The Identification of Insoluble Adducts of Lewis Acids with Bases by Extension of the Continuous Variation Method to Solid-Liquid Reactions

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A method has been developed for identifying occurrence and composition of all the insoluble adducts formed in solid-liquid reactions by extension of the continuous variation method to the heterogeneous systems that were produced by the reactions of PbX_2 (X=Cl, Br, and I) with ethylenediamine(=en) in ethanol solution. Four new adducts, $PbX_2 \cdot i(en)$ (i=1/2 and 1; X=Cl and Br), were found. The developed method was effective in identifying formation of the adducts such as $PbCl_2 \cdot 1/2(en)$ and $PbBr_2 \cdot 1/2(en)$ whose formation is liable to be overlooked in extending the mole ratio method to solid-liquid reactions.

In previous papers,[1-3] we have developed the methods to identify the insoluble adducts formed in solid-liquid reactions by extending either the mole ratio method[4] or the continuous variation method[5] to the heterogeneous reactions. However, the mole ratio method extended to the reactions has a drawback that formation of insoluble adducts is liable to be overlooked when the region of occurrence is narrow as in the cases of $PbI_2 \cdot 2/3(en)$[1] and $PbI_2 \cdot 1/2$(diethylenetriamine)(=dien).[2] The purpose of this psper is to develop theoretically a method for identifying occurrence and composition of insoluble adducts by extending the continuous variation method discussed in the preceding paper[3] to solid-liquid reactions in order to overcome the drawback of the mole ratio method.

Theoretical

Let us assume that an insoluble Lewis acid, A, reacts with a soluble Lewis base, B, in a solution according to Eqs. 1 and 2 to yield two insoluble adducts:

$$\mathrm{A(solid)} + m\mathrm{B(soln.)} = \mathrm{A}\cdot m\mathrm{B(solid)}, \qquad (1)$$

$$\mathrm{A}\cdot m\mathrm{B(solid)} + n\mathrm{B(soln.)} = \mathrm{A}\cdot(m+n)\mathrm{B(solid)}. \qquad (2)$$

Suppose that A and B react in varying proportions at fixed temperature and pressure in a fixed volume of the reaction solution so that the sum of A and B is kept constant at D mol. Provided that the concentration of B remaining unreacted in solution ([B] mol dm^{-3}) is determined after an equilibrium has been reached, the relation between [B] and B at the beginning of the reaction is depicted by a curve in Fig. 1, which is termed "concentration curve".

As discussed on the basis of the phase rule in a previous paper,[2] the region where [B] increases and the region where [B] becomes constant appear alternately on the concentration curve. Two regions 2 and 4, where the concentration curve is flat, represent two invariant states. Accordingly, A and $\mathrm{A}\cdot m\mathrm{B}$ coexist in region 2 and $\mathrm{A}\cdot m\mathrm{B}$ and $\mathrm{A}\cdot(m+n)\mathrm{B}$, in region 4 in each solid phase. On the other hand, three regions 1, 3, and 5 where the curve has a certain slope represent three monovariant states and correspond to the presence of A, $\mathrm{A}\cdot m\mathrm{B}$, and $\mathrm{A}\cdot(m+n)\mathrm{B}$ in the solid phase, respectively.

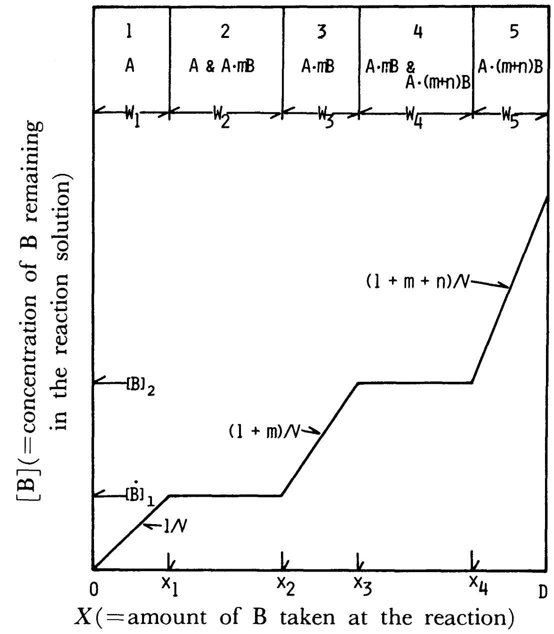


Fig. 1. A typical phase diagram for a ternary system consisting of A, B, and solvent where two insoluble adducts, $\mathrm{A}\cdot m\mathrm{B}$ and $\mathrm{A}\cdot(m+n)\mathrm{B}$, form.

