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INFRARED AND RAMAN SPECTRA OF (THIOACETOXYTHIO)TRIORGANO DERIVATIVES OF SILICON, GERMANIUM, TIN AND LEAD

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Summary

The IR and Raman spectra of (thioacetoxythio)trimethyl-Group IVb metals were recorded and an attempt was made to elucidate the structures by spectra. It is concluded that the bonding is similar to that of organic dithio acetates and that intramolecular coordination of the thiocarbonyl sulfur to Group IVB metals is small or negligible. Characteristic absorption bands of C(S)—S groups are found near 880-860 cm^{-1}.

Introduction

Although the structures of Group IVb organometallic esters of acetic [1] and *N,N*-dimethyldithiocarbamic acid [2] have been investigated in detail by IR spectroscopy and X-ray diffraction, the corresponding esters of dithioacetic acid have not been reported. We have described [3] the successful isolation of crystalline piperidinium salts of aliphatic dithio acids (except those of dithioacetic acid) and through subsequent efforts to crystallize dithioacetic acid using amines under various conditions we managed to obtain two crystalline ammonium salts (trimethylammonium and piperidinium). This result prompted us to prepare a series of (thioacetoxythio)triorgano-Group IVB metals (CH_3CS_2X, X = CH_3, Me_3Si, Me_3Ge, Me_3Sn and Et_3Pb) and to investigate their structures by IR and Raman spectroscopy.

Results and discussion

The assignment of the principal absorption bands in the spectra of (thioacetoxythio)trimethyl-Group IVB metals are indicated in Tables 1 (IR) and 2

(continued on p. 227)

TABLE I

FREQUENCIES (cm^{-1}) AND ASSIGNMENTS[a] OF PRINCIPAL ABSORPTION BANDS OF IR SPECTRA IN (THIOACETOXYTHIO)TRIORGANO-GROUP IVB METAL[b]

$CH_3CS_2CH_3$ (Ia)	$CH_3CS_2Si(CH_3)_3$ (Ib)	$CH_3CS_2Ge(CH_3)_3$ (Ic)	$CH_3CS_2Sn(CH_3)_3$ (Id)	$CH_3CS_2Pb(C_2H_5)_3$ (Ie)	Assignment
2892 w	2964 w	2982 w	2992 w	2975 w	$\nu(CH_3)_{asym}$
				2940 w	$\nu(CH_2)_{asym}$
2868 w	2909 w	2919 w	2924 w	2925 w	$\nu(CH_3)_{sym}$
				2850 w	$\nu(CH_2)_{sym}$
				2830 w(sh)	(1420 + 1420)
				1462 w	
1419 w	1428 w	1430 w	1433 w	1455 m	$\delta(CH_3)_{asym}$
1410 m	1408 w	1412 w	1420 w	1420 w	$\delta(CH_3(-M))_{asym}$
1360 m	1367 w	1355 w	1357 w	1375 m	$\delta(CH_3)_{sym}$
				1350 vw	$\delta(CH_2)_{sym}$
				1222 vw	(785 + 450)
1251 m	1251 w	1237 w	1198 w	1194 w	$\delta(CH_3(-M))_{sym}$
	1194 vs	1187 vs	1184 s	1165 vs(sh)	
1194 vs					$\nu(C=S)_{asym}$
	1178 m(sh)	1178 s	1172 vs	1154 vs	

