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Structure of Trisodium Monothioarsenate Dodecahydrate

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Abstract. $Na_3AsO_3S.12H_2O$, $M_r = 440{\cdot}14$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}220\,(1)$, $b = 12{\cdot}831\,(2)$, $c = 13{\cdot}906\,(3)$ Å, $V = 1645{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 2{\cdot}32$ mm^{-1}, $F(000) = 904$, $T = 213$ K, $R = 0{\cdot}038$ for 2043 unique observed reflections. Units of three face-sharing distorted $[Na(OH_2)_6]^+$ octahedra are each connected by two common vertices into zigzag chains parallel to the *c* axis. These endless chains of composition $[Na_3(OH_2)_{11}]^{3+}$, discrete AsO_3S^{3-} anions and discrete H_2O molecules, not coordinated to Na^+ cations, are linked *via* O—H···O and/or O—H···S hydrogen bonds. The title compound $[Na_3(OH_2)_{11}][AsO_3S].H_2O$ is structurally closely related to the hydrate $[Na_3(OH_2)_{11}][AsO_2S_2]$.

Introduction. Palazzi (1971, 1978) studied the properties of the crystalline hydrate $Na_3AsO_3S.12H_2O$ by means of thermoanalytical and X-ray powder diffraction methods. From the powder pattern the space group $P2_12_12_1$ with $Z = 4$ and the cell constants $a = 9{\cdot}212\,(3)$, $b = 12{\cdot}865\,(3)$, and $c = 13{\cdot}973\,(3)$ Å had been deduced.

We are interested in structures, hydrogen bonding and melting characteristics of crystalline salt hydrates (Felsche, 1988). In the course of these investigations we have carried out a single-crystal X-ray structure analysis of the title compound. The results are reported below.

Experimental. Crystals of the compound $Na_3AsO_3S.12H_2O$, which slowly decomposed in air, were grown from an aqueous solution by cooling. One of the crystals of approximate size 0·3 × 0·2 × 0·2 mm was sealed in a thin-walled glass capillary for the X-ray studies on an Enraf–Nonius CAD-4 diffractometer (graphite monochromator) equipped with a low-temperature device. Cell constants were determined from the setting angles of 25 strong reflections in the range $34 < 2\theta < 38°$. Intensities were measured by a variable $\omega/2\theta$-scan technique. A total decay in intensity of 12·5% during the measurements was indicated by the standard reflections monitored every hour. 2706 unique reflections were registered up to $(\sin\theta)/\lambda = 0{\cdot}703$ Å^{-1} in the hemisphere $0 \leq h \leq 12$, $0 \leq k \leq 18$, $0 \leq l \leq 19$. A linear decay correction and an empirical absorption correction based on the ψ scans of nine reflections were applied. Minimum and maximum relative transmission factors were 0·797 and 0·999, respectively. 663 reflections with $F^2 < 1{\cdot}5\sigma(F^2)$ were considered unobserved.

The structure was solved by direct methods. The observed reflections were weighted according to $w = 4F^2/[\sigma^2(I) + (0{\cdot}04F^2)^2]$ and included in the full-matrix least-squares refinement with the function minimized $\sum w(\Delta F)^2$. 23 out of the total 24 H atoms were located by difference Fourier methods. In the final refinement 181 parameters were varied: one scale factor, coordinates and anisotropic displacement parameters of the non-H atoms; the coordinates and arbitrary isotropic displacement parameters of the H atoms were kept fixed; $R = 0{\cdot}038$, $wR = 0{\cdot}042$, $S = 1{\cdot}390$. Maximum Δ/σ in the last cycle was 0·01. $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ in the final difference Fourier synthesis were $-0{\cdot}67$ and $+0{\cdot}68$ e Å^{-3} near the As atom, respectively. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Digital PDP11/23 computer using the Enraf–Nonius (1978) *SDP* program system. Illustrations were generated with the program *ORTEP*II (Johnson, 1976). Final atomic parameters of the non-H atoms are listed in Table 1.*