Let us consider how the slope on the concentration curve changes in each monovariant region. If the volume of reaction solution (V dm^3) remains unchanged during the reaction and species involving A dissolve sparingly into the solution, [B] is given by:

$$[\mathrm{B}] = (x - yz)/V, \qquad (3)$$

where x and z are the amounts of B and A in mol at the beginning of the reaction, respectively, and y is the mole ratio of B/A in the sediment. Since the reaction is carried out under the condition that D is constant,

$$D = x + z = \text{constant}. \qquad (4)$$

Equation 5 is obtained from Eqs. 3 and 4 by eliminating z:

$$[\mathrm{B}] = \frac{x - y(D - x)}{V} = \frac{(1 + y)}{V}x - \frac{yD}{V}. \qquad (5)$$

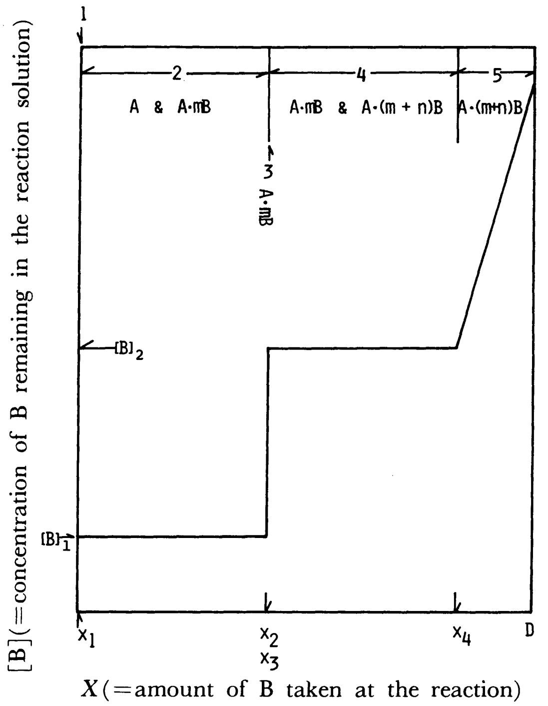


Fig. 2. A typical phase diagram for a ternary system where both $[B]_1$ and $[B]_2$ are very low.

The value of the slope equals $1/V$ in region 1 where only A is present in the solid phase, because $y=0$. Similarly, the values of the slope are $(1+m)/V$ and $(1+m+n)/V$ in regions 3 and 5, respectively, because $y=m$ and $y=m+n$. Therefore, once the concentration curve is obtained experimentally, the composition of the formed adducts can be determined by the slope of the concentration curve in each monovariant region.

If the equilibrated concentrations of B are $[B]_1$ and $[B]_2$ in the respective invariant regions 2 and 4, the amount of B in the boundary between monovariant and invariant region is given by substituting either $[B]_1$ or $[B]_2$ for [B] in Eq. 5 and solving for x:

$$x_1 = [B]_1V, \tag{6}$$

$$x_2 = (mD + [B]_1V)/(1 + m), \tag{7}$$

$$x_3 = (mD + [B]_2V)/(1 + m), \tag{8}$$

$$x_4 = ((m + n)D + [B]_2V)/(1 + m + n). \tag{9}$$

The width of each region, $W_1, \cdots, W_5$, is given by calculating successively the difference in each x with Eqs. 6—9:

$$W_1 = x_1 - 0 = [B]_1V, \tag{10}$$

$$W_2 = x_2 - x_1 = m(D - [B]_1V)/(1 + m), \tag{11}$$

$$W_3 = x_3 - x_2 = ([B]_2 - [B]_1)V/(1 + m), \tag{12}$$

$$W_4 = x_4 - x_3 = n(D - [B]_2V)/(1 + m + n)(1 + m), \tag{13}$$

$$W_5 = D - x_4 = (D - [B]_2V)/(1 + m + n). \tag{14}$$

Let us consider how each width depends on $[B]_1$ and $[B]_2$ when they are less than 10^{-3} M (1 M=1 mol dm^{-3}).

