# Synthesis and vibrational study of some polydentate ligands

M. F. GARGALLO ESTEBAN, R. VILAPLANA SERRANO and F. GONZÁLEZ VILCHEZ\*

Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain

(Received 10 December 1984; in final form 16 November 1986; accepted 12 January 1987)

Abstract—Sodium salts of iminodiacetic acid (IDA), ethylenediaminetetraacetic acid (EDTA), 1,2propylenediaminetetraacetic acid (PDTA) and 1,2-diaminocyclohexanetetraacetic acid (DCTA) were prepared by modification of the literature methods and their i.r. and Raman spectra were studied. The results obtained by application of both techniques allowed a better characterization of these polydentate ligands. Raman spectroscopy was specially useful in elucidating structural aspects in compounds containing acetate groups.

### INTRODUCTION

The published literature concerning i.r. studies of polyamine-polycarboxylic acids as polydentate ligands deals mostly with a partial study of the vibrational properties of the substances described, i.e., characteristic peak identifications, assignment of the main bands, and other important spectral features.

CHAPMAN [1, 2], SAWYER [3], and NAKAMOTO [4, 5], were interested in studying several ligands with acid character and some of their sodium salts. Their results indicated important structural changes when the spectra of the solid compounds were compared with those of the same compounds in solution. These authors proposed structures for the solid compounds in which the only oxygen atoms were protonated atoms, while NOVAK *et al.* [6–8] reached different conclusions, in proposing protonation of the nitrogen atoms.

We have synthesized the sodium salts of some important polydentate chelating agents (IDA, EDTA, PDTA, DCTA) and investigated their vibrational behavior. Both i.r. and Raman spectra of these solid compounds are reported for the first time in this paper. Until now, few references dealing with Raman studies of similar compounds have appeared in the literature [9, 10]. The comparative study of the results provided by both techniques provides a useful tool in order to obtain information about the behaviour of polycarboxylic acids, very recently used as "secondary" ligands in neutral complexes formed between platinum metals and this type of compound [11].

### EXPERIMENTAL

### Starting materials

The starting chemicals were purchased from commercial firms as follows: IDA (BDH Chemicals Ltd., England); EDTA and Na<sub>2</sub>-EDTA (Riedel de Haen, A. E., F.R.G.) and PDTA, DCTA (Fluka Chem. Fabrik, Switzerland).

#### Chemical analyses

The elemental analyses were performed by the General Organic Chemistry Institute, Madrid. The sodium content was determined by flame spectrophotometry using an M6a Lange GmbH instrument. Water was determined by thermogravimetry (TG) using an automatic HT-M Stanton Redcroft thermobalance. The experimental data of C,H,N,Na and H<sub>2</sub>O analyses (%), were in good agreement with the theoretical values expected for the substances.

#### Potentiometry and conductimetry

The techniques were used to investigate the optimal pH in the synthesis of the studied sodium salts. The titration of the acids was carried out with 0.099 M NaOH. A Radiometer automatic instrument was used, with a TTT 11 titrator, a 28 pH meter, an SBR-2 plotter, and an ABU-1 autoburette. Solutions to be titrated were prepared by dissolving 10-20 mg of acid in 30-40 ml of distilled water.

The conductimetric titrations were carried out with a CDM-104 model. NaOH 0.099 M was added using the same autoburette and pH values were recorded with the same pH meter described above. The solutions were prepared by dissolving 10-20 mg of acid in 60 ml of distilled water, keeping them in a cell at 25°C to a calorimetric thermostat.

#### I.r. and Raman spectra

I.r. spectra were collected in the range of 4000-200 cm<sup>-1</sup> on a Perkin-Elmer model 577 spectrophotometer using KBr pellets. Raman spectra were recorded on a Varian Cary 82 Raman spectrophotometer. Excitation was accomplished with the 488.0 nm line of a Spectra-Physics model 165-03 argon ion laser. Compact powder samples were irradiated with 599 mW laser beam power.

