Table 4. *Torsion angles (°) for the gluconate ion*

O(0)–C(1)–C(2)–O(2)	130·4 (6)	O(1)–C(1)–C(2)–O(2)	51·5 (6)
C(1)–C(2)–C(3)–C(4)	54·4 (7)	C(2)–C(3)–C(4)–C(5)	178·2 (5)
C(3)–C(4)–C(5)–C(6)	−172·8 (6)	C(4)–C(5)–C(6)–O(6)	65·3 (6)
O(2)–C(2)–C(3)–C(4)	175·5 (6)	O(2)–C(2)–C(3)–O(3)	62·2 (7)

modification of potassium D-gluconate monohydrate (Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974) and in one of two different gluconate ions in manganese(II) D-gluconate dihydrate (Lis, 1979), by rotating 125° about C(2)—C(3) (see Fig. 1 and Table 4). Other types of bent-chain conformations were found earlier in the monoclinic modification of $KC_6H_{11}O_7.H_2O$ (Panagiotopoulos *et al.*, 1974), in trisodium 6-phospho-D-gluconate dihydrate (Smith, Fitzgerald, Caughlan, Kerr & Ashmore, 1974) and in one of the gluconate ions of $Mn(C_6H_{11}O_7)_2.2H_2O$ (Lis, 1979). The most interesting fact is that contrary to all other α-hydroxycarboxylic moieties (Newton & Jeffrey, 1977) the $-C(OH)COO^-$ group is not planar (Table 4). It may be assumed that the deviation of the O(2) atom from the plane of the carboxylate group is brought about by the hydrogen bonds in this salt. It is noteworthy that each O atom is involved in two H bonds (Table 3).

The author thanks Mr Jerzy Okruciński for assistance.

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Structures of Tris(2-cyanoethyl)phosphine Sulphide, $P(CH_2CH_2CN)_3S$ and Tris(2-cyanoethyl)phosphine Selenide, $P(CH_2CH_2CN)_3Se$

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(*Received* 10 *November* 1980; *accepted* 22 *April* 1981)

Abstract. $C_9H_{12}N_3PS$ and $C_9H_{12}N_3PSe$, triclinic, $P\bar{1}$, $Z = 2$. Cell dimensions, $(PCH_2CH_2CN)_3S$: $a = 8{\cdot}363$ (8), $b = 9{\cdot}026$ (4), $c = 9{\cdot}777$ (6) Å, $\alpha = 98{\cdot}75$ (4), $\beta = 107{\cdot}31$ (5), $\gamma = 115{\cdot}85$ (5)°, $V = 599{\cdot}1$ (3) Å^3, $D_c = 1{\cdot}252$ (3), $D_o = 1{\cdot}247$ (5) Mg m^{-3}, final $R = 0{\cdot}095$ for a total of 738 independent observed reflections; $P(CH_2CH_2CN)_3Se$: $a = 8{\cdot}497$ (5), $b = 9{\cdot}148$ (2), $c = 9{\cdot}972$ (8) Å, $\alpha = 98{\cdot}85$ (2), $\beta = 107{\cdot}20$ (6), $\gamma = 116{\cdot}96$ (3)°, $V = 621{\cdot}1$ (3) Å^3, $D_c = 1{\cdot}467$ (3), $D_o = 1{\cdot}477$ (3) Mg m^{-3}, final $R = 0{\cdot}081$ for a total of 701 independent observed reflections. The two compounds are isostructural and the individual molecules have C_1 internal symmetry: two of the cyanoethyl groups are related by an imaginary mirror plane which includes the P—S(Se) bond but the third cyanoethyl group does not lie in this plane.

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0567-7408/81/101959-04$01.00

Introduction. Tris(2-cyanoethyl)phosphine sulphide and tris(2-cyanoethyl)phosphine selenide, $P(CH_2CH_2CN)_3X$ (X = S,Se), are triclinic, with almost identical unit-cell dimensions and closely related X-ray powder diffraction patterns (Blake, Howie & McQuillan, 1979). The corresponding oxide is trigonal, with C_3 internal molecular symmetry (Blake, Howie & McQuillan, 1981). The vibrational spectrum of the oxide is much simpler than those of the sulphide or selenide (Blake, 1980) suggesting a lower molecular symmetry for the latter compounds. We now report structure determinations for $P(CH_2CH_2CN)_3S$ and $P(CH_2CH_2CN)_3Se$.