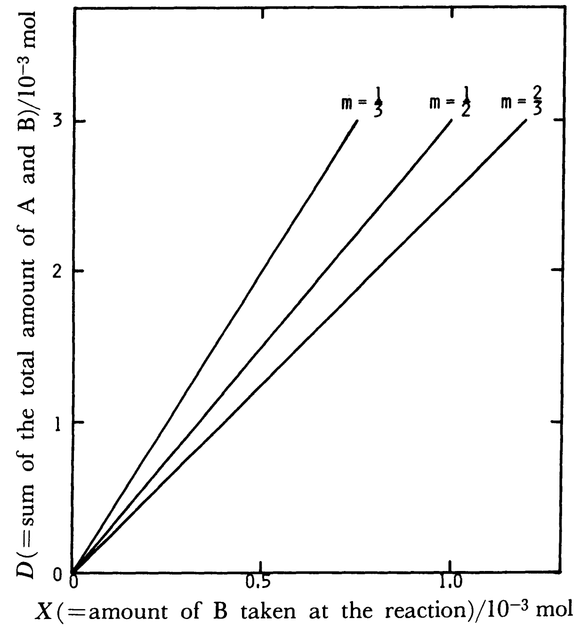


Fig. 3. Relation between the point of phase boundary and D when $[B]_1$ and $[B]_2$ are low.

Solid-liquid reactions are usually carried out under the condition that D is 1—2 mmol and V is 10 cm^3. The value of $[B]_1V$ or $[B]_2V$ ($10^{-3}\,M\times10^{-2}$ dm^3=10^{-5} mol) is much smaller than mD ($m\times10^{-3}$ mol). Therefore, both W_1 and W_3 are nearly equal to zero, as is shown in Fig. 2. Hence, Eq. 15 is derived from Eqs. 7 snd 8, because $[B]_1\approx[B]_2\approx0$:

$$x_2 = x_3 = mD/(1 + m). \tag{15}$$

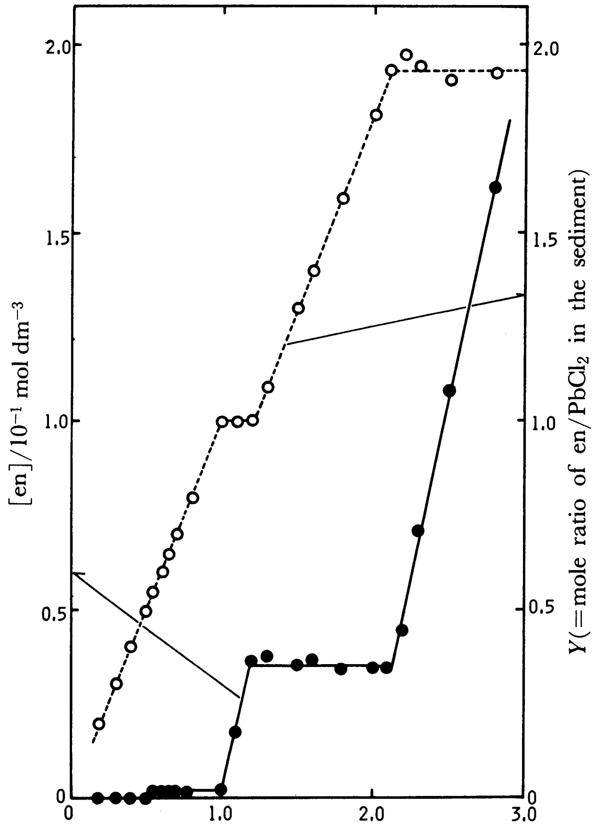
Equation 15 shows that the B value in the boundary between invariant regions 2 and 3, and between 3 and 4, depends on D and composition m. This relation is illustrated in Fig. 3, which shows how the value changes with D. Accordingly, if equilibrated concentration of B is low in invariant regions, the composition of adducts can be determined by Eq. 15.

Experimental

Apparatus. A Toa Denpa HM-18E pH meter was used to determine potentiometrically the concentration of en in equilibrated reaction solutions. Low concentration of en was determined by a Shimazu MPS-2000 double beam spectrophotometer to measure the absorbance at 430 nm. The reactions were carried out in a Taiyo WB-3 incubator with mechanical shaking.