#### **RESULTS AND DISCUSSION**

### Preparation of the sodium salts

The following sodium salts were studied in this work: Na-EDTA and disodium salts of IDA, PDTA and DCTA; tri-and tetrasodium salts of EDTA, PDTA and DCTA. The chemical structures of the ligands are shown in Scheme 1.

The method used by SAWYER and PAULSEN for synthesizing similar compounds [12] was experimentally modified in order to produce the sodium salts under the most suitable conditions.

Stoichiometric amounts of sodium bicarbonate and the respective acid were weighed, dissolved separately in a minimum amount of distilled water and mixed. The mixed solutions were allowed to react by heating  $(60-70^{\circ}C)$  until CO<sub>2</sub> evolution ceased and then were cooled to room temperature. The pH was adjusted when necessary with 0.099 M NaOH. Solutions were reduced to half volume by gentle heating, cooled in

$$(HOOC---H_2C)_2N---(CH_2)_2N(CH_2COOH)_2 \qquad EDTA$$

$$(HOOC - H_2C)_2N - CH(CH_3) - CH_2 - N - (CH_2 - COOH)_2$$
 PDTA

$$\begin{array}{c} N(CH_2 - COOH)_2 \\ N(CH_2 - COOH)_2 \end{array}$$
CDTA

Scheme 1.

salted ice, and ice cold absolute ethanol (sometimes acetone, see Table 1) was added until a light cloudiness appeared. By keeping the temperature below  $0^{\circ}$ C, white crystals were obtained, which were then filtered, purified and dried under vacuum over  $P_2O_5$ . Most of these sodium salts are hygroscopic, but they keep well in a desiccator over  $P_2O_5$ .

## Spectroscopy

The complete interpretation of i.r. and Raman spectra would be difficult. For that reason we carried out a comparative study of these spectra, choosing IDA, EDTA, and their sodium salts as the most representative compounds.

 $4000-2000 \ cm^{-1}$ 

The  $CH_2$  stretching frequencies close to 3000 cm<sup>-1</sup> give more and better resolved bands in Raman than i.r. spectra especially in the case of the sodium salts.

As can be seen in Fig. 1 (Table 2), the Raman spectrum of the sodium salt of IDA clearly shows two main strong peaks of the same intensity at 2970 and 2920 cm<sup>-1</sup>. This type of vibration is nearly absent in the i.r. spectrum. This fact reveals a unique kind of methylenic group in the solid substance. The  $NH^+$  stretching vibration occurs in the same region, but it is not always easy to identify. The IDA spectra show a single band at  $3100 \text{ cm}^{-1}$  which is ascribed to the asymmetric stretching vibration (N–H bond) in the

Table 1. I.r. and Raman bands,  $cm^{-1}$ , of EDTA and Na<sub>2</sub>-EDTA

EDTA			Na <sub>2</sub> –EDTA			
i.r.	Raman	Assignment	i.r.	Raman	Assignment	
3018 } 2982 }s	3024 } 2990 } vs	vCH <sub>2</sub>	3520 3315 s		H <sub>2</sub> O	
			3030 2975 <sup>s</sup>	3018 2978 <sup>vs</sup>	vCH <sub>2</sub>	
1685 vs	1690 s	vC=O	1620 vs	1615 m	v_COO <sup>-</sup>	
1412 vs	1415 vs	vC-O	1395 s	1400 s	v <sub>a</sub> COO⁻	
1445 s	1445 vs	$\delta$ (C–H)CH <sub>2</sub>	1475 s	1480 vs	$\delta(C-H)CH_{2}$	
		· / •	1360 s	1360 m	δNH <sup>+</sup>	
1090 w	1094 m	vC-N		1090 s	vC-N	
	912 s	C-C(CH <sub>2</sub> -COO <sup>-</sup> )		926 908 s	C-C(CH <sub>2</sub> -COO <sup>-</sup>	

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table 2. I.r. and Raman bands,  $cm^{-1}$ , of IDA and Na<sub>2</sub>-IDA.

