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Preliminary communication

SOLVENT-INDUCED LINKAGE ISOMERISM AND IONIZATION IN SOLUTIONS OF TRIPHENYLLEAD SELENOCYANATE*

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Summary

Infrared spectra in the ν(CN) region of $Ph_3PbSeCN$ solutions show that different solvents cause ionization and/or linkage isomerism of the solute depending on the donor power and dielectric constant of the solvent.

There are many examples of linkage isomerism involving thiocyanate coordination to transition metal ions but few sets of analogous selenocyanate isomers have been reported [1—3]. Very few examples of main group or related (d^{10} or $d^{10}s^2$) metal ion systems are known, and only for cadmium thiocyanate complexes [4] and $R_3PAuSCN$ [5] have linkage isomers definitely been identified and then, only in solution. Recently [6], we observed ambidentate behaviour by the selenocyanate ligand in adducts of triphenyllead selenocyanate with *O*-donor ligands, and infrared spectra of benzene solutions of the adducts showed the presence of both N- and Se-bonded adduct isomers. This was claimed to be the first example of linkage isomerism involving selenocyanate coordination to a main group metal. We now report that all three types of NCSe bonding, ionic, N-bonded, and Se-bonded are found in $Ph_3PbSeCN$ solutions depending on the solvent used.

Infrared spectral data in the ν(CN) region for solutions of $Ph_3PbSeCN$ in various solvents are given in Table 1, together with an assignment of the peaks to different bonding of selenocyanate, employing the usual criteria [7]. The varying solvent effects can be rationalized in terms of the following equilibria, where L is the donor solvent. This causes, first, complete formation of the adduct which may then isomerize. Strong donors, e.g., DMF and TMP, then coordinate further causing complete ionization while lead remains five-coordinate. In acetone, a weaker donor, only partial ionization occurs.

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*Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday by M.O., who had the privilege of being inspired and guided by him during 1954—56.

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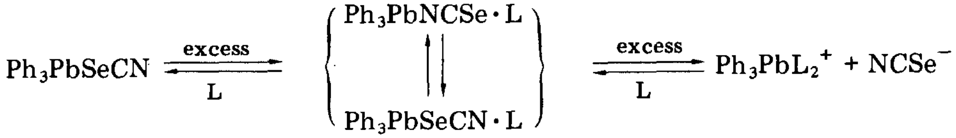
TABLE 1

INFRARED SPECTRA (2300—1900 cm^{-1}) OF $Ph_3PbSeCN$ IN NEAT SOLVENTS

Solvent ([$Ph_3PbSeCN$])	DN[a] (ϵ)[b]	Assignment of ν(CN)[c] peak to			
		$Ph_3PbSeCN$	$Ph_3PbSeCN \cdot L$	$(NCSe)^-$	$Ph_3PbNCSe \cdot L$
Benzene (C_6H_6) [6]	0.1	2139 sp			
(very dilute)		(—)			
Dichloromethane (CH_2Cl_2) [6]	0.1	2136[d]			
(0.012 *M*)	(9.1)	(11)			
N.N-Dimethylformamide (DMF)	26.6			2066[e]	
(0.017 *M*)	(36.1)			(14)	
Trimethylphosphate (TMP)	23.0			2068[f]	
(0.032 *M*)	(20.6)			(14)	
Acetone (Me_2CO)	17.0			2066 sh	2056
(0.015 *M*)	(20.7)			(—)	(—)
Acetonitrile (MeCN)	14.1			2066	[g]
(0.012 *M*)	(38.0)			(~16)	
Tetrahydrofuran (THF)	20.0		2129 s		2036 wm
(0.016 *M*)	(7.6)		(11)		(41)
Pyridine (py)	33.1		2117 wm	2066 vs	2047 sh
(0.024 *M*)	(12.3)		(14)	(~16)	(—)
Pyridine (py)	33.1		2117 sm	2064 s	2049 vs
(0.099 *M*)	(12.3)		(14)	(~20)	(~41)

[a] The donor number as given by Gutmann et al. [8]. [b] Dielectric constant. [c] Follows criteria in ref. 7; values in parentheses are of $\Delta\nu_{1/2}$ (cm^{-1}) (the peak width at half-height), approximate values are when peaks overlap; values of A_{CN} below are the integrated molar absorptivity, M^{-1} cm^{-1} $(NCSe)^{-1}$. [d] $A_{CN} = 0.5 \times 10^4$. [e] $A_{CN} = 2.5 \times 10^4$. [f] $A_{CN} = 2.7 \times 10^4$. [g] Asymmetry to low frequency shows some N-bonded adduct is present.



$$\mathrm{Ph_3PbSeCN} \underset{\mathrm{L}}{\overset{\text{excess}}{\rightleftharpoons}} \left\{\begin{matrix} \mathrm{Ph_3PbNCSe \cdot L} \\ \updownarrow \\ \mathrm{Ph_3PbSeCN \cdot L} \end{matrix}\right\} \underset{\mathrm{L}}{\overset{\text{excess}}{\rightleftharpoons}} \mathrm{Ph_3PbL_2^+} + \mathrm{NCSe^-}$$

However, coordinative ability as given by Gutmann's donor number (DN) concept [8] does not provide a complete explanation. High solvent dielectric constant also favours ionization as is shown by MeCN, the weakest donor used here. In contrast, in THF, a stronger donor than acetone but which has a much lower dielectric constant, no ionization occurs. Partial ionization occurs in pyridine but the high donor power of this ligand may also be inhibited by steric hindrance as suggested elsewhere [6].

