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Raman spectra of some heavy metal oxalates

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ABSTRACT

The Raman spectra of microcrystalline powders of $\text{Ag}_2\text{C}_2\text{O}_4$, $\text{Tl}_2\text{C}_2\text{O}_4$ and HgC_2O_4 are recorded and discussed on the basis of their structural peculiarities and in comparison with the spectra of other previously investigated metallic oxalates. In the case of $\text{Tl}_2\text{C}_2\text{O}_4$ also IR data were used to complement the spectral analysis.

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KEYWORDS

Silver oxalate;
Thallium(I) oxalate;
Mercury(II) oxalate;
Raman spectra.

INTRODUCTION

Vibrational spectra of calcium oxalates, as well as those derived from first row transition metals or from the alkaline cations, has been often investigated^[1-5]. Notwithstanding, information concerning the heavy metal oxalates, remain relatively scarce. Only data concerning the spectroscopic behavior of PbC_2O_4 ^[6], SnC_2O_4 ^[7], $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and CdC_2O_4 ^[8], the two hydrates of SrC_2O_4 ^[9] and $\text{Tl}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ ^[10] are so far known. In this paper, and in order to extend this information, we report the results of an investigation of the Raman spectra of $\text{Ag}_2\text{C}_2\text{O}_4$, $\text{Tl}_2\text{C}_2\text{O}_4$ and HgC_2O_4 .

EXPERIMENTAL

Synthesis of the investigated oxalates

Silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4$, was obtained by slow addition of an aqueous 0.1 M solution of sodium oxalate to an equimolecular 0.1 M silver nitrate so-

lution, at room temperature and under continuous stirring. After filtration, the precipitated oxalate was washed with several portions of warm water and finally dried in vacuum over H_2SO_4 , in the dark^[11]. For the preparation of thallium(I) oxalate, $\text{Tl}_2\text{C}_2\text{O}_4$, 0.01 mol of oxalic acid were dissolved in 40 mL of boiling water and 0.01 mol of solid Tl_2CO_3 were slowly added in small portions, under stirring. The white precipitate was filtered off, recrystallized twice from water and dried in vacuum over H_2SO_4 ^[12]. For the synthesis of mercury(II) oxalate, HgC_2O_4 , 200 mL of a 0.5 M aqueous solution of oxalic acid was dropwise added, under continuous stirring, to 150 mL of a 0.5 M $\text{Hg}(\text{NO}_3)_2$ solution, slightly acidified with drops of nitric acid. The filtered precipitate was washed with several portions of hot water and dried in air^[13].

The purity of the compounds was confirmed by elemental analysis and X-ray powder diffractometry.

Spectroscopic measurements

The infrared spectra were recorded as KBr pel-

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lets with a FTIR-Bruker-EQUINOX-55 spectrophotometer. In the case of the Ag(I) and Hg(II) oxalates rapid interaction with the pellet material was observed, a situation generated in ionic exchange processes, which has often been found for salts of this type of cations^[14]. Only in the case of the Tl(I) compound reasonable good IR spectra could be obtained. IR measurements with Nujol mulls between CsI plates gave also relatively poor-quality spectra.

For this reason the vibrational behavior of the three investigated oxalates was only analyzed on the basis of their Raman spectra. Only for $Tl_2C_2O_4$ the information is also complemented with IR results.

Raman spectra of the three oxalates were registered on the microcrystalline powders of the compounds with a Raman Horiba Jobin Yvon T64000 instrument, using the 514.5 nm line of an argon laser for excitation. Unfortunately, the $Ag_2C_2O_4$ sample was partially destroyed during irradiation with this laser, even if its potency was drastically reduced. Therefore, this sample was finally measured with a Perkin Elmer FT-Raman RFs 110/s spectrometer, using the 1064 nm line of a solid state Nd:YAG laser for excitation.

RESULTS AND DISCUSSION

Structural characteristics of the compounds

The crystal structures of the three oxalates are known. Pertinent crystallographic data are shown in TABLE 1.

In the three compounds, the oxalate anions are practically planar but coordination numbers of the cations are different. In $Ag_2C_2O_4$ each Ag^+ cation is coordinated to four O-atoms from three different

anions, forming a flattened AgO_4 -tetrahedron, and another Ag^+ ion, generating Ag-Ag pairs with a short bond distance (2.945 Å). A very interesting feature of this structure is the presence of relatively elongated C-C bonds (1.60 Å)^[15]. In thallium(I) oxalate, the cation has an irregular coordination geometry, conformed by seven O-atoms, from four different oxalate anions and a lone pair which clearly squeezes the Tl-O bonds in the coordination polyhedra^[16,17]. In HgC_2O_4 the coordination number of Hg^{2+} is eight and is derived from two practically perpendicular HgO_4 planes presenting the shape of a slightly deformed box^[13].

