Crystal Structure of a Complex of Caesium Thiocyanate with Phenacylkojate: 5-Phenacyl-2-(hydroxymethyl)-4*H*-pyran-4-one–Caesium Thiocyanate

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The structure of the title complex has been determined by three-dimensional *X*-ray crystal-structure analysis. Crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions a = 7·809(18), b = 11·270(13), c = 11·152(12) Å, α = 92·70(8), β = 101·08(7), γ = 119·21(10)°, Z = 2. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares to R 0·071 for 2217 independent diffractometer observations.

The caesium ions lie in pairs (4·157 Å apart) related by centres of symmetry, with four bridging contacts of the type Cs–X–Cs. Each ion is co-ordinated by three oxygen atoms from its associated phenacylkojate (pak) molecule, one shared oxygen atom from the centrosymmetrically related pak, and one oxygen atom from a further pak. The co-ordination number of eight is completed by the nitrogen atom of one NCS and a bridging sulphur atom from each of two further NCS ions. The triply bridging NCS ions hold the overall structure together with hydrogen bonding between the hydroxy-group of the pak molecule and the NCS sulphur atom. Cs^+–O distances are 3·008—3·322 Å, Cs^+–S 3·799 and 3·602 Å, and Cs^+–N 3·452 Å. The O · · · S hydrogen-bond distance is 3·219 Å.

ALKALI-METAL halides form complexes with phenacylkojate[1] (pak) in one of two stoicheiometries, $[MX(pak)_2]$ or [MX(pak)] depending on the sum of the radii of the anion and cation.[2] Complexes having the 1 : 2 stoicheiometry are formed when the radius sum is <3·60 Å and the structure of such a complex, $[KI(pak)_2]$, has already been determined.[3] The three 1 : 1 complexes of the series, namely [RbI(pak)], [CsBr(pak)], and [CsI(pak)], are not suitable for accurate crystallographic work because of the presence of two heavy atoms for each ligand molecule. Preliminary *X*-ray photographs of the complex [Cs(NCS)(pak)] showed it to have the same stoicheiometry, space group, and similar unit-cell dimensions as the [CsI(pak)] complex and to provide a suitable subject for structure analysis.

The crystals are triclinic, the unit cell containing two [Cs(NCS)(pak)] units. Observations were collected on an automatic diffractometer and the structure was solved by conventional Patterson and Fourier methods, the space group proving to be $P\bar{1}$ with [Cs(NCS)(pak)] corresponding to one asymmetric unit. Full-matrix least-squares refinement was carried out for all atoms and the final parameters are given in Table 1.

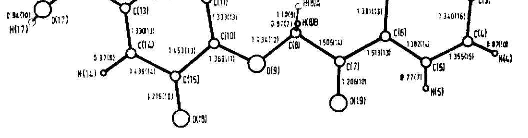

FIGURE 1 The pak molecule projected on its mean plane showing the crystallographic numbering scheme and the bond lengths (Å), with standard deviations. Refinement of hydrogen atom parameters resulted in the distorted position of H(2)

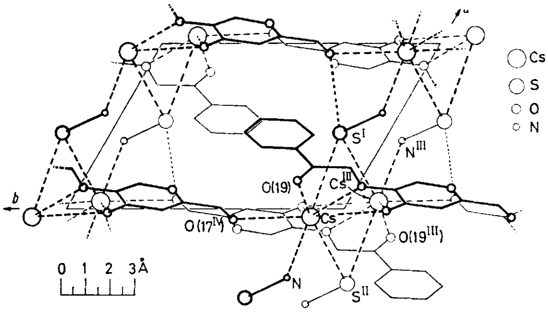

FIGURE 2 Structure of [CsNCS(pak)] projected along the *c* axis; the projected directions of the *a* and *b* axes are indicated. Co-ordination to the caesium ions is shown by broken lines and the O(17) · · · S hydrogen bonds by dotted lines. Roman numeral superscripts refer to other asymmetric units as follows:

