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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XL. ORGANOLEAD(IV) AZIDO AND MIXED AZIDO—THIOCYANATO COMPLEX ANIONS

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Summary

Tetraphenylarsonium and tetramethylammonium salts of the complex anions $Ph_3Pb(N_3)_2^-$, $Ph_3Pb(N_3)(NCS)^-$, $Ph_2Pb(N_3)_4^{2-}$ and $Ph_2Pb(N_3)(NCS)_2^-$ have been prepared and characterized. Infrared spectra and solution conductance data are reported. Possible configurations of the complex anions are discussed.

Introduction

Some synthetic and spectroscopic studies of organotin(IV) azido and mixed azido—thiocyanato complex anions have been previously reported [1]. This paper is concerned with the preparation of analogous organolead(IV) species, and was undertaken mainly because little information exists on the coordination chemistry of Pb^{IV} compounds containing the N_3^- ligand. $Ph_2Pb(N_3)_2$ [2], Me_3PbN_3 [3] and Ph_3PbN_3 [2, 4—6] were the only stable compounds previously prepared. Lead atoms with coordination number higher than 4 probably exist in solid $Ph_2Pb(N_3)_2$, its insolubility in common solvents suggesting the presence of intermolecular bonding by bridging azido groups. It has been pointed out that in R_3PbN_3 there is a consistent ionic character of the lead—azide bond, but no clear structural evidence, even on the symmetry of the R_3Pb^{IV} moieties, emerged from the studies of these compounds [2—6]. The corresponding R_3SnN_3 compounds have been shown by Mössbauer spectroscopy [7, 8] to be polymeric compounds containing pentacoordinate tin(IV) atoms. Probably there are not close stereochemical analogies between the R_3MN_3 (M = Sn, Pb) series with M = Sn and that with M = Pb, since Me_3PbN_3, unlike Me_3SnN_3, does not show a marked shift in the $\nu_{as}(N_3)$ frequency on dissolution [3], and the crystals of the triphenylderivatives are not isomorphous [2, 6].

Experimental

The organolead derivatives Ph_3PbN_3 [6], $Ph_2Pb(N_3)_2$ [2] and $Ph_2Pb(NCS)_2$ [11] were obtained by published methods. The salts Me_4NN_3, Ph_4AsN_3 and Ph_4AsNCS were prepared as previously described [1].

The complex salts $[Me_4N][Ph_3Pb(N_3)_2]$ (I), $[Ph_4As][Ph_3Pb(N_3)_2]$ (II) and $[Ph_4As][Ph_3Pb(N_3)(NCS)]$ (III) were isolated as crystalline solids by cooling alcoholic solutions of Ph_3PbN_3 (1.6 g in 25 ml of abs. EtOH) containing a stoichiometric amount of the appropriate AN_3 or ANCS ($A = Me_4N$, Ph_4As) salt, and were recrystallized from the same solvent.

The compounds $[Me_4N]_2[Ph_2Pb(N_3)_4]$ (IV) and $[Ph_4As]_2[Ph_2Pb(N_3)_4]$ (V) were prepared by refluxing 0.8 g of $Ph_2Pb(N_3)_2$ and an excess of AN_3 (mole ratio 1/3) in 40 ml of acetonitrile until the reactants had almost completely dissolved. After filtering the warm solution, the tetramethylammonium derivative separated out on cooling but the tetraphenylarsonium salt had to be precipitated from the solution by the addition of diethyl ether. Both compounds were recrystallized from acetonitrile containing equimolar amounts of AN_3.

The compound $[Ph_4As][Ph_2Pb(N_3)(NCS)_2]$ (VI) was prepared by refluxing 0.4 g of $Ph_2Pb(NCS)_2$ with the stoichiometric amount of Ph_4AsN_3 in 25 ml of acetonitrile. From the filtered solution the compound was precipitated by addition of diethyl ether.

Infrared spectra were recorded with Nujol mulls in the range 4000 to 250 cm^{-1} on a Perkin—Elmer 457 spectrometer. Conductance measurements were performed at 30° with an LKB 5300 B instrument.

