atoms, this distance being inconceivable for an O···O interaction in this type of structure. In any case, these assumptions have to be supported by additional data and further investigations are planned for the location of the hydrogen atoms of the water molecules by neutron diffraction. Nevertheless, our assumptions are consistent with the interpretation of the DTA, TG and DTG experiments.

All the computations have been performed on an IBM 370-168 computer at Orsay (CIRCE), through the terminal of the Institut de Recherches sur la Catalyse, Lyon, and by means of programs available at the Laboratoire de Chimie Analytique II, Université Claude-Bernard, Lyon I.

References

BÄRNIGHAUSEN, H. & WEIDLEIN, J. (1967). *Acta Cryst.* **22**, 252–258.

CLAUDEL, B., MENTZEN, B. F., PUAUX, J. P. & SAUTEREAU, H. (1977). *C. R. Acad. Sci. Sér. C*, **285**, 425–428.

DREW, M. G. B. (1977). *Prog. Inorg. Chem.* **23**, 69.

GRUENINGER, H. W. & BÄRNIGHAUSEN, H. (1969). *Z. Anorg. Chem.* **368**, 53–61.

GUILLERMET, J. (1974). *Spectroscopies Infrarouge et Raman, Monographie du CAST de l'INSA de Lyon*, edited by B. F. MENTZEN, Vol. 9, pp. 158–178. Paris: Masson.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MENTZEN, B. F. (1977). *Acta Cryst.* B**33**, 2546–2549.

MENTZEN, B. F., PUAUX, J. P. & LOISELEUR, H. (1977). *Acta Cryst.* B**33**, 1848–1851.

MENTZEN, B. F., PUAUX, J. P. & SAUTEREAU, H. (1978). *Acta Cryst.* B**34**, 1846–1849.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, a Practical Guide*, pp. 454–458. New York: Macmillan.

TELLGREN, R., THOMAS, J. O. & OLOVSSON, I. (1977). *Acta Cryst.* B**33**, 3500–3504.

Acta Cryst. (1978). B**34**, 2711–2714

The Crystal Structure of Phenylmercury Cyanide–Phenanthroline

BY A. RUIZ-AMIL

Instituto de Química Inorgánica 'Elhuyar', Serrano 113, *Madrid* 6, *Spain*

AND S. MARTÍNEZ-CARRERA AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto 'Rocasolano', Serrano 119, *Madrid* 6, *Spain*

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The title compound, $C_{19}H_{13}N_3Hg$, crystallizes in the monoclinic system, space group $P2_1/a$, with unit-cell dimensions $a = 10.152$ (1), $b = 18.502$ (2), $c = 8.861$ (1) Å, $\beta = 99.59$ (1)° and $Z = 4$. The structure was solved by the heavy-atom method and successive Fourier syntheses and refined by the full-matrix least-squares method to a final R of 0·071 for 3355 observed reflections. The Hg atom presents fourfold coordination. The three rings of the phenanthroline are in the same plane, forming an angle of 89° with the plane of the phenyl group.

Introduction

It is well known that the Hg atoms in organomercury derivatives show very little tendency to increase their coordination number by interaction with donor molecules. However, the organomercury derivatives of the type Ph—Hg—C≡X (X = N, C—R; Ph = C_6H_5) should have an acceptor capacity intermediate between that of Ph_2Hg and that of the corresponding $(X{\equiv}C)_2Hg$. A strong donor ligand, such as 1,10-phenanthroline (phen), is capable of forming adducts with the organomercury derivative Ph—Hg—C≡N and with zinc, cadmium and mercury dicyanides (Cano Esquivel, Santos & Ballester, 1977).

In the present paper the structure of the complex of Ph—Hg—CN with phenanthroline is reported.

Experimental

Samples of phenylmercury cyanide–phenanthroline were provided by Drs M. Cano and A. Santos of the Instituto de Química Inorgánica 'Elhuyar' del CSIC, Madrid, Spain.

Colourless crystals were obtained by the reaction of phenylmercury cyanide with phenanthroline and by slow evaporation from a solution in methanol.