Discussion. In the crystal structure of the salt hydrate $Na_3AsO_3S.12H_2O$ units of three face-sharing $[Na(OH_2)_6]^+$ octahedra are each connected by two common vertices into one-dimensional zigzag chains parallel to the *c* axis. These endless chains of composition $[Na_3(OH_2)_{11}]^{3+}$, discrete AsO_3S^{3-} anions and discrete H_2O molecules, not coordinated to Na^+ cations, are linked *via* hydrogen bonds to form a

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* Lists of anisotropic displacement parameters of the non-H atoms, H-atom parameters, interatomic distances and angles in which the H atoms take part, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52510 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Coordinates and equivalent isotropic displacement parameters* ($Å^2$) *of the non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (1/24\pi^2)\Sigma_i\Sigma_jB_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
As	0·24841 (5)	0·45298 (3)	0·27059 (3)	0·01022 (6)
S	0·2671 (1)	0·29250 (8)	0·22779 (8)	0·0181 (2)
Na1	0·2606 (3)	0·2125 (1)	0·6037 (1)	0·0249 (4)
Na2	0·2480 (3)	0·0081 (1)	0·4771 (1)	0·0224 (4)
Na3	0·2400 (2)	−0·2226 (1)	0·3909 (1)	0·0200 (4)
O1	0·1958 (4)	0·4604 (3)	0·3867 (2)	0·0189 (7)
O2	0·1245 (4)	0·5142 (2)	0·2010 (2)	0·0167 (7)
O3	0·4102 (3)	0·5153 (2)	0·2587 (2)	0·0147 (6)
O4	0·3902 (4)	0·2752 (3)	0·7480 (2)	0·0238 (9)
O5	0·3542 (4)	0·3731 (3)	0·5320 (2)	0·0208 (7)
O6	0·0534 (4)	0·3133 (3)	0·6455 (3)	0·0227 (7)
O7	0·4460 (4)	0·1143 (3)	0·5293 (3)	0·0242 (9)
O8	0·1648 (4)	0·1786 (3)	0·4299 (3)	0·0270 (9)
O9	0·0875 (4)	0·0726 (3)	0·5990 (2)	0·0237 (9)
O10	0·3506 (4)	−0·0657 (3)	0·3373 (3)	0·0251 (9)
O11	0·3452 (4)	−0·1499 (3)	0·5476 (3)	0·0244 (9)
O12	0·0486 (4)	−0·1058 (3)	0·4290 (3)	0·0219 (7)
O13	0·1410 (4)	−0·3635 (3)	0·4832 (3)	0·0249 (9)
O14	0·4536 (4)	−0·3240 (3)	0·3865 (3)	0·0233 (9)
O15	0·1438 (4)	0·0005 (4)	0·2165 (3)	0·051 (1)

three-dimensional network. As illustrated in Fig. 1, this network might be considered topologically as being composed of layers parallel to the *bc* plane which are stacked along the **a** direction following the symmetry of 2_1-screw axes. However, there are more independent interlayer (13) than intralayer (11) hydrogen bonds. Selected interatomic distances and angles are listed in Table 2.

The $[Na(OH_2)_6]^+$ coordination octahedra are moderately or strongly distorted. The bond lengths and angles in the AsO_3S^{3-} anion correspond to values reported for the hydrates $Na_3AsO_3S.7H_2O$ (Palazzi, 1976) and $Na_3AsO_2S_2.11H_2O$ (Jaulmes & Palazzi, 1976). With the help of the 23 roughly located H atoms a reasonable system of unfurcated hydrogen bonds has been deduced. Atom H82 is the only H atom which has not been located from the ΔF maps. It is probably situated between atoms O8 and O5 (O···O distance 2·988 Å), with O8 being the donor of the hydrogen bond, because the other O··O contacts with appropriate lengths, O8···O7 (3·052 Å) and O8···O9 (2·810 Å), are extended along the edges of $[Na(OH_2)_6]^+$ polyhedra which, for electrostatic reasons, are unfavourable positions for H atoms (Baur, 1972).

