambda = 5.73 \times 10^{-3}$ pm^{-1}) in blocked-matrix least-squares refinement with all non-hydrogen atoms anisotropic. All H atoms were refined as parts of rigid H_2O molecules with O–H = 96.0(5) and H ⋯ H = 156.0(5) pm. The minimized function was $\Sigma w||F_o| - |F_c||^2$ with $w = 7.5/[\sigma^2(F_o) + 1.5 \times 10^{-4} F_o^2]$, SHELX-76 system.[6] Final refinement converged to $R = 0.0602$, $R' = 0.0544$ ($R = \Sigma||F_o| - |F_o||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$). Scattering factors, f' and f'' were from International Tables.[7]

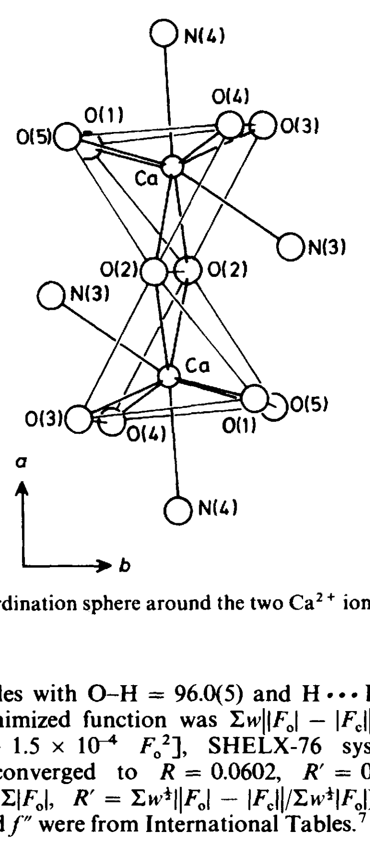

Figure 1. Co-ordination sphere around the two Ca^{2+} ions

Discussion

Final atomic parameters are given in Table 1. The co-ordination sphere of the two Ca^{2+} ions is shown in Figure 1. Six O atoms with an average distance of 247 pm form a distorted trigonal prism, which is bicapped by two N atoms with Ca–N distances of 255 for N(4) and 272 pm for N(3). Two prisms share a common edge producing a dimeric unit, $(CaO_4O_2N_2)_2$.

Dimeric, oligomeric, and polymeric units containing Ca^{2+} ions are common in the stereochemistry of calcium. In compounds with eight-co-ordinated calcium there are usually bisdisphenoids (triangulated dodecahedrons) or Archimedean antiprisms as co-ordination polyhedra.[8]

The hexahydrates of the halides $CaX_2·6H_2O$ (X = Cl, Br, or I) contain tricapped trigonal-prismatic co-ordinated Ca^{2+} with nine O atoms at distances of 245.1—262.2 pm.[9,10] By sharing of

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† *Supplementary data available* (No. SUP 56352, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

‡ First prepared by Gompper and Topfl.[4]

Table 1. Final atomic co-ordinates (all atoms with site-symmetry 1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ca	0.740 1(2)	0.995 8(1)	0.413 1(1)	O(4)	0.366 9(5)	0.114 9(3)	0.769 5(4)
S(1)	0.006 2(2)	0.175 6(1)	0.783 1(1)	O(5)	0.334 9(4)	0.699 4(3)	0.197 8(4)
S(2)	0.267 4(2)	0.993 5(2)	0.960 5(1)	H(1A)	0.306(9)	0.747(3)	0.497(5)
C(1)	0.055 4(8)	0.467 7(5)	0.365 4(5)	H(1B)	0.234(8)	0.849(7)	0.398(1)
C(2)	0.084 7(8)	0.049 2(6)	0.151 5(5)	H(2A)	1.003(8)	0.125(2)	0.373(4)
C(3)	0.062 2(8)	0.170 7(6)	0.089 2(5)	H(2B)	0.993(8)	0.025(4)	0.336(3)
C(4)	0.260 1(8)	0.025 9(6)	0.235 5(5)	H(3A)	0.658(15)	0.727(3)	0.491(11)
N(3)	0.061 2(8)	0.230 1(5)	0.549 4(5)	H(3B)	0.537(9)	0.844(10)	0.488(9)
N(4)	0.405 8(7)	0.485 9(5)	0.801 8(5)	H(4A)	0.426(8)	0.041(5)	0.819(5)
O(1)	0.313 1(5)	0.838 3(3)	0.476 3(3)	H(4B)	0.273(7)	0.146(7)	0.779(6)
O(2)	1.001 7(5)	0.032 8(3)	0.393 2(3)	H(5A)	0.243(6)	0.752(6)	0.196(6)
O(3)	0.636 3(5)	0.822 9(4)	0.480 5(3)	H(5B)	0.429(7)	0.759(6)	0.211(9)

