

Experimental

The crystals were produced by precipitation crystallization. One double-ended crystal was found, $0.12 \times 0.17 \times 0.58$ mm in dimensions, from which the optical goniometer measurements of Fig. 1 were made. $(001) \wedge (101) = 21.5^\circ$, giving $c/a = 0.394$. The general form $\{21\bar{1}\}$ clearly demonstrates that the point group is $\bar{4}$ and this was supported by a positive result in the Giebe-Scheibe test for piezoelectric effect. Subsequent recrystallization by the Soxhlet technique produced a crop of double-ended crystals showing similar forms to those of Fig. 1.

Axial lengths were obtained by a modified Farquhar & Lipson (1946) technique. Twelve 5° oscillations were superimposed on the same film $[0, 14, 0$ and $0, \bar{1}4, 0$ ($\theta = 76^\circ$) and $0, 10, 4$; $0, 10, \bar{4}$; $0, \bar{1}0, \bar{4}$ and $0, \bar{1}0, 4$ ($\theta = 81.5^\circ$) on both sides of the film] with just sufficient missetting of the crystal to prevent overlapping. The film holder was checked for concentricity and the effective radius deduced from measurements of cassette diameter and film and paper thickness. The film was held against the film holder by sprung rings above and below the zero layer line. Errors were calculated from the maximum possible errors in measurement of spot position and film radius, and of the effect of film shrinkage.

The density was measured by the flotation method.

Intensities were measured by photometry of integrating Weissenberg photographs about **a** and **c**. The methods used were those described in the references given in the *Introduction*.

The crystals were ground nearly spherical by Bond's (1951) method and the corrections applied and individual weights calculated as described by Jeffery & Rose (1964). Scale factors for the various layers were obtained from a correlation program, which included symmetry-related as well as common reflexions, and was based on the method suggested by Rollett & Sparks (1960). This method has since been criticized and modified, but judging from the *R* value finally obtained it cannot have given rise to appreciable errors in this case. A check run with the original data using the modified method (Hamilton, Rollett & Sparks, 1965), but without utilizing the symmetry-related reflexions, gave values in good agreement with the earlier ones. Some 1300 measurements were reduced by correlation and averaging to 360 independent F^2 values. All the independent reflexions were measured up to $2 \sin \theta = 1.95$ for Cu $K\alpha$ radiation. Another program calculated a Wilson plot (which gave initial values for the absolute scale and temperature factors) and $N(z)$ coordinates (which gave a curve lying well below the standard acentric curve). All programs, except where otherwise specified, were written in CHLF autocode by one of the authors (J.W.J.) with the occasional incorporation of library routines from London University Institute of Computer Science.

Crystal data

$a = 11.109 \pm 2$; $c = 4.379 \pm 2$ Å; $c/a = 0.3942 \pm 3$ at $18 \pm 3^\circ\text{C}$.

$V = 540.5 \pm 4$ Å³; $D_m = 3.020 \pm 5$ g.cm⁻³; $Z = 2$;

$D_x = 3.018 \pm 3$ g.cm⁻³,

Cu $K\alpha$ radiation, $\lambda_{\alpha_1} = 1.54050$; $\lambda_{\alpha_2} = 1.54434$ Å.

Absorption coefficient, $\mu = 460$ cm⁻¹.

Laue symmetry: $4/m$. Point group: $\bar{4}$. Reflexions absent only for $h+k+l=2n+1$. Space group: $I\bar{4}$. C, N and S are probably in general positions. Hg and Co must be on special positions $(000; \frac{1}{2}\frac{1}{2}\frac{1}{2}) + (a) 000$; $(b) 00\frac{1}{2}$; $(c) \frac{1}{2}0\frac{1}{2}$; $(d) \frac{1}{2}0\frac{3}{4}$. If the origin is taken at a Hg atom, the Co atom can be at (b) , (c) or (d) . The 'molecule' must have $\bar{4}$ symmetry at both the Hg and Co positions.

The crystals were deep purple, square prisms, with large (110) and very small (100) faces, terminated by two pairs of sphenoid faces. Thin sections perpendicular to the prism axis gave uniaxial negative interference figures between crossed polarizers. Sections parallel to **c** were dichroic; purple \parallel c, blue \perp c.

Structural data

Patterson synthesis

If the positive *z* coordinate is chosen for the S, the S-Co peak in the three-dimensional synthesis fixes Co at $\frac{1}{2}, 0, \frac{3}{4}$. Taking the negative coordinate shifts Co to $\frac{1}{2}, 0, \frac{1}{4}$, but this is merely equivalent to turning the cell through a right angle. Coordinates for C and N (assuming S-C-N) were also obtained from the Patterson synthesis.*

Least-squares refinement

Seven cycles using Rollett's S.F.L.S. program (*World List of Crystallographic Computer Programs*, no. 4036) with atomic scattering factors from *International Tables for X-ray Crystallography* (1962) (Hg and Co amplitudes corrected for both anomalous scattering components) and anisotropic temperature factors, brought the shifts to less than one tenth of the standard deviations. $R = 4.2\%$. Table 1 gives the fractional coordinates and average temperature factors of the crystal chemical unit.

Table 1. Fractional coordinates (σ in brackets) ($\times 10^4$) and average temperature factors

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>B</i>
Hg	0	0	0	2.38
S	1528 (3)	1260 (3)	2980 (10)	2.70
C	2733 (11)	804 (12)	1179 (34)	2.45 (or 2.4*)
N	3601 (9)	480 (11)	-228 (62)	3.40 (or 2.4*)
Co	5000	0	-2500	2.63

* From electron density distribution.

* Mills's (1961) program was used for all Fourier syntheses.