The single crystal (approximately 0·3 × 0·4 × 0·2 mm), which was used for both the determination of the lattice parameters and for the data collection, was mounted along the *b* axis.

The unit-cell parameters and the intensity data were measured on a Philips PW 1100 automatic diffractometer monochromated with a graphite crystal. The crystal data are summarized in Table 1. A θ–2θ scanning mode with Mo $K\alpha$ radiation was used to measure 4787 independent reflections with 2θ values below 30°; of these reflections, 3355 were considered as observed [$I > 2\sigma(I)$, where $\sigma(I)$ was determined from counting statistics]. The intensity data were reduced to structure factors and an absorption correction was applied with the program *ORABS* (Schwarzenbach, 1972) and the XRAY 70 system (Stewart, Kundell & Baldwin, 1970).

Structure determination and refinement

Structure-factor calculations based on the coordinates of the Hg atom, obtained from a three-dimensional Patterson function, gave an *R* index of 0·270. A subsequent Fourier map revealed six C atoms. The remaining thirteen C and the three N atoms of the molecule appeared in an electron-density map calculated from the phases of the Hg atom and the previous six C atoms. The final *R* value was 0·210 for all non-hydrogen atoms. This model was refined with isotropic thermal parameters by a full-matrix least-squares analysis of the 3355 observed reflections (unit weight was assigned for each reflection). At convergence the standard residual was $R = 0{\cdot}161$.

In the anisotropic refinement the weighting scheme $w = K/\sigma_1^2$, where $\sigma_1 = a + b|F_o|$ and $K = 0{\cdot}588$ with the coefficients given in Table 2 (Martinez-Ripoll & Cano, 1975), was used. The positions of the H atoms were calculated geometrically and included with fixed parameters, their isotropic thermal parameters being equal to those of the atoms to which they are bonded. Atomic scattering factors and the real and imaginary parts of the anomalous scattering factors for Hg were taken from *International Tables for X-ray Crystallography* (1974). The final *R* and R_w $[=|\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2}]$ indices were 0·071 and 0·084 respectively. A final difference synthesis had no electron density greater than 0·28 e Å^{-3}.

Final atomic coordinates are presented in Tables 3 and 4.* The perspective view in Fig. 1 shows the

Table 1. *Crystal data*

Molecular formula: $C_{19}H_{13}N_3Hg$
FW: 483·94
Crystal system: monoclinic
Space group: $P2_1/a$

$a = 10{\cdot}152\ (1)$ Å
$b = 18{\cdot}502\ (2)$
$c = 8{\cdot}861\ (1)$
$\beta = 99{\cdot}59\ (1)°$
$\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å

$D_x = 1{\cdot}95$ g cm^{-3}
$Z = 4$
$F(000) = 912$
$V = 1664{\cdot}65$ Å^3
$\mu = 95{\cdot}29$ cm^{-1}

Table 2. *Coefficients for the weighting scheme*

	a	*b*
$F_o \le$ 0·750	0	0
0·750 $\le F_o \le$ 7·270	1·776	0·853
7·270 $\le F_o \le$ 12·340	3·863	−0·175
12·340 $\le F_o \le$ 42·640	1·008	0·024
42·640 $\le F_o \le$ 118·000	−1·252	0·083

Table 3. *The positional parameters* ($\times 10^4$) *for non-hydrogen atoms*

Standard deviations are given in parentheses.

