

SYNTHESIS AND VIBRATIONAL SPECTRA OF DIPHENYL-LEAD
DI-ISOTHIOCYANATE ADDUCTS WITH SOME O- AND
N-DONOR LIGANDS

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Summary

Diphenyl-lead di-isothiocyanate forms: (a) 1:2 complexes with hexamethylphosphoramide, dimethylsulphoxide, N,N-dimethylacetamide, N,N-dimethylformamide, piperidine, and ethylenediamine; (b) 1:1 complexes with 2,2'-bipyridyl and 1,10-phenanthroline; (c) the condensation product $\text{Ph}_2\text{Pb}(\text{NCS})(\text{ox})$ with 8-hydroxyquinoline. All complexes are solids, insoluble in common polar and nonpolar organic solvents, and most melt with decomposition at about 200°. Only $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$ (m.p. 232°) can be recrystallized from benzene in which it is monomeric. Attempts to isolate complexes of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ with triethylphosphate, tetrahydrofuran, dioxane, pyridine, aniline, acetonitrile, triphenylphosphine, acetylacetonate, and tetramethylethylenediamine were unsuccessful. The infrared and Raman spectra of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ and its complexes show: (a) bands near 2100 cm^{-1} which are attributed to $\nu(\text{CN})$ of -NCS- bridging groups; (b) bands near 800 cm^{-1} which are

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assigned to $\nu(\text{CS})$ of $-\text{NCS}-$ bridging and $-\text{NCS}$ terminal groups; (c) bands in the range $460 - 495 \text{ cm}^{-1}$ due to the $\delta(\text{NCS})$ vibration. These observations and the physical properties of the compounds suggest that weak Pb-S bonds of the $-\text{NCS}-$ bridges in polymeric $\text{Ph}_2\text{Pb}(\text{NCS})_2$ are broken up by ligands to produce complexes containing lead-ligand bonds, Pb-NCS bonds, and $-\text{NCS}-$ bridge bonds to a degree which depends upon the donor power of the ligand.

The coordinating abilities of diphenyl-lead dihalides and dipseudohalides have not been as thoroughly studied as those of the corresponding diphenyltin(IV) compounds [1]. Adducts of either 1:1 or 1:2 stoichiometry have been prepared and characterized for diphenyl-lead dihalides with pyridine [2], *N,N*-dimethylformamide [2], dimethylsulphoxide [2], 2,2'-bipyridyl [2,3], 1,10-phenanthroline [2], terpyridyl [3], and triphenylphosphine oxide [4], but their vibrational spectra and structures have not yet been determined. The only complexes of diphenyl-lead di-isothiocyanate reported to date are the complex anions $[\text{Ph}_2\text{Pb}(\text{NCS})_4]^{2-}$ and $[\text{Ph}_2\text{Pb}(\text{N}_3)(\text{NCS})_2]^-$, isolated by Bertazzi, et al. [5,6], as their tetramethylammonium or tetraphenylarsonium salts. Infrared data were obtained in support of N-bonded thiocyanate groups, and a trans-octahedral structure was suggested for $[\text{Ph}_2\text{Pb}(\text{NCS})_4]^{2-}$ by analogy with the related $(\text{CH}_3)_2\text{Sn}(\text{NCS})_4^{2-}$ [7].

As part of our interests in the coordination chemistry of Pb(IV) and Pb(II) , and our particular interest in the mode of bonding of thiocyanate, we report the preparation and vibrational spectra of the first neutral complexes of diphenyl-lead di-isothiocyanate.

Experimental

Materials

Diphenyl-lead di-isothiocyanate, $\text{Ph}_2\text{Pb}(\text{NCS})_2$, was prepared by the reaction of diphenyl-lead diacetate with potassium thiocyanate [8], and its infrared spectrum was the same as that reported by Bertazzi, et al. [5]. Solvents and liquid ligands were dried by conventional methods and distilled just prior to use. Reagent grade 2,2'-bipyridyl, 1,10-phenanthroline, and 8-hydroxyquinoline were used as received.

