

PII: S0277-5387(98)00119-3

Interaction of divalent metal ions with D-aldonic acids in the solid phase-II. Structural information¹

Alejandro A. Frutos,^a Sandra Signorella,^a Luis F. Sala,^a* Graciela M. Escandar,^b Juan M. Salas Peregrin^c and Virtudes Moreno^d

^aDepartamento de Química Fisica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531 (2000) Rosario, Argentina

^bDepartamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531 (2000) Rosario, Argentina

^eDepartamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada España

^dDepartament de Química Inorgánica, Universitat de Barcelona, E-08028 Barcelona, España

(Received 3 November 1997; accepted 16 March 1998)

Abstract—Complexes formed between D-glucoheptonate, D-galactonate, D-gulonate and D-ribonate, and several metal ions were obtained in the solid state. Specifically: D-glucoheptonates, $Be(C_7H_{13}O_8)_2 \cdot 1/2H_2O$, $Mn(C_7H_{13}O_8)_2 \cdot 2H_2O$, $Co(C_7H_{13}O_8)_2 \cdot 2H_2O$, $Co(C_6H_{11}O_7)_2 \cdot 3H_2O$, $Co(C_6H_{11}O_7)_2 \cdot 3H_2O$, $Cu(C_6H_{11}O_7)_2 \cdot 3H_2O$, $Cu(C_6H_{11}O_7)_2$, $Pb(C_6H_{11}O_7)_2$; D-gulonates, $Co(C_6H_{11}O_7)_2 \cdot H_2O$, $Ni(C_6H_{11}O_7)_2 \cdot 2H_2O$, $Cu(C_6H_{11}O_7)_2 \cdot 2H_2O$, $Co(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2$, $Pb(C_6H_{11}O_7)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2$, $Pb(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2$, $Pb(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, $Cu(C_5H_9O_6)_2 \cdot 2H_2O$, $Ni(C_5H_9O_6)_2 \cdot 2H_2O$, Ni

Keywords: D-aldonic acids; metal sugar complexes; divalent metal ions.

INTRODUCTION

Solid complexes formed between the metal ions beryllium (II), manganese (II), cobalt (II), nickel (II), copper (II) and lead (II), and ligands of biological interest, such as D-glucoheptonic acid (I), D-galactonic acid (II), D-gulonic acid (III) and D-ribonic acid (IV) (Fig. 1), were isolated. This work is part of our program on the coordination chemistry of sugar acids [1–8]. In previous papers, studies were carried out on equilibrium reactions in aqueous solution and in the solid state for metal complexes of both D-gluconolactone and D-lactobionic acid [1, 2]. The importance of studying the interaction between carbohydrates and transition metal ions is related to the use of this type of ligands as sequestering agents for metal ions present in biological media [9, 10]. The present work complements previous information afforded with metal ions cobalt (II), nickel (II) and copper (II), and the ligands I, II, III and IV in solution studies [2, 4, 8]. Interactions of the above-mentioned D-aldonic acids with beryllium (II), manganese (II) and lead (II) are given as additional information.

The studies in the solid state were performed by elemental, thermogravimetric and susceptibility analyses, and by FT–IR, diffuse reflectance and EPR spectroscopies.

These studies represent a contribution to future crystallographic analyses, which are complicated by the difficulties in obtaining X-ray quality crystals of complexes containing carbohydrates with nonblocked hydroxyl groups.

¹Presented at the X Physicochemical Argentine Meeting, April 21 to 25, 1997, Tucumán, Argentina.

^{*} Author to whom correspondence should be addressed. Fax: 54-41-350214; E-mail: inquibir@satlink.com.

A. A. Frutos et al.



Fig. 1. Ligands.

EXPERIMENTAL

Reagents

D-glucoheptono- γ -lactone, D-galactono- γ -lactone, D-gulono- γ -lactone and D-ribono- γ -lactone were purchased from Sigma. Their purities were checked by elemental analysis, chromatography and potentiometric titrations. The metal carbonates or oxides used were: Co(CO₃) · xH₂O (Aldrich), 2NiCO₃ · 3Ni(OH)₂ · 4H₂O (Aldrich), CuCO₃ · Cu(OH)₂ (Aldrich), MnCO₃ (BDH), BeCO₃ · 5H₂O (BDH) and PbCO₃ (Aldrich).