	x	*y*	*z*
Hg	3177·3 (4)	7075·1 (1)	2119·6 (4)
C(1)	2036 (11)	6867 (6)	3796 (12)
C(2)	2315 (15)	7203 (7)	5262 (15)
C(3)	1462 (17)	7043 (7)	6324 (14)
C(4)	382 (14)	6580 (11)	5985 (15)
C(5)	115 (13)	6300 (12)	4555 (15)
C(6)	952 (12)	6423 (9)	3464 (12)
C(7)	1648 (12)	5740 (7)	−436 (12)
C(8)	1305 (13)	5074 (7)	−1165 (14)
C(9)	2051 (13)	4480 (7)	−725 (14)
C(10)	3167 (11)	4541 (6)	439 (12)
C(11)	3981 (14)	3947 (6)	967 (16)
C(12)	5043 (13)	4017 (6)	2053 (15)
C(13)	5400 (10)	4707 (6)	2774 (13)
C(14)	6465 (12)	4799 (7)	3970 (15)
C(15)	6732 (11)	5461 (8)	4619 (14)
C(16)	5926 (13)	6040 (7)	4028 (14)
N(2)	4896 (9)	5986 (5)	2899 (10)
C(17)	4622 (9)	5320 (5)	2285 (11)
C(18)	3470 (9)	5241 (5)	1091 (10)
N(1)	2703 (8)	5823 (4)	654 (9)
C(19)	4138 (13)	7504 (6)	448 (14)
N(3)	4620 (17)	7755 (6)	−475 (15)

Table 4. *Positional parameters* ($\times 10^4$) *for hydrogen atoms*

The positional parameters were determined geometrically by the *H SEARCH* program

	x	*y*	*z*
H(2)	3190	7470	5540
H(3)	1610	7300	7380
H(4)	−180	6470	6790
H(5)	−670	5910	4290
H(6)	740	6200	2440
H(7)	1090	6180	−770
H(8)	490	5050	−1990
H(9)	181	4000	−1180
H(11)	3780	3460	470
H(12)	5610	3580	2450
H(14)	7050	4360	4360
H(15)	7530	5520	5480
H(16)	6120	6520	4490

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33493 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

essential relative configurational features of the molecule; the H atoms have been omitted for clarity. Each non-hydrogen atom is represented by an ellipsoid consistent with the anisotropic thermal parameters. Table 5 shows a list of bond angles and bond lengths together with their standard deviations.

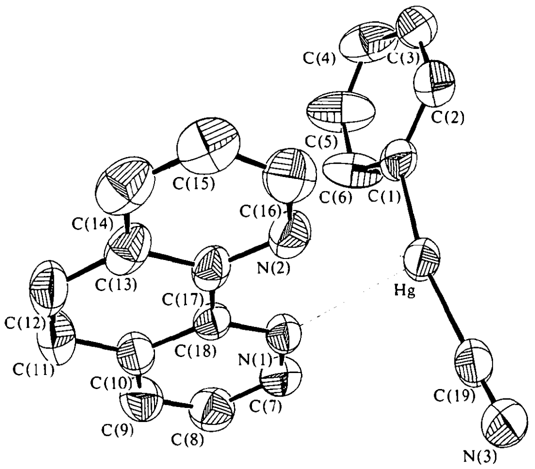

Fig. 1. *ORTEP* drawing of $C_{19}H_{13}N_3Hg$ (Johnson, 1965).

Table 5. *Bond distances* (Å) *and angles* (°)

Standard deviations are given in parentheses.