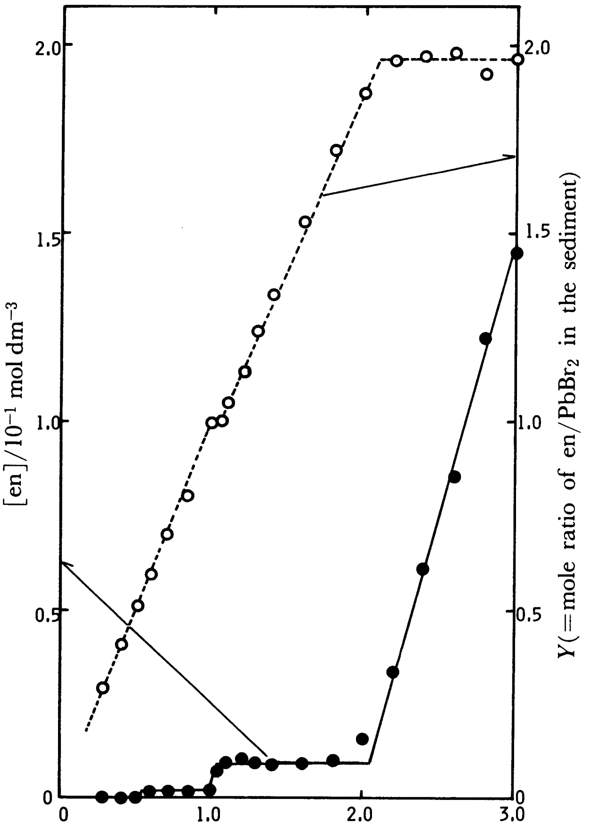
Reagents. The preparation of PbI_2 was described previously.[2] $PbBr_2$ was prepared by mixing a solution of $Pb(NO_3)_2$ with that of KBr in the stoichiometric ratio, the sediment was separated from the solution, dried at 110 °C for about 12 h, and stored in the dark. $PbCl_2$ was purified by recrystallization from distilled water. Ethylenediamine (99.0% pure) purchased from Wako Pure Chemical Co. was used without further purification. Ethanol was dehydrated with molecular sieves (3A1/16) and then distilled.

The Solid-Liquid Reactions of PbX_2 (X=Cl, Br, and I) with en. (1) Extension of the Mole Ratio Method. 0.500 g



X/Z(=mole ratio of en/PbCl$_2$ taken at the reaction)

Fig. 4. Relation between the concentration of ethylenediamine remaining in the solution and mole ratio of en/PbCl$_2$ taken at the reaction when the mole ratio method was extended to the reaction of PbCl$_2$ with en: —●—●—, concentration curve; --○--○--, composition curve (definition, see text).



X/Z(=mole ratio of en/PbBr$_2$ taken at the reaction)

Fig. 5. Relation between the concentration of ethylenediamine remaining in the solution and mole ratio of en/PbBr$_2$ taken at the reaction when the mole ratio method was extended to the reaction of PbBr$_2$ with en: —●—●—, concentration curve; --○--○--, composition curve.

of finely powdered PbX$_2$ (X=Cl and Br) suspended in 10.0 cm^3 ethanol solution containing various amounts of en was put into ampoule. After several glass beads (about 0.2 cm in diameter) were added, the ampoule was sealed and shaked at 25.0±0.2 °C for about one month in the incubator. The mole ratio of en/PbX$_2$ at the beginning of reaction varied in the range of 0.3—3.0. Each ampoule was covered with an aluminium film in the case of the reaction of PbBr$_2$ with en to prevent the PbBr$_2$ from turning black owing to exposure to light. Reaction solution was separated from sediment after the reaction reached the equilibrium and then was subjected to chemical analysis.

(2) Extension of the Continuous Variation Method. Various amounts of finely powdered PbX$_2$ (X=Cl, Br, and I) and 10 cm^3 of ethanol solution containing various amounts of en were mixed in ampoule in varying proportions that the sum of PbX$_2$ and en is constant. The suspension was then treated as described above. The adopted D was 2.0 mmol for PbCl$_2$, PbBr$_2$, and PbI$_2$ and 1.5 mmol for PbCl$_2$.

Chemical Analysis of the Equilibrated Reaction Solutions. The concentration of en in the equilibrated reaction solutions was determined either potentiometrically when the concentration is high and spectrophotometrically[6)] when low. [Pb^{2+}] was determined complexometrically[7)] for some solutions.

Results and Discussion

Preliminary experiments confirmed that PbX$_2$ (X=Cl, Br, and I) does not react with ethanol and is sparingly soluble in it even in the presence of en.

