present structure from 108.0 to 112.1° (Table III), are in the middle of the range 106.0–114.3° found for the other structures[1-4] containing this heterocycle and are very close to the tetrahedral angle. The range of C–O–C angles found previously[1-4] was 112.3–114.6°; one of our two C–O–C angles (113.0, 116.4°) falls slightly outside these limits. It is satisfying to note that the average C–O and C–C bond distances found here are precisely the same, 1.430 and 1.495 Å, respectively, as the respective averages of 36 determinations of the C–O distance and 18 determinations of the C–C distance in the previous four structures,[1-4] and that the individual values all fall within three standard deviations of these averages. The mean C–H bond distance, 0.98 Å, is as usual shorter than the true internuclear separation,[11] presumably about 1.09 Å, because of the bias of the electron density of the hydrogen atoms toward the bonding region. Some systematic errors in bond distances may occur because of thermal motion, but no correction for these was attempted.

The structure contains no atoms with unusually large thermal amplitudes (Table II and Figure 1). The oxygen atoms of the hexahydrated magnesium unit exhibit their largest components of thermal vibration in directions approximately perpendicular to the Mg–O bonds. The cation itself shows the smallest thermal amplitudes and is nearly isotropic. In contrast to those structures where the heterocycle functions as a tetradentate ligand,[1-4] the ring oxygens show considerable anisotropy.

Acknowledgment. We thank P. P. North for assistance with the experimental data.

Registry No. $Mg(H_2O)_6Cl_2 \cdot C_8H_{16}O_4$, 53993-08-1.

Supplementary Material Available. A listing of calculated and observed structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40465C.

References and Notes

(1) F. P. van Remoortere and F. P. Boer, *Inorg. Chem.*, **13**, 2071 (1974).

(2) F. P. Boer, M. A. Neuman, F. P. van Remoortere, and E. C. Steiner, *Inorg. Chem.*, **13**, 2826 (1974).

(3) F. P. van Remoortere, E. C. Steiner, and F. P. Boer, *Acta Crystallogr.*, in press.

(4) P. P. North, E. C. Steiner, F. P. van Remoortere, and F. P. Boer, submitted to *Acta Crystallogr.*

(5) H. W. Rinn, F. P. Boer, and E. C. Steiner, unpublished results.

(6) P. A. Agron and W. R. Busing, ORNL-4437, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1969, p 117.

(7) M. A. Neuman, "Fournier Summation Program for the IBM 1130 Computer," Dow Internal Reports SL 203078, 203082, 203083, 203084.

(8) F. P. van Remoortere and F. P. Boer, "A FORTRAN Crystallographic Least-Squares Program (FXLS) for the IBM 1130," Dow Internal Report FL 314.

(9) Atomic scattering factors were obtained from the "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 201 ff.

(10) (a) J. Gvildys, "A FORTRAN Crystallographic Least-Squares Refinement Program," Program Library 14E7043, Argonne National Laboratory, Argonne, Ill.; (b) J. Gvildys, "Two- and Three-Dimensional Fourier Summation Program," Program Library B-149, Argonne National Laboratory, Argonne, Ill.; (c) C. K. Johnson, "ORTEP: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.; (d) J. Gvildys, "ANL-FFE, FORTRAN Crystallographic Function and Error Program," Program Library B115, Argonne National Laboratory, Argonne, Ill.

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); hydrogen scattering factors were obtained from this source.

(12) Supplementary material.

(13) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 60 ff.

(14) R. G. Delaplane and J. A. Ibers, *J. Chem. Phys.*, **45**, 3451 (1966).

(15) For $ax + by + cz = D$, $a^2 + b^2 + c^2 = 1$ and x', y', and z' are a set of orthogonal axes in Å coincident with a, b, and c^*. D is the perpendicular distance from the plane to the origin.

(16) Reference 13, Appendix.

(17) The definition follows that suggested by W. Klyne and V. Prelog, *Experientia*, **16**, 521 (1960).

