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Chelating Properties of Lactate Anion. Perturbing Effect of Additional Ligands on Bis(DL-lactato)-metal(II) Complexes

F. CARIATI, F. MORAZZONI, G. M. ZANDERIGHI

Istituto di Chimica Generale ed Inorganica dell'Università, Via Venezian 21, 20133 Milano,

G. MARCOTRIGIANO

Cattedra di Chimica, Facoltà di Medicina Veterinaria dell'Università, Bari

G. C. PELLACANI

Istituto di Chimica Generale ed Inorganica dell'Università, Modena, Italy

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Dilactate complexes of copper(II), nickel(II), cobalt(II), zinc(II) and their adducts with bases have been considered. Tetragonal structure of the complexes and chelating behaviour of the lactate anion, coordinated through one oxygen of the carboxylate group and the oxygen of the hydroxo group, is suggested. The strength of the metal–lactate bond greatly depends on the presence of the base molecule axial with respect to the plane of the lactate anion.

Introduction

A possible scheme of coordination has been proposed [1, 2] and a structural analysis on aquobis(DL-lactato)copper(II) hemyhydrate has appeared [3]. However no comprehensive investigation on the molecular properties of these compounds is available. The principal aspects we are going to consider in this paper are: a) Symmetry of dilactate copper(II), cobalt(II), nickel(II) and zinc(II) compounds, and of their adducts with bases. b) Electronic effects of additional ligands (H_2O, pyridine, 4-Methylpyridine, *etc.*) on bis(DL-lactato)metal(II) complexes.

Experimental

Preparation of Compounds

Aquobis(DL-lactato)copper(II) n hydrate, Diaquobis(DL-lactato)metal(II) n hydrate (metal = cobalt, nickel, zinc)

The metal carbonates (or hydroxocarbonates) were reacted with aqueous lactic acid, in a stoichiometric ratio, at 60 °C. The filtered solution was concentrated and on cooling it separated a microcrystalline compound, which was recrystallized from water.

Bis(DL-lactato)copper(II)

Thermal dissociation of the hydrated aquolactate complexes, carried out at 110 °C, gave the anhydrous compound. Analogous result could be obtained by recrystallisation of the aquocomplexes from ethanol.

Bis(DL-lactato)metal(II) (metal = cobalt, nickel, zinc)

Thermal dissociation of the hydrated diaquolactate complexes, carried out at 160 °C, gave the anhydrous compounds.

Bis(DL-lactato)pyridinemetal(II), Bis(DL-lactato)-4-Methylpyridinemetal(II) (metal = copper, zinc), Bis(DL-lactato)dipyridinemetal(II), Bis(DL-lactato)bis(4-Methylpyridine)metal(II) (metal = cobalt, nickel)

The adducts with bases were obtained by dissolving the aquolactato complexes in pyridine and 4-Methylpyridine, and heating at about 70 °C. The solid compounds separated after concentration of the mother liquor, by addition of diethyl ether and cooling to 4–5 °C.

Bis(DL-lactato)α,α'-bipyridylmetal(II) (metal = copper, cobalt, nickel, zinc)

A stiochiometric amount of α,α'-bipyridyl was added to an ethanol suspension of the aquolactate complexes and heated at 50–60 °C. The unconverted, insoluble lactate complex has been removed by filtration, and a mixture of acetone and diethyl ether (1/1) has been added to the solution. By cooling to 4–5 °C a microcrystalline hygroscopic compound separated, which was washed with diethyl ether and dried *in vacuo*.

Tris(1,2-diaminoethane)metal(II) dilactate (metal = copper, cobalt, nickel, zinc)

A small excess of 1,2-diaminoethane was added to a suspension of aquolactate complexes, in a 1/1 methanol–acetone mixture. For the copper com-

TABLE I. Analytical Data.[a]

