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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXXI. STUDIES ON ORGANOLEAD(IV) THIOCYANATE COMPOUNDS

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SUMMARY

The configurations of $(CH_3)_3PbNCS$, $(C_6H_5)_3PbNCS$, $(C_6H_5)_2Pb(NCS)_2$, $(C_6H_5)_3Pb(NCS)_2^-$ and $(C_6H_5)_2Pb(NCS)_4^{2-}$ have been investigated in the solid and (except for the insoluble diphenyl derivative) in solution. From infrared spectroscopy it is deduced that the compounds are isothiocyanates in both states, and there is evidence for a polymeric nature of the solid neutral species involving bridging through NCS. PMR and osmometric investigations show that five-coordinate species $(CH_3)_3Pb(NCS)\cdot(CH_3)_2CO$ are present in acetone solution. Possible configurations are discussed

INTRODUCTION

The preparation and the solution chemistry of the complex anions $Ph_2Pb(NCS)_4^{2-}$ and $Ph_3Pb(NCS)_2^-$, Me_4N^+ and Ph_4As^+ salts, have been described previously[1]. We have now investigated structural aspects of organolead(IV) thiocyanate derivatives; the configurations of the neutral salts Me_3PbNCS, Ph_3PbNCS and $Ph_2Pb(NCS)_2$ [dialkyllead(IV) thiocyanates do not exist[2]], as well as those of the above-mentioned complex anions, were studied by infrared spectroscopy in the solid state and in solution [except for the almost insoluble $Ph_2Pb(NCS)_2$]. The solution chemistry of Me_3PbNCS was also investigated by PMR spectroscopy and by osmometry. The nature of the Pb^{IV} thiocyanate interaction, which cannot be determined for inorganic Pb^{IV}, owing to the non-existence of Pb^{IV} thiocyanates (not reported in the literature), has thus been elucidated.

EXPERIMENTAL

Analytical grade reagents were used throughout. Organolead(IV) thiocyanate derivatives were prepared as elsewhere reported[1,3,4]. The IR spectra were recorded with Beckman IR 9 and Perkin-Elmer 457 spectrometers.

Solids were investigated as Nujol mulls and as KBr pellets. The assignment of vibrational bands has been achieved by comparison of the spectra of organolead

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TABLE 1

INFRARED DATA FOR ORGANOLEAD(IV) THIOCYANATE DERIVATIVES

For solids, assignments of bands to NCS stretching and bending vibrational modes are indicated. For solutions (3×10^{-2} *M*), the apparent integrated absorption intensities per mole of NCS [*A* (cm^{-2}/mole)] of the ν_{as}(NCS) are listed. Frequencies in cm^{-1}.

Compound	*Solids*				*Solutions*		
	ν_{as}	ν_{sym}	$2 \times \delta$	δ	*Solvent*	ν_{as}	$A \times 10^4$
Me_3PbNCS^a	2090 vs 2042 (sh)	760 w(sh)	930 w^b 907 w	463 m 452 w	Me_2CO	2045	6
Ph_3PbNCS	2092 vs 2050 (sh)	^{c}	930 vw 905 vw	464 w 458 w	Me_2CO	2039	10
$Ph_2Pb(NCS)_2$	2098 vs 2050 (sh)	832 w^d 765 w^d	926 w 904 vw	462 m 440 m^d		^{e}	^{e}
$[Me_4N][Ph_3Pb(NCS)_2]$	2090 s 2045 (sh)	^{c}	927 vw 905 vw	462 w 452 w	Me_2CO	2040	9
$[Ph_4As][Ph_3Pb(NCS)_2]$	2093 s 2055 vs	^{c}	^{c}	480 m 467 m	MeCN	2043	12
$[Me_4N]_2[Ph_2Pb(NCS)_4]$	2054 vs	832 vw^d 790 w^d	^{c}	490 w 472 w	MeCN	2039	12
$[Ph_4As]_2[Ph_2Pb(NCS)_4]$	2088 m 2046 s	845 vw^d	^{c}	478 m 464 m	Me_2CO	2032	14

[a] $\nu_{as}(PbC_3)$ at 494 cm^{-1}.

[b] Previously assigned to ν_{sym}(NCS)[4].

[c] Not observed.

[d] Assignment uncertain.

[e] Not determined owing to insufficient solubility.

thiocyanates with those of Me_3PbCl[5], Ph_2PbCl_2 and Ph_3PbCl[6], Me_4NNCS and Ph_4AsNCS. The solution phase studies were carried out on freshly prepared solutions, using cells with CaF_2 windows, 0.1 mm thick. The apparent integrated absorption intensity of the ν_{as}(NCS) band was calculated by the Ramsay method of direct integration[7]. The results are reported in Table 1.

The PMR spectrum of Me_3PbNCS was determined with a JEOL C 60 spectrometer using $(CD_3)_2CO$ as the solvent and TMS as the internal standard. The coupling constant $J(^{207}\text{Pb–CH}_3)$ was 79.5 Hz.

The osmometry was carried out with a Mechrolab 301–A vapour pressure osmometer on acetone solutions at 37°. Results are reported in Table 2.