1093 m	1093 m	1093 m	1093 m	1093 m	$\rho(CH_3)$
				1060 vw	(594 + 460)
				1020 w	ν(C—C)
				958 w	
				940 w	(460 + 460)
862 vs	876 vs	873 vs	870 vs	873 vs	$\nu(C(S)—S—M)_{asym}$ (?)
				785 m	
				720 m	
	841 vs	827 vs	777 vs	670 s	$\rho(CH_3(—M)$ or $\rho(CH_2—(M))$
	805 vw	805 vw	805 vw		
	760 vw	760 vw	[c]		
		612 m	539 m	460 m	
	689 m	(split)	(split)	(split)	$\nu(C—M)_{asym}$
		605 m	531 m	457 m	
578 m	624 m	565 m	510 m	435 m	$\nu(C(S)—S)_{asym}$
	583 m	586 m	590 m	600 m	
454 m	458 m	456 m	456 m	437 m	ρ(C—C(S)) in-plane bend
	489 m	417 m	395 m	372 m	$\nu(M—S)_{asym}$
339 w	365 vw	357 vw	355 vw	362 w	
	331 m	266 m	235 m	245 m (?)	$\nu(M—S)_{sym}$

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[a] Abbrevation: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; (sh), shoulder [b] Recorded as Nujol nulls. [c] Hidden in strong absorption at 777 cm^{-1}.

TABLE 2

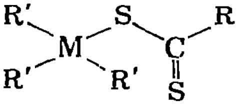
FREQUENCIES (cm^{-1}) AND ASSIGNMENTS[a] OF PRINCIPAL ABSORPTION BANDS OF RAMAN SPECTRA IN (THIOACETOXYTHIO)TRIORGANO-GROUP IVB METAL[b]

$CH_3CS_2CH_3$ (Ia)	$CH_3CS_2Si(CH_3)_3$ (Ib)	$CH_3CS_2Ge(CH_3)_3$ (Ic)	$CH_3CS_2Sn(CH_3)_3$ (Id)	$CH_3CS_2Pb(C_2H_5)_3$ (Ie)	Assignment
2960 vw	2960 vw	2980 vw			$\nu(CH_3)_{asym}$
2905 m	2906 m	2906 m	2906 m	2906 m	$\nu(CH_3)_{sym}$
				2870 vw	$\nu(CH_2)_{sym}$
1360 vw	1360 vw	1360 vw	1360 vw		
	1220 w	1220 w			
			1180 (sh)		
1200 s	1190 s	1180 s		1160 s	$\nu(C{=}S)_{asym}$
			1170 s		
1100 vw	1100 vw	1100 vw	1100 vw		
862 m	880 m	874 m	870 m	873 m	$\nu(C(S){-}S)_{asym}$ (?)
730 vw					
		590 w	690 m		
578 vs					
	586 vs	566 vs	507 vs	440 vs	$\nu(C(S){-}S)_{sym}$
	480 m	420 m	395 m	385 w	$\nu(C{-}S)_{sym}$
385 vw					
340 vw	330 m	260 m	237 m	243 m	$\nu(M{-}S)_{sym}$
230 m	180 m	172 m	156 m	160 m	

[a] Abbreviation. vs, very strong; s, strong; m, medium; w, weak; vw, very weak, (sh), shoulder. [b] Recorded as Nujol mulls.

(Raman). Our approach has been empirical. First, bands attributable to $CH_3C(S)$, Me_3M (M = Si, Ge and Sn) and Et_3Pb were selected, on the basis of intensity and frequency, using available correlations with $CH_3CO_2CH_3$ [4], CH_3CS_2H [5], $CH_3CO_2SiMe_3$ [6] and $CH_3CO_2SnMe_3$ [1]. Next, bands ν(C=S) and ν(S—M) (M = Group IVB metal) were assigned using available correlations with i-$PrCS_2MMe_3$ [7] and $Ph_3MSM'Ph_3$ (M, M' = Group IVB metals) [8]. This left a number of bands unassigned.