Synthesis of complexes in the solid state

The complexes were prepared following the procedures described previously [11]. Briefly, the metal ion was added to a previously refluxed (1 h) solution of the lactone, in order to promote the opening of the sugar ring affording the aldonic acid. This mixture was boiled for 2 hrs. The metal–lactone ratio was 1:2. Ethanol was added to the clear solution and a solid phase was obtained. The precipitate was separated by filtration and recrystallized four times from a mixture of ethanol–water (4:1). Finally, the product was washed with ethanol, dried under vacuum over phosphorus pentoxide at room temperature and again dried for 2 hrs. at 80°C under vacuum over phosphorus pentoxide.

The purity of the obtained complexes was checked by elemental analysis.

Analysis of the solid complexes

Microanalyses of C and H were performed using a Fisons 1108 CHNS microanalyser. The nickel (II) percentages in its complexes was determined by complexometric titration with EDTA and zinc nitrate solutions employing eriochrome black T as an indicator [12]. The content of beryllium was calculated from the thermogravimetrical residue. The metal percentage in the other complexes were determined by atomic absorption using a Metrolab 250 AA atomic absorption spectrophotometer. Thermogravimetric curves were obtained in an atmosphere of pure air using a Shimadzu TGA-50 H, with a heating speed of 20° C min⁻¹, equipped with a Nicolet model 550 IR gas analyzer and Fisons model Thermolab mass detector. DSC data were obtained on a Shimadzu DSC-50 differential scanning calorimeter, using a heating speed of 10°C min⁻¹. The diffuse reflectance spectra were obtained with a Cary-5E refractometer provided with a praying mantis module. IR spectra were performed on a FT-IR Nicolet 20 SX8 spectrophotometer. Susceptibility magnetic measurements were carried out on Manics DSM-8 instrument in the 80–290 K temperature range. X-band (\sim 9.2 GHz) EPR spectra were recorded as the first derivative of absorption at 77 and 298 K, on a Bruker ESP 300E EPR spectrometer with 100 kHz field modulation. The microwave frequency was generated with a Bruker 04 ER and measured with a Racal-Dana frequencymeter. The magnetic field was measured with a Bruker NMR-probe gaussmeter.

RESULTS AND DISCUSSION

Elemental Analysis

The analytical results for the synthesized complexes are reported in Table 1. All the complexes present a 1:2 metal-ligand ratio and were obtained either in

3372

	colors	%	%C		%H		%M	
Complexes		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	
D-glucoheptonates:								
$Be(C_7H_{13}O_8)_2 \cdot 1/2H_2O$	white	35.90	35.62	5.81	5.83	1.92	1.94	
$Mn(C_7H_{13}O_8)_2 \cdot 2H_2O$	light pink	31.06	30.78	5.59	5.75	10.32	10.42	
$Co(C_7H_{13}O_8)_2 \cdot 2H_2O$	pink	30.84	30.46	5.54	5.78	10.81	10.50	
$Ni(C_7H_{13}O_8)_2 \cdot 2H_2O$	green	30.85	30.84	5.37	5.88	10.77	10.29	
$Cu(C_7H_{13}O_8)_2 \cdot 2H_2O$	blue	30.58	29.45	5.50	5.25	11.56	11.80	
$Pb(C_7H_{13}O_8)_2$	white	25.57	25.22	3.99	4.03	31.51	31.10	
D-galactonates:								
$Mn(C_6H_{11}O_7)_2 \cdot 2H_2O$	white	29.95	29.69	5.44	5.36	11.41	11.20	
$Co(C_6H_{11}O_7)_2 \cdot 3H_2O$	pink	28.64	28.79	5.61	5.70	11.71	12.01	
$Ni(C_6H_{11}O_7)_2 \cdot 3H_2O$	green	28.65	28.43	5.61	5.87	11.68	11.17	
$Cu(C_6H_{11}O_7)_2$	blue	31.76	31.88	4.89	5.16	14.00	13.65	
$Pb(C_6H_{11}O_7)_2$	white	24.12	24.07	3.71	3.59	34.68	34.68	
D-gulonates:								
$Co(C_6H_{11}O_7)_2 \cdot H_2O$	pink	30.85	31.28	5.18	5.27	12.61	12.40	
$Ni(C_6H_{11}O_7)_2 \cdot 2H_2O$	green	29.71	29.69	5.40	5.40	12.10	11.90	
$Cu(C_6H_{11}O_7)_2 \cdot 2H_2O$	blue	29.42	29.69	5.35	4.81	12.97	12.65	
D-ribonates:								
$Mn(C_5H_9O_6)_2$	light pink	31.18	30.84	4.71	4.70	14.26	14.40	
$Co(C_5H_9O_6)_2 \cdot 2H_2O$	pink	28.25	28.75	5.21	5.23	13.86	13.60	
$Ni(C_5H_9O_6)_2 \cdot 2H_2O$	green	28.27	28.51	5.22	5.46	13.81	13.28	
$Cu(C_5H_9O_6)_2 \cdot 2H_2O$	blue	27.95	27.71	5.16	4.67	14.79	14.52	
$Pb(C_5H_9O_6)_2$	white	22.35	22.29	3.38	3.41	38.55	38.73	

