Journal of Organometallic Chemistry, 99 (1975) 31—40
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MERCURY β-DIKETONATO COMPLEXES

II. THE CRYSTAL AND MOLECULAR STRUCTURE OF 3,3-BIS(CHLOROMERCURY)-2,4-PENTANEDIONE

L.E. McCANDLISH and J.W. MACKLIN*

Department of Chemistry, University of Washington, Seattle, Washington 98195 (U.S.A.)

(Received October 17th, 1974)

Summary

The structure of 3,3-bis(chloromercury)-2,4-pentanedione is reported. The space group indicated is $C2/c$ with unit cell dimensions: a = 15.048(2), b = 10.921(6), c = 16.080(4) Å, and β = 134.74(1)°. Three-dimensional absorption-corrected diffractometer data were used in the refinement of the structure to a conventional $R(F)$ value of 0.079. Anisotropic temperature factors were used for Hg and Cl atoms while C and O atoms were refined isotropically. Both Hg atoms are bound to the γ-carbon of acetylacetone. Solid state Raman and infrared spectra are reported. Lowering of the C=O stretching frequency is discussed in terms of the crystal structure.

Introduction

Several mercury acetylacetonate compounds, prepared from mercuric chloride and containing chloride ion, have been reported [1-3]. In each of these studies a structurally different compound is concluded. Some workers indicate that mercury is bound to an oxygen [1] atom of acetylacetone while others indicate that mercury is bound to the γ-carbon [2]. The most recent report suggests that compounds exist which have both modes of mercury—acetylacetonate binding [3].

Bonati and Minghetti [2] report a preparation of $Hg_2(C_5H_6O_2)Cl_2$. Using their room temperature preparation method at 0°C in attempt to improve the yield we obtain a microcrystalline solid which has chemical composition and IR spectrum identical to that of the solid obtained at room temperature. Crystals obtained from methanol or ethanol solutions of this compound have the same chemical composition as the dissolved material but give a distinctly different set of IR and Raman spectra*. We have determined the crystal structure of this latter form and have studied the vibrational spectra of the crystals with a view toward establishing the structural characteristics of this and other mercury acetylacetonate compounds.

We have obtained at least three other crystalline forms with the same chemical composition but still different vibrational spectra. Spectral differences are believed to be due to variations in molecular conformation and solid state structure. Two of these variations other than the crystal which is the topic of this paper, have been obtained as single crystals and will be the subjects of further X-ray crystallographic studies. In light of these observations, and the fact that other chemical compositions are possible, e.g., $Hg(C_5H_7O_2)Cl$ or $Hg_2(C_5H_6O_2)$-$(C_5H_7O_2)Cl$, it is not surprising that various workers have suggested diverse structures for chloromercury acetylacetonate compounds.

Experimental

Weissenberg photographs of a single crystal of 3,3-bis(chloromercury(II))-2,4-pentanedione showed monoclinic symmetry with systematic absences for reflections of the type *hkl* with $h + k \neq 2n$ and $h0l$ with $h \neq 2n$ and $l \neq 2n$. These observations are consistent with space groups $C2/c$ and Cc. The crystals have a density greater than that of 1,1,3,3-tetrabromoethane (2.96 g/cm^3) indicating the number of molecules per unit cell to be at least six. The space group $C2/c$ was assumed and nothing in the subsequent solution indicated that this assumption is wrong. The cell constants were determined by least-squares refinement of the 2θ(Mo-K_α) values obtained for 21 diffractometer-measured reflections. The crystal data are summarized in Table 1.

Three-dimensional data were collected on a Picker card-punch-controlled diffractometer equipped with a pulse height analyzer. The intensities of 1269 reflections to a 2θ value of 45° were measured using Nb-filtered Mo-K_α radiation. The X-ray source was a standard tube operated at 50 kV and 14 mA with a 3.5° take-off angle. The θ—2θ scan mode with a 2°/min scan rate was used. 2θ scan ranges were calculated from the relation $\Delta 2\theta = 1.8° + \tan\theta$. Backgrounds were counted for 10 seconds at each of the scan limits for each reflection.