While the O atoms in the anion accept three or four hydrogen bonds, the S atom accepts a total of six hydrogen bonds with donor—acceptor distances covering the range from 3·271 to 3·621 Å, typical for strong and weak O—H···S interactions (Mereiter, Preisinger & Guth, 1979; Mereiter & Preisinger, 1988). 11 of the 12 H_2O molecules are bonded to (one or two) Na^+ ions. The O atoms of these H_2O molecules have coordination numbers four (nine cases) or five (two cases, atoms O5 and O11). One H_2O molecule (O15) does not belong to any $[Na(OH_2)_6]^+$ polyhedron. It accepts one and donates two O—H···O bonds in a trigonal-planar surrounding of O atoms of H_2O molecules and the anion. This special coordination sphere as well as the weak interactions (O15···O11 at 3·034 Å is the longest O—H···O bond in the structure) account for the comparatively large and strongly anisotropic displacement parameters of atom O15 (the longest axis of the displacement ellipsoid is approximately normal to the plane of the three hydrogen-bonded O atoms). All O···O distances in the hydrogen bonds fall into a range that is typical for H_2O molecules in salt hydrates (Chiari & Ferraris, 1982).

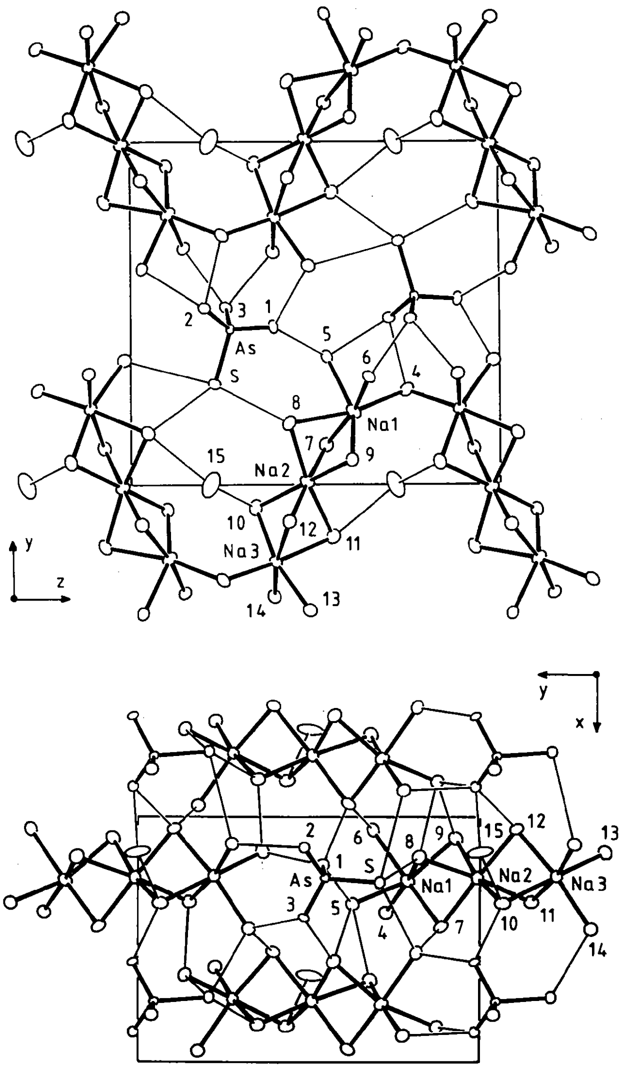

Fig. 1. A layer in the structure of $[Na_3(OH_2)_{11}][AsO_3S].H_2O$ as viewed along the *a* axis (top) and stacking of the layers as viewed along the *c* axis (bottom). All ellipsoids correspond to the 50% probability level. O atoms are designated by numbers only. H atoms are omitted for clarity.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