Table 2. Observed and calculated structure factors

H K			H K			H K			H K			H K		
L	F(obs)	F(calc)	L	F(obs)	F(calc)	L	F(obs)	F(calc)	L	F(obs)	F(calc)	L	F(obs)	F(calc)
0	0		0	0		0	0		0	0		0	0	
0	21663	21663	1	8278	9234	1	3748	3623	1	3067	2993	0	1867	1794
2	2045	2045	3	3633	3620	3	4796	4598	3	1801	1805	2	3354	3201
4	3231	3078	5	1216	1266	5	259	494	5	8		4	778	948
0	1		0	6930	7541	0	754	8511	0	3197	3313	0	3197	3795
1	6066	6563	2	3646	3538	2	963	1044	2	1720	1715	1	3986	1935
3	3447	4578	4	3417	2974	4	2520	2533	4	2786	2655	3	1930	1935
5	676	757	0	6960	7554	0	4240	4303	0	1648	1773	0	2297	2264
0	6972	8654	1	3859	3721	1	2414	2167	1	10		2	2642	2479
2	4333	4292	3	1333	1373	3	876	953	3	3016	3168	0	9	
4	2973	2626	5	7136	8313	5	6		5	1137	1211	1	2723	2643
0	7978	8763	0	3780	3594	0	3307	3443	0	11		3	1941	1877
2	2273	2256	2	2191	2186	2	3988	3957	2	1951	1959	0	7	
5	1906	1936	4	5		4	1830	1867	0	12		2	2745	2797
0	4		0	5731	5983	0	7		0	2411	2456	0	2314	2190
0	3994	3863	1	2731	2677	1	4127	4046	0	1		0	9	
2	4978	4935	3	2680	2677	3	1435	1401	2	4304	4002	0	1018	1084
4	1859	1834	5	984	1038	0	8		4	1249	1337	2	2477	2427
0	5		0	7065	7817	0	3577	3706	0	7		0	9	
1	5908	5774	2	3117	2938	2	2755	2733	1	5008	4709	0	2176	2210
3	2865	2898	4	2517	2396	4	1343	1427	3	1397	1316	0	1	
5	1402	1456	0	4056	3997	0	1635	3642	0	7		10	1	
0	7260	7371	1	3947	2926	1	2007	2248	2	5515	5383	3	2198	2169
2	2145	1919	3	8		3	10		4	464	676	0	3	
4	2735	2696	0	6231	6457	0	4697	4838	0	4		0	4758	4895
0	1		2	2170	2080	2	761	811	1	4154	3998	2	1222	1191
1	3596	3528	4	1677	1729	4	11		3	1778	1857	0	10	
3	3189	3143	0	9		0	2360	2279	0	5		1	2710	2697
0	8		0	4240	4177	3	1985	1987	0	2796	2819	3	1913	1883
0	6224	6255	1	4177		1	12		2	3332	3130	0	10	
2	1616	1495	3	2433	2365	0	3229	3278	4	1119	1229	0	4273	4346
4	1852	2032	0	20		2	1472	1528	0	6		2	1724	1598
0	9		0	2447	2358	0	13		1	3045	3057	0	10	
1	3147	2928	2	2366	2232	1	1377	1906	3	2776	2711	1	2750	2646
3	2022	2041	0	11		0	5		0	7		3	1416	1477
0	10		1	3053	2966	0	4578	4217	0	3423	3445	0	2710	2763
2	2581	2515	3	949	1079	2	6220	6114	2	2459	2345	0	2199	1981
4	2405	2330	0	12		4	1923	1943	0	1595	1507	0	10	
0	11		0	2386	2483	0	5		0	8		1	2469	2841
1	3297	3176	2	1673	1713	1	5462	5222	1	2957	2876	0	10	
3	1183	1205	0	13		3	3203	3378	3	2036	2081	0	8	
0	12		0	1416	1451	0	876	929	0	9		0	2204	2343
0	2583	2605	0	1		0	3		0	1759	1765	2	1476	1444
2	1628	1597	3	5158	5136	0	5450	5459	2	3187	3177	0	10	
0	13		2	7124	7444	2	4441	4250	0	10		1	2016	2094
1	2081	2043	4	1453	1361	0	1920	1891	1	2504	2494	0	11	
0	1		0	3		0	4		0	11		0	2730	2772
0	5541	5427	1	5564	5312	1	4504	4424	0	1044	1118	2	2742	2649
2	4497	4550	3	3374	3399	3	3616	3552	2	2291	2317	0	11	
4	1968	1875	5	769	812	5	812	832	0	12		1	2632	2486
0	2		0	3		0	5		1	1797	1932	3	2444	2396
1	4159	4059	0	7122	8007	0	3374	3399	0	8		0	3	
3	2622	2883	2	4485	4475	2	4511	4411	1	4883	4725	0	3445	3479
5	1444	1486	4	2072	2015	4	1183	1353	3	2348	2756	2	1653	1607
0	3		0	4		0	5		0	8		0	4	
0	544	121	1	5423	5595	1	4985	5016	0	1679	1635	1	2511	2494
2	7072	7704	3	3539	3542	3	1682	1693	2	1499	1477	3	1801	1773
4	1481	1445	5	343	580	0	7		4	1611	1703	0	11	
0	4		0	3		0	1148	1095	0	3		0	769	802
1	5553	5536	0	3593	3568	2	4863	4729	1	4444	4330	2	2781	2729
3	2032	1988	2	4644	4571	4	1050	1009	3	1392	1321	0	11	
5	1624	1672	4	1526	1437	0	8		0	4		1	2122	2207
0	5		0	6		1	3918	3942	0	3571	3532	0	11	
0	2179	2046	3	5034	5263	3	1586	1638	2	3219	3055	0	8	
2	5154	5243	0	7		0	9		4	1812	1826	2	2573	2579
4	1476	1507	3	2509	2484	0	3493	3537	0	5		0	11	
0	6		0	706	813	2	2647	2672	1	2855	2753	1	1463	1549
1	4594	4670	2	4417	4387	0	10		3	2411	2372	0	12	
3	3702	3608	4	836	938	0	2072	2091	0	8		1	1958	1925
5	635	788	0	3		3	2216	2205	0	5601	5844	0	12	
0	7		1	3453	3419	0	5		2	836	930	0	3166	3271
0	5235	5547	3	1778	1795	0	11		4	1657	1636	2	876	889
2	2463	2272	0	9		0	2562	2576	0	7		0	3	
4	1238	1318	3	2498	2483	2	1339	1542	1	2612	2529	1	1808	1846
0	8		2	3187	3103	0	5		0	2565	2507	0	12	
1	3785	3765	4	1307	1342	0	1944	1975	3	8		0	2514	2605
3	2982	2916	0	10		1	5108	5195	0	3221	3228	2	1194	1202
0	9		2	4644	4571	4	1050	1009	2	1265	1267	0	12	
0	2560	2551	0	6		1	3918	3942	0	9		1	2120	2170
2	3822	3716	3	5034	5263	3	1586	1638	1	2774	2685	0	12	
4	120	998	0	7		0	9		3	1005	1028	0	12	
0	10		2	2509	2484	2	3301	3035	0	10		0	1348	1427
1	1405	1348	0	12		4	1906	1782	0	1612	1660	1	1830	1997
3	1005	1055	1	2735	2764	0	3		2	2078	2069	0	13	
0	11		0	13		1	4648	4535	0	11		2	2016	2037
2	1222	1134	3	1238	1297	3	2488	2343	1	1763	1832	0	13	
4	3969	3842	0	4		0	6		0	9		1	2026	2039
0	12		1	6122	6118	2	5084	5272	0	2822	2867	0	13	
1	2578	2554	3	2388	2222	2	3210	3126	2	3843	3666	0	3	
0	13		5	1166	1241	4	1888	1835	0	1490	1498	0	1271	1339
0	1789	1871	0	2		0	5		4	9		1	2006	2136
2	1530	1595	0	7378	8063	1	4823	4791	1	3313	3129	0	13	
			2	1297	1117	0	6		3	1677	1711	0	5	
			4	2261	2231	2	4856	5131					1397	1510
						2	2173	2107						
						4	1565	1680						

