Crystal Structure of a Complex of Potassium Iodide with Phenacyl Kojate: Bis(5-phenacyloxy-2-hydroxymethyl-4*H*-pyran-4-one)potassium Iodide

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The structure of the title complex has been determined by three-dimensional *X*-ray crystal-structure analysis from diffractometer data. Crystals are monoclinic, space group $P2_1/n$ with dimensions $a = 12{\cdot}095(17)$, $b = 15{\cdot}885(22)$, $c = 15{\cdot}037(32)$ Å, $\beta = 98{\cdot}87(13)°$, $Z = 4$. The structure was solved by Patterson and Fourier methods, and full-matrix least-squares refinement gave R 0·165 for 3080 independent diffractometer observations.

The structure consists of layers of planar ligand molecules linked by sandwiched potassium ions and hydrogen-bonded chains of the form $-K^+-O-H \cdots I^- \cdots H-O-K^+-$. The potassium ion is eight-co-ordinated by three oxygen atoms from each of two ligands and by hydroxy-groups from two more ligand molecules. The K^+-O distances are in the range 2·74—2·92 Å and the $I^- \cdots O$ hydrogen-bonded distances are 3·39 and 3·43 Å.

In the first preparation of phenacyl kojate, (pak),[1] the product was found to have taken up sodium bromide from the reaction mixture in proportions which suggested formation of a complex. In fact pak readily forms complexes with alkali-metal halides (except lithium) in 2 : 1 and 1 : 1 stoicheiometries according to the sum of the radii of the anion and cation, and a series of these has been prepared.[2] The potassium iodide complex was taken as being representative of the 2 : 1 complexes, as well as being suitable for crystal-structure analysis.

Preliminary *X*-ray photographs showed the crystal to be monoclinic with space group $P2_1/n$, $KI(pak)_2$, corresponding to one asymmetric unit. Observations were collected on an automatic diffractometer and the structure was solved by Patterson and Fourier methods.

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[1] C. D. Hurd and R. J. Sims, *J. Amer. Chem. Soc.*, 1949, **81**, 2441.

