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THERMAL BEHAVIOUR AND VIBRATIONAL SPECTRA OF $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ AND $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$

I. L. Botto, E. J. Baran and *A. C. Garcia*

QUÍMICA INORGÁNICA, FACULTAD DE CIENCIAS EXACTAS,
U.N.L.P., CALLES 47 Y 115 LA PLATA (1900), ARGENTINA

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The IR and Raman spectra and the thermal behaviour of the isomorphous compounds $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ and $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ were investigated. Detailed stoichiometries, sustained by TG, DTA and IR spectroscopic analyses, were found in both cases. Different results, associated with the different polarizing powers of the metal cations, were obtained. The first evidence was found of the formation of basic gallium carbonates.

The isomorphous salts $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ and $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ belong to the triclinic system, space group PI and $Z = 2$ [1]. In these compounds the Ga and the Al atoms are coordinated by six oxygen atoms from oxalate groups, in the form of a distorted octahedron [1]. These polyhedra are linked together by hydrogen-bonding. The three oxalate groups act as bidentate ligands, and the bond lengths and bond angles are similar to the values found for other oxalato complexes [1]. A peculiarity of these structures is the non-equivalence of the water molecules. They seem to be situated at several different sites in the lattice. Consequently, the characteristics of the hydrogen-bonding are unclear. Further, the gallium and aluminium compounds are structurally different from the similar compounds of other elements of group III. The coordination number for In(III) in the same stoichiometry is eight, and that for Y is nine [2, 3].

As the polarizing powers of Ga(III) and Al(III) differ in magnitude, one might expect that their complex salts will differ in thermal behaviour.

IR spectroscopy can be used to characterize the constitution of the intermediates generated during the pyrolysis process.

On the other hand, the vibrational behaviour can contribute to a better knowledge of the properties of the M—O bonds and their effects on other bond lengths and bond strengths.

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Experimental

$(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ and $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ were obtained as transparent crystals by slow evaporation from dilute aqueous solution according to Bulc et al. [1]. The purity of the substances was checked by X-ray diffractometry.

Thermogravimetric and differential thermal analyses were carried out simultaneously on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2), using a Pt – Pt/Rh thermoelement. The measurements were performed under a constant N_2 flow (0.4 l/min). The heating rate was 10 deg/min. α-Al_2O_3 was used as DTA standard; the maximum heating temperature was 700°. Sample weight ranged between 20 and 30 mg.

For further characterization of the pyrolysis residues or intermediates, samples of the different compounds were heated at selected and controlled temperatures in a crucible furnace, according to the information obtained from the thermograms.

The IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer, using the KBr pellet technique.

Raman spectra were obtained with a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a SCAMP data processor. The 514.5 nm line of an Ar ion laser was used for excitation.

X-ray powder diagrams were obtained with a Philips 1010 diffractometer, using CuK_α radiation (Ni-filter) and NaCl as an external calibration standard. The X-ray powder diagrams of samples collected after the first heat treatment, showed that the materials were amorphous.

Results and discussion

Thermal behaviour

TG and DTA traces recorded in typical experiments on $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ and $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ are shown in Fig. 1. It is evident that the thermal behaviour is not totally similar in the two compounds.

A) $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$

As seen in Fig. 1*A*, the DTA curve of this compound shows two well-defined endothermic peaks, at 63° and 100°. They correspond to the loss of two and one molecules of hydration water, respectively, generating the anhydrous oxalate. On further heating, intramolecular water (1.5 H_2O), NH_3, CO and CO_2 are lost between 170° and 380°. A total mass loss of 87.3% (theoretical 87.5%) leads to Al_2O_3 as the final product. Hence, from the IR spectra of the decomposition intermediates collected in the different stages, as well as from the TG data, the