(18) A reviewer pointed out that the correct expression for the Lorentz–polarization factor in the case of the Picker diffractometer where diffractions at the monochromator and sample occur in planes perpendicular to one another should be $(Lp)^{-1} = (\sin 2\theta)(1 + \cos^2 2\theta_m)/(\cos^2 2\theta_m + \cos^2 2\theta)$. The errors introduced in the structure factors are negligible for low 2θ values, 0.5% at $2\theta = 38°$ and 1% at $2\theta_{max} = 54.9°$.

Contribution from the Department of Chemistry,
University of Montreal, C.P. 6210, Montreal, Quebec, Canada H3C 3V1

Crystal Structure of Tetraphenylphosphonium Trithiocyanatomercurate(II)

AMAR SAKHRI and ANDRE L. BEAUCHAMP*

Received August 13, 1974 AIC405727

$[(C_6H_5)_4P][Hg(SCN)_3]$ crystallizes in the space group $P2_1/c$ with unit-cell parameters a = 11.574 (4) Å, b = 20.014 (8) Å, c = 12.144 (4) Å, β = 103.56 (3)°, and Z = 4. The structure was refined on 1899 independent observed reflections to an R factor of 0.039. The anionic part of the compound can be described as infinite chains of $[Hg(SCN)_3]^-$ ions, in which one of the SCN groups is bridging. The Hg–S bonds of the two nonbridging groups are of reasonable lengths (2.46 Å) for a basically three-coordinate species. For the bridging group, the Hg–S bond is much longer (2.59 Å) and nitrogen is close (2.40 Å) to the mercury atom of the next ion. As a result of this interionic Hg···N interaction, the metal is displaced by 0.45 Å from the trigonal plane toward the nitrogen atom and its overall coordination corresponds to a flattened tetrahedron of one nitrogen and three sulfur atoms. The $[[Hg(SCN)_3]^-]_n$ chains run parallel to the c axis and the space between the chains is filled with $[(C_6H_5)_4P]^+$ cations.

Introduction

Compounds of the type $MHgX_3$ are known for a variety of monovalent cations (M) and halide or pseudohalide anions (X).[1,2] Crystallographic studies have shown that chloro compounds with small cations (Na,[3] NH_4,[4] and Cs)[5] are double salts in which linear $HgCl_2$ molecules and chloride ions are packed in such a way that an approximate octahedral geometry is achieved around mercury. According to Zhdanov and Sanadze,[6] $KHg(SCN)_3$ and $NH_4Hg(SCN)_3$ are double salts as well. In those cases, the $Hg(SCN)_2$ molecule is bent at mercury and the metal is surrounded by a very distorted tetrahedron of sulfur atoms. Trigonal $[HgX_3]^-$ ions have been observed in crystals of $[(CH_3)_4N][HgBr_3]$[7] and $[(CH_3)_3S][HgI_3]$.[8]

The existence of discrete trihalogenomercurate anions in presence of larger cations prompted us to investigate similar systems with thiocyanate ions. The structure of the $[(C_6H_5)_4P]^+$ salt is reported here.