Linkage isomerism is clearly favoured by solvents with low dielectric constant. Since lead in Ph_3Pb^+ has borderline soft acid character [9], the above trend that decreasing solvent dielectric constant promotes increasing Se-bonding compared with N-bonding to a soft metal contradicts that suggested in the literature [1,2]. Moreover, it must be noted that all previous studies of this type have involved transition metal systems and that the effect of solvent variation on linkage isomerism is still a controversial topic.

The effects of dilution of a donor solvent by a non-coordinating one on the infrared spectra of $Ph_3PbSeCN$ solutions are shown in Table 2. Diluting THF with CH_2Cl_2 causes adduct dissociation which becomes significant in 10% (v/v) THF/CH_2Cl_2. For DMF, dilution with CH_2Cl_2 (while keeping the $Ph_3PbSeCN$ concentration in the range 0.14—0.17 *M*) first decreases ionization which by 5%

TABLE 2

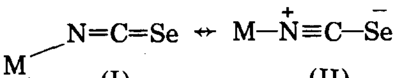
INFRARED SPECTRA (2300—1900 cm^{-1}) OF $Ph_3PbSeCN$ IN MIXED SOLVENTS

Donor solvent	Diluent ($[Ph_3PbSeCN]$)	Assignment of $\nu(CN)^a$ peak to			
		$Ph_3PbSeCN$	$Ph_3PbSeCN \cdot L$	$(NCSe)^-$	$Ph_3PbNCSe \cdot L$
THF	Dichloromethane	2135 sh	2127 vs		~2050 w, vbr
(20)	(0.017 *M*)	(—)	(~15)		(—)
THF	CH_2Cl_2	2135 vs, sp	2128 s, sp		~2050 w, vbr
(10)	(0.016 *M*)	(—)	(—)		(—)
DMF	CH_2Cl_2		2121 w	2067 vs	^{b}
(20)	(0.017 *M*)		(15)	(~21)	
DMF	CH_2Cl_2	2135 sh	2122 sm	2064 vs	2056 sh
(10)	(0.014 *M*)	(—)	(14)	(—)	(—)
DMF	CH_2Cl_2	2136 sh	2122 s		2055 vs
(10)	(0.052 *M*)	(—)	(15)		(42)
DMF	CH_2Cl_2	2135 sh	2122 vs		2054 sm
(5)	(0.016 *M*)	(—)	(14)	(41)	(41)
DMF	CH_2Cl_2	2134 sh	2122 vs		2051 m
(2)	(0.016 *M*)	(—)	(14)	(37)	(37)
DMF	CH_2Cl_2	2135 vs, sp	2123 vs, sp		2051 wm
(1)	(0.015 *M*)	(—)	(—)		(—)
DMF	Benzene		2125 m	2065 vs	2046 br sh
(10)	(0.015 *M*)		(12)	(~18)	(—)
DMF	C_6H_6		2125 sm	2064 sh	2045 vs
(10)	(0.055 *M*)		(14)	(—)	(~42)
DMF	C_6H_6		2126 vs	2064 s	2044 sm
(5)	(0.016 *M*)		(12)	(~18)	(~45)

^{a} See Table 1, footnote *c*. ^{b} Low frequency peak asymmetry shows some N-bonded adduct is present.

DMF/CH_2Cl_2 has disappeared. Further dilution causes adduct dissociation. Equally interesting is the increase in the Se-bonded to N-bonded adduct concentration ratio as DMF (ϵ = 36.1) is diluted with CH_2Cl_2 (ϵ = 9.1), a trend the same as noted above.

The changes caused by diluting DMF with benzene were also examined. For solutions of equal DMF concentration, benzene favours ionization compared with CH_2Cl_2, but the study was limited by the very low solubility of $Ph_3PbSeCN$ in benzene. Of greater interest is the ~10 cm^{-1} increase in ν(CN) of the N-bonded isomer on going from C_6H_6 to CH_2Cl_2 as the major solvent. The same trend but even larger (17—20 cm^{-1}) was observed earlier [6] when solution spectra of $Ph_3PbSeCN \cdot L$ (L = O-donor) in the same two solvents were compared, and was then ascribed to a change in bonding, i.e., from N-bonding to ionic selenocyanate. However, since ν(CN) for the $NCSe^-$ ion can now be assigned to a sharp peak at ~2065 cm^{-1} in both C_6H_6 and CH_2Cl_2, the above trend must reflect a solvent effect on the N-bonded isomer itself. Bonding in N-bonded metal chalcocyanates is generally considered in terms of the resonance forms:



(I) (II)

Remembering that the species are solvated, it is suggested that the more polar solvent (CH_2Cl_2) preferentially stabilizes the polar resonance form II which will increase the carbon—nitrogen bond order, and thus ν(CN), in agreement with experiment.

These preliminary results show that triphenyllead selenocyanate provides a useful probe for investigating solvent effects on metal chalcocyanate systems, and quantitative studies are now in progress.

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References

1 A.H. Norbury, Adv. Inorg. Chem. Radiochem., 17 (1975) 337.
2 R.J. Balahura and N.A. Lewis, Coord. Chem. Rev., 20 (1976) 109.
3 V.V. Skopenko, G.V. Tsintsadze, E.I. Ivanova, Russ. Chem. Rev., 51 (1982).
4 A.Yu. Tsivadze, Yu.Ya. Kharitonov and G.V. Tsintsadze, Russ. J. Inorg. Chem., 17 (1972) 1529.
5 J.B. Melpolder and J.L. Burmeister, Chem. Commun., (1973) 613; Inorg. Chim. Acta, 49 (1981) 115.
6 R. Wojtowski, I. Wharf and M. Onyszchuk, Can. J. Chem., in press.
7 Ref. 1, p. 254.
8 V. Gutmann and R. Schmid, Coord. Chem. Rev., 12 (1974) 263.
9 S. Stafford, H.-J. Haupt and F. Huber, Inorg. Chim. Acta, 11 (1974) 207.