JOURNAL OF SOLID STATE CHEMISTRY 46, 41–45 (1983)

An Iodine Mössbauer Study of Lead(II) Iodide and Lead Oxyiodide

FRANK J. BERRY

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT, England

AND COLIN H. W. JONES AND M. DOMBSKY

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

Received June 28, 1982

The ^{127}I and ^{129}I Mössbauer spectra of lead(II) iodide are characterized by single resonances showing no measurable quadrupole coupling and with chemical isomer shifts within the range expected for ionic iodides. The ^{127}I Mössbauer spectrum of lead oxyiodide also shows a single line typical of an ionic iodide. No evidence was found for the presence of intercalated iodine in a compound of composition $Pb^{II}OI$ nor for the existence of iodate in a compound of formula $[Pb_2{}^{II}O]^{2+}OI^-I^-$. The Mössbauer spectrum is consistent with a mixed-valence lead oxyiodide of composition $Pb^{II}_{4-x}Pb^{IV}_xO_4I_{2x}(1 < x < 2)$ with a $Pb_4O_4Cl_2$-type structure.

Introduction

The ^{127}I Mössbauer spectra of single-crystal and polycrystalline samples of lead(II) iodide recorded at 4.2K with a Zn ^{127m}Te source have been reported (*1*) to show significant quadrupole couplings consistent with appreciable covalent character in the bonding. However, the layered structure of lead(II) iodide resembles that of cadmium(II) iodide (*2*) with metal to iodine bond lengths comparable to the sum of the ionic radii which might reasonably be considered as being indicative of appreciable ionic properties. The use of ^{129}I Mössbauer spectroscopy is a potentially more sensitive means by which such uncertainty may be clarified. The ^{129}I Mössbauer resonance (*3*) has an intrinsically narrower linewidth (0.59 mm sec^{-1}) than that of ^{127}I (2.54 mm sec^{-1}), chemical isomer shifts which are approximately three times those of ^{127}I ($\delta^{129}I/\delta^{127}I = -2.9$), and quadrupole coupling constants which are comparable to those of ^{127}I ($e^2qQ\ ^{129}I/e^2qQ\ ^{127}I = 0.701$). We have therefore reinvestigated lead(II) iodide by remeasuring the ^{127}I Mössbauer spectrum and, in order to achieve a more accurate interpretation of the quadrupole coupling and isomer shift data, have recorded the ^{129}I Mössbauer spectrum of $Pb\ ^{129}I_2$.

We also report here on an investigation of the recently reported (*4*) lead oxyiodide to clarify uncertainty over the nature of iodine in the material.

Experimental

Lead(II) iodide was prepared by the addition of sodium iodide to lead ion in aqueous

0022-4596/83/010041-05$03.00/0

solution. $Pb^{129}I_2$ was prepared by a similar method from $Na^{129}I_2$.

Lead oxyiodide was prepared by stirring the yellow orthorhombic high-temperature variation of lead(II) oxide, massicot, with iodine in water (*4*). The solid was air-dried at room temperature.

Mössbauer spectra were recorded with a conventional constant acceleration spectrometer using $Zn^{127m}Te$ and $Zn^{129m}Te$ sources with both source and absorber at 4.2K. The spectra were computer fitted to Lorentzian peaks. ^{127}I and ^{129}I Mössbauer spectra of potassium iodide and $K^{129}I$ were recorded for standardization purposes.

Results and Discussion

Lead(II) Iodide

The ^{127}I Mössbauer spectrum of lead(II) iodide (Fig. 1) showed a single, rather broad line which did not exhibit a measurable quadrupole coupling. The ^{129}I Mössbauer spectrum (Fig. 2) also yielded a single line and gave no evidence for quadrupole hyperfine interaction. The ^{127}I and ^{129}I Mössbauer parameters are given in Table I. The ratios of the ^{129}I and ^{127}I chemical isomer shifts ($\delta^{129}I/\delta^{127}I$) for both lead(II) iodide and potassium iodide are, within the rather large errors, consistent with the reported (*3*) ratio of -2.9 in which the negative sign arises from the difference in sign of the change in nuclear radius in the Mössbauer transition for the two isotopes.