Interaction of divalent metal ions with D-aldonic acids in the solid phase-II. Structural information 3373

Table 1. Analytical data and colors for D-aldonic complexes

anhydrous or solvated form. It was not possible to prepare pure Be(II) D-ribonate because it was contaminated with the starting material ($BeCO_3$). This fact would be due to low acidity of the ribonic acid which makes it less reactive towards the carbonate.

Thermogravimetric curves

As was already reported [1, 2, 6], the thermogravimetric curves of this type of complexes present two steps: dehydration (between 100–200°C) and pyrolytic processes (above 200°C). Figure 2 shows two typical thermal decompositions for both hydrated and anhydrous complexes, respectively. Thermoanalytical data are in good agreement with the elemental analysis. The temperature of water loss and the sharp peak on the DSC diagram may indicate that these molecules are coordinated to the metal. The pyrolitic process took place in two, three or four steps. The pyrolitic products identified by IR spectra were: water, carbon monoxide and carbon dioxide. The pyrolitic residues at 400–800°C were determined to be oxides or mixture of carbonates and oxides of the corresponding metal ion. Thermoanalytical data are given in supplementary material.

Reflectance spectra

As an example, Fig. 3 shows reflectance spectra for different complexes of cobalt (II), copper (II) and nickel (II). The bands of the recorded spectra are shown in Table 2 (A and B). In this table both the calculated and experimental frequency ratios according to the DQ/B values are presented [14]. The band of the spectra of cobalt (II) complexes were these expected for the electronic transition of a d^7 metal ion in an octahedral arrangement [15](a)[16](b). The spectra of the nickel (II) complexes also show three absorption bands and the relationship between the first two bands (1.7) suggests octahedral geometries for these complexes [15](b)[16](a). In all cases, the second bands were found to split into two signals. This fact can be attributed either to interactions with the nearest electronic level ¹Eg or to spin-orbit coupling. The copper (II) complexes showed spectra with a single wide band with maxima in the range 799-





Fig. 2. Thermogravimetric curves for (a) Cu (II) D-galactonate (initial mass: 5.973 mg); (b) Co (II) D-gulonate (initial mass: 5.093 mg).



Fig. 3. Reflectance spectra for (a) Cu (II) D-gulonate; (b) Co (II) D-galactonate; (c) Ni (II) D-glucoheptonate.

814 nm. The frequencies of these maxima are coincident with the value of the crystal field splitting and correspond to the electronic transitions ${}^{2}T_{2}g \leftarrow {}^{2}Eg$. According to these results tetragonal distortion of octahedral arrangements was proposed for these complexes [15](c)[16](c).

IR spectra

The IR spectra of the solid complexes were carried out between $4000-400 \text{ cm}^{-1}$ and the interpretation was based on a comparison with both the corresponding sugar acids and structurally related compounds.