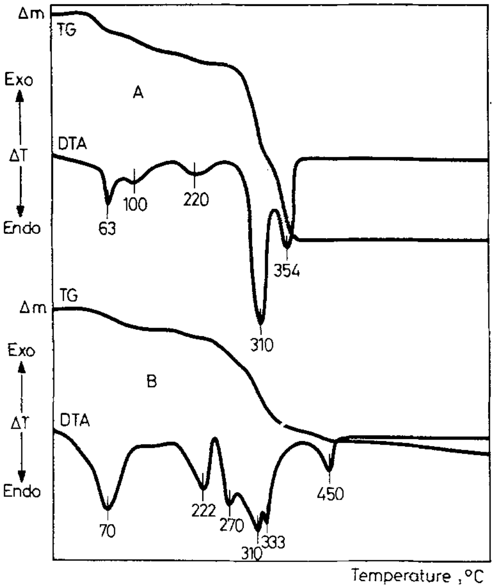

Fig. 1 TG and DTA plots of *A*: $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$; *B*: $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$

degradation process can be formulated as follows:

$$(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O \xrightarrow{63^\circ} (NH_4)_3Al(C_2O_4)_3 \cdot H_2O + 2\ H_2O \quad (1)$$

$$(NH_4)_3Al(C_2O_4)_3 \cdot H_2O \xrightarrow{100^\circ} (NH_4)_3Al(C_2O_4)_3 + H_2O \quad (2)$$

$$(NH_4)_3Al(C_2O_4)_3 \xrightarrow{170\text{–}380^\circ} 1.5\ H_2O + 3\ NH_3 + + 3\ CO + 3\ CO_2 + 0.5\ Al_2O_3 \quad (3)$$

B) *$(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$*

As can be observed in Fig. 1*B*, the DTA curve of this compound shows a first endothermic peak at 70°, which corresponds to the loss of the three molecules of hydration water. From then on, there is different thermal behaviour from that for the Al compound. In a second step, intramolecular water (one molecule) is liberated; the theoretical weight loss of 4.07% agrees well with the value found experimentally. The loss of NH_3, CO and CO_2 occurs on continued heating. However, before the final DTA signal (approx. 400°) the presence of basic gallium carbonate is observed. This can be formulated as $Ga_2O_3 \cdot 2CO_2 \cdot H_2O$ or

$Ga_2O(CO_3)_2 \cdot H_2O$. It is very hygroscopic in air. After 450° the product seems to be $Ga_2O_3 \cdot CO_2 \cdot H_2O$ or $Ga_2O_2CO_3 \cdot H_2O$. The weight loss of 5% between 380 and 470° coincides perfectly with the value found experimentally at this last DTA signal. Further, the remaining water is slowly lost between 500 and 700°, providing a total mass loss of 74% (theoretical 73.8%). Subsequent heating up to 1100° leads to the formation of Ga_2O_3.

It is interesting to note that the behaviour of the Ga compound is similar to that observed for the corresponding lanthanum oxalate [4–6] and especially to that for the decomposition of the anhydrous rare earth carbonates [7].

On the other hand, the IR spectra of the products obtained between 400 and 500° show small differences, attributable to the presence of monoxydicarbonate and dioxymonocarbonate species [7, 8].

It is well known that the "free" carbonate ion has three IR active vibrations, as a result of its D_{3h} symmetry: ν_2, ν_3 and ν_4; ν_2 is the out-of-plane deformation, ν_3 the asymmetric C—O stretching, and ν_4 the in-plane deformation. They lie in the infrared spectral regions 860–870, 1430–1500 and 700–750 cm^{-1} [8, 9]. Likewise, the symmetric C—O stretching (ν_1) is only Raman-active and lies in the region 1000–1100 cm^{-1} [9]. It is also known that symmetry lowering produces splitting and eventually the IR activation of the ν_1 mode. In the present case, the symmetry is evidently low and for this reason the ν_1 mode can be observed for the monoxydicarbonate form at 1042 cm^{-1} in the infrared spectrum. The other bands observed are: ν_2 at 883 cm^{-1}, ν_3 at 1440 and 1412 cm^{-1}, and ν_4 at 768 cm^{-1}. This IR spectrum is shown in Fig. 2. Bands in the 600 cm^{-1} region correspond to the Ga—O bond vibrations. On the other hand, the narrow band at 3522 cm^{-1} is

