

## Crystal and Molecular Structure of Dithiocyanato(triphenylarsine)mercury(II)

JOSEPH HUBERT, ANDRÉ L. BEAUCHAMP, AND ROLAND RIVEST

Département de Chimie, Université de Montréal, C.P. 6210, Montréal, Québec H3C 3V1

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The crystal and molecular structure of dithiocyanato(triphenylarsine)mercury(II) has been determined from X-ray diffraction data. The crystals are monoclinic, space group  $P2_1/c$ , with  $a = 10.290(7)$ ,  $b = 21.199(23)$ ,  $c = 10.719(7)$  Å,  $\beta = 112.00(2)^\circ$ , and  $Z = 4$ . The structure has been solved by the heavy-atom method and refined by block-diagonal least-squares calculations. The agreement factor  $R$  obtained for 2607 'observed' reflections is 0.030. The crystal consists of single molecules. The 'characteristic' coordination number of mercury is three, with two sulfur and one arsenic atoms at the apexes of a triangle. The nitrogen atoms of the thiocyanate groups are at 2.67 and 2.74 Å from the adjoining mercury atoms and therefore link the different molecules together.

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Les structures cristalline et moléculaire du dithiocyanato(triphénylarsine)mercure(II) ont été déterminées par diffraction de rayons X. Les cristaux sont monocliniques, de groupe d'espace  $P2_1/c$  et de paramètres de maille:  $a = 10.290(7)$ ,  $b = 21.199(23)$ ,  $c = 10.719(7)$  Å,  $\beta = 112.00(2)^\circ$  et  $Z = 4$ . La structure a été résolue par la méthode de l'atome lourd et affinée par moindres carrés (matrice à blocs diagonaux). Le facteur d'accord  $R$  obtenu pour les 2607 réflexions 'observées' est de 0.030. Le cristal est constitué de molécules monomères. Le nombre de coordination 'caractéristique' du mercure est de trois, et la coordination est assurée par deux atomes de soufre des thiocyanates et l'atome d'arsenic. Les atomes d'azote des groupements thiocyanates se trouvent à des distances de 2.67 et 2.74 Å d'atomes de mercure voisins et relient les diverses molécules entre elles.

### Introduction

Reactions of mercuric halides with monodentate ligands often lead to dimeric halide-bridged 1:1 complexes in which mercury has a tetrahedral coordination. Several examples of similar thiocyanate complexes are also known. On the basis of preliminary X-ray results (1), we recently reported that mercury is three-coordinated in  $\text{Hg}(\text{SCN})_2 \cdot \text{As}(\text{C}_6\text{H}_5)_3$ . The complete crystal structure analysis on that compound is described in the present paper.

### Experimental Section

#### Crystal data

$\text{C}_{20}\text{H}_{15}\text{AsHgN}_2\text{S}_2$  f.w. = 622.99  
Monoclinic,  $P2_1/c$ ,  $a = 10.290(7)$ ,  $b = 21.199(23)$ ,  $c = 10.719(7)$  Å,  $\beta = 112.00(2)^\circ$ ,  $V = 2168$  Å<sup>3</sup>,  $\rho_o = 1.90(1)$ ,  $Z = 4$ ,  $\rho_c = 1.909$  g cm<sup>-3</sup>,  $\mu = 90.72$  cm<sup>-1</sup> (23 °C;  $\text{MoK}\alpha$ ,  $\lambda = 0.71069$  Å).

The complex was prepared by reaction of 1.9 mmol of  $\text{Hg}(\text{SCN})_2$  and 2.1 mmol of  $\text{As}(\text{C}_6\text{H}_5)_3$  in 125 ml of ethanol. By slow evaporation of the solution, well-shaped crystals were obtained.