Experimental Section

Preparation. When KSCN and $[(C_6H_5)_4P]Cl$ both dissolved in

Table I. Refined Atomic Coordinates (×10^4) and Temperature Factors (×10^3)[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	4,274 (1)	2322 (1)	2191 (1)	72.1 (4)	73.7 (3)	48.4 (6)	−10.3 (2)	10.6 (3)	−6.2 (3)
S(1)	3,071 (3)	3185 (2)	3061 (3)	73 (3)	62 (3)	49 (2)	2 (1)	10 (1)	3 (1)
S(2)	6,281 (4)	2702 (3)	2130 (4)	68 (2)	111 (4)	87 (3)	−9 (1)	13 (1)	−18 (1)
S(3)	3,556 (4)	1221 (2)	2640 (4)	95 (3)	65 (3)	65 (3)	−3 (1)	1 (1)	5 (1)
P	8,486 (3)	454 (2)	2514 (3)	43 (2)	46 (2)	42 (2)	0 (1)	4 (1)	−0 (1)
C(1)	3,271 (12)	2843 (7)	4322 (12)	52 (9)	49 (12)	49 (10)	7 (3)	9 (4)	1 (4)
C(2)	6,068 (14)	2986 (9)	795 (16)	71 (10)	85 (14)	102 (14)	−3 (5)	28 (5)	−10 (5)
C(3)	2,294 (13)	1192 (7)	1591 (13)	75 (11)	54 (11)	70 (12)	2 (4)	19 (4)	5 (4)
N(1)	3,349 (11)	2384 (7)	201 (10)	85 (9)	59 (9)	55 (9)	−2 (4)	8 (3)	−1 (3)
N(2)	5,958 (13)	3162 (9)	−116 (14)	99 (12)	137 (16)	116 (14)	9 (5)	33 (5)	16 (5)
N(3)	1,415 (12)	1163 (7)	914 (13)	67 (10)	91 (13)	99 (13)	−1 (4)	4 (4)	0 (5)
C(11)	7,645 (12)	−30 (7)	3286 (11)	46 (9)	46 (10)	35 (9)	−2 (3)	5 (3)	−1 (3)
C(12)	6,477 (13)	168 (8)	3266 (13)	62 (10)	61 (13)	52 (11)	1 (4)	10 (4)	3 (4)
C(13)	5,794 (14)	−210 (10)	3836 (14)	66 (11)	110 (17)	59 (12)	−14 (5)	11 (4)	−3 (5)
C(14)	6,253 (16)	−770 (9)	4407 (14)	101 (14)	83 (15)	52 (12)	−18 (5)	8 (5)	−5 (5)
C(15)	7,403 (16)	−971 (9)	4413 (14)	96 (13)	67 (14)	53 (12)	−3 (5)	4 (5)	1 (5)
C(16)	8,108 (13)	−608 (8)	3843 (12)	70 (10)	60 (12)	42 (10)	−6 (4)	5 (4)	1 (4)
C(21)	8,961 (11)	1216 (7)	3236 (12)	35 (8)	41 (11)	60 (11)	2 (3)	−1 (3)	−2 (4)
C(22)	9,782 (13)	1614 (8)	2817 (16)	54 (10)	64 (13)	97 (16)	−6 (4)	8 (5)	−0 (5)
C(23)	10,198 (15)	2200 (8)	3406 (18)	62 (11)	54 (14)	123 (17)	−6 (5)	9 (5)	−4 (6)
C(24)	9,787 (18)	2360 (10)	4377 (20)	109 (14)	70 (15)	130 (20)	1 (6)	−7 (7)	−30 (7)
C(25)	9,007 (18)	1976 (11)	4799 (18)	89 (17)	96 (16)	109 (17)	−1 (6)	11 (6)	−13 (6)
C(26)	8,566 (13)	1402 (8)	4190 (13)	64 (10)	65 (13)	58 (12)	1 (4)	9 (4)	−12 (5)
C(31)	9,782 (12)	−1 (7)	2408 (11)	50 (10)	42 (11)	33 (9)	3 (3)	3 (4)	1 (4)
C(32)	10,738 (12)	10 (8)	3314 (13)	52 (10)	68 (13)	51 (10)	7 (4)	4 (4)	0 (4)
C(33)	11,737 (13)	−358 (9)	3280 (15)	54 (10)	89 (15)	86 (15)	10 (5)	−4 (5)	3 (5)
C(34)	11,808 (13)	−722 (8)	2382 (16)	56 (10)	61 (13)	101 (15)	10 (4)	16 (5)	4 (5)
C(35)	10,824 (15)	−725 (8)	1425 (15)	79 (12)	64 (13)	88 (13)	8 (5)	15 (5)	−6 (5)
C(36)	9,826 (13)	−363 (8)	1451 (13)	63 (10)	83 (14)	57 (11)	0 (4)	8 (4)	−6 (5)
C(41)	7,535 (11)	615 (7)	1156 (11)	47 (8)	47 (10)	33 (9)	−4 (3)	9 (3)	−1 (3)
C(42)	7,261 (14)	1250 (7)	753 (13)	83 (12)	35 (11)	52 (11)	5 (4)	5 (4)	3 (4)
C(43)	6,457 (16)	1347 (9)	−277 (14)	116 (15)	63 (13)	62 (12)	22 (5)	9 (5)	8 (5)
C(44)	5,937 (16)	824 (9)	−864 (14)	87 (14)	98 (15)	47 (12)	16 (6)	1 (5)	2 (5)
C(45)	6,163 (13)	182 (9)	−516 (14)	59 (10)	95 (15)	57 (12)	−6 (5)	4 (4)	−13 (5)
C(46)	6,971 (12)	74 (8)	534 (13)	46 (9)	59 (12)	58 (11)	−3 (4)	2 (4)	2 (4)

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

absolute ethanol are mixed together (1:1 ratio), KCl precipitates immediately and the starting compound $[(C_6H_5)_4P]SCN$ is isolated by evaporation of the filtered solution.