$[Na(OH_2)_6]^+$ polyhedra			
Na1—O4	2·470 (4)	Na1—O5	2·446 (4)
Na1—O6	2·380 (4)	Na1—O7	2·363 (4)
Na1—O8	2·611 (4)	Na1—O9	2·403 (4)
O4—Na1—O5	83·5 (1)	O4—Na1—O6	90·8 (1)
O4—Na1—O7	100·3 (1)	O4—Na1—O8	166·0 (1)
O4—Na1—O9	125·9 (1)	O5—Na1—O6	85·7 (1)
O5—Na1—O7	90·9 (1)	O5—Na1—O8	83·2 (1)
O5—Na1—O9	148·5 (1)	O6—Na1—O7	168·0 (1)
O6—Na1—O8	92·6 (1)	O6—Na1—O9	83·1 (1)
O7—Na1—O8	75·5 (1)	O7—Na1—O9	94·0 (1)
O8—Na1—O9	68·0 (1)		
Na2—O7	2·390 (4)	Na2—O8	2·411 (4)
Na2—O9	2·397 (4)	Na2—O10	2·360 (4)
Na2—O11	2·423 (4)	Na2—O12	2·442 (5)
O7—Na2—O8	79·0 (1)	O7—Na2—O9	93·5 (1)
O7—Na2—O10	99·9 (1)	O7—Na2—O11	94·2 (1)
O7—Na2—O12	177·6 (1)	O8—Na2—O9	71·5 (1)
O8—Na2—O10	105·5 (1)	O8—Na2—O11	170·9 (1)
O8—Na2—O12	103·2 (1)	O9—Na2—O10	165·6 (2)
O9—Na2—O11	103·4 (1)	O9—Na2—O12	86·4 (1)
O10—Na2—O11	81·3 (1)	O10—Na2—O12	80·6 (1)
O11—Na2—O12	83·6 (1)		
Na3—O10	2·377 (4)	Na3—O11	2·561 (4)
Na3—O12	2·375 (4)	Na3—O13	2·397 (4)
Na3—O14	2·361 (4)	Na3—O4′	2·419 (4)
O10—Na3—O11	78·2 (1)	O10—Na3—O12	81·7 (1)
O10—Na3—O13	165·9 (1)	O10—Na3—O14	95·8 (1)
O10—Na3—O4′	101·0 (1)	O11—Na3—O12	82·1 (1)
O11—Na3—O13	87·9 (1)	O11—Na3—O14	84·7 (1)
O11—Na3—O4′	171·5 (1)	O12—Na3—O13	94·2 (1)
O12—Na3—O14	166·8 (1)	O12—Na3—O4′	89·4 (1)
O13—Na3—O14	85·3 (1)	O13—Na3—O4′	92·3 (1)
O14—Na3—O4′	103·8 (1)		
AsO_3S^{3-} anion			
As—S	2·150 (1)	As—O1	1·689 (3)
As—O2	1·691 (3)	As—O3	1·700 (3)
S—As—O1	110·0 (1)	S—As—O2	109·9 (2)
S—As—O3	110·7 (1)	O1—As—O2	109·1 (1)
O1—As—O3	108·6 (1)	O2—As—O3	108·6 (1)
Hydrogen bonds O—H···O			
O4···O2′	2·784 (4)	O5···O1	2·734 (4)
O5···O2′	2·766 (4)	O6···O3′	2·725 (4)
O7···O1′	2·755 (4)	O7···O6′	2·784 (5)
O8···O5′	2·988 (5)	O9···O3′	2·803 (4)
O9···O5′	2·904 (5)	O10···O3′	2·779 (5)
O10···O15	2·679 (5)	O11···O13′	2·766 (5)
O12···O2′	2·860 (4)	O12···O14′	2·858 (5)
O13···O1′	2·677 (5)	O14···O3′	2·753 (4)
O15···O2′	2·733 (5)	O15···O11′	3·034 (5)
Hydrogen bonds O—H···S			
O4···S′	3·597 (3)	O6···S′	3·452 (3)
O8···S′	3·304 (3)	O11···S′	3·271 (3)
O13···S′	3·622 (3)	O14···S′	3·375 (3)

A prime indicates an atomic position which is symmetry equivalent with that of the same number given in Table 1.

