Magic-angle-spinning nuclear-magnetic-resonance spectra for ^{27}Al in as-synthesized AlPO$_4$-17 contain two peaks (Blackwell & Patton, 1984). The peak showing a chemical shift of 31 p.p.m. with respect to aqueous Al(NO$_3$)$_3$ is attributed to tetrahedrally coordinated Al [six Al(2) atoms and four Al(1) atoms], and the peak at 14 p.p.m. to trigonal-bipyramidal Al [eight Al(1) atoms]. Although the height of the first peak is less than that of the second peak, its area could be greater if the peak is asymmetric like those for AlPO$_4$-5 and 11 (Blackwell & Patton's Fig. 2). Furthermore, the peak area may not be related linearly to the number of atoms if the bonding characteristics differ. The greater enhancement by cross-polarization from ^{1}H of the peak at 14 p.p.m. than the one at 31 p.p.m. is consistent with the proposal that O(7) represents a hydroxyl species. The additional spectra of calcined and rehydrated AlPO$_4$-17 can be interpreted in terms of removal of the hydroxyl species and the piperidine upon calcination, and adsorption of H$_2$O near the Al(1) atom upon hydration. Further X-ray structure determinations of calcined and hydrated specimens are needed to provide a detailed interpretation.

In conclusion, the subtle modification of the erionite structure type to accommodate a non-framework hydroxyl or H$_2$O into the coordination group of framework Al atoms is a further illustration of the fascinating properties of the new family of synthetic aluminophosphates. In addition to the changes of Al coordination, there are important phenomena related to the organic compounds used as possible templates. Whereas in AlPO$_4$-21 (Bennett *et al.*, 1985), the organic species (*N,N,N',N'*-tetramethyl-1,3-propanediamine) is fissioned into three parts, in AlPO$_4$-17 the piperidine has apparently reacted with a water molecule to yield a piperidinium ion and a hydroxyl, which then interacts with the aluminophosphate framework.

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X-ray Structure and Thermal Motion of Barium *N*-Dithiocarboxylatoglycinate Trihydrate

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Abstract. $Ba^{2+}.C_3H_3NO_2S_2^{2-}.3H_2O$, $M_r = 340{\cdot}6$, triclinic, $P\bar{1}$, $a = 7{\cdot}906\ (1)$, $b = 7{\cdot}905\ (1)$, $c = 8{\cdot}000\ (1)$ Å, $\alpha = 96{\cdot}34\ (1)$, $\beta = 100{\cdot}08\ (1)$, $\gamma = 93{\cdot}54\ (1)°$, $V = 487{\cdot}6\ (1)$ Å^3, $Z = 2$, $D_m = 2{\cdot}31\ (1)$, $D_x = 2{\cdot}320$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 4{\cdot}47$ mm^{-1}, $F(000) = 324$, room temperature, final

$R = 0.044$ ($wR = 0.050$) for 3235 observed reflexions. The anionic group is not planar and the S—C [1·717 (6) Å] and C(sp^2)—N [1·322 (8) Å] bonds show a high double-bond character. The structure consists of infinite layers of organic anions along [100] with barium ions connected on both sides of these layers, where an extended two-dimensional hydrogen-bonding system, involving the water molecules, holds together the adjacent anions. Thermal-motion analysis reveals a good fit to a simple rigid-body model for the anion and no significant internal modes should exist.

Introduction. Barium *N*-dithiocarboxylatoglycinate trihydrate has been prepared in the Inorganic Chemistry Department of this University according to:

$$H_2N{-}CH_2{-}COOH \xrightarrow[(2)\,CS_2]{(1)\,Ba^{2+}} Ba^{2+}\,(S_2C{-}NH{-}CH_2{-}COO)^{2-}.$$

The synthesis of this compound and other similar substances has been described (Beck, Girnth, Castillo & Zippel, 1978). Their spectroscopic properties and their capacity as ligands in coordination compounds will be reported elsewhere (Castillo, Criado, Macias & Criado, 1986). The X-ray crystal analysis was suggested to elucidate the structural details in order to explain some spectroscopic results and reaction mechanisms.