Analysis of the raman spectra

The Raman spectra of the three investigated oxalates are shown in Figure 1 and the propose assignment is presented in TABLE 2 and briefly discussed as follows:

- The symmetric (C-O) stretching vibration is found at comparable energies in the three spectra and appears clearly splitted only in the case of HgC_2O_4 . For silver oxalate, two weak shoulders (1437 and 1420 cm^{-1}) are observed on the high energy side of this band.
- The corresponding antisymmetric vibrational mode, which is usually only observed in the IR spectra of oxalates, was detected for HgC_2O_4 in the high energy range (1671/1631 cm^{-1}). Consistent with this finding, in the IR spectrum of $Tl_2C_2O_4$ these ν_{as} (C-O) vibrations were clearly identified as a very strong band at 1597 cm^{-1} , with a shoulder on the low energy side (1542 cm^{-1}), and a strong doublet at 1308/1290 cm^{-1} . Interestingly, in the case of the previously investigated SnC_2O_4 a similar band was also found

TABLE 1 : Crystallographic data of the three investigated oxalates

Compound	Cr. system	Space group and unit cell parameters*	Ref.
$Ag_2C_2O_4$	monoclinic	Space group: $P2_1/c$ $a = 3.4603(5)$; $b = 6.1972(9)$; $c = 9.548(2)$; $\beta = 103.47(1)$; $Z = 2$	[15]
$Tl_2C_2O_4$	monoclinic	Space group: $P2_1/c$ $a = 6.6141(9)$; $b = 5.8404(11)$; $c = 6.6620(15)$; $\beta = 99.22(2)$; $Z = 2$	[16]
HgC_2O_4	monoclinic	Space group: $P2_1$ $a = 5.033(1)$; $b = 5.237(1)$; $c = 6.453(1)$; $\beta = 108.74(1)$; $Z = 2$	[13]

