

Síntesis, caracterización espectroscópica y electroquímica de complejos de níquel(II) y cobalto(II) con nuevos ligandos N_2S_2 , N,N' -alquil-bis(2-amino-1-ciclopentencarboditioato de etilo y bencilo)

Synthesis, spectroscopic and electrochemical characterization of nickel(II) and cobalt(II) complexes with new N_2S_2 ligands, ethyl- and benzyl- N,N' -alkyl-bis(2-amino-1-cyclopentencarbodithioate)

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Resumen

Se reporta la síntesis y caracterización (UV-Visible, FTIR, RMN- 1H y ^{13}C , análisis elemental, espectrometría de masas y voltamperometría cíclica) de complejos de níquel(II) y cobalto(II) con los nuevos ligandos nitrógeno-sulfurados, N,N' -alquil-bis(2-amino-1-ciclopentencarboditioato de etilo) con alquil = etileno (L^1), propileno (L^2), butileno (L^3) y N,N' -butil-bis(2-amino-1-ciclopentencarboditioato de bencilo) (L^4). Las propiedades espectroscópicas y electroquímicas de los complejos metálicos indican que tienen importancia como posibles compuestos modelo en biomimética inorgánica

Palabras clave: Complejos de níquel (II) y cobalto (II), ligandos nitrógeno-sulfurados, β -ditiolato enaminas, biomimética inorgánica.

Abstract

The synthesis of nickel(II) and cobalt(II) complexes with the new nitrogen-sulphur ligands, ethyl- N,N' -alkylbis(2-amino-1-cyclopentencarbodithioate) with alkyl = ethylene (L^1), propylene (L^2), butyl (L^3) and benzyl- N,N' -butyl-bis(2-amino-1-cyclopentencarbodithioate) (L^4), and their characterization (UV-Visible, FTIR, 1H - and ^{13}C - NMR, elemental analysis, mass spectra and cyclic voltametry) are reported. The spectroscopic and electrochemical properties of metallic complexes have a potential importance as models in inorganic biomimetic.

Key words: Nickel (II) and cobalt (II) complexes, nitrogen-sulfur ligand, β -dithiolate enamine, inorganic biomimetic.

1 Introducción

There is a considerable interest in nitrogen-sulphur N_2S_2 ligands for their great versatility in coordination chemistry, especially in four-coordinate $M^{II}[N_2S_2]$ com-

plexes, as possible models for physicochemical properties mimics or biomimetic (Ibers et al., 1980) of metallobio-molecules active sites found in nature (Bertini et al., 1994). They have importance also in catalytic studies, electrochem-istry and medicinal chemistry. Metal complexes exhibits

interesting electronic properties when coordinated to nitrogen-sulfur donor ligands connected by alkyl bridges, which simulate the spectral and geometrical N_2S_2 metal coordination sphere, derived from two histidine residues, cysteine and methionine residues, prevalent in metalloenzymes such as: (a) blue copper proteins as the azurin (Gray, 1997; Gray et al., 2000), (b) nickel hydrogenases, CO dehydrogenases (Lancaster, 1988), and (d) zinc finger proteins (Lipscomb et al., 1996). The use of a reported method (Bordás et al., 1972), allows the introduction of N,N' -alkyl variable length chains, in new benzyl- and ethyl- N,N' -alkylbis(2-amino-1-cyclopentencarbodithioate) ligand series (Contreras et al., 2006; Fontal et al., 2002). Our laboratory reported the complete characterization of homologous series of nitrogen-sulphur ligand (Avila et al., 2009; Contreras et al., 2008), with electronic and steric variations, and their respective metal complexes: copper(II) (Contreras et al., 2004), nickel(II) (Contreras et al., 2004) and cobalt(II) (Contreras et al., 2005) as well as their electrochemical properties (Menolasina et al., 2009; Menolasina et al., 2007; Contreras et al., 2003). In this article, we report the synthesis and characterization of nickel(II) and cobalt(II) complexes with ethyl- N,N' -alkylbis(2-amino-1-cyclopentencarbodithioate) where alkyl = ethylene, L^1 ; propylene, L^2 ; butyl, L^3 ; and benzyl- N,N' -butyl-bis(2-amino-1-cyclopentencarbodithioate), L^4 .