Compound	Colour	C%		H%		N%		L%	
		calc.	found	calc.	found	calc.	found	calc.	found
$Cu(lact)_2\ 2H_2O$	blue	25.95	25.86	5.08	5.02	–	–	12.97	12.6
$Cu(lact)_2\ 1.5H_2O$	blue	26.82	26.78	4.88	4.60	–	–	10.05	10.42
$Cu(lact)_2$	blue	29.82	29.27	4.17	5.05	–	–	–	–
$Cu(lact)_2py$	blue	41.18	41.37	4.71	4.85	4.36	4.30	24.63	24.58
$Cu(lact)_2pic$	blue	43.05	43.32	5.12	5.12	4.18	4.06	27.82	26.80
$Cu(lact)_2\ bipy$	blue	48.30	47.92	4.56	4.88	7.04	7.00	–	–
$Cu(en)_3\ (lact)_2$	blue	34.13	34.45	8.12	8.27	19.92	20.33	–	–
$Ni(lact)_2\ 2.5H_2O$	green	25.55	25.30	5.32	5.40	–	–	15.97	16.24
$Ni(lact)_2\ 2H_2O$	green	26.41	26.53	5.17	5.21	–	–	13.20	12.80
$Ni(lact)_2$	green	30.43	29.60	4.26	4.10	–	–	–	–
$Ni(lact)_2\ 2py$	blue	48.64	48.86	5.11	5.08	7.09	6.94	40.04	40.12
$Ni(lact)_2\ 2pic$	blue	51.09	51.30	5.72	5.84	6.62	6.70	43.98	44.08
$Ni(lact)_2\ bipy$	blue	48.89	48.78	4.62	4.92	7.13	6.92	–	–
$Ni(en)_3(lact)_2$	violet	34.53	34.67	8.22	8.35	20.15	19.96	–	–
$Co(lact)_2\ 3H_2O$	pink	24.75	24.68	5.51	5.42	–	–	18.55	18.07
$Co(lact)_2\ 2H_2O$	pink	26.38	26.78	5.17	5.20	–	–	13.19	12.75
$Co(lact)_2$	violet	30.39	30.93	4.25	4.17	–	–	–	–
$Co(lact)_2\ 2py$	pink	48.62	48.43	5.10	4.95	7.09	6.96	40.02	39.85
$Co(lact)_2\ 2pic$	pink	51.07	51.20	5.71	5.69	6.62	6.66	43.96	44.26
$Co(lact)_2\ bipy$	pink	48.86	47.70	4.61	4.78	7.12	6.85	–	–
$Co(en)_3(lact)_2$	orange	34.51	34.40	8.21	8.27	20.14	19.75	–	–
$Zn(lact)_2\ 3H_2O$	white	24.20	24.27	5.42	5.35	–	–	18.16	17.54
$Zn(lact)_2\ 2H_2O$	white	25.78	25.97	5.05	5.14	–	–	12.88	12.74
$Zn(lact)_2$	white	29.59	29.32	4.14	3.98	–	–	–	–
$Zn(lact)_2py$	white	40.92	39.91	4.69	5.10	4.34	4.21	24.51	24.75
$Zn(lact)_2pic$	white	42.81	42.70	5.09	4.85	4.16	4.06	27.65	30.20
$Zn(lact)_2bipy$	white	48.06	48.12	4.54	4.84	7.01	7.12	–	–
$Zn(en)_3(lact)_2$	white	33.99	33.96	8.09	8.20	19.84	19.75	–	–

[a] Lact = lactate; L = pyridine(py); 4-Methylpyridine(pic); water; derived from thermal analyses; bipy = α,α'-bipyridyl; en = 1,2-diaminoethane.

pound the suspension was in ethanol. The suspension was heated at 50–60 °C until complete dissolution. By addition of diethyl ether and cooling to 4–5 °C, a microcrystalline hygroscopic compound separated, which was finally washed with ether and dried *in vacuo*.

Analytical data for all lactato complexes, derived from elemental and thermal analyses, have been reported in Table I.

Spectroscopic, Magnetic and Thermal Measurements

Infrared spectra were recorded with a Perkin–Elmer 621 spectrophotometer, in KBr phase (4000–200 cm^{-1}) and in nujol mull (800–200 cm^{-1}); and with a Perkin–Elmer FIS 3 spectrophotometer, in nujol mull on polythene (400–60 cm^{-1}).

Electronic reflectance spectra were recorded on a Beckmann DK-2A spectrophotometer.

E.s.r. spectra were recorded on a Varian 4502-11 spectrometer at a field modulation of 100 kHz. The resonance frequencies were derived by standardisation with diphenylpicrylhydrazyl. Magnetic susceptibilities were measured by the Gouy method.