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

TABLE 1

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

	x/a	y/b	z/c	U_{iso}
I	2768(1)	2540(1)	4711(1)	*
K	5252(3)	3830(2)	2383(3)	*
C(1)	1769(16)	5093(12)	−0429(12)	657(54)
C(2)	0705(22)	4972(17)	−0923(17)	1090(83)
C(3)	0371(20)	4165(16)	−1174(15)	955(74)
C(4)	1008(20)	3518(15)	−0907(16)	940(73)
C(5)	2007(17)	3614(13)	−0364(13)	706(57)
C(6)	2413(13)	4413(11)	−0136(11)	478(44)
C(7)	3487(14)	4479(11)	0406(11)	472(44)
C(8)	3949(15)	5364(11)	0638(11)	553(48)
O(9)	5020(9)	5274(7)	1165(7)	547(31)
C(10)	5518(13)	5993(10)	1551(10)	452(42)
C(11)	5094(13)	6783(10)	1406(11)	478(44)
O(12)	5645(9)	7472(8)	1801(7)	649(32)
C(13)	6613(14)	7352(12)	2372(11)	586(48)
C(14)	7022(13)	6600(10)	2577(11)	474(44)
C(15)	6521(14)	5825(11)	2194(11)	556(48)
C(16)	7006(15)	8178(12)	2760(12)	603(52)
O(17)	8040(11)	8080(8)	3332(8)	738(37)
O(18)	6873(10)	5119(8)	2391(8)	662(35)
O(19)	4064(10)	3870(8)	0654(8)	661(35)
C′(1)	8305(16)	5105(12)	5609(13)	670(54)
C′(2)	9347(20)	5099(15)	6199(15)	931(71)
C′(3)	9994(18)	4407(15)	6249(14)	844(65)
C′(4)	9683(20)	3739(15)	5755(15)	907(70)
C′(5)	8685(19)	3666(14)	5165(15)	857(67)
C′(6)	8018(16)	4406(12)	5100(12)	634(53)
C′(7)	6907(15)	4387(12)	4467(12)	557(48)
C′(8)	6186(15)	5190(11)	4391(12)	571(49)
O′(9)	5203(9)	5019(7)	3798(7)	543(31)
C′(10)	4493(13)	5676(10)	3586(10)	427(41)
C′(11)	4627(16)	6442(13)	3940(13)	700(56)
O′(12)	3903(9)	7101(7)	3709(7)	567(32)
C′(13)	2997(13)	6939(11)	3073(11)	471(43)
C′(14)	2781(14)	6194(11)	2733(11)	513(46)
C′(15)	3512(15)	5471(11)	2928(11)	564(48)
C′(16)	2312(17)	7714(13)	2901(13)	791(62)
O′(17)	1282(9)	7574(8)	2325(7)	667(33)
O′(18)	3398(9)	4784(7)	2566(7)	559(31)
O′(19)	6633(11)	3774(8)	4037(8)	725(38)
H(1) †	2075	5726	−0294	760
H(2)	0102	5503	−1113	760
H(3)	−0440	4076	−1585	760
H(4)	0687	2882	−1084	760
H(5)	2511	3055	−0145	760
H(8)	3426	5688	1011	633
H(8)	4050	5687	0041	633
H(11)	4369	6858	0912	633
H(14)	7807	6539	3021	633
H(16)	6408	8432	3152	633
H(16)	7102	8613	2238	633
H′(1)	7737	5653	5534	760
H′(2)	9582	5637	6627	760
H′(3)	746	4403	6711	760
H′(4)	272	3218	5800	760
H′(5)	8436	3096	4782	760
H′(8)	6631	5695	4146	633
H′(8)	5979	5342	5031	633
H′(11)	5358	6557	4448	633
H′(14)	2008	6081	2276	633
H′(16)	2773	8177	2585	633
H′(16)	2120	7965	3515	633

* Anisotropic vibration parameters ($U_{ij} \times 10^4$ Å^2) in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	847(10)	673(9)	657(8)	−186(9)	−41(7)	−54(8)
K	548(24)	406(23)	552(25)	−23(20)	−2(19)	−20(20)

† Parameters for H atoms were not refined. The atoms are numbered according to the carbon atom to which they are bonded (see Figure 1).

Full-matrix least-squares refinement was carried out on all non-hydrogen atoms with calculated hydrogen atom positions taken into account. Final parameters for non-hydrogen atoms and the calculated hydrogen atom parameters are given in Table 1.

The arrangement of oxygen atoms in the molecules of pak (see Figure 1) is such that O(9), O(18), and O(19) are favourably positioned for chelation. It is not unexpected, therefore, that the potassium ion is co-ordinated by these three oxygen atoms from each of the two independent molecules of pak, the eight-fold co-ordination shell being completed by the hydroxy-oxygen atoms of two further ligand molecules. The co-ordination shell of the potassium ion is irregular, with six of the co-ordinated oxygen atoms on one side and only two left to fill the remaining space (see Figure 2). The two neighbouring iodide ions are well out of range, ruling out the possibility of ion-pairing as an explanation of this effect. The two independent molecules of pak lie in approximately parallel planes with the potassium ion sandwiched between them, their hydroxy-oxygen atoms co-ordinated to two further potassium ions and apparently hydrogen-bonded to iodide ions. The system, apart from the iodide ions, shows an approximate two-fold axis (Figure 2), but this does not apply to the structure as a whole.