Four standard reflections were measured periodically during data collection in order to estimate a scale factor for each reflection and to estimate an instability constant for the diffractometer. The experimental instability constant was $P = 0.0085$. A linear fit was obtained for the intensity of each standard reflection as a function of time. The scale factor for each reflection was calculated as the average scale factor determined from these functions. The crystal suffered significant radiation damage as indicated by the range (1.0-1.09) of scale factors. The data were corrected for background, coincidence loss, absorption, and the usual Lorentz and polarization effects. Pertinent data on the absorption correction are collected in Table 2.

---

* Bonati and Minghetti report recrystallization of this compound unchanged from several solvents, especially methyl ethyl ketone. We have not been able to recrystallize the compound and obtain a substance which has the same vibrational spectra as the initial precipitate; however, we have occasionally found crystals of the initial form along with the common variation described in this paper.

TABLE 1

ROOM TEMPERATURE CRYSTAL DATA

Space Group	$C2/c$	
Cell Constants	$a = 15.048(2)$ Å $b = 10.921(6)$ Å $c = 16.080(4)$ Å $\beta = 134.74°(1)$	
Density	$\rho_c = 4.035$ g/cm^3	($Z = 8$)

Infrared spectra were recorded using a Perkin—Elmer 225 infrared spectrometer. Solid state spectra were measured as a Nujol oil mull on both polyethylene and KBr as well as a Kel F fluorocarbon oil mull on KBr. Through this procedure one obtains full spectra free of interfering bands due to the sampling media. The estimated maximum error in observed frequencies is ± 5 cm^{-1}.

Raman spectra were recorded using a Spex 1401 double monochromator spectrometer equipped with an RCA-C31034 thermoelectrically cooled phototube with red sensitive response and a dc amplifier. The excitation source was a CRL Model 52MG Ar$^+$, Kr$^+$ mixed gas laser. Laser emission at 5145 Å was used as the exciting frequency. Solid state spectra were measured using single crystals in

TABLE 2

ABSORPTION CORRECTION DATA

U Matrix (from the program ABSOR[a])

0.065386	0.067003	—0.000196
0.000056	—0.000339	—0.091573
—0.001645	0.087244	—0.000221

Data were collected in the bisecting position ($\omega = 0$)

Boundary planes of crystal

h	k	l	Distance from origin (cm)
1	0	0	0.0054
0	0	1	0.0161
—1	0	0	0.0044
0	0	—1	0.0219
1	0	—1	0.0229
1	—2	—2	0.0394
—1	—2	1	0.0399
—1	2	—1	0.0246

Crystal volume $V = 3.33 \times 10^{-2}$ mm^3

Absorption coefficient μ(Mo-K_α) = 338.4 cm^{-1}

Maximum correction 227.3 × I

Minimum correction 15.3 × I

[a] Analytical calculation based on the method of De Meulenaer and Tompa [4]. The program ABSOR is a revision of AGNOST as described by Templeton and Templeton [13]. The U matrix in our case is related to the instrument angles χ and φ by the relation:

$$\vec{h}U = [\sin\varphi\cos(180-\chi), \cos\varphi\cos(180-\chi), -\sin(180-\chi)]$$

where $\vec{h}$ is the reciprocal lattice vector specifying the reflecting plane.

a number of orientations. Estimated maximum error in observed frequency shifts is ±3 cm^{-1}.

Solution and refinement of the structure

The two independent Hg atoms in the asymmetric unit were found from a Patterson synthesis and the remaining light atoms found from a delta F synthesis using phases based on the Hg positions.

The initial model was refined using standard least-square techniques. Carbon, oxygen, chlorine and mercury scattering factors were those of Cromer and Mann [5]. Real and imaginary dispersion corrections for both Hg and Cl were taken from the International Tables (1960).

Full-matrix least-squares refinement of the model converged to a conventional value of $R(F) = 0.079$ with a goodness-of-fit of 4, based on 1219 reflections. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is the statistical weight defined as $1/\sigma(F_o)^2$. A reflection was considered to be observed if the condition $F_o > 2\sigma(F_o)$ was satisfied. "Unobserved" reflections were allowed to contribute to the refinement with $F_o \equiv 2\sigma(F_o)$ if $F_c > 2\sigma(F_o)$*.