Fourier syntheses

An observed Fourier synthesis (O.F.) was computed from the final structure factors (S.F.) (Table 2) and the atomic peak positions calculated from Sparks's 19 point program (W.L. 4048). Without cut-off correction, these were within 2.5σ of the least-squares positions. A composite diagram through the atomic positions is shown in Fig. 2. (The complete atomic arrangement is given in Fig. 10). A difference Fourier synthesis (D.F.) was featureless apart from diffraction effects round Hg and Co.

Interatomic distances and angles

The interatomic distances and angles were calculated by a modified version of the program (W.L. 4045) of Sparks. The values obtained are given without correction (W) in Table 3, together with the bond lengths corrected for thermal vibrations (Busing & Levy, 1964) for 'riding' (R) and 'independent' (I) motions. The limits of the corrected bond lengths are given as 'MIN' and 'MAX' in the table and correspond to 'in-phase' and 'anti-phase' vibration of the atom pair respectively. The latter is physically so unlikely that it can be disregarded except as defining the maximum possible correction.

In both cases the tetrahedral arrangement about Hg and Co is slightly flattened in the c direction, so that the larger angle refers to two S 's or N 's which have the same z coordinate.

Vibration ellipsoid axes

The vibration ellipsoid axes (r.m.s. displacement), obtained from a modified version of Sparks's program (W.L. 4044), are given in Table 4.

Secondary extinction

Inspection of the S.F. table suggested that secondary extinction might be present. For secondary extinction the effective absorption coefficient $\mu' = \mu + g'q$ and

$$g' = g(1 + \cos^2 2\theta) (1 + \cos^2 2\theta)^{-2}$$

(Zachariasen, 1963) where g is a constant and q is the integrated reflexion. This change is equivalent to a

Table 4. *Vibration ellipsoid parameters*
(3σ in brackets)

	r.m.s. displacement	Direction cosines		
		a	b	c
Hg	0.211(1)	0	0	1
	0.152(1)	0	1	0
	0.152(1)	1	0	0
S	0.221(7)	0.085	-0.559	0.825
	0.168(5)	-0.257	0.787	0.561
	0.159(5)	0.963	0.260	0.077
C	0.193(20)	0.068	-0.925	0.374
	0.190(20)	-0.162	0.360	0.919
	0.138(12)	0.984	0.124	0.125
N	0.240(25)	-0.220	0.504	0.836
	0.204(5)	0.185	0.862	-0.471
	0.173(4)	0.958	-0.051	0.283
Co	0.228(5)	0	0	1
	0.156(3)	0	1	0
	0.156(3)	1	0	0

change in the absorption correction factor, A^* and for small changes:

$$\frac{\delta q}{q} = \frac{\delta A^*}{A^*} = \frac{1}{A^*} \cdot \frac{dA^*}{d(\mu r)} \cdot \delta(\mu r)$$

$$= \frac{rg'q}{A^*} \cdot \frac{dA^*}{d(\mu r)}$$

$$q_c = qF_c^2(1 + \cos^2 2\theta) \frac{L}{A^*},$$

where L is the Lorentz factor and q a constant.

$$\therefore \frac{\delta q}{q} = \frac{F_c^2 - F_o^2}{F_c^2} = rg'qF_c^2(1 + \cos^2 2\theta) \frac{L}{A^{*2}} \cdot \frac{dA^*}{d(\mu r)}$$

Making the approximations

$$F_c^2 - F_o^2 = (F_c - F_o)(F_c + F_o) \simeq 2F_c(F_c - F_o)$$

and

$$\frac{dA^*}{d(\mu r)} \simeq kA^*,$$

where k is a constant we have:

Table 3. *Distances and angles* (σ in brackets)

Distances	W	R	I	MIN	MAX
Hg-S	2.558 (4) Å	2.559 Å	2.586 Å	2.558 Å	2.614 Å
S-C	1.635 (14)	1.638	1.678	1.635	1.720
C-N	1.199 (21)	1.207	1.261	1.200	1.322
N-Co	1.921 (16)	1.926	1.959	1.921	1.997
Angles					
	S-Hg-S(1)	118.7 (1)°			
	S-Hg-S(2)	105.1 (1)			
	Hg-S-C	97.3 (5)			
	S-C-N	178 (2)			
	C-N-Co	179 (1)			
	N-Co-N(1)	118 (1)			
	N-Co-N(2)	106 (1)			

