angles are close to 180° though packing restraints force some deviation from linearity. As the figure shows, each of these water molecules is involved in three hydrogen bonds (the fourth possible interaction, with an O···O separation of 2·9 Å, is deemed too weak to be included).

Even longer 'hydrogen bonds', both inter- and intramolecular, between coordinated waters and nitrate ligands, have been ignored in Table 3, although such interactions have been discussed by others (*e.g.* Burns, 1979) for O···O distances up to 2·95 Å.

The different water sites are reflected in different $\bar{\nu}$ values for their bending modes (Raman: 1650, 1634; IR: 1680 and 1640 cm^{-1}). As is often the case (*e.g.* Chakravorty, 1974) the O—H stretching absorptions are extremely broad (over 1000 cm^{-1}) with a vague maximum at about 2800 cm^{-1}. Metal–water vibrations occur at 320 (Raman), metal–nitrate vibrations at 225 and 200 cm^{-1} (Raman).

References

ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D. (1971). *Q. Rev. Chem. Soc.* **25**, 289–322.
BERGMAN, J. G. & COTTON, F. A. (1966). *Inorg. Chem.* **5**, 1208–1213.
BURNS, J. (1979). *Inorg. Chem.* **18**, 3044–3047.
CHAKRAVORTY, A. (1974). *Coord. Chem. Rev.* **13**, 1–46.
CHIEH, C., TOOGOOD, G. E., BOYLE, T. D. & BURGESS, C. M. (1976). *Acta Cryst.* B**32**, 1008–1011.
FULLER, C. C. & JACOBSON, R. A. (1976). *Cryst. Struct. Commun.* **5**, 349–352.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MILINSKI, N., RIBÁR, B. & SATARIC, M. (1980). *Cryst. Struct. Commun.* **9**, 473–476.
MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Q. Rev. Chem. Soc.* **21**, 109–194.
RIBÁR, B., MILINSKI, N. & BUDOVALCEV, Z. (1980). *Cryst. Struct. Commun.* **9**, 203–206.
RUMANOVA, I. M., VOLODINA, G. F. & BELOV, N. V. (1965). *Sov. Phys. Crystallogr.* **9**, 545–550.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TAYLOR, N. J., JACOBSON, S. E. & CARTY, A. J. (1975). *Inorg. Chem.* **14**, 2648–2653.
TOOGOOD, G. E. & CHIEH, C. (1975). *Can. J. Chem.* **53**, 831–835.

Calcium Cesium Triazide Monohydrate, CaCs(N₃)₃.H₂O

BY H. KRISCHNER AND F. A. MAUTNER

Institut für Physikalische und Theoretische Chemie, Abteilung für Strukturforschung, Technische Universität Graz, Rechbauerstrasse 12, A-8010 Graz, Austria

AND CH. KRATKY

Institut für Physikalische Chemie der Universität Graz, Heinrichstrasse 28, A-8010 Graz, Austria

Abstract. $M_r = 317\cdot06$, triclinic, $P\bar{1}$, $a = 6\cdot846$ (1), $b = 7\cdot557$ (1), $c = 8\cdot810$ (1) Å, $\alpha = 71\cdot59$ (1), $\beta = 82\cdot80$ (1), $\gamma = 81\cdot09$ (1)°, $V = 425\cdot82$ Å^3, $Z = 2$, $D_x = 2\cdot47$ Mg m^{-3}, $F(000) = 304\cdot01$, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å (graphite monochromator), $\mu = 4\cdot9$ mm^{-1}, $T = 298$ K. The crystal structure was solved by Patterson and Fourier methods and refined to $R = 0\cdot034$ for 1475 independent counter reflections. Ca is seven-coordinated to six N atoms of azide groups and to one water molecule. The polyhedra around Ca are pentagonal bipyramids sharing one edge. Cs is nine-coordinated to eight azide groups and one water molecule. The mean N—N distance is $1\cdot17$ (2) Å.

