Both such systems are normally obtained when the metal is manganese or rhenium, especially the dimeric system. In fact the only mononuclear manganese compound identified, $Mn(CO)_5SC_6F_5$, is unstable at ambient temperature.[16] The rhenium analogs are more stable and the monomers $Re(CO)_5SCF_3$[15] and $Re(CO)_5SC_6F_5$[16] are known. They undergo condensation to dimers under mild activation. The stability of the group VI metal anions $M(CO)_5SR^-$ is in contrast to this behavior since no evidence for a similar condensation reaction was observed when the $M(CO)_5SR^-$ salts were subjected to irradiation or refluxing in THF. If irradiation was carried out in the presence of Ph_3P, substitution of a carbonyl group by the phosphine occurred and displacement of the sulfur ligand was not observed. The bis-substituted products appear to

$$M(CO)_5SR^- + Ph_3P \longrightarrow M(CO)_4(SR)Ph_3P^- + CO$$
$$R = CH_3 \text{ or } CF_3$$

have a cis configuration since four $\nu_{C=O}$ stretching frequencies are observed in the infrared spectrum (see Table II).

Since only singly bridged species were obtained upon reaction of $(n\text{-}C_4H_9)_3SnSR$ with chlorocarbonyl anions,[4] $M(CO)_5Cl^-$, it was felt that the sulfur in the presumed mononuclear mercaptide intermediate was highly nucleophilic. However, attempts to demonstrate this nucleophilicity failed and no reaction was observed between the anion $W(CO)_5SCH_3^-$ and $W(CO)_6$ or the photochemically produced $W(CO)_5 \cdot THF$. Conversion of the $M(CO)_5SR^-$ anions to the bridged mercaptide derivatives $M_2(CO)_{10}SR^-$ occurred readily in the presence of organotin mercaptides. For example treatment of the anion $W(CO)_5SCH_3^-$ with $(n\text{-}C_4H_9)_3SnSCH_3$ resulted in the formation of $W_2(CO)_{10}SCH_3^-$ in good yield. The source of the bridging mercapto group was shown to be the mercapto group bonded to tin and not to the pentacarbonyl moiety since the following reaction was observed. No evidence for an equilibrium mixture was observed using ¹H nmr. This reaction is completely analogous to the reaction of the $M(CO)_5Cl^-$ anions with the organotin mercaptides.[4]

$$2W(CO)_5SCH_3^- + (n\text{-}C_4H_9)_3SnSCH_3 \longrightarrow W_2(CO)_{10}SCH_3^- + SCH_3^- + (n\text{-}C_9H_4)_3SnSCH_3$$

$$2W(CO)_5SCH_3^- + (n\text{-}C_4H_9)_3SnSC_6H_5 \longrightarrow W_2(CO)_{10}SC_6H_5^- + SCH_3^- + (n\text{-}C_4H_9)_3SnSCH_3$$

Since the organotin compound was intimately involved in the conversion of $M(CO)_5SR^-$ to $M_2(CO)_{10}SR^-$ anions, the recently reported compound $Cr(CO)_5S(CH_3)Sn(CH_3)_3$ was felt to be a likely intermediate. Therefore the known compound $Cr(CO)_5S(CH)_3Sn(CH_3)_3$ and its tungsten analog were prepared. When $W(CO)_5S(CH_3)Sn(CH_3)_3$ was allowed to react with either $W(CO)_5SCH_3^-$ or $W(CO)_5Cl^-$, the known dinuclear carbonyl mercaptide derivative was formed according to the following equation. The new bridged mixed-metal mercaptide $[(CO)_5CrS(CH_3)W(CO)_5]^-$ was formed when $Cr(CO)_5S(CH_3)Sn(CH_3)_3$ was allowed to react with either $W(CO)_5Cl^-$ or $W(CO)_5SCH_3^-$. This compound was found to be similar to other dinuclear carbonyl tungsten mercaptides reported earlier,[4] as determined by its analytical data and infrared spectrum. These results suggest the following reaction scheme. The trialkytin mercaptide R_3SnSR' reacts with the tungsten pentacarbonyl halide or mercaptide anion to form the neutral compound $W(CO)_5S(R')SnR_3$. Thus displacement of halide or mercaptide ion occurs rather than sulfur–tin bond cleavage. The sulfur in the trialkyltin mercaptide would be expected to be more nucleophilic than the sulfur in a related alkyl sulfide due to the electropositive character of the tin atom compared to that of a carbon atom. This was demonstrated by addition of diethyl sulfide to the mononuclear carbonyl mercaptide. No reaction occurred and the starting mercaptide derivative was recovered. Attack on the neutral intermediate by another tungsten pentacarbonyl halide or mercaptide ion results in sulfur–tin bond cleavage as shown above. The lability of the sulfur–tin bond has been demonstrated by Ehrl and Vahrenkamp[17] by allowing compounds of the type R_nEY (Y = alkyl or halogen; E = Li, Mg, B, C, P, As, or S) to react with the neutral carbonylthiotin derivative $Cr(CO)_5S(CH_3)SnR_3$. Cleavage of the sulfur–tin bond resulted (*e.g.*, $Cr(CO)_5S(CH_3)SnR_3 + CH_3MgBr \rightarrow SnCH_3 + Cr(CO)_5S(CH_3)MgBr$). This reaction scheme explains the formation of the singly bridged species from both $M(CO)_5Cl^-$ and $M(CO)_5SR^-$ ions and the formation of the mixed-metal-bridged compound.