$[(C_6H_5)_4P][Hg(SCN)_3]$ was obtained by evaporation of a 1:1 solution of $Hg(SCN)_2$ and $[(C_6H_5)_4P]SCN$ in ethanol. Pure samples of the alkali salts had been prepared by this method,[9] but in the present case, mixtures were obtained. They consisted of a colorless crystalline material and large pieces of a yellowish porous solid, which were mechanically separated. On the basis of elemental analyses and powder patterns, it was assumed that the crystalline fraction corresponds to the expected compound with some unreacted $Hg(SCN)_2$. Elongated crystals of $Hg(SCN)_2$ could be identified under the microscope and prismatic crystals of the new compound were selected for the present work.

Crystal Data: Formula $C_{27}H_{20}N_3S_3PHg$; FW 713.8; monoclinic, space group $P2_1/c$; $a = 11.574$ (4) Å, $b = 20.014$ (8) Å, $c = 12.144$ (4) Å, $\beta = 103.56$ (3)°, $V = 2844.5$ Å^3, $Z = 4$, $d_{obsd} = 1.68$ (1) g/cm^3 (flotation in CCl_4–1,1,2,2-tetrabromoethane), $d_{calcd} = 1.66$ g/cm^3; λ(Mo K$\bar{\alpha}$) 0.71068 Å (graphite monochromator); μ(Mo Kα) = 58.1 cm^{-1}.

Crystallographic Measurements. A crystal of dimensions 0.04 mm × 0.06 mm × 0.08 mm was used for the present work. Space group $P2_1/c$ was established from a set of precession photographs. Accurate cell parameters were obtained by refinement of the setting angles 2θ, ω, and χ of twelve reflections automatically centered on a Picker FACS-1 diffractometer.

Intensities of 2557 independent reflections within a sphere $2\theta \leq 40°$ were measured with the FACS-1 diffractometer using the θ–2θ scan technique. The scan rate was 1° (2θ)/min and the 2θ range (minimum 1.5°) was increased by $114.6 \sin\theta\, (\lambda(K\alpha_2) - \lambda(K\alpha_1))/\lambda(K\alpha_1)$ to account for the $\alpha_1\alpha_2$ separation. Stationary-background counts (B_1 and B_2) of 20 sec each were taken at the limits of the scan. Three standard reflections (51$\bar{4}$, 0,10,$\bar{1}$, and 036) showed fluctuations of ±3% during data collection.

Net intensities I were calculated from $I = I_t - T(B_1 + B_2)/40$, where I_t is the total scan count and T the scan time. A total of 658 reflections with $\sigma(I) = [I_t + T^2(B_1 + B_2)/160 + 0.0004I^2]^{1/2} > 0.4I$ were considered as unobserved.[10] An absorption correction based on the crystal geometry was applied (NRC-3 Program, Ahmed and Singh). A grid of 10 × 10 × 10 was used and the transmission factor ranged from 0.49 to 0.68. Lorentz and polarization corrections were finally applied. The 1899 observed reflections were used to solve and refine the structure.

Solution and Refinement of Structure. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Isotropic refinement of all the nonhydrogen atoms converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.108$ (observed reflections only). At this stage, the hydrogen atoms were fixed at the calculated positions (C–H distance = 1.0 Å) and were assigned isotropic temperature factors between 5.0 and 7.0 Å^2, depending on the factors of the carbon atoms to which they were attached. The hydrogen parameters were not refined, but shifts equal to those of the carbon atoms were applied to the coordinates of the corresponding hydrogen atoms. Weights $w = 1/\sigma_F^2$ were used[10] and corrections were made for anomalous scattering of Hg, P, and S.[11] Anisotropic refinement of all nonhydrogen atoms converged to $R = 0.039$ and $R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.044$ (observed reflections only).

