Inorganica Chimica Acta, 145 (1988) 81–84

Infrared and Raman Spectra of Metal 1,2,4,5-Benzenetetracarboxylates: Evidence for Very Short, Strong Hydrogen Bonds

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(Received August 12, 1987)

Abstract

Salts of 1,2,4,5-benzenetetracarboxylic acid with copper, aluminum, ammonium, cobalt(II), thallium(I), tin(II), uranyl ion, zinc, manganese, iron(II), nickel, potassium and sodium have been prepared and characterized by their IR spectra. The salts of aluminum, ammonium, thallium(I), tin(II), zinc, iron(II), nickel, potassium and sodium had not been reported before with adequate characterization. Raman spectra of selected compounds also aided structural interpretation. The IR spectra of $Na_2C_{10}H_4O_8 \cdot 2H_2O$, $Fe(C_{10}H_5O_8)_2 \cdot 12H_2O$, $Zn(C_{10}H_5O_8)_2 \cdot 12H_2O$, $Ni(C_{10}H_5O_8)_2 \cdot 12H_2O$, $(NH_4)_3C_{10}H_3O_8 \cdot H_2O$ and $CoC_{10}H_4O_8 \cdot 6H_2O$ indicate very short, strong hydrogen bonds in these compounds. The IR and Raman spectra can be used to determine the mode of coordination (if any) of the carboxylate groups of 1,2,4,5-benzenetetracarboxylate to metal ions.

Introduction

Although a number of salts of 1,2,4,5-benzenetetracarboxylic acid or pyromellitic (PMA) have been reported [1–14], in many cases they have not been well characterized. We report salts of aluminum, ammonium, thallium(I), tin(II), zinc, iron(II), nickel, potassium and sodium not previously reported with adequate characterization. Only a few IR studies [6–9] and no Raman studies have been reported on salts of PMA. Because of the various ways that a carboxylate group can coordinate to a metal ion, it is very desirable to have single crystal X-ray structure information to assist in the interpretation of IR and Raman spectra of metal carboxylates [15].

Recently the single crystal X-ray structure determinations of $Cu_2C_{10}H_2O_8 \cdot 10H_2O$, $CoC_{10}H_4O_8 \cdot 6H_2O$, $UO_2C_{10}H_4O_8 \cdot 2H_2O$ and two neptunium salts of PMA were reported in addition to the dihydrate of PMA done some time ago [10–14, 16]. These demonstrate a variety of modes of hydrogen bonding and coordination of carboxylate groups to the cations. A single crystal X-ray study of $Tl_4C_{10}H_2O_8$ shows that the anion is not coordinated to the metal ion and exhibits no hydrogen bonding [17]. Therefore it is valuable as a basis for comparison with other compounds where the benzenetetracarboxylate is coordinated to metal ions or hydrogen bonded or both. Now there is sufficient single crystal X-ray diffraction structural information to permit interpretation of IR and Raman spectra of benzenetetracarboxylates in terms of metal coordination, anion structure, and hydrogen bonding even for those compounds which have not had single crystal X-ray diffraction studies.

Because of the practical importance of salts of PMA [9, 12] and availability of single crystal X-ray structure information, this study to improve the characterization of salts of PMA by elemental analysis and IR and Raman spectroscopy was undertaken.

Experimental

The dihydrate of PMA was prepared by recrystallizing Aldrich 1,2,4,5-benzenetetracarboxylic anhydride from water. Anhydrous PMA was prepared by drying the dihydrate at 115 °. The weight loss of 12.45% agreed closely with the calculated value of 12.41% for the loss of water of hydration from the dihydrate. The salts of the divalent cations were prepared by mixing solutions of equimolar amounts of a soluble salt of the metal and the PMA neutralized with two equivalents of sodium carbonate. Most of these salts were slightly soluble and precipitated immediately. They were filtered off and air dried. The cobalt (II) and nickel salts were more soluble and required that crystallization be forced by solution evaporation or addition of more sodium carbonate. It was difficult to obtain $CoC_{10}H_4O_8 \cdot 6H_2O$ without contamination by several other phases, but the crystals were often large enough to pick by hand from the other phases. The $Tl_4C_{10}H_2O_8$ was so soluble that it could only be prepared by adding $Na_4C_{10}H_2O_8$ solutions to saturated thallium(I) perchlorate solutions and evaporating until crystals

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0020-1693/88/$3.50

deposited upon cooling. Salts of the alkali metals were prepared by adding stoichiometric amounts of the metal carbonate or hydroxide to a solution of the acid and evaporating until crystals formed upon cooling. It was necessary to add dimethyl sulfoxide to the concentrated solution of $K_4C_{10}H_2O_8$ to force formation of crystals of the tetrahydrate which were filtered off, washed with ethanol, and air dried. The IR spectrum showed no trace of ethanol or dimethyl sulfoxide.

