Inorganica Chimica Acta, *192* (1992) 237–242

Synthesis and characterization of metal derivatives of dihydrolipoic acid and dihydrolipoamide

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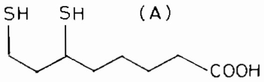
(Received July 1, 1991; revised October 28, 1991)

Abstract

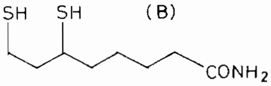
Complexes formed by the dianions LH^{2-} and L'^{2-} deriving from dihydrolipoic acid (LH_3) and dihydrolipoamide ($L'H_2$), respectively, by substitution of the hydrogen atoms of the thiol groups with Ni(II), Co(II), Hg(II) and Cu(I) ions were synthesized, isolated and characterized. In all these compounds the metal ions are coordinated to the thiolic sulfur atoms of the ligands. Potentiometric and spectroscopic data (IR, UV–Vis, EPR and XPS) obtained for these complexes or for their solutions are discussed.

Introduction

The coordinating ability of the thiolate groups of dihydrolipoic acid LH_3 (**A**) ($L = C_8H_{13}S_2O_2$) and dihydrolipoamide, $L'H_2$ (**B**) ($L' = C_8H_{15}S_2ON$), allowed the use of these compounds in the removal of Fe(III) and Fe(II) ions from the transport and storage proteins involved in iron metabolism in man, namely transferrin [1] and ferritin respectively [2, 4].



A



B

Dihydrolipoic acid plays an important role in the enzymatic biosynthesis of the active site in iron–sulfur proteins, and represents a convenient reactant for the chemical synthesis of analogs of these structures [5–7]. It was also found to accelerate the uptake of iron by transferrin and ferritin [8], so that hypotheses about a possible shuttle role for the two dithiols in the intracellular metabolism of iron were advanced.

These observations prompted us to examine the formation and properties of other metal derivatives of the two dithiols. Mercury(II) and nickel(II) complexes, corresponding to the formulae Hg(LH) and Ni(LH), were already described some time ago [9], but information of these compounds was not complete and was to some extent incorrect. In the present paper we report the synthesis, as well as the spectroscopic and magnetic characterization of compounds formed by anions of dihydrolipoic acid and dihydrolipoamide with nickel(II), cobalt(II), mercury(II) and copper(I). While the mercury(II) and copper(I) complexes are water insoluble at any pH value, the cobalt(II) and nickel(II) complexes are water soluble at pH 8–9. Consequently, potentiometric titrations of nickel(II) and cobalt(II) chloride solutions in the presence of dihydrolipoic acid have been carried out to determine the stability of these metal complexes in solution.

Experimental

Preparation of the ligands

Dihydrolipoic acid and dihydrolipoamide were prepared according to already described methods [10].

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Their purity was assessed by IR and NMR spectroscopy, and by potentiometric titration.

Preparation of the metal derivatives of LH_3 and $L'H_2$

To avoid the oxidation of the ligands and any possible decomposition of the products, all manipulations were performed under Ar on rigorously degassed solutions, and the products were stored under Ar. Two methods of preparation were utilized.

Method 1. Typically 4.8 mmol of the ligand were dissolved in 100 ml of 0.3 M Tris {(tris[hydroxymethyl]-aminomethane)} brought to pH = 9.0 with HCl. To this solution, 10 ml of an aqueous solution of the metal salt (4.3 mmol) were added. A precipitate was obtained when the pH of the solution was lowered to 5.0 by addition of 0.1 M HCl. The solid was filtered, washed with 100 ml of water and 25 ml of CH_2Cl_2 and dried under dynamic vacuum.

Method 2. To 4.3 mmol of the metal salt suspended in 2 ml of DMF solution of the ligand (4.81 mmol) were added. After stirring for 3 h, 250 ml of water were added. A solid compound was obtained, filtered, washed with 100 ml of water and 25 ml of CH_2Cl_2 and dried under dynamic vacuum.