The Hg and Cl atoms were refined using anisotropic temperature factors while C and O atoms were refined isotropically. The rather large value of the goodness-of-fit is attributed to systematic errors remaining in the data after absorption correction. Small errors in the measurement of the crystal dimensions, for example, become significant when the linear absorption coefficient is large. The final atomic coordinates and thermal parameters are given in Table 3. A listing of the calculated and observed structure factor amplitudes is available**.

Discussion

The molecular structure is consistent with spectroscopic evidence indicating mercury-to-carbon rather than mercury-to-oxygen bonding. The structure is similar in this respect to crystal structures previously reported for mercury derivatives of dipivaloylmethane [6,7].

Two Hg atoms replace the two hydrogen atoms on the γ-carbon, C(3), of acetylacetone. In accord with the tetrahedral geometry at C(3), the acetylacetone portion of the molecule is found in the keto form and has a twisted conformation. The angle between the plane defined by atoms C(1), C(2), and O(2) and the plane defined by the atoms C(5), C(4), and O(4) is ca. 77°.

Each Hg atom is also bonded to a Cl atom. The C—Hg—Cl bond angles are 174(1)° and 172(2)°. The deviation from linearity is significant and may be at-

---

* The $\sigma(F_o)^2$ were derived from the $\sigma(I)^2$ which were calculated as

$$\sigma(I)^2 = \left[\frac{K}{(1-\tau S)^2}\right]^2 S + (RK)^2 B + P^2(S+B)^2$$

where S = total scan counts, B = total background counts, K = scale factor, R = ratio of scan time to background counting time, τ = coincidence loss parameter, P = instrumental instability constant.

** The table of structure factors has been deposited as NAPS Document No. 02672 with ASIS/NAPS, c/o Microfische Publications, 440 Park Ave. So., New York, New York 10016. A copy may be secured by citing the document and remitting $3.00 for microfiche or $5.00 for photocopies. Advance payment is required. Outside of the U.S.A. and Canada, postage is $2.00 for a photocopy or $1.00 for a fiche. Make checks payable to Microfiche Publications.

TABLE 3a

POSITIONAL PARAMETERS AND THEIR LEAST-SQUARES STANDARD DEVIATIONS

	X/a	Y/b	Z/c
Hg(1)	0.40284(10)	0.18716(11)	0.40356(09)
Hg(2)	0.10184(10)	0.11444(11)	0.20824(09)
Cl(1)	0.5245(7)	0.3578(8)	0.4608(7)
Cl(2)	−0.0981(7)	0.1902(8)	0.0905(7)
C(1)	0.214(3)	−0.115(4)	0.399(3)
C(2)	0.301(3)	−0.027(3)	0.425(3)
C(3)	0.284(3)	0.034(3)	0.333(3)
C(4)	0.302(3)	−0.050(3)	0.274(2)
C(5)	0.319(3)	−0.065(4)	0.196(3)
O(2)	0.400(2)	−0.014(3)	0.529(2)
O(4)	0.314(2)	−0.156(3)	0.294(2)

tributed to secondary interactions with electronegative atoms surrounding the mercury atoms.

The secondary interactions involving the two mercury atoms are quite different. One mercury atom, Hg(2), is weakly bonded to an oxygen atom in a symmetry-related molecule. The distance between Hg(2) in the first molecule and O(4)′ in the molecule related to the first by the 2-fold screw operation is 2.82(3) Å. This distance may be compared to the sum of Van der Waals radii of Hg and O, 1.51 + 1.40 = 2.91 Å [6]. The C(3)—Hg(2)—O(4)′ and Cl(2)—Hg(2)—O(4)′ angles are 95° and 90° respectively. Thus the nearest neighbor geometry about Hg(2) is approximately 'T' shaped, as observed in tetrakis(pentafluorophenyl)-μ-bis(diphenylarsino)methanedimercury(II) [8]. The Hg(2)—O(4)′ interaction binds the individual molecules into weakly linked chains along the b-axis of the crystal. In general, one would expect the crystal growth rate to be fastest in the direction along a "polymeric" chain. Thus the suggestion that the Hg(2)—O(4)′ interaction is attractive is consistent with the observation that the crystal habit is elongated along the direction of the b-axis. Compared to the initial reaction