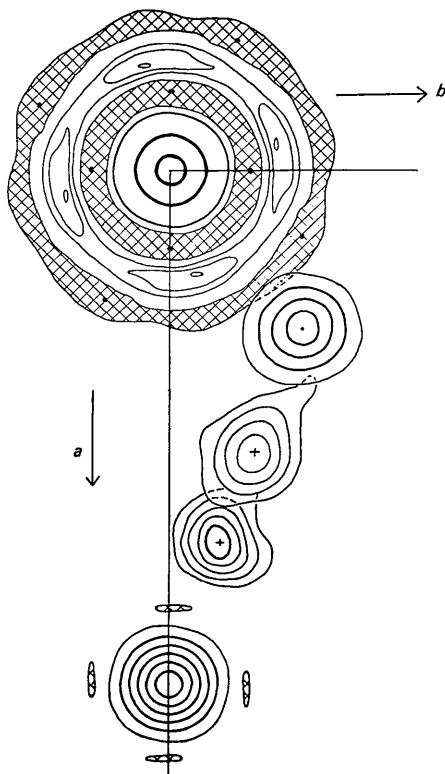


Fig. 2. A composite diagram of the nearest sections to the atomic centres of the atoms. Cross hatched areas are negative. Thin contours are at intervals of $2 \text{ e.}\text{\AA}^{-3}$, thick at $10 \text{ e.}\text{\AA}^{-3}$ except around the mercury atom, where the two very thick contours are at 100 and $200 \text{ e.}\text{\AA}^{-3}$. Zero contour not shown. Crosses mark the L.S. centres; length of arm $= 3\sigma$.

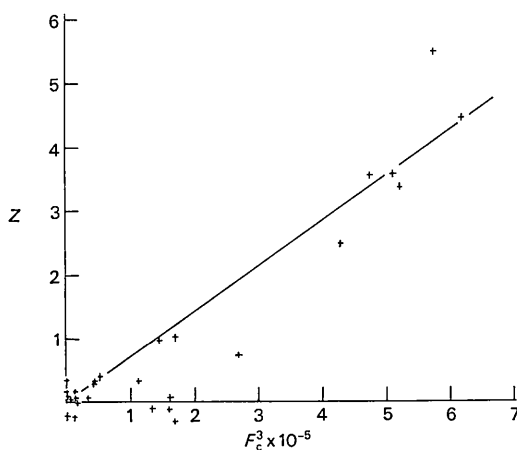


Fig. 3. The effect of secondary extinction. The ordinates are values of $Z = (F_c - F_o) (1 + \cos^2 2\theta) A^* \times 10^{-4} / (1 + \cos^4 2\theta) \sin 2\theta$ plotted against $F_c^3 \times 10^{-5}$. The slope of the line is a measure of the amount of secondary extinction present, although if a small amount of primary extinction is present as well it would have a similar effect.

$$F_c - F_o = 2krgqF_c^3 \frac{(1 + \cos^4 2\theta)}{A^*(1 + \cos^2 2\theta)} L$$

$$= KF_c^3 \frac{(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)} \frac{L}{A^*}$$

$$\therefore (F_c - F_o) \frac{(1 + \cos^2 2\theta)}{(1 + \cos^4 2\theta)} \cdot \frac{A^*}{L} = KF_c^3$$

Thus if the left-hand side is plotted against F_c^3 it should give a straight line of slope K . Fig. 3 gives the plot for 27 $hk0$ reflexions and clearly shows that secondary extinction is present. For these 27 reflexions, correction for secondary extinction from the graph reduced R from 5.4% to 3.2%.

Atomic arrangement

Up to this point it had been tacitly assumed (and apparently justified by the results) that the arrangement was S-C-N, in accordance with the chemical evidence, and not S-N-C. In an attempt to confirm this, C and N were interchanged and a further series of L.S. refinements undertaken.

Fig. 4 shows the relevant D.F. sections. As would be expected, a positive peak appears in the original nitrogen position (on the right) and a negative one on the left in (2) but a comparison of (1) and (6) shows that the evidence of the D.F.'s gives very little indication of the relative positions of C and N. However, the O.F. gives a different result. Fig. 5 shows the O.F.'s corresponding to Fig. 4(1) on top and Fig. 4(6) below. There is remarkably little difference between them and there would appear to be no doubt which is C and which N. This must mean that the position of the atomic centres (which changed very little during the L.S. refinements after interchanging C and N) is the main factor determining the phases and an inspection shows that only 4 out of 283 phases able to vary ($l \neq 0$) had altered by more than 2° during the course of this second refinement. The greatest alteration was 3.25° and most changes were less than 1° .

The only parameters which changed significantly during the L.S. refinement were the anisotropic temperature factors and it is clear that this was responsible for the almost complete disappearance of the D.F. peaks of Fig. 4(2) at the end of the refinement [Fig. 4(6)].

Since this left the evidence very much as it was before, a further attempt at confirming the identification of C and N was made using the radial electron density distribution.

Radial distribution of electron density

The average radius of each contour on the three O.F. sections of Figs. 5(a) and 6 was obtained from 36 measurements for each electron density. The standard deviation of electron density at a general position, xyz , was obtained from the formula

$$\sigma(\varrho) = \frac{1}{V} \left[\sum_{hkl} (\Delta F)^2 \right]^{\frac{1}{2}}$$

(Cruickshank & Rollett, 1953). For a single point $\sigma(\varrho) = 0.2 \text{ e.}\text{\AA}^{-3}$. For the average of 36 measurements $3\sigma = 0.1 \text{ e.}\text{\AA}^{-3}$. Allowing for errors arising from bonding and anisotropic vibration distortion it would seem reasonable to take the maximum error as $0.2 \text{ e.}\text{\AA}^{-3}$.

A series of radial distribution curves was calculated from the atomic form factors for various values of the temperature factor, B , and the upper limit of $\sin \theta/\lambda$. The upper limit of $\sin \theta/\lambda$ for the experimental data was 0.63 and for this limit there is little variation of the radial distribution curve with B from $r=0.4$ to 0.7 \AA . The observed points can best be fitted to the curves in this region if the zero of electron density on the Fourier is assumed to be $0.4 \text{ e.}\text{\AA}^{-3}$ too high. Such an error could easily arise from faulty f curves, even although the scale factor error was less than 1% . If this correction is made the observed points are shown on Fig. 7 together with the errors as given above. The curves give the calculated values for $B=2.4$, which appears to give the best fit at the peaks, but $B=2.3$ or 2.5 would do this nearly as well. The curve from $r=0.4$ to 0.7 \AA would not be appreciably affected by the choice.