Introduction. Crystal structures of several compounds between alkaline azides and alkaline-earth azides have been determined during the last few years (Krischner & Maier, 1980; Paar & Krischner, 1981). In the ternary system cesium azide/calcium azide/water, the title compound is formed at room temperature together with three other calcium cesium azide hydrates of different composition (Krischner & Hofer, 1983). Crystals are colorless and transparent. They dissolve readily in water, are stable for several days at room temperature and are not explosive.

Experimental. Crystal dimensions $0\cdot25 \times 0\cdot25 \times 0\cdot30$ mm, Stoe four-circle diffractometer. Cell dimensions from setting angles of 11 reflections with $2\theta \simeq 30°$. Intensity data: all reflections of one hemisphere with $2\theta \le 50°$ ($\sin\theta/\lambda \le 0\cdot595$ Å^{-1}), range of

hkl: -7, -8, $0/8$, 8, 9, ω scan, $\Delta\omega = 2°$, 1493 unique reflections, all reflections used $[|F_o| \geq 0\sigma(F_o)]$. Reference reflections 443, 006; their intensities dropped by about 2% in the course of data collection. Test measurements revealed, however, that the intensities of several strong low-order reflections had increased during X-ray exposure of the crystal, possibly due to partial removal of extinction. The nine strongest reflections were therefore subsequently excluded, together with nine reflections with strongly asymmetric backgrounds. All the remaining 1475 independent reflections were processed (Lp correction, no absorption correction, scattering factors from *International Tables for X-ray Crystallography*, 1974) and used for structure solution and refinement. Positions of the heavy atoms were obtained from a Patterson function, the remaining atoms (including protons) were observed in F_o and $(F_o - F_c)$ Fourier syntheses. Least-squares refinement of F magnitudes included anisotropic tensor components for all atoms except H, whose isotropic temperature factors were fixed at $U = 0.06$ Å^2. The O—H distances were constrained to 1.02 Å. Refinement [1475 observations, 115 parameters, no secondary-extinction correction, weighting system $w_i = 1/\sigma^2(F_o) + 0.0032F_o^2$] converged at $R = 0.034$, $R_w = 0.041$. Maximal shift to error except H atoms $= 0.9$, final $(F_o - F_c)$ Fourier synthesis showed peaks up to 1.1 e Å^{-3} in the vicinity of metal atoms and minima of 1.8 e Å^{-3}. Computer programs used: *SHELX76* (Sheldrick, 1976), XRAY76 (Stewart, 1976), *ORTEP* (Johnson, 1965); Univac 1108 computer, Rechenzentrum Graz.

Discussion. Final atomic parameters are given in Table 1.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38525 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
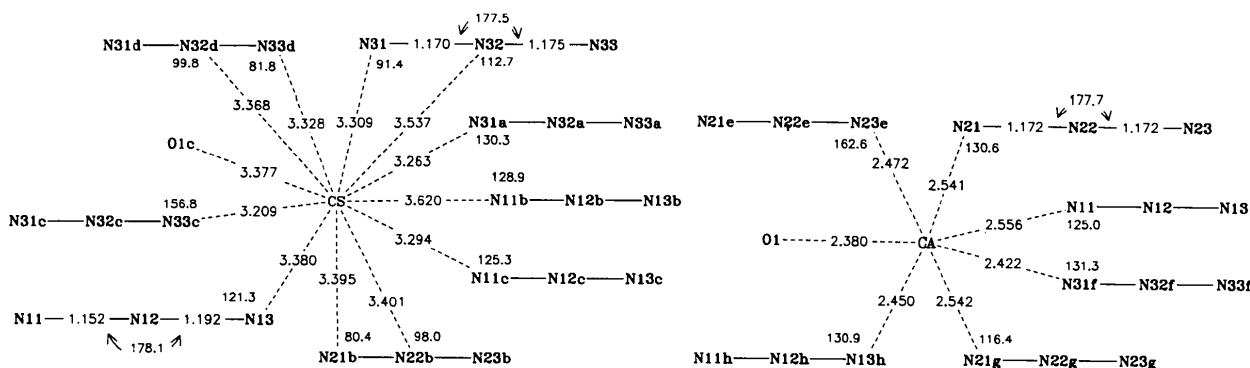
Ca is surrounded by six terminal azide N atoms [average Ca—N = 2.50 (6) Å] and the water O. The coordination polyhedra have the form of distorted pentagonal bipyramids; pairs of these related by a center of symmetry share a common edge. Adjacent pairs are linked *via* azide ions and hydrogen bonds [H(1)—N(13) = 2.03 (3); H(2)—N(33) = 1.19 (9) Å].