2 Experimental

2.1 Reagents and methods

The reagents and solvents (Aldrich Chemical, Merck Co, Baker and Eastman Co.) were used directly as supplied, except CS_2 which was purified as described in the literature (Gordon, 1972).

2.2 Physical measurements

UV-visible absorption spectra (190 – 1,100 nm) were obtained with a Shimadzu Uv/Vis Uvmini-1240 spectrophotometer. Vibrational spectra (4000 – 400 cm^{-1} , KBr pellets) were recorded with a Fourier Transform Perkin-Elmer 1725X spectrophotometer. Room temperature 1H NMR spectra (DMSO, TMS internal standard) were obtained with a Bruker Avance DRX 400-MHz spectrometer. Microanalytical data (C, H, N) were collected using a FISON EA 1108 instrument. Mass spectra were obtained with a Hewlett-Packard gas chromatograph-mass spectrometer, GC-MS Model 5988A, using chemical ionization. Electrochemical experiments were carried out with a BAS100B/W system. Measurements were conducted employing an H cell, a vitreous carbon working electrode (area = 0.08 cm^2), $Ag/AgNO_3$ reference electrode and 200 $mV s^{-1}$ scan rate; CH_2Cl_2 was used as solvent and tetrabutylammonium tetrafluoroborate (TBAFB) as supporting electrolyte. Conductivity measurements were made with a Schott Gerate C6857 conductance bridge.

2.3 Ligand synthesis

Synthesis of ethyl- N,N' -alkylbis(2-amino-1-cyclopentencarbodithioate) where alkyl = ethylene, L^1 ; propylene, L^2 ; butyl, L^3 :

6.8 g (40 mmol) of the cyclopentendithiocarboxylic acid, prepared by Bordás's method (Bordás et al., 1972) was placed in a flask containing 50 cm^3 of NaOH (1 mmol cm^{-3}) solution, and stirred for 15 min. at 0 °C to obtain a suspension. 2.6 cm^3 (20 mmol) of dimethylsulfate were added dropwise with stirring for 20 min at 5 °C. The yellow solid ethyl-2-amino-1-cyclopentencarbodithioate was filtered and recrystallized from dioxane. Yield and melting points: 4.41 g (60 %), m.p.: 35-36 °C. 3.7 g (20 mmol) of the ethyl-2-amino-1-cyclopentencarbodithioate was placed in a flask with MeOH (30 cm^3) and 10 mmol of the appropriate diamine: 1,2-diaminoethane for L^1 ; 1,3-diaminopropane for L^2 , and 1,4-diaminobutane for L^3 with stirring during 72 h. at room temperature. The compounds (yellow solids) were dried under vacuum and recrystallized from methanol. Melting points and overall yields: L^1 , 1.44 g (36 %), 152-153 °C; L^2 , 0.75 g (18 %), 96-99 °C; and L^3 , 2.06 g (48%), 128-130 °C.

Elemental analysis:

L^1 : found: C, 53.90; H, 7.02; N, 6.85; S, 31.98, calcd. for $[C_{18}H_{28}N_2S_4]$: C, 53.95; H, 7.04; N, 6.99; S, 32.01.

L^2 : found: C, 54.89; H, 7.03; N, 6.68; S, 30.90, calcd. for $[C_{19}H_{30}N_2S_4]$: C, 55.03; H, 7.29; N, 6.75; S, 30.93.

L^3 : found: C, 56.02; H, 7.50; N, 6.51; S, 29.90, calcd. for $[C_{20}H_{32}N_2S_4]$: C, 56.03; H, 7.52; N, 6.53; S, 29.92.

Mass spectrometry (CI), P^+ , m/z (I%): L^1 , 400.2(6.0); L^2 , 414.4(17.0); L^3 , 428.4(8.0).