Hg–C(1)	2·067 (12)	C(10)–C(11)	1·408 (16)
Hg–C(19)	2·063 (14)	C(10)–C(18)	1·431 (13)
Hg–N(1)	2·660 (8)	C(11)–C(12)	1·327 (18)
Hg–N(2)	2·680 (9)	C(12)–C(13)	1·447 (16)
C(1)–C(2)	1·425 (16)	C(13)–C(14)	1·393 (15)
C(1)–C(6)	1·366 (18)	C(13)–C(17)	1·408 (14)
C(2)–C(3)	1·411 (22)	C(14)–C(15)	1·360 (20)
C(3)–C(4)	1·384 (22)	C(15)–C(16)	1·398 (19)
C(4)–C(5)	1·354 (20)	C(16)–N(2)	1·325 (15)
C(5)–C(6)	1·407 (19)	C(17)–C(18)	1·488 (12)
C(7)–C(8)	1·409 (18)	C(17)–N(2)	1·356 (12)
C(7)–N(1)	1·326 (13)	C(18)–N(1)	1·348 (12)
C(8)–C(9)	1·355 (18)	C(19)–N(3)	1·122 (21)
C(9)–C(10)	1·404 (15)		
C(1)–Hg–C(19)	167·5 (4)	C(9)–C(10)–C(11)	123 (1)
C(1)–Hg–N(2)	95·4 (4)	C(9)–C(10)–C(18)	118 (1)
N(2)–Hg–N(1)	61·8 (2)	C(11)–C(10)–C(18)	120 (1)
C(19)–Hg–N(1)	93·1 (4)	C(10)–C(11)–C(12)	122 (1)
Hg–C(1)–C(2)	121·6 (9)	C(11)–C(12)–C(13)	121 (1)
Hg–C(1)–C(6)	119·0 (8)	C(12)–C(13)–C(14)	123 (1)
Hg–N(2)–C(16)	122·3 (8)	C(12)–C(13)–C(17)	119 (1)
Hg–N(2)–C(17)	119·9 (6)	C(14)–C(13)–C(17)	117 (1)
Hg–N(1)–C(7)	120·9 (7)	C(13)–C(14)–C(15)	120 (1)
Hg–N(1)–C(18)	120·4 (6)	C(14)–C(15)–C(16)	118 (1)
Hg–C(19)–N(3)	177 (1)	C(15)–C(16)–N(2)	124 (1)
C(2)–C(1)–C(6)	119 (1)	C(16)–N(2)–C(17)	117 (1)
C(1)–C(2)–C(3)	118 (1)	C(13)–C(17)–C(18)	119 (1)
C(2)–C(3)–C(4)	122 (1)	N(2)–C(17)–C(18)	118 (1)
C(3)–C(4)–C(5)	118 (1)	C(13)–C(17)–N(2)	123 (1)
C(4)–C(5)–C(6)	122 (1)	C(10)–C(18)–C(17)	119 (1)
C(1) C(6) C(5)	120 (1)	C(10)–C(18)–N(1)	122 (1)
C(8)–C(7)–N(1)	123 (1)	C(17)–C(18)–N(1)	119 (1)
C(7)–C(8)–C(9)	120 (1)	C(7)–N(1)–C(18)	118 (1)
C(8)–C(9)–C(10)	119 (1)		

Discussion

The average values of the C–C and C–N bond distances and the C–C–C bond angle in the phenanthroline group (1·391, 1·338 Å and 119·7° respectively) agree well with those in the literature.

In the phenyl group, the average C–C bond distance and C–C–C bond angle are 1·391 Å and 120° respectively (also in agreement with the literature values).

The bond distance C(19)–N(3), 1·122 Å, in the cyanide group is comparable with the C–N distance, 1·13 Å, of phenylmercury cyanide (Gilli, Cano & García-Blanco, 1976) and other compounds of this type (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958, 1965). The angle Hg–C(19)–N(3), 177°, is very similar to the angle of 176° observed in phenylmercury cyanide.

Table 6. *Least-squares planes and dihedral angles*

(*a*) Equations of the planes

1 $-0{\cdot}5228X+0{\cdot}7837Y-0{\cdot}3353Z-8{\cdot}0696=0$
2 $0{\cdot}6949X+0{\cdot}2054Y-0{\cdot}6892Z-3{\cdot}6601=0$
3 $0{\cdot}6985X+0{\cdot}1897Y-0{\cdot}6900Z-3{\cdot}5302=0$
4 $0{\cdot}7242X+0{\cdot}1917Y-0{\cdot}6624Z-3{\cdot}7303=0$
5 $0{\cdot}7025X+0{\cdot}1986Y-0{\cdot}6834Z-3{\cdot}6188=0$

(*b*) Distances (Å) of atoms from the planes. Italicized values belong to atoms defining the planes.