Instruments

Infrared spectra were recorded in the range $250\text{--}4000\text{ cm}^{-1}$ on a Perkin-Elmer 521 grating spectrophotometer, with samples as Nujol mulls held between CsI plates. Matched NaCl cells of 0.1 mm thickness were used to record solution spectra. Far infrared spectra were obtained in the range $33\text{--}400\text{ cm}^{-1}$ on a Perkin-Elmer Model 180 spectrophotometer through the courtesy of Dr. A.N. Jones and Mr. A. Nadeau of The National Research Council of Canada, Ottawa, Ontario. Samples were examined as dilute polythene disks. A Jarrell-Ash 25-300 Raman spectrometer equipped with an Argon ion laser (514.5 nm) was used to record Raman spectra in the range 25 to 2200 cm^{-1} . Measurements were made on powdered samples sealed in thin glass capillary tubes.

Microanalyses for C, H, and N were done by Chemalytics Inc., Tempe, Arizona, or Galbraith Laboratories, Inc., Knoxville, Tennessee. Lead was determined gravimetrically as PbSO_4 promptly after the preparation of a complex. Only one complex $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$, was sufficiently soluble in benzene for its molecular weight to be determined by vapour pressure osmometry (Galbraith Laboratories Inc.).

TABLE 1
ANALYTICAL RESULTS FOR COMPLEXES OF $\text{Pb}_2\text{Pb}(\text{NCS})_2$

Complex ^a	C		H		N		Pb		S		Melting pt °C
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$	36.29	37.36	5.38	5.55	13.06	13.40	25.04	24.79	8.14	7.67	232
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmso}$	34.56	34.11	3.18	3.50	4.72	4.42					155
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmf}$	37.49	38.51	3.50	3.88	8.13	8.98					180 ^b
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dma}$	39.77	40.54	3.61	4.33	8.41	8.60	32.00	31.79	9.63	9.83	116
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{pipy}$	44.41	44.49	3.10	4.98	8.59	8.65	31.61	31.98			206 ^b
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot \text{bipy}$	45.50	45.49	2.84	2.86	8.73	8.84	32.84	32.69			210 ^b
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot \text{phen}$	47.38	47.48	2.76	2.76	8.43	8.52			9.60	9.75	218 ^b
$\text{Pb}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{en}$	36.29	36.17	4.20	4.38	13.10	14.06	34.30	34.66			170 ^b
$\text{Pb}_2\text{Pb}(\text{NCS})_2 (\text{ox})$	46.33	46.88	3.14	2.86	5.54	4.97					210 ^b

^aLigand abbreviations are: hmpa = hexamethylphosphoramide, dmso = dimethyl sulphoxide, dmf = N,N-dimethylformamide, dma = N,N-dimethylacetamide, pipy = piperidine, bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline, en = ethylenediamine, ox = 8-hydroxyquinolate.

^bDecomposition occurred simultaneously.

Preparations

In Table 1 the complexes prepared are listed together with elemental analyses and melting or decomposition temperatures.

The reaction of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.90 g, 6.1 mmol) with hmpa (10.0 g, 55.8 mmol) in benzene (50 ml) produced a clear solution from which the complex $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$ crystallized. This complex and all others to be described below were filtered off, washed with ethanol, and dried in a vacuum at 25°C. After the addition of a 2% ethanolic solution of dmsO (1.00 g, 12.8 mmol) to a mixture of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.52 g, 5.3 mmol) and ethanol (100 ml), and stirring of the mixture for 2 days, the resulting white powder was $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmsO}$. To a mixture of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.00 g, 4.2 mmol) in ethanol (100 ml) was slowly added a solution of dmf (2.36 g, 32.3 mmol) in ethanol (50 ml), and the mixture was stirred for 2 days after which the precipitate was found to be $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmf}$. $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.00 g, 4.2 mmol) dissolved in a solution of dma (6.56 g, 75.3 mmol) in benzene (100 ml) to produce a clear solution from which $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dma}$ precipitated after the addition of diethyl ether (25 ml). $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{pipy}$ was obtained when a 5% ethanolic solution of pipy (1.72 g, 20.2 mmol) was added to a mixture of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.00 g, 4.2 mmol) in ethanol (100 ml), and the resulting mixture was stirred for 2 days. Complexes of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ with bipy and phen were prepared by stirring for 3 days an ethanolic (100 ml) mixture of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ and ligand in a 1:2 mole ratio. To a mixture of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (2.41 g, 5.0 mmol) and ethanol (100 ml) was added 5% ethanolic ethylenediamine (1.20 g, 20.0 mmol), and the mixture was stirred for 4 days at 25°C, after which $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{en}$ was isolated. The interaction

of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ (1.22 g, 2.55 mmol) with 8-hydroxyquinoline (1.16 g, 8.0 mmol) in ethanol (100 ml) for 3 days with rapid stirring produced a yellow precipitate which proved to be $\text{Ph}_2\text{Pb}(\text{NCS})(\text{ox})$.