Nuclear magnetic resonance data and assignments (See Fig. 1): 1H -NMR 400 MHz, DMSO- d_6 (s = singlet, d = doublet, t = triplet, c = quartet, q = quintet, m = multiplet): L^1 : δ 8.20 (N-H, s, 2H); 3.59a,b (m, 4H); 3.07j (c, 4H, J = 7.5 Hz); 2.72e (t, 4H, J = 7.5 Hz); 2.60g (t, 4H, J = 7.1 Hz); 1.71f (q, 4H, J = 7.5 Hz); 1.17k (t, 6H, J = 7.16 Hz). L^2 : δ 12.40 (N-H, s, 2H); 3.50a,c (c, 4H, J = 6.4 Hz); 3.20j (c, 4H, J = 7.4 Hz); 2.77e (t, 4H, J = 7.3 Hz); 2.69g (t, 4H, J = 7.7 Hz); 2.00b (q, 2H, J = 6.5 Hz); 1.84f (q, 4H, J = 7.5 Hz); 1.30k (t, 6H, J = 7.4 Hz). L^3 : δ 8.30 (N-H, s, 2H); 3.80a (c, 4H, J = 7.1 Hz); 3.06j (c, 4H, J = 7.7 Hz); 2.74e (t, 4H, J = 7.5 Hz); 2.62g (t, 4H, J = 7.1 Hz); 1.75f (q, 4H, J = 7.6 Hz); 1.16b (t, 4H, J = 7.1 Hz); 1.09k (t, 6H, J = 7.1 Hz).

^{13}C -NMR 400 MHz, DMSO- d_6 : L^1 : δ 195.4j; 169.8d; 117.2h; 40.6a,b; 33.4g; 31.9e; 25.1i; 20.7f; 12.5k. L^2 : δ 197.2i; 169.1d; 118.3h; 41.9a,c; 33.4g; 32.8e; 29.5b; 26.9j; 20.5f; 13.7k. L^3 : δ 196.1i; 170.9d; 117.7h; 39.9a; 33.8g; 32.9e; 28.4b; 26.8j; 20.6f; 12.4k.

Electronic spectral data, λ (cm^{-1}) (ϵ , M-1 cm^{-1}): L^1 :

37,879 (9,100); 31,348 (7,300); 26,316 (9,900); 24,631 (12,200). L2: 31,348 (13,800); 26,316 (19,900); 24,691 (18,000). L3: 31,645 (15,700); 26,316 (24,400); 24450 (18,400).

FT-IR vibrational spectra band positions and assignments, ν (cm⁻¹) (s = strong, m = medium, w = weak, br=broad): L1: $\nu_{\text{N-H}}$, 3452m,br; $\nu_{\text{a(C=C)+v}_{\text{a(C=N)}}$, 1586s; $\nu_{\text{s(C=C)}}$, 1479m; $\nu_{\text{s(C=N)+v}_{\text{a(C=S)}}$, 1313w; $\nu_{\text{a(S-CH}_3)}$, 1270s; ρ -CH₂, 948w; $\nu_{\text{a(CS}_2\text{CH}_3)}$, 919w; $\nu_{\text{s(CS}_2\text{CH}_3)}$, 757w. L2: 3502m,br; 1589s; 1484m; 1322w; 1274m; 949m; 915w; 774w. L3: 3532m; 1589s, 1480s; 1336s; 1271s; 951m; 911m; 761w.

2.4 Synthesis of benzyl-N,N'-butyl-bis(2-amino-1-cyclopentencarbodithioate), L4

5 g (30 mmol) of the cyclopentendithiocarboxylic acid, prepared by Bordas's method (Bordás et al., 1972), was placed in a flask containing a 25 cm³ solution of NaOH (2 mol dm⁻³), and stirred for 15 minutes at 0 °C to get a suspension. A mixture of 5.4 cm³ (40 mmol) of benzyl chloride dissolved in 25 cm³ of a water suspension of 6.8 g (45 mmol) of NaI (1:1.5 mmol) was added dropwise, and the mixture stirred for 1 hour at -5 °C. A brown-yellow solid was collected by suction. 5 g (20 mmol) of the ester product was placed in a flask with 30 ml of THF and 0.9 cm³ (10 mmol) of 1,4-diaminobutane with stirring during 24 hours at ambient temperature; the obtained solution is evaporated to dryness and ethyl acetate is added until the product precipitates as a yellow solid which was re-crystallized in toluene. Melting point, overall yield and color: decomposes above 200 °C, 75 %, clear yellow.