$Ni(LH)\cdot 0.5H_2O$: method 1 (from $NiCl_2\cdot 6H_2O$, 1.00 g). Colour: brownish red. *Anal.* Calc.: C, 35.07; H, 5.48; O, 14.61; S, 23.68; Ni, 21.45; H_2O, 3.29. Found: C, 35.00; H, 5.12; O, 15.10; S, 23.20; Ni, 21.88; H_2O, 3.00%.

$Co(LH)\cdot 0.75H_2O$: method 1 (from $CoCl_2\cdot 6H_2O$, 1.00 g). Colour: dark red. *Anal.* Calc.: C, 34.48; H, 5.57; O, 15.80; S, 22.99; Co, 21.16; H_2O, 4.85. Found: C, 34.48; H, 5.04; O, 15.68; S, 22.98; Co, 20.99; H_2O, 4.74%.

Hg(LH): method 2 (from $HgCl_2$, 1.17 g). Colour: white. *Anal.* Calc.: C, 23.61; H, 3.44; O, 7.85; S, 15.70; Hg, 49.33. Found: C, 24.16, H, 4.51; O, 7.72; S, 15.68; Hg, 49.06%.

$Cu_2(LH)\cdot 0.2H_2O$: method 2 (from CuCl, 0.85 g). Colour: yellow. *Anal.* Calc.: C, 28.51; H, 4.28; O, 10.45; S, 19.01; Cu, 37.75; H_2O, 1.07. Found: C, 28.29; H, 3.90; O, 10.00; S, 18.50; Cu, 38.03; H_2O, 0.95%.

$NiL'\cdot 0.5H_2O$: method 2 (from $NiCl_2\cdot 6H_2O$, 1.00 g). Colour: brownish red. *Anal.* Calc.: C, 35.20; H, 5.87; O, 8.80; S, 23.46; N, 5.13; Ni, 21.52; H_2O, 3.30. Found: C, 35.20; H, 5.43; O, 8.71; S, 23.40; N, 5.11; Ni, 21.42; H_2O, 3.93%.

$CoL'\cdot 0.5H_2O$: method 2 (from $CoCl_2\cdot 6H_2O$, 1.00 g). Colour: dark red. *Anal.* Calc.: C, 35.17; H, 5.86; O, 8.79, S, 23.45; N, 5.13; Co, 21.59; H_2O, 3.30. Found: C, 34.96; H, 5.79; O, 8.75; S, 23.47; N, 5.10; Co, 20.55; H_2O, 3.89%.

HgL′: method 2 (from $HgCl_2$, 1.18 g). Colour: white. *Anal.* Calc.: C, 23.66; H, 3.69; O, 5.92; S, 15.78; N, 3.45; Hg, 49.05. Found: C, 22.95; H, 3.90; O, 5.90; S, 15.75; N, 3.42; Hg, 48.99%.

$Cu_2L'\cdot 0.5H_2O$: method 2 (from CuCl, 0.86 g). Colour: yellow. *Anal.* Calc.: C, 28.14; H, 4.69; O, 7.03; S, 18.76; N, 4.10; Cu, 37.26; H_2O, 2.64. Found: C, 30.25; H, 5.00; O, 7.00; S, 18.78; N, 4.41; Cu, 36.62; H_2O, 2.08%.

Physical measurements

Nitrogen, carbon, oxygen and hydrogen were analyzed with a Perkin-Elmer elemental analyzer model 2400. Sulfur was analyzed with a LECO sulfur determinator. Metals contents were determined with a Perkin-Elmer atomic absorption instrument model 4000. Water content was determined as weight loss by thermoanalysis with a Dupont TG model 1090 instrument.

IR spectra were obtained on KBr pellets of sample using a Jasco FT-IR 5000 spectrophotometer. UV–Vis spectra were recorded on an Hewlett Packard diode array spectrophotometer on samples dissolved in aqueous buffer or in DMF. Magnetic susceptibility data on solid samples were obtained at room temperature according to Faraday's methods using a Cahn–Ventron magnetic apparatus equipped with a Cahn 1000 balance. EPR spectra were obtained at 123 K on a Varian E-109 spectrometer operating at X-band.