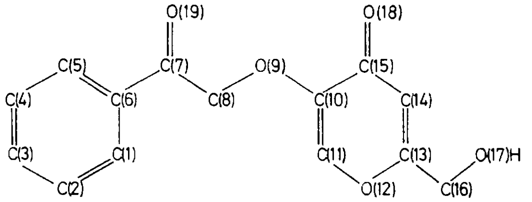

FIGURE 1 Crystallographic numbering scheme for one of the independent molecules of pak [molecule (1)]; molecule (2) has the same scheme but each atom designation is primed. Hydrogen atoms, except the hydroxy-hydrogen, are omitted

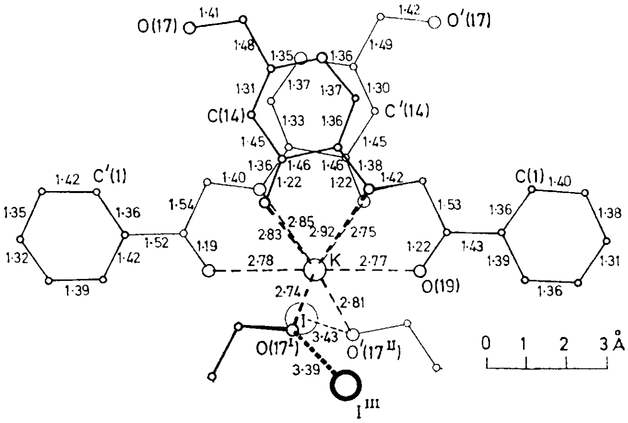

FIGURE 2 Asymmetric unit of $KI(pak)_2$ structure with one additional I^- ion and fragments of two additional molecules of pak. Roman numeral superscripts relate the atoms to those of Table 1 as x,y,z by the following operations: I, $1\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; II, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; III, $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$. Standard deviations in bond lengths are: benzene rings C–C ±0·03, other C–C ±0·025, C–O ±0·02, K–O contacts ±0·014, and I · · · O ±0·013 Å

DISCUSSION

Bond lengths and angles in the ligand molecules are as expected (Figures 2 and 3) with a few exceptions. A large spread of bond lengths in the benzene rings is immediately obvious, but since the spread only amounts to 0·1 Å and 3σ (C–C) is as high as 0·09 Å due to poor refinement, this is not regarded as a real effect. The angles about the ether oxygens of 117 and 116° respectively, differ significantly from the tetrahedral angle (3σ 3·9°). Angles about C(10) and C′(10) also show a tendency to bring O(18) and O(19), and O′(18) and O′(19) closer together, but other angles along the chain are not significantly affected. The K^+–O co-ordination distances are normal [3a] range 2·74—2·92 (± 0·01) Å, mean 2·81 Å. Both ligand molecules are approximately planar, the largest deviation of an atom from the weighted mean plane being 0·20(1) Å for O(9). The departure from planarity in each molecule takes the form of a slight arching of the molecule along its longest axis such that the two carbonyl oxygen atoms are brought into closer contact with the K^+ ion. This effect is more marked in molecule (1) than in molecule (2). The benzene rings are arranged in parallel pairs related by centres of symmetry, the separation of their weighted mean planes being 3·55(2) and 3·73(2) Å respectively for the two independent molecules. The angle between the weighted mean planes of the two independent ligand molecules is 12·32° and the distances of the associated K^+ ion from each are 1·421(4) and 1·156(4) Å. The equations of the planes are given in Table 2.

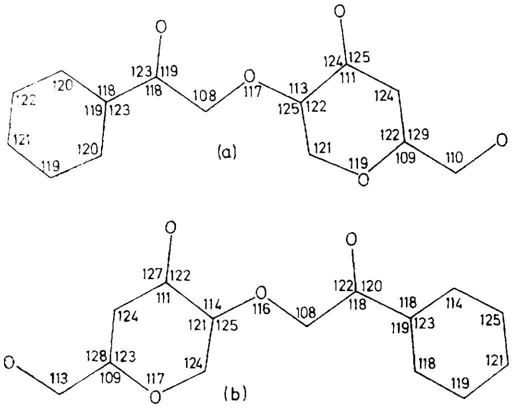

FIGURE 3 Bond angles in the two independent ligand molecules: (*a*) molecule 1, (*b*) molecule 2. Standard deviations are ±1·5°, except for benzene rings angles, ±2·5°