The set of data used to solve the structure (1) was collected with  $\text{CuK}\alpha$  radiation on a relatively large crystal of complicated geometry. Refined values of some temperature factors were high, presumably because of the high absorption coefficient for copper radiation and problems

in describing the crystal faces. For those reasons, another crystal of simpler geometry was selected and a new set of data was collected with  $\text{MoK}\alpha$  radiation. This crystal had dimensions  $0.35 \times 0.12 \times 0.20$  mm perpendicular to [011], [010], and [110] respectively. The crystal was mounted on a Picker FACS-1 automatic four-circle diffractometer equipped with a graphite monochromator. The lattice parameters were calculated by least-squares refinement (2) on the setting angles of 12  $\text{MoK}\alpha$  reflections ( $12 < 2\theta \leq 30^\circ$ ).

A total of 3046  $\text{MoK}\alpha$  reflections ( $hkl$  and  $h\bar{k}l$ ) were measured up to a  $2\theta$  value of  $48^\circ$ . The intensities were collected by the  $\theta/2\theta$  scan technique at a constant speed of  $1^\circ$  per min. The scan range was  $1.75^\circ$  symmetrically disposed with respect to the calculated peak center and backgrounds were counted for 20 s on each side of the scanning range. During data collection, three standard reflections were measured every 50 reflections as a test on crystal and instrument stability. No systematic changes were observed and the intensity fluctuations were within  $\pm 5\%$ .

Integrated intensities  $I = N - (B_1 + B_2) \times T/2t$  were calculated and standard deviations  $\sigma(I)$  were estimated according to the formula

$$\sigma^2(I) = N + 0.25 \times (T/t)^2 \times (B_1 + B_2) + (cI)^2$$

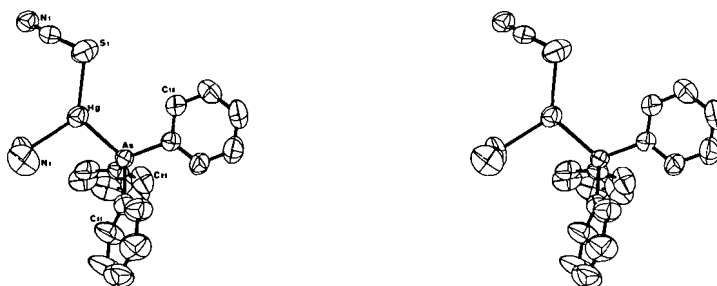
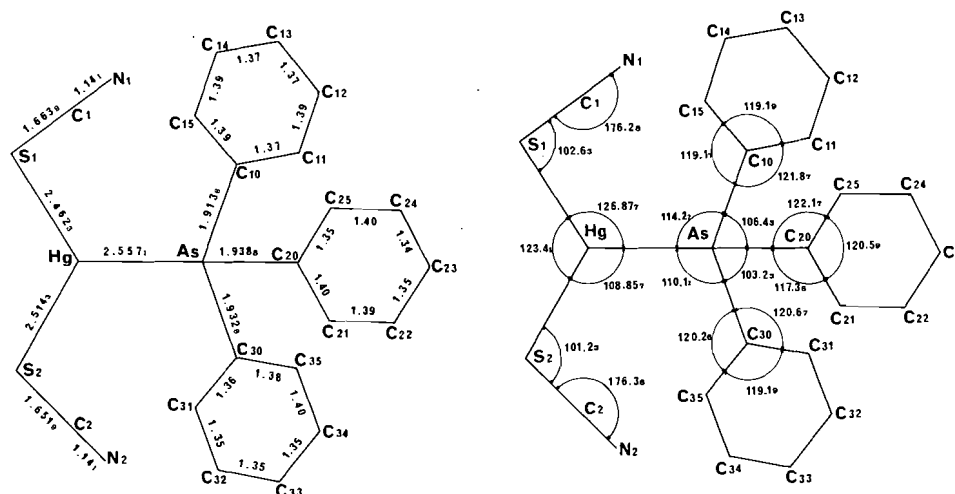
where  $N$  is the total counts from scanning for  $T$  s,  $B_1$  and  $B_2$  are the background counts measured during  $t$  s each, and  $c$ , the instability factor, is 0.05.

A set of 2607 reflections for which  $I \geq 2.5\sigma(I)$  were considered as observed and later used in least-squares refinement.