The compounds were prepared and unit-cell parameters determined as described previously (Blake *et al.*, 1979). Single-crystal diffraction data were obtained using the equi-inclination multiple-film Weissenberg technique, and intensities were measured by the SRC

Daresbury Laboratory microdensitometer service (Machin & Elder, 1977). For the sulphide, a total of 738 independent reflections with intensities above background were measured over the layers (h,0–7,l); the corresponding total for the selenide was 701 reflections over the layers (0–4,k,l). All measurable reflections were treated as 'observed'. The data were corrected for Lorentz and polarization effects, but not for absorption.

The sulphide structure was solved by conventional methods with the space group initially assumed to be $P1$ (Z = 2) with 28 non-H atoms in the asymmetric unit. A three-dimensional Patterson synthesis located the P and S atoms but did not distinguish between them. A Fourier synthesis treating both 'heavy' atoms as P established the approximate C and N positions and hence identified the P and S atoms. At this stage, the position of one P atom was fixed, to define the unit-cell origin, and the coordinates of the other atoms were adjusted accordingly. After several cycles of block-diagonal least-squares refinement, with all atoms isotropic, the computed atomic coordinates clearly indicated a centrosymmetric unit cell and the refinement was therefore continued in space group $P\bar{1}$ (Z = 2) with 14 non-H atoms in the asymmetric unit. Anisotropic temperature factors were introduced for all atoms and the calculation was concluded when all parameter shifts were <0·3 e.s.d. At this point, the conventional R value was 0·095.

For the selenide, an initial structure-factor calculation using the final positional parameters from the sulphide structure yielded an R value of 0·27. Block-diagonal least-squares refinement, with anisotropic temperature factors in the later stages, was continued until all parameter shifts were <0·3 e.s.d. and R had fallen to 0·081. No attempt was made to include the H atoms in either calculation.

The weighting scheme used in both cases was of the form $w = [1 + \{(|F_o| - P_2)/P_1\}^2]^{-1}$ with $P_1 = 8$ and $P_2 = 14$ for the sulphide and $P_1 = 10$ and $P_2 = 15$ for the selenide. Crystallographic programs were based on those of Ahmed, Hall, Pippy & Huber (1966) and neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Positional parameters for both compounds are given in Tables 1 and 2 and bond length and angle data in Tables 3 and 4.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35900 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. P($CH_2CH_2CN)_3$S: *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
P(1)*	0·3978 (5)	0·1814 (4)	0·1621 (4)	2·3 (1)
S(1)	0·2875 (6)	0·1453 (4)	−0·0552 (4)	3·4 (1)
C(11)	0·2506 (19)	0·0033 (16)	0·2154 (15)	3·4 (3)
C(12)	0·1843 (21)	−0·1753 (15)	0·1082 (15)	3·9 (3)
C(13)	0·0591 (22)	−0·3189 (18)	0·1499 (18)	4·7 (4)
N(10)	−0·0346 (23)	−0·4242 (18)	0·1877 (20)	7·2 (6)
C(21)	0·4180 (20)	0·3738 (16)	0·2789 (15)	3·4 (3)
C(22)	0·5180 (23)	0·5325 (17)	0·2352 (17)	4·0 (4)
C(23)	0·5209 (21)	0·6836 (17)	0·3199 (16)	3·6 (3)
N(20)	0·5183 (21)	0·7934 (17)	0·3870 (15)	5·1 (4)
C(31)	0·6439 (19)	0·2103 (18)	0·2237 (15)	3·5 (3)
C(32)	0·7362 (19)	0·2274 (18)	0·3865 (17)	3·6 (3)
C(33)	0·9347 (24)	0·2738 (23)	0·4245 (19)	5·0 (4)
N(30)	1·0914 (26)	0·3164 (25)	0·4504 (20)	8·3 (7)

* Numbering system is indicated in the diagrams.

Table 2. P($CH_2CH_2CN)_3$Se: *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
P(1)*	0·4031 (8)	0·1815 (5)	0·1658 (5)	1·8 (1)
Se(1)	0·2856 (4)	0·1422 (3)	−0·0640 (3)	2·8 (1)
C(11)	0·2535 (32)	0·0035 (21)	0·2235 (23)	2·7 (3)
C(12)	0·1964 (27)	−0·1711 (22)	0·1146 (21)	2·3 (3)
C(13)	0·0665 (37)	−0·3182 (25)	0·1475 (30)	6·1 (6)
N(10)	−0·0254 (32)	−0·4292 (23)	0·1880 (26)	6·1 (6)
C(21)	0·4166 (32)	0·3689 (21)	0·2887 (21)	2·4 (3)
C(22)	0·5145 (32)	0·5296 (21)	0·2342 (23)	3·2 (3)
C(23)	0·5171 (32)	0·6762 (21)	0·3248 (22)	2·9 (3)
N(20)	0·5249 (35)	0·7919 (22)	0·3943 (22)	5·9 (6)
C(31)	0·6497 (31)	0·2141 (25)	0·2232 (26)	3·3 (4)
C(32)	0·7380 (37)	0·2273 (27)	0·3977 (24)	3·8 (4)
C(33)	0·9395 (44)	0·2799 (32)	0·4274 (30)	5·6 (6)
N(30)	1·0980 (40)	0·3226 (31)	0·4553 (27)	7·0 (6)