Several examples of potassium complexes with chelating ligands have been reported, the distance of the cation from the plane of the rest of the chelate ring varying from less than 0·5 to 1·5 Å. In the complex of isonitrosoacetophenone with potassium *o*-nitrophenolate [4] the cation lies 1·494 Å out-of-plane of the rest of the six-membered chelate ring formed with the *o*-nitrophenolate, but only 0·580 Å from the plane of the five-membered ring formed with the isonitrosoacetophenone (one of the chelating atoms being nitrogen in this case). In the complex of potassium with two isonitrosoacetophenone molecules only,[5] the corresponding distances are 0·802 and 1·023 Å respectively. Potassium iodide forms a complex KI(diacetamide)$_2$ [6] where the potassium ion is only 0·4 Å from the plane of the chelating atoms, packing considerations being held responsible for forcing it out of the plane.

TABLE 2

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

Plane (1)

[molecule (1)]: $0{\cdot}596X + 0{\cdot}077Y - 0{\cdot}799Z - 2{\cdot}519 = 0$

[*C(1) −0·05, C(2) −0·18, C(3) −0·19, C(4) −0·16, C(5) −0·15, C(6) −0·06, C(7) 0·01, C(8) 0·14, O(9) 0·20, C(10) 0·14, C(11) 0·12, O(12) 0·08, C(13) 0·01, C(14) −0·06, C(15) −0·01, C(16) −0·12, O(17) −0·15, O(18) −0·11, O(19) 0·02,* K −1·42]

Plane (2)

[molecule (2)]: $0{\cdot}602X + 0{\cdot}285Y - 0{\cdot}746Z - 1{\cdot}426 = 0$

[*C′(1) −0·07, C′(2) −0·05, C′(3) 0·04, C′(4) 0·13, C′(5) 0·11, C′(6) 0·04, C′(7) 0·01, C′(8) −0·06, O′(9) −0·11, C′(10) −0·06, C′(11) −0·06, O′(12) 0·00, C′(13) 0·06, C′(14) −0·01, C′(15) −0·05, C′(16) 0·13, O′(17) 0·03, O′(18) 0·01, O′(19) 0·07,* K 1·16]

Hydrogen Bonds.—The existence of the hydrogen bonding can only be inferred because the hydrogen atoms could not be located in electron-density maps, but there are several factors which support the hypothesis. Assuming the sum of the radii of I^- and O to be 3·56 Å,[7] the I · · · O distances of 3·39 and 3·43 Å suggest a close I · · · O contact even if the hydrogen atom is not between these atoms. This is, however, the most probable hydrogen atom position, and the angles of the type C(16)–O(17) · · · I^- of 102 and 99° are consistent with this. Further evidence is that the OH stretching frequency in the i.r. spectrum is at 3325 cm^{-1}, compared with 3490 cm^{-1} in the anhydrous crystalline form [2] of pak and 3644 cm^{-1} for a monomeric MeOH.[8] The high m.p. (>205 °C) is consistent with hydrogen bonding throughout the crystal.

The overall structure is shown in the packing diagram (Figure 4) and the layered arrangement of the ligand molecules can be seen clearly. In fact, nearly all the scattering matter lies in planes parallel to the plane (20$\bar{4}$) giving rise to the large observed amplitude and negative phase of the reflection. The approximate two-fold axis mentioned above is located close to

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[3] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, (*a*) p. 258; (*b*) pp. 202—206.

[4] M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 745.

[5] M. A. Bush, H. Luth, and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 740.

[6] J. P. Roux and J. C. A. Boeyens, *Acta Cryst.*, 1965, **B25**, 2395.

[7] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, chs. 7, and 13.

[8] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, 1969, **A25**, 319.

$x = \frac{1}{2}$, $z = \frac{1}{4}$, *i.e.* alternating with the two-fold screw axis in the x direction. The interplanar cross-linking is also shown with $^{-}$O · · · I^{-} · · · O^{-} links joining alternate layers and K^{+}–O^{-} co-ordination linking adjacent layers. The crystal morphologies and preliminary X-ray diffraction results on the other 2 : 1 complexes of pak with alkali-metal halides show marked similarities to $\mathrm{KI(pak)_2}$, so the structures are probably similar.