The title compound $[Na_3(OH_2)_{11}][AsO_3S].H_2O$ is structurally closely related to the undecahydrate $Na_3AsO_2S_2.11H_2O$, which crystallizes in the minimal lattice-equivalent supergroup *Pnma* of space group $P2_12_12_1$ (Jaulmes & Palazzi, 1976). In the latter hydrate with the structural formula $[Na_3(OH_2)_{11}]$-$[AsO_2S_2]$, in which no discrete H_2O molecules are present, the units of three face-sharing $[Na(OH_2)_6]^+$ octahedra within the chains have point symmetry $\bar{1}$ and are symmetry related by mirror planes through the linking O atoms (see Fig. 2). Similarly, inversion centres and mirror planes exist in the dodecahydrate, but only approximately as pseudosymmetry elements. On the other hand, $Na_3AsO_3S.12H_2O$ is not structurally related to $Na_3PO_3S.12H_2O$. In the phosphorus compound the trimeric units of face-sharing octahedra are not connected with each other, *i.e.* they are finite units of composition $[Na_3(OH_2)_{12}]^{3+}$, and the PO_3S^{3-} anions are orientationally disordered (Goldstein, 1982).

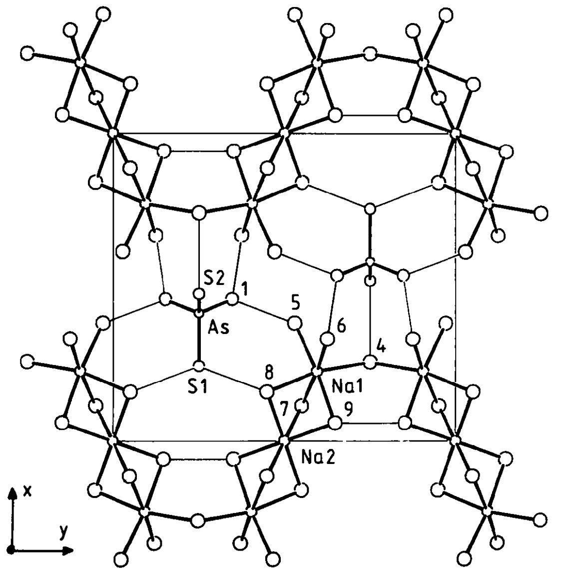

Fig. 2. A layer in the structure of $[Na_3(OH_2)_{11}][AsO_2S_2]$. Atomic coordinates were taken from Jaulmes & Palazzi (1976), but the atomic symbols have been changed.

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The Structures of [Sn{Co(CO)$_4$}$_4$] and [Pb{Co(CO)$_4$}$_4$]

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Abstract. Tetrakis(tetracarbonylcobaltio)tin, [SnCo$_4$(CO)$_{16}$], $M_r = 802·59$, cubic, $F\bar{4}3c$, $a = 17·255$ (2) Å, $V = 5136·7$ (19) Å^3, $Z = 8$, $D_x = 2·08$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 35·60$ cm^{-1}, $F(000) = 3056$, $T = 296$ K, $R = 0·017$, $wR = 0·022$ for 196 observed unique reflections [$I > 3\sigma(I)$]. The tetrahedral Sn atom sits on a site of 23 symmetry and is surrounded by four trigonal bipyramidal Co(CO)$_4$ groups. Tetrakis(tetracarbonylcobaltio)lead, [PbCo$_4$(CO)$_{16}$], $M_r = 891·10$, orthorhombic, $Pccn$, $a = 12·184$ (2), $b = 12·267$ (3), $c = 17·220$ (2) Å, $V = 2574$ (1) Å^3, $Z = 4$, $D_x = 2·30$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 91·64$ cm^{-1}, $F(000) = 1656$, $T = 296$ K, $R = 0·077$, $wR = 0·100$ for 1139 observed unique reflections [$I > 3\sigma(I)$]. Pb{Co(CO)$_4$}$_4$ is isostructural to Sn{Co(CO)$_4$}$_4$ but possesses only twofold crystallographic symmetry.