I $1 + x, y, z$
II $-1 - x, -y, -z$
III $-x, -y, -z$
IV $x, 1 + y, z$
V $x - 1, y, z$

Co-ordination and Overall Structure.—As in the structure of $[KI(pak)_2]$,[3] four of the five oxygen atoms in the pak molecule (see Figure 1) are involved in co-ordination, namely O(9), O(17), O(18), and O(19). The caesium ions occur in pairs, **4·157**(1) Å apart, related by a centre of symmetry; their environment is shown in the packing diagram, Figure 2. Each caesium ion lies close to the plane of its associated ligand molecule and is co-ordinated by O(9), O(18), and O(19) of that molecule, the centrosymmetrically related O(18) atom forming bridges between the similarly related caesium ions. The cation is also co-ordinated by an O(17) atom from a further ligand molecule making a total of five oxygen atoms around each caesium ion. The eight-fold co-ordination of the caesium ion is completed by thiocyanate ions, the sulphur atoms of two thiocyanate ions bridging each pair of caesium ions and two further thiocyanate ions, each co-ordinating one caesium through the nitrogen atom. Co-ordination distances (Table 2) are as expected for eight-co-ordinate caesium. Thus each thiocyanate ion is co-ordinated to three caesium ions and this is largely responsible for holding the overall structure together in the direction of the crystallographic *a* axis. The O(17)–Cs^+ co-ordination

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[2] D. E. Fenton, *J.C.S. Dalton*, 1973, 1380.

[3] D. L. Hughes, S. E. V. Phillips, and M. R. Truter, *J.C.S. Dalton*, 1974, 907.

TABLE 1

Fractional co-ordinates ($\times 10^4$) and isotropic vibration parameters ($U_{\mathrm{iso}} \times 10^2$ Å^2), with standard deviations in parentheses