Wharf et al. prepared PbX$_2$·2(en) (X=Cl, Br, and I).[8)] We ascertained, however, the formation of PbI$_2$·2/3(en) and PbI$_2$·en in addition to PbI$_2$·2(en).[1)] Therefore, solid-liquid reactions of PbX$_2$ (X=Cl and Br) with en were carried out by extension of the mole ratio method in order to confirm if any other adducts than PbX$_2$·2(en) are formed. Figures 4 and 5 show the results of the reactions of PbCl$_2$ and PbBr$_2$ with en, respectively. The concentration curve of Fig. 4 ascends slightly near 0.5 of x/z and then becomes flat when x/z approaches 1.0. It ascends again at 1.0 of x/z and becomes flat between 1.2 and 2.1 of x/z. Namely, three plateaus appear on the concentration curve in the ranges of x/z of 0.3—0.5, 0.55—1.0, and 1.2—2.1. The concentration curve of Fig. 5 behaves in the same manner as that of Fig. 4 except that the concentration of en in the range of 1.1—2.1 of x/z is lower than that in Fig. 4. According to the phase rule, these facts mean that three insoluble adducts form in each solid-liquid reaction.

As discussed in Refs. 1 and 2 on extension of the mole ratio method, the slope of monovariant regions on the concentration curve is equal to a certain fixed value depending on the adopted experimental conditions and independent of the composition of the formed adducts. Their compositions can be calculated by Eq. 16, which is converted from Eq. 3:

$$y = (x - [\mathrm{B}]V)/z = (x - [\mathrm{en}]V)/z, \qquad (16)$$

where [en] is the concentration of en in the equilibrated reaction solution. The compositions calculated from Eq. 16 are also shown in open circles in Figs. 4 and 5, where the broken line is termed "composition curve." Two plateaus appear clearly on each composition curve in monovariant regions where each concentration curve has specific slope; nearly equal to 1 and 2 of y in the right ordinate. Two insoluble adducts, $\mathrm{PbX_2 \cdot en}$ and $\mathrm{PbX_2 \cdot 2(en)}$, seem to correspond to each reaction. On the other hand, each composition curve shows no plateau corresponding to the rise in the concentration curve which occurs near 0.5 of x/z. The occurrence of these adducts is liable to be overlooked because of disappearance of the plateau in the composition curve and slight increase in the concentration curve. This is a drawback in extension of the mole ratio method to solid-liquid reactions. A similar situation was noticed when $\mathrm{PbI_2 \cdot 2/3(en)}$[1] and $\mathrm{PbX_2 \cdot 1/2(dien)}$[3] are formed. In the case of $\mathrm{PbI_2 \cdot 1/2(dien)}$, its formation can be confirmed of not only by a slight concentration rise but also by the powder X-ray diffraction of the solid sediments.

In order to show that extension of the continuous variation method overcomes the drawback of the mole ratio method, the former was applied to the reactions of $\mathrm{PbX_2}$ (X=Cl, Br, and I) with en in ethanol. Figure 6 shows the results of the reactions. When D is 2 mmol, each concentration curve has two plateaus and ascends sharply at 0.7 and 1.0 mmol of x for the reactions of $\mathrm{PbCl_2}$ and $\mathrm{PbBr_2}$. The reaction of $\mathrm{PbI_2}$ with en also shows two plateaus and ascends at 0.8 mmol of x. When D is 1.5 mmol, the concentration curve ascends at 0.5 mmol of x in the reaction of $\mathrm{PbCl_2}$. According to Eq. 15, the value of x where [B] increases sharply is 0.67 mmol for m=1/2, 0.8 mmol for m=2/3, and 1.0 mmol for m=1 when D is 2 mmol, while it is 0.5 mmol for m=1/2 when D is 1.5 mmol. Since each value of x found in Fig. 6 is equal to x calculated by Eq. 15, three insoluble adducts, $\mathrm{PbCl_2 \cdot 1/2(en)}$, $\mathrm{PbBr_2 \cdot 1/2(en)}$, and $\mathrm{PbI_2 \cdot 2/3(en)}$, seem to be identified. Similarly, each sharp concentration rise at 1.0 mmol of x in Fig. 6 corresponds to formation of $\mathrm{PbCl_2 \cdot en}$ and $\mathrm{PbBr_2 \cdot en}$.

In order to prepare adducts with a mole ratio of en/$\mathrm{PbX_2}$ higher than two, suspended $\mathrm{PbX_2}$ powders were made to react with en without solvent. However, resulting adducts were found to be $\mathrm{PbX_2 \cdot 2(en)}$ by chemical analysis and powder X-ray diffractometry.