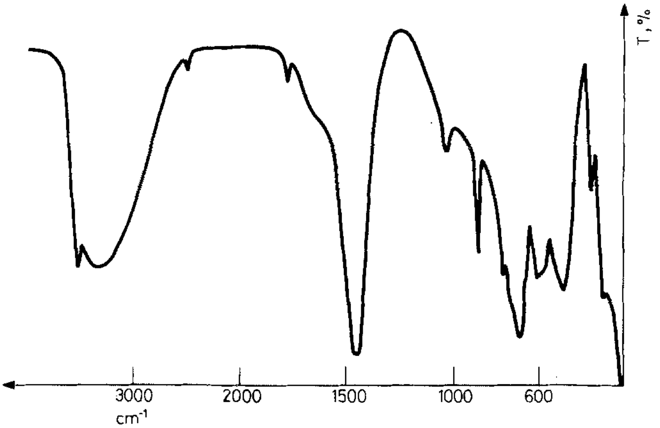

Fig. 2 IR spectrum of $Ga_2O(CO_3)_2 \cdot H_2O$

attributable to the OH groups. The presence of water, in different proportions depending on the time of exposure to air, is due to adsorbed atmospheric water.

For the samples heated up to 500°, additional bands appear in the out-of-plane deformation region (862–868 cm^{-1}).

The partial degradation of the complex is associated with a weakening of the degenerate in-plane bending mode [7].

In the spectrum shown in Fig. 2, some weak overtones or combination bands may also be observed, so that bands at 2490 and 1778 cm^{-1} can be attributed to $\nu_1+\nu_3$ and $\nu_1+\nu_4$ combination modes [7].

In conclusion, the following decomposition scheme can be proposed on the basis of all the previous results:

$$(NH_4)_3Ga(C_2O_4)_3\cdot 3H_2O \xrightarrow{70^\circ} (NH_4)_3Ga(C_2O_4)_3+3\ H_2O \qquad (1)$$

$$\begin{aligned}(NH_4)_3Ga(C_2O_4)_3 &\xrightarrow{170\text{–}380^\circ} H_2O+3\ NH_3+3\ CO+\\ &+2\ CO_2+0.5\ Ga_2O(CO_3)_2\cdot H_2O\end{aligned} \qquad (2)$$

$$0.5\ Ga_2O(CO_3)_2\cdot H_2O \xrightarrow{450^\circ} 0.5\ Ga_2O_2CO_3\cdot H_2O+CO_2 \qquad (3)$$

$$0.5\ Ga_2O_2CO_3\cdot H_2O \xrightarrow{500\text{–}700^\circ} 0.5\ Ga_2O_2CO_3+H_2O \qquad (4)$$

$$Ga_2O_2CO_3 \xrightarrow{1100^\circ} Ga_2O_3+CO_2 \qquad (5)$$

Vibrational behaviour

As an example, the IR and Raman spectra of $(NH_4)_3Ga(C_2O_4)_3\cdot 3H_2O$ are shown in Fig. 3. Table 1 shows the characteristic frequencies for both compounds.

According to Hester and Plane [10] and other literature data [11, 12], it is possible to make a detailed assignment of all bands, considering that the original D_{2h} oxalate symmetry finally becomes D_3. It is also evident that the difference in the cationic masses affects the M—O bonds. The difference between $\nu_{as}-\nu_s$ corresponding to the M—O bond for each metal becomes higher as the metal atomic weight increases. This is due to the fact that in all Raman-active modes, the Ga(III) ion remains more stationary than the Al(III) ion, because of its higher mass. The M—O bond-strengths therefore indirectly affect the C—O and C=O vibrations, as can be observed in Table 1.

The NH_4^+ bands are also found in the ranges characteristic of the vibrations of this cation [9].