On the final difference Fourier map, four peaks of ±0.3 e/Å^3 were found at <1 Å from mercury, the remaining peaks being lower than ±0.12 e/Å^3. The programs used are listed elsewhere.[12] The form factors were those of Cromer and Waber.[13]

The refined atomic parameters are given in Table I.

Description of the Structure and Discussion

The environment of mercury is shown in Figure 1. Interatomic distances and bond angles are found in Table II.

The anionic part of the compound can be described as $[Hg(SCN)_3]^-$ ions in which mercury is surrounded by a triangle of sulfur atoms. The metal is displaced by 0.45 Å from the plane of the triangle toward atom N(1) of the next ion. In this manner, S(1)–C(1)–N(1) groups bridge consecutive $[Hg(SCN)_3]^-$ ions and form infinite chains.

Figure 1. Stereoscopic illustration of a chain of bridged $[Hg(SCN)_3]^-$ ions. The numerical part of the symbol is the same for all three atoms of a given SCN group. Successive ions are linked by the dashed Hg· · ·N bond. The ellipsoids correspond to 50% probability.

Therefore, the overall coordination of mercury in the chains corresponds to a very flattened tetrahedron of one nitrogen and three sulfur atoms.

The present structure bears a certain relationship to $[(CH_3)_4N][HgBr_3]$, which contains trigonal $[HgBr_3]^-$ ions.[7] One bromine atom from the next ion is found above the center of the triangle and mercury is displaced by 0.3 Å from the plane toward this fourth neighbor. In the resulting infinite chain, $[HgBr_3]^-$ trigonal ions are bridged by a bromine atom playing the same role as S(1)–C(1)–N(1) in the present case.

The Hg–S bond lengths of the nonbridging groups (2.46 Å) are reasonable for a basically three-coordinate species, since they fall between the distances observed for two-coordinate digonal (2.38 Å)[14] and four-coordinate tetrahedral compounds (2.55 Å).[15] The third Hg–S bond (2.59 Å) is much longer and comparable with those found in $Hg(SCN)_2(1,10\text{-phen})_2$, a six-coordinate molecule.[16] Consequently, in contrast with $[HgBr_3]^-$ where bridging does not significantly affect the corresponding Hg–Br bond, a considerably weakened Hg–S bond is observed here for the bridging group. The Hg···N(1) distance (2.40 Å) is greater than the sum of the covalent radii (2.2 Å),[2] but it certainly denotes much stronger attractions than the intermolecular interactions found in $Hg(SCN)_2$ (Hg···N, 2.81 Å)[14] and $Hg(CN)_2$ (2.74 Å).[17] Apparently, this is the first crystallographic example of a Hg–SCN–Hg bridge in which both ends of the SCN group interact about equally with the metal, the Hg–S bond being usually greatly favored.

The usual characteristics are observed for the SCN groups: linear, Hg–S–C angles close to 100°, normal lengths for the S–C (1.67 Å) and C–N (1.14 Å) bonds.

The $[(C_6H_5)_4P]^+$ ions have the expected tetrahedral structure, with P–C bond lengths between 1.78 (1) and 1.80 (1) Å and C–P–C angles varying from 106.6 (6) to 111.8 (6)°. Within the phenyl rings, the C–C distances range from 1.36 (2) to 1.43 (2) Å (average 1.38 Å), and the C–C–C angles, from 116 (1) to 124 (1)° (average 120°). The rings are planar within 1σ. Such values are similar to those already reported for the same ion.[18,19]