	1	2	3	4	5
Hg	0·0472	−0·2237	−0·2892	−0·3383	−0·2382
C(1)	*−0·0099*	−2·2894	−2·3552	−2·4007	−2·3036
C(2)	*0·0117*	−2·9984	−3·0748	−3·0821	−3·0090
C(3)	*0·0034*	−4·4084	−4·4846	−4·4931	−4·4194
C(4)	*−0·0213*	−5·1076	−5·1739	−5·2192	−5·1224
C(5)	*0·0237*	−4·3942	−4·4515	−4·5338	−4·4131
C(6)	*−0·0075*	−2·9891	−3·0456	−3·1278	−3·0074
N(1)	−1·2002	*−0·0016*	−0·0308	−0·1264	*−0·0098*
C(7)	−0·5255	*−0·0087*	−0·0380	−0·1836	*−0·0283*
C(8)	−1·1521	*0·0094*	−0·0010	−0·1727	*−0·0072*
C(9)	−2·5051	*−0·0004*	0·0085	−0·1369	*−0·0022*
C(10)	−3·2599	*−0·0094*	*0·0004*	−0·0921	*0·0012*
C(11)	−4·6673	−0·0336	*−0·0043*	−0·0670	*−0·0073*
C(12)	−5·3634	−0·0227	*0·0070*	−0·0056	*0·0151*
C(13)	−4·7078	−0·0159	*−0·0058*	*0·0080*	*0·0187*
C(14)	−5·3982	−0·0728	−0·0629	*0·0032*	*−0·0264*
C(15)	−4·7206	−0·0902	−0·0993	*−0·0165*	*−0·0475*
C(16)	−3·3239	−0·0224	−0·0504	*0·0073*	*0·0045*
C(17)	−3·3009	0·0119	*0·0022*	*−0·0121*	*0·0311*
C(18)	−2·5464	*0·0107*	*0·0005*	−0·0683	*0·0174*
C(19)	0·5206	1·7949	1·7226	1·6662	1·7759
N(2)	−2·6129	0·0254	−0·0034	*0·0043*	*0·0407*
N(3)	0·8280	2·8810	2·8044	2·7428	2·8590

(*c*) Dihedral angles (°)

Planes		Planes	
1–2	88·356	2–4	2·403
1–3	89·149	3–4	2·162
1–4	89·638	2–5	0·668
1–5	88·997	3–5	0·671
2–3	0·919	4–5	1·776

The Hg atom is bonded to two N and two C atoms, presenting fourfold coordination. The coordination geometry is irregular, the angles around the Hg atom being very different: C(1)–Hg–C(19) = 167·5, C(19)–Hg–N(1) = 93·1, N(1)–Hg–N(2) = 61·8 and N(2)–Hg–C(1) = 95·4°.

The bond distance Hg–C(19), 2·063 Å, is shorter than that of 2·094 Å in Ph–Hg–CN, and it is considerably longer than the 2·015 Å in $Hg(CN)_2$ (Gilli, Cano & García-Blanco, 1976). The difference in these values is in agreement with the difference in IR stretching frequencies of the Hg–C(cyanide) bond observed for the title compound, Ph–Hg–CN and $Hg(CN)_2$; these IR frequencies are 395, 385 and 412 cm^{-1} respectively (Cano Esquivel, Santos & Ballester, 1977).

On the other hand, the bond distances Hg–C(1)-(phenyl) in the present structure (2·067 Å) and Ph–Hg–CN (2·051 Å) are comparable. However, the angle C(1)–Hg–C(19) (167·5°) is smaller than the angle C–Hg–C (177·5°, approximately linear) of Ph–Hg–CN (Gilli, Cano & García-Blanco, 1976).

Table 6 lists computed least-squares planes with their equations and the distances of various atoms from these planes. The three rings of phenanthroline are in the same plane, forming an angle of 89° with the plane of the phenyl group.

A projection of the structure along the *c* axis showing the arrangement of the molecules in the crystal is given in Fig. 2. The structure consists of discrete molecular units. There are no particularly short intermolecular contacts and the molecules are held together by van der Waals forces only. Intermolecular contacts of less than 3·8 Å, between non-hydrogen atoms, are listed in Table 7.