Experimental. Single crystals in the form of colourless prisms elongated along [001]. D_m by flotation method. Crystal 0·08 × 0·14 × 0·25 mm. Unit-cell parameters by least squares from 25 reflexions, $5 < \theta < 20°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $2\theta < 64°$ ($0 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 11$), ω–2θ scan mode. Two standard reflexions ($31\bar{2}$, $1\bar{2}\bar{3}$), variation in intensity less than 2% of mean value. 3604 independent reflexions measured, 369 considered unobserved [$I < 2\sigma(I)$]. Lorentz and polarization correction, no correction for absorption ($\mu R \sim 0.3$) or extinction. Patterson function and heavy-atom method with initial set of phases on Ba-atom position. Full-matrix least-squares refinement on F, anisotropic; difference Fourier synthesis revealed H atoms; isotropic temperature factor for each H atom equal to that of atom bonded to it; further least-squares refinement including positional parameters of H atoms and anomalous-dispersion correction for Ba and S atomic scattering factors (*International Tables for X-ray Crystallography*, 1974) reduced R to 0·044 ($wR = 0.050$); weighting scheme based on statistical count criterion ($w = 1/\sigma^2$). $(\Delta/\sigma)_{\max} = 0.01$, $S = 2.0$ for 136 refined parameters. RR = number of reflexions/number of parameters = 23·8. Final difference synthesis showed $0.25 > \Delta\rho > -0.30$ e Å^{-3}. Crystallographic programs of *XRAY70* system (Stewart, Kundell & Baldwin, 1970) used throughout.*

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-hydrogen atoms are listed in Table 1. Atom numbering and bond lengths and angles involving non-hydrogen atoms of the *N*-dithiocarboxylatoglycinate group are given in Fig. 1. The two sulfur–carbon distances (of equal value) and the carbon-(sp^2)—nitrogen bond all have high double-bond character. A valence-bond description, based on Pauling's (1960) formula relating bond distance to bond order and the values S—C = 1·81, S=C = 1·59, N—C = 1·48 and N=C = 1·275 Å, gives the percentages of double-bond character of 20 and 60% for S—C and N—C

Table 1. *Atomic fractional coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^5)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ba	2350·7 (5)	504·2 (4)	3839·9 (4)	183 (1)
S(1)	3668 (2)	1732 (2)	333 (2)	258 (4)
S(2)	3468 (3)	4387 (2)	3228 (2)	329 (5)
C(1)	3038 (7)	3671 (7)	1078 (7)	208 (14)
C(2)	1740 (8)	4222 (3)	−1830 (7)	217 (15)
C(3)	470 (7)	2656 (7)	−2425 (7)	177 (13)
N	2172 (7)	4633 (6)	34 (6)	222 (13)
O(1)	−685 (5)	2340 (5)	−1565 (5)	214 (11)
O(2)	582 (6)	1785 (6)	−3798 (6)	285 (13)
O(3)	5047 (6)	1688 (6)	−3295 (6)	242 (12)
O(4)	6932 (8)	1902 (8)	3847 (7)	416 (19)
O(5)	9475 (7)	1438 (8)	1679 (7)	395 (18)

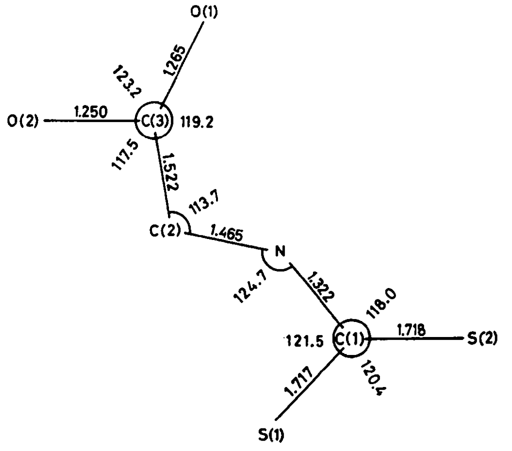

Fig. 1. Bond lengths (Å) and angles (°) in the anion. (Standard deviations are in the ranges 0·006–0·008 Å and 0·3–0·5°, respectively.)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42623 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds, respectively. The three angles at C(1), which are opposite to those three bonds with high double-bond character, show a mean value of 120·0°. The two C—O distances in the carboxylate group are equal within experimental error and the observed configuration is near to that predicted for this ion group [O—C=O 125·3° and each C—O bond length 1·27 Å (Pauling, 1960)]. The organic anion is not planar as indicated by the torsion angles: S(1)—C(1)—N—C(2) = −3·4 (8), C(1)—N—C(2)—C(3) = 66·7 (7) and N—C(2)—C(3)—O(1) = 33·6 (7)°.