* Numbering system is indicated in the diagrams.

Table 3. *Bond lengths* (Å)

	P($CH_2CH_2CN)_3$S	P($CH_2CH_2CN)_3$Se
P(1)–S(1)	1·957 (5)	–
P(1)–Se(1)	–	2·108 (5)
P(1)–C(11)	1·811 (15)	1·86 (3)
C(11)–C(12)	1·54 (2)	1·56 (3)
C(12)–C(13)	1·48 (2)	1·46 (4)
C(13)–N(10)	1·13 (2)	1·18 (4)
P(1)–C(21)	1·837 (15)	1·88 (2)
C(21)–C(22)	1·51 (2)	1·60 (3)
C(22)–C(23)	1·47 (2)	1·48 (3)
C(23)–N(20)	1·12 (2)	1·14 (3)
P(1)–C(31)	1·847 (18)	1·86 (3)
C(31)–C(32)	1·50 (2)	1·64 (3)
C(32)–C(33)	1·43 (3)	1·47 (5)
C(33)–N(30)	1·12 (3)	1·15 (5)

Table 4. *Bond and torsion angles* (°)

	$P(CH_2CH_2$-$CN)_3S$	$P(CH_2CH_2$-$CN)_3Se$
S(Se)(1)–P(1)–C(11)	113·2 (0·5)	114·8 (0·8)
S(Se)(1)–P(1)–C(21)	112·7 (0·5)	114·3 (0·8)
S(Se)(1)–P(1)–C(31)	110·8 (0·5)	109·5 (0·8)
C(11)–P(1)–C(21)	104·3 (0·7)	99·2 (1·0)
C(11)–P(1)–C(31)	107·9 (0·7)	109·0 (1·1)
C(21)–P(1)–C(31)	107·5 (0·7)	109·6 (1·1)
P(1)–C(11)–C(12)	112·1 (1·0)	107 (2)
C(11)–C(12)–C(13)	111·4 (1·3)	110 (2)
C(12)–C(13)–N(10)	177·0 (1·9)	174 (3)
P(1)–C(21)–C(22)	111·2 (1·1)	106 (2)
C(21)–C(22)–C(23)	111·5 (1·4)	106 (2)
C(22)–C(23)–N(20)	176·8 (1·8)	178 (3)
P(1)–C(31)–C(32)	115·0 (1·2)	111 (2)
C(31)–C(32)–C(33)	109·2 (1·4)	103 (2)
C(32)–C(33)–N(30)	176·3 (2·2)	178 (3)
P(1)–C(11)/C(12)–C(13)	177·8 (1)	176·1 (1)
P(1)–C(21)/C(22)–C(23)	174·6 (1)	177·2 (1)
P(1)–C(31)/C(32)–C(33)	171·9 (1)	171·4 (1)

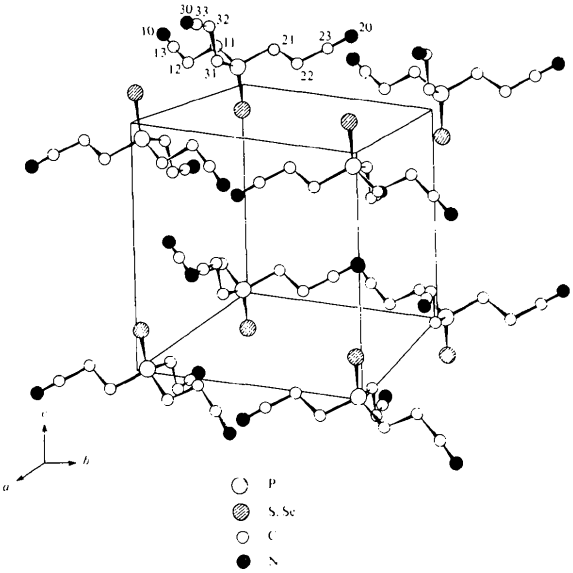

Fig. 1. Unit cell of $P(CH_2CH_2CN)_3S(Se)$.