The wide bands at $3500-3100 \text{ cm}^{-1}$ in the spectra of the free ligands were assigned to strongly hydrogenbonded OH groups. The interaction between the hydroxyl groups of the aldonolactones and the metals produces broadening, but not shifting, of the sugar OH stretching vibrations. The carbonyl stretching bond in the spectra of the studied lactones appeared at $1700-1800 \text{ cm}^{-1}$. In the spectra of the complexes, this band disappeared and two new bands were detected at about 1600 and 1400 cm^{-1} . The latter were assigned to the antisymmetric and symmetric frequencies of stretching carboxyl groups, respectively [17]. The difference in frequency between these two bands allowed us to infer the coordination mode of the metal center towards the carboxylate groups. Most of the complexes under study showed values which were equal to, or higher than, 200 cm⁻¹, always related to a monodentate coordination [18]. Lead (II) D-glucoheptonate and cobalt (II), nickel (II) and copper (II) D-galactonate presented values in the range 160-200 cm⁻¹, which were in agreement with an additional hydrogen-bonded coordination between the carbonyl oxygen and protons of the carbonate chain [18]. Lead (II) D-ribonate complex spectrum showed a splitting of the signals corresponding to symmetric and antisymmetric stretching, suggesting that the metal ion is not located in a symmetric environment. In the spectral region of 1400–1100 cm⁻¹, shifting and broadening for the CH₂, OH and COH bending modes were observed in the presence of the metal ions, and were attributed to the metal-OH interaction in the complexation. Both the sugar C-O stretching vibrations $(1100-940 \,\mathrm{cm}^{-1})$ and the deformation modes of the lactone ring skeletal (900-500 cm⁻¹) showed major changes upon metal ion chelation. Selected infrared absorption frequencies for complexes and aldonolactones are given in supplementary material.

A. A. Frutos et al.

Table 2. Electronic absorption spectral data in the solid pl	iase
--	------

Complex	v ₁	v ₂	v ₃	$\Delta_{\rm o} ({\rm cm}^{-1})$	B^{*} (cm ⁻¹)
Co(II) D-glucoheptonate	${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$ (8123 cm ⁻¹)	${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$ (15699 cm ⁻¹)	${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ (18762 cm ⁻¹)	7576	673
Ni(II) D-glucoheptonate	$^{3}T_{2g} \leftarrow ^{3}A_{2g}$ (8772 cm ⁻¹)	${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ (14881 cm ⁻¹)	${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ (25381 cm ⁻¹)	8772	904
Cu(II) D-glucoheptonate	$^{2}T_{2g} \leftarrow ^{2}E_{g}$ (12285 cm ⁻¹)			12285	—
Co(II) D-galactonate	${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$ (7949 cm ⁻¹)	${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$ (15798 cm ⁻¹)	${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ (18349 cm ⁻¹)	7849	687
Ni(II) D-galactonate	$^{3}T_{2g} \leftarrow ^{3}A_{2g}$ (8734 cm ⁻¹)	${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ (15106 cm ⁻¹)	${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ (24752 cm ⁻¹)	8734	890
Cu(II) D-galactonate	$^{2}T_{2g} \leftarrow ^{2}E_{g}$ (12438 cm ⁻¹)		_	12438	—
Co(II) D-gulonate	${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$ (8052 cm ⁻¹)	${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$ (15337 cm ⁻¹)	${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ (18939 cm ⁻¹)	7285	675
Ni(II) D-gulonate	$^{3}T_{2g} \leftarrow ^{3}A_{2g}$ (8873 cm ⁻¹)	${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ (14925 cm ⁻¹)	${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ (25445 cm ⁻¹)	8873	894
Cu(II) D-gulonate	$^{2}T_{2g}\leftarrow^{2}E_{g}$ (12516 cm ⁻¹)	_	_	12516	
Co(II) D-ribonate	${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$ (8071 cm ⁻¹)	${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$ (15384 cm ⁻¹)	${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ (18692 cm ⁻¹)	7313	658
Ni(II) D-ribonate	${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$ (8636 cm ⁻¹)	${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ (14925 cm ⁻¹)	${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ (25445 cm ⁻¹)	8636	925
Cu(II) D-ribonate	${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$ (12346 cm ⁻¹)	_	_	12346	—

*Calculated according to Ref. [13].

(B)

Complex	Dq/B	v_1/v_2	v_{3}/v_{1}	v_{3}/v_{2}
Co(II) D-glucoheptonate	1.1	1.933 (2.138)	2.310 (2.414)	1.195 (1.129)
Ni(II) D-glucoheptonate	1.0	1.696 (1.648)	2.893 (2.852)	1.706 (1.731)
Co(II) D-galactonate	1.1	1.987 (2.138)	2.308 (2.414)	1.161 (1.129)
Ni(II) D-galactonate	1.0	1.730 (1.648)	2.834 (2.852)	1.639 (1.731)
Co(II) D-gulonate	1.1	1.905 (2.138)	2.352 (2.414)	1.235 (1.129)
Ni(II) D-gulonate	1.0	1.682 (1.648)	2.868 (2.852)	1.705 (1.731)
Co(II) D-ribonate	1.1	1.906 (2.138)	2.316 (2.414)	1.215 (1.129)
Ni(II) D-ribonate	0.9	1.728 (1.667)	2.946 (3.000)	1.705 (1.800)

()According to Ref. [14].