Analysis of the metal content was generally by titration with EDTA after ashing. Thallium was determined as the chromate [18] and nickel as the dimethylglyoximate. Alkali metals and C, H, N analyses were by MTU Analytical Services or Spang Microanalytical Lab. Uranium was determined by reducing to U(IV) with excess Ti(III) and then titrating potentiometrically with Ce(IV) with Fe^{3+} as a catalyst.

The IR spectra were taken on a Perkin-Elmer 283B Infrared Spectrophotometer as potassium bromide disks except for the copper salt which had to be done as a nujol mull since the copper salt appeared to react with the potassium bromide. This sort of problem has been observed before [15]. The Raman instrument and data collection system have been described [19]. One to five scans at twenty cm^{-1} min^{-1} and one cm^{-1}/step were summed to give an excellent signal to noise ratio. The slit width was two cm^{-1}.

Results

The compounds obtained are listed in Table I. Satisfactory elemental analyses were obtained. (See 'Supplementary Material'.) The cobalt(II), copper, uranyl and manganese salts have been reported before [8, 10–12], but no detailed IR spectra were given. Different salts of nickel, cobalt(II), and zinc were obtained by Brzyska and Kowalewicz under different conditions [8].

TABLE I. 1,2,4,5-Benzenetetracarboxylate Salts

$Al_4(C_{10}H_2O_8)_3 \cdot 6H_2O$
$(NH_4)_3C_{10}H_3O_8 \cdot H_2O$
$Cu_2C_{10}H_2O_8 \cdot 10H_2O$
$CoC_{10}H_4O_8 \cdot 6H_2O$
$Tl_4C_{10}H_2O_8$
$Sn_2C_{10}H_2O_8 \cdot 2H_2O$
$UO_2C_{10}H_4O_8 \cdot 6H_2O$
$Zn(C_{10}H_5O_8)_2 \cdot 12H_2O$
$Mn_2C_{10}H_2O_8 \cdot H_2O$
$Fe(C_{10}H_5O_8)_2 \cdot 12H_2O$
$Ni(C_{10}H_5O_8)_2 \cdot 12H_2O$
$K_2C_{10}H_4O_8 \cdot 2H_2O$
$K_4C_{10}H_2O_8 \cdot 4H_2O$
$Na_2C_{10}H_4O_8 \cdot 2H_2O$

The IR spectra of $CoC_{10}H_4O_8 \cdot 6H_2O$, $Na_2C_{10}H_4O_8 \cdot 2H_2O$, $Fe(C_{10}H_5O_8)_2 \cdot 12H_2O$, $Ni(C_{10}H_5O_8)_2 \cdot 12H_2O$, $Zn(C_{10}H_5O_8)_2 \cdot 12H_2O$ and $(NH_4)_3C_{10}H_3O_8 \cdot H_2O$ display very broad, intense envelopes from 1800 to 900 cm^{-1}. (See 'Supplementary Material'.) Broad, intense envelopes in this region are known to be indicative of very strong, short hydrogen bonds [20–22].

Discussion

The IR spectra of anhydrous PMA and the dihydrate above 600 cm^{-1} were reported long ago [23]. For the most part, the results of this study agree with the literature values for the most intense bands. However, it is hard to understand why no bands were reported above 2700 cm^{-1} for the anhydrous PMA unless they actually had the anhydride. We find an intense, very broad band from 3500 to 2200 cm^{-1} for anhydrous PMA. This had been found to be characteristic of cyclic dimers of carboxylic acids [24–26]. This broad band is not present in the IR spectrum of the dihydrate although a number of sharper bands are present in the 3540–3140 cm^{-1} region which may be assigned to carboxyl hydrogens or water. The X-ray single crystal study of the dihydrate shows that no simple dimer rings are present although there is still hydrogen bonding between carboxyl groups as well as between the waters and carboxyl groups [16]. Because the dihydrate has a center of symmetry, no bands should be coincident in the Raman and IR spectra. With such a large molecule, there are a large number of fundamental modes, so it is more difficult to apply the mutual exclusion rule. There are several cases where IR and Raman frequencies of bands are within experimental error, but these must be accidental coincidences. The total number of bands observed in the IR and Raman spectra for the dihydrate of PMA is much less than the theoretical number possible. The broadness of many of the bands suggests that a number of fundamental modes have similar frequencies and overlap.