IDA			Na <sub>2</sub> –IDA		
i.r.	Raman	Assignment	i.r.	Raman	Assignment
3100 s	3100 m	$v_a NH_2^+$	3450		H₂O
3020 } 2970 } <sup>m</sup>	3020 2980 s	CH <sub>2</sub>	3320 sh	3325 m	NH
2590} 2420}m		OH(COOH)	2945 } 2900 } w	2970 } 2920 } vs	СН
1710 s 1600 sh	1712 m	$C = O$ $NH_2^+ (7)$	1590 vs 1416 s	1590 m 1422 vs	v_COO~ v_COO~
1580 vs 1390 s	1582 w 1400 vs	$v_{a} COO^{-}$ $v_{s} COO^{-}$	1470 w	1475 s	(C-H)CH <sub>2</sub>
1005 8	941 s 915 s	$C-C(CH_2-COO^-)$		935 vs	C–C(CH <sub>2</sub> –COO

See Table 1 for abbreviations.

ionized  $-NH_2^+$  group and is not present in its disodium salt, indicating the deprotonation of one of the carboxylic groups of the free acid. The i.r. spectrum of Na<sub>2</sub>-IDA (Fig. 1) shows, instead, a shoulder at 3320 cm<sup>-1</sup> and a clear band in the Raman spectrum at the same wavenumber not being masked by any water absorption. We assigned this band to the N-H stretching vibration in the >NH group.

Also, the same band is clearly registered at  $3030 \text{ cm}^{-1}$  (PDTA) and  $3020 \text{ cm}^{-1}$  (DCTA), whereas the i.r. spectra only give a weak shoulder.

The acids investigated do not show any i.r. absorption above  $3100 \text{ cm}^{-1}$ , indicating the absence of free –COOH groups. However, they exhibit broad bands with a series of minor peaks in the  $3000-2500 \text{ cm}^{-1}$  range (i.e., Fig. 1). This is indicative of strong H bonds [13]. These broad absorptions have been ascribed to the NH<sup>+</sup> stretching vibration [6], but they can also be

assigned to complex vibrations involving -OH and >NH bonds.

### 2000-800 cm<sup>-1</sup>

The assignment of absorptions below 2000 cm<sup>-1</sup> is only tentative. The single absorption of the C=O groups at 1690 cm<sup>-1</sup> in the EDTA spectra confirms the equivalence of all the carboxylic groups, as deduced from the symmetric H bonds postulated for this compound. IDA, PDTA, and DCTA exhibit characteristic vibrations of both protonated and ionized carboxylic groups (Table 2).

It should be noted that anti-symmetrical  $(1600 \text{ cm}^{-1})$  vibrations of the COO<sup>-</sup> structure have their intensities reversed in Raman and i.r., in accordance with the normal behaviour of such modes.

The large number of bands between 1500- $1300 \text{ cm}^{-1}$  makes correct assignment difficult because



Fig. 1. I.r. and Raman spectra of Na<sub>2</sub>-IDA.

 $\delta NH^+$ , CH<sub>2</sub> deformation and various COO<sup>-</sup> vibrations occur in the same region.

SHIMANOUCHI et al. [14] have found a Raman band between 1250 and 1200 cm<sup>-1</sup>, characteristic of the -CH<sub>2</sub>-COOH group due to CH<sub>2</sub>, but with some contribution of C-O and C-C vibrations. Every compound investigated exhibits one or two peaks in this region of its Raman spectrum.

The C-N asymmetric stretching is assigned as a prominent band, [15] in the Raman spectra of these compounds near  $1090 \text{ cm}^{-1}$  (Tables 1 and 3; Fig. 2).

