Acta Cryst. (1978). B**34**, 3382–3384

The Adduct Bis(phenylethynyl)mercury–1,10-Phenanthroline

By E. Gutiérrez-Puebla[*] and A. Vegas[*]

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

and S. García-Blanco

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

(*Received* 20 *June* 1978; *accepted* 18 *July* 1978)

Abstract. $Hg(C_6H_5-C{\equiv}C)_2.C_{12}H_8N_2$, $M_r = 583{\cdot}06$, monoclinic, $P2_1/n$, $a = 22{\cdot}564\,(3)$, $b = 9{\cdot}577\,(5)$, $c = 10{\cdot}339\,(5)$ Å, $\beta = 96{\cdot}20\,(1)^\circ$, $Z = 4$, $D_c = 1{\cdot}73$ g cm^{-3}, μ(Mo $K\alpha$) = 71·0 cm^{-1}. The structure was refined by least-squares procedures to $R = 5{\cdot}9\%$ for all measured reflexions. The Hg atom is four-coordinated, with geometry far from tetrahedral. The two Hg–N distances and the C(11)–Hg–C(1) angle indicate a weak interaction between the phenanthroline molecule and the Hg-containing moiety.

Introduction. An IR study of several bisalkynyl derivatives of Hg with 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline has been reported by Cano-Esquivel, Santos-Macias & Ballester-Reventos (1977). For $Hg(C_6H_5-C{\equiv}C)_2.C_{12}H_8N_2$, the absence of some IR absorption bands prevented a clear understanding of the donor–acceptor interactions between the two moieties, so the crystal structure determination was undertaken.

A crystal 0·17 × 0·07 × 0·37 mm was chosen for the data collection on an automatic four-circle PW 1100 diffractometer with Mo $K\alpha$ radiation monochromated by graphite ($\lambda = 0{\cdot}7107$ Å). 4834 independent reflexions were measured in the $\omega/2\theta$ scan mode within $2 \leq \theta \leq 27^\circ$. 1231 reflexions for which $I \leq 2\sigma(I)$ were considered as unobserved. The systematic absences were $h0l$ for $h + l$ odd and $0k0$ for k odd. The intensities were corrected for absorption by *ORABS* (Schwarzenbach, 1972) and Lorentz and polarization corrections were applied.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Anomalous dispersion factors for Hg were those of Cromer & Liberman (1970).

The structure was solved by Patterson and Fourier syntheses allowing the location of all the non-hydrogen atoms. After anisotropic block full-matrix least-squares refinement, R was 5·9% for the measured reflexions. A difference synthesis with reflexions with $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1} showed 8 of the 18 H atoms, the remainder being located by geometry. Weights assigned by *PESOS* (Martínez-Ripoll & Cano, 1975) are given in Table 1. Further refinement with isotropic temperature factors for the H atoms gave a final $R = 4{\cdot}6\%$ and $R_w = 4{\cdot}9\%$ for observed reflexions only, where $R_w = (\sum w\Delta^2 F/\sum w|F_o|^2)^{1/2}$. A final difference synthesis showed no significant electron density. The final positional parameters are listed in Table 2.[*]

Table 1. *Weighting scheme applied in the least-squares refinement*

$w = K/\sigma^2$	$K = 0{\cdot}5263$	$\sigma = a + b\vert F_o\vert$
a	b	
4·2999	−0·0717	$24 > F_o$
2·2942	−0·0165	$53 > F_o > 24$
0·4018	0·0189	$F_o > 53$

Discussion. The interatomic distances and angles are listed in Table 3. The atoms are labelled as in Fig. 1. The Hg atom has four-coordination. The phenanthroline molecule is practically planar with an average deviation of 0·047 A from the best least-squares plane and forms an angle of 85·83° with the plane defined by Hg and the four C atoms of the two acetylenic groups which bond to Hg and to the phenyl groups in a non-linear fashion.

The Hg–C length is longer than in $Hg(CN)_2$ (Seccombe & Kennard, 1969) but shorter than in $(C_6H_5)Hg(CN)$ (Gilli, Cano & García-Blanco, 1976) and $(C_6H_5)Hg(CN).C_{12}H_8N_2$ (Ruiz-Amil, Martínez-Carrera & García-Blanco, 1978) in which both Hg and *sp*-hybridized C are involved. The C≡C length appears unaffected by coordination when compared with that obtained in other acetylenic hydrocarbons not bonded to metal atoms. The value of 1·180 (5) Å found in $C_{17}H_{13}N$ (Pérez-Salazar, Cano, Martinez-Carrera &

---

[*] Also at Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, Madrid, Spain.