TABLE I. Final fractional coordinates ( $\times 10^4$ ), and thermal parameters ( $\times 10^3$ ) in  $\text{Hg}(\text{SCN})_2 \cdot \text{As}(\text{C}_6\text{H}_5)_3^a$

Atom	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Hg	4162.9(4)	506.5(2)	2148.1(3)	76.4(2)	67.8(2)	56.3(2)	3.1(2)	25.7(1)	3.8(1)
As	2588.3(7)	1421.9(4)	909.9(7)	54.2(4)	58.5(4)	47.6(4)	-6.0(3)	20.1(3)	0.1(3)
S(1)	6604(2)	575(1)	3757(3)	60(1)	155(2)	108(1)	-10(1)	24(1)	64(1)
S(2)	2993(2)	-514(1)	1146(2)	109(1)	72(1)	118(1)	-19(1)	79(1)	-15(1)
C(1)	6613(7)	91(3)	4980(7)	44(3)	74(5)	61(4)	-1(3)	15(3)	-5(3)
N(1)	6698(7)	-233(3)	5851(6)	75(4)	87(6)	55(3)	-2(3)	20(3)	7(3)
N(2)	4427(8)	-824(4)	-523(7)	100(5)	124(6)	87(5)	-17(5)	57(4)	-24(5)
C(2)	3842(8)	-678(3)	148(7)	59(4)	71(5)	60(4)	-10(3)	18(3)	2(3)
C(10)	3562(7)	2199(3)	997(6)	55(4)	61(4)	51(3)	-0(3)	22(3)	-0(3)
C(11)	3125(9)	2632(4)	-32(7)	101(6)	71(5)	55(4)	-14(4)	24(4)	6(3)
C(12)	3853(11)	3196(4)	61(9)	137(8)	70(5)	76(5)	-18(5)	45(5)	3(4)
C(13)	5024(11)	3315(4)	1182(10)	130(8)	66(5)	111(7)	-31(5)	61(6)	-5(5)
C(14)	5475(10)	2889(4)	2219(10)	94(7)	84(6)	99(6)	-25(5)	23(5)	-15(5)
C(15)	4760(8)	2323(4)	2116(8)	69(5)	71(5)	76(5)	-4(4)	22(4)	6(4)
C(20)	1037(7)	1611(4)	1458(7)	58(4)	81(5)	55(4)	-8(3)	22(3)	-10(3)
C(21)	524(9)	1120(5)	2013(8)	67(5)	132(8)	61(5)	-2(5)	28(4)	10(5)
C(22)	-635(10)	1232(7)	2342(10)	79(6)	198(13)	93(7)	-6(7)	51(5)	20(7)
C(23)	-1251(11)	1805(7)	2148(12)	78(7)	207(14)	129(9)	-4(8)	61(6)	-46(9)
C(24)	-729(12)	2279(6)	1647(16)	103(8)	128(10)	200(13)	8(7)	79(9)	-53(9)
C(25)	427(10)	2189(4)	1274(12)	92(7)	86(6)	145(9)	-0(5)	61(7)	-17(6)
C(30)	1671(8)	1222(3)	-977(7)	74(5)	64(4)	55(4)	-6(3)	23(3)	-2(3)
C(31)	291(10)	1051(6)	-1494(9)	92(7)	173(11)	70(5)	-64(7)	34(5)	-28(6)
C(32)	-329(14)	874(8)	-2797(10)	128(9)	242(16)	72(6)	-115(11)	30(6)	-55(8)
C(33)	385(13)	853(6)	-3624(9)	143(10)	136(9)	57(5)	-47(8)	21(5)	-22(6)
C(34)	1748(12)	1028(5)	-3148(9)	132(8)	127(9)	59(5)	-6(7)	47(5)	-21(5)
C(35)	2423(9)	1223(5)	-1809(8)	79(5)	114(7)	63(5)	-3(5)	26(4)	-2(4)

<sup>a</sup>The expression for the anisotropic temperature factor is  $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$ .