Magnetic susceptibility measurements

Table 3 shows the magnetic data for the studied complexes. In all cases the Curie–Weiss law was verified: $\chi_M = C/(T-\theta)$, where χ_M is the corrected molar susceptibility, *C* is the Curie Constant, *T* is the absolute temperature and θ is the Weiss Constant. Copper (II) and nickel (II) D-galactonates, and manganese (II) D-glucoheptonate showed ferromagnetic interactions while the rest of the isolated compounds displayed an antiferromagnetic coupling. The values of the effective magnetic moment (μ_{eff}) for all the complexes studied suggest that the metal ions are in an octahedral high spin environment. The plots of $\chi_M vs$. *T* (not shown)

for both cobalt (II) and copper (II) D-ribonates present a significant deviation of the linearity at values lower than 170 and 150 K respectively.

EPR measurements

Cu(II) D-aldonic acids complexes. The polycrystalline samples exhibit rhombic EPR spectra with EPR parameters (g factors and hyperfine splitting constants A) summarized in Table 4. The spectra recorded at 77 K are very similar to those at room temperature, indicating no significant change in the coordination geometry (Fig. 4).

(A)

Interaction of divalent metal ions with D-aldonic acids in the solid phase-II. Structural information 3377

	Temperature	θ	μ_{eff}	
Complex	(K)	(K)	(BM)	
Mn (II) D-glucoheptonate	93–290	0.85	6.08	
Co (II) D-glucoheptonate	119-290	-8.95	4.96	
Ni (II) D-glucoheptonate	79–290	-2.57	3.24	
Cu (II) D-glucoheptonate	85-290	-18.4	1.99	
Mn (II) D-galactonate	140-290	-8.48	5.60	
Co (II) D-galactonate	100-290	-10.31	5.14	
Ni (II) D-galactonate	81-280	0.47	3.27	
Cu (II) D-galactonate	90-290	2.18	1.75	
Co (II) D-gulonate	99–290	-12.25	4.92	
Ni (II) D-gulonate	90-290	-9.83	3.37	
Cu (II) D-gulonate	130-290	-14.0	2.04	
Mn (II) D-ribonate	101-290	-0.33	5.81	
Co (II) D-ribonate	170-290	-11.9	5.22	
Ni (II) D-ribonate	122-290	-4.98	3.34	
Cu (II) D-ribonate	150-290	-24.58	1.95	

Table 3. Magnetic moments for complexes

 Table 4. Room temperature (or 77 K) EPR parameters for copper (II) complexes

Compound	$gz\left(g_{\parallel}\right)$	$A_{\parallel}({\rm G})$	$gx,gy\left(g_{\bot}\right)$
Cu (II) D-gluconate	2.36	135	2.05, 2.02
Cu (II) D-lactobionate	2.34	143	2.05
Cu (II) D-gulonate	2.34	143	2.05
Cu (II) D-glucoheptonate	2.34	143	2.05
Cu (II) D-gluconate Cu (II) D-lactobionate Cu (II) D-gulonate Cu (II) D-glucoheptonate	2.36 2.34 2.34 2.34	135 143 143 143	2.05, 2.05 2.05 2.05 2.05 2.05



Fig. 4. EPR spectra for Cu (II)-D-gulonate (77 K).

The EPR spectral patterns and parameters observed for the Cu(II) D-gluconate, Cu(II) D-lactobionate [1], Cu(II) D-gulonate and Cu(II) D-glucoheptonate were typical for molecules of pseudo-axial symmetry, having $qz > qx \approx qy > 2$; generally showing a hyperfine structure due to the nuclear spin (I = 3/2) at the g_{\parallel} region and were indicative for a predominantly dx^2 dy^2 ground state with small mixing of a dz^2 contribution [19, 20]. The rhombic signal was probably a consequence of the bulkiness of the carbohydrate moiety as well as its tendency to form intermolecular hydrogen bonds [21]. For Cu(II) D-galactonate a rhombic signal centered at \approx 3135 G was observed. In this case the coordination sphere of the copper center was less distorted than for the other complexes and the different anisotropic components of g were not resolved.