Table II. Interatomic Distances and Bond Angles around Mercury

Bond	Distance, Å	Bonds	Angle, deg
Hg–S(1)	2.591 (4)	S(1)–Hg–S(2)	113.9 (1)
Hg–S(2)	2.462 (4)	S(1)–Hg–S(3)	105.3 (1)
Hg–S(3)	2.460 (4)	S(2)–Hg–S(3)	130.9 (1)
Hg–N(1)[a]	2.40 (1)	S(1)–Hg–N(1)[a]	102.8 (3)
Hg–N(2)[b]	3.53 (3)	S(2)–Hg–N(1)[a]	98.8 (3)
S(1)–C(1)	1.64 (1)	S(3)–Hg–N(1)[a]	100.1 (3)
S(2)–C(2)	1.69 (1)	S(1)–C(1)–N(1)	176 (1)
S(3)–C(3)	1.70 (1)	S(2)–C(2)–N(2)	178 (1)
C(1)–N(1)	1.15 (1)	S(3)–C(3)–N(3)	176 (1)
C(2)–N(2)	1.12 (2)	Hg–S(1)–C(1)	97.5 (5)
C(3)–N(3)	1.13 (2)	Hg–S(2)–C(2)	101.8 (5)
		Hg–S(3)–C(3)	97.7 (5)
		C(1)[a]–N(1)[a]–Hg	147 (1)

[a] $x, {}^1/_2 - y, -{}^1/_2 + z$. [b] $x, {}^1/_2 - y, {}^1/_2 + z$.

Table III. Interionic Contacts (Å)[a]

S(1)· · ·C(15)[b]	3.37	N(2)· · ·H(14)[b]	2.56
S(1)· · ·C(16)[b]	3.39	N(3)· · ·H(22)[e]	2.39
S(2)· · ·H(34)[c]	2.87	N(3)· · ·H(36)[f]	2.53
S(2)· · ·H(43)[d]	2.89	C(15)· · ·H(32)[g]	2.86
C(2)· · ·H(43)	2.86	C(16)· · ·H(32)[g]	2.68
C(2)· · ·H(14)[b]	2.80	C(44)· · ·H(34)[h]	2.80
C(3)· · ·H(22)[e]	2.80	C(45)· · ·C(45)[f]	3.30

[a] The esd's are 0.01 Å for bonds involving sulfur and 0.02 Å for the others. [b] $1 - x, {}^1/_2 + y, {}^1/_2 - z$. [c] $2 - x, {}^1/_2 + y, {}^1/_2 - z$. [d] $x, {}^1/_2 - y, {}^1/_2 + z$. [e] $-1 + x, y, z$. [f] $1 - x, \bar{y}, \bar{z}$. [g] $2 - x, \bar{y}, 1 - z$. [h] $2 - x, \bar{y}, \bar{z}$.

Figure 2 shows the packing of ions in the crystal. Chains of bridged $Hg(SCN)_3$ units run parallel to the *c* axis, and the *c* glide plane of the space group generates the alternation of parallel–antiparallel chains in the *b* direction. Space between the chains is occupied by cations.

$[(C_6H_5)_4P]^+$ ions sometimes assume suitable conformations and relative orientations to allow the stacking of phenyl rings at 3.5–3.6 Å. In crystals of $[(C_6H_5)_4P]_2[Hg(SCN)_4]$,[18] for instance, cations define a three-dimensional network with "holes" filled with discrete $[Hg(SCN)_4]^{2-}$ anions. The interionic contacts listed in Table III indicate that stacking effects are not important in the present case; most of the contacts involve one atom from the anion and one from the cation. Apparently, the approach of donor atoms above and/or below the trigonal plane cannot easily be avoided and the complex ions in the solid state tend to associate rather than to exist as monomeric species, even when favorable cations are present.

Acknowledgment. We wish to thank "La Société Nationale des Matériaux de Construction d'Algérie" for a scholarship and the National Research Council of Canada for a research grant.

Registry No. $[(C_6H_5)_4P][Hg(SCN)_3]$, 53516-71-5.