Potentiometric titrations were performed at 25 ± 1 °C with a Metrohm E654 pH-meter equipped with an automatic Metrohm Dosimat 665 burette which was governed by the TITOBAS program [11]. A combined pH-electrode (Metrohm) was used for highly alkaline solutions. Water solutions (20 ml) of $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$ and LH_3 in the molar ratios (metal/LH_3) 1/1, 1/2, 1/3 and 1/4, were titrated with 0.1 M KOH. Ionic strength was kept constant at 0.1 M by addition of KNO_3.

Measurements were performed under an argon atmosphere by adding 0.05 ml aliquots of a KOH solution up to a five-fold molar excess of alkali over LH_3. A one-minute time interval was allowed between two successive additions of the KOH solution. Each experimental curve consisted of about sixty experimental points. Potentiometric data for the electrode standardization were analyzed by the MAGEC program [12]. The ionization constants of dihydrolipoic acid and the formation constants of its adducts with Ni(II) and Co(II) were calculated by a slightly modified version of the PSEQUAD program [13]. XPS measurements were carried out on a VG-ESCA 3 photoelectron spectrometer, employing an Al Kα source ($h\nu$= 1486.6 eV). Measurements were always performed both at liquid nitrogen temperature and at room temperature, and at a base pressure of 1×10^{-9} Torr, and in the shortest possible time from preparation of the compounds to be analyzed. Samples were dusted and pressed on a metal tip. Quantitative measurements were obtained from relative peak area ratios, after correction for atomic cross-section values [14] and for an $E^{-1/2}$ dependence of mean free-path values.

Results and discussion

Figures 1 and 2 show distribution curves derived from titration experiments on cobalt and nickel salts respectively, in the presence of dihydrolipoic acid.

In the case of cobalt, the following compounds were progressively formed as the pH was raised: $[CoL_2H_6]^{2+}$, $[CoL_2H_5]^+$, $[CoL_2H_4]$, $[CoL_2H_3]^-$ and $[CoL]^-$. In the presence of an excess of ligand at alkaline pH values, formation of $[CoL_4H_6]^{4-}$ was observed. In the formulae written above, charges are calculated by assigning to L a net charge of -3. Taking in account the protonation equilibria of the ligand, the compounds listed above should correspond to: $[Co(LH_3)_2]^{2+}$, $[Co(LH_2)(LH_3)]^+$, $[Co(LH_2)_2]$, $[Co(LH_2(LH)]^-$, $[CoL]^-$ and $[CoL_2(LH_3)_2]^{4-}$.

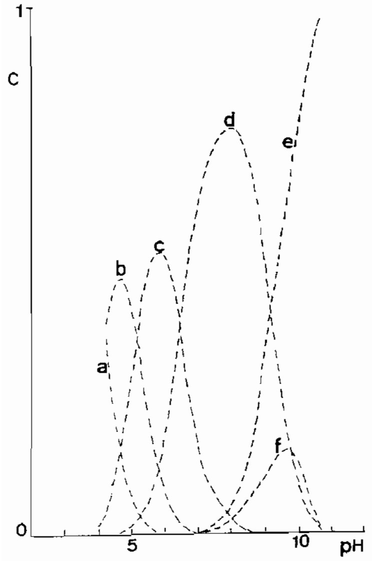

Fig. 1. Distribution curves for the formation of the Co complexes: a, $[CoL_2H_6]^{2+}$; b, $[CoL_2H_5]^+$; c, $[CoL_2H_4]$; d, $[CoL_2H_3]^-$; e, $[CoL]^-$; f, $[CoL_4H_6]^{4-}$; as a functions of pH for a ½ molar ratio [Co]/[L].