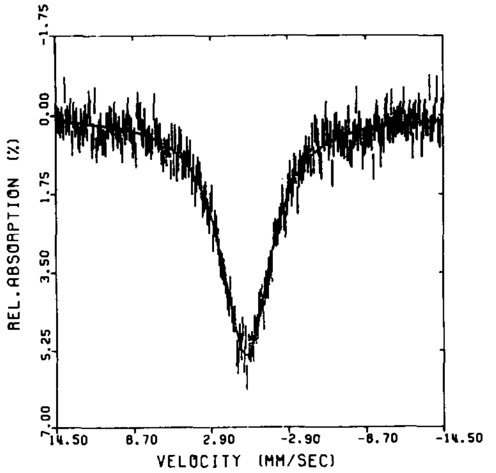

FIG. 1. ^{127}I Mössbauer spectrum of lead(II) iodide.

TABLE I

^{127}I AND ^{129}I MÖSSBAUER DATA FOR LEAD(II) IODIDE AND LEAD OXYIODIDE

	$^{127}I\delta^{a}$ (mm sec^{-1})	$^{129}I\delta^{a}$ (mm sec^{-1})	$\Gamma_{expt.}$ (mm sec^{-1})
KI	0.12 ± 0.05		3.9 ± 0.2
		-0.46 ± 0.01	1.07 ± 0.05
PbI_2	-0.02 ± 0.03		4.6 ± 0.2
		0.24 ± 0.02	1.04 ± 0.05
$Pb^{II}_{4-x}Pb^{IV}_{x}O_4I_{2x}$	0.01 ± 0.06		4.5 ± 0.2

[a] δ with respect to ZnTe in both cases, source and absorbers at 4.2K.

The ^{127}I chemical isomer shift for lead(II) iodide ($\delta = -0.02$ mm sec^{-1}) is more positive than that recorded ($\delta = -0.20$ and -0.28 mm sec^{-1}) during the previous (*1*) investigation. Furthermore, while the earlier work (*1*) reported a significant ^{127}I quadrupole coupling of 776 to 799 MHz, no quadrupole hyperfine interaction was observed in either the ^{127}I or ^{129}I Mössbauer spectra recorded during this investigation. We are unable therefore to confirm the earlier results (*1*) and their interpretation in terms of significant covalent character in lead(II) iodide. Indeed, the chemical isomer shift data recorded here clearly fall within the general area reported for ionic halides (*3*) and, together with the lack of spectral evidence for quadrupole coupling, are consistent with a predominantly ionic formulation for lead(II) iodide. It must be acknowledged, however, that the ^{129}I chemical isomer shift for $Pb^{129}I_2$ ($\delta = +0.24$ mm sec^{-1}) is more positive than that observed for $K^{129}I$ and might reasonably be associated with deshielding of the iodine $5s^2$ electrons from the iodine nucleus as a

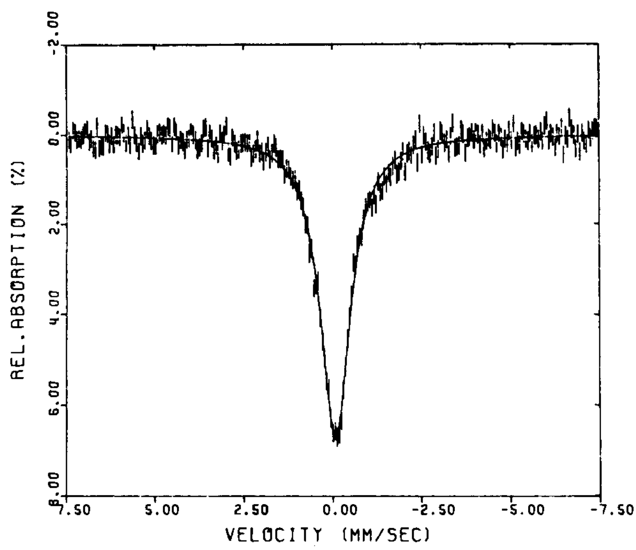

FIG. 2. ^{129}I Mössbauer spectrum of lead(II) iodide.