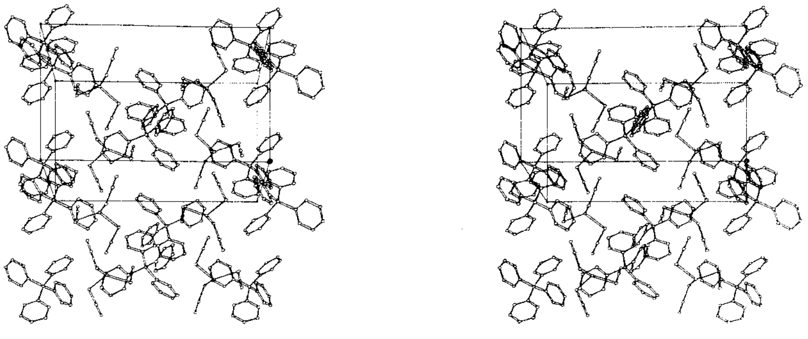

Figure 2. Stereoscopic diagram of the packing of ions in the crystal of $[(C_6H_5)_4P][Hg(SCN)_3]$. The origin of the cell is represented by a black dot. The axes are oriented as follows: *a*, approximately perpendicular to the drawing, away from the reader; *b*, horizontal and to the left; *c*, vertical and up. Two antiparallel chains of bridged $[Hg(SCN)_3]$ ions are seen to run parallel to the *c* axis of the cell.

Supplementary Material Available. A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC405727.

References and Notes

(1) P. Pascal, "Nouveau traité de chimie minérale," Vol. V, Masson et Cie, Paris, 1962.

(2) D. Grdenic, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965).

(3) A. Weiss and K. Damm, *Z. Naturforsch. B*, **9**, 82 (1954).

(4) E. J. Harmsen, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **100**, 208 (1938).

(5) S. V. Zvonkova, V. V. Samodurova, and L. G. Vorontsova, *Dokl. Akad. Nauk SSSR*, **102**, 1115 (1955).

(6) G. S. Zhdanov and V. V. Sanadze, *Zh. Fiz. Khim.*, **26**, 469 (1952). Very recently, the corresponding Rb and Cs salts were investigated by G. Thiele and D. Messer, and a trigonal-planar coordination was observed for mercury (private communication). Since the Rb, NH_4, and K salts are isostructural,[9] the original work on the latter two compounds seems to be erroneous.

(7) J. G. White, *Acta Crystallogr.*, **16**, 397 (1963).

(8) R. H. Fenn, J. W. H. Oldham, and D. C. Phillips, *Nature (London)*, **198**, 381 (1963).

(9) A. Larbot and A. L. Beauchamp, *Rev. Chim. Miner.*, **10**, 465 (1973).

(10) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N.Y., 1969, p 457.

(11) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(12) A. Terzis, A. L. Beauchamp, and R. Rivest, *Inorg. Chem.*, **12**, 1166 (1973).

(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(14) A. L. Beauchamp and D. Goutier, *Can. J. Chem.*, **59**, 977 (1972).

(15) R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Dalton Trans.*, 2247 (1973).

(16) A. L. Beauchamp, B. Saperas, and R. Rivest, *Can. J. Chem.*, **49**, 3579 (1971).

(17) R. C. Seccombe and C. H. L. Kennard, *J. Organometal. Chem.*, **18**, 243 (1969).

(18) M. R. Churchill and J. Cooke, *J. Chem. Soc. A*, 2046 (1970); P. Goldstein, K. Seff, and K. N. Trueblood, *Acta Crystallogr. Sect. B*, **24**, 778 (1968); M. Colapietro and L. Zambonelli, *ibid.*, **27**, 739 (1971).

(19) A. Sakhri and A. L. Beauchamp, *Acta Crystallogr.*, in press.

Contribution from the "Laboratoire de Chimie de
Coordination du C.N.R.S." 31030 Toulouse Cedex, France

Dinuclear-Bridged d^8 Metal Complexes. IV. Crystal and Molecular Structure of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ and Isomerization in Solution of $[RhCl(CO)(PR_3)]_2$ Complexes[1]

