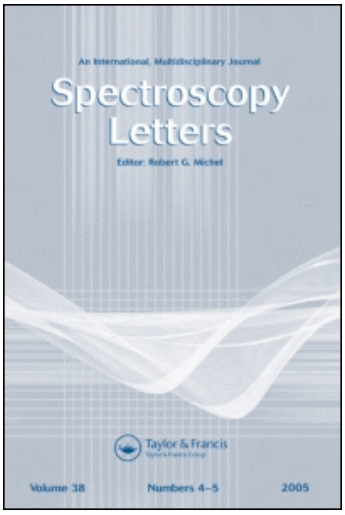

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J. G. Contreras[a]; C. A. López[a]; G. V. Seguel[a]
[a] Departamento de Química, Universidad de Concepción Casilla 3-C,

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"VIBRATIONAL SPECTRA OF TETRAPROPYLAMMONIUM TRICHLOROZINCATE (II)"

Keywords: Far-infrared, Raman, Trichlorozincate (II) complexes.

J.G. Contreras*, C.A. López and G.V. Seguel

Departamento de Química
Universidad de Concepción
Casilla 3-C, Concepción
Chile

ABSTRACT

The IR and Raman spectra of Crystalline Tetrapropylammonium trichlorozincate (II) have been measured at room and liquid nitrogen temperatures. The spectra have been interpreted in terms of halogen bridged structures. The complete coincidence of the IR and Raman bands suggests a symmetry lower than D_{2h} and rules out any centrosymmetric structure.

INTRODUCTION

Anionic complexes of the type MX_3^- where M is a group IIb metal ion and X = Cl, Br or I have been studied in aqueous solution,

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TBP extracts and melts[1-4]. Conductivity measurements in TBP show that the maximum conductance occurs for MX_2/LIX = 1 molar ratio[4,5]. On the other hand, Raman spectra of molten compositions $ZnCl_2$-MCl (M = Li, K, Rb or Cs) are consistent with the presence of $ZnCl^+$, $ZnCl_2$, $(ZnCl_2)_n$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ species[2]. The $ZnCl_3^-$ species being the more important one.

In aqueous solution[3] or TBP extract[4,6] the $ZnCl_3^-$ skeleton might be bent. The appearance of an IR active ν_1 mode[4] and the four-band Raman spectrum with two polarized bands[3] support a C_{3v} symmetry. The shift of ca 50 cm^{-1} in the P-O stretching mode of the TBP would imply that the solvent is coordinated to produce the C_{3v} tetracoordinate species. It seems clear that in solution the $ZnCl_3^-$ anion can only be investigated in the presence of appreciable amounts of $ZnCl_2$ and $ZnCl_4^{2-}$ species. Therefore, we have prepared and isolated this anionic species as salt ot tetrapropylammonium. The far infrared and Raman spectra at room and liquid nitrogen temperatures have been recorded and interpreted on the basis of the previously reported structure found for the tetrapropylammonium trichloromercurate (II)[6], tribromomercurate[7] (II) and triiodomercurate (II)[8].

EXPERIMENTAL

$(C_3H_7)_4NZnCl_3$ was prepared as follows: zinc (II) chloride was suspended in a solution containing the stoichiometric amount of tetrapropylammonium chloride dissolved in methanol. The suspension was left with stirring for 1-2 hrs and then allowed to slowly eva-

porate to yield colorless crystals. The solid was recrystallized twice from either methanol/acetonitrile or methanol/dichloromethane. Carbon, hydrogen, nitrogen and zinc analysis agree well with the formula given above. Conductivity measurements and molecular weight determination were carried out as described previously[9], Raman spectra were recorded as described elsewhere[10], whereas far-IR were obtained on a purged Bruker IFS 113V Fourier transform spectrophotometer using a mercury arc lamp and a DTGS detector at a resolution of 2 cm^{-1}. The samples were ground and mixed with polyethylene powder and pressed to disks of ca. 13 mm diameter. For all samples the same concentration was used: 5 mg of sample in 200 mg of polyethylene. -Pure polyethylene was used as reference. In the room temperature spectrum two beam splitters were used. A Mylar beamsplitter of 6μ for the range 530-55 cm^{-1} and one of 50μ for 55 down to 20 cm^{-1}. In the low temperature measurements, a Mylar 6μ beamsplitter was used in the whole range. The samples were cooled in an Oxford crystal type CF 104 with polymethylpentene windows.