result of covalency involving the iodine 5p orbitals. Such effects may be evaluated, albeit approximately, by assuming the 5s^2 electrons to be localized on the iodine and relating (*5*) the ^{129}I Mössbauer chemical isomer shift to the number of 5p electrons, h_p, removed from the iodide $5s^25p^6$ configuration using the expression

$$\delta = 1.5h_p - 0.54.$$

Hence the ^{129}I chemical isomer shift of +0.24 mm sec^{-1} recorded from $Pb^{129}I_2$ corresponds to an h_p value of ca. 0.5. On the other hand, the absence of a quadrupole coupling is indicative of equal population of the iodine 5p orbitals. In resolving these observations it must be noted that the cadmium(II) iodide structure of lead(II) iodide involves the pyramidal coordination of the halogen by three lead atoms such that equal population of the iodine 5p orbitals would occur even with some covalency in the lattice. Hence we conclude that the ^{127}I and ^{129}I Mössbauer data are consistent with a predominantly ionic lead(II) iodide in which the degree of covalency is small. In this respect it is relevant to note that while lead(II) iodide is an intensely yellow solid it dissolves in hot water to give a colorless solution containing Pb^{2+} and I^- ions.

Although our results and their interpretation may be readily related to the properties of lead(II) iodide, we believe it pertinent to comment on our failure to observe a quadrupole coupling in both the ^{127}I and ^{129}I Mössbauer spectra which is in sharp contrast to the relatively large coupling reported earlier (*1*). In this respect we find it relevant to note that the previous study (*1*) did not report a spectrum for a single-line standard absorber such as potassium iodide. Hence it is not impossible that the quadrupole coupling recorded earlier arose from the source rather than the lead(II) iodide under investigation.

Lead Oxyiodide

A recent investigation of the reaction between yellow orthorhombic lead(II) oxide, iodine, and water reported (*4*) the isolation of a mixed-valence lead oxyiodide of variable composition $Pb^{II}_{4-x}Pb^{IV}_{x}O_4I_{2x}$ $(1 < x < 2)$. It might be presumed that such a compound would be somewhat analogous to the tetragonal bismuth oxyiodide BiOI (*6*) having a crystal structure of the general PbFCl type containing a mixture of Pb^{2+} and Pb^{4+} ions in random distribution over the metal ion positions of the PbFCl lattice. Such random mixing of Pb^{2+} and Pb^{4+} ions in the outer layers Pb$_n$ of each (Pb$_n$O$_{2n}$Pb$_n$) sandwich could be envisaged in a material in which $x = 2$, i.e., a compound of formula Pb(II)Pb(IV)O$_2$I$_2$. However, X-ray investigations (*4*) suggested that the oxyiodide was more likely to correspond with the composition Pb(II)$_3$Pb(IV)O$_4$I$_2$, i.e., $x = 1$, and be analogous to the lead oxychloride Pb$_4$O$_4$Cl$_2$ (*7*). Such a structural proposal agrees well with earlier extensive studies (*8, 9*) on a large group of structurally related compounds. Among these, two simple types of structures "X_1" and "X_2" were identified in which the iodide ions were said to be present, respectively, in single and double layers alternating with the metal oxide sandwiches (*10*). The lead oxyiodide of approximate composition Pb$_4$O$_4$I$_2$ was reported (*4*) to represent the X_1 structure but, like Pb$_4$O$_4$Cl$_2$, to exhibit considerable variation in chemical composition as indicated by the general formula $\mathrm{Pb}^{II}_{4-x}\mathrm{Pb}^{IV}_x\mathrm{O}_4\mathrm{I}_{2x}$ ($1 < x < 2$).