FIG. 1. The molecular structure of  $\text{Hg}(\text{SCN})_2 \cdot \text{As}(\text{C}_6\text{H}_5)_3$ .FIG. 2. Bond lengths and angles in  $\text{Hg}(\text{SCN})_2 \cdot \text{As}(\text{C}_6\text{H}_5)_3$ . The values for  $\text{Hg}-\text{As}-\text{C}(20)$  and  $\text{C}(10)-\text{As}-\text{C}(30)$  are  $115.7(2)$  and  $106.3(3)^\circ$  respectively. Standard deviations are given as subscripts.

An absorption correction based on the crystal faces was applied.<sup>1</sup> The calculated transmission factor ranged from 0.16 to 0.37. The usual corrections for polarization and Lorentz effects were finally applied. During the absorption correction the coefficient  $dA^*/d\mu$  was evaluated for secondary extinction correction (3).

Mercury was located from an origin-removed sharpened Patterson map. After two cycles of least-squares refinement, a difference Fourier map revealed all nonhydrogen atoms. Block-diagonal least-squares refinement with unit weights, of the scale factor, the positional and individual isotropic temperature factors led to  $R = (\sum||F_o| - |F_c||) / \sum|F_o| = 0.089$ . The  $R$  factor reduced to 0.033 by introducing and refining anisotropic temperature factors and a secondary extinction coefficient (4). At this stage, the phenyl hydrogen atoms were placed at the

<sup>1</sup>The computer programs used were locally modified versions of the following: F. R. Ahmed and C. P. Huber, NRC-2 (data reduction); F. R. Ahmed and P. Singh, NRC-3 (absorption correction); R. J. Doedens and J. A. Ibers, NUCLS (least-squares refinement with block diagonal option); A. Zalkin, FORDAP (Fourier, Patterson) and C. K. Johnson, ORTEP (drawings).

calculated position ( $\text{C}-\text{H} = 0.95 \text{ \AA}$ ) and were included in structure factor calculations with fixed isotropic factors ( $B = 7 \text{ \AA}^2$ ). The function minimized in least-squares refinements was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2$  and  $\sigma = a + bF_o + cF_o^2$  (5). After three additional least-squares cycles the final  $R$  and  $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$  were respectively 0.030 and 0.040. The values of  $a$ ,  $b$ , and  $c$  were adjusted in order to minimize the variations of the  $\sum w\Delta F^2$  function vs.  $F_o$  (final values  $a = 5.38$ ,  $b = -0.08$ , and  $c = 0.0006$ ). The standard deviation of an observation of unit weight was 1.65. In the final least-squares cycle the highest and the average shifts were respectively  $0.6\sigma$  and  $0.4\sigma$ .

On the final difference Fourier map, the highest peaks had an intensity of  $+0.6 e/\text{\AA}^3$  and were located at less than  $1 \text{ \AA}$  from the mercury atom.

The scattering factors used for the nonhydrogen atoms were taken from Cromer and Waber (6), the scattering curve of hydrogen was from Stewart *et al.* (7), and the anomalous dispersion coefficients for the heavy atoms (Hg, As, S) from Cromer (8).

The final positional and thermal parameters are given in Table 1. The carbon atoms belonging to phenyl rings are identified with labels of the type  $\text{C}(ij)$ , where  $i$  is the

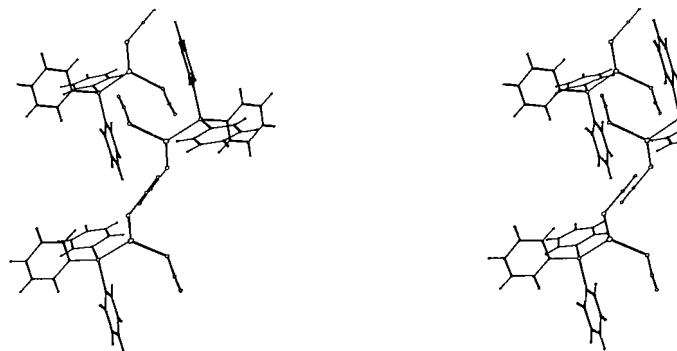


FIG. 3. Stereoscopic drawings of the molecular packing in  $\text{Hg}(\text{SCN})_2 \cdot \text{As}(\text{C}_6\text{H}_5)_3$ .