RESULTS AND DISCUSSION

The Raman spectrum of Pr_4NZnCl_3 (Pr_4N = tetrapropylammonium cation) in acetonitrile shows one strong polarized band at ca. 285 cm^{-1} in good agreement with previously reported results[1,4]. This band can confidently be assigned tc the symmetric Zn-Cl stretching mode of the solvated C_{3v} species. The above results are also in keeping with our conductivity data which demonstrate that the entitled compound is monomeric and behaves as a 1:1 electrolite in solution.

In the solid state, the Rast method indicates that the dimeric anionic species are present (M.W. Calc. 355.9; MWobs. 701) and hence the compound is better formulated as $(Pr_4N)_2Zn_2Cl_6$. These results imply that the $Zn_2Cl_6^{2-}$ anionic species must undergo extensive dissociation in solution. The far-IR and Raman spectra of the crystalline $(Pr_4N)_2Zn_2Cl_6$ show the typical features of a halogen-bridged species. A non-planar halogen-bridged $Zn_2Cl_6^{2-}$ species belongs to the D_{2h} (or lower) point group. The eighteen normal modes can be distributed in eight stretching modes and ten bendings, twisting, rocking and ring deformation modes[11].

In D_{3h} symmetry the mutual exclusion selection rule must operate and hence two terminal and two bridging Zn-Cl stretching modes are to be observed in the Raman and the corresponding in the IR. Since the bendings, twistings, rocking and ring deformation modes lie in the region where the lattice modes also occur, we will confine our discussion to the stretching modes only.

Zinc-chloride stretching vibrations occur in the range 330-200 cm^{-1}, the Zn-Cl Terminal stretching modes are observed in the upper limit. Thus, a range of 330-270 cm^{-1} is in good agrement with that found in other halide complexes of post-transitional metals[6,12]. The Zn-Cl bridging modes are observed from 250 down to 200 cm^{-1}. Table I gives the IR and Raman spectra of the crystalline $(Pr_4N)_2Zn_2Cl_2$. According with the previously established ranges for termal and bridging stretching modes the assignment of the vibrational bands is straightforward. Figure 1 shows the IR and Raman spectra at ca. 77°K.

TABLE I

IR and Raman of crystalline $(Pr_4N)_2Zn_2Cl_6$

IR (300 °K)	IR (77 °K)	Raman (77 °K)	Raman (300 °K)	Assignment[a]
322 vs	324 vs	322 ms	316 s	T
298 vs	303 vs	297 m	298 m	T
--	281 w	287 m	286	T
--	274 w	269 vs	271 ms	T
--	245 vs	249 m	248 m	B
236 s	239 vs	231 s	233 ms	B
--	208 vw	210 m	216 s	B
--	200 w	201 mw	206 mw	B
--	--	173 w	176 w	
--	163 w	--	--	
--	--	138 m	134 mw	bending
128 m	128 s	--	--	modes
107 ms	107 s	105 w	--	
--	93 w	93 mw	92 w	
79 vw	81 w	--	--	
--	69 w	--	--	Lattice
55 mw	59 m	60 mw	--	modes
52 m	--	53 w	54 w	
48 w	--	--	--	
44 m	--	44 w	--	

[a] T and B denote terminal and bridging respectively.