Thermal analyses were carried out on a Dupont 990 thermal analyzer equipped with a Dupont 951 thermogravimetric analyzer, at a heating rate of 20 °C min^{-1}, under a stream of nitrogen of 40 $cm^3\ min^{-1}$.

Results and Discussion

Thermal Behaviour

Aquolactate complexes of different metals crystallize with a variable number of water molecules. Both coordinated and uncoordinated water are lost within the same temperature range (see Table II). The uncoordinated water has a modifying effect on the temperature range where the water is lost; the dissociation temperature decreases on increasing the hydratation degree. The highest temperature has been found when only coordinated water is present. The N donor ligands pyridine and 4-Methylpyridine did not show any tendency to enter in the crystals as uncoordinated molecules. All lactate complexes decompose above 200 °C.

TABLE II. Thermal Dissociation Range of Additional Ligand L (water, pyridine, 4-Methylpyridine) (a). Thermal decomposition range of lactate complexes (b).

Compound	t °C (a)	t °C (b)
$Cu(lact)_2 2H_2O$	40– 74	230–270
$Cu(lact)_2 1.5H_2O$	75–135	250–300
$Cu(lact)_2 py$	175–210	215–295
$Cu(lact)_2 pic$	160–210	215–280
$Ni(lact)_2 2.5H_2O$	60–150	250–335
$Ni(lact)_2 2H_2O$	170–225	345–420
$Ni(lact)_2 2py$	150–210	325–400
$Ni(lact)_2 2pic$	175–240	325–400
$Co(lact)_2 3H_2O$	70–130	230–270
$Co(lact)_2 2H_2O$	135–180	305–500
$Co(lact)_2 2py$	130–195	250–455
$Co(lact)_2 2pic$	150–195	285–445
$Zn(lact)_2 3H_2O$	60–105	235–460
$Zn(lact)_2 2H_2O$	125–155	235–445
$Zn(lact)_2 py$	100–155	235–445
$Zn(lact)_2 pic$	160–190	235–445

TABLE III. Magnetic Moments at Room Temperature.

Compound	μ_{eff}, B.M.
$Cu(lact)_2 1.5H_2O$	1.92
$Cu(lact)_2$	1.93
$Cu(lact)_2 py$	1.84
$Cu(lact)_2 pic$	1.85
$Cu(lact)_2 bipy$	a
$Cu(en)_3(lact)_2$	1.90
$Ni(lact)_2 2H_2O$	3.10
$Ni(lact)_2$	3.11
$Ni(lact)_2 2py$	3.01
$Ni(lact)_2 2pic$	3.05
$Ni(lact)_2 bipy$	3.21
$Ni(en)_3(lact)_2$	2.92
$Co(lact)_2 2H_2O$	4.63
$Co(lact)_2$	4.64
$Co(lact)_2 2py$	4.87
$Co(lact)_2 2pic$	4.67
$Co(lact)_2 bipy$	4.32
$Co(en)_3(lact)_2$	4.53

[a] hindered by a difficult packing.

TABLE IV. E.s.r. Parameters of Copper Complexes.[a]

Compound	$g_{\parallel}$	$g_{\perp}$
$Cu(lact)_2 1.5H_2O$	2.28	2.07
$Cu(lact)_2 py$	2.23	2.06
$Cu(lact)_2 pic$	2.27	2.09
$Cu(lact)_2 bipy$	2.27	2.06

[a] Recorded on polycrystalline samples at room temperature.

Electronic and Magnetic Properties

Magnetic susceptibility values at room temperature of all copper complexes are in the usual range for octahedral or tetragonal compounds (Table III). The cobalt and nickel complexes have high spin configurations, corresponding to cubic or tetragonal symmetries. Since these values do not show significant change passing from the lactate complexes to their adducts with bases, the possibility of planar geometry in nickel and cobalt anhydrous compounds is ruled out.

Polycrystalline samples of copper complexes show two types of resonance in their e.s.r. spectra (Table IV), the lines at higher field being more intense. Therefore the symmetry appears to be always axial, except in tris(1,2-diaminoethane)copper(II) dilactate, which shows isotropic resonances ($g = 2.178$) like tris(1,2-diaminoethane)copper(II) sulphate [4].