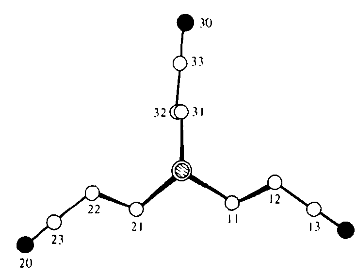

Fig. 2. $P(CH_2CH_2CN)_3S(Se)$ molecule viewed along the P–S(Se) bond direction.

Discussion. The two compounds are isomorphous and fully isostructural: Figs. 1 and 2 apply to both molecules. The slightly smaller R value obtained for the selenide reflects the influence of the relatively heavy Se atom: the P, C and N atomic positions are all more precisely defined in the sulphide than in the selenide structure.

The unit cell contains two $P(CH_2CH_2CN)_3X$ molecules related by a centre of symmetry. There are no significant intermolecular contacts; the closest P–P, S–S, Se–Se or P–S(Se) distances are all greater than 4·85 Å and the N–S(Se) and N–N distances greater than 4·0 and 3·7 Å respectively. The structure contrasts markedly with that of $P(CH_2CH_2CN)_3O$, in which the molecules are arranged head-to-tail in columns with a non-bonded O–P distance of only 3·635 Å (Blake *et al.*, 1981). The electronegativity of the O atom will cause the P–O bond to be significantly more dipolar than P–S or P–Se and the strong $\overset{\delta+}{P}-\overset{\delta-}{O}\cdots\overset{\delta+}{P}-\overset{\delta-}{O}$ non-bonded interaction presumably is the major ordering influence in the oxide structure. The sulphide and selenide, with weaker P–X dipoles, are not subject to a comparable effect and adopt less regular structures.

The $P(CH_2CH_2CN)_3S$ and $P(CH_2CH_2CN)_3Se$ molecules have no overall internal symmetry but the cyanoethyl groups C(11)–N(10) and C(21)–N(20) are related by a mirror plane containing the P–S(Se) bond and bisecting the C(11)–P–C(21) angle. However, the third cyanoethyl group [C(31)–N(30)] is somewhat displaced from this plane and hence the molecular point group is C_1 rather than C_s (Fig. 2). The individual cyanoethyl groups are approximately planar, with PC–CCN torsion angles between 170–180° in all cases. The unique group C(31)–N(30) displays the lowest torsion angle (171–172°), and thus makes the most noticeable departure from strict planarity, in both molecules (Table 4).

The P–S and P–Se bond lengths are comparable with those in other phosphine sulphides and selenides, insofar as such information (especially for the latter compounds) is available [see *e.g.* Cameron & Dahlén (1975); Dreissig, Plieth & Zäske (1972); Lee & Goodacre (1969, 1970, 1971); Wilkins, Hagen, Hedberg, Quang Shen & Hedberg (1975)]. The values obtained (P–S, 1·96; P–Se, 2·11 Å) are very close to the calculated P=X double-bond distances (1·94 and 2·07 Å respectively).

We thank Dr M. Elder and Dr M. Pickering of the SRC Daresbury Laboratory for microdensitometer measurements, and SRC for a maintenance grant (AJB).

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SHORT COMMUNICATION

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Acta Cryst. (1981). B**37**, 1962

X-ray structure analysis and molecular conformation of *N*-propionylproline: erratum. By M. E. KAMWAYA,* O. OSTER and H. BRADACZEK, *Institut für Kristallographie, Freie Universität Berlin, Takustrasse* 6, *D*-1000 *Berlin* 33, *Federal Republic of Germany*

(*Received* 23 *July* 1981)

Abstract

Corrections are given to the paper by Kamwaya, Oster & Bradaczek [*Acta Cryst.* (1981), B**37**, 364–367]. In Table 2 the atomic nomenclature for three entries requires correction: the correct entries are $N'-C_4^{\alpha}-C_5^{\beta}$ 101·8 (3), $O_3-C'_8-O_2$ 124·0 (3)°, $C_4^{\alpha}-C_5^{\beta}$ 1·527 (5) Å. In Table 3 the torsion angle $C'_3-N'-C_4^{\alpha}-C'_8$ should be designated φ. See also *Acta Cryst.* (1981), B**37**, 1161.

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All the relevant information is given in the *Abstract*.