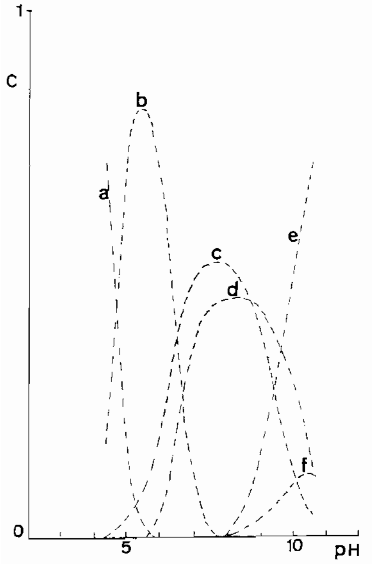

Fig. 2. Distribution curves for the formation of the Ni complexes: a, $[NiL_2H_6]^{2+}$; b, $[NiL_2H_4]$; c, $[NiLH]$; d, $[NiL_3H_4]^{3-}$; e, $[NiL]^-$; f, $[NiL_4H_5]^{5-}$; as a function of pH for a ½ molar ratio [Ni]/[L].

In the case of nickel, formation of the following compounds was observed as the pH was raised: $[NiL_2H_6]^{2+}$, $[NiL_2H_4]$, $[NiLH]$, $[NiL_3H_4]^{3-}$ and $[NiL]^-$. In the presence of excess ligand at alkaline pH values, formation of $[NiL_4H_5]^{5-}$ was observed. In analogy to that reported for cobalt, the nickel species could also be presented as: $[Ni(LH_3)_2]^{2+}$, $[Ni(LH_2)_2]$, $[NiLH]$, $[Ni(LH)_2(LH_2)]^{3-}$, $[NiL]^-$ and $[Ni(LH)_3(LH_2)]^{5-}$.

Table 1 reports the formation constants for nickel and cobalt compounds, and provides information on the protonation equilibria for dihydrolipoate. As a consequence of the wide range of bonding possibilities of the ligands we were not able to obtain our compounds in a form suitable for single crystal analysis. Therefore we have made use of different spectroscopic methods to characterize these products and infer some structural information.

Electronic spectra were recorded in the 800–300 nm range, on solutions of nickel and cobalt at pH 9 in the presence of equimolar amounts of ligand. Under these conditions, the compounds $[NiL]^-$ and $[CoL]^-$ represent the most abundant chemical species present in solution. The electronic spectrum of $[NiL]^-$ presents three bands at 530 ($\epsilon=800$), 450 ($\epsilon=1400$) and 335 ($\epsilon=2300$) nm. The electronic spectrum of $[CoL]^-$ shows

TABLE 1. Logarithms of the formation constants β_{mlh} for complexes of dihydrolipoate and cobalt(II) and nickel(II)[a]

Compound[b]	Co(II)	Ni(II)
[MHL]		19.31 (2)
$[ML]^-$	9.96 (1)	9.92 (1)
$[ML_2H_6]^{2+}$	61.84 (2)	60.05 (2)
$[ML_2H_5]^+$	57.62 (2)	
$[ML_2H_4]$	52.45 (2)	50.68 (2)
$[ML_2H_3]^-$	46.02 (2)	
$[ML_3H_4]^{3-}$		62.91 (2)
$[ML_4H_6]^{4-}$	90.11 (2)	
$[ML_4H_5]^{5-}$		79.80 (2)
LH_3	25.611 (2)	$pK_1=4.73$
LH_2	20.881 (2)	$pK_2=9.86$
LH	11.02 (2)	$pK_3=11.02$

$$\beta_{mlh}=\frac{[M_mL_lH_h]}{[M]^m[L]^l[H]^h}$$

[a] The values in parentheses are the standard deviations of the calculated constants. [b] The concentration values utilized were: $10^4[LH_3]$, 2.700; $10^4[Co]$, 2.850, 1.425, 1.000, 0.715; $10^4[Ni]$, 2.700, 1.395, 1.000, 0.700.

three bands at 470 ($\epsilon=4160$), 382 ($\epsilon=4800$) and 337 ($\epsilon=4800$) nm. According to the literature [16], all these bands should arise from electronic charge transfer.

The EPR spectrum at 77 K of an alkaline solution of cobalt and dihydrolipoate, presents two g values at $g_1=2.31$ and $g_2=2.061$. The g_2 signal shows the eight lines splitting due to the ^{59}Co hyperfine coupling. Such an observation could be interpreted by assigning to the cobalt atom the electronic configuration d^7 with a spin state $S=1/2$ (low spin) [16].