Elemental analysis: found: C, 65.04; H, 6.48; N, 4.98; S, 22.87, calcd. for [C₃₀H₃₆N₂S₄]: C, 65.17; H, 6.56; N, 5.07; S, 23.20.

Mass spectrometry (EI): P⁺, [P⁺-2(C₇H₇S)] and ion tropylium (C₇H₇), m/z (I%): C₁₆H₂₂N₂S, 274.05(7); 91.15(16).

Nuclear magnetic resonance data and assignments (See Figure 1): ¹H-n.m.r. 400 MHz, CDCl₃ (s = singlet, d = doublet, t = triplet, c = quartet, q = quintet, m = multiplet): 12.4 (N-H, s, 2H); 7.36_o (d, 4 H, J = 7.6 Hz); 7.27_m (t, 4 H, J = 7.6 Hz); 7.21_p (d, 2 H, J = 7.6 Hz); 4.49_j (s, 4H); 3.42_a (s, 4H); 2.77_e (d, 4H, J = 6.8 Hz); 2.66_g (d, 4H, J = 7.2 Hz); 1.80_f (m, 4H); 1.85_b (m, 4H). The ¹³C NMR spectra data: 204.5_i; 169.9_d; 137.6_k; 129.3_o 128.4_m; 127.1_p; 116.9_h; 42.9_a 39.9_b; 38.0_j; 33.4_e; 32.7_g; 20.7_f.

Electronic spectral data, λ (cm⁻¹) (ϵ , M⁻¹cm⁻¹): 44,053 (10,250); 31,546 (10,780); 25,000 (15,410).

FT-IR vibrational spectra band positions and assignments, ν (cm⁻¹) (s = strong, m = medium, w = weak, br=broad): $\nu_{\text{N-H}}$, 3439m; $\nu_{\text{a(C=C)+v}_{\text{a(C=N)}}$, 1596s; $\nu_{\text{s(C=C)}}$, 1487m; $\nu_{\text{s(C=N)+v}_{\text{a(C=S)}}$, 1328w; $\nu_{\text{a(S-CH}_2)}$, 1272s; ρ -CH₂, 947w; $\nu_{\text{a(CSS-)}}$, 909m; $\nu_{\text{s(CSS-)}}$, 752w.

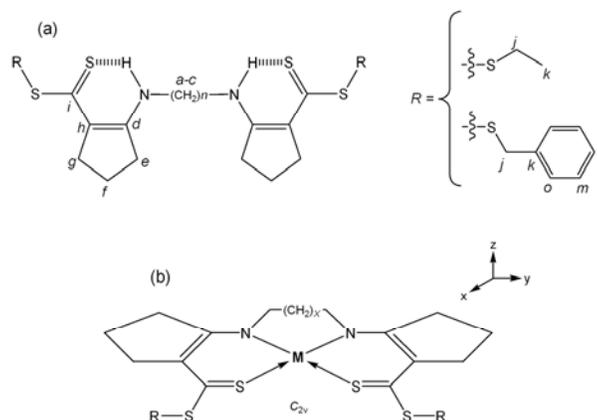


Fig. 1. (a) Proposed structure for the metal(II) complexes. L1: ethyl-N,N'-ethylenebis(2-amino-1-cyclopentencarbodithioate) with x=2; L2: ethyl-N,N'-propylenebis(2-amino-1-cyclopentencarbodithioate) with x=3; L3: ethyl-N,N'-butylenebis(2-amino-1-cyclopentencarbodithioate) with (x=4) and L4: benzyl-N,N'-butylenebis(2-amino-1-cyclopentencarbodithioate) with (x=4); ¹H- and ¹³C-NMR spectral data assignments scheme. (b) Structure proposed of the metallic complexes MLn with M = Ni(II) and Co(II) in C_{2v} symmetry