In the Raman spectrum of every compound investigated a strong vibration appears near  $900 \text{ cm}^{-1}$ ,

ranging from  $877 \text{ cm}^{-1}$  (nitrilotriacetic acid) to 941 cm<sup>-1</sup> (IDA). This band has been assigned [9] to the C-C bond vibration in the acetate group. The wavenumber for acetic acid is  $886 \text{ cm}^{-1}$ , for the acetate ion 926 cm<sup>-1</sup> [16, 17].

The existence of a single or multiple band in this region can account for the existence of equivalent or different acetate groups. In fact, EDTA exhibits only one band at 912 cm<sup>-1</sup>, ascribed to the C-C vibration since the four acetate groups are equivalent and linked to these of the next molecules by H bonds. This is right only if the zwitterion structure (NH<sup>+</sup>) ascribed to this compound is correct. The intensity of the band

Table 3. I.r. and Raman bands,  $cm^{-1}$ , of Na<sub>3</sub>-EDTA and Na<sub>4</sub>-EDTA. (see Table 2)

Na <sub>3</sub> -EDTA			Na₄–EDTA			
i.r.	Raman	Assignment	i.r.	Raman	Assignment	
3410		H <sub>2</sub> O	3420		H <sub>2</sub> O	
3030)	3025)	-	2960			
2980 \m	2980 \s	v CH <sub>2</sub>	m	2950 vs	v CH <sub>2</sub>	
2800	2800 <sup>)</sup>	-	2820		-	
1625 vs	1620 w	v <sub>a</sub> COO <sup>-</sup>	1580 vs	1580 m	v <sub>a</sub> COO <sup>-</sup>	
1400 vs	1411 vs	v <sub>s</sub> COO <sup>-</sup>	1410 1440 <sup>vs</sup>	1420 1450 vs	v <sub>s</sub> COO <sup>-</sup>	
1475 m	1471 s	$\delta$ (C-H)CH <sub>2</sub>				
1365 s	1360 m	δNH <sup>+</sup>				
	1092 m	vC-N		1090 m	v C-N	
918 s	922 s 912 m	C-C(CH <sub>2</sub> -COO <sup>-</sup> )	920 m	922 s	C-C(CH <sub>2</sub> -COO <sup>-</sup> )	

See Table 1 for abbreviations.



Fig. 2. Raman spectra of EDTA and its sodium salts.

becomes gradually smaller in mono-, di-, and trisodium salts, disappearing completely in the spectrum of the tetrasodium salt. At the same time, a new band occurs at 925 cm<sup>-1</sup>, ascribed to acetate groups bonded to sodium, increasing in its intensity with a greater number of Na<sup>+</sup>. This band is the only one present in the Raman spectrum of the tetrasodium salt.

A similar explanation can account for the two bands  $(915-941 \text{ cm}^{-1})$  in the IDA Raman spectrum showing the presence of two different acetate groups. The Raman spectrum of its disodium salt shows, however, a single band  $(935 \text{ cm}^{-1})$  due to the equivalent acetate groups (Fig. 1).

#### CONCLUSIONS

A few general conclusions can be deduced from this study.

(1) We have repeatedly found in this research that it is more convenient and profitable to work with crystalline starting materials instead of powdered ones, because of the higher resolution and better splitting of the spectral bands, especially those registered in the range  $3500-2800 \text{ cm}^{-1}$ . This is the main reason why the synthesis or recrystallization of new and commercial products have been performed in all cases.

(2) The additional information derived from Raman spectroscopy when applied to this type of sequestering agent is valuable and complementary to that provided only by i.r. spectroscopy. As an illustrative example, Fig. 1 shows the very strong, sharp and narrow peak appeared at  $3320 \text{ cm}^{-1}$  in the Raman spectrum, now certainly assigned to the N-H stretching vibration. The overlapping broad absorption from water registered at this wavenumber in the infrared spectrum is completely absent from the Raman one.

(3) Raman spectroscopy reveals itself to be particularly useful to differentiate the free from bonded acetate groups in coordination compounds. This fact can lead to a better interpretation of structural aspects of coordination compounds containing acetate groups.

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