	x/a	y/b	z/c	U_{iso}
Cs	−0486(1)	1061(1)	1346(1)	*
S	−5385(5)	1730(3)	0940(3)	*
C	−4700(17)	1056(11)	2073(9)	*
N	−4169(16)	0622(11)	2859(9)	*
C(1)	4492(18)	2634(13)	7136(10)	*
C(2)	5388(19)	3563(15)	8230(11)	*
C(3)	5473(20)	4845(15)	8268(11)	*
C(4)	4686(18)	5151(13)	7235(11)	*
C(5)	3775(18)	4242(12)	6161(10)	*
C(6)	3666(16)	2978(11)	6098(9)	*
C(7)	2552(15)	1982(10)	4881(8)	*
C(8)	2485(17)	0623(12)	4803(9)	*
O(9)	1345(10)	−0154(7)	3589(6)	*
C(10)	1104(15)	−1438(10)	3358(9)	*
C(11)	1561(17)	−2078(11)	4230(10)	*
O(12)	1222(11)	−3386(7)	3981(6)	*
C(13)	0426(15)	−4046(10)	2788(9)	*
C(14)	−0021(17)	−3452(11)	1872(9)	*
C(15)	0256(15)	−2092(10)	2067(9)	*
C(16)	0124(20)	−5469(13)	2718(12)	*
O(17)	−0585(13)	−6161(8)	1480(8)	*
O(18)	−0178(12)	−1538(7)	1248(6)	*
O(19)	1718(13)	2271(8)	4016(6)	*
H(1)	4383(125)	1696(89)	7201(76)	5(2)
H(2)	5983(191)	3089(133)	8715(121)	12(4)
H(3)	6268(135)	5599(95)	9136(86)	6(3)
H(4)	5123(154)	6029(112)	7369(96)	8(4)
H(5)	3591(109)	4543(76)	5582(68)	3(2)
H(8)A	1853(146)	0151(102)	5567(93)	8(3)
H(8)B	3752(120)	0895(75)	4852(65)	3(2)
H(11)	2103(124)	−1711(87)	4978(78)	5(3)
H(14)	−0527(107)	−3952(73)	1029(70)	5(2)
H(16)A	1478(137)	−5397(89)	3049(80)	6(3)
H(16)B	−0480(185)	−5704(127)	3264(115)	11(5)
H(17)	−1997(151)	−6621(100)	1208(89)	7(3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	101·3(6)	63·2(5)	49·5(4)	61·7(5)	6·6(3)	0·8(3)
S	93(2)	62(2)	68(2)	45(2)	−4(2)	7(1)
C	87(8)	68(7)	48(6)	47(7)	5(5)	5(5)
N	104(8)	109(9)	70(6)	68(8)	8(6)	19(6)
C(1)	88(9)	77(8)	55(6)	41(7)	7(6)	7(5)
C(2)	86(9)	101(10)	62(7)	45(8)	6(6)	9(7)
C(3)	89(9)	99(10)	62(7)	43(8)	17(6)	−7(7)
C(4)	87(9)	68(8)	68(7)	37(7)	14(6)	−8(6)
C(5)	97(9)	72(7)	58(7)	60(7)	12(6)	−2(6)
C(6)	80(7)	70(7)	49(5)	47(6)	11(5)	2(5)
C(7)	65(7)	60(6)	55(6)	39(6)	6(5)	−1(5)
C(8)	68(8)	71(7)	57(6)	46(6)	2(5)	−4(5)
O(9)	81(5)	59(4)	58(4)	48(4)	4(3)	−1(3)
C(10)	66(7)	55(6)	67(6)	44(6)	13(5)	10(5)
C(11)	77(7)	68(7)	58(7)	52(6)	8(5)	1(5)
O(12)	88(5)	69(5)	65(4)	55(4)	10(4)	13(4)
C(13)	66(7)	57(6)	64(6)	43(6)	12(5)	6(5)
C(14)	82(7)	67(7)	56(6)	55(6)	13(5)	9(5)
C(15)	66(7)	62(6)	58(6)	44(6)	14(5)	9(5)
C(16)	81(8)	64(7)	96(9)	48(7)	16(7)	5(6)
O(17)	95(6)	59(5)	101(6)	54(5)	16(5)	3(4)
O(18)	116(6)	65(5)	60(4)	67(5)	10(4)	10(3)
O(19)	130(7)	79(5)	54(4)	74(5)	−13(4)	−11(4)

* Anisotropic vibration parameters ($U_{ij} \times 10^3$ Å^2) in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

links the units along the *b* axis, assisted by a hydrogen bond from O(17) to the sulphur atom of the *N*-co-ordinated thiocyanate ion. The structure is held along the *c* axis by van der Waals contacts between adjacent ligand molecules.

The Hydrogen Bond.—The existence of the hydrogen bond was confirmed by the location on the difference map, and subsequent refinement, of the hydrogen atom bonded to O(17). The O · · · S distance for this bond [3·219(10) Å] compares well with values [3·27 (ref. 4) and 3·225 (ref. 5)] reported for similar O · · · S hydrogen bonds involving thiocyanate ions and water molecules. Other distances and angles associated with the hydrogen bond are given in Table 2. These observations are consistent with the observed O–H stretching frequency in the i.r. spectrum which occurs at **3275** compared with **3325** for [KI(pak)$_2$],[2] **3490** cm^{-1} for the anhydrous crystalline form of pak,[2] and **3644** cm^{-1} for monomeric MeOH.[6] The bond length and i.r. information together indicate that the hydrogen bond is strong and makes a definite contribution to the binding together of the structure.