[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33791 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^4$, *for* Hg $\times 10^5$, *for* H $\times 10^3$) *of* $Hg(C_6H_5{-}C{\equiv}C)_2.C_{12}H_8N_2$

E.s.d.'s are given in parentheses.

	x	*y*	*z*
Hg	50604 (1)	58752 (3)	29621 (4)
N(1)	5433 (4)	8300 (8)	2068 (8)
N(2)	4602 (3)	8263 (7)	3797 (7)
C(1)	5813 (4)	5675 (10)	4243 (11)
C(2)	6285 (4)	5617 (9)	4834 (10)
C(3)	6867 (4)	5663 (9)	5558 (8)
C(4)	7265 (5)	6702 (10)	5257 (10)
C(5)	7829 (4)	6778 (10)	5896 (11)
C(6)	8012 (4)	5806 (12)	6842 (10)
C(7)	7629 (5)	4778 (14)	7156 (10)
C(8)	7048 (5)	4688 (11)	6508 (10)
C(11)	4346 (5)	5553 (10)	1624 (11)
C(12)	3951 (5)	5224 (10)	841 (10)
C(13)	3445 (4)	4787 (10)	−57 (9)
C(14)	3339 (6)	5400 (12)	−1297 (11)
C(15)	2849 (7)	4969 (15)	−2132 (13)
C(16)	2487 (6)	3909 (16)	−1780 (12)
C(17)	2598 (5)	3286 (16)	−577 (14)
C(18)	3074 (5)	3734 (12)	306 (11)
C(20)	5862 (6)	8346 (12)	1269 (12)
C(21)	6013 (6)	9556 (14)	639 (13)
C(22)	5722 (5)	10757 (12)	815 (11)
C(23)	5274 (4)	10776 (9)	1677 (9)
C(24)	5149 (4)	9500 (8)	2281 (9)
C(25)	4715 (4)	9488 (8)	3215 (8)
C(26)	4226 (5)	8272 (11)	4671 (11)
C(27)	3934 (5)	9465 (12)	5074 (11)
C(28)	4040 (4)	10690 (11)	4476 (11)
C(29)	4437 (4)	10736 (9)	3511 (9)
C(30)	4548 (5)	11982 (10)	2834 (12)
C(31)	4956 (6)	12006 (10)	1960 (13)
H(4)	712 (3)	716 (8)	456 (8)
H(5)	815 (3)	730 (8)	573 (7)
H(6)	842 (4)	586 (12)	723 (10)
H(7)	777 (5)	423 (15)	787 (12)
H(8)	669 (4)	414 (11)	694 (9)
H(14)	357 (4)	597 (11)	−155 (9)
H(15)	297 (9)	526 (22)	−297 (20)
H(16)	210 (7)	369 (19)	−228 (17)
H(17)	233 (5)	298 (13)	−17 (12)
H(18)	317 (5)	335 (12)	130 (11)
H(20)	608 (5)	744 (13)	119 (11)
H(21)	630 (4)	957 (11)	4 (10)
H(22)	580 (4)	1167 (12)	24 (10)
H(26)	418 (4)	745 (12)	505 (10)
H(27)	368 (4)	939 (10)	590 (9)
H(28)	390 (5)	1161 (12)	489 (11)
H(30)	427 (4)	1273 (11)	305 (9)
H(31)	512 (5)	1279 (14)	136 (12)

García-Blanco, 1977) agrees with 1·18 (1) and 1·19 (1) Å in this work.

From the results reported in this work, only the C(11)–Hg–C(1) angle and the two Hg–N distances can be taken into account to explain the donor–acceptor interaction. The magnitudes may be compared with the respective values of 180° and 2·8–3·0 Å found in $(Ph)_2Hg(dmp)_2$ and in $(Ph)_2Hg(tmp)_2$ (Canty & Gatehouse, 1972). In this last case, the existence of

Table 3. *Bond lengths* (Å) *and angles* (°) *for* $Hg(C_6H_5{-}C{\equiv}C)_2.C_{12}H_8N_2$

Standard deviations	σ(Å)	σ(°)
Involving Hg	0·01	0·4
Involving H atoms	0·1	10·0
Involving C and N	0·02	1·0