Results and Discussion

Properties

All complexes in Table 1 are stable white solids except $\text{Ph}_2\text{Pb}(\text{NCS})(\text{ox})$ which is yellow. Some melt sharply, but most melt with decomposition at about 200°. All are insoluble in common non-polar and polar organic solvents, except $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$ which is soluble and monomeric in benzene as evident from its molecular weight (Found: 839, 842; Calcd: 836.0).

Attempts to prepare complexes with triethylphosphate, tetrahydrofuran, dioxane, pyridine, aniline, acetonitrile, triphenylphosphine, acetylacetonate, and tetramethylethylenediamine were unsuccessful by the above method. For most ligands there appears to be a correlation between the formation of stable complexes and ligand electron-pair donor powers expressed by donor numbers or donicities as defined by Gutmann [9]. Ligands which have donor numbers greater than 26, e.g., dmf, dma, dmsO, and hmpa, form stable complexes; whereas ligands with donor numbers less than 26, e.g., triethylphosphate and tetrahydrofuran, do not. However, pyridine does not appear to follow this correlation: with a donor number of 33.1, it is expected to form a complex, but all attempts to isolate one were unsuccessful. This is surprising because the corresponding tin complex, $\text{Ph}_2\text{Sn}(\text{NCS})_2 \cdot 2\text{py}$, has been isolated [10] and one would not expect analogous tin and lead compounds to differ so greatly in acceptor strength, especially toward such a strong donor

as pyridine. Unfortunately, donor numbers are not yet available for all the other ligands used in this work, otherwise a better test of the apparent relationship with donor numbers would be possible.

Comparisons with $\text{Ph}_2\text{Sn}(\text{NCS})_2$ adducts

All of the monodentate ligands in Table 1 except piperidine formed 1:2 complexes with $\text{Ph}_2\text{Pb}(\text{NCS})_2$; $\text{Ph}_2\text{Sn}(\text{NCS})_2$ behaves similarly forming 1:2 complexes with pyridine [10], pyridine-N-oxide [10], and dimethylsulphoxide [11], whereas 1:1 complexes of $\text{Ph}_2\text{Sn}(\text{NCS})_2$ are obtained with triphenylphosphine oxide and triphenylarsine oxide [10]. Both $\text{Ph}_2\text{Sn}(\text{NCS})_2$ [12,11] and $\text{Ph}_2\text{Pb}(\text{NCS})_2$ form 1:1 complexes with the bidentate ligands bipy and phen, but those of $\text{Ph}_2\text{Sn}(\text{NCS})_2$ are soluble and monomeric in benzene, whereas those of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ are insoluble. Quinoline-N-oxide, also a potential bidentate ligand, forms 1:1 and 1:2 complexes with $\text{Ph}_2\text{Sn}(\text{NCS})_2$ [10]. Ethylenediamine produced a 1:2 complex with $\text{Ph}_2\text{Pb}(\text{NCS})_2$, whereas tetramethylethylenediamine did not coordinate presumably because of its larger steric requirements.

The condensation product $\text{Ph}_2\text{Pb}(\text{NCS})(\text{ox})$ was obtained when $\text{Ph}_2\text{Pb}(\text{NCS})_2$ combined with 8-hydroxyquinoline, and there was no evidence of a product which could arise from the replacement of the second NCS by an oxinate group. The complex is yellow, melts with decomposition at 210° , and is insoluble in common organic solvents, whereas the tin analog, $\text{Ph}_2\text{Sn}(\text{NCS})(\text{ox})$, decomposes above 76°C and is monomeric in benzene solution [12].

Vibrational spectra and thiocyanate bonding(i) $\text{Ph}_2\text{Pb}(\text{NCS})_2$