TABLE 3b

THERMAL PARAMETERS AND THEIR LEAST-SQUARES STANDARD DEVIATIONS ($U_{ij} \times 10^2$)

	Hg(1)	Hg(2)	Cl(1)	Cl(2)
U_{11}	2.66(7)	2.23(7)	3.5(4)	2.9(4)
U_{22}	2.23(8)	2.66(8)	4.1(5)	4.8(5)
U_{33}	2.56(7)	2.51(7)	4.1(5)	3.5(4)
U_{12}	−0.22(5)	0.50(5)	−0.3(4)	1.7(4)
U_{13}	1.86(6)	1.72(6)	2.8(4)	2.4(3)
U_{23}	−0.16(5)	0.65(5)	−0.3(4)	1.4(4)
	C(1)	C(2)	C(3)	C(4)
U	4.4(8)	3.2(7)	3.5(8)	2.3(6)
	C(5)	O(2)	O(4)	
U	3.7(8)	5.8(7)	4.3(6)	

product, the recrystallized product is much less readily dissolved in methanol. This fact also supports the existence of a "polymeric" structure.

Hg(1) on the other hand experiences two intermolecular contacts with oxygen atoms at 3.01(4) and 3.02(2) Å in addition to an intramolecular contact with O(2) at 3.00(4) Å. These contacts are all longer than the Hg(1) · · · C(2) and Hg(1) · · · C(4) distances at 2.95(4) and 2.98(3) Å respectively.

Hg(1) has an intermolecular contact of 3.30(1) Å with a chlorine atom. Hg(2) has three intermolecular contacts with chlorine atoms at 3.28(1), 3.38(1), and 3.40(1) Å. The sum of Van der Waals radii for mercury and chlorine is 1.51 + 1.80 = 3.31 Å. Thus, each Hg atom is surrounded by a combined total of 4 Cl and O atoms at distances near the sum of the appropriate Van der Waals radii in addition to the covalently bound C and Cl atoms. The polyhedron formed by the 6 atoms which are either bonded to or in contact with each Hg atom is, however, an extremely irregular octahedron.

The standard deviations of positional parameters for carbon and oxygen atoms are large due to the dominance of the mercury and chlorine atoms in the scattering of X-rays. Bond lengths and angles which involve the carbon and oxygen atoms do not deviate in a statistically significant way from normal values expected for the various kinds of bonds in the acetylacetone portion of the molecule. Fig. 1 is a drawing of the molecule and Fig. 2 is a packing diagram. Interatomic distances and bond angles are given in Table 4.

The crystal structure presented here suggests a reinterpretation of a part of the results reported by Bonati and Minghetti [3]. Their outline of the chemistry of acetylacetone mercury derivatives is given in Fig. 3.

Our data indicate that compound IV in Fig. 3 differs from compound I only in its solid state structure and is in fact the structure of the present X-ray

