Inorganica Chimica Acta, 45 (1980) L47–L48

Raman Spectra of Trihalogenoanions of Lead(II) in Solution in Tri-n-butylphosphate and N,N-dimethyl Formamide

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Received March 10, 1980

K. Balasubramanyan and L. Nanis [1] studied the molten mixture of $PbCl_2$–KCl system by Raman spectra and they found that two types of ionic species $PbCl_3^-$ and $PbCl_4^{2-}$ appear to exist in the molten mixture. But the series of Raman bands reported by them was not observed by the recent work done by Maroni, Victor A, [2] in using the Ar–Kr ion laser of PbX_2–KX melts containing ≤67 mole% KX, X = Cl or Br. They have observed a single polarized Raman band which has attributed to the stretching mode of a simple unidentified complex ion, PbX_n^{2-n}. In order to obtain more direct evidence for the existence of complex ions in solution, Raman spectroscopic studies of solutions of lead(II) halides in tri-n-butylphosphate (TBP) and N,N-dimethylformamide (DMF) containing added halide ion were performed. The solvents TBP and DMF combine the desirable properties of possessing a good solubility for all these complexes with relatively weak Raman bands in the frequency region of interest. It has accordingly proved possible to obtain well defined spectra from all the solutions and thus to attempt the structure of the species.

Reagent grade TBP was purified [3] and dried by vacuum pumping (0.1 torr) at 50 °C for 24 h. The water content was thereby reduced to less than0.2% (Karl Fischer). The commercial grade N,N-dimethylformamide (DMF) was distilled under vacuum and dried using a Linde 5A molecular sieve.

Raman spectra were recorded on Cary 81 and Spex Ramalog instruments with He–Ne 6.32.8 nm excitation.

Results and Discussion

The observed Raman bands of the extracts by shaking the solutions of lead(II) halides and hydrogen halides with tri-n-butylphosphate(TBP) as well as the solutions prepared by dissolving lead(II) halides and

TABLE I. Raman Spectra of Trihalogenoanions of Lead(II) in TBP and DMF and Their Comparison with Isoelectronic Species SnX_3^- (X = Cl or Br) [4].

Sample	Species	Vibrational frequencies, cm^{-1}			
		ν_1 (a_1)	ν_2 (a_1)	ν_3 (e)	ν_4 (e)
Solution of $PbCl_2$ (0.5*M*) and anhydrous LiCl (0.5*M*) in DMF	$PbCl_3^-$	249s(p)	–	–	–
Extract of $SnCl_2$ (2*M*) and HCl (6*M*) aqueous solution in diethyl ether [4]	$SnCl_3^-$	297s(p)	128w(p)	256m(dp)	103m(dp)
Extract of $PbBr_2$ (0.5*M*) and HBr (8.4*M*) aqueous solution in TBP	$PbBr_3^-$	180s(p)	–	166m(dp)	–
Solution of $PbBr_2$ (0.5*M*) and anhydrous LiBr (0.5*M*) in TBP	$PbBr_3^-$	176s(p)	–	164m(dp)	58w
Solution of $PbBr_2$ (0.5*M*) and anhydrous LiBr (0.5*M*) in DMF	$PbBr_3^-$	164s(p)	–	152m(dp)	–
Extract of $SnBr_2$ (1.5*M*) and HBr (4*M*) aqueous solution in diethyl ether [4]	$SnBr_3^-$	211s(p)	83m(p)	181m(dp)	65m(dp)
Extract of PbI_2 (0.5*M*) and HI (6.3*M*) aqueous solution in TBP	PbI_3^-	137s(p)	–	127m(dp)	30–45wb
Solution of PbI_2 (0.5*M*) and anhydrous LiI (0.5*M*) in TBP	PbI_3^-	137s(p)	–	127m(dp)	30–45wb
Solution of PbI_2 (0.5*M*) and anhydrous LiI (0.5*M*) in DMF	PbI_3^-	122s(p)	–	–	–

m = medium, s = strong, w = weak, p = polarized, dp = depolarized, wb = weak broad.

anhydrous lithium halides in TBP and DMF are inserted in Table I.

The spectrum of each extract in TBP consists of three lines (Table I), one of which at the highest frequency is polarised. The spectra of the bromide and iodide complexes in DMF are at a slightly lower frequency than in TBP but are less complete in regard to the remaining lines. No spectra could be observed for $PbCl_3^-$ in TBP, but in DMF, a single polarized line was observed. This may be the same type of Raman spectrum expected according to the rules of selection and polarization for a species of the type MX_3^- of pyramidal shape of point group, C_{3v}. The ions $PbCl_3^-$, $PbBr_3^-$ and PbI_3^- in which the metal atom has a valency octet including one unshared electron pair are expected to have a pyramidal shape and are isoelectronic with the ions $SnCl_3^-$, $SnBr_3^-$ and SnI_3^- [4]. The comparison of the Raman spectra of the isoelectronic pairs in Table I provides strong evidence that the species prepared and extracted into tri-n-butylphosphate (TBP) and N,N-dimethylformamide (DMF) are trihalogeno anions of lead(II). In each pair the spectra are analogous to each of the frequencies of $PbCl_3^-$ and $PbBr_3^-$ being less than the corresponding one $SnCl_3^-$ and $SnBr_3^-$. This is in accordance with the parallel behaviour exhibited by other series of ions within a given group of the periodic table, where a decrease in vibrational frequencies is normally associated with an increase in the mass of the central atom.

Maroni, Victor, A [2] in their studies of PbX_2–KX melts observed a single polarised Raman band centered at 218 cm^{-1} for X = Cl and at 144 cm^{-1} for X = Br. We have also observed a single polarized Raman band at 249 cm^{-1} for $PbCl_3^-$ and at 176 cm^{-1} for $PbBr_3^-$ alongside with other depolarized bands. We have tentatively assigned it to the stretching mode, $\nu_1(a_1)$ of a complex ion, PbX_3^- (X = Cl or Br) of pyramidal shape of point group, C_{3v} and compared its bands with the isoelectronic species SnX_3^- (X = Cl or Br) in Table I.

References

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