Bertazzi, et al. [5] suggested that the structure of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ is polymeric with octahedrally bound lead, bridging NCS groups, and trans-linear C-Pb-C linkages, a structure analogous to that of $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ [13] and Ph_2PbCl_2 [14] which were determined by X-ray methods. Although our infrared spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ is the same as that reported by Bertazzi et al [5], we differ in the assignments of bands at 832 and 440 cm^{-1} . A weak band near 832 cm^{-1} is observed in the spectra of diphenyl- and triphenyl-lead derivatives [15], as well as in corresponding tin compounds [16]. This band is undoubtedly due to a phenyl group vibration, mode (g) in Whiffen's notation [17], a possibility mentioned by Bertazzi, et al. [5], but left uncertain because weak bands due to $\nu(\text{CS})$ were thought to occur in the same region. In fact, the weak band they observed at 765 cm^{-1} (764 cm^{-1} in our spectrum) is now confidently assigned to the $\nu(\text{CS})$ vibration because no bands are observed near 765 cm^{-1} in the spectra of diphenyllead dihalides [15]. Unfortunately, all attempts to observe the $\nu(\text{CS})$ band in the Raman spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ were unsuccessful due to fluorescence and decomposition of the sample in the laser beam.

The moderately intense band previously reported at 441 cm^{-1} [5] (also present in our spectrum) is probably due to the (γ) mode of the phenyl group rather than to the bending mode $\delta(\text{NCS})$ proposed by Bertazzi, et al. [5]. Bands near 441 cm^{-1} are usually observed in spectra of phenyllead(IV) [15] and phenyltin(IV) [16] derivatives which do not contain thiocyanate groups. The band at 462 cm^{-1} in the spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ is assigned to $\delta(\text{NCS})$ because a similar band occurs in the spectra of Ph_3PbNCS [18], $\text{Ph}_2\text{Sn}(\text{NCS})_2$ [10],

and Ph_3SnNCS [18], and because these bands are invariably weaker than the band near 440 cm^{-1} now attributed to the phenyl (γ) vibration.

The intense band at 2097 cm^{-1} in the Nujol mull spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ must be associated with bridging NCS groups because this band disappears or its intensity decreases appreciably in spectra of acetone or ethanol solutions of $\text{Ph}_2\text{Pb}(\text{NCS})_2$. Even though $\text{Ph}_2\text{Pb}(\text{NCS})_2$ is only very slightly soluble in acetone and ethanol, we observed $\nu(\text{CN})$ bands at 2065 cm^{-1} in dilute ethanol, and at 2080 and 2061 cm^{-1} in a dilute acetone solution. These observations together with similar ones of Ph_3PbNCS [5,18] and $\text{Ph}_2\text{Sn}(\text{NCS})_2$ [12], lead us to conclude that the band at 2097 cm^{-1} in crystalline $\text{Ph}_2\text{Pb}(\text{NCS})_2$ indicates the presence bridging NCS groups. After bridges are ruptured by solvent molecules, terminal N-bonded thiocyanate groups remain and they are characterized by absorption bands near 2060 cm^{-1} . However, $\nu(\text{CN})$ bands near 2060 cm^{-1} are not necessarily characteristic of only terminal NCS groups, since a band at 2050 cm^{-1} is present in the infrared spectrum of crystalline $\text{Ph}_2\text{Pb}(\text{NCS})_2$ which is thought to have only bridging NCS groups. The 2097 and 2050 cm^{-1} bands in the infrared spectrum of crystalline $\text{Ph}_2\text{Pb}(\text{NCS})_2$ might be due to components of the $\nu(\text{CN})$ vibration arising from coupling between adjacent NCS groups and/or to crystal lattice splitting effects. Crystalline organotin(IV) thiocyanates such as Me_3SnNCS [19], $\text{Me}_2\text{Sn}(\text{NCS})_2$ [13,20], $[(\text{Me}_2\text{SnNCS})_2\text{O}]_2$ [21], and Ph_3SnNCS [22] have only bridging NCS groups, whereas the 1:1 terpyridyl complex [23], $\text{Me}_2\text{Sn}(\text{NCS})_2 \cdot \text{terpy}$, has only N-bonded NCS groups in a crystal structure which consists of well-separated discrete seven-coordinate molecules.

The correlation of $\nu(\text{CN})$ frequency with NCS bonding

type as summarized in Table 2, has been successfully used to decide bonding type in a wide range of transition metal complexes for which X-ray crystallographic data are available [24,25]. However, these criteria must be used cautiously and conclusions based on them can only be tentative because ambiguities arise when frequency ranges overlap and because factors causing frequency shifts are uncertain [24]. Moreover, the validity of using these criteria for main group compounds has not yet been adequately tested. In spite of these doubts, the most reliable criterion of bond type is considered by Burmeister [26] to be $\nu(\text{CS})$, which varies in the order $\text{M-SCN} < \text{NCS}^- < \text{M-NCS}$, and for which "no definitive example has yet appeared in the literature which contradicts this order". In the absence of X-ray structural data tentative thiocyanate bonding types are proposed for complexes of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ in the following sections based upon $\nu(\text{CN})$, $\nu(\text{CS})$, and $\delta(\text{NCS})$ frequencies, with particular attention paid to $\nu(\text{CS})$ frequencies. Thiocyanate absorption frequencies of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ and its adducts are summarized in Table 3.