2.5 Metal complexes síntesis

A suspension of M^{II}[OAc]₂ (1 mmol) in MeOH (15 cm³) was added dropwise, with stirring to a solution of the appropriate ligand (1 mmol) in MeOH (20 cm³). After 1 h. reflux, the colored solids formed were dissolved in CH₂Cl₂, filtered through a glass fiber filter and vacuum dried. A minimum amount of MeOH was added to precipitate the complexes which were collected by suction using a Millipore® (0.8 μM) filter, vacuum dried and recrystallized from EtOH. All complexes formed decomposed above 150 °C. Metallic complexes colors and yields (%): NiL¹: intense red, 0.37 g (81%); NiL²: red, 0.34 g (73%); NiL³: red, 0.32 (67%); NiL⁴: brown reddish, 0.48 (79%); CoL¹: greenish brown, 0.34 g (74%); CoL²: brown, 0.37 g (80%); CoL³: brown, 0.43 (89%); CoL⁴: brown, 0.52 (86%).

Nickel(II) complexes. Elemental analysis:

NiL¹: found: C, 47.15; H, 5.68; N, 6.01; S, 27.78, calcd. for [C₁₈H₂₆N₂NiS₄]: C, 47.27; H, 5.73; N, 6.12; S, 28.04.

NiL²: found: C, 48.25; H, 5.86; N, 5.78; S, 26.81, calcd. for [C₁₉H₂₈N₂NiS₄]: C, 48.41; H, 5.99; N, 5.94; S, 27.21.

NiL³: found: C, 49.27; H, 6.02; N, 5.58; S, 26.23, calcd. for [C₂₀H₃₀N₂NiS₄]: C, 49.49; H, 6.23; N, 5.77; S, 26.42.

NiL⁴: found: C, 58.95; H, 5.36; N, 4.39; S, 20.79, calcd. for [C₃₀H₃₄N₂NiS₄]: C, 59.11; H, 5.62; N, 4.60; S, 21.04.

Derived molecular ions of the metallic isotopes observed in the mass spectrum: ⁵⁸Ni, P⁺ and ⁶⁰Ni, P⁺+2; NiL¹: 457.1; 459.2. NiL²: 471.1; 473.0. NiL³: 485.1; 487.3. NiL⁴: 609.1; 611.4.

Electronic spectral data, λ (cm⁻¹) (ϵ , M⁻¹cm⁻¹): NiL¹: 37,313 (9,500); 31,056 (9,700); 26,315 (10,500); 24,876 (11,500). NiL²: 36,630 (19,600); 31,152 (15,600); 26,317 (11,900); 25,189 (12,700). NiL³: 36,232 (16,600); 31,447

(18,800); 26,316 (20,100); 25,253 (19,000). NiL⁴: 31,645 (22,700); 25,773 (33,240); 24,813 (25,580); 20,284 (2,020); 15,625 (130).

FTIR vibrational spectra band positions and assignments, ν (cm⁻¹) (s = strong, m = medium, w = weak): NiL¹: $\nu_a(\text{C}=\text{C})+\nu_a(\text{C}=\text{N})$, 1580s; $\nu_s(\text{C}=\text{C})$, 1477s; $\nu_s(\text{C}=\text{N})+\nu_a(\text{C}=\text{S})$, 1315m; $\nu_a(\text{S}-\text{CH}_3)$, 1270s; $\rho-\text{CH}_2$, 951m; $\nu_a(\text{CS}_2\text{CH}_3)$, 917m; $\nu_s(\text{CS}_2\text{CH}_3)$, 769m; $\nu_s(\text{M}-\text{N})$, B₂, 522w; $\nu_a(\text{M}-\text{N})$, A₁, 456w. NiL²: 1581s; 1478s; 1321s; 1279s; 947m; 914m; 776w; 521w; 473w. NiL³: 1587s; 1488s; 1341s; 1274s; 950m; 916m; 746w; 523w; 437w. NiL⁴: 1591s; 1493s; 1337w; 1281m; 949w; 915w; 767w; 533w; 457w.

¹H-NMR 400 MHz, DMSO-*d*₆ (See Figure 1): NiL¹: 3.51*a,b*; 3.21*j*; 2.67*e*; 2.55*g*; 1.87*f*; 1.24*k*. NiL²: δ 3.34*a,b*; 3.23*j*; 2.63*e*; 2.59*g*; 1.85*b,f*. NiL³: 3.64*a*; 3.23*j*; 2.63*e*; 2.52*g*; 1.87*b,f*. NiL⁴: 7.39*o*; 7.28*m*; 7.27*p*; 4.53*j*; 3.46*a*; 2.80*e*; 2.70*g*; 1.85*f,b*.