With the metalloidal IVB esters, two characteristic intense IR bands were observed at 1200-1150 cm^{-1} and 880-860 cm^{-1}, and there are strong Raman bands for each compound in the range 440 to 590 cm^{-1}, which are reasonable for C—S stretching bands. A very strong infrared band between 1150 and 1200 cm^{-1} is attributed to the C=S stretching vibration, because with the amine salts of dithioacetic acid this band was observed near 870 cm^{-1}. In addition, these C=S stretching bands showed a tendency towards a small red shift (ca. 10-15 cm^{-1}) of ν(C=S) with increasing atomic number of Group IVB metal. Moreover, the molecular weight of $CH_3CS_2Sn(CH_3)_3$ in benzene was 248 (calcd. 255). These phenomena suggest that these shifts are probably caused by the heavy metal atom effect, and that any intramolecular coordination effects of the thiocarbonyl sulfur atom to Ge, Sn and Pb atoms are small or negligible. This result was supported by Mössbauer spectral data for (thiobenzoylthio)triphenylstannane [9] and X-ray structure determination for trimethylstannyl dimethyldithiocarbamate [10, 11]. Thus, it seems that the Group IVB metal esters of dithio acid in a mull have the metal in a 4-coordinate structure (I).



(I)

M = Si, Ge, Sn, Pb, C

As mentioned above, alkyl and triorgano-Group IVB metal esters of dithioacetic acid show a characteristic intense absorption band in the range 880-860 cm^{-1}, as well as in the region 1200-1150 cm^{-1} which can be assigned to the ν(C=S). However, it would also be difficult to assign the bands in the 880-850 cm^{-1} region to the symmetrical thiocarbonyl stretching frequency or the ν(C—S) band, because a relatively small absorption band was observed in the same range of their Raman spectra and it is well known that the C—S stretching vibration normally appears in the infrared as a weak absorption below 700 cm^{-1} [12]. Interestingly, this characteristic intense band did not show a tendency towards a red shift with increasing atomic number of the Group IVB metal atom. The order Si > Ge > Pb > Sn > C for this band is clearly inconsisten with the operation of a simple inductive or heavy atom effect, and may possibly reflect a capacity for d_π—p_π bonding between the IVB element and the sulfur atom, resulting in the formation of a S=C—S—M conjugate system. A similar order was observed in the n—π^* transition of these esters (see Experimental section). These results, and the possibility of a contribution of the resonance form II to the C(S)—S stretching vibration in dithio esters suggests that the inten

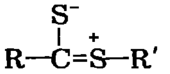
TABLE 3

YIELDS AND SPECTRAL DATA OF (THIOACETOXYTHIO)TRIALKYL-GROUP IVB METALS

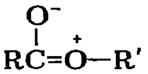
No.	Compounds	B.p. (°C/mmHg)	Yield (%)	NMR ($CDCl_3$) δ (ppm)		UV (cyclo-C_6H_{12}) λ max (nm), (ε max)
Ia	$CH_3CS_2CH_3$	53.5-55/39-40	99	2.75 (CH_3–CS_2, s, 3H) 2.53 (CH_3–S, s, 3H)		303(10700) 457(16)
Ib	$CH_3CS_2SiMe_3$	66-67/17	89	2.89 (CH_3–CS_2, s, 3H) 0.47 (CH_3–Si, s, 9H)		295(10800) 484(12)
Ic	$CH_3CS_2GeMe_3$	53-54/5	96	2.90 (CH_3–CS_2, s, 3H) 0.68 (CH_3–Ge, s, 9H)		310(10540) 482(15)
Id	$CH_3CS_2SnMe_3$	61-62/0.5	97	2.94 (CH_3–CS_2, s, 3H) 0.59 (CH_3–Sn, s, 9H)	$J(^{117}Sn$–CH) 55.0 Hz $J(^{119}Sn$–CH) 57.3 Hz	317(9800) 474(17)
Ie	$CH_3CS_2PbEt_3$	27-29[a]	95	2.95 (CH_3–CS_2, s, 3H) 2.07 (CH_2, q, 6H) 1.73 (CH_3, t, 9H)		330(9000) 476(17)

[a] Melting point

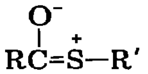
absorption band in the 880-860 cm^{-1} region may be reasonably attributed to an


$R-\overset{S^-}{C}=\overset{+}{S}-R'$

(II)


$R\overset{O^-}{C}=\overset{+}{O}-R'$

(III)


$R\overset{O^-}{C}=\overset{+}{S}-R'$

(IV)

asymmetric C(S)—S—M (M = IVB element) stretching frequency in alkyl and Group IVB metal esters of dithioacetic acid. Although the difference between the ν(C—S) frequency in —C(O)—S— and —C(S)—S— must result principally from the change on the S=C—S—M conjugate system which results from replacing O by S, the greater relative importance of the resonance structures (III and IV) for ordinary aliphatic esters [13] and thiol esters [14, 15] has been noted.