For acetates the separation between the symmetric and antisymmetric carbyxylate stretching frequencies indicates whether the acetate is coordinated in a monodentate, chelating, or bridging mode or not coordinated at all to the cation [15]. Both frequencies are at much lower values in salts than in acetic acid [24–26]. That shift was also observed in this study of PMA and its salts.

An examination of the IR and Raman spectra finds that the spectra are more complicated than for acetates because of the greater number of carboxylates per ion and the presence of the benzene ring. However, the separation between symmetric and antisymmetric carboxylate stretching vibrations is 180 cm^{-1} in the thallium(I) salt which is known from the crystal structure determination to have no coordination of the carboxylate to the cation or hydrogen bonding [17]. This is close to the value of about 170 cm^{-1} for ionic acetates. The value of 208 cm^{-1} for the separation in the copper compound, which is known to have monodentate coordination of the carboxylate groups [11], is consistent with the values of over 200 cm^{-1} for monodentate acetates [15]. However, the cobalt(II) salt has a difference of 240 cm^{-1}, and it has no coordinated carboxylates [12]. Apparently being hydrogen bonded to water has the same effect as being a monodentate ligand to a metal ion. (The carboxyl group bands used to calculate these splittings are denoted in the Tables by asterisks.)

The iron(II), nickel and zinc IR spectra are so similar as to indicate that the compounds are isostructural. The separation between the symmetric and antisymmetric carboxylate stretching frequencies are over 200 cm^{-1}, but they have substantial amounts of water of hydration available for hydrogen bonding (as previously seen with the cobalt salt), so no conclusion about the nature of coordination for the carboxylate group is possible for these compounds. Each of these three compounds has a band around 1700 cm^{-1} which is characteristic of a free protonated carboxylate group [26]. These are in addition to the usual deprotonated carboxylate bands at lower energy.

From the X-ray crystal study, $UO_2C_{10}H_4O_8 \cdot 2H_2O$ is known to have a chelating carboxylate group [10]. The difference between the broad symmetric and antisymmetric stretching bands is 150 cm^{-1} which is in the range established for chelating or bridging acetate groups (90–150 cm^{-1}) [15]. The tin(II) and aluminum compounds also show differences small enough to be in this range.

Thus, IR and Raman spectroscopy have the potential to distinguish the mode of coordination (if any) of the carboxylate group in metal salts of PMA now that a number of structures have been determined by single crystal X-ray work which can be correlated with the vibrational spectra of this study.

In view of the extensive coupling of vibrational modes below 1200 cm^{-1}, even in simpler polycarboxylates which have been analyzed by normal coordinate analysis [27, 28], no attempt will be made to assign bands below 1200 cm^{-1}. Examination of the results shows that even the strongest bands below 1200 cm^{-1} are not in the same position in this series of compounds. The similarity of band positions found for IR spectra of lanthanide salts of PMA [6] was not observed in the wider variety of metal salts in this study.

In conclusion, an important result of this work is the observation of broad envelopes from 1800 to 900 cm^{-1} in the IR spectra which indicate the presence of the relatively uncommon very strong hydrogen bond in $Na_2C_{10}H_4O_8 \cdot 2H_2O$, $(NH_4)_3C_{10}H_3O_8 \cdot H_2O$, $CoC_{10}H_4O_8 \cdot 6H_2O$, $Zn(C_{10}H_5O_8)_2 \cdot 12H_2O$, $Fe(C_{10}H_5O_8)_2 \cdot 12H_2O$ and $Ni(C_{10}H_5O_8)_2 \cdot 12H_2O$.

IR and Raman spectra for salts of PMA for which single crystal studies have been done generally appear to follow the same pattern as the more thoroughly characterized acetates; the separation between the symmetric and antisymmetric stretching vibrations of the carboxylate group can be used to determine the mode of coordination (if any) of the carboxylate group. These results suggest that the mode of coordination (if any) of the carboxylate group can be inferred from the IR spectra in other PMA salts which have not had single crystal X-ray studies. However, caution must be exercised because H-bonding to waters of crystallization can lead to effects which mimic cation coordination. It would be desirable to have single crystal X-ray data for the tin(II) and aluminum compounds to further test this suggestion.

Supplementary Material

Tables IA through XIII, giving the elemental analyses and IR and Raman spectra of the compounds prepared, are available from the authors on request.

Acknowledgements

Fred Robinson, Michael Berrigan, Shawn Mealey, and Thomas Eisele did preliminary work preparing several of the compounds.

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