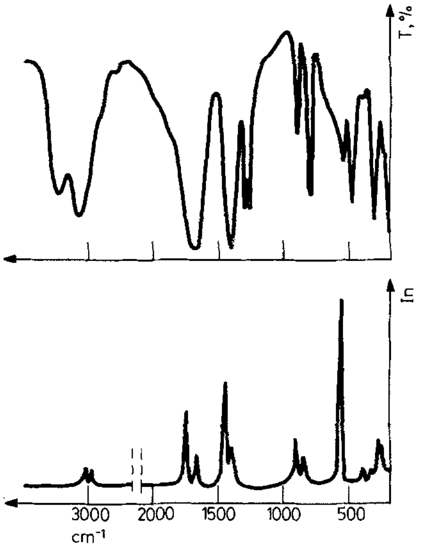

Fig. 3 IR (above) and Raman (below) of $(NH_4)_3Ga(C_2O_4)_3\cdot 3H_2O$

Conclusions

From the previous results, the following conclusions can be inferred:

— The thermal behaviour of the two studied compounds is affected by the polarizing power of the cation.

— Two basic gallium carbonates can be obtained as pyrolysis intermediates, and in this sense the behaviour of this element is reminiscent of that observed for La(III) in lanthanum oxalate and the lanthanide carbonates.

— The formation of an intermediate hydrate is evident in the case of the Al(III) compound. In contrast, the Ga(III) compound decomposes to the anhydrous oxalate directly.

— The M—O stretching vibrations are affected by the mass of the metal atom.

— The C—O and C=O stretching frequencies are similar to those observed in other oxalato-metallates. The hydrogen-bonds do not play an important role, as is deduced from a comparison of our results with those obtained by Hester and Plane [10] for different anhydrous oxalates.

* * *

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Table 1 Vibrational spectra of $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ and $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$

$(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$		$(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$		Assignment
IR	Raman	IR	Raman	
3450 vs	—	3540 sh	—	ν_1, ν_3 OH
3335 s	—	3427 m	—	ν_3 NH_3^+
3125 vs	—	3122 vs	—	H-bonding
3020 sh	3050 w	3025 s	3020 m	
2845 sh	2830 w			
1865 sh	—	1777 sh	1790 vw	ν_s C=O, ν_{as} C=O
1715 s	1747 m	1725 vs	1739 w	ν_2 NH_4^+ δ H_2O
1695 vs	—	1700 vs	1664 m	
1680 vs	1670 w	1662 vs	1661 w	
1412 s	1443 s	1400 s	1446 sh	ν_s C—O
1362 sh	1403 w	1385 s	1426 s	
			1406 sh	ν_4 NH_4^+
1305 s	—	1295 s	—	ν_{as} C—O
1275 s	—	1272 s	—	
905 m	911 m	912 m	918 s	ν C—C
855 w	857 w	864 w	858 w	δ O—C—O
815 s	—	825 m	—	
800 s	—	807 m	—	crystal water
720 sh	—	725 sh	—	
597 sh	599 sh	582 m	585 vs	ν_s M—O
—	571 vs	—	—	
557 m	—	—	—	ν_{as} M—O
492 s	—	492 s	—	
—	—	477 s	479 vw	
—	—	435 w	—	δ O—C—O
395 vw	393 w	380 w	374 m	δ C—C—O
322 s	323 w	337 w	290 m	δ C—O—M
—	267 m	—	276 m	
—	245 m	—	256 m	

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

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Zusammenfassung — Die IR- und Raman-Spektren der isomorphen Verbindungen $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ und $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ wurden aufgenommen. Das thermische Verhalten dieser Verbindungen wurde untersucht. Durch TG, DTA und IR-Spektroskopie gestützte stöchiometrische Zusammenhänge wurden in beiden Fällen in Einzelheiten geklärt. Abhängig von der Polarisationswirkung der Metallkationen wurden unterschiedliche Ergebnisse erhalten. Die Bildung von basischem Galliumkarbonat wurde erstmals bewiesen.

Резюме — Исследовано термическое поведение, ИК спектры и спектры комбинационного рассеяния двух изоморфных соединений $(NH_4)_3Ga(C_2O_4)_3 \cdot 3H_2O$ и $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$. С помощью ТГ, ДТА и ИК спектроскопии установлен стехиометрический состав обоих соединений. Различные результаты, полученные для двух соединений, обусловлены различной поляризуемостью катионов металла. Впервые найдено доказательство образования основного карбоната галлия.