



ELSEVIER

Journal of Molecular Liquids 107/1-3 (2003) 69-75

www.elsevier.com/locate/molliq

journal of  
MOLECULAR  
LIQUIDS

## ESR and NMR study of galacturonic and galactaric acids complex formation in solution

A.I. Shestavin, S.N. Bolotin, V.A. Volynkin, V.T. Panyushkin\*

Chemistry Department, Kuban State University,  
Stavropolskaya Str., 149, 350040, Krasnodar, Russia

Received 14 February 2002; accepted 8 March 2003

The complexation of copper(II) with D-galacturonic (HGal) and galactaric acids (H<sub>2</sub>Gala) was investigated by the ESR method in aqua and DMSO solutions. The spin Hamiltonian parameters, the complex composition and its structure were determined. The complexation of *f*-elements (Pr, Nd) with the same ligands was investigated by NMR <sup>1</sup>H. The coordination modes and structure of complexes formed in the solution were determined also.

© 2003 Elsevier B.V. All rights reserved.

### 1. INTRODUCTION

Galacturonic and galactaric acids, being hydroxyl acids, are of great importance in processes taking place in human and animal organisms. The galacturonic acid is the main monomer of pectin and a number of papers [1-9] have been devoted to study its binding with metals ions. While this, in these works various types of binding are offered: only through the carboxy group [1-2], with the additional coordination on the oxygen atom of the ring [3-6], with the additional coordination on one of the alcoholic O atoms [7-8].

The galactaric acid complex formation has been investigated a little because the low solubility of the acid in water and other solvents. The galactarat structure has been studied by IR spectroscopy [10, 11] and X-ray structural method [12]. In the last work [CuGala], [CuGalaH<sub>1</sub>] and [CuGalaH<sub>2</sub>]<sup>2-</sup> complexes stability constants obtained by the potentiometric method have been reported also.

The aim of the present paper was the determination of the complex structure formed by galacturonic and galactaric acids with copper(II), praseodymium(III) and neodymium(III) ions in the solution.

### 2. RESULTS AND DISCUSSION

#### 2.1. ESR study

The complexation of galacturonic acid with Cu(II) was investigated by ESR. The ESR spectra analysis of aqueous solutions containing copper(II) nitrate and galacturonic acid (Fig. 1) shows the complexation (change of the spectrum lineshape) at pH more than 3.0. The further pH increase leads to magnification of the signal intensity of the complex and the

\* Correspondence address: e-mail: [NMR\\_ESR@chem.kubsu.ru](mailto:NMR_ESR@chem.kubsu.ru)

appearance of a line in the upfield, that can evidence the helatic complex  $[\text{CuGalH}_1]$  formation.

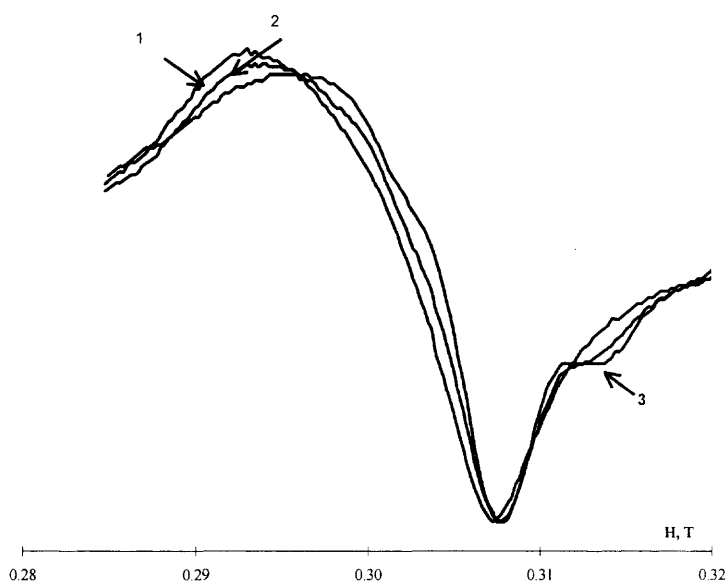


Fig. 1. ESR spectra of the copper(II)- galacturonic acid system at a ligand-to-metal concentration ratio 1.0 (1); 2.0 (2); 4.0 (3) at pH 5.0.

The parameter  $g$ , the hf coupling constant  $A$ , the data for line widths, mean lifetime  $\tau$  and the stability constant of each species were varied, until the sum of the squares of differences between the calculated and measured intensities reached its minimum. The theoretical spectrum was calculated using the method of the spin density matrix [13, 14]. Data obtained for the  $[\text{CuGala}]^-$  and  $[\text{CuGalaH}_1]^-$  complexes are collected in Table 1.