This behaviour suggests a ionic situation of the lactate anions, and hexacoordination by 1,2-diaminoethane.

Electronic reflectance spectra of copper complexes (Fig. 1) in the near infrared and visible regions are characteristic of copper complexes with tetragonal symmetry. The broad band between 1500 and 500 nm has a complex structure in which the position of the components and the shape of the absorption give the measure of the tetragonal distortion.

Relative magnitudes of g values are consistent with the ground state configuration $(xz)^2(yz)^2(xy)^2(z^2)^2 \times (x^2 - y^2)$, if the x and y molecular axes lie along M–O bonds. This corresponds to an elongated tetragonal geometry, the two lactate anions being very probably equatorial ligands, the coordinated water and the base molecules axial ligands. The anhydrous compound exhibits magnetic parameters identical to those of the aquocomplexes suggesting that the axial position is occupied by a lactate oxygen of another molecule.

As for the magnitude of tetragonal distortion, the increase mainly involves [6] a) increase in the energy of $^2B_1 \rightarrow {}^2A_1$ transition (with the highest intensity), b) relative approach of three transitions $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$ $^2B_1 \rightarrow {}^2E$, and a more symmetrical shape of the broad band.

On these bases the monoadduct with 4-Methylpyridine is more distorted than the analogous pyridine adduct. The anhydrous compound shows distorsion higher than the aquocomplexes, though its electronic spectrum does not suggest a planar geometry.

It can be observed that the comparisons have been made among complexes having similar ligands. Different ligands, like α,α'-bipyridyl or 1,2-diaminoethane could involve differences in the absorption bands not all due to differences in tetragonal distortions. Cobalt and nickel lactate complexes have electronic spectra characteristic of the hexacoordinated compounds of these metals (Fig. 2, 3, Table V, VI).

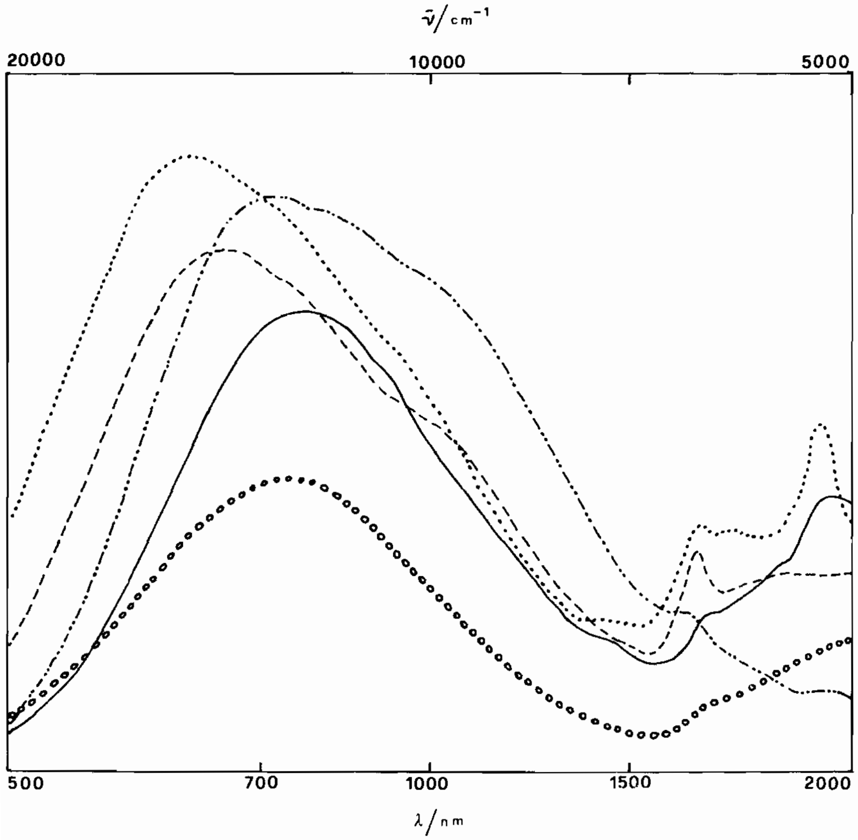

Fig. 1. Reflectance electronic spectra: (——) $Cu(lact)_2 1.5H_2O$; (– – – –) $Cu(lact)_2py$; (–..–..) $Cu(lact)_2bipy$; (.........) $Cu(lact)_2$-pic; (∘∘∘∘∘∘∘) $Cu(lact)_2$.