Cyclic voltammetry: E_{ox} (V), E_{red} (V), E_{1/2}(V, *i* = irreversible), and couple: NiL¹: -0.40; -0.59; -0.50*i*; Ni^{II}/Ni^I. NiL²: -0.49 (E_{red}), Ni^{II}/Ni^I and 0.87 (E_{ox}), Ni^{III}/Ni^{II}. NiL³: -0.50; -0.73; -0.62*i*.

Cobalt(II) complexes. Elemental analysis:

CoL¹: found: C, 47.08; H, 5.47; N, 5.88; S, 27.79, calcd. for [C₁₈H₂₆N₂CoS₄]:C, 47.24; H, 5.73; N, 6.12; S, 28.03.

CoL²: found: C, 48.18; H, 5.64; N, 5.68; S, 26.91, calcd. for [C₁₉H₂₈N₂CoS₄]:C, 48.39; H, 5.98; N, 5.94; S, 27.20.

CoL³: found: C, 49.28; H, 6.09; N, 5.66; S, 26.14, calcd. for [C₂₀H₃₀N₂CoS₄]:C, 49.46; H, 6.23; N, 5.77; S, 26.41.

CoL⁴: found: C, 58.83; H, 5.49; N, 4.38; S, 20.90, calcd. for [C₃₀H₃₄N₂CoS₄]:C, 59.09; H, 5.62; N, 4.59; S, 21.03.

Derived molecular ions observed in the mass spectrum: ⁵⁹Co, P⁺; CoL¹: 457.2. CoL²: 471.4. CoL³: 485.1. CoL⁴: 610.2.

Electronic spectral data, λ (cm⁻¹) (ϵ , M⁻¹cm⁻¹): CoL¹: 31,348 (6,400); 26,316 (6,700); 24,938 (7,400). CoL²: 31,546 (10,700); 26,317 (11,100); 25,000 (13,100). CoL³: 31,545 (13,900); 26,315 (18,500); 25,062 (18,100). CoL⁴: 25,773 (15,150); 25,000 (12,510); 24,813 (25,580); 20,284 (2,020); 9,766 (99).

FTIR vibrational spectra band positions and assignments, ν (cm⁻¹) (s = strong, m = medium, w = weak): CoL₁: 1581s; 1478s; 1314m; 1269s; 950m; 916m; 767m; 526w; 457w. CoL₂: 1589s; 1478s; 1322s; 1273s; 951m; 914m; 770w; 520w; 465w. CoL₃: 1588s; 1479s; 1319m; 1275s; 950m; 915m; 747w; 523w; 456w.

Cyclic voltammetry, E_{ox} (V), E_{red} (V), E_{1/2}(V, *i* = irreversible), and couple: CoL¹: -0.60; -0.84; -0.72*i*, Co^{II}/Co^I. CoL²: -0.74 (E_{red}), Co^{II}/Co^I. CoL³: -0.53; -0.75; -0.64*i*.

The nonelectrolytic behavior of these compounds is evident from their low Λ_M values $\approx 1 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in PhNO₂.

3 Results and discussion

3.1 Mass spectrometry

The ligand and metallic complexes presented a low molar conductance which indicates a nonelectrolytic behavior, and consequently the formation of neutral nickel(II) and cobalt(II) complexes where the coordination sphere has been completely satisfied with 1:1 chelates. The metal(II) complex monomeric composition is suggested by the ⁵⁸Ni/⁶⁰Ni and ⁵⁹Co isotopes patterns (see experimental section), accompanied by a mass scan up to 2,000 m/z, to discard cluster impurities. The complexes fragmentation pattern is rather complicated but initial fragmentations certainly take place only at the peripheral parts of the molecule as evidenced by the presence of positives ions derived of the subsequent breakdown of a -CH₃, -SCH₂CH₃ and two -SCH₂CH₃ groups observed for L¹, L² and L³ or -CH₂C₆H₅ in L⁴. The L⁴ ligand showed also the tropylium ion characteristic of a benzyl group. The high intensity peaks corresponding to C₆H₆NS₂ and C₈H₁₁NS₂ fragments were also observed, a common pattern previously observed for ligands derived from cyclopentendithiocarboxylic acid (Contreras et al., 2005).