Hg–C(1)	2·05	
–C(11)	2·03	
–N(1)	2·67	
–N(2)	2·69	
	(*X* = 0)	(*X* = 1)
C(*X*1)–C(*X*2)	1·17	1·18
C(*X*2)–C(*X*3)	1·44	1·45
C(*X*3)–C(*X*4)	1·40	1·41
–C(*X*8)	1·38	1·39
C(*X*4)–C(*X*5)	1·37	1·40
C(*X*5)–C(*X*6)	1·38	1·38
C(*X*6)–C(*X*7)	1·37	1·38
C(*X*7)–C(*X*8)	1·41	1·40
C(*X*4)–H(*X*4)	0·9	0·8
C(*X*5)–H(*X*5)	0·9	1·0
C(*X*6)–H(*X*6)	1·0	1·0
C(*X*7)–H(*X*7)	0·9	0·8
C(*X*8)–H(*X*8)	1·1	1·1

N(1)–C(20)	1·34
–C(24)	1·35
C(21)–C(20)	1·39
–C(22)	1·35
C(23)–C(22)	1·42
–C(24)	1·41
–C(31)	1·43
C(24)–C(25)	1·45
N(2)–C(25)	1·36
–C(26)	1·31
C(27)–C(26)	1·40
–C(28)	1·36
C(29)–C(25)	1·40
–C(28)	1·41
–C(30)	1·42
C(20)–H(20)	1·0
C(21)–H(21)	0·9
C(22)–H(22)	1·1
C(26)–H(26)	0·9
C(27)–H(27)	1·1
C(28)–H(28)	1·0
C(30)–H(30)	1·0
C(31)–H(31)	1·0

C(1)–Hg–C(11)	165·6	C(1)–Hg–N(2)	101·1
N(1)–Hg–N(2)	61·2	C(11)–Hg–N(1)	98·8
C(1)–Hg–N(1)	92·0	C(11)–Hg–N(2)	92·5

	(*X* = 0)	(*X* = 1)
Hg–C(*X*1)–C(*X*2)	170	173
C(*X*1)–C(*X*2)–C(*X*3)	176	176
C(*X*2)–C(*X*3)–C(*X*4)	119	121
C(*X*2)–C(*X*3)–C(*X*8)	122	119
C(*X*4)–C(*X*3)–C(*X*8)	119	120
C(*X*3)–C(*X*4)–C(*X*5)	121	119
C(*X*4)–C(*X*5)–C(*X*6)	120	121
C(*X*5)–C(*X*6)–C(*X*7)	120	120
C(*X*6)–C(*X*7)–C(*X*8)	121	121
C(*X*7)–C(*X*8)–C(*X*3)	119	119
C(*X*3)–C(*X*4)–H(4)	111	121
C(*X*5)	128	120
C(*X*4)–C(*X*5)–H(5)	131	100
C(*X*6)	109	133
C(*X*5)–C(*X*6)–H(6)	117	122
C(*X*7)	123	117
C(*X*6)–C(*X*7)–H(7)	115	123
C(*X*8)	124	109
C(*X*3)–C(*X*8)–H(8)	116	116
C(*X*7)	122	125

C(21)–C(20)–N(1)	123	C(20)–N(1)–Hg	121
C(20)–C(21)–C(22)	120	C(24)–N(1)–Hg	121
C(21)–C(22)–C(23)	119	C(25)–N(2)–C(26)	118
C(22)–C(23)–C(24)	117	C(25)–N(2)–Hg	120
C(22)–C(23)–C(31)	123	C(26)–N(2)–Hg	122
C(24)–C(23)–C(31)	120	H(20)–C(20)–C(21)	122
C(23)–C(24)–C(25)	119	H(20)–C(20)–N(1)	115
C(23)–C(24)–N(1)	123	H(21)–C(21)–C(20)	123
C(25)–C(24)–N(1)	118	H(21)–C(21)–C(22)	117
C(24)–C(25)–C(29)	119	H(22)–C(22)–C(21)	120
C(24)–C(25)–N(2)	119	H(22)–C(22)–C(23)	121
C(29)–C(25)–N(2)	122	H(26)–C(26)–C(27)	121

Table 3 (*cont.*)