For carbon the B value is in good agreement with the average value of Table 4, but the value for nitrogen in the table is too high. This may be connected with the much larger error in the z coordinate for nitrogen, and the evidence of the Fourier synthesis that the B values are nearly the same is probably to be preferred in this case.

Electron transfer and bond electrons

The general agreement between observed and calculated electron density distribution would seem to establish the identity of the Fourier peaks beyond reasonable doubt (it would be necessary to assume a value of $B \approx 1.5$ for carbon and 3.5 for nitrogen to get anywhere near a fit the other way round), but the observed points for nitrogen appear to lie significantly below the calculated curve and those for carbon above. If this is a real effect it indicates an appreciable electron transfer from nitrogen to carbon. Such a transfer would be consistent with the very short C-N bond [$1.20 \pm 0.06 (3\sigma)$] which gives rise by overlap to the appreciable electron concentration in the bond shown in the sections perpendicular to \mathbf{b} [Fig. 6(b)] which are only 18° from the vertical plane containing the bond.

Anomalous dispersion

Theoretical

When the original data were collected the possibility of anomalous dispersion effects was not appreciated. This did not affect most of the work on comparison of symmetry-related reflexions since this was done on the $hk0$ zone in which symmetry-related reflexions are

all affected in the same way. However, this does not apply to the non-zero layer reflexions and the adjustment of the amplitudes of the Hg and Co atomic scat-

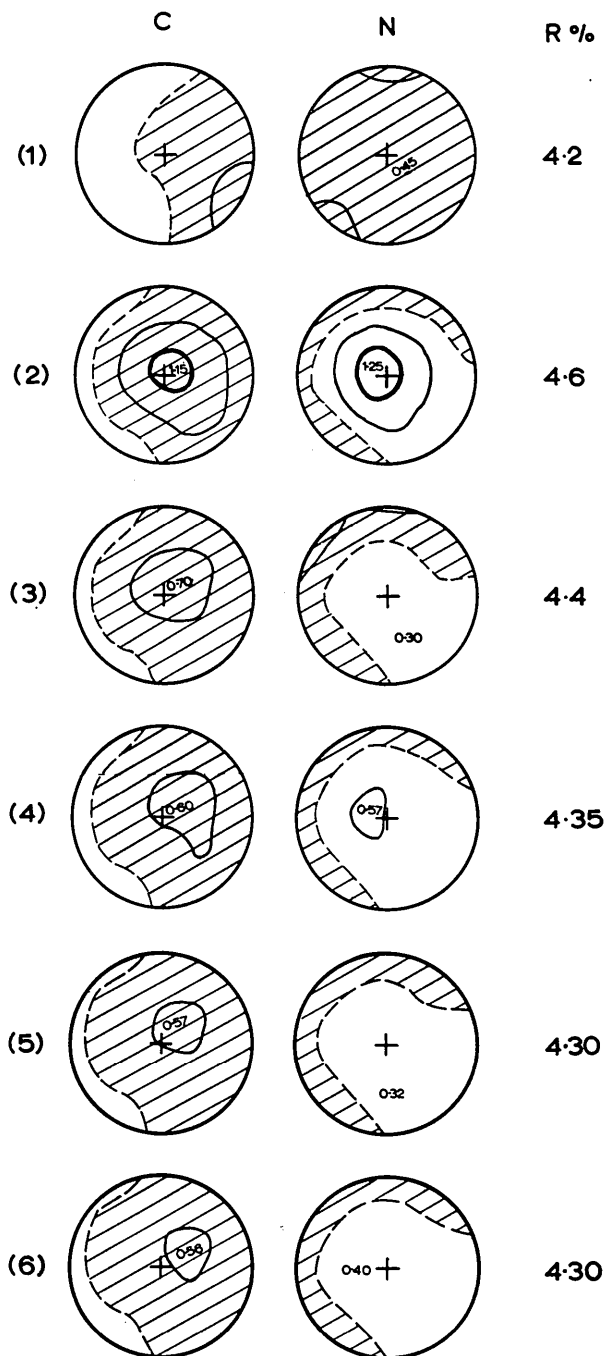


Fig. 4. Difference Fourier ($F_o - F_c$) sections perpendicular to \mathbf{c} through the centres (+) of the C and N atoms. Diameter of circles = 1.5 \AA . Zero contour dashed; $0.5 \text{ e.}\text{\AA}^{-3}$, light line; $1.0 \text{ e.}\text{\AA}^{-3}$, heavy line. Negative areas hatched. Figures give approximate position and magnitude of maximum electron density. (1) After completion of refinement with atom order S-C-N. (2) After interchanging C and N to give S-N-C. (3), (4), (5) and (6) After 1, 2, 3 and 4 rounds of L.S. refinements maintaining the order S-N-C. Second refinement then complete.

tering factors does nothing to take account of the difference in intensity of symmetry-related reflexions due to the anomalous dispersion.

The expected value of R from the known errors in the data was 1.6% (Rose, 1965). The value found was 4.2% and this could at best be reduced to 3.2% by correcting for extinction. Some of the remaining differences could be due to the assumption that

$$I_{hkl} = I_{hk\bar{l}} = I_{\bar{h}k\bar{l}} = I_{\bar{h}kl} = I_{khl} = I_{\bar{k}h\bar{l}} = I_{k\bar{h}l} = I_{k\bar{h}\bar{l}}.$$

Since

$$\alpha_{hkl} = -\alpha_{hk\bar{l}} = \alpha_{\bar{h}k\bar{l}} = -\alpha_{\bar{h}kl} = \\ -\alpha_{\bar{k}hl} = \alpha_{k\bar{h}l} = -\alpha_{k\bar{h}\bar{l}} = \alpha_{k\bar{h}\bar{l}}$$

($\alpha \neq 0$ or π in general) anomalous dispersion could destroy the equality of intensities. The extent of the effect was therefore calculated, using the S.F. tables and scattering factor values as follows.