Discussion

The compounds prepared, shown in Table 1, were shown to be tetraorganoammonium or -arsonium salts of the organolead anions by the analytical data. Their existence is evidence of the ability of Pb^{IV} in Ph_2Pb^{IV} and Ph_3Pb^{IV} to expand its coordination number in the presence of an azide ligand. The formation of anionic diphenyllead complexes is suggested by the dissolution of $Ph_2Pb(N_3)_2$ in the solvent containing AN_3. Some dissolution of $Ph_2Pb(N_3)_2$ was noticed after the addition of one mole of AN_3, probably indicating the formation of formally pentacoordinate lead species. Similar solubility was observed on addition of ANCS or AN_3 to $Ph_2Pb(N_3)_2$ or $Ph_2Pb(NCS)_2$ (which is also practically insoluble in common solvents), and evidence of formation of $Ph_2Pb(N_3)_x(NCS)_{n-x}^{2-n}$ ($n = 3, 4$) species was observed. Compounds IV, V and VI were, however, the only pure products we were able to isolate. From treatment of Me_3PbN_3 with AN_3 in suitable solvents only starting materials were isolated. Similar results were previously obtained for treatment of Me_3PbNCS with ANCS [9].

The compounds I—III and VI behave as 1/1 and V as 1/2 electrolytes, as shown by their molar conductivities in MeOH solutions (Table 1) [10], the results show that complex anions are also present in solution.

Infrared peaks arising from internal vibrations of the pseudohalide groups are listed in Table 2. For the mixed azido—thiocyanato complex salts III and VI, both coordination through the S atom and bridging behaviour by the NCS ligand can be excluded on the basis of the $\nu_{as}(NCS)$ and $\delta(NCS)$ frequencies [9]. The

TABLE 1

ANALYTICAL DATA AND MOLAR CONDUCTANCES IN METHANOL

Compound		M p. (°C)	Analysis found (calcd.) (%)				Conc. (mM)	Λ_m (Ω^{-1} cm^2 mol^{-1})
			C	H	N	S		
I	$[Me_4N][Ph_3Pb(N_3)_2]$	176–177	44.51 (44.28)	4.62 (4.56)	16.28 (16.43)		2.23 1.34 0.45	112 118 128
II	$[Ph_4As][Ph_3Pb(N_3)_2]$	183–185	54.83 (55.68)	3.99 (3.89)	9.10 (9.10)		1.32 0.88 0.44	92 96 101
III	$[Ph_4As][Ph_3Pb(N_3)(NCS)]$	157–159	55.81 (56.01)	3.97 (3.83)	6.02 (6.08)	3.33 (3.48)	2.23 1.34 0.45	98 108 129
IV	$[Me_4N]_2[Ph_2Pb(N_3)_4]$	208–209	35.42 (35.44)	5.19 (5.06)	28.77 (28.93)		*a*	
V	$[Ph_4As]_2[Ph_2Pb(N_3)_4]$	185–186	55.49 (55.59)	4.18 (3.89)	12.78 (12.97)		1.40 0 56	163 184
VI	$[Ph_4As][Ph_2Pb(N_3)(NCS)_2]$	179–181	50.45 (50.54)	3.45 (3.35)	7.59 (7.76)	7.25 (7.10)	3.43 1.72 0.69	102 116 131

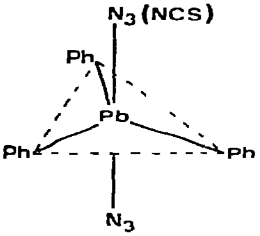
[a] Poorly soluble in MeOH.