TABLE V. Electronic Bands and Assignment in Nickel Compounds.

Compound	$\nu_1^{a,b}$	$\nu_2^{a,b}$	$\nu_3^{a,b}$
$Ni(lact)_2 2H_2O$	8.6	13.9	15.1
$Ni(lact)_2$	8.7	13.9	15.0
$Ni(lact)_2 2py$	10.0	15.0	17.1
$Ni(lact)_2 2pic$	9.6	13.7	16.4
$Ni(lact)_2 bipy$	10.0	13.4	16.6

[a] Symbols are in accordance to O_h symmetry: ν_1 ($^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$), ν_2 ($^3A_{2g} \rightarrow {}^1E_g$), ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$). [b] $10^3 cm^{-1}$

TABLE VI. Electronic Bands and Assignment in Cobalt Compounds.

Compound	$\nu_1^{a,b}$	$\nu_2^{a,b}$	$\nu_3^{a,b}$
$Co(lact)_2 2H_2O$	8.4	16.0	19.5 20.9
$Co(lact)_2$	8.8	16.2	20.3 21.6
$Co(lact)_2 2py$	9.3	18.8	19.8 21.1
$Co(lact)_2 2pic$	8.3	16.8	19.8 20.7
$Co(lact)_2 bipy$	9.1	(c)	20.0

[a] Symbols are in accordance to O_h symmetry: ν_1 ($^4T_{1g}(^4F) \rightarrow {}^4T_{2g}(^4F)$), ν_2 ($^4T_{1g}(^4F) \rightarrow {}^4A_{2g}(^4F)$), ν_3 ($^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$). [b] $10^3 cm^{-1}$. [c] Not observed.

Diaquobis(DL-lactato)nickel(II) has an electronic spectrum similar to that of hexaquonickel(II) cation [7], showing no difference in the ligand field strength between water and the lactate oxygens. The other nickel lactate complexes show broader bands and, in some cases, evident shoulders arising mainly on $^3A_{2g} \rightarrow {}^3T_{1g}$ (ν_3) and $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)O_h$ transitions and representative of the tetragonal distortions.

The electronic spectra of cobalt(II) complexes, compared with that of hexaquocobalt(II) cation [8], show the splitting of the octahedral $^4T_{1g}(^4F) \rightarrow {}^4T_{1g}(^4P)$ (ν_3) transition as the main effect of the tetragonal distortions. The differences in the distorsion power of the various axial ligands could be difficult to rationalize; however, from the analogy between the spectra of the anhydrous compounds and those of hexaquocobalt(II), nickel(II) cations, it is now quite sure that the anhydrous compounds are hexacoordinated through intermolecular interactions.

The electronic spectra of tris(1,2-diaminoethane)-metal(II) dilactate complexes are very similar to those of the analogous tris(1,2-diaminoethane)metal(II) cations [9–11], according to a completely ionic situation of the lactate anions.