In Fig. 8 OA is the normal atomic scattering factor with zero phase relative to the atomic centre as origin. AB is $\Delta f'$ and BC $\Delta f''$, the two components due to the anomalous dispersion effect. \overrightarrow{OC} is therefore the

true scattering factor, with a non-zero phase angle, δ . $OD = OC$ is the atomic scattering factor (f') used in the S.F. calculations, with zero phase angle. To take account of the phase angle, δ , it is therefore necessary

to add the vector \overrightarrow{DC} (modified by the temperature factor) to the Argand diagram of the calculated S.F.,

so that \overrightarrow{DC} makes an angle of $\pi/2 - \delta/2$ with the scattering factor used in the calculations. The two components of this vector are $BC = \Delta f''$ and $DB = \Delta f''' = \Delta f'' \tan \delta/2$. $\sin \delta = BC/OC = \Delta f''/f'$.

Only Hg and Co in the structure have significant anomalous scattering for Cu $K\alpha$ radiation. The normal phase of the Hg scattering is always zero and the Co scattering can have phase angles of 0, $\pi/2$, π or $3\pi/2$, depending on the indices. To get the maximum effect Co and Hg should have the same phase, so that the anomalous effects are added, the X component of the S.F. (A) should be as small as possible [large θ and negative (SCN)₄ contribution] and the Y component [B , contributed by (SCN)₄] should be as large as possible (up to the value for a maximum

$$[(\Delta f''_{\text{Hg}} + \Delta f''_{\text{Co}})^2 + A^2]^{\frac{1}{2}}$$

which is not approached for any reflexion of this crystal) so that the resultant amplitudes are as different as possible for two symmetry-related reflexions. Inspection showed that the 224 reflexions, with $A = 31$, $B = -15$ and $\sin \theta = 0.731$ satisfied these requirements and Fig. 9 shows the Argand diagram for 224 and $\bar{2}\bar{2}\bar{4}$ and Table 5 the scattering factor values.

Table 5. Scattering factors for Hg and Co

	f'	$\Delta f''$	$\Delta f'''$	$\exp(-B \sin^2 \theta/\lambda^2)$
Hg	43.8	8	0.75	0.586
Co	11.3	3.8	0.65	0.555

The true amplitudes of 224 and $\bar{2}\bar{2}\bar{4}$, OR and OS , are very different and the ratio $I_{224}/I_{\bar{2}\bar{2}\bar{4}}$ is 1.40, although the average intensity, 1.19×10^3 , is not significantly different from the original calculated intensity ($ON^2 = OM^2$) of 1.18×10^3 , and the error in intensity involved in measuring only one reflexion is of the order of 17%. Thus, where symmetry-related reflexions were averaged, no appreciable error is likely to have been caused, but where only one reflexion was measured the error may be considerable. In only a few cases is it likely to be more than 10%, but in spite of the large number of averaged results, it is probable that part of the residual is, in fact, due to errors arising from anomalous dispersion.

Experimental

A spherical crystal, very similar to that from which the a -axis data had been collected, was used for an experimental test of the effect of anomalous dispersion. The a axis was taken as positive upwards along the

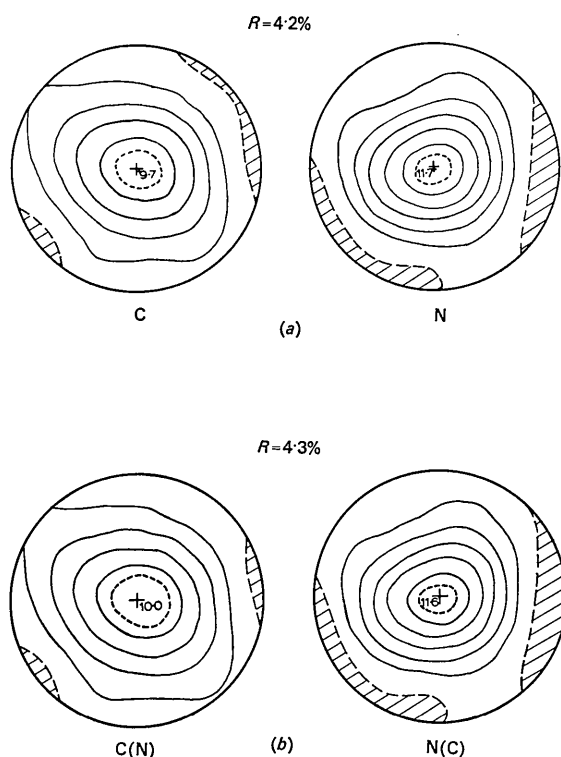


Fig. 5. (a) Observed electron-density sections perpendicular to c through the centres (+) of the C and N atoms; corresponds to Fig. 4(1). Diameter of circles 1.5 Å. Zero contour: long dashes; full lines at 2 e.Å^{-3} intervals; central, short-dashed contours at 9 and 11 e.Å^{-3} for C and N respectively. Maximum electron density marked. The large crosses mark the centres as obtained from L.S. refinement. The lengths of the arms are equal to 3σ . The small crosses mark the centres obtained by peak location from the 3-D Fourier synthesis. (b) As for (a) after second refinement with C and N interchanged; corresponds to Fig. 4(6).

rotation axis of the camera and the original choice then determined the directions of positive \mathbf{b} and \mathbf{c} . However, since the Laue symmetry is $4/m$, rotation of 90° about \mathbf{c} would not normally be detectable, so that the direction along the rotation axis might equally well be $\pm \mathbf{b}$ or $-\mathbf{a}$. Since there is a twofold axis in the space group passing through the origin, it is not possible to distinguish between the positive or negative directions of the axes, but anomalous dispersion effects should make it possible to determine whether \mathbf{a} or \mathbf{b} was along the camera rotation axis. Four pairs of $\{224\}$ reflexions were therefore registered with an integrating Weissenberg camera. The photometer results are given in Table 6.

Table 6. *Photometer results*

hkl	Density	Ratio	Average
224	0.373	1.44	0.316
$\bar{2}\bar{2}4$	0.259		
$2\bar{2}\bar{4}$	0.362	1.25	0.333
$\bar{2}2\bar{4}$	0.304		
$\bar{2}\bar{2}4$	0.334	1.27	0.299
$2\bar{2}4$	0.264		
$\bar{2}2\bar{4}$	0.367	1.30	0.325
$22\bar{4}$	0.283		
Overall average		1.32 ± 8	0.318 ± 13

On the basis of the original choice of the z coordinate of S from the Patterson synthesis, \mathbf{b} is along the rotation axis, not \mathbf{a} . The average ratio of the pairs, 1.32, is rather less than the expected value of 1.40, but the standard deviation shows that this is probably not significant.