TABLE 2

CORRELATION OF THIOCYANATE BINDING TYPE WITH THIOCYANATE VIBRATIONAL FREQUENCIES (cm^{-1})

Bonding type	$\nu(\text{CN})$	$\nu(\text{CS})$	$\delta(\text{NCS})$
NCS^-	2053	746	486,471
M-NCS	2100-2050	870-820	485-475
M-SCN	2130-2085	760-700	470-430
M-NCS-M	2165-2065	800-750	470-440

TABLE 3

VIBRATIONAL FREQUENCIES (cm^{-1}) OF THE NCS GROUP^a

Compound	$\nu(\text{CN})$			$\nu(\text{CS})$			$\delta(\text{NCS})^b$		
	Infrared	Raman		Infrared	Raman		Infrared	Raman	
K^+NCS^-	2053s		d	744w		d	483, 470, 459		d
$\text{Ph}_2\text{Pb}(\text{NCS})_2$	2097s, 2050m	2107w, 2093w, 2080s		764w		d	462		d
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$	2040s, br	2052s, 2043s		795vw	808w, 797w		c		c
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmso}$	2094s, 2015s, br	2108s, 2092s		790w, 762w	800w, 768w		495, 471, 462		500
$\text{Ph}_2(\text{NCS})_2 \cdot 2\text{dmf}$	2095s, 2035s, br		d	808vw, 765w		d	483, 474, 463		d
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dma}$	2096m, 2056m, 2015s, br	2031s		802w, 794w	806w, 800w		493, 485, 473		490
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{pipx}$	2056s, 1960m	2050s		770w	770w		472, 464		481w
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot \text{bipy}$	2092s, 2035s	2078s, 2034s		814m, 796m	815w, 795w		489, 479, 464		487, 465
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot \text{phen}$	2091w, 2030s, 2000s, br		d	807w, 798w		d	495, 481, 472		d
$\text{Ph}_2\text{Pb}(\text{NCS})_2(\text{ox})$	2092s, 2064s, 2010m, sh		d	b		d	490, 481, 474		d
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{en}$	2055s, 2010m, sh	2055s		773w	775w		482, 476, 465		475

a Abbreviations are: w = weak, m = medium, s = strong, br = broad, sh = shoulder

b All of these bands are weak

c Overlapped by ligand bands

d Not observed due to decomposition and/or fluorescence of the sample in the laser beam

(ii) $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$

In the reaction of hmpa with $\text{Ph}_2\text{Pb}(\text{NCS})_2$ the high polarity and strong donor activity of hmpa [9] should facilitate the complete break-up of NCS bridges in solid $\text{Ph}_2\text{Pb}(\text{NCS})_2$ and the formation of molecular species, found by molecular weight measurements in benzene solution to be monomeric $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$.

Single bands occur for the $\nu(\text{CN})$ and $\nu(\text{CS})$ vibrations at 2028 and 795 cm^{-1} , respectively, in the infrared spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$, whereas each band is split into a doublet, (2052 and 2043 cm^{-1}) and (808 and 797 cm^{-1}), respectively, in the Raman spectrum (Table 3). This splitting might be due to a crystal lattice effect or to a cis-arrangement of NCS groups in an octahedral coordination sphere around lead. The $\nu(\text{CN})$ and $\nu(\text{CS})$ frequencies are consistent with the presence of N-bonded NCS groups (Table 2). Owing to the absence of a broad band near 2100 cm^{-1} , which is attributed to -NCS- bridges in $\text{Ph}_2\text{Pb}(\text{NCS})_2$, we suggest that $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$ exists as a molecular crystal free from thiocyanate bridge bonding. Consistent with this conclusion is its sharp melting point (232°C) and solubility in benzene.

Considering all of these observations, it seems reasonable to propose that $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hmpa}$ is a six-coordinate, octahedral complex with N-bonded NCS groups. A single crystal X-ray structure is now necessary to test this proposal and to reveal the relative arrangement of the six groups around the central lead atom.