TABLE 2

Important interatomic distances (Å) and angles (°) in the complex and the thiocyanate ion

(*a*) Distances

S–C	1·638(10)	Cs–O(18)	3·053(7)
C–N	1·131(12)	Cs-O(18$^{\mathrm{III}}$)	3·062(8)
Cs-S$^{\mathrm{I}}$	3·799(10)	Cs–O(19)	3·008(8)
Cs–S$^{\mathrm{II}}$	3·602(8)	Cs–O(17$^{\mathrm{IV}}$)	3·167(8)
Cs–N	3·452(12)	S–H(17$^{\mathrm{IV}}$)	2·32(10)
Cs–O(9)	3·322(7)	S–O(17$^{\mathrm{IV}}$)	3·219(10)

(*b*) Angles

S–C–N	177·9(12)	Cs$^{\mathrm{V}}$–S–C	101·9
Cs–S$^{\mathrm{I}}$–C$^{\mathrm{I}}$	101·9(4)	Cs$^{\mathrm{II}}$–S–C	107·7
Cs–S$^{\mathrm{II}}$–C$^{\mathrm{II}}$	107·7(4)	Cs$^{\mathrm{V}}$–S–H(17$^{\mathrm{IV}}$)	145·3
Cs–N–C	84·9(8)	Cs$^{\mathrm{II}}$–S–H(17$^{\mathrm{IV}}$)	140·0
S–H(17$^{\mathrm{IV}}$)O(17$^{\mathrm{IV}}$)	161(8)	H(17$^{\mathrm{IV}}$)–S–C	88·4
Cs$^{\mathrm{V}}$–S–Cs$^{\mathrm{II}}$	68·3		

Angles *A*–Cs–*B* about the caesium ion

A *B*	S$^{\mathrm{I}}$	S$^{\mathrm{II}}$	N	O(9)	O(18)	O(19)	O(18$^{\mathrm{III}}$)	O(17$^{\mathrm{IV}}$)
S$^{\mathrm{I}}$		111·7	158·3	72·7	67·4	84·8	65·0	110·1
S$^{\mathrm{II}}$			84·6	110·5	67·8	149·7	70·1	114·4
N				88·5	108·8	74·5	136·2	73·2
O(9)					49·8	48·5	133·2	129·0
O(18)						98·1	94·3	177·4
O(19)							139·6	80·6
O(18$^{\mathrm{III}}$)								85·3

Roman numeral superscripts are defined in the legend to Figure 2.

Thiocyanate Ion.—The thiocyanate ion is able to take part in co-ordination in several different ways because the nitrogen end of the ion constitutes a 'hard' and the sulphur end a 'soft' base. This tends to give rise to *N*-bonding with class *A* metal ions and *S*-bonding with class *B* metal ions though not all systems fall clearly into one or other of these categories.

Several different types of bridging have been reported including a few cases having the $\begin{smallmatrix}\mathrm{M}\\ \mathrm{M}\end{smallmatrix}\!\!>\!\mathrm{SCN{-}M}$ form similar to that found in [CsNCS(pak)], *e.g.* [Co(NCS)$_6$Hg$_2$(C$_6$H$_6$)],[7] and [Ag(NCS)(PPr$_3$)].[8] The use of Pauling's method[9] to calculate the resonance contri-

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[8] C. Panattoni and E. Frasson, *Acta Cryst.*, 1963, **16**, 1258.

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butions fails as the observed C–N bond length (Table 2) is, in fact, less than the expected value for the C:N triple bond calculated from covalent radii, though the C–S bond length is less than the expected C–S single distance. We assumed that the major contributing form was N:C·S$^-$, as in the free ion,[10] and used for sulphur the scattering-factor curve corresponding to S$^-$. The i.r. spectrum is consistent with these bond lengths, the frequencies being assigned by comparison with the i.r. spectrum of [CsI(pak)] which is almost identical apart from the thiocyanate bands. The observed frequencies for the thiocyanate ion are listed in Table 3 together with the free-ion values.[11]

TABLE 3

Thiocyanate bands (cm^{-1}) in i.r. spectrum for [CsNCS(pak)] and free NCS$^-$

Assignment	[CsNCS(pak)]	NCS$^-$
ν(CN)	2064	2053 *
ν(CS)	736	746 *
δ(NCS)	(431) †	486,471 *

* From ref. 11. † Band observed at 862 cm^{-1} assumed to be first overtone of δ(NCS).