$$W(CO)_5S(CH_3)Sn(CH_3)_3 + W(CO)_5L^- \longrightarrow W_2(CO)_{10}SCH_3^- + (CH_3)_3SnL \quad (L = Cl, SCH_3)$$

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Enthalpies of Decomposition of Mercuric Halide–Dioxane Complexes

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There has been renewed interest in the complexes of 1,4-dioxane (DX) with the mercuric halides. The far-infrared spectra[1] and nuclear quadrupole resonance spectra[2] of $HgX_2 \cdot DX$ and the dipole moments of HgX_2 in dioxane solution[3] have been reported. Each of these studies suggests that the interaction of DX with HgX_2 decreases in the order $HgCl_2 > HgBr_2 > HgI_2$. The enthalpies of decomposition reported by Crenshaw, Cope, Finklestein, and Rogan (CCFR)[4] appear to indicate the order of stability to be $HgBr_2 \cdot DX > HgI_2 \cdot DX > HgCl_2 \cdot DX$. CCFR reported ΔH for reac-

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tion 1 to be −3.725, −7.253, and −4.880 kcal/mol for

$$HgX_2(s) + DX(l) \longrightarrow HgX_2 \cdot DX(s) \qquad (1)$$

X = Cl, Br, and I, respectively. These values were obtained from unreproachable measurements of the vapor pressures over the solids left by evaporating DX from HgX_2 solutions.

CCFR were not aware that, in addition to $HgX_2 \cdot DX$, complexes $HgX_2 \cdot 2DX$ also exist. These 1:2 complexes decompose under vacuum by reaction 2. $HgBr_2 \cdot 2DX$ and $HgI_2 \cdot 2DX$ are very unstable. There is no doubt that reaction 2 occurred during the removal of the last traces of free solvent so that CCFR did indeed study the decomposition of $HgBr_2 \cdot DX$ and $HgI_2 \cdot DX$ according to reaction 3. However, $HgCl_2 \cdot 2DX$ is relatively stable. It can be crystallized readily from dioxane solution below 40°. Comparison of the vapor pressures reported by CCFR with those given for $HgCl_2 \cdot 2DX$ and $HgCl_2 \cdot DX$ by Daasch[5] and values obtained in the present work shows that CCFR assigned values appropriate to $HgCl_2 \cdot 2DX$ to the 1:1 compound. Values of ΔH, ΔG, and ΔS for reactions 2 and 3 are summarized in Table I.

$$HgX_2 \cdot 2DX(s) \longrightarrow HgX_2 \cdot DX(s) + DX(g) \qquad (2)$$

$$HgX_2 \cdot DX(s) \longrightarrow HgX_2(s) + DX(g) \qquad (3)$$

TABLE I

THERMODYNAMIC QUANTITIES FOR DISSOCIATION REACTIONS OF COMPLEXES[a]

Compound	Reaction	$\Delta H/10^3$J mol^{-1}	$-\Delta G/10^3$J mol^{-1}	ΔS/J mol^{-1} K^{-1}	Ref
$HgCl_2 \cdot 2DX$	2	53.02	9.54	210	*b*
	2	54.28 ± 0.43	9.70 ± 0.05	215 ± 5	*c*
	2	36.96 ± 6.1	10.17 ± 0.2	158 ± 20	*d*
$HgCl_2 \cdot DX$	3	65.5 ± 0.39	22.71 ± 0.40	297 ± 5	*c*
	3	64.26 ± 0.6	21.43 ± 0.40	287 ± 10	*d*
$HgBr_2 \cdot DX$	3	66.57	17.71	281	*b*
$HgI_2 \cdot DX$	3	58.31	11.35	233	*b*
$SbCl_3 \cdot 2DX$	4	47.30	7.70	184	*e*
	4	35.08	9.42	149	*d*
$AgClO_4 \cdot 3DX$	5	58.96 ± 0.61	14.24 ± 0.21	246 ± 10	*f*
	5	45.00	13.61	197	*d*
$AgClO_4 \cdot DX$	6	92.09 ± 1.10	26.87 ± 0.40	399 ± 12	*f*
	6	35.62	16.74	176	*d*

[a] All data refer to 298°K. [b] Data from ref 4, expressed in terms of reactions 2 or 3 (errors cannot be estimated from the smoothed data presented). [c] Present work. [d] Reference 5, estimates of error by present author. [e] Calculated from data of C. J. Kelley and P. A. McCusker, *J. Amer. Chem. Soc.*, **65**, 1307 (1943). [f] J. C. Barnes and C. S. Duncan, *J. Chem. Soc., Dalton Trans.*, in press.