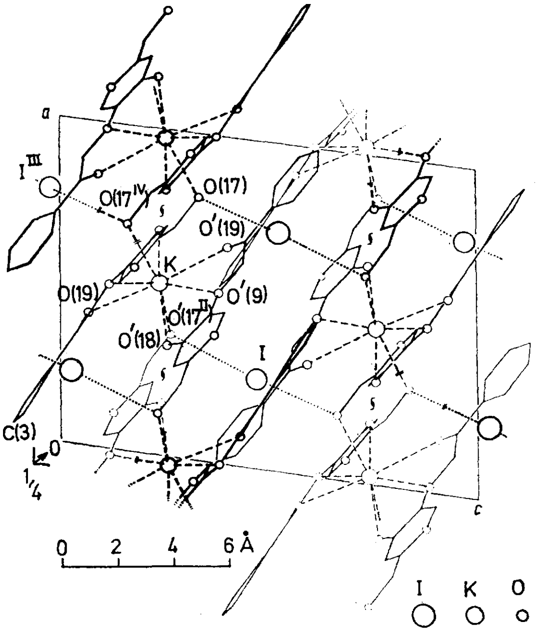

FIGURE 4 The structure projected along the b axis. K–O contacts and hydrogen bonds are shown by broken and dotted lines respectively. For Roman numeral superscripts see Figure 2; IV is at $1\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$, which eclipses I in this projection.

EXPERIMENTAL

A rod-shaped crystal *ca.* 0·01 × 0·01 × 0·03 cm, parallel to the crystallographic a, b, and c axes, was mounted on a set of eucentric arcs on a Picker four-circle automatic diffractometer. Accurate unit-cell dimensions were obtained by careful manual centring of 14 reflections and refinement of the parameters by least-squares methods.

Crystal Data.—$\mathrm{(C_{14}H_{12}O_5)_2KI}$, $M = 686{\cdot}5$, Monoclinic, $a = 12{\cdot}095(17)$, $b = 15{\cdot}885(22)$, $c = 15{\cdot}037(32)$ Å, $\beta = 98{\cdot}87(13)^\circ$, $U = 2855$ Å^3, D_m (flotation) $= 1{\cdot}60$, $Z = 4$, $D_c = 1{\cdot}60$, $F(000) = 1376$. Space group $P2_1/n$ (C_{2h}^5) uniquely determined. This is a non-standard setting of $P2_1/c$ and the equivalent positions are: x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $-x, -y, -z$. No molecular symmetry is required. Mo-K_α radiation, Zr-filtered, $\lambda(\text{Mo-}K_{\alpha 1}) = 0{\cdot}70926$ Å (1 Å = 10^{-10} m). Single-crystal diffraction intensities measured by counter; $\mu(\text{Mo-}K_\alpha) = 13{\cdot}4$ cm^{-1}, no absorption correction applied.

Intensities were collected in shells of reciprocal space for the (hkl) and ($hk\bar{l}$) octants to 2θ 42°. Scanning was carried out at 0·5° min^{-1} from 0·5° below Mo-$K_{\alpha 1}$ peak to 0·7° above Mo-$K_{\alpha 2}$ peak and backgrounds were counted for 25 s at the ends of each scan. Three standard reflections, ($22\bar{3}$), (331), and (112) were measured after every 50 reflections. 3080 Unique reflections were measured, 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). Reflections were considered unobserved if the intensity (I) was < 15 counts, in which case it was reset to 7, or if the intensity was $< 2\sigma(I)$.