Table 1  
Parameters of the copper (II)-galactaric acid complexes

|                        | $\lg K$ | $g$   | $A, G$ | $-\lg \tau$ |
|------------------------|---------|-------|--------|-------------|
| $[\text{CuGala}]^-$    | 1.9     | 2.178 | 32     | 7.8         |
| $[\text{CuGalaH}_1]^-$ | 5.2     | 2.156 | 54     | 6.2         |

The complexation of copper(II) with galactaric acid in a DMSO solution was studied. The value  $g = 2.116$  evidences the bidentate coordination of the ligand and allows to assume the structure of the  $[\text{CuGala}]$  complex in Fig. 2.

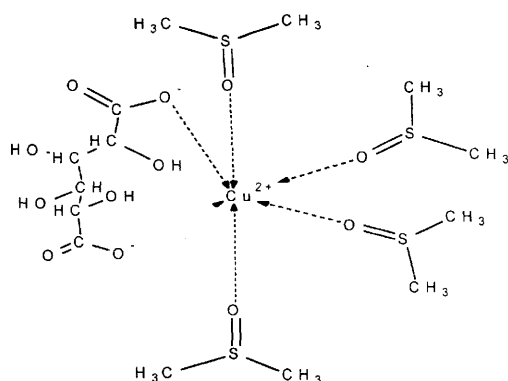


Fig. 2. Structure of the  $[\text{CuGal}]$  complex in the DMSO solution.

## 2.2. NMR study

The NMR spectrum of galacturonic acid in  $\text{D}_2\text{O}$  is illustrated in Fig. 3(a), the spectrum of Pr (III) chloride – galacturonic acids with the ratio 1:3 is illustrated in Fig. 3(b).

To determine the character of the observed process (one or more complexes are present), the equilibrium constants and lanthanide induced chemical shifts were calculated using the observed chemical shift analysis [15].

The dependencies of the lanthanide induced proton chemical shifts of  $\text{H}^2$  and  $\text{H}^4$  atoms upon the metal-to-ligand concentration ratio are given in Fig. 4. The analysis of this dependence has shown the formation of complexes 1:1, 1:2 and 1:3.

The signals of  $\text{H}^1$ ,  $\text{H}^2$ ,  $\text{H}^3$  protons are shifting downfield, but  $\text{H}^4$ ,  $\text{H}^5$  signals shifting upfield are observed. The greatest downfield shift and line broadening under the influence of the praseodymium ion are observed for  $\text{H}^1$ . It testifies that the oxygen atom of the ring takes part in bonding. Taking into consideration all the above facts, we propose the structure in Fig. 6 as most probable modes of co-ordination for the complexes of galactarat-ion-lanthanide.

As the signals of  $\text{H}^3$  and  $\text{H}^5$  atoms overlap with the signal of the water protons and the signal of  $\text{H}^1$  is rather broadened, that made the determination of the shift difficult. Therefore spectra processing was held according to the  $\text{H}^2$  and  $\text{H}^4$  signals. The results are listed in table 2.

Table 2

Chemical shifts of protons  $\text{H}^2$  and  $\text{H}^4$  and stability constants of complexes of praseodymium(III) and neodymium(III) with a galacturonic acid

|                       | $\Delta$ , ppm |              | lgK |
|-----------------------|----------------|--------------|-----|
|                       | $\text{H}^2$   | $\text{H}^4$ |     |
| $[\text{PrGal}]^{2+}$ | 2.56           | -1.75        | 2.9 |
| $[\text{PrGal}_2]^+$  | 2.75           | -2.01        | 2.0 |
| $[\text{PrGal}_3]$    | 4.98           | -5.63        | 1.2 |
| $[\text{NdGal}]^{2+}$ |                | -0.60        | 2.7 |
| $[\text{NdGal}_2]^+$  |                | -0.62        | 1.6 |
| $[\text{NdGal}_3]$    |                | -3.35        | 1.2 |