Table 2. Interatomic distances (pm) and angles (°)

(*a*) The Ca^{2+} ion

Ca–O(1)	248.0(3)	Ca–O(4)	250.3(5)
Ca–O(2)	251.2(3), 252.4(4)	Ca–O(5)	242.5(4)
		Ca–O	246.9(4) (average)
Ca–O(3)	236.7(4)		
Ca–N(3)	272.2(5)	Ca–N(4)	254.9(4)
Ca–N(3)–C(3)	141.05(47)	Ca–N(4)–C(4)	167.13(43)
Ca–Ca	395.6(2)		

(*b*) The i-mnt dianion

C(1)–S(1)	174.1(5)	S(1)–C(1)–S(2)	120.41(24)
C(1)–S(2)	169.9(5)	S(1)–C(1)–C(2)	117.53(40)
S(1)–S(2)	298.5(2)	S(2)–C(1)–C(2)	122.04(43)
C(2)–C(1)	139.6(6)	C(1)–C(2)–C(3)	123.16(46)
C(2)–C(3)	144.2(8)	C(1)–C(2)–C(4)	123.37(53)
C(2)–C(4)	140.7(7)	C(3)–C(2)–C(4)	113.36(42)
C(3)–N(3)	112.9(8)	C(2)–C(3)–N(3)	172.79(59)
C(4)–N(4)	114.6(7)	C(2)–C(4)–N(4)	175.71(59)

(*c*) The hydrogen-bond geometry

OH ··· S bonds	H ··· S	O ··· S	Angle O–H ··· S
O(1)–H(1A) ··· S(2)	242(3)	329.6(4)	152(5)
O(1)–H(1B) ··· S(1)	236(3)	328.7(4)	163(5)
O(2)–H(2A) ··· S(1)	235(3)	328.8(3)	164(4)
O(2)–H(2B) ··· S(1)	226(4)	321.4(3)	174(3)
O(3)–H(3A) ··· S(2)	240(4)	335.9(4)	173(11)
O(4)–H(4B) ··· S(1)	242(3)	336.6(2)	167(6)

OH ··· O bonds	H ··· O	O ··· O	Angle O–H ··· O
O(3)–H(3B) ··· O(1)	192(2)	284.8(3)	163(9)
O(5)–H(5B) ··· O(4)	210(4)	305.6(3)	176(8)

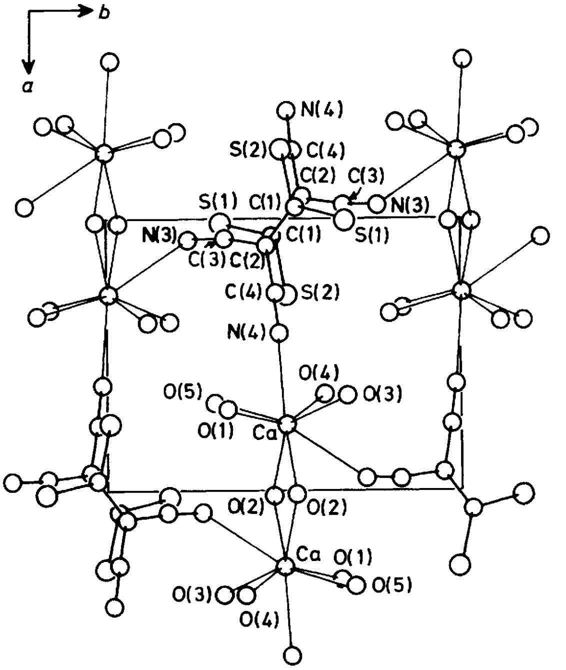

Figure 2. Projection of the structure of $Ca(i\text{-}mnt)\cdot 5H_2O$ on the *ab* plane. Only one layer generated by connection of $[Ca(NC)_2C]_\infty$ chains *via* Ca–O–Ca bridges is depicted

six oxygen atoms, linear one-dimensional infinite chains, $[Ca(OH_2)_3(OH_2)_{\frac{6}{2}}]_\infty$, are formed.

In the present compound only the nitrogen atoms of i-mnt are directed towards Ca^{2+}, while in the corresponding compound $K_2(i\text{-}mnt)\cdot H_2O$, both sulphur and nitrogen ligate potassium.[3] Besides the various amounts of crystal water in both structures, differences in 'softness' character of K^+ and Ca^{2+} may be responsible for the differing donation of i-mnt.[11]

A projection of the structure of $Ca(i\text{-}mnt)\cdot 5H_2O$ on the (001) plane is shown in Figure 2. The N atoms of one i-mnt are co-ordinated to two different Ca^{2+} ions, generating one-dimensional infinite undulatory chains $[Ca(NC)_2C]_\infty$. These chains are connected *via* Ca–O–Ca bridges forming two-dimensional parallel layers which are linked only by hydrogen bonds.