Structure Determination.—The solution of the Patterson synthesis was ambiguous, in that the iodine ion could lie close to either (0, 1/4, 1/4) or (1/4, 1/4, 1/2), *i.e.* approximately on the n-glide plane, the two cases producing different relative positions for two of the four potassium ions. A Fourier synthesis phased on the basis of the former solution did not show a recognisable structure and was abandoned after several attempts. A synthesis based on the iodine and potassium positions given by the second solution did show the structure, albeit rather obscurely, and all non-hydrogen atoms were located from this map. Refinement was carried out by use of block-diagonal least-squares to refine the iodine and potassium anisotropically, and the remaining atoms isotropically, the R factor falling from 0·34 to 0·14 in four cycles for observed reflections only, with weights derived from counting statistics. A difference-Fourier synthesis computed at this point failed to show the hydrogen atom positions and several weighting schemes were tried in an attempt to produce constant values of $\langle w\Delta^2\rangle$ [weight × $(|F_o| - |F_c|)^2$] for ranges of $|F_o|$. Location of hydrogen atoms remained impossible and so their parameters were calculated for all except hydroxy-hydrogen atoms and their contributions were included in subsequent structure-factor calculations with isotropic temperature factors corresponding to their adjacent atoms. Derivation of a weighting scheme was difficult and the one finally chosen has the form: for $|F_o| < 48{\cdot}0$, $w = 1/\{13\,375/(156{\cdot}3 + [|F_o| - 23{\cdot}3]^2)\}$; $|F_o| \geqslant 48{\cdot}0$, $w = 0{\cdot}482$. Final refinement was carried out with the full-matrix least-squares program NUCLS.[9] Comparison of runs made by use of all data and observed data only showed that the former gave more reasonable benzene-ring bond distances as well as lower standard deviations in the parameters; the latter gave a lower R factor. Thus final refinement was carried out with all data leading to an R value of 0·165 for 3080 planes, R being 0·082 for the 1356 observed planes. The maximum shift to standard deviation in the final cycle of least squares was 0·13 for the x co-ordinate of C(4). A final electron-density difference map failed to show the positions of the hydroxy-hydrogen atoms; there were several peaks as high as 0·85 eÅ^{-3} not attributable to anisotropic motion or to extra atoms. The poor refinement was not due to absorption or extinction effects. The position of the iodide ion, *i.e.* almost exactly on the n-glide plane, produces an approximately B centred lattice of heavy atoms. The photographs clearly show systematic weaknesses for reflections with $h + l$ odd and this had a marked effect on the intensity measurements. While 980 reflections were considered observed for $h + l$ even, only 376 were considered observed for $h + l$ odd. Using the final parameters and all data, the R value for planes with $h + l$ even was 0·114 and for planes with $h + l$ odd it was 0·285. The overall effect was to reduce drastically the number of reliable data available for the refinement.

Bond lengths and angles with errors were calculated, by

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[9] IBM 360 programs: full-matrix least squares, NUCLS, R. J. Doedens and J. A. Ibers; interatomic distances and errors, ORFFE, W. R. Busing, K. O. Martin, and H. A. Levy.

the program ORFFE,[9] from the variance–covariance matrix. Scattering-factor curves were taken from ref. 10 for hydrogen atoms, ref. 11 for iodide ions, and ref. 3b for all other atoms. Anomalous scattering corrections were applied for I^-, the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 12. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20910 (19 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, and interatomic distances were computed on an IBM 1130.[13] Full-matrix least-squares and calculation of bond lengths and angles with standard deviations from a full correlation matrix were carried out on the University College IBM 360/H65 computer.[9]

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

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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[12] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[13] *X*-RAY ARC: IBM 1130 program system for crystallography compiled by B. L. Vickery, D. Bright, and P. R. Mallinson. This includes the following programs: least squares, BLOK, B. L. Vickery; Fourier, FODAP, A. Zalkin and D. Bright; Picker setting, PICK3, W. C. Hamilton and D. Bright; data reduction, PRED, B. L. Vickery and P. R. Mallinson; mean planes, MPLN (NRC22), M. E. Pippy and F. R. Ahmed; and intermolecular contacts, JANE, P. R. Mallinson.