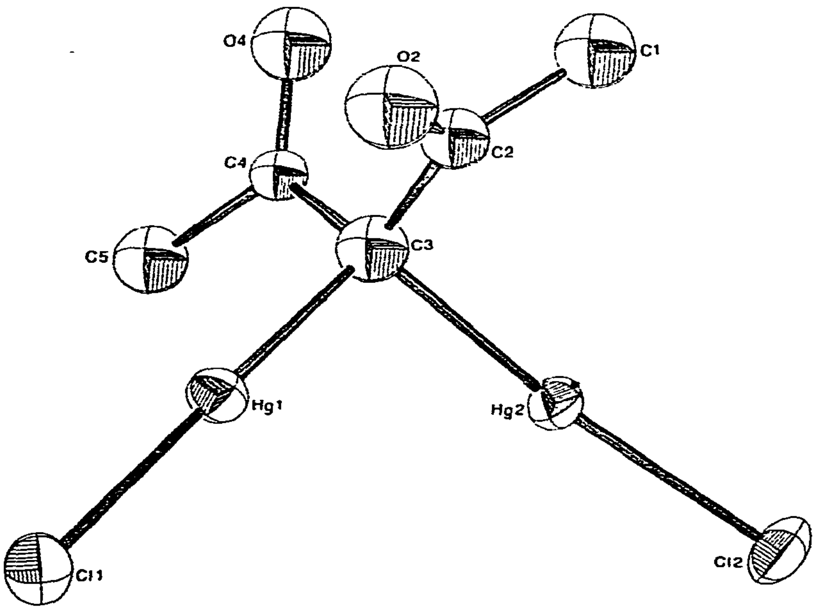

Fig. 1. Molecular structure of 3,3-bis(chloromercury)-2,4-pentanedione (ORTEP [14] drawing).

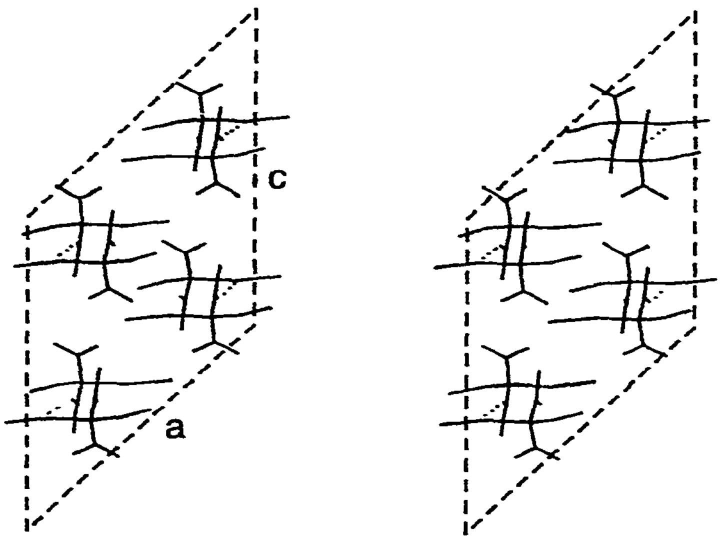

Fig. 2. Stereopacking diagram viewed down the *b* axis. Hg(2) and O(4)′ are connected by dotted lines.

crystallographic determination. The observations are as follows: (1) Compound IV and our crystals both decompose in the temperature range 200-210°C; (2) The IR spectrum of IV is identical to the spectrum obtained from our crystals; (3) The solution PMR spectra of I and IV as reported by Bonati and Minghetti are not significantly different.

The IR spectrum obtained from IV by Bonati and Minghetti is reproduced in Table 5 along with the IR and Raman spectra of our crystals.

Support for the structure of IV, as proposed by Bonati and Minghetti, rests largely on the assignment of the 1596 cm^{-1} band to ν(C=C) lowered in frequency by conjugation. In light of the crystal structure we assign this band to ν(C=O) for the one carbonyl group which is weakly coordinated to Hg(2) as discussed above. We attribute its low frequency to this interaction. The 1667 cm^{-1} band is

TABLE 4

BOND LENGTHS AND BOND ANGLES

Distances (Å)		Angles (°)	
C(1)—C(2)	1.42(6)	C(1)—C(2)—C(3)	122(3)
C(2)—C(3)	1.47(7)	C(1)—C(2)—O(2)	117(4)
C(2)—O(2)	1.23(3)	C(3)—C(2)—O(2)	120(4)
Hg(1)—C(3)	2.11(4)	Hg(1)—C(3)—C(2)	110(2)
Hg(1)—Cl(1)	2.302(10)	Hg(1)—C(3)—C(4)	112(3)
		Hg(1)—C(3)—Hg(2)	103(1)
C(4)—C(5)	1.53(7)	C(3)—Hg(1)—Cl(1)	174(1)
C(3)—C(4)	1.47(7)	C(3)—C(4)—C(5)	123(3)
C(4)—O(4)	1.18(4)	C(5)—C(4)—O(4)	117(4)
Hg(2)—C(3)	2.14(3)	C(3)—C(4)—O(4)	120(4)
Hg(2)—Cl(2)	2.302(8)	Hg(2)—C(3)—C(4)	111(2)
		C(2)—C(3)—C(4)	113(3)
		Hg(2)—C(3)—C(2)	109(3)
		C(3)—Hg(2)—Cl(2)	172(2)