(iii) Complexes of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ with dmsO, dmf, dma and pipy

Partial retention of the thiocyanate bridged polymeric framework of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ in dmsO and dmf complexes is strongly suggested by the persistence of two bands in the $\nu(\text{CN})$ region

and the reversal of their relative intensities. The strong band at 2097 cm^{-1} in $\text{Ph}_2\text{Pb}(\text{NCS})_2$ persists as a medium intensity band at 2094 cm^{-1} and 2095 cm^{-1} in dmsO and dmF complexes respectively; whereas the medium intensity band at 2050 cm^{-1} in $\text{Ph}_2\text{Pb}(\text{NCS})_2$ becomes strong and broad at $2060\text{--}2025$ and $2055\text{--}2020\text{ cm}^{-1}$ in dmsO and dmF complexes respectively. On the basis of these observations we suggest that NCS bridges of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ are partially broken by dmsO and dmF to give a chain structure in which bridging and terminal N-bonded thiocyanate groups are present and the coordination number of lead is greater than six. Two $\nu(\text{CS})$ bands in each complex are also suggestive of N-bonded and bridging NCS groups. The presence of coordinated dmsO is confirmed by the shift of $\nu(\text{SO})$ from 1042 cm^{-1} in free dmsO to 943 cm^{-1} , in the complex, a shift similar to that report for $\text{Ph}_2\text{Sn}(\text{NCS})_2 \cdot 2\text{dmsO}$ [10]. Coordination of dmF is evident from the decrease of $\nu(\text{CO})$ from 1670 cm^{-1} in liquid dmF to 1638 cm^{-1} in the solid complex.

More extensive cleavage of NCS bridges appears to occur when dma reacts with $\text{Ph}_2\text{Pb}(\text{NCS})_2$ to form $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dma}$, as evident from the further decrease in intensity of the $\nu(\text{CN})$ band at 2096 cm^{-1} and the disappearance of the $\nu(\text{CS})$ band present at 764 cm^{-1} in the spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2$. The appearance of two $\nu(\text{CS})$ bands (at 794 and 802 cm^{-1}) and of two $\nu(\text{CN})$ bands (at 2056 and 2015 cm^{-1}) might be due to a cis-arrangement of N-bonded thiocyanate groups around octahedral lead(IV). However, NCS bridge bonding, inferred from the $\nu(\text{CN})$ band at 2096 cm^{-1} , must be sufficiently strong to prevent the complex from melting sharply and dissolving in polar organic solvents. Coordination of dma is confirmed by the decrease of the amide I band (mainly $\nu(\text{CO})$) from 1638 cm^{-1} in the free ligand to 1597 cm^{-1} in the complex. Corresponding shifts of about

40 cm^{-1} have been reported recently for dma complexes of Ph_2SnCl_2 , Ph_2SnBr_2 , and Ph_2SnI_2 [27].

In the spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{pipy}$ the weak $\nu(\text{CS})$ band at 770 cm^{-1} is consistent with the presence of bridging NCS groups, but there is no $\nu(\text{CN})$ band near 2100 cm^{-1} usually characteristic of such bonding. That the complex is not molecular is suggested by its insolubility in common solvents and failure to melt sharply. Perhaps the complex is polymeric but with additional bridging at the nitrogen atom, i.e., >NCS- , rather than the usual -NCS- bridging. The additional Pb-N bonding might decrease the electron density at the CN bond thereby reducing its vibrational frequency to 1960 cm^{-1} , the lowest value observed among the complexes prepared. Such a low frequency has also been reported for the thiourea (tu) complex $\text{Pb}(\text{NCS})_2 \cdot 4\text{tu}$ [28], the structure of which is not known, and for several tetraalkyl distannoxanes in which >NCS- bridging was first proposed [7].

(iv) Complexes of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ with bidentate ligands

The strong and sharp band at 2092 cm^{-1} in the spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot \text{bipy}$ is likely due to the $\nu(\text{CN})$ vibration of bridging NCS groups so characteristic of the parent $\text{Ph}_2\text{Pb}(\text{NCS})_2$. The insolubility of this complex and its failure to melt sharply are also consistent with an NCS bridged polymeric structure. However, the presence of terminal N-bonded NCS in the complex is indicated by a $\nu(\text{CN})$ band at 2035 cm^{-1} and $\nu(\text{CS})$ bands at 814 and 796 cm^{-1} . A similar pattern of $\nu(\text{CS})$ bands is shown by the phenanthroline complex, but in the $\nu(\text{CN})$ region the band at 2092 cm^{-1} is weak rather than strong and a new strong and broad band is centered at 2000 cm^{-1} . These differences might be due to less extensive or weaker NCS bridging in the phenanthroline than in the bipyridyl complex. Ligand ring vibrations are

increased by 10 to 20 cm^{-1} due to coordination, a behaviour characteristic of phenanthroline [29,30] and 2,2'-bipyridyl [31,30] complexes.