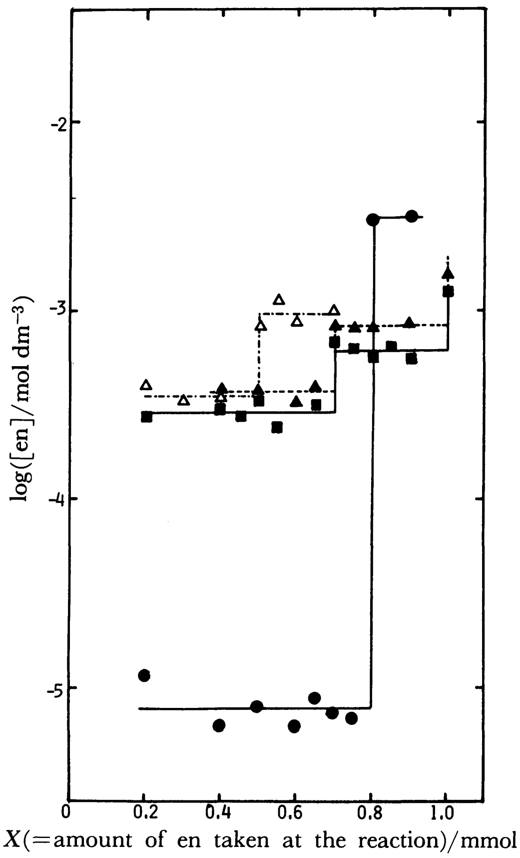


Fig. 6. Relation between the concentration of ethylenediamine remaining in the solution and the amount of en taken at the reaction when the continuous variation method was extended to the reaction of $\mathrm{PbX_2}$ with en: —●—●—, $\mathrm{PbI_2}$, D=2 mmol; —■—■—, $\mathrm{PbBr_2}$, D=2 mmol; --▲--▲--, $\mathrm{PbCl_2}$, D=2 mmol; ---△---△---, $\mathrm{PbCl_2}$, D=1.5 mmol.

When the equilibrated concentration of Lewis bases is high at invariant regions, the composition of formed adducts can be determined by extension of the continuous variation method to the reaction of $\mathrm{PbI_2}$ with pyridine[3] on the basis of the slope at monovariant regions on the concentration curve. In the present work, the extension has been examined in the reactions of $\mathrm{PbX_2}$ (X=Cl, Br, and I) with en where the equilibrated concentration of en is very low at the invariant regions. In this case, their compositions are determined on the basis of the values of sharp rises in the concentration curve. The values are proportional to D, the sum of Lewis acid and base, as shown in Fig. 3. This fact was also demonstrated by the reaction of $\mathrm{PbCl_2}$ with en where formation of the same adduct, $\mathrm{PbCl_2 \cdot 1/2(en)}$, was confirmed at two different D's, 1.5 and 2.0 mmol. If low concentration of Lewis bases can be accurately determined, the continuous variation method is effective in identifying formation of the adducts such as $\mathrm{PbCl_2 \cdot 1/2(en)}$ and $\mathrm{PbBr_2 \cdot 1/2(en)}$ whose formation is liable to be overlooked in the mole ratio method, because the composition curve tends to lose the plateaus corresponding to the rises in the concentration curve.

Formation of $PbX_2 \cdot 2(en)$ (X=Cl, Br, and I) has been reported by Wharf et al.[8] By extension of the mole ratio method, three adducts, $PbI_2 \cdot i(en)$ (i=2/3, 1, and 2), were identified.[1] In the present paper, $PbX_2 \cdot i(en)$ (X=Cl and Br; i=1/2, 1, and 2) were confirmed. The mole ratio method as well as the continuous variation method are necessary to confirm all the adducts formed in solid-liquid reactions. Many adducts have been reported on PbX_2 with monodentate Lewis bases.[8–10] Most of them have the compositions of 1 : 1 and/or 1 : 2 PbX_2: base ratio. $PbCl_2 \cdot 1/2(en)$ and $PbBr_2 \cdot 1/2(en)$ correspond to adducts with PbX_2/base ratio of 1 : 1 and $PbX_2 \cdot en$ with the ratio of 1 : 2, because ethylenediamine is considered to be a bidentate ligand. Therefore, $PbX_2 \cdot 2(en)$ and $PbI_2 \cdot 2/3(en)$ have unusual compositions.

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