Each barium ion is surrounded by two sulfur atoms [Ba—S(1) = 3·376 (2) and Ba—S(2) = 3·254 (2) Å] and seven oxygen atoms at distances ranging between 2·688 (5) and 2·871 (4) Å; three of these oxygen atoms belong to two anions of adjacent organic layers and the others belong to water molecules. Details of these contacts are: Ba···O(1) ($-x$, $-y$, $-z$) = 2·827 (4), Ba···O(2) (x, y, $1+z$) = 2·688 (5), Ba···O(2) ($-x$, $-y$, $-z$) = 2·845 (5), Ba···O(3) ($1-x$, $-y$, $-z$) = 2·831 (5), Ba···O(3) (x, y, $1+z$) = 2·871 (4), Ba···O(4) ($1-x$, $-y$, $1-z$) = 2·812 (6) and Ba···O(5) ($1-x$, $-y$, z) = 2·795 (6) Å.

The structure (Fig. 2) consists of infinite layers of organic anions, extending parallel to [100], connected on both sides to layers of barium ions. The layers of organic anions are held together by an extended two-dimensional hydrogen-bonding system involving the water molecules. Each anion is linked to the neighbour related by a centre of symmetry by hydrogen bonds N—H···O(1) ($-x$, $1-y$, $-z$). On the other hand, the water molecules are involved in five hydrogen bonds linking organic anions. The characteristics and geometrical details of these interactions are quoted in Table 2.

The N—H···O(1) contacts between centrosymmetrically related adjacent anions in the layers have a weak hydrogen-bond character as shown by the N···O distance of 2·969 (7) Å, but the angle N—H···O of 166 (11)° is satisfactory. For the O(4)—H(41)···O(5), O(5)—H(51)···O(1) and O(5)—H(52)···O(1) contacts involving water molecules the value of the d parameter, defined as the difference between the sum of the van der Waals radii of H and O (1·20 and 1·50 Å) and the interatomic distance (Taylor & Kennard, 1982) are 0·78, 0·78 and 0·46 Å, respectively, and the angles O—H···O agree with the mean value of 165·8 (12)° for bonds with O···H > 1·812 Å (Allen, Kennard & Taylor, 1983). Finally, the three interactions O(4)—H(41)···S(1), O(3)—H(32)···S(1) and O(3)—H(31)···S(2) show values for the d parameter of 0·49, 0·73 and 0·76 Å respectively (van der Waals radius of S = 1·80 Å) and angles O—H···S of 165 (9), 175 (9) and 173 (10)° and so can be considered as hydrogen bonds. No other contact significantly shorter than the sum of the van der Waals radii has been detected. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983).

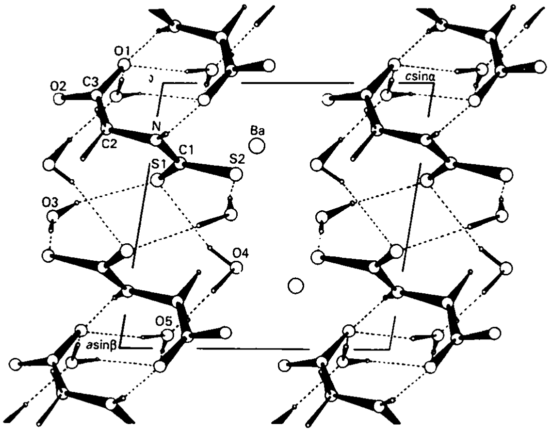

Fig. 2. A view along [010] of the unit-cell contents. Hydrogen bonds are indicated by dashed lines.

Table 2. *Geometry of the possible hydrogen bonds*

X—H···Y	X···Y(Å)	H···Y(Å)	X—H(Å)	X—H···Y(°)
O(3)—H(32)···S(1^0)	3·271 (5)	2·24 (12)	1·03 (12)	175 (9)
O(4)—H(42)···O(5^0)	2·891 (9)	1·92 (14)	0·98 (14)	168 (12)
O(4)—H(41)···S(1^0)	3·452 (6)	2·51 (10)	0·96 (11)	165 (9)
O(3)—H(31)···S($2^{\rm i}$)	3·240 (5)	2·27 (12)	0·98 (12)	173 (10)
O(5)—H(51)···O($1^{\rm ii}$)	2·750 (7)	1·91 (12)	0·87 (13)	160 (11)
N—H···O($1^{\rm iii}$)	2·969 (7)	2·15 (12)	0·83 (11)	166 (11)
O(5)—H(52)···O($1^{\rm iv}$)	3·188 (8)	2·24 (12)	0·98 (12)	161 (10)

Symmetry code: (0) x, y, z; (i) $-x+1$, $-y+1$, $-z$; (ii) $x+1$, y, z; (iii) $-x$, $-y+1$, $-z$; (iv) $-x+1$, $-y$, $-z$.