3.2 Electronic absorption spectra

Electronic spectral data for the M^{II}[N₂S₂] complexes are listed in the Experimental section. All the free ligand spectra exhibit three bands in the 37,000 – 24,000 cm⁻¹ region, their high intensities indicate $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ intraligand transitions characteristic of -C=C-, -C=N- and -C=S groups. All the observed bands are shifted to the red of the normal values reported for these chromophores (Silverstein et al., 2005), due to strong charge delocalization over the cyclopentene, the double bond, the nitrogen group and the carbodithioate group. All the complexes spectra are similar in the UV region where ligand absorptions predominate. The NiL⁴ electronic spectra exhibit one band at 15,625 cm⁻¹ assignable to *d-d* transition. The bands observed are assigned according to their energy to ³B₂ ← ³A₂ transitions, corresponding to a Ni(II) in C_{2v} symmetry, *d*⁸ (ground state derived from ³F). The CoL⁴ complexes exhibit spectra with *d-d* transitions at 9,766 cm⁻¹, assignable to ⁴B₂ ← ⁴A₂ transitions according to Co(II), C_{2v} symmetry, *d*⁷ (ground state derived from ⁴F). All complexes electronic spectra exhibit strong bands in the range 26,000 - 24,000 cm⁻¹ reported previously as S(thiolate) → M^{II}, *d*_π → *d*_σ and *d*_π → *d*_π bands respectively in M^{II}[N₂S₂] complexes with a coordination sphere distorted from planarity (Halcrow et al., 1994). The S → M^{II} LMCT bands has biomimetic importance, for example in the nickel-hydrogenase is observed at 33,000 – 22,000 cm⁻¹, while in Azurin substituted with cobalt(II) (Co^{II}Az) appears in the range 30,000 – 25,000 cm⁻¹ (Engeseth et al., 1982).

3.3 FTIR spectra

Ligand and metal complex IR bands are listed in the Experimental section. The band assignments have been made by comparison with analogue complexes of dithioamides, dithiocarboxylates and dithioester ligands (Nakamoto, 1997). The ligands show a strong broad band around 1590 cm^{-1} assigned to $\nu_a(\text{C}=\text{C})+\nu_a(\text{C}=\text{N})$, and a weak broad band centered at 3500 cm^{-1} corresponding to $\nu(\text{N-H})$ in secondary amines; these bands indicate important electron delocalization over the cyclopentene, the double bond, the nitrogen group and the carbodithioate group according to a bathochromic effect observed in electronic absorption bands. Metal imine complexation (*N,S*-chelated structure), with the \mathbf{L}^2 and \mathbf{L}^3 ligands is supported by the $\nu(\text{N-H})$ band disappearance and the 1590 cm^{-1} band red shifted, due to $\text{C}=\text{N}$ double bond character reduction, but maintaining the $\text{C}=\text{C}$ bond. The $\nu_a(\text{CS}_2\text{CH}_2^-)$ band splitting and the $\nu_s(\text{CS}_2\text{CH}_2^-)$ band hypsochromic effect, compared with the free ligand, indicate a monodentate carbodithioate group, similar to dithiocarbamate complexes reported (Nag et al., 1975; Nag et al., 1980). Assuming metallic center C_{2v} symmetry, the $\text{M}^{\text{II}}-\text{N}_2$ group exhibits in the infrared range two $\text{M}^{\text{II}}-\text{N}$ bands: $\nu_a[\text{M}^{\text{II}}-\text{N}]$ stretching (B_2 mode) near 520 cm^{-1} ; $\nu_a[\text{M}^{\text{II}}-\text{N}]$ stretching (A_1 mode) at 470 cm^{-1} , similar to values reported for the $\text{M}(\text{II})-\text{N}$ bond (Ferraro, 1971).