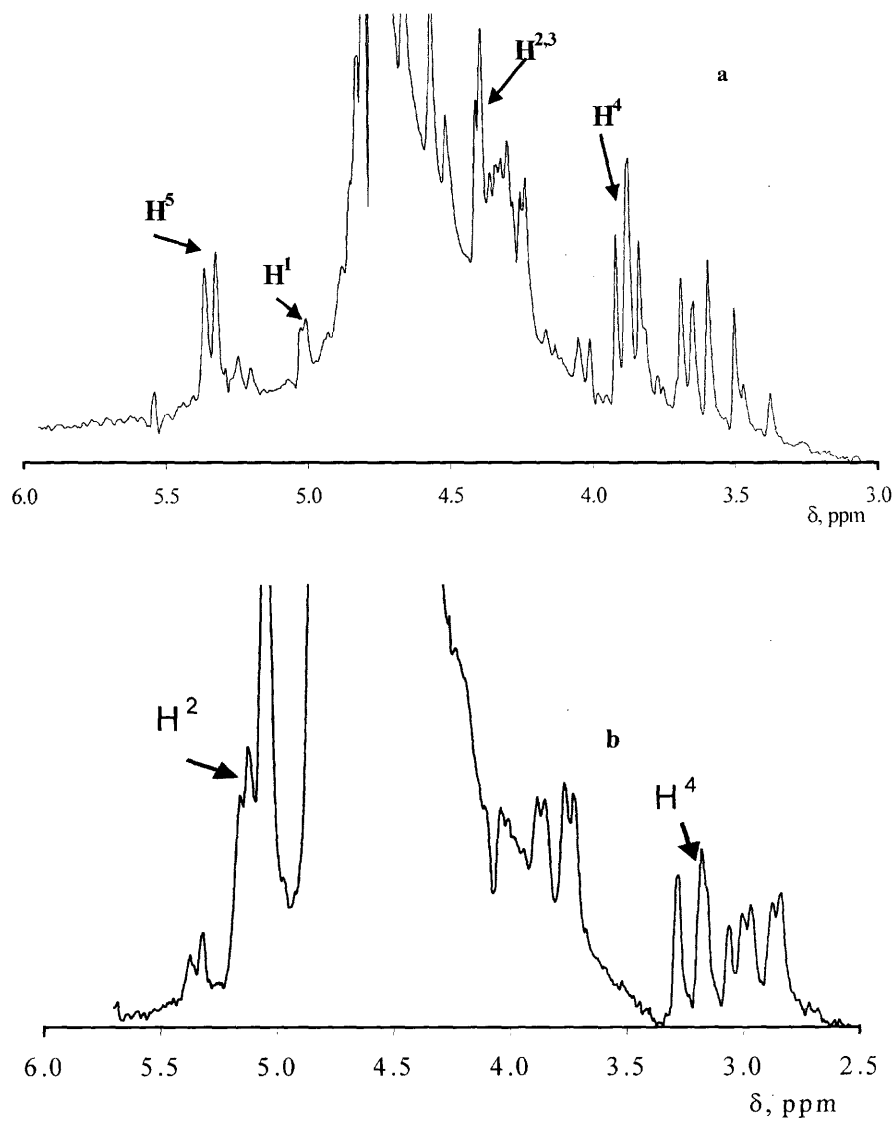


Fig. 3. NMR spectra of galacturonic acid in  $D_2O$  (a); Pr(III) chloride – galacturonic acids system at  $C_M/C_L = 0.33$  (b).

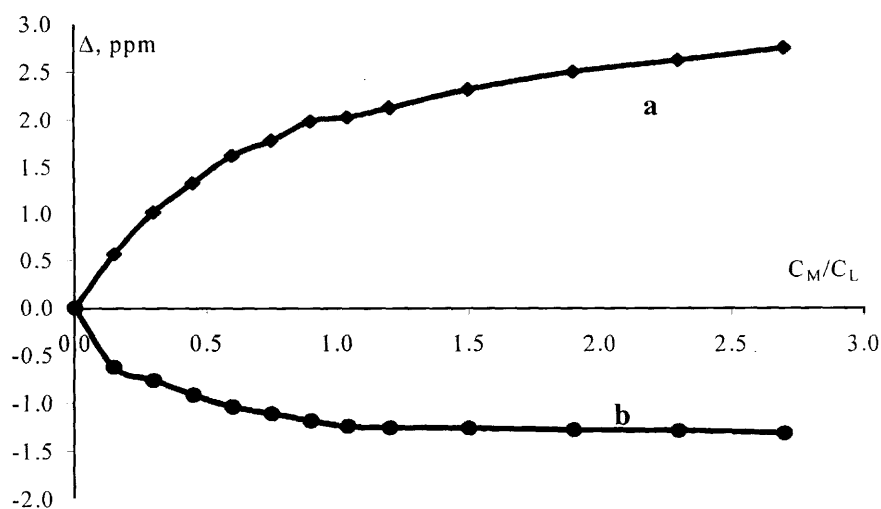


Fig. 4. Paramagnetic shifts in NMR spectra induced by  $Pr^{3+}$  cations for  $H^2$  (a) and  $H^4$  protons at pH 5.0.

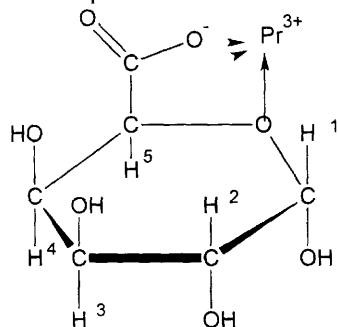


Fig. 6. The fragment of the  $[PrGal_3]$  complex structure.