CONCLUSION

All isolated complexes presented a 1:2 metal-ligand stoichiometry, with different hydration degrees. Both the presence or absence of water in the compounds was confirmed by thermogravimetric analyses. The water molecules would be coordinated to the metal center. The infrared spectra suggest that the carboxylic groups of sugars are involved in the chelation. The structural data obtained from magnetic measurements would indicate that the metal ions in manganese (II), cobalt (II), nickel (II) and copper (II) complexes are in an octahedral environment. For cobalt (II), nickel (II) and copper (II) complexes was confirmed an octahedral geometry by diffuse reflectance spectra. In the case of the copper (II) complexes, the EPR measurements confirm also octahedral environment. The molecular flexibility of the studied sugar acids would enable on octahedral coordination mode.

Acknowledgements—We are grateful for financial support from the Universidad Nacional de Rosario (UNR), Argentine and from the Agreement between Consejo Nacional de Investigaciones Científicas y Tecnicas (CONICET, Argentine) and the Universidad de Granada, Spain.

REFERENCES

- Frutos, A. A., Escandar, G. M., Salas Peregrín, J. M., Gonzalez Sierra, M. and Sala, L. F., *Can. J. Chem.*, 1997, **75**, 405.
- Escandar, G. M., Salas Peregrin, J. M., Gonzalez Sierra, M., Martino, D., Santoro, M. I., Frutos, A. A., García, S. I., Labadié, G. and Sala, L. F., *Polyhedron*, 1996, 15, 2251.
- Escandar, G. M., Gandolfo, F. H. and Sala, L. F., Anal. Asoc. Quim. Argent., 1990, 78, 37.
- Escandar, G. M. and Sala, L. F., *Can. J. Chem.*, 1992, **70**, 2053.
- Escandar, G. M., Olivieri, A. C., Gonzalez Sierra, M. and Sala, L. F., J. Chem. Soc. Dalton Trans., 1994, 1189.
- 6. Escandar, G. M., Gonzalez Sierra, M., Salas Per-

egrin, J. M., Labadié, G., Santoro, M., Frutos, A. and Sala, L. F., *Polyhedron*, 1994, **13**, 909.

- Escandar, G. M., Olivieri, A. C., Gonzalez Sierra, M., Frutos, A. A. and Sala, L. F., *J. Chem. Soc. Dalton Trans.*, 1995, 799.
- Escandar, G. M., Gonzalez Sierra, M. and Sala, L. F., *Polyhedron*, 1994, 13, 143.
- Whitfield, D. M., Stojkooski, S. and Sarkas, B., *Coord. Chem. Rev.*, 1993, **122**, 171.
- Bandwar, R. P., Rao, C. P., Giralt, H., Hidalgo, J. and Kulckarni, G. U., *J. Inorg. Biochem.*, 1997, 66, 37.
- 11. Melson, G. A., Pickering, Aust. J. Chem., 1969, 21, 2889.
- 12. Schwarzenbach, G., *Complexometric Titrations*. Interscience, New York, 1960, pp. 79–82.
- 13. Dou, Yu-sheng, J. Chem. Ed., 1994, 67, 134.
- 14. Lever, A. B. P., J. Chem. Ed., 1968, 45, 711.
- 15. Lever, A. B. P., Inorganic Electronic Spectroscopy,

2nd edn., Elsevier, New York, 1984, a: pp. 480– 490, b: pp. 507–511 and p. 742, c: pp. 560–567.

- Sutton, D., Espectros Electrónicos de los Complejos de los Metales de Transición. Reverté, Barcelona, 1975, a: pp. 119–122, b: p. 139, c: p. 141.
- Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds. John Wiley & Sons, 1967, pp. 231–233.
- Deacon, G. B. and Phillips, R. J., Coord. Chem. Rev., 1980, 33, 227.
- Addison, A. W. In Copper coordination chemistry: Biochemical and Inorganic perspectives, eds. K. D. Varlin and J. A. Zubieta, Adenine Press, Guiderland, New York, 1983.
- Hathaway, B. H. and Billing, D. E., Coord. Chem. Rev., 1970, 5, 143.
- Diaz, A., García, I., Cao, R., Beraldo, H., Salberg, M., West, D., Gonzalez, L. and Ochoa, E., *Polyhedron*, 1997, 16, 3549.