The Cs$^+$ is surrounded in a seemingly irregular arrangement by eight terminal N atoms of different azide groups [average Cs—N = 3.35 (12) Å] and the water molecule. Again, the coordination polyhedra are

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and isotropic thermal parameters* $(\text{Å}^2 \times 10^4)$

U_{eq} was calculated as one third of the trace of the orthogonalized U_{ij} tensor. The temperature factor has the form $T = \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

	x	y	z	U or U_{eq}
Cs(1)	2462 (1)	1824 (1)	962 (1)	309 (3)
Ca(1)	6894 (1)	8144 (1)	3990 (1)	160 (5)
O(1)	8901 (5)	5998 (5)	2796 (5)	336 (23)
N(11)	4710 (5)	7014 (6)	2425 (5)	339 (26)
N(12)	3953 (5)	5666 (5)	2919 (4)	225 (21)
N(13)	3123 (7)	4299 (5)	3407 (5)	312 (24)
N(21)	3311 (6)	9198 (6)	4782 (5)	253 (23)
N(22)	1836 (5)	8667 (5)	4661 (5)	228 (22)
N(23)	362 (6)	8173 (6)	4488 (7)	410 (32)
N(31)	7243 (8)	660 (6)	1502 (5)	352 (27)
N(32)	7470 (6)	2229 (6)	1252 (5)	254 (24)
N(33)	7766 (8)	3791 (6)	970 (7)	464 (32)
H(1)	10341 (28)	5550 (99)	2908 (98)	600
H(2)	8443 (99)	4983 (95)	2410 (86)	600

Fig. 1. Stereoscopic *ORTEP* drawing of the crystal structure of CaCs(N$_3$)$_3$.H$_2$O. Atoms are drawn with increasing radii in the sequence H, N, O, Ca, Cs.

Fig. 2. Relevant distances and angles in the crystal structure of CaCs(N$_3$)$_3$.H$_2$O. Approximate standard deviations are as follows: N—N, $\sigma \simeq 0.007$ Å; Ca—N or O, $\sigma \simeq 0.006$ Å; Cs—N or O, $\sigma \simeq 0.005$ Å; N—N—Cs, $\sigma \simeq 0.5°$; N—N—Ca, $\sigma \simeq 0.5°$. The equivalent positions are as follows: (a) $1-x$, $-y$, $-z$; (b) x, $-1+y$, z; (c) $1-x$, $1-y$, $-z$; (d) $-1+x$, y, z; (e) $1+x$, y, z; (f) x, $1+y$, z; (g) $1-x$, $2-y$, $1-z$; (h) $1-x$, $1-y$, $1-z$.

arranged in centrosymmetric pairs. Fig. 1 shows the packing in a stereoscopic *ORTEP* drawing.

The average angles between azide ions and the metal atoms (M—N—N) are 133 (15)° around Ca and 114 (27)° around Cs. Two Cs—N—N angles are below 90°. This results in a rather close contact between Cs and the middle N atoms (Fig. 2). Close contacts of Cs to the central azide N atoms have been observed in several other complex azides (Krischner, Saracoglu & Kratky, 1982).

Bond lengths and angles within the azide groups are as expected (Pringle & Noakes, 1968).