3.4 NMR spectra

The room temperature $^1\text{H-NMR}$ spectra peak positions and assignments for the \mathbf{L}^1 , \mathbf{L}^2 , \mathbf{L}^3 and \mathbf{L}^4 compounds and the Ni complexes are given in the Experimental section. (see Fig. 1). In all cases, the nickel complexes spectra show variations compared with the free ligands, some peak displacements and superpositions. Peak areas and coupling changes, compared with the ligands, helped in chemical shift assignments for metal complex spectra. The first change observed is the N-H signal disappearance, implying metal substitution; the decrease in multiplicity of the vicinal protons (*c*- CH_2) and a shift to lower frequency, characteristic of protons close to a coordinated nitrogen. The protons that are located further from the coordinated nitrogen show little chemical shift change. The cyclopentene protons (*d*- CH_2 and *f*- CH_2) are shifted to lower frequency as a result of the inductive effects, due to metal coordination and electronic delocalization through the chelate ring formed (Drago, 1966).

3.5 Electrochemistry

Cyclic voltammetry of the metal(II) complexes ($1.10^{-4}\text{ mol L}^{-1}$, CH_2Cl_2 solutions) versus $\text{Ag}/\text{Ag}^+/\text{NO}_3^-$ (+ 1.3 to -1.2 V range at 100 mV s^{-1} scan rate) show two redox processes in the -0.73 to -0.40 V range. We attribute these redox processes to $[\text{M}^{\text{II}}\text{L}^n]^{2+} \rightarrow [\text{M}^{\text{I}}\text{L}^n]^+$ generic nickel and cobalt complexes reduction. Peak current ratios (i_{pc}/i_{pa}) over the

500 to 50 mV s^{-1} scan rates and peak to peak separation indicates a slow irreversible electrochemical process (Hamann et al., 2007; Gosser, 1993). Additionally, the NiL^2 complex showed an $[\text{Ni}^{\text{II}}\text{L}^n]^{2+} \rightarrow [\text{Ni}^{\text{III}}\text{L}^n]^{3+}$ oxidation process around +0.87 mV. The presence of this couple in the nickel complexes is interesting since the redox process in nickel hydrogenases corresponds to a reversible nickel(II) to nickel(III) oxidation at low potential in planar geometries (Holm et al., 1996). Cobalt complexes showed a $[\text{Co}^{\text{II}}\text{L}^n]^{2+} \rightarrow [\text{Co}^{\text{III}}\text{L}^n]^{3+}$ couple for \mathbf{L}^2 with oxidation potential of 0,15 V. This probably is explained by considering the stabilization of cobalt(III) with the \mathbf{L}^2 ligand that favors planar symmetry.

3.6 Crystallization

We have already made numerous efforts to crystallize the complexes for X-ray diffraction studies. However, until now, no single crystals have been obtained.

4 Conclusions

Nickel(II) and cobalt(II) metal complexes with the new nitrogen-sulphur ligands ethyl-*N,N'*-alkylbis(2-amino-1-cyclopentencarbodithioate) with alkyl = ethylene (\mathbf{L}^1), propylene (\mathbf{L}^2), butyl (\mathbf{L}^3) and benzyl-*N,N'*-butyl-bis(2-amino-1-cyclopentencarbodithioate) (\mathbf{L}^4), have been prepared and characterized. FTIR and $^1\text{H-NMR}$ corroborated the metal imino quelating type $\text{M}^{\text{II}}(\text{N}_2\text{S}_2)$; mass spectra and elemental analysis indicates a mononuclear M^{II} complexes containing one ligand. Cyclic voltammetric studies show irreversible $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ and $\text{M}^{\text{II}}/\text{M}^{\text{I}}$ (Ni, Co) couples. The $\text{S} \rightarrow \text{M}^{\text{II}}$ LMCT bands observed in the $26,000 - 24,000\text{ cm}^{-1}$ range have biomimetic importance, for example in the nickel-hydrogenase is observed at $33,000 - 22,000\text{ cm}^{-1}$, while in azurin substituted with cobalt(II) ($\text{Co}^{\text{II}}\text{Azurin}$) appears in the $30,000 - 25,000\text{ cm}^{-1}$ range. The spectroscopic and electrochemical properties observed by metallic complexes have a potential importance as models in inorganic biomimetic.

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