The sulphur atom has four neighbours which subtend angles (Table 2) consistent with a distorted tetrahedral environment as expected for the N:C·S$^-$ form. Contact from the nitrogen atom to caesium is not collinear with, but normal to, the anion, the Cs–N–C angle being 84·9°; this may account for the Cs–N contact [3·452(12) Å], being long compared with the Cs–O (3·20 Å) and Cs–NCS contacts (3·26 Å) reported[12] for eight-co-ordinate caesium.

The Ligand.—Bond lengths and angles in the ligand molecule are as expected and none differs significantly from the corresponding values found in the [KI(pak)$_2$] structure[3] (see Figures 1 and 3). The spread of bond lengths in the benzene ring is large (**1·340—1·413**, mean **1·376** Å), and values are rather short for C–C bonds in benzene rings, but this effect was observed[3] for [KI(pak)$_2$] and for [(pak)(H$_2$O)],[13] and is probably due to librational effects. The angle about the ether oxygen atom in the chain [116·6(7)°] is significantly greater than the tetrahedral angle, as before,[3] and the angles about C(10) again differ from 120° in a way which tends to bring O(18) and O(19) closer together. Torsion angles have been calculated for the molecule with standard deviations computed using a method that assumes the estimated standard deviations in the atomic co-ordinates to be isotropic,[14] and those angles differing significantly from 0 or ±180° are given in Table 4, together with the corresponding values for [KI(pak)$_2$]. The torsion angles about the C(6)–C(7) bond show a tendency to bring O(19) closer to the associated caesium ion and those about the O(9)–C(10) bond tend to bring O(18) closer to the centrosymmetrically related caesium ion to which it is also co-ordinated. Although there are several bonds in the molecule about which rotation could be free, none of the torsion angles is very different from 0 or ±180° and all have values similar to those for the corresponding angles in [KI(pak)$_2$].

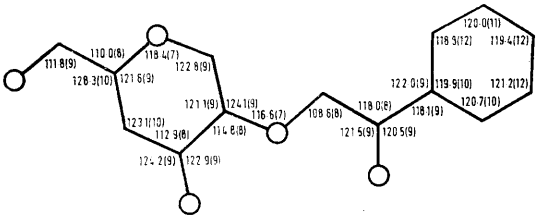

FIGURE 3 Bond angles and standard deviations involving carbon and oxygen atoms in the (pak) molecule

TABLE 4

Torsion angles (°) differing significantly from 180° in the pak molecule. Corresponding values for [KI(pak)$_2$] are given [a]

Angle [b]	[CsNCS(pak)]	[KI(pak)$_2$]
C(1)–C(6)–C(7)–O(19)	174·5(11)	−179·0(17); −178·0(18)
C(8)–O(9)–C(10)–C(11)	11·4(15)	−5·25(22); −4·5(23)
C(8)–O(9)–C(10)–C(15)	−169·8(9)	170·5(14); 176·8(14)
O(12)–C(13)–C(16)–O(17)	−176·3(10)	−177·6(13); −173·0(14)

[a] From ref. 3. [b] Positive angle corresponds to clockwise rotation of the nearest to eclipse the furthest bond.

The weighted mean plane of the ligand molecule was computed (Table 5) and this shows the molecule to be almost planar but slightly arched along its long axis, as in [KI(pak)$_2$],[3] the largest deviation from the plane being O(19) at 0·20(1) Å. Weighted mean planes calculated for the two six-membered rings show that both are planar, the angles between their normals being 7·08°. The associated caesium ion lies 0·309(1) Å from the mean plane of the molecule while the centrosymmetrically related caesium ion lies 1·850(1) Å from the other side of the plane.