TABLE 2. Selected intermolecular distances and angles

Atoms	Distance (Å)	Bonds	Angle (deg)
Hg-N(1) <sup>a</sup>	2.673(7)	As-Hg-N(1) <sup>a</sup>	104.2(2)
Hg-N(2) <sup>b</sup>	2.736(9)	As-Hg-N(2) <sup>b</sup>	82.3(2)
N(1)-H(12) <sup>c</sup>	2.68	S(1)-Hg-N(1) <sup>a</sup>	90.5(2)
N(1)-H(21) <sup>a</sup>	2.74	S(1)-Hg-N(2) <sup>b</sup>	77.6(2)
N(2)-H(35) <sup>b</sup>	2.70	S(2)-Hg-N(1) <sup>a</sup>	84.6(2)
		S(2)-Hg-N(2) <sup>b</sup>	102.9(2)
		N(1) <sup>a</sup> -Hg-N(2) <sup>b</sup>	168.1(3)

<sup>a</sup>1 - x, -y, 1 - z.

<sup>b</sup>1 - x, -y, -z.

<sup>c</sup>1 - x, -½ + y, ½ - z.

ring number and *j* corresponds to sequential numbering of the ring vertices with *j* = 0 for the atom bound to arsenic. The structure factor table is available.<sup>2</sup>

### Results and Discussion

The crystal consists of single molecules as shown in Fig. 1. Intramolecular bond lengths and angles are given in Fig. 2.

#### Molecular Structure

Mercury forms strong bonds to one arsenic and two sulfur atoms and its so-called 'characteristic' coordination number (9) is three. The Hg-S bonds are significantly different (2.514(3) and 2.462(3) Å) but still in the range observed for  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{Hg}(\text{SCN})_3]$ , another (12) three-coordinate mercury complex. Mercury is shifted toward N(1) of another molecule and is only 0.14 Å above the plane defined by As, S(1), and S(2). Intramolecular nonbonded interactions with the phenyl rings of triphenylarsine could

<sup>2</sup>Complete set of tabular data is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

be partly responsible for the angular distortions around the mercury atom. S(1) lies close to the plane of ring (1) and increasing the S(1)-Hg-As angle to 126.9° probably helps to minimize S(1)... H(15) (3.3 Å) repulsions. Ring (3) which is closest to S(2), is approximately perpendicular to the coordination plane and S(2)-Hg-As can reduce to 108.9° before appreciable S(2)... C(31) (3.04 Å) repulsions are experienced. The S(1)-Hg-S(2) angle is normal at 123.4°.

As commonly observed in mercury-thiocyanate compounds, the SCN groups are linear, the Hg-S-C angles are close to 100°, and the S-C and C-N bond lengths are 1.65-1.66 and 1.14 Å respectively.

The three As-C bonds (1.91-1.93 Å) in triphenylarsine are equal within experimental errors and the expected tetrahedral geometry is observed with some distortions. The phenyl rings are planar within 1σ. Their C-C distances and bond angles range from 1.34 to 1.40 Å (average = 1.37(1) Å) and 118.5 to 121.5° (average = 120(1)°) respectively.

### *Molecular Packing*

The molecules are linked in infinite zigzag chains along the *c* direction by weakly bridging SCN groups (Fig. 3).

The Hg–N distances (2.67 and 2.74 Å, Table 2), although shorter than the sum of the van der Waals radii (3.0 Å), correspond to the weak intermolecular contacts found in  $\text{Hg}(\text{SCN})_2$  (10) and  $\text{Hg}(\text{CN})_2$  (11). The type of bridging reported for  $[\text{Hg}(\text{SCN})_3]^-$  ions (12), though geometrically similar, involves much greater participation of the terminal nitrogens, with Hg–N distances of 2.40 Å.

When the two Hg–N contacts are taken into account, the effective coordination of mercury corresponds to a very distorted trigonal bipyramid (Table 2).

The chains are held together by normal van der Waals contacts.

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