The complexation of a galactaric acid with a neodymium (III) ion in DMSO solution was investigated by NMR. The complex formation leads to the shifting of  $\alpha$ - and  $\beta$ -proton signals downfield. The analysis of chemical shift dependencies upon the metal-to-ligand ratio has shown the formation of the complexes 1:1 and 1:2. The greater shift occurs for  $\alpha$ -protons that indicates the coordination through carboxylic groups only.

The character of the galacturonic acid spectrum does not change when adding lanthanide salts, that shows the participation of both ligand carboxylic groups in the binding with the metal ion (symmetrical character of the helatic ring). The structure of the galactarate - ion complex with praseodymium (III) is represented in Fig. 6.

The data obtained when treating the dependencies of the observed chemical shifts are listed in table 3.

Table 3.

Chemical shifts of  $\alpha$ -protons and stability constant of lanthanide complexes with the galactaric acid

|         | $\Delta_1$ .ppm | $\Delta_2$ .ppm | $\lg K_1$       | $\lg K_2$       |
|---------|-----------------|-----------------|-----------------|-----------------|
| Nd(III) | 0.51            | 0.22            | $1.95 \pm 0.03$ | $1.60 \pm 0.02$ |
| Pr(III) | 0.91            | 0.56            | $3.20 \pm 0.05$ | $2.48 \pm 0.03$ |

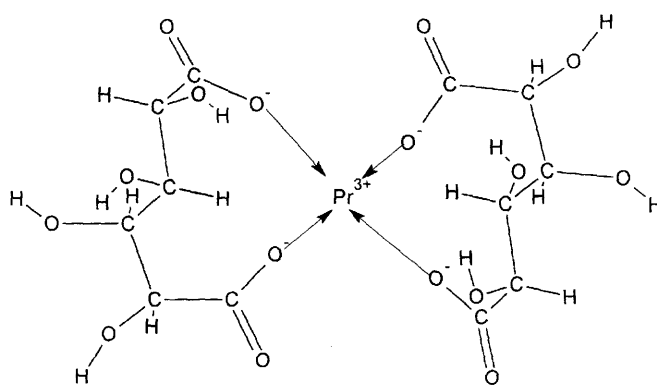


Fig. 6. Structure of the  $[\text{PrGal}_2]$  complex in DMSO solution.

### 3. EXPERIMENTAL

Galacturonic and galactaric acids were Merck products and used without further purification. Copper (II) nitrate, neodymium (III) and praseodymium (III) chlorides were standardized complexometrically. All other reagents were products of analytical grade.

ESR spectra were recorded on a Radiopan SE/X 2543 spectrometer in the X-band at 298 K with 100 kHz field modulation.

$^1\text{H}$  NMR spectra were recorded on a Varian FT-80 spectrometer (80 MHz). Spectra were run in  $\text{D}_2\text{O}$  and  $\text{DMSO-d}_6$  (purity 99.8%) with *t*-butanol as internal standard.

### REFERENCES

1. Macridou C., Cromet-Morin M. Schaft J.P. // *Bull. Soc. Chim. Fr.*, No 1-2 (1977) 59.
2. Deiana S., Gessa G., Solinas V. // *Analitica Chimica Acta*. 226 (1989) 315.
3. Aruga R. // *Bull. Chem. Soc. Jap.*, 54 (1981) 1233.
4. Angyal S.J. Greeves D., Littlemore L. // *Carbohydrate Research*, 174 (1988) 121.
5. Grasdalen H., Svare L., Smidsrod O. // *Acta Chem. Scand.* 28 (1974) 966.
6. Grasdalen H., Anthonsen T., Larsen B., Smidsrod O. // *Acta Chem. Scand.* 29 (1975) 17.

7. Anthonsen T., Larsen B., Smidsrod O. // *Acta Chem. Scand.* 26 (1972) 2988.
8. Anthonsen T., Larsen B., Smidsrod O. // *Acta Chem. Scand.* 27 (1973) 2671.
9. Dubois B., Vandotpe B. Olivier I. // *Bull. Soc. Chim. Fr.*, 2 (1991) 184.
10. Wen Tian, Li-Min Yang, Yi-Zhuang Xu, Shi- Fu Weng, Jin-Guang Wu. // *Carbohydrate Research*, 324 (2000) 45.
11. Wen Tian, Hua Liao, Jin-Guang Wu, Guang-Di Yang. // *Polyhedron*, 16 (1997) 2055.
12. Saladini M., Candini M., Iacolino D., Menabue M. // *Inorg.Chim. Acta*, 292 (1999) 189.
13. Abramenko V.A., Bolotin S.N., Nikolaienko I.A. // *Journal of Molecular Liquids*, 91 (2001) 219.
14. Panyuskin V.T., Bolotin S.N., Vashchuk A.V. // *Zhurnal strukturnoy khimii (J. Struct. Chem., Russia)*, No 2 (1997) 385.
15. Fielding L. // *Tetrahedron*, 59 (2000) 6151.