TABLE 5

Weighted mean planes through the ligand molecule. The equations refer to an orthogonal system of axes a, b', and c' where c' lies in the plane of a and c. Deviations of the atoms from these planes (Å) are shown in square brackets; atoms designated in italics were used to define the plane

Plane (1): $0{\cdot}8826X + 0{\cdot}4186Y - 0{\cdot}2135Z + 0{\cdot}7706 = 0$

[*C(1) 0·14, C(2) 0·15, C(3) 0·09, C(4) 0·04, C(5) 0·01, C(6) 0·06, C(7) −0·03, C(8) 0·06, O(9) −0·07, C(10) −0·02, C(11) −0·09, O(12) −0·11, C(13) −0·02, C(14) 0·08, C(15) 0·08, C(16) −0·09, O(17) 0·09, O(18) 0·14, O(19) −0·20,* Cs −0·31, Cs$^{\mathrm{III}}$ 1·85, H(17) −0·71]

Plane (2): $0{\cdot}8581X + 0{\cdot}4491Y - 0{\cdot}2484Z + 0{\cdot}8797 = 0$

[*C(1) 0·01, C(2) 0·00, C(3) −0·01, C(4) 0·01, C(5) 0·00, C(6) 0·00,* C(7) −0·07, C(8) −0·03, O(19) −0·18]

Plane (3): $0{\cdot}9012X + 0{\cdot}4103Y - 0{\cdot}1394Z + 0{\cdot}4870 = 0$

[*C(10) −0·01, C(11) 0·01, O(12) 0·00, C(13) 0·00, C(14) 0·01, C(15) 0·00,* O(9) −0·05, C(16) −0·06, O(17) 0·03, H(17) −0·81, O(18) −0·02]

Roman numerals are defined in the legend to Figure 2.

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DISCUSSION

Comparison of the co-ordination geometries of [CsNCS(pak)] and [KI(pak)$_2$] is interesting in that the differences in stoicheiometry are the reverse of what would be expected on the basis of the cation radii. It is clear that the observed multiple bridging is essential in order to bring the co-ordination number of caesium up to 8, the minimum normally observed. The preferred co-ordination number and packing restriction seem to cause the caesium ion to lie only 0·309 Å from the plane of its associated ligand while the smaller potassium ion in [KI(pak)$_2$] lies 1·421 and 1·156 Å respectively out of the planes of its corresponding ligands.[3]

The similarities in cell dimensions and i.r. spectra of [CsNCS(pak)] and [CsI(pak)] suggest that the latter compound may also contain the [Cs$^+$(pak)]$_2$ unit.

EXPERIMENTAL

Crystals of the complex [CsNCS(pak)] (m.p. 150—152 °C) were prepared by dissolving equimolar quantities of Cs(NCS) and pak in warm methanol and allowing the solution to cool slowly. Quite large single crystals may be produced in this way and the sample chosen was reduced in size by dipping it in methanol, the final dimensions being 0·015 × 0·025 × 0·030 cm. The crystal was set on a rigid mount * on a Picker four-circle automatic diffractometer and accurate cell dimensions were obtained by least-squares refinement of the ϕ, χ, and 2θ settings of 19 manually centred reflections.

Crystal Data.—$C_{15}H_{12}CsNO_5S$, $M = 451{\cdot}2$, Triclinic, $a = 7{\cdot}809(18)$, $b = 11{\cdot}270(13)$, $c = 11{\cdot}152(12)$ Å, $\alpha = 92{\cdot}70(8)$, $\beta = 101{\cdot}08(7)$, $\gamma = 119{\cdot}21(10)°$, $U = 829{\cdot}1$ Å^3, $D_m = 1{\cdot}80$ (flotation), $Z = 2$, $D_c = 1{\cdot}81$, $F(000) = 440$. Space group = $P\bar{1}$. Mo-$K_\alpha$radiation, Zr-filtered, λ(Mo-$K_{\alpha1}$) = 0·70926 Å (1 Å = 10^{-10} m). Single-crystal diffraction intensities measured by counter, μ(Mo-K_α) = 24·2 cm^{-1}.