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–174. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KRISCHNER, H. & HOFER, F. V. (1983). *Z. Anorg. Allg. Chem.* In preparation.
KRISCHNER, H. & MAIER, H. E. (1980). *Z. Anorg. Allg. Chem.* **460**, 217–220.
KRISCHNER, H., SARACOGLU, A. I. & KRATKY, CH. (1982). *Z. Kristallogr.* **159**, 225–229.
PAAR, W. & KRISCHNER, H. (1981). *Z. Anorg. Allg. Chem.* **479**, 212–218.
PRINGLE, G. E. & NOAKES, D. E. (1968). *Acta Cryst.* B**24**, 262–269.
SHELDRICK, G. M. (1976). *SHELX*76. Univ. of Cambridge, England.
STEWART, J. M. (1976). Editor. The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Structures of Ba₈Ga₇, Sr₈Ga₇ and Sr₈Al₇

BY MARIA L. FORNASINI

Istituto di Chimica Fisica, Università di Genova, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

Abstract. Ba_8Ga_7, cP60, $M_r = 1586 \cdot 8$, cubic, $P2_13$, $a = 12 \cdot 990$ (6) Å, $V = 2192$ Å³, $Z = 4$, $D_x = 4 \cdot 81$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å, $\mu(Mo\ K\alpha) = 23 \cdot 4$ mm⁻¹, $F(000) = 2660$, $R = 0 \cdot 040$ for 784 reflections. Sr_8Ga_7, $M_r = 1189$, $P2_13$, $a = 12 \cdot 484$ (6) Å, $V = 1946$ Å³, $D_x = 4 \cdot 06$ Mg m⁻³, $\mu(Mo\ K\alpha) = 32 \cdot 7$ mm⁻¹, $F(000) = 2084$, $R = 0 \cdot 048$ for 224 reflections. Sr_8Al_7, $M_r = 889 \cdot 8$, $P2_13$, $a = 12 \cdot 753$ (5) Å, $V = 2074$ Å³, $D_x = 2 \cdot 85$ Mg m⁻³, $\mu(Mo\ K\alpha) = 21 \cdot 6$ mm⁻¹, $F(000) = 1580$, $R = 0 \cdot 031$ for 555 reflections. For this last phase a previous structural proposal for equiatomic stoichiometry was revised and the new formula Sr_8Al_7 determined. The three compounds are isotypic and their structure is characterized by the presence of isolated tetrahedral and triangular clusters of Ga (or Al) atoms included in cages of 16 and 13 alkaline-earth atoms, respectively.

Introduction. After the structure determination of $Ba_{10}Ga$ (Fornasini & Merlo, 1979), work was continued on the study of the other alkaline-earth-rich phases present in the Ba–Ga, Sr–Ga (Bruzzone, 1966) and Sr–Al (Bruzzone & Merlo, 1974) systems. This paper deals with the structure determination of the compounds reported as Ba_3Ga_2, Sr_3Ga_2 and Sr_3Al_2 in the corresponding phase diagrams. In the case of Sr_3Al_2

a previous structural proposal for equiatomic stoichiometry (Fornasini & Merlo, 1976) is re-examined.

Experimental. Metals used: Ba (99·5 wt%) from Fluka, Switzerland, Sr (99wt%) and Ga (99·999wt%) from Koch-Light, England. Ba_3Ga_2 prepared by melting in a sealed tantalum container, and slowly cooling the alloy; single crystals examined by X-ray precession technique; cubic Laue symmetry $m3$ with the systematic absence of $h00$ reflections with $h = 2n + 1$ led univocally to the space group $P2_13$. A nearly spherical crystal with mean radius 0·08 mm sealed in a thin glass capillary under vacuum, mounted on an Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice constant determined by least-squares over 25 diffractometer-measured high-angle reflections; equivalent hkl, lhk and klh reflections collected in the ω scan mode up to $2\theta = 55°$. Intensities corrected for Lp and absorption, applying both the semi-empirical method of North, Phillips & Mathews (1968) with ψ-scan data of four top reflections and the spherical correction, the maximum transmission-factor ratio being 2·4; equivalents merged ($R_{int} = 0 \cdot 069$), 944 unique reflections obtained, 784 with $F_o > 2\sigma(F_o)$ used in the refinement. The structure already proposed for SrAl (Fornasini & Merlo, 1976)