XPS data on those compounds which did not show modification by exposure to X-ray are collected in Table 2. A first experimental finding emerging from the XPS data, presented in Table 2, is the constant presence of two inequivalent sulfur atoms in the S 2p peak for all the listed LH_3 compounds. The first component (162–162.5 eV) could be attributed to a thiolic sulfur terminally bound to a central metal atom, in analogy to that reported in the literature for several cysteine and penicilamine complexes [17]. The second component (163.9–164.4 eV) is practically coincident with the S 2p binding energy presented by free LH_3 and $L'H_2$. However, the values of S 2p binding energy are also compatible with a bridging S–R group [18]. A much lower value (161.5 eV) has been assigned to bridging S atoms like those present in the Fe–S–Fe moieties [19, 20]. The analysis of metal ionization peaks was also informative. As expected for a diamagnetic Cu(I) complex, no satellite lines were evident in the Cu 2p spectra of the $Cu_2(LH)\cdot 0.2H_2O$ complex. On the basis of the absence of a satellite structure accompanying the main Ni 2p ionization peaks and a FWHM value typical for Ni in a single environment, we may regard both $Ni(LH)\cdot 0.5H_2O$ and $NiL'\cdot 0.5H_2O$ species as Ni(II) complexes. The Ni(II) complex with $L'H_2$ did not show a binding energy shift for the central metal atom. On the other hand, lowering of the S 2p binding energy and, more significantly, a clear narrowing in S 2p FWHM to a value typical in our experimental conditions of a single S species, suggest a different coordinative situation for the ligand in this complex. The ligand is coordinatively bound to Ni(II) through terminal thiolic groups. The N 2p binding energy for the amide group is only marginally shifted to a lower binding energy upon coordination, suggesting the absence of a direct involvement of the amide group in coordinative bonds The presence of strong satellite lines in the Co 2p XPS spectrum confirms the paramagnetic nature of Co(II) in $Co(LH)\cdot 0.75H_2O$.

TABLE 2. XPS binding energies (eV)

Compound	M	S 2p	N 1s
LH_3		164.1	
$L'H_2$		164.1	399.9
$Ni(LH)\cdot 0.5H_2O$	2p 854.4	162.3 164.1	
$Co(LH)\cdot 0.75H_2O$	2p 779.6 +satellite lines	162.0 164.3	
Hg(LH)	4f 101.2	162.4 163.9	
$Cu_2(LH)\cdot 0.2H_2O$	2p 933.2	162.3 164.1	
$NiL'\cdot 0.5H_2O$	2p 854.4	163.0	399.9
HgL'	4f 101.3	163.7	399.9

Hg(LH) presented a metal core ionization peak 4f falling at a binding energy comparable with that of S 2p, thus allowing an XPS semiquantitative analysis of the Hg/S ratio with much more confidence than for all the other complexes reported here. The resulting ratio (Hg/S = 2.0) confirms bulk chemical analysis results and suggests that a surface structural arrangement different from the bulk of the complex should not occur in this case.

The $\nu_s(COO)$, $\nu_{as}(COO)$, $\nu(CO)+\delta(NH_2)$ and $\nu(CN)$ IR vibrational frequency values for the complexes were obtained on solid samples and are reported in Table 3. Frequencies were assigned according to the data reported in the literature [21, 22].

It is important to note that the $\nu_{as}(COO)$ and $\nu_s(COO)$ stretching frequencies values for these compounds are more similar to those of LH_3 than to those of LH_2Na. As a consequence, it can be concluded that the LH^{2-} species is present in our compounds and that this species is coordinated to the metal atom through its thiolic groups. In previous literature reports [9], the 1570 cm^{-1} $\nu(COO)$ stretching frequency for the nickel(II) complex of dihydrolipoic acid was wrongly assigned. From the present work, it appears that this value is in better accord with the spectrum of LH_2Na than with the spectrum of LH_3. By comparing the $\nu(CO)+\delta(NH_2)$ and $\nu(CN)$ frequencies of our complexes with those of the free ligand, we can conclude that the amide group of L' does not take part in the binding of the metal.