DISCUSSION

The assignments to ν_{sym}(NCS) (virtually a C–S stretch[8]) and to the bending mode δ(NCS) of the bands occurring at 760 cm^{-1} and 463, 452 cm^{-1}, respectively, in solid Me_3PbNCS (Table 1), suggest an isothiocyanato configuration for this compound. According to established views, ν_{sym}(NCS) should lie between 760 and 880 cm^{-1}, and δ(NCS) at about 475 cm^{-1}, for isothiocyanates (see *e.g.* ref. 9). On the other hand, the fact that ν_{as}(NCS) (virtually a C–N stretch[8]) for the solid lies in the neighborhood of 2100 cm^{-1} (Table 1) may indicate a bridging nature for NCS[10] in Me_3Pb-NCS. This is supported by the fact that an intense band occurring at 494 cm^{-1} may

TABLE 2

OSMOMETRY IN ACETONE SOLUTIONS OF Me_3PbNCS, Me_4NNCS, AND EQUIMOLAR MIXTURES

Van 't Hoff factors, *i*, are listed.

	Concn. (mM)	*i*
Me_3PbNCS	1.2	1.3
	3	1.2
	10	1.0
	30	1.0
Me_4NNCS	1.54	1.8
	15.4	1.2
$Me_3PbNCS + Me_4NNCS$	1	2.9
	10	1.9

be safely assigned to $\nu_{as}(PbC_3)^5$, while no band may be reasonably attributed to $\nu_{sym}(PbC_3)$. The PbC_3 unit would then assume a planar trigonal configuration, and solid Me_3PbNCS would be a trigonal bipyramidal polymer, as proposed for Me_3Sn-NCS[11].

The polymeric structure of Me_3PbNCS is obviously destroyed in solution phase where $\nu_{as}(NCS)$ is shifted to 2045 cm^{-1} (Table 1) a value characteristic of isothiocyanates (see *e.g.* refs. 9 and 12). Coordination of NCS to Pb through the N atom in acetone solution is also inferred from the apparent integrated absorption intensity of the $\nu_{as}(NCS)$ band (Table 1). The latter parameter was reported to range between 9 and 12×10^{-4} cm^{-2}/mole for *N*-bonded compounds, and between 0.8 and 2.3×10^{-4} cm^{-2}/mole for *S*-bonded derivatives[13]. According to this analysis the value $A = 6 \times 10^{-4}$ cm^{-2}/mole determined for Me_3PbNCS (Table 1) would appear low for a nitrogen–metal bond, but at the same time it would exclude the possibility of the existence of a sulphur–metal bond. Since osmometric data (Table 2) clearly indicate the occurrence of monomeric undissociated Me_3PbNCS in acetone for concentrations of the same order of that used in the infrared study, an *N*-bonded configuration is assumed for Me_3PbNCS in solution.

The nature of the species present in acetone solutions of Me_3PbNCS is indicated by PMR and osmometric data. The value of 79.5 Hz for $(J\,^{207}Pb\text{–}CH_3)$ is consistent with the presence of a solvated five-coordinated species in which the NCS group and a solvent molecule would axially coordinate to Pb and the PbC_3 moiety would be located in a trigonal plane. Previously $J(^{207}Pb\text{–}CH_3)$ values ranging between 63 and 87 Hz have been reported for compounds with this type of configuration[14]. Slight dissociation of Me_3PbNCS occurs at higher dilution while the coordinated acetone molecule is not displaced by NCS^- ligands (Table 2). This is consistent with the failure of attempts to prepare $Me_3Pb(NCS)_2^-$ by addition reaction of NCS^- to the neutral salt in donor solvents.

Solid Ph_3PbNCS also seems to be an essentially *N*-bonded compound, with a possible polymeric structure due to a bridging behaviour of the NCS group; $\delta(NCS)$ is again located at a wavenumber consistent with *N*-bonding, and $\nu_{as}(NCS)$ is not inconsistent with the presence of bridging NCS (Table 1). A trigonal bipyramidal polymeric structure can thus be advanced for solid Ph_3PbNCS, analogous to that assumed for Me_3PbNCS. Infrared data (Table 1) and osmometry[1] in acetone solution indicate again the presence of monomeric species, with NCS bonded to Pb through N.

In solid $Ph_2Pb(NCS)_2$, one of the two bands occurring at 832 and 765 cm^{-1} (Table 1) could be tentatively assigned to $\nu_{sym}(NCS)$, even if the presence of phenyl ring vibrations in this region[6] makes the attribution uncertain. This assignment, together with the $\delta(NCS)$ value quoted in Table 1, is consistent with *N*-bonding. Again, polymerization through bridging by NCS is not ruled out by $\nu_{as}(NCS)$, and is supported by the insolubility of $Ph_2Pb(NCS)_2$ even in donor solvents. The structure of $Ph_2Pb(NCS)_2$ could be analogous to those of Me_2PbCl_2[5], Ph_2PbCl_2[15] and $Ph_2Sn(NCS)_2$[16], which are assumed to be octahedral polymeric compounds, with bridging Cl or NCS groups, and *trans* linear C–M–C linkages. On the other hand, deviations from the regular octahedral configuration have often been detected in related solid organotin compounds, such as Me_2SnCl_2[17], Ph_2SnCl_2[16] and $Me_2Sn(NCS)_2$[18].

As for the anionic complexes, $\delta(NCS)$ for solids and the integrated absorption intensities for solutions (Table 1) are fully consistent with *N*-bonding in both physical states. A *trans* octahedral structure is suggested for $Ph_2Pb(NCS)_4^{2-}$, and a trigonal bipyramidal one for $Ph_3Pb(NCS)_2^-$ (with the PbC_3 group located in the trigonal plane) in keeping with those proposed[19] for the related anions $Me_2Sn(NCS)_4^{2-}$ and $Me_3Sn(NCS)_2^-$.

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