Discussion

The general arrangement of the structure, and, in particular, the tetrahedral coordination of Hg by S which was suggested earlier (Jeffery, 1947) and which was also found by Scouloudi (1953) in $\text{Hg}(\text{SCN})_4 \cdot \text{Cu}(\text{en})_2$, has been confirmed. The tetrahedral coordination of Co by N has been established. The distortions of the tetrahedra are similar to those found in other structures with tetrahedrally coordinated cobalt (Figgis, Gerloch & Mason, 1964). The S, C, N and Co atoms lie in a line, straight to within the limits of error (2°). This is in contradistinction to the findings of Scouloudi (1953) that the SCN bridge is kinked at C by about 20° . The difference is probably due to the much lower symmetry of the $\text{Hg}(\text{SCN})_4 \cdot \text{Cu}(\text{en})_2$ structure.

Since the strains in the structure would tend to open up the Hg-S-C angle, its measured value of 97° is probably greater than its value unstrained.

The combination of two tetrahedrally coordinated atoms in the structure has produced a very unusual arrangement. The Hg atoms are separated vertically by the height of the unit cell (4.38 \AA) which is considerably greater even than the van der Waals bonding distance. The connexion between them, through a

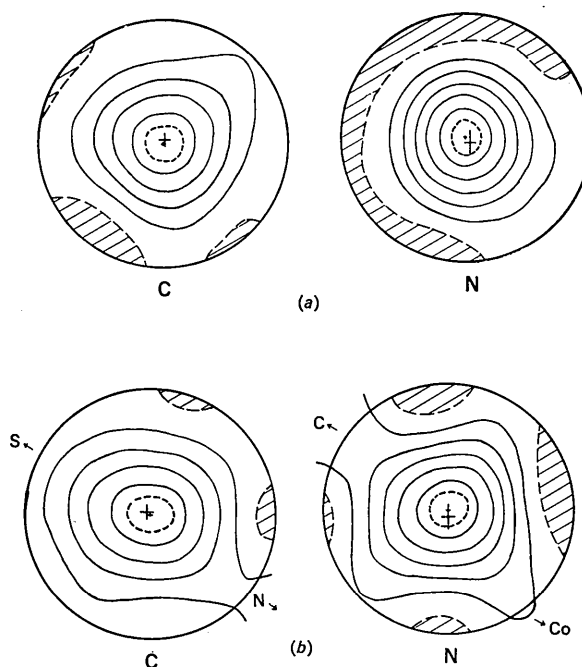


Fig. 6. Observed electron-density sections through the centres of the C and N atoms: (a) perpendicular to \mathbf{a} ; (b) perpendicular to \mathbf{b} . Contours, etc. as for Fig. 5(a).

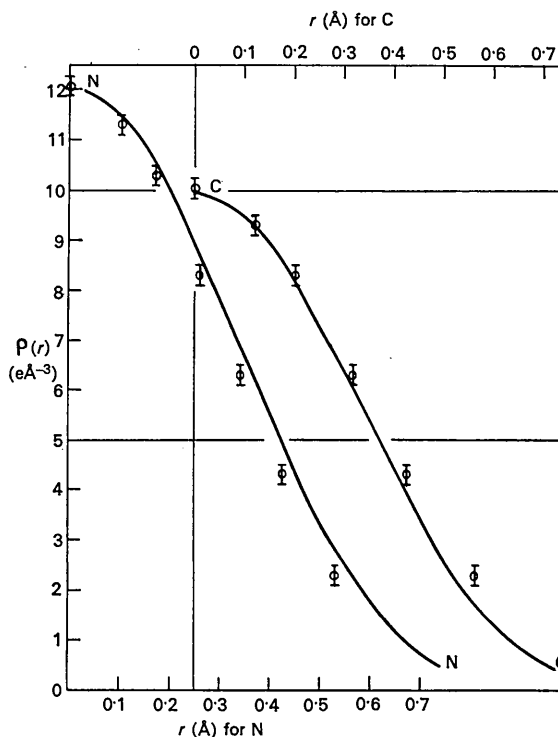


Fig. 7. Calculated electron density radial distribution curves for C and N atoms. $B = 2.4$, cut-off for $\sin \theta/\lambda$ at 0.63, corresponding to the experimental conditions ($\text{Cu } K\alpha$, $2 \sin \theta = 1.95$). The observed points and estimated errors (on the basis of 3σ) are shown. The curves have been separated laterally to avoid overlap.

'square spiral' of four S-C-N arms (Fig. 10) is very indirect. If we start at Hg ($x=0, y=0, z=1$), this is linked to Co($\frac{1}{2}0\frac{3}{4}$) in the a direction [via S($z=1.30$), C(1.12), N(0.98)]; thence to Hg ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) in the b direction; to Co($0\frac{1}{2}\frac{1}{4}$) in the $-a$ direction; and to Hg(000) in the $-b$ direction. A similar spiral links the two, going from Co($\frac{1}{2}0\frac{3}{4}$) in the $-b$ direction and two more

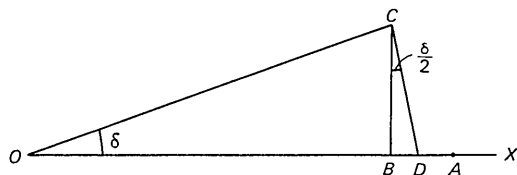


Fig. 8. Diagram showing the relation between the true atomic scattering vector OC , the normal (real) scattering factor OA and the modified (real) factor OD .

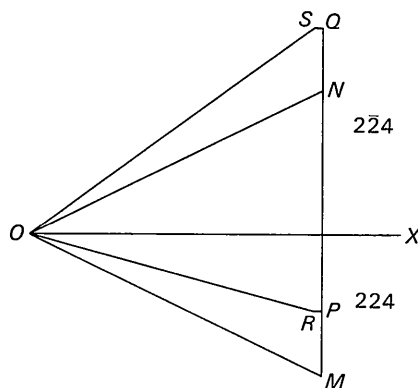


Fig. 9. The Argand diagram for 224 and $\bar{2}\bar{2}4$ reflexions. OM and ON are the original calculated structure factors for the two cases. $MP=NQ=\Sigma \Delta f'' e^{-M}$ and $PR=QS=\Sigma \Delta f''' e^{-M}$.