C(27)–C(26)–N(2)	125	H(26)–C(26)–N(2)	115
C(26)–C(27)–C(28)	117	H(27)–C(27)–C(26)	119
C(27)–C(28)–C(29)	120	H(27)–C(27)–C(28)	123
C(25)–C(29)–C(28)	118	H(28)–C(28)–C(27)	117
C(25)–C(29)–C(30)	120	H(28)–C(28)–C(29)	121
C(28)–C(29)–C(30)	122	H(30)–C(30)–C(29)	115
C(29)–C(30)–C(31)	121	H(30)–C(30)–C(31)	129
C(23)–C(31)–C(30)	121	H(31)–C(31)–C(23)	104
C(20)–N(1)–C(24)	118	H(31)–C(31)–C(30)	135

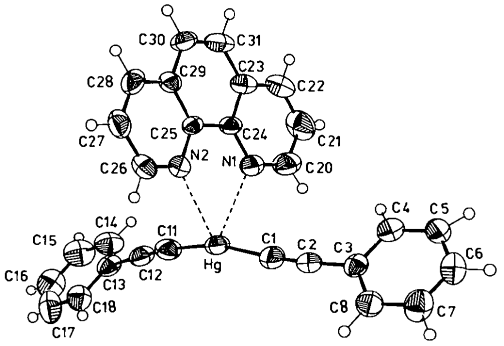

Fig. 1. *ORTEP* drawing of $Hg(C_6H_5-C\equiv C)_2.C_{12}H_8N_2$ (Johnson, 1965). The labels of the H atoms have been omitted for clarity: their numbering is that of the C atoms to which they are bonded.

interaction cannot be inferred because of the lack of precision in the Hg–N length. However, in our study, a shorter Hg–N distance (2·68 Å) corresponds to a smaller value in the C–Hg–C angle (165°) indicating a weak but clear donor–acceptor interaction between the two moieties.

Most of the calculations were performed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of CPD del MEC for the use of the 1108 Univac computer.

References

Cano-Esquivel, M., Santos-Macias, A. & Ballester-Reventos, L. (1977). *An. Quím.* **73**, 1051–1056.

Canty, A. J. & Gatehouse, B. M. (1972). *Acta Cryst.* B**28**, 1872–1878.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

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. 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.

Pérez-Salazar, A., Cano, F. H., Martínez-Carrera, S. & García-Blanco, S. (1977). *Acta Cryst.* B**33**, 2276–2278.

Ruiz-Amil, A., Martínez-Carrera, S. & García-Blanco, S. (1978). *Acta Cryst.* B**34**, 2711–2714.

Schwarzenbach, D. (1972). *ORABS* program. Zürich.

Seccombe, R. C. & Kennard, C. H. L. (1969). *J. Organomet. Chem.* **18**, 243–247.

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

Acta Cryst. (1978). B**34**, 3384–3387

(+)-*trans*-*N'*,*O*-Cyclohexylidene-*N*-(2-hydroxycyclohexyl)guanidinium *p*-Toluenesulfonate

By Hikaru Nakamura and Yoichi Iitaka

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, *Japan*

(*Received* 22 *March* 1978; *accepted* 16 *May* 1978)

Abstract. $C_{13}H_{24}N_3O^+.C_7H_7O_3S^-$, FW 409·5, monoclinic, $P2_1$, $Z = 2$, $a = 10{\cdot}130\,(5)$, $b = 10{\cdot}593\,(5)$, $c = 10{\cdot}011\,(5)$ Å, $\beta = 100{\cdot}22\,(4)°$, $V = 1057{\cdot}2$ Å^3, $D_x = 1{\cdot}287$ g cm^{-3}. $R = 0{\cdot}04$ for 1988 observed structure factors. The complex is formed by the hydrogen bonds between the guanidinium and sulfonate groups which form a helical structure around the screw diad.

Introduction. In the course of synthetic studies on dihydrostreptomycin it became necessary to establish the structure of the product obtained by the reaction of (+)-*trans*-2-guanidinocyclohexanol with 1,1-dimethoxycyclohexane in order to clarify the unusual reaction of the *trans*-diequatorial guanidino and hydroxyl groups in the streptidine moiety (Takagi, Kawashima, Tsuchiya, Sano & Umezawa, 1976). The guanidino compound was converted to its *p*-toluenesulfonic acid salt in order to make the compound soluble in organic solvents.

Crystals of the *p*-toluenesulfonate salt grown from ethanol solutions were colorless, transparent prisms elongated along the *b* axis. The lattice constants were