Although we cannot claim high accuracy for the H atoms, they appear to be sufficiently well established from *X*-ray data and stereochemical considerations. With the exception of $H_2O(5)$, all water molecules are involved in OH ··· S type hydrogen bonds (Table 2, Figure 3). Three interlayer distances S(1) ··· O <331 pm include the possibility of hydrogen bonds [S(1) to O(1), O(2), and O(4)].[12] S(1) has also one attractive intralayer contact with O(2) while S(2) is involved in two OH ··· S hydrogen bonds within the same layer. The mean value of O ··· S (330.2 pm) is close to the 331 pm for S–O obtained from a statistical treatment of *X*-ray data on intermolecular OH ··· S hydrogen bonds in organic homonuclear crystals.[12] Two O–O distances are in the range (260—310 pm) indicative of O–H ··· O bridge bonds, based on various neutron diffraction data.[13] The bond O(1) ··· O(3)

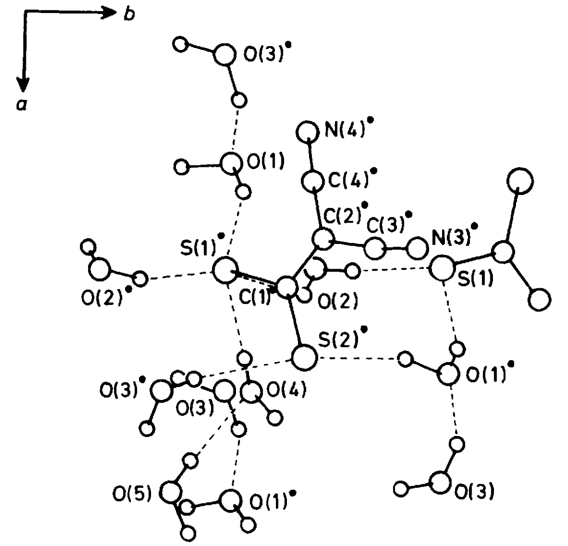

Figure 3. The hydrogen bonds in Ca(i-mnt)$\cdot$5H_2O. Hydrogen bonds within the same layer are marked with a bold dot

connects different layers while O(5)$\cdots$O(4) is of intralayer type. The i-mnt dianion is nearly planar with a maximum deviation from the least-squares plane for the whole molecule of 9.60 pm. The observed C–S distances are smaller than expected for a C–S single bond (182 pm).[14] The observed distance for S(1)–C(1) corresponds to a value expected for a S–C(sp^2) bond and is significantly elongated with respect to S(2)–C(1).[15] According to the decreased bond order for S(1)–C(1), S(1) forms more OH$\cdots$S hydrogen bonds. All C–C distances indicate delocalization of the π-electron system. The value for the C–N triple bond length in i-mnt is reduced compared with that in the highly symmetrical $C(CN)_3^-$ ion (117 pm).[16] This could be caused by the lowering of the contribution of the cyanide groups to the π-system in i-mnt.

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References

1 E. Söderbäck, *Acta Chem. Scand.*, 1963, **17**, 362.
2 L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Am. Chem. Soc.*, 1968, **90**, 7357.
3 H.-U. Hummel, *Acta Crystallogr., Sect. C*, in the press.
4 R. Gompper and W. Topfl, *Chem. Ber.*, 1962, **95**, 2861.
5 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
6 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.
7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
8 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Clarendon Press, Oxford, 1975.
9 A. Leclaire and M. M. Borel, *Acta Crystallogr., Sect. B*, 1977, **33**, 2938.
10 Z. Herrmann, *Z. Anorg. Allg. Chem.*, 1931, **197**, 339.
11 G. Klopmann, *J. Am. Chem. Soc.*, 1968, **90**, 223.
12 L. N. Kuleshova and P. M. Zorkii, *Acta Crystallogr., Sect B*, 1981, **37**, 1363.
13 G. Ferraris and M. Franchini-Angela, *Acta Crystallogr., Sect. B*, 1972, **28**, 3572.
14 M. Drager, *Z. Anorg. Allg. Chem.*, 1977, **428**, 243.
15 G. F. Gasparri, M. Nardelli, and A. Villa, *Acta Crystallogr.*, 1967, **23**, 384.
16 J. R. Witt and D. Britton, *Acta Crystallogr., Sect. B*, 1971, **27**, 1835.

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