Alternative models of the lead oxyiodide requiring the presence of only Pb(IV) in a material of composition Pb^{4+} (e)O^{2-}I$^-$ containing the electron in a conduction band were discounted (*4*) on the grounds of the small electrical conductivity of the material. Another formulation involving only the presence of Pb(II) in a material Pb^{2+}O^{2-}I containing iodine intercalated between the sandwich type lead(II) oxide layers at the positions of the Cl$^-$ ions in the PbFCl structure is, however, worthy of consideration despite the failure of the compound to give an ESR signal (*4*). Moreover, the formulation $[\mathrm{Pb}^{II}_2\mathrm{O}]^{2+}\mathrm{OI}^-\mathrm{I}^-$, which would also be compatible with a material in which lead is present only in the oxidation state of two and in which iodine has undergone disproportionation to iodate and iodide, has not been previously considered.

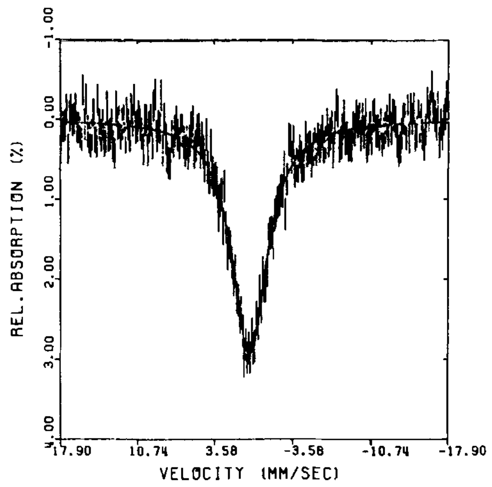

FIG. 3. ^{127}I Mössbauer spectrum of lead oxyiodide.

The ^{127}I Mössbauer spectrum of the lead oxyiodide was characterized by a single line with a chemical isomer shift comparable to that of lead(II) iodide (Fig. 3). It seems, therefore, that the formulation of the lead oxyiodide as $\mathrm{Pb}^{II}_{4-x}\mathrm{Pb}^{IV}_x\mathrm{O}_4\mathrm{I}_{2x}$ is correct and that the iodine is present as the iodide ion. Certainly the presence of intercalated iodine or iodate ion in either of the alternative formulations would have been expected to yield a significant quadrupole hyperfine interaction.

Acknowledgment

One of the authors (C.H.W.J.) wishes to acknowledge a grant in support for this research from the National Sciences and Engineering Research Council of Canada.

References

1. G. TURNBULL AND E. E. SCHNEIDER, *Solid State Commun.* **11,** 547 (1972).
2. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Vol. 1, p. 271, Interscience, New York (1963).

3. N. N. GREENWOOD AND T. C. GIBB, "Mössbauer Spectroscopy," p. 462, Chapman and Hall, London (1971).
4. M. A. BREDIG, C. E. BARNBERGER, AND D. M. RICHARDSON, *J. Inorg. Nucl. Chem.* **40**, 1497 (1978).
5. A. P. MARKS, R. S. DRAGO, R. H. HERBER, AND M. L. POTASEK, *Inorg. Chem.* **15**, 259 (1976).
6. R. A. HOWIE AND W. MOSER, *Nature* **219**, 372 (1968).
7. M. GASPERIN, *Bull. Soc Fr. Mineral. Crystallogr.* **87**, 278 (1964).
8. L. G. SILLEN AND E. JORNSTAD, *Z. Anorg. Allg. Chem.* **250**, 178 (1942).
9. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Vol. 4, p. 18, Interscience, New York (1968).
10. M. A. BREDIG, *J. Chem. Phys.* **24**, 1039 (1956).