J. J. BONNET, Y. JEANNIN, P. KALCK, A. MAISONNAT, and R. POILBLANC*

Received July 22, 1974 AIC40493V

The crystal and molecular structure of *cis*-di-μ-chloro-dicarbonylbis(dimethylphenylphosphine)dirhodium(I) has been solved by single-crystal X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ with two asymmetric units per unit cell. Lattice constants are $a = 10.495 \pm 0.009$, $b = 12.086 \pm 0.009$, and $c = 10.337 \pm 0.007$ Å; $\alpha = 112.71 \pm 0.04$, $\beta = 97.50 \pm 0.04$, and $\gamma = 103.69 \pm 0.04°$. The structure has been refined by a full-matrix least-squares procedure to a conventional R factor of 0.037 for 2370 observed reflections. Each rhodium atom is surrounded approximately in a square-planar fashion but there is a dihedral angle of 123° between these two planes. Bond distances of interest are as follows: two Rh–Cl trans to phosphorus, 2.410 (3) and 2.427 (3) Å; two Rh–Cl trans to carbonyl groups, 2.408 (3) and 2.406 (2) Å; Rh–P 2.230 (3) and 2.220 (2) Å; Rh–Rh, 3.167 (1) Å. In conjunction with X-ray results, a careful discussion of the infrared spectra in the solid state and in solution indicates an isomerization phenomenon in solution which is extented to the parent compounds.

Introduction

A previous infrared and nmr study[2] showed that complexes of the type $[RhCl(CO)(PR_3)]_2$ have a double square-planar structure. However a definitive conclusion about the cis or trans configuration could not be clearly set up. Moreover, nmr spectra[2] of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ at room temperature showed an apparent equivalence of the methyl protons which could be interpreted as an entirely planar structure. However, previous crystal structures of dinuclear chloro-bridged rhodium(I) complexes such as $[RhCl(CO)_2]_2$,[3] $[RhCl(C_2H_4)_2]$,[4] $C_8H_{12}Rh_2Cl_2[P(OC_6H_5)_3]_2$,[5] $[RhCl(C_6H_{10})_2]_2$,[6] and $[RhCl(C_8H_{12})]_2$[7] showed that each rhodium atom is in a square-planar configuration but the dihedral angle between these two planes departs from 180° except in the last case. The present study was undertaken to elucidate these two points of interest.

The X-ray structural determination has been carried out on a single crystal of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$. Discussing results in comparison with those of a careful infrared study in the solid state and in solution, an interpretation of isomerization is given; it is extented to the parent compounds such as trimethyl- and tris(dimethylamino)phosphine complexes of Rh(I).

Experimental Section

The compounds $[RhCl(CO)PR_3]_2$ were prepared as previously described.[2] All attempts to crystallize the $[RhCl(CO)P(CH_3)_3]_2$ compound failed to give suitably sized crystals. However beautiful clear brown-yellow prisms of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ were obtained using the following technique. Hexane, in which the compound is slightly soluble, was added to a solution of the complex in toluene without stirring. At −20° the slow diffusion of toluene in hexane and of hexane in toluene led to suitable crystals. *Anal.* Calcd for $RhClC_9H_{11}OP$: C, 35.49; H, 3.65; P, 10.17; Cl, 11.64. Found: C, 34.77; H, 3.81; P, 10.35; Cl, 11.62.

Infrared Studies. The infrared spectra were recorded with a Perkin-Elmer 225 grating spectrometer equipped with a scale expander, either in cyclohexane solutions or in cesium bromide pellets. In the carbonyl stretching region, the spectra were calibrated by water vapor lines. Line shape analyses were performed with a Dupont 310 curve resolver. The part due to diffusion in the Lorentz shape analysis of the spectra in the solid state has not been taken into account. We checked that this neglected part does not affect our conclusions.

Crystal Data. Examination of crystals of $Rh_2Cl_2(CO)_2(P(CH_3)_2C_6H_5)_2$ by precession methods using Mo Kα radiation did not reveal any symmetry but the center imposed by the Friedel law. Hence the space group is either $P1$ or $P\bar{1}$. The lattice constants, obtained after alignment of a crystal on a four-circle diffractometer, are $a = 10.495 \pm 0.009$, $b = 12.086 \pm 0.009$, and $c = 10.337 \pm 0.007$ Å; $\alpha = 112.71 \pm 0.04$, $\beta = 97.50 \pm 0.04$, and $\gamma = 103.69 \pm 0.04°$ (T 21°, λ(Mo Kα) 0.71069 Å).

Based on a calculated volume of 1139 Å^3 and two asymmetric units per unit cell, the calculated density of 1.783 g cm^{-3} is in good agreement with the density of 1.77 g cm^{-3} measured by flotation in an aqueous solution of zinc chloride.

Data Collection. Diffraction data were collected at room temperature from a truncated hexagonal bipyramid of average dimension