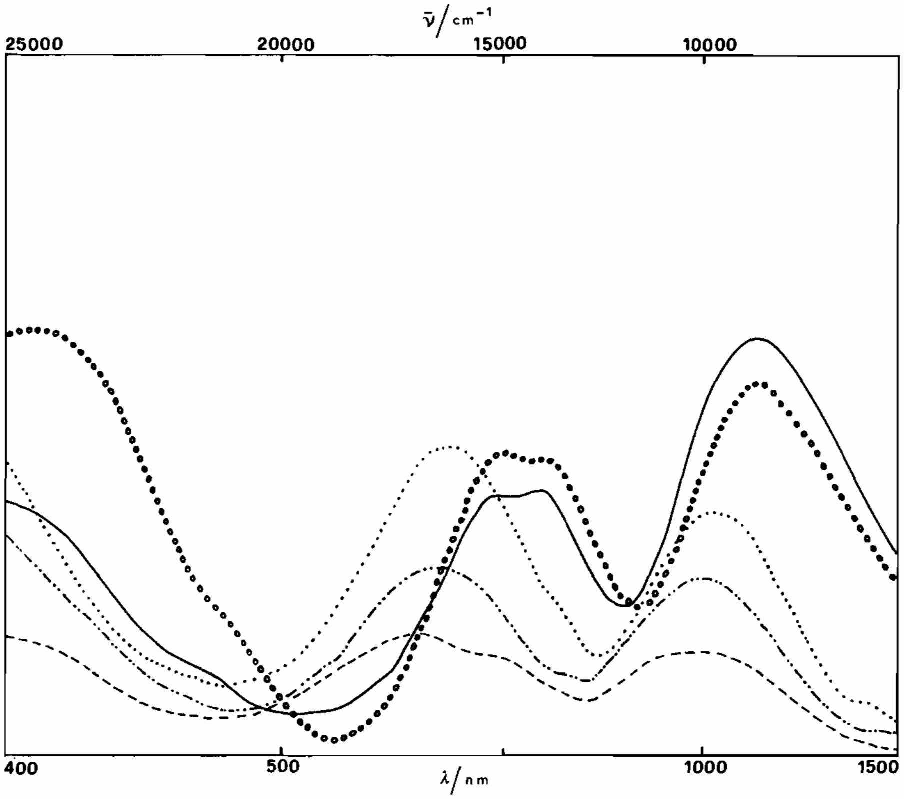

Fig. 2. Reflectance electronic spectra: (——) $Ni(lact)_2 2H_2O$; (– – – –) $Ni(lact)_2 2py$; (–··–··) $Ni(lact)_2 bipy$; (·········) $Ni(lact)_2$ 2pic; (●●●●●●) $Ni(lact)_2$.

TABLE VII. H_2O and CO_2^- Stretching Frequencies.[a,b]

Compound	Water ν(OH)	ν(CO_2^-)	
		as	s
$Cu(lact)_2 2H_2O$	3530w 3400 m,b 3240w,b	1585vs	1405s
$Cu(lact)_2 1.5H_2O$	3500w 3360m,b 3200w,b	1585vs	1405s
$Cu(lact)_2$		1585vs	1405s
$Cu(lact)_2 py$		1600vs,b	1390s
$Cu(lact)_2 pic$		1600vs,b	1400s
$Cu(lact)_2 bipy$		1585vs	1385s
$Ni(lact)_2 2.5H_2O$	3530w 3360m,b 3230w,b	1595vs	1425s
$Ni(lact)_2 2H_2O$	3440w 3240m,b	1600vs,b	1405s
$Ni(lact)_2$		1640vs	1380s
$Ni(lact)_2 2py$		1580vs	1410s
$Ni(lact)_2 2pic$		1600vs,b	1420s
$Ni(lact)_2 2bipy$		1600vs,b	1370s
$Co(lact)_2 3H_2O$	3530w 3360m,b 3200w,b	1585vs	1420s
$Co(lact)_2 2H_2O$	3440w 3240m,b	1600vs,b	1410s
$Co(lact)_2 2py$		1585vs	1405s
$Co(lact)_2 2pic$		1600vs,b	1420s
$Co(lact)_2 bipy$		1600vs	1375s
$Zn(lact)_2 3H_2O$	3520w 3340m,b 3240m,b	1590vs	1430s
$Zn(lact)_2 2H_2O$	3440w 3220m,b	1600vs,b	1405s
$Zn(lact)_2 py$		1600vs,b	1385s
$Zn(lact)_2 pic$		1600vs,b	1415s
$Zn(lact)_2 bipy$		1590vs,b	1375s

[a] Spectra have been recorded in KBr phase. [b] cm^{-1}. s = strong, m = medium, w = weak, vs = very strong, b = broad.

Vibrational Properties

The vibrational properties have been considered in order to discuss the strength of metal–lactate bond as well as the electronic perturbation of the coordinated lactate. Moreover they are the only structural data for zinc(II) complexes. Three different frequency ranges have been considered: i) The range characteristic of the stretching vibrations of water (3700–1300 cm^{-1}). ii) The range diagnostic for the coordination mode of the carboxylate [12] anion (1700–1300 cm^{-1}).