Thermal motion analysis

The individual atomic vibration tensors derived from least-squares refinement for the organic anionic group have been analysed in terms of the **TLS** rigid-body model (Schomaker & Trueblood, 1968) using the *THMB* program (Trueblood, 1978). The rigid-bond test (Hirshfeld, 1976) was used to estimate the acceptability of the data. The fit of the assumed model can be expressed in terms of an agreement factor R_{wU} defined as

$$R_{wU} = [\sum w_{ij}(U^{ij}_{\rm obs}-U^{ij}_{\rm cal})^2/\sum w_{ij}(U^{ij}_{\rm obs})^2]^{1/2},$$

where $U^{ij}_{\rm obs}$ are the observed atomic thermal parameters and $U^{ij}_{\rm cal}$ those evaluated from the derived rigid-body tensors.

Representative results of thermal-motion analysis carried out in the inertial molecular frame are listed in Table 3. As indicated by the low value of the agreement factor, a good fit is obtained assuming that the entire organic anion vibrates as a simple rigid body. So, it can be expected that internal modes should not be significant. The major component of molecular translation (T_{33}) is along a direction normal to the anion axis

Table 3. *Molecular thermal motion in the organic anion*

The analysis is carried out in the inertial frame with *x* along the elongated axis of the anion.

Translation tensor, **T** (Å^2 × 10^4)

$$\begin{pmatrix} 181\,(20) & 37\,(14) & -33\,(12) \\ & 169\,(15) & -10\,(8) \\ & & 223\,(10) \end{pmatrix}$$

Libration tensor, L (rad^2 × 10^4)

$$\begin{pmatrix} 21\,(3) & 19\,(3) & 15\,(3) \\ & 4\,(4) & 7\,(3) \\ & & 25\,(11) \end{pmatrix}$$

Cross tensor, **S** (rad Å × 10^4)

$$\begin{pmatrix} 20\,(5) & -26\,(5) & 5\,(4) \\ 10\,(5) & -25\,(4) & 10\,(4) \\ 7\,(9) & -12\,(6) & 6\,(5) \end{pmatrix}$$

$R_{wU} = 0{\cdot}045$

$\langle \Delta^2\, U_{ll}\rangle^{1/2} = 0{\cdot}0006$

$\langle \sigma^2\, U_{ll}\rangle^{1/2} = 0{\cdot}0017$

(lower inertia moment) and the least librational motion (L_{22}) is also about a direction normal to the anion axis. A major limitation of the model is the assumption that the anionic groups in the crystal are vibrating independently, whereas they are actually coupled by ionic and H-bonding interactions.

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Structure of the 1:1 Adduct between Titanium(IV) Chloride and Pentanedinitrile

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Abstract. $TiCl_4.C_5H_6N_2$, $M_r = 283{\cdot}83$ orthorhombic, *Pbcm*, $a = 6{\cdot}009\,(1)$, $b = 12{\cdot}729\,(2)$, $c = 14{\cdot}243\,(2)$ Å, $V = 1089{\cdot}4\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}731$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 17{\cdot}20$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}041$ for 1266 observed reflections. Equal amounts of $TiCl_4$ and $NC(CH_2)_3CN$ produce the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct whose crystal structure has been found to be one-dimensionally polymeric with $NC(CH_2)_3CN$ acting as a bridge between two $TiCl_4$ units. Ti atoms are octahedrally coordinated with N atoms in the *cis* configuration.

Introduction. The interesting chemistry of transition-metal–nitrile complexes has been extensively reviewed (Storhoff & Lewis, 1977). With two —C≡N groups, a dinitrile is able to react with more than one transition-metal center, while titanium tetrachloride is coordinatively unsaturated, capable of increasing its coordination number from 4 to 6 by reacting with suitable organic ligands (Cotton & Wilkinson, 1980). The 1:1 $TiCl_4$–$NC(CH_2)_nCN$ adducts (n = 1–8) can be chelated complexes, cyclic di/trimers, or linear polymers based on spectroscopic data (Jain & Rivest, 1963). The 1:1 $TiCl_4$–$NC(CH_2)_nCN$ adducts (n = 2, 4, and 5), whose molecular weights as determined by cryoscopy are

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