Intensities were collected in shells of reciprocal space for the (hkl), $(hk\bar{l})$, $(h\bar{k}l)$, and $(h\bar{k}\bar{l})$ octants to a maximum 2θ of 50°. Scanning was carried out at 0·5° min^{-1} from 0·5° below Mo-$K_{\alpha1}$ peak to 0·7° above Mo-$K_{\alpha2}$ peak and backgrounds were counted for 25 s at the ends of each scan. Three standard reflections [(012), $(1\bar{3}\bar{4})$, and $(2\bar{3}\bar{1})$] were measured after every 50 reflections. 2946 Unique reflections were measured and an absorption correction was applied using an n-point Gaussian integration method,[15] the crystal being divided into 6 × 6 × 6 elements for the integration. Lorentz and polarisation factors (LP) were applied and the standard deviations were calculated from the formula $\sigma^2(F) = \sigma^2(I)/(4.I.LP)$ where $\sigma^2(I)$ = total count + (0·25 background) × (scan time/background time)^2. Reflections were considered unobserved if the intensity (I) was $<$15 counts, or $I < 3\sigma(I)$.

Structure Determination.—A Patterson synthesis was computed from the 2217 planes considered as observed, and the highest peak (apart from the origin peak) taken to be the Cs · · · Cs vector. Two Cs · · · S vectors could be assigned, suggesting that the space group was $P\bar{1}$ rather than $P1$. Structure factors were calculated using the Cs position only and a Fourier synthesis was computed for all planes where $F_c > 0{\cdot}5 \times F_c$ (1944 planes) which showed the S atom in the position indicated by the Patterson map together with the other 21 non-hydrogen atoms. Refinement was carried out by use of block-diagonal least-squares to refine the caesium and sulphur anisotropically and the remaining atoms isotropically, the R factor falling from 0·24 to 0·088 in four cycles for observed reflections only, using weights derived from counting statistics. Refinement was continued with all atoms anisotropic and a second-order polynomial weighting scheme, calculated to produce constant values of $\langle w\Delta^2\rangle$, when R was reduced to 0·075. A difference-Fourier synthesis at this stage revealed all the hydrogen atom positions. Refinement continued by use of the full-matrix least-squares program NUCLS,[16] hydrogen atom co-ordinates and isotropic temperature factors being refined in addition to the 23 anisotropic atoms. A third-order polynomial weighting scheme, based on the same criterion as the previous one, was used for the final cycles, the form being: $1/w = 1/[w(\text{counting})\ (-0{\cdot}4758 + 0{\cdot}3157|F_o| - 0{\cdot}0122|F_o|^2 + 0{\cdot}0005|F_o|^3)]$. Owing to the large number of parameters, it was necessary to refine co-ordinates and temperature factors in alternate cycles, the refinement converging to R 0·071 and a weighted factor R' of 0·087. Bond lengths and angles with errors were calculated, by the program ORFFE,[16] from the variance–covariance matrix of the final cycle of refinement of the atomic co-ordinates. Scattering factor curves were taken from ref. 17 for hydrogen atoms, ref. 18 for S$^-$ and nitrogen atoms, and ref. 19 for all other atoms. Anomalous scattering corrections were applied for Cs$^+$, the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 20. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21155 (12 pp., 1 microfiche).†

Computing.—The determination of the orientation matrix for the Picker diffractometer and the unit-cell dimensions, data reduction, Patterson and Fourier synthesis, block-diagonal least-squares refinement, calculation of planes through various groups of atoms, torsion angles and interatomic distances were computed on an IBM 1130.[21]

Full-matrix least-squares and calculation of bond lengths and angles with standard deviations from a full correlation matrix [16] were carried out on an IBM 360/65X computer at University College, London.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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[20] D. T. Cromer, *Acta Cryst.*, 1965, **17**, 17.

[21] *X*-RAY ARC: 1130 program system; for details see ref. 13 of ref. 3.