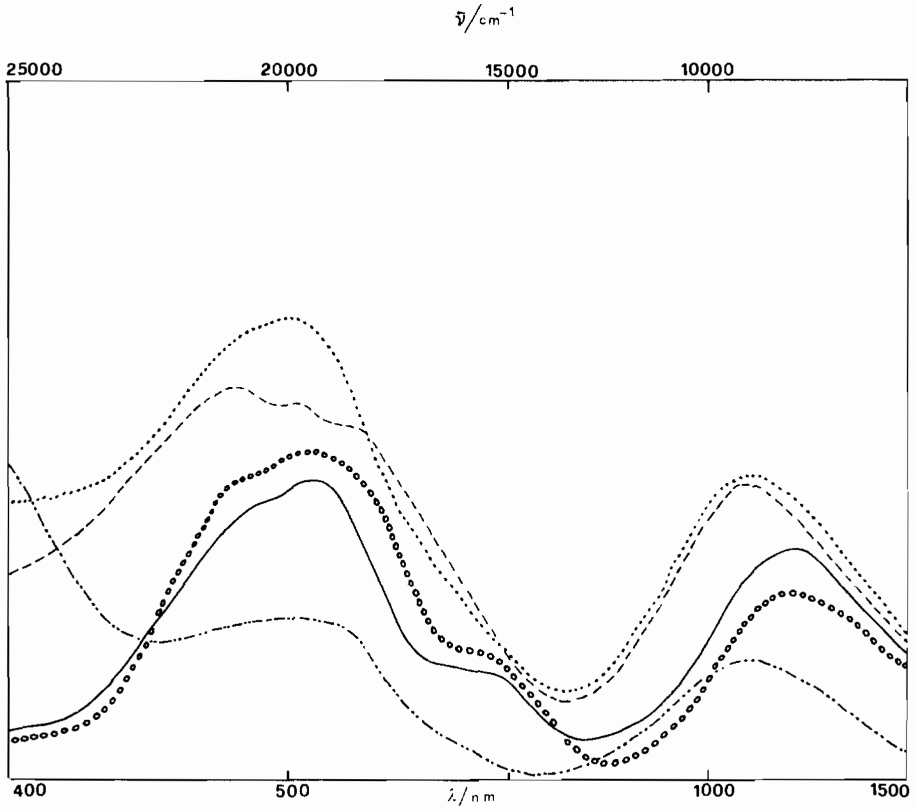

Fig. 3. Reflectance electronic spectra: (——) $Co(lact)_2 2H_2O$; (– – – –) $Co(lact)_2 2py$; (–..–..) $Co(lact)_2bipy$; (.........) $Co(lact)_2$-2pic; (∘∘∘∘∘∘∘) $Co(lact)_2$.

TABLE VIII. M–O and M–N Stretching Frequencies[a,b]

Compound	$\nu(M-OH_2)$	$\nu(M-N)$	$\nu(M-O)$ + ring deformations
$Cu(lact)_2 1.5H_2O$	375		495m, 415m, 385m, 320m
$Cu(lact)_2$			510w, 430m, 395m, 320m
$Cu(lact)_2py$		263m	480m, 420m, 360m, 297m
$Cu(lact)_2pic$		270m	(c), 410m, 330sh, 290m
$Ni(lact)_2 2H_2O$	390w		485w, 425m, 340sh, 285m
$Ni(lact)_2$			500w, 430m, 335sh, 315m
$Ni(lact)_2 2py$		280m	491m, 400m, 340m, 300m
$Ni(lact)_2 2pic$		270m	(c), 400m, 320m, 286m
$Co(lact)_2 2H_2O$	380w		475w, 420m, 335m, 285m
$Co(lact)_2$			495w, 425m, 330sh, 295m
$Co(lact)_2 2py$		265m	480m, 395m, 329m, 295m
$Co(lact)_2 2pic$		260m	(c), 410m, 315sh, 275m
$Zn(lact)_2 2H_2O$	370w		475w, 420m, 300sh, 265m
$Zn(lact)_2$			495w, 430m, 300sh, 270m
$Zn(lact)_2py$		240mw	480m, 405m, 320m, 270m
$Zn(lact)_2pic$		270m	(c), 430m, 330m, 280m

[a] Recorded in nujol mull. [b] cm^{-1} [c] Obscured by ligand absorptions.

iii) The range diagnostic for the M–O (metal–lactate and metal–water) [13] and M–N stretching vibrations (500–200 cm^{-1}) [14].