TABLE 5

VIBRATION SPECTRA

IR		Raman Single crystals
Reference 3 (cm^{-1})	Nujol,Kel F mull (cm^{-1})	(cm^{-1})
	200 w	188
	223 w	
272 vw	276 vw	277
309 m	310 m	316
331 s	335 s	334
367 m	371 m	371
498 m	502 m	502
		553
566 m	571 m	573
612 m	619 m	618
670 w		
	722 w	
	739 w	742
800 w		
		834
856 w	863 w	865
		882
990 m	992 m	993
1015 m	1012 m	1016
		1030
		1072
1183 s	1184 s	1186
1213 s	1215 s	1212
1258 w		
1357 s	1350 m	1348
1375 m	?[a]	
	1418 w(br)	1424
1450 s(br)	?[a]	
1596 s(br)	1601 s(br)	1601
1652 (sh)	1650 (sh)	
1669 s	1667 s	1668

[a] The only significant differences are the strong band at 1450 cm^{-1} and the medium band at 1375 cm^{-1} reported by Bonati and Minghetti [3]. We believe these two bands may be attributed to the well known bands of Nujol oil near these frequencies. We note the otherwise excellent agreement between the two sets of spectra.

assigned to $\nu(C{=}O)$ for the carbonyl group which is relatively free from close secondary interactions. These assignments are verified by Raman studies of oriented single crystals to be published elsewhere. One might expect these two carbonyl groups to be nearly equivalent in solution. This expectation is borne out by the Raman spectrum in acetonitrile which shows a single broad band at 1690 cm^{-1}. An increase in stretching frequency is expected as oxygen-bonded interactions decrease. The carbonyl frequencies for the keto-tautomer of acetylacetone are 1720 and 1700 cm^{-1}.

It is useful to compare the solid state IR spectrum of our crystals with the solid state IR spectrum of $KPt(acac)_2Cl$. Single crystal X-ray analysis [9] shows that this compound has one carbon-bonded and one oxygen-bonded acetylacetone ligand. The potassium ions are of two kinds. The first is six-coordinated by pairs of oxygen atoms at 2.73, 2.76, and 2.89 Å. The second is surrounded by a pair of oxygen atoms at 2.84 Å and two pairs of chlorine atoms at 3.22 and 3.25 Å. Thus we have a situation similar to that in our crystal insofar as the atoms involved in secondary interactions with the carbonyl oxygen atoms of the γ-carbon-bonded acetylacetone molecule are found roughly at two different distances. The IR spectrum of $KPt(acac)_2Cl$ has two bands at 1695 and 1653 cm^{-1} which are assigned to $\nu(C=O)$ for the carbonyl groups of the carbon-bonded acetylacetone ligand [10]. In addition, two bands appear at 1565 and 1546 cm^{-1} which are assigned to a mixture of C=O and C=C vibrations of the oxygen-bonded acetylacetone ligand. It is a general result that for molecules containing acetylacetone groups bonded via oxygen, the highest frequencies in the 1500-1750 cm^{-1} region are below 1600 cm^{-1}, whereas for molecules in which the acetylacetone group is bonded through the γ-carbon, frequencies are found above 1600 cm^{-1}. Thus, it would appear that the observation of a carbonyl stretching frequency at 1601 cm^{-1} in our crystal would indicate a strong secondary mercury—oxygen association.

Finally we suggest that "mercury acetylacetone", substance II in Fig. 3, is a mixture whose major component is $(C_5H_7O_2)Hg(C_5H_6O_2)Hg(C_5H_7O_2)$. This structure is consistent with the known chemistry associated with the substance and has a composition consistent with the range of compositions reported for the substance. The calculated composition for this compound is C, 25.9; H, 2.88; O, 13.8; Hg, 57.4%, very near the average composition of the mixtures reported by Bonati and Minghetti, C, 26.3; O, 12.1; H, 3.0; Hg, 59%. This structure has previously been suggested [11] for the reaction product obtained from sodium acetylacetonate and mercuric chloride. The compound can be readily obtained in pure form and a report of preparations and spectroscopic studies in our laboratory is forthcoming [12].