Introduction. Cobalt carbonyl compounds of tin and lead have been known for years. The complex [Sn{Co(CO)$_4$}$_4$] has been reported from the reactions of metallic tin, SnCl$_4$ or [SnCl{Co(CO)$_4$}$_3$] with [Co$_2$(CO)$_8$] (Schmid & Etzrodt, 1977; Patmore & Graham, 1968; Bigorgne & Quintin, 1967). [Sn{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}$_4$] has been prepared by treating [Sn{Co(CO)$_4$}$_4$] with P(C$_6$H$_5$)$_3$ (Schmid & Etzrodt, 1977). Species such as [RSn{Co(CO)$_4$}$_3$] (R = C$_6$H$_5$, CH$_3$, CH$_2$=CH, n-C$_4$H$_9$), [XSn{Co(CO)$_4$}$_3$] (X = Cl, Br, I), and [R_nX_{3-n}SnCo(CO)$_4$] (R = C$_6$H$_5$; X = Cl, Br, I; n = 0, 1, 2) have been obtained from reactions of tin halides or alkyl halides with [Co$_2$(CO)$_8$] or [Co(CO)$_4$]$^-$ (Patmore & Graham, 1966, 1968). The complex [Pb{Co(CO)$_4$}$_4$] has been reported from the reaction of metallic Pb with [Co$_2$(CO)$_8$] (Schmid & Etzrodt, 1977). Reactions of metallic Pb with [HCo(CO)$_4$] or Pb(NO$_3$)$_2$ with [NaCo(CO)$_4$] (Vizi-Orosz, Bor & Markó, 1969; Krumholz & Bril, 1960) initially were reported to form [Pb{Co(CO)$_4$}$_2$], but were later shown to give [Pb{Co(CO)$_4$}$_4$] (Schmid & Etzrodt, 1977). [Pb{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}$_4$] and [Pb{Co(CO)$_3${P(C$_6$H$_5$)$_3$}}Co(CO)$_4$] have been prepared by treating [Pb{Co(CO)$_4$}$_4$] with P(C$_6$H$_5$)$_3$ (Schmid & Etzrodt, 1977).

None of these complexes, however, has been structurally characterised using X-ray crystallography. Thus, we present here the crystal structures of [Sn{Co(CO)$_4$}$_4$] and [Pb{Co(CO)$_4$}$_4$]. These molecules, which are isostructural, consist of four trigonal bipyramidal [Co(CO)$_4$] groups tetrahedrally surrounding a group 14 atom.

Experimental. [Sn{Co(CO)$_4$}$_4$] was prepared from the dropwise addition over a 10 min period of an aqueous solution of SnCl$_4$.5H$_2$O (1·08 g, 3·08 mmol in 100 ml N$_2$ bubbled H$_2$O) to a stirred aqueous solution of Na[Co(CO)$_4$] (12·3 mmol in 60 ml N$_2$ bubbled H$_2$O). After stirring several hours the resulting burnt-orange precipitate was then isolated by filtration, washed with 100 ml H$_2$O, and dried under vacuum to give [Sn{Co(CO)$_4$}$_4$] in 65% yield (1·61 g, 2·01 mmol). Crystals of the compound were grown from a CH$_2$Cl$_2$ solution cooled at 253 K overnight. A cube of edge approximately 0·5 mm was mounted on the tip of a glass fiber with epoxy cement. The unit-cell parameters were derived from the least-squares best fit of 22 reflections ($26·88 \leq 2\theta \leq 41·13°$), which indicated an F-centered cubic lattice. Data were collected (2θ–ω scans, 4° ω min^{-1}) using a Rigaku AFC5S automated four-circle diffractometer [Rigaku *CRYSTAN/TEXTL* (3:2:1) *Automatic Data Collection Series* (Molecular Structure Corporation, 1987)] through the range h 0 to 22, k 0 to 22, l 0 to 22, measuring 353 nonequivalent reflections with 196

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