The vibrational data are reported in Table VII and VIII.

The absorption frequencies associated to the stretching modes of water show that in aquocomplexes it is not easy to distinguish between coordinated and uncoordinated water [15]; surely the sharp band, at higher frequency, can be associated to the coordinated water. One can observe that the energy of the O–H stretching increases with the hydration of the compound.

The so called asymmetrical (higher frequency) and symmetrical stretchings show frequency differences $\Delta\nu = 160 - 290$ cm^{-1}. These values exclude bidentation [14]. Since aquobis(DL-lactato)copper(II) hemihydrate, in which the carboxylate anion is monodentate [3], has a $\Delta\nu$ value = 180 cm^{-1}, a monodentate coordination is assigned to the lactate anion in our complexes, with similar or higher $\Delta\nu$ values. This agrees with the results of the electronic and magnetic measurements and it is also in accordance with the coordination scheme found in glycolate metal complexes [13]. $\Delta\nu$ values depend on the metal, within the series of bis(DL-lactato)metal(II) complexes; they change on passing from anhydrous to aquocomplexes and to the base adducts of the same metal (with exception of the copper complexes), and on changing the hydration degree of the aquocomplexes of the same metal with the exception of the copper complexes). The highest $\Delta\nu$ values have been found in anhydrous cobalt, nickel and zinc lactato complexes. The addition of ligands in the fifth and sixth position leads to a large reduction of the $\Delta\nu$ values. This reduction varies with the different ligand molecules. The vibrational properties of tris(1,2-diaminoethane)metal(II) lactate, in the carboxylate frequency range, are almost identical to those of the alkali lactate. This behaviour is expected for a completely ionic lactate, without perturbations from the metal.

The bis(DL-lactato)metal(II) complexes show four bands in the range 510–270 cm^{-1}, which may be assigned to combined vibrations of the M–O stretchings and ring deformations [13]. The four bands suggest local C_{2v} symmetry. Their frequencies decrease in the order $Cu > Ni > Co > Zn$, this sequence corresponding to the order of M–O bond strength for these metals. Additional ligands in axial position lower the ν(M–O) frequency, indicating that the transfer of electron density lowers the metal–lactate coordination strength. As for the relation between ν(M–O) and $\Delta\nu$ value, it can be observed that the higher the bond strength between metal and lactate, the higher the $\Delta\nu$ value. Copper complexes are the only exception, as there is no variation of the $\Delta\nu$ value corresponding to that of the ν(M–O) frequency. It can be suggested that the out-of-plane position of copper(II) ion, found in aquobis(DL-lactato)copper(II) hemyhydrate [3], is common to all copper lactato complexes; so that the influence of the electron transfer from the axial ligand is limited to the M–O bond. The perturbation of the carboxylate group requires planarity, as in cobalt, nickel and zinc complexes, with no displacement of the metal ion from the plane of lactate ligands.

Conclusions

The results reported in this paper show that the lactate anions always act as chelate ligands through one oxygen of the carboxylate group and the oxygen of the hydroxo group. None of the metal ions considered shows any tendency to assume the fourcoordinate geometry. Five or sixcoordination is reached even in the absence of any additional ligand, by intermolecular interactions.

Sixcoordination has been found peculiar for the cobalt and nickel lactate complexes, fivecoordination for the copper complexes. The zinc complexes showed both kinds of coordination, being hexacoordinate in the aquocomplexes and pentacoordinate in the pyridine and 4-Methylpyridine adducts. Therefore the different conclusions on the geometry of the metal lactate compounds, reached by Bolard [1], have now been definitely ruled out.

The coordination to cobalt, nickel and zinc ions has a perturbing effect on the electronic distribution of the ionic lactate, as well as the addition of water or of basic ligands in axial position affects the energy of the metal–lactate bonds. The latter effect may be considered the most important conclusion in this paper. In fact it shows the possibility of being related to the perturbing effects of the basic groups in biological systems. The stabilisation of the metal–lactate bond in metalloenzymes can be related to the presence of basic ligands in the coordination sphere.

As for zinc, which is of direct interest in the lactato dehydrogenase chemistry [16], the comparison with the electronic distributions of the complexes here reported, indicates zinc similar to nickel and mainly to cobalt, copper being completely different.

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