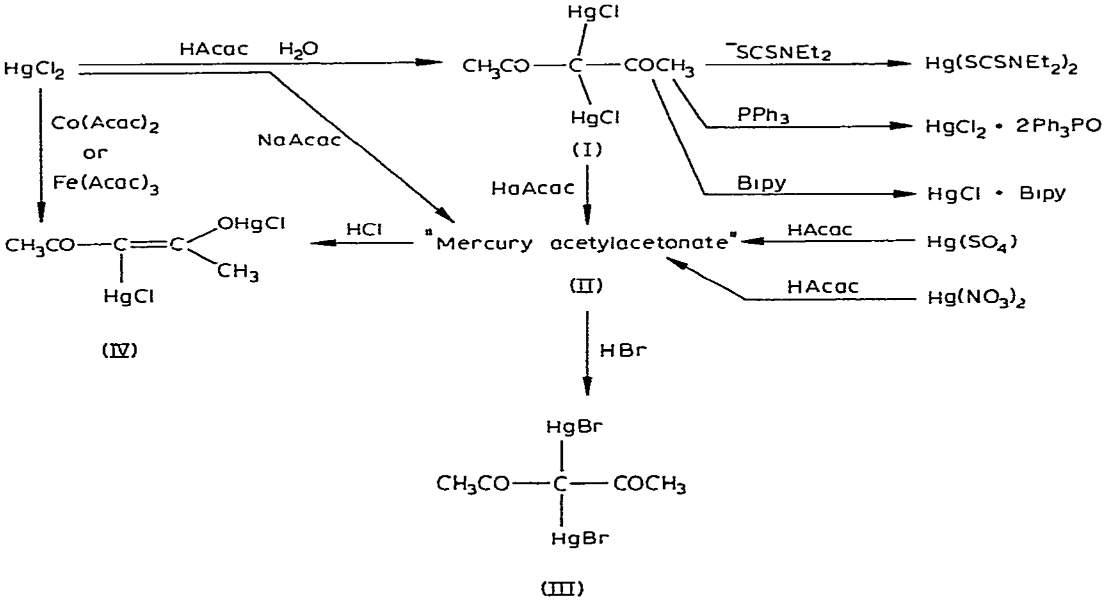

Fig. 3. Chemistry of acetylacetonemercury derivatives from ref. 3.

Acknowledgements

The authors would like to thank Professor G.H. Stout for helpful discussions. This work was supported in part by an NSF Graduate School Research Fund Grant No. GU 3129.

References

1 L. Paoloni, Gaz. Chim. Ital., 89 (1959) 2171.
2 F. Bonati and G. Minghetti, Angew. Chem. Intern. Ed., 7 (1968) 629.
3 F. Bonati and G. Minghetti, J. Organometal. Chem., 22 (1970) 5.
4 J. DeMeulenaer and H. Tompa, Acta Cryst., 19 (1965) 1014.
5 D. Cromer and J. Mann, Acta Cryst., A24 (1968) 321.
6 R. Allman, K. Flatau and H. Musso, Chem. Ber., 105 (1972) 3067.
7 R. Allman and H. Musso, Chem. Ber., 106 (1973) 3001.
8 A. Canty and B. Gatehouse, J. Chem. Soc. D, (1971) 443.
9 B.N. Figgis, J. Lewis, R.F. Long, R. Mason, R.S. Nyholm, P.J. Pauling and G.B. Robertson, Nature, 195 (1969) 1278.
10 J. Lewis, R.F. Long and C. Oldham, J. Chem. Soc., (1965) 6740.
11 D. Gibson, Coord. Chem. Rev., 4 (1969) 225.
12 Spectrochim. Acta, submitted.
13 L. Templeton and D. Templeton, Abstract E10, Amer. Cryst. Assoc. Meeting, Storrs, Conn., 1973.
14 C.K. Johnson, Report ORNL-3794 revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.