Table 7. *Intermolecular distances* (Å) *less than* 3·8 Å (*between non-hydrogen atoms*), *with their estimated standard deviations in parentheses*

Symmetry code

(i) $x, \quad y, \quad 1+z$
(ii) $x-1, \quad y, \quad z$
(iii) $1-x, \quad 1-y, \quad 1-z$
(iv) $1-x, \quad 1-y, \quad -z$
(v) $-x, \quad 1-y, \quad -z$
(vi) $x-\frac{1}{2}, \quad \frac{3}{2}-y, \quad z+1$
(vii) $x-\frac{1}{2}, \quad \frac{3}{2}-y, \quad z$

C(2)–C(16^{vii})	3·639 (18)	C(11)–C(18^{iv})	3·722 (18)
C(3)–C(17^{i})	3·721 (17)	C(11)–C(19^{iv})	3·637 (18)
C(3)–N(3^{vi})	3·667 (23)	C(11)–N(3^{iv})	3·512 (18)
C(4)–C(7^{i})	3·573 (18)	C(12)–C(16^{iii})	3·765 (20)
C(4)–C(8^{i})	3·773 (21)	C(12)–C(18^{iv})	3·650 (17)
C(4)–N(3^{vi})	3·572 (21)	C(12)–N(1^{iv})	3·593 (17)
C(5)–C(15^{ii})	3·778 (20)	C(12)–C(19^{iv})	3·761 (18)
C(9)–C(9^{vii})	3·582 (17)	C(12)–N(3^{iv})	3·604 (17)
C(7)–N(3^{vii})	3·460 (17)	C(13)–C(15^{iii})	3·434 (17)
C(8)–C(8^{v})	3·630 (20)	C(13)–C(16^{iii})	3·610 (18)
C(9)–C(14^{iv})	3·710 (19)	C(14)–C(15^{iii})	3·700 (18)
C(10)–C(13^{iv})	3·678 (16)	C(14)–C(16^{iii})	3·590 (20)
C(10)–C(17^{iv})	3·568 (15)	C(14)–N(2^{iii})	3·604 (17)
C(11)–N(2^{iv})	3·788 (18)	C(14)–C(17^{iii})	3·674 (17)
C(11)–C(17^{iv})	3·677 (18)	C(15)–C(17^{iii})	3·572 (17)

We wish to thank the 'Centro de Proceso de Datos' del Ministerio de Educación y Ciencia, Madrid, Spain, for the facilities provided for all calculations, which were performed with the help of the XRAY 70 system on a Univac 1108 computer.

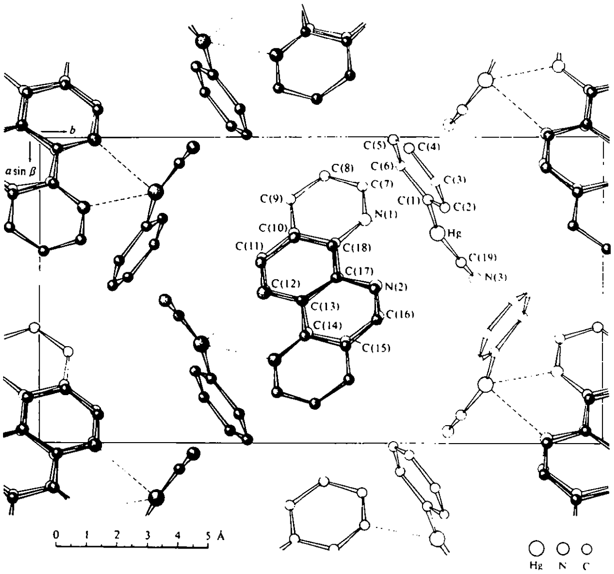

Fig. 2. The crystal structure viewed along the *c* axis. The intermolecular distances are listed in Table 7.

References

Cano Esquivel, M., Santos, A. & Ballester, L. (1977). *Inorg. Chim. Acta*, **21**, 41–46.

Cano Esquivel, M., Santos, A. & Ballester, L. (1977). *J. Inorg. Nucl. Chem.* **39**, 1153–1156.

Gilli, G., Cano, F. H. & García-Blanco, S. (1976). *Acta Cryst.* B**32**, 2680–2682.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 150. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Serrano 119, Madrid 6, Spain.

Schwarzenbach, D. (1972). A modification of the program *ORABS*, Zürich.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1958), *Supplement* (1965). Spec. Publ. Nos. 11 and 18. London: The Chemical Society.