The lack of a band near 2100 cm^{-1} in the spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{en}$ suggests the absence of NCS bridges. Nevertheless, this complex has properties such as insolubility in common solvents and indefinite melting point which indicate a polymeric structure. Perhaps ethylenediamine molecules rather than NCS groups form a bridging network similar to that found in an ethylenediamine complex of Pt(IV) [32]. However, the $\nu(\text{CS})$ band at 770 cm^{-1} in the complex is only slightly different from that of 764 cm^{-1} in $\text{Ph}_2\text{Pb}(\text{NCS})_2$, whereas a larger increase is expected if only N-bonded NCS were present in the complex. Two broad bands centered at 3224 and 3130 cm^{-1} are characteristic of $\nu(\text{NH})$ of coordinated ethylenediamine [33,34], but its bonding mode and conformation are uncertain because absorption bands due to ethylenediamine are overlapped by bands characteristic of the phenyl group in the range 700 - 300 cm^{-1} .

There are three well-defined $\nu(\text{CN})$ bands at 2092, 2060, and 2010 cm^{-1} in the infrared spectrum of $\text{Ph}_2\text{Pb}(\text{NCS})(\text{ox})$; these are consistent with the presence of both bridging and N-bonded groups. Unfortunately, ligand bands overlap the $\nu(\text{CS})$ region so severely that it is not possible to identify $\nu(\text{CS})$ confidently, although the weak band at 761 cm^{-1} is probably $\nu(\text{CS})$ and suggestive of NCS bridge bonding. The insolubility of the complex and its melting with decomposition at 210° support a polymeric structure.

(v) Far-infrared spectra

Peaks in the far-infrared spectra of $\text{Ph}_2\text{Pb}(\text{NCS})_2$ and its complexes are listed in Table 4. Apart from the assignment of the symmetric and asymmetric $\text{Pb}-\text{C}_6\text{H}_5$ stretch-

TABLE 4
 FAR-INFRARED BANDS (33-400 cm^{-1}) OF $\text{Ph}_2\text{Pb}(\text{NCS})_2$ COMPLEXES

Compound	ν_{as} (Pb-Ph)	ν_{s} (Pb-Ph)	Unassigned
$\text{Ph}_2\text{Pb}(\text{NCS})_2$	237m	206w	257m ^c , 175m, 151s, 125s, 107s, 78m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{hupa}$	235m	203m	377m ^b , 350m ^b , 295w ^b , 258m, 148s, br, 113s, br
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmso}$	234m	204m	333m ^b , 307m ^b , 254m ^c , 170s, 150s, 126s, 104s, 75m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dmf}$	230m	206m	373m ^b , 340w ^b , 256m ^c , 175m, 148s, 128s, 106s, 80m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{dma}$	238m	210m	354w ^b , 257m ^c , 180s, 160s, 130s, 104s, 73m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot 2\text{pipy}$	230w	196m	357w ^b , 307w ^b , 256s ^c , 178w, 120w, 92w, 78w
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot \text{bipy}$	238w	218s, 194m	398m ^b , 341w ^b , 258s ^c , 167s, br, 150s, br, 133s, 106m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 \cdot \text{phen}$	235m	218m, 195m, sh	277w ^b , 271w ^b , 259m ^c , 172s, br, 157s, sh, 120m
$\text{Ph}_2\text{Pb}(\text{NCS})_2 (\text{ox})$	236w	213m, 202m	386s ^b , 276w ^b , 256m ^c , 172s, sh, 150s, 128s, 107s, 76m

a Abbreviations are: w = weak, m = medium, s = strong, br = broad, sh = shoulder

b Ligand bands

c Probably the phenyl γ -mode

ing modes [15] and the recognition of some ligand bands, it was not possible to assign the remaining peaks. Spectra were poorly resolved in the 100-180 cm^{-1} range, in which Pb-NCS, Pb-ligand, and phenyl ring vibrations are expected.

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