The order of stability is now $HgCl_2 \cdot DX > HgBr_2 \cdot DX > HgI_2 \cdot DX$ as expected by analogy with other mercury(II) halide complexes and as indicated by the infrared spectra,[1] nqr spectra,[2] and dipole moment measurements.

Table I shows that the values reported by Daasch[5] for ΔH_{298} and ΔS_{298} are smaller than those reported by other workers not only for the mercury compounds but also for the decomposition reactions 4, 5, and 6.

$$2[SbCl_3 \cdot 2DX](s) \longrightarrow (SbCl_3)_2 \cdot 3DX(s) + DX(g) \qquad (4)$$

$${}^1/_2 AgClO_4 \cdot 3DX(s) \longrightarrow {}^1/_2 AgClO_4 \cdot DX(s) + DX(g) \qquad (5)$$

$$AgClO_4 \cdot DX(s) \longrightarrow AgClO_4(s) + DX(g) \qquad (6)$$

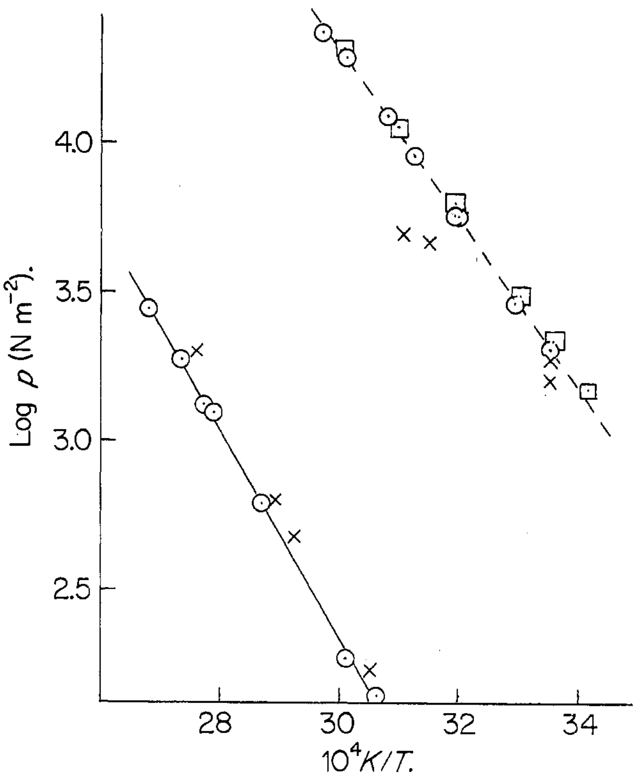

Figure 1.—Decomposition of $HgCl_2 \cdot DX$ and $HgCl_2 \cdot 2DX$: dotted line, $HgCl_2 \cdot 2DX$; full line, $HgCl_2 \cdot DX$; circles, present data; squares, smoothed data presented by CCFR;[4] crosses, data presented by Daasch.[5]

Since the alternative data have been collected independently over 35 years, it appears that the values obtained by Daasch are in error. The error may lie in the method used to determine the vapor pressures. Daasch measured the intensities of the 1258- and 881-cm^{-1} bands of dioxane in a gas cell connected to a thermostated flask containing the sample. The calibration of the transmittance scale with dioxane vapor was not described. Each of the other workers including the present authors used conventional monometric techniques.

Experimental Section

$HgCl_2 \cdot DX$ was prepared by allowing a boiling saturated solution of analytical grade $HgCl_2$ in reagent grade dioxane to crystallize. $HgCl_2 \cdot 2DX$ was obtained from dilute solutions which formed crystals only below 40°. Since both compounds have been described previously,[4,5] the dried products were analyzed only for mercury, using the gravimetric $Cu(en)_2HgI_4$ method.[6] *Anal.* Calcd for $C_4H_8Cl_2HgO_2$: Hg, 55.81. Found: Hg, 55.5. Calcd for $C_8H_{16}Cl_2HgO_4$: Hg, 44.82. Found: Hg, 44.9.

Vapor pressure measurements were made in an apparatus differing from that used by CCFR[4] only in being arranged to use previously prepared solid complexes whereas in the original the samples were prepared *in situ*. The sample cell and the adjacent mercury-filled trap were heated in a water bath thermostatically controlled to ±0.05°. Pressures were measured by a mercury manometer to ±0.1 Torr and the usual corrections applied. Readings were accepted only when the same pressure was obtained three times, exhausting the sample cell to 0.1 Torr between each reading. In this way errors due to traces of trapped, uncomplexed dioxane could be avoided.

Figure 1 shows the experimental results obtained in this work compared with those reported by CCFR[4] and by Daasch.[5]

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