Experimental

The IR spectra in the 4000-200 cm^{-1} region were recorded on a JASCO DS-701G instrument as mulls between CsI plates. The KBr region was calibrated with polystyrene. A JASCO Model CT-40D Raman spectrometer equipped with Spectra-Physics Model 165 Argon Ion 5144 Å, max 800 mW was used to obtain the Raman spectra. In this instrument, the laser beam passes through a glass ampoule tube and the Raman signal is collected at 90° to the incident laser beam. The mechanical slit width was 500 μ (SBW 10.6 cm^{-1}) sensitivity 1-4, response 0.5-2 sec, and scanning speed 240-30 cm^{-1} min^{-1}. The Raman spectra of (thioacetoxythio)triethyllead was obtained in cyclohexane and CCl_4 * solution (ca. 20%) by the rotatory reflection method. The other Raman spectra were obtained on liquids at room temperature. The power of the excitation line (5144 Å) was reduced to 35 mW, to avoid boiling or destruction of the sample. There was no evidence of sample degradation as a result of exposure to the laser beam except for (thioacetoxythio)triethyllead. The reported infrared and Raman frequencies below 1500 cm^{-1} are believed accurate to ± 2 cm^{-1}.

Materials

Piperidinium dithioacetate was prepared according to the previously reported method [3], except that the reaction temperature was kept below —30°C: m.p. 68-73°C; IR(Nujol) $\nu(H_2N)$ 3000-2500, $\nu(CS_2)$ 875 cm^{-1}; NMR (CH_2Cl_2), δ 8.00 (NH_2, s, 2H), 3.28 (ring CH_2N, t, 4H), 3.07 (CH_3, s, 3H), 1.73 (ring CH_2, m, 6H). Chlorotrimethylgermane (EGA-Chemie DG) and chlorotriethyllead (Ventron Corporation, Alfa Products), were commercially available. Methyldithioacetate (Ia), (thioacetoxythio)trimethyl-silane (Ib), -germane (Ic) and -stannane (Id), and (thioacetoxythio)triethyllead (Ie) were prepared by the reaction of piperidinium dithioacetate with the corresponding organo-Group IVB metal chloride according to the previously reported procedures [7]. Their yields, spectral data (except for IR and Raman spectral data) and elemental analyses are summarized in Tables 3 and 4.

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* The power of the excitation line (5144 Å). 20 mW.

TABLE 4

ELEMENTAL ANALYSES

No	Compound	Formula	Analysis found (calcd) (%)		
			C	H	S
Ia	$CH_3CS_2CH_3$	$C_3H_6S_2$	33.89 (33.93)	5.61 (5.69)	60.46 (60.38)
Ib	$CH_3CS_2Si(CH_3)_3$	$C_5H_{12}S_2Si$	36.61 (36.54)	7.33 (7.36)	39.20 (39.02)
Ic	$CH_3CS_2Ge(CH_3)_3$	$C_5H_{12}S_2Ge$	28.83 (28.75)	5.80 (5.79)	30.91 (30.70)
Id	$CH_3CS_2Sn(CH_3)_3$	$C_5H_{12}S_2Sn$	23.48 (23.55)	4.77 (4.74)	25.26 (25.15)
Ie	$CH_3CS_2Pb(C_2H_5)_3$	$C_8H_{18}S_2Pb$	24.80 (24.92)	4.76 (4.71)	16.59 (16.63)

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