All the compounds except $Co(LH)\cdot 0.75H_2O$ and $CoL'\cdot 0.5H_2O$ were found to be diamagnetic. At room temperature these two cobalt derivatives gave magnetic moments, $\mu=1.97$ BM for the LH_3 compound and $\mu=1.84$ BM for the $L'H_2$ compound. These values are clearly indicative of cobalt(II) low-spin compounds [23]. The principal values of the g tensor for cobalt(II) compounds were obtained from EPR spectra taken at 123 K on powdered samples. The values $g_{\parallel}=2.313$, $g_{\perp}=2.006$ for $Co(LH)\cdot 0.75H_2O$ and $g_{\parallel}=2.313$, $g_{\perp}=2.006$ for $CoL'\cdot 0.5H_2O$ were assigned [24] on the basis of the relative signal intensities because, as typical for the spectra of powders, the $g_{\perp}$ value is correlated to the more intense signal. These g values make it clear that we are dealing with two cobalt(II) low-spin com-

TABLE 3. IR selected frequencies (cm^{-1})

Compound	$\nu_{as}(COO)$	$\nu_s(COO)$	$\nu(CO)+\delta(NH)$	$\nu(CN)$
LH_3	1710(vs)	1412(s)		
LH_2Na	1570(vs)	1440(ms)		
$L'H_2$			1659(vs), 1634(vs)	1418(ms)
$Ni(LH)\cdot 0.5H_2O$	1705(vs)	1415(ms)		
$Co(LH)\cdot 0.75H_2O$	1705(vs)	1415(ms)		
$Hg(LH)$	1700(vs)	1415(m)		
$Cu_2(LH)\cdot 0.2H_2O$	1705(vs)	1415(m)		
$NiL'\cdot 0.5H_2O$			1640(vs)	1400(m)
$CoL'\cdot 0.5H_2O$			1660(vs)	1405(m)
HgL'			1650(vs)	1415(m)
$Cu_2L'\cdot 0.5H_2O$			1655(vs)	1410(m)

ν_{as} = asymmetric stretching; ν_s = symmetric stretching; δ = bending; vs = very strong; m = medium; ms = medium strong.

plexes. When considering that only two g values have always been observed, the cobalt(II) complexes are likely to have a tetragonally distorted octahedral coordination. Moreover, since the $g_{\parallel}$ value is always greater than the $g_{\perp}$ value, a compressed tetragonal distortion [25] having the $(xy)^2\ (xz,yz)^4\ (x^2\text{–}y^2)$ ground state configuration can be attributed to these cobalt compounds.

Since nickel(II) and cobalt(II) complexes are soluble in water at pH 9 and in DMF, electronic and EPR spectra of their solutions were recorded. No difference was found between the electronic spectra of isolated compounds and those of the buffered equimolar mixture of LH_3 and metal considered in the previous section of this paper.

Conclusions

The principal conclusions ensuing from the work reported here can be summarized as follows.

Dihydrolipoic acid behaves in solution either as the neutral ligand, LH_3, or as one of the anions LH_2^-, LH^{2-}, L^{3-}. In the solid compounds we have isolated, dihydrolipoic acid was always found as the LH^{2-} anion, which was coordinated to the metal atom by its thiolate groups. In an identical fashion, dihydrolipoamide was found in the isolated solid compounds as the L'^{2-} anion, and it was coordinated to the metal through its thiolate groups. On the basis of spectroscopic and magnetic data, it has been possible to determine the oxidation number and the electronic spin state for the metal atoms of the compounds reported here. On the same grounds, the isolated compounds were found to show a tetragonally distorted octahedral geometry around the metal atom.

Finally, XPS spectra made it possible to hypothesize that a polymeric structure stabilized by bridging sulfur atoms can be envisaged for compounds of dihydrolipoic acid when isolated as solids. On the other hand, XPS spectra of metal derivatives of dihydrolipoamide left some uncertainties as to their interpretation, making it difficult to formulate hypotheses about the structures of these latter compounds.

Acknowledgement

The authors are grateful to C.N.R. Centro di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione for the availability of the EPR instrumentation.

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