TABLE 2

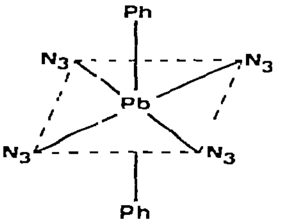
INFRARED ABSORPTIONS (cm^{-1}) FROM THE PSEUDOHALIDE GROUPS

Compound		ν_{as}(N_3 and/or NCS)	$\nu_s(N_3)$	$\delta(N_3)$	δ(NCS)
I	$[Me_4N][Ph_3Pb(N_3)_2]$	2040 (sh) 2020 vs (br)	1279 w	645 w	
II	$[Ph_4As][Ph_3Pb(N_3)_2]$	2033 s (sh) 2020 vs	1270 vw	640 w	
III	$[Ph_4As][Ph_3Pb(N_3)(NCS)]$	2062 s (sh) 2040 vs	1265 w	642 w	480 m
IV	$[Me_4N]_2[Ph_2Pb(N_3)_4]$	2020 vs (br)	1268 w	650 w (sh)	
V	$[Ph_4As]_2[Ph_2Pb(N_3)_4]$	2030 (sh) 2020 s	1260 vw		
VI	$[Ph_4As][Ph_2Pb(N_3)(NCS)_2]$	2079 s 2030 s (br)	1280 m (br)		478 w (sh)

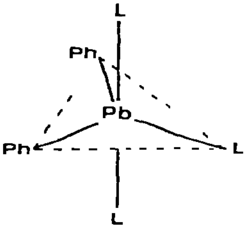
spectra are complicated by the relatively intense bands due to phenyl groups, but a close correspondence (band frequencies, shape and intensity) was found, however, between the absorptions of I, II and III and those of $A[Ph_3Pb(NCS)_2]$ [9, 11], and between the spectra of IV and V and those of $A_2[Ph_2Pb(NCS)_4]$ [9, 11] (for the same A, allowance being made for contributions of the azide groups). Thus, similar structures can be reasonably assigned to the correspondent complex anions. Trigonal bipyramidal, with equatorial PbC_3 and apical pseudohalide ligands (a), and *trans*-Ph_2 octahedral (b) structures are suggested, in agreement with those deduced by means of vibrational and Mossbauer spectroscopy for the related $Ph_3Sn(N_3)_2^-$, $Ph_3Sn(N_3)(NCS)^-$ and $Me_2Sn(N_3)_4^{2-}$, $Ph_2Sn(N_3)_2(NCS)_2^{2-}$ species [1].



(a)



(b)



(c)

The stoichiometry of VI corresponds to that of $A^I[R_2PbX_3]$ (R = Ph, 3-$NO_2C_6H_4$; X = Cl, Br) salts [12, 13], the structures of which have not been investigated. Analogous $A^I[Me_2SnCl_3]$ compounds contain the bipyramidal pentacoordinate $R_2SnCl_3^-$ anion with the organic substituents in equatorial positions [14], and a similar stereochemistry (c) may apply to $R_2PbL_3^-$ (L = halide, pseudohalide) species. The present data, however, do not exclude for VI bridging by the azide groups with formation of, for example, a dimeric anion.

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References

1 R. Barbieri, N. Bertazzi, C. Tomarchio and R.H. Herber, J. Organometal. Chem., (1974) in press
2 E. Lieber, C.N. Rao and F.M Keane, J. Inorg. Nucl. Chem., 25 (1962) 631.
3 J.S. Thayer and R. West, Inorg. Chem., 3 (1964) 889.
4 E. Lieber and F.M. Keane, Chem. Ind. (London), (1961) 747.
5 W.T. Reichle, Inorg. Chem., 3 (1964) 402.
6 J.S. Thayer and R. West, Inorg. Chem., 3 (1964) 406.
7 R.H. Herber, H.A. Stockler and W.T. Reichle, J. Chem. Phys., 42 (1965) 2247.
8 H.S. Cheng and R.H. Herber, Inorg. Chem., 9 (1970) 1686.
9 N. Bertazzi, G. Alonzo, A. Silvestri and G. Consiglio, J. Organometal. Chem., 37 (1972) 281.
10 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
11 N. Bertazzi and R. Barbieri, Inorg. Nucl Chem. Lett., 5 (1968) 591.
12 F. Huber and S. Schönafinger, Angew. Chem Int. Ed. Engl., 7 (1968) 72.
13 E. Kunze and F. Huber, J. Organometal. Chem., 57 (1973) 345.
14 F.W.B. Einstein and B.R. Penfold, Chem. Commun., (1966) 780, J. Chem. Soc. A, (1968) 3019.