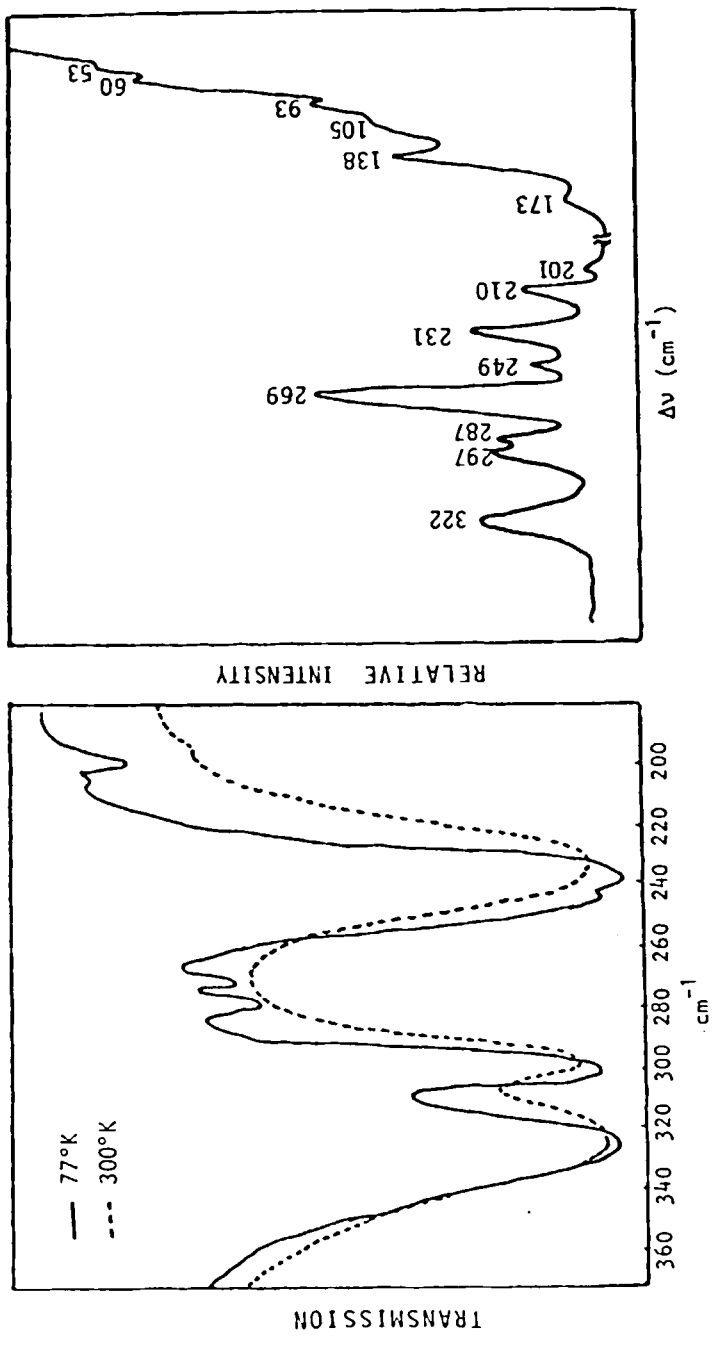

Fig. 1. IR and Raman Spectra of Crystalline $(Pr_4N)_2Zn_2Cl_6$ at ca. 77 °K.

From Table I it can be inferred that the mutual exclusion selection rule does not apply for the $Zn_2Cl_6^{2-}$ species in the solid state and hence this anionic species must possess a symmetry lower than D_{2h}. (Probably C_1 or C_{2v}). This conclusion is in keeping with findings for the $Hg_2Cl_6^{2-}$ and $Hg_2Br_6^{2-}$ species for which the X-ray crystal structure determinations show[6,7] that a C_1 symmetry occurs in these complexes. An alternative explanation for the complete coincidence of the IR and Raman bands is that the anionic complex possesses a D_{2h} symmetry but the factor group is not a centrosymmetric one.

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