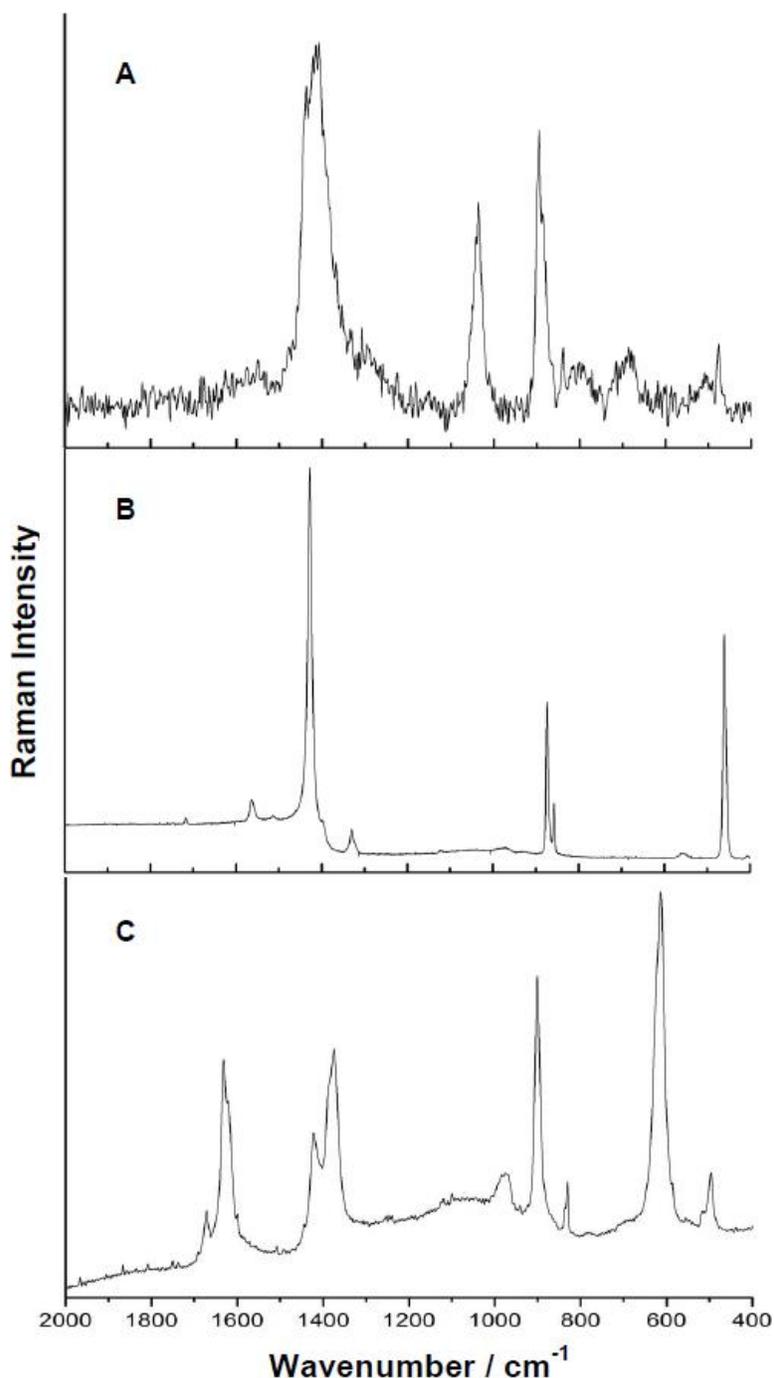


Figure 1 : Raman spectra of $\text{Ag}_2\text{C}_2\text{O}_4$, $\text{Tl}_2\text{C}_2\text{O}_4$ and HgC_2O_4 (A: $\text{Ag}_2\text{C}_2\text{O}_4$, B: $\text{Tl}_2\text{C}_2\text{O}_4$, C: HgC_2O_4)

- in the Raman spectrum, at 1617 cm^{-1} [7].
- In the case of $\text{Ag}_2\text{C}_2\text{O}_4$ the strong Raman line observed at 1036 cm^{-1} can also be assigned to another $\nu_{\text{as}}(\text{C-O})$ mode. Its important displacement to lower frequencies, in comparison with the values observed in the IR spectrum of $\text{Tl}_2\text{C}_2\text{O}_4$, may be a consequence of the peculiar arrangement of the Ag^+ and oxalate ions in this structure^[15].
- The $\nu(\text{CC})$ stretchings are observed as three group of bands, those at lower energy partially coupled with one (OCO)-deformation. Interestingly, in the case of $\text{Ag}_2\text{C}_2\text{O}_4$ no bands above 900 cm^{-1} are observed for this stretching; instead, an additional band at lower energies (838 cm^{-1}) is found. This behavior can surely be related to mentioned elongation of the C-C bond in this case.

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TABLE 2 : Assignment of the raman spectra of $\text{Ag}_2\text{C}_2\text{O}_4$, $\text{Tl}_2\text{C}_2\text{O}_4$ and HgC_2O_4 (band positions in cm^{-1})

$\text{Ag}_2\text{C}_2\text{O}_4$	$\text{Tl}_2\text{C}_2\text{O}_4$	HgC_2O_4	Assignment
		1671 w, 1631 s	$\nu_{\text{as}}(\text{C-O})$ cf. text
1555 vw	1563 vw		
1437 sh, 1420 sh			
1407 vs	1427 vs	1422 m, 1374 s	$\nu_{\text{s}}(\text{C-O})$ cf. text
1295 vw	1330 w		
1036 s			$\nu_{\text{as}}(\text{C-O})$
	971 vw	975 m	$\nu(\text{C-C})$
895 s	874 s, 858 m	901 vs	$\nu(\text{C-C})$
838 w		831 m	$\nu(\text{C-C}) + \delta_{\text{as}}(\text{OCO})$
815 w, 800 w			$\delta_{\text{as}}(\text{OCO})$
689 m			$\delta_{\text{as}}(\text{OCO}) + \rho(\text{OCO})$
	562 vw	613 vs	$\rho(\text{OCO})$
507 w, 476 m	460 s	496 m, 460 s	$\delta_{\text{s}}(\text{OCO}) + \rho(\text{OCO})$

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder

- For $\text{Tl}_2\text{C}_2\text{O}_4$ the $\delta_{\text{as}}(\text{OCO})$ vibration is found as a very strong IR band located at 754 cm^{-1} .
- The assignment of the $\delta_{\text{s}}(\text{OCO})$ and $\rho(\text{OCO})$ vibrations were performed by comparison with the results of the spectral analysis of PbC_2O_4 [6].
- Some weak bands found for the silver and thallium(I) oxalates above 1500 cm^{-1} and at around 1300 cm^{-1} surely originated in combinations or overtone modes.
- Metal-to-ligand vibrations could not be identified in any case. In all cases the Raman spectra show relatively strong bands around or below 200 cm^{-1} , but these bands are surely related to external ("lattice") vibrational modes.

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