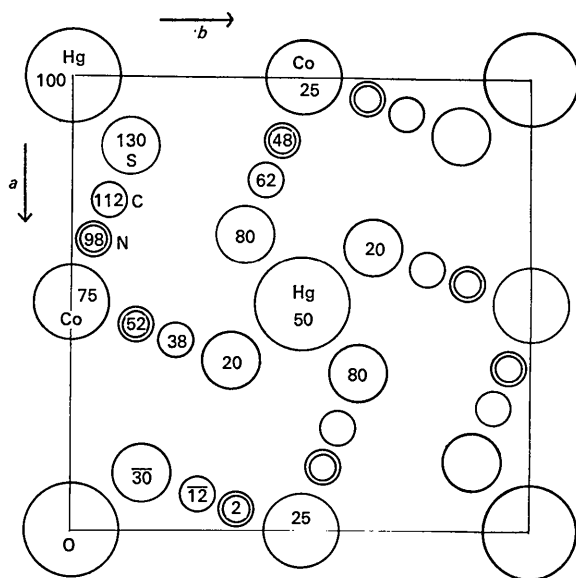


Fig. 10. Diagram of the structure. The figures are hundredths of the cell height.

arms start from Hg(001) in the $-a$ direction. By starting from Hg(001) in the $\pm b$ direction, four spirals go up to Hg(002). The Co atoms, vertically above one another (also 4.38 \AA apart), are linked in the same way, except that a and b are interchanged.

Each SCN arm takes part in eight such 'square spirals' (2 linking Hg at $z=0$ and 1; 2 Hg at $\frac{1}{2}, \frac{1}{2}$; 2 Co at $\frac{3}{4}, \frac{1}{4}$ and 2 Co at $\frac{1}{4}, \frac{1}{4}$). Each such spiral is a spring holding the Hg and Co atoms apart and straining the bonds in the process. It is almost certainly this strain which flattens the tetrahedral coordination round Hg and Co in the c direction. If the arrangement could be reproduced mechanically it would probably provide the ideal spring mattress! On the atomic scale it provides the possibility for considerably greater thermal vibrations in the c direction than in the ab plane. The SCN arms will also tend to vibrate like strings stretched between the Hg and Co atoms. There is some slight evidence that the C atom is at a partial node in this vibrating string, and for all the atoms on the string the longitudinal vibrations (nearly the a direction for the atoms in Table 4) are less than the transverse.

Conclusion

Accurate intensity measurements have enabled C and N to be distinguished in a structure containing a large proportion of Hg, Co and S atoms, and many structural details have been elucidated. The discrepancy between the measured R value of 4.2% and the expected value of 1.6% has been shown to be partly due to extinction and probably partly to the effects of anomalous dispersion. For work of the highest accuracy it will be necessary to take account of the phase alteration introduced by anomalous dispersion (and not just the alteration in amplitude) even in centrosymmetric structures, when the effect is of the same order as in this case.

The crystals were prepared in the Chemistry Department at Birkbeck College and a sample kindly supplied by Professor Wardlaw. Parts of the paper appeared in extended form in theses by both authors (J.W.J., 1952; K.M.R., 1965) accepted for the degree of Ph.D. in London University. Professor Bernal's encouragement and advice are gratefully acknowledged.

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On a Simple Approximate Matrix in the Least-Squares Determination of Positional Parameters

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The use of a simple approximate matrix in the least-squares determination of positional parameters with X-ray data is discussed. In the approximate matrix the summation over the structure-factor derivatives is no longer carried out, but rather, expected values of the matrix elements are used. The approximate matrix consists of a 3×3 block-diagonal matrix. Each block contains the metric tensor of the crystal, a factor being the square of the number of the electrons of the particular atom, and a universal scale factor. The approximation becomes more legitimate as more structure factors are used. It is shown theoretically that the quality of the approximation can be improved when fewer parameters are refined. Hence the approximation is improved when the number of parameters is reduced by introducing stereochemical restraints. The approximation is tested numerically by means of criteria which have been introduced by Sparks. It is concluded that the approximation is sufficient in the initial stages of a refinement for 1000, 2000, and 5000 data with about 27, 47, and 80 parameters respectively.

Introduction

In least-squares refinement of crystal structures one often does not use the full matrix in the normal equations, but rather approximations (diagonal matrix, block-diagonal matrix *etc.*) in order to save storage space and computing time. As is well known, the use of approximations is permissible because the least-squares postulate only requires that the sequence of the right-hand sides of the normal equations shall converge towards zero (at the correct structure minimum). The form of the matrix is unimportant as long as it ensures that convergence occurs at the correct structure minimum.

Recently a further, very rough approximation for the normal matrix of positional parameters of the single atoms was described by Scheringer (1965*a*). This approximation, however, was intended to be used for re-adjusting positional parameters of the single atoms by means of a set of stereochemical restraints. In the present paper we shall investigate how far this approximation may also be used for the direct refinement of positional parameters. As the calculation of the approximate matrix is very rapid, one could save much computing time. The approximation will normally be too poor for the refinement of the parameters of the

single atoms, but it can be improved by introducing stereochemical restraints. In the following we shall establish this theoretically; further we shall give some criteria to judge the quality of a given approximation [similar to those given by Sparks (1961)], and we shall give some numerical values of the criteria with two structures. With the numerical results thus obtained we shall estimate the range (number of data, number of parameters) in which the approximation may be used.

The approximate matrix

For positional parameters of the single atoms the normal matrix \mathbf{A} can be approximated by

$$\mathbf{Q} = k\mathbf{ZH} \quad (1)$$

(*cf.* Scheringer, 1965*a*). k is a scale factor which can be roughly determined by setting trace (\mathbf{A}) equal to trace (\mathbf{Q}). (How the scale can be improved will be discussed below.) \mathbf{ZH} is a 3×3 block-diagonal matrix with elements $Z_i^2 h_{st}$ for the i th block. Z_i is the number of electrons of the i th atom; h_{st} is a component of the metric tensor of the unit cell. \mathbf{Q} is positive-definite and symmetric. The assumptions made in the approximation are: