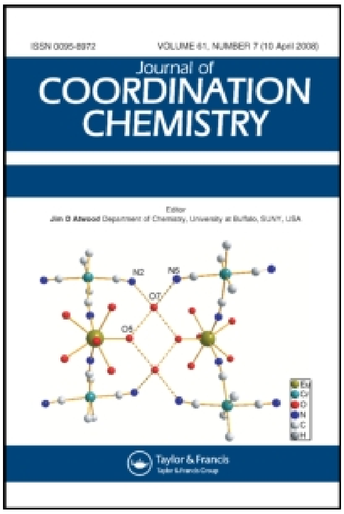

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Thermodynamic stability and crystal structure of lanthanide complexes with di-2-pyridyl ketone‖

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The di-2-pyridylketone ligand (dpk) exhibits several coordination modes and is a good candidate for preparation of a variety of metal complexes. In this work we present a potentiometric study (in water and in ethanol : water mixtures) of Ln-dpk and Cu(II)-dpk complexes. The thermodynamic stability of the species with La, Sm and Yb is compared to that of Cu(II). In addition, $[Ln(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ $(Ln = Pr, Sm, Gd)$ and $[Cu(SCN)_2\{(py)_2C(OEt)(OH)\}]_2 \cdot 2EtOH$ have been prepared and characterized by X-ray diffraction.

Keywords: Di-2-pyridylketone; Lanthanide complexes; Copper(II) complexes; Crystal structure; Chemical speciation

1. Introduction

Neutral di-2-pyridylketone [dpk, $(py)_2CO$] has three potential donor groups, the two 2-pyridyl nitrogens and the carbonyl oxygen [figure 1(a)]. Many complexes containing this ligand can be found in the literature, mostly with 3d metal ions [1–4]. Upon metal-promoted solvation, the ligand exhibits four donor sites [figure 1(b)], and can chelate either in the protonated or deprotonated state. The presence of deprotonated hydroxy groups produces coordination flexibility [figure 1(c)] which has been used in the synthesis of mononuclear [1, 5–12] and polynuclear complexes [13–23].

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‖Dedicated to Professor Alfredo Mederos on the occasion of his retirement as Professor of Inorganic Chemistry of Universidad de La Laguna, Tenerife, Spain.

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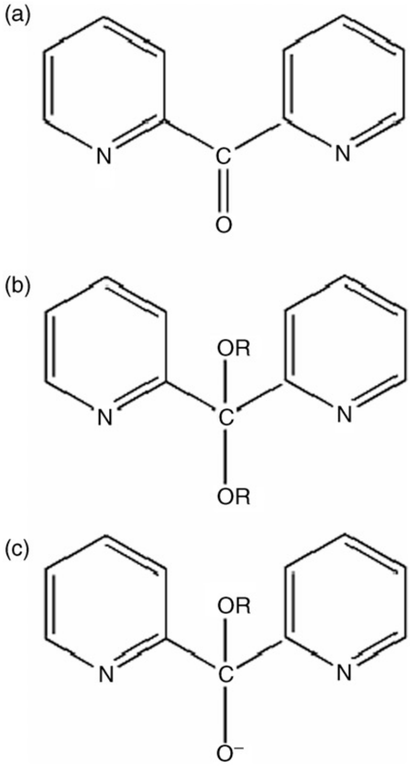

Figure 1. Schematic representation of dpk and its derivatives. R = H, Me, Et.

Recently, the interaction of dpk with lanthanide ions (Ln) has begun to be explored. The structures of the mononuclear $[Er(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ and the dinuclear $[Er_2(NCS)_3\{(py)_2C(OMe)O\}_3]$ and $[Er_2(NO_3)_3\{py)_2C(OMe)O\}_2\{(py)_2C(OH)O\}]$ complexes [24, 25] reveal that Ln ions also promote solvation of the ligand. In these complexes, dpk can coordinate as the neutral solvated [$(py)_2C(OR)(OH)$; R = Et, Me] or as the deprotonated solvated [$(py)_2C(OR)(O)$; R = Me, H] ligand. In the latter, the formation of polynuclear compounds containing a dpk bridge is verified. The complexes exhibit interesting photoluminescence.

In this work we present a potentiometric study (in water and in ethanol : water 1 : 1, v : v mixtures) of the Ln(III)–dpk complexes. The thermodynamic stability of the species with La, Sm and Yb is compared to that of Cu(II). In addition, $[Ln(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ (Ln = Pr, Sm, Gd) and $[Cu(SCN)_2\{(py)_2C(OEt)(OH)\}]_2 \cdot 2EtOH$ have been characterized by X-ray diffraction.

2. Experimental

2.1. *General*

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. $LaCl_3 \cdot 7H_2O$, $SmCl_3 \cdot 6H_2O$,

$YbCl_3 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were used as metal sources for the potentiometric titrations. The dpk acid solutions were prepared by weighing the Sigma reagent and adding HCl stock solution.

The infrared spectra, as KBr pellets, were obtained from a Bomen MB 102 FT-IR spectrophotometer. Elemental analysis (C, H, N, S) was performed on a Carlo Erba EA 1108 instrument.

2.2. *Potentiometric titrations*

Solutions of the metals were standardized according to standard techniques [26]. Solutions were freed of carbon dioxide by Ar bubbling. Standard HCl solutions were prepared from Merck standard ampoules. The titrant solutions [0.1 M solution of $Me_4N(OH)$ in 0.5 M Me_4NCl] were prepared by dissolving $Me_4N(OH) \cdot 5H_2O$ (Fluka) in water or water : ethanol (1 : 1, v : v) and standardized with potassium biphthalate.

The protonation constants of the ligand (dpk) were determined in water or water : ethanol (1 : 1, v : v; $pK_w = 14.26$) mixtures through three potentiometric titrations (ca. 100 experimental points each) in the concentration range 3–10 mM. The Ln(III) hydrolysis constants (Ln = La, Sm, Yb) in water : ethanol were analogously determined covering pH values between 2 and those causing precipitation of the corresponding hydroxide. Those in water were taken from previously reported studies [27, 28], except for Yb hydrolysis constants that were also determined in this work.

The behavior of dpk in the presence of Cu(II), La(III), Sm(III) and Yb(III) ions was analyzed through at least five potentiometric titrations (ca 100 experimental points each) at concentrations ranging from 2 to 5 mM, and dpk : metal ion molar ratios varying from 0.5 to 5.

In all cases, the solutions were poured into a 20 mL titration cell. After thermal equilibrium was reached, hydrogen ion concentrations were determined in successive readings, each performed after a small incremental addition of standard 0.1 M $Me_4N(OH)$ solution. The titrant was added from a Metrohm 765 Dosimat autoburette. The e.m.f. was recorded by a Metrohm 713 pH meter using a glass electrode and a Ag/AgCl reference electrode. A BASIC program [29] was used to monitor each titration point. The ionic strength was kept constant throughout the titrations by using solutions containing 0.5 M Me_4NCl and relatively low concentrations of the metal ions. Pre-saturated argon (free of CO_2) was bubbled through the solutions during titrations to eliminate the effect of atmospheric carbon dioxide, and the temperature was kept at 25.0 (±0.1)°C. The cell constants E° and the liquid junction potentials were determined according to the methods of Biedermann and Sillén [30] and Liberti and Light [31], both in water or water : ethanol (1 : 1, v : v) mixtures. Data were analyzed using the HYPERQUAD program [32] and species distribution diagrams were produced using the HySS program [33]. The fit of the values predicted by the model to the experimental data was estimated on the basis of the parameter σ, corresponding to the scaled sum of square differences between predicted and experimental values.

2.3. *Preparation of complexes*

2.3.1. $[Ln(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ [Ln = Pr (1), Sm (2), Gd (3)]. About 3 mmol (291 mg) of KSCN was dissolved in 11.5 mL of hot ethanol. Then, $LnCl_3 \cdot 6H_2O$

(1 mmol) was added and the mixture stirred at room temperature for 30 min. A white solid of KCl was removed by filtration and a clear solution (solution A) was obtained. Also, 0.4 mmol (74 mg) of dpk was dissolved in 7 mL of ethanol (solution B). To 2.5 mL of solution A, 1 mL of ethanol was slowly added avoiding the premature mixing of the solutions. Then 7 mL of solution B was added as a third layer on top. The mixture was allowed to diffuse in a closed container over 2–3 days. A polycrystalline solid (containing some X-ray suitable crystals) was obtained, collected by filtration and washed with ethanol. Yield: 78% (**1**), 75% (**2**) and 63% (**3**). Anal. Calcd for **1**, $C_{42}H_{42}N_9O_6S_3Pr$ (%): C, 50.1; H, 4.2; N, 12.6; S, 9.6. Found: C, 50.9; H, 4.2; N, 12.8; S, 9.5. Anal. Calcd for **2**, $C_{42}H_{42}N_9O_6S_3Sm$ (%): C, 49.7; H, 4.2; N, 12.4; S, 9.5. Found: C, 48.6; H, 3.9; N, 11.9; S, 9.3. Anal. Calcd for **3**, $C_{42}H_{42}N_9O_6S_3Gd$ (%): C, 49.3; H, 4.1; N, 12.3; S, 9.4. Found: C, 49.6; H, 3.9; N, 12.6; S, 9.4.

2.3.2. $[Cu(SCN)_2\{(py)_2C(OEt)(OH)\}]_2 \cdot 2EtOH$ (4). About 0.39 mmol (72 mg) of dpk and 0.79 mmol (60 mg) of NH_4SCN were dissolved in 20 mL ethanol. Also, 0.40 mmol (97 mg) of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 10 mL ethanol was added and the resulting mixture was allowed to stand at room temperature in a closed container. A polycrystalline green solid (containing some X-ray suitable crystals) was obtained, collected by filtration and washed with ethanol. Yield: 75% based on Cu(II). Anal. Calcd for **4**, $C_{34}H_{40}N_8O_6S_4Cu_2$ (%): C, 44.8; H, 4.4; N, 12.3; S, 14.1. Found: C, 43.8; H, 4.0; N, 12.9; S, 14.7.

Alternatively, **4** can be obtained from **2**. 0.049 mmol (50 mg) of **2** and 0.099 mmol (17 mg) of $CuCl_2 \cdot 2H_2O$ were dissolved in EtOH (8 mL). The mixture was stirred at room temperature for 30 min and the resulting solution was filtered through paper. After slow evaporation of the solvent, green crystals of **4** were obtained. Yield: 30% (based on Cu).

2.4. *X-ray crystallography*

Diffraction data of **1** and **3** were collected at room temperature using a Bruker–Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Frames were collected with the COLLECT program [34], indexed and processed using Denzo SMN and the files scaled together using the HKL2000 program [35]. The absorption correction was applied using a semi-empirical method based on multiple scanned reflections on PLATON program [36]. The structure solution was obtained by direct methods using the SIR2004 program [37] and refined using the SHELXL-97 program [38]. All H atoms were placed in geometrically calculated positions. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. All other H atoms were allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The rest of the atoms were refined with anisotropic thermal.

The crystallographic data of **2** and **4** were collected on a Bruker P4 diffractometer at 173 K. The structures were solved by direct methods using SIR2004 [37] and refined by a full-matrix least-squares method on F^2 using SHELXL-97 [38]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model. SADABS [39] was used to perform area-detector scaling and absorption corrections.

Crystallographic details for structures **1**–**4** are summarized in table 1.

Table 1. Crystallographic data and structure refinements for **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{42}H_{42}N_9O_6PrS_3$	$C_{42}H_{42}N_9O_6S_3Sm$	$C_{42}H_{42}GdN_9O_6S_3$	$C_{34}H_{40}Cu_2N_8O_6S_4$
Formula weight	1005.97	1015.38	1022.31	912.06
Crystal system	Trigonal	Trigonal	Trigonal	Monoclinic
Space group	$P3_1$	$P3_1$	$P3_1$	$C2/c$
Unit cell dimensions (Å, °)				
a	12.335(1)	12.114(5)	12.198(1)	17.428(5)
b	12.335(1)	12.114(5)	12.198(1)	14.972(5)
c	29.494(1)	28.929(5)	29.281(1)	17.784(5)
α	90	90	90	90
β	90	90	90	119.115(5)
γ	120	120	120	90
V	3886.4(5)	3677(2)	3773.1(5)	4067(2)
Z	3	3	3	4
D_{Calcd} (g cm^{-3})	1.289	1.368	1.350	1.490
$F(000)$	1536	1536	1551	1880
μ (mm^{-1})	1.110	1.377	1.493	1.304
R_1 [$I > 2\sigma(I)$]	0.0740	0.0340	0.0461	0.0398
wR_2 [$I > 2\sigma(I)$]	0.1287	0.0868	0.1057	0.1128

Table 2. Protonation constants of dpk and formation constants for Cu–dpk complexes at 25.0°C, $I = 0.5$ M Me_4NCl, in water and water : ethanol (1 : 1, v : v).

Equilibrium	log K, water	σ	log K, water : ethanol	σ
$HL + H^+ \leftrightarrow H_2L^+$	2.965(6)	1.4	2.307(7)	1.5
$HL \leftrightarrow L^- + H^+$	−13.15(7)		−12.70(3)	
$Cu^{2+} + HL + H_2O \leftrightarrow [CuL(OH)] + 2H^+$	−5.92(7)	0.1		1.2
$Cu^{2+} + HL \leftrightarrow [CuL]^+ + H^+$	−1.5(1)		−2.43(6)	
$Cu^{2+} + HL \leftrightarrow [Cu(HL)]^{2+}$	4.1(1)		2.7(1)	
$Cu^{2+} + 2HL \leftrightarrow [Cu(HL)_2]^{2+}$	7.92(7)		5.71(5)	
$Cu^{2+} + 2HL \leftrightarrow [CuL_2] + 2H^+$	−3.0(2)		−7.6(1)	

HL represents the neutral form of the ligand.

3. Results and discussion

3.1. *Chemical speciation*

The obtained data of protonation constants of the ligand and the stability constants of Cu(II)-dpk species in water and water : ethanol are depicted in table 2. The log K values for dpk are in line with those previously reported in water [40, 41]. The ligand can be protonated at one of the nitrogens and, at very high pH values, a mono-protonated geminal diol is formed. The protonation constants slightly change when the solvent contains ethanol. Dpk is less basic in water: ethanol while acidity of the geminal diol is enhanced in this medium.

Stable Cu(II)-dpk species were detected in both solvents, with 1 : 1 or 1 : 2 stoichiometry and the ligand in the neutral or deprotonated form. Figure 2 shows the species distribution diagrams in both solvents. Dpk exhibits better coordination capability in water. This is reflected in the almost 20% of free copper ion detected at acidic pH values for the ethanol-containing mixture. In neutral or basic aqueous

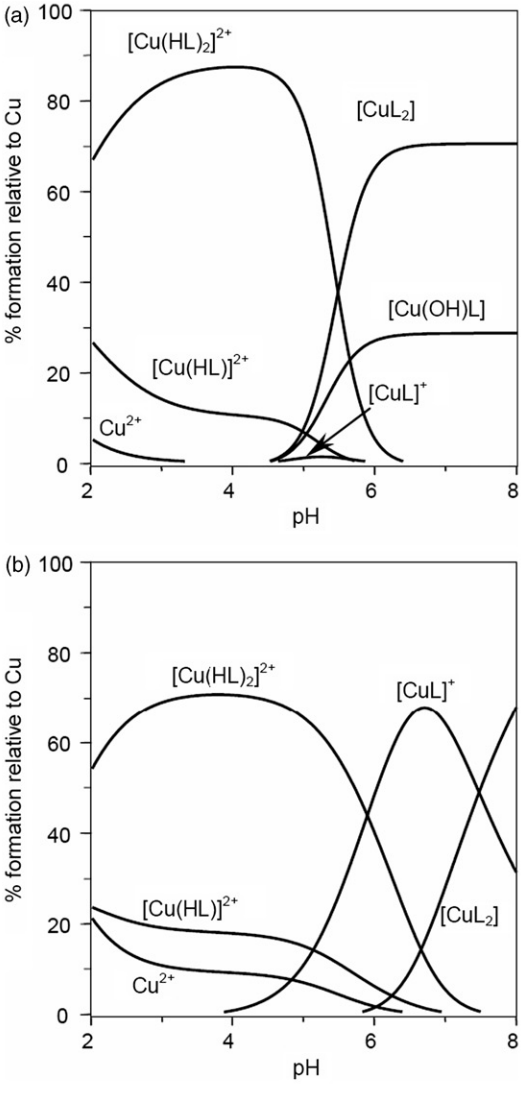

Figure 2. Species distribution diagram for the Cu(II)–dpk system: (a) water (b) water : ethanol (1 : 1, v : v). In all cases, [dpk] = 20 mM, [Cu] = 10 mM, $T = 25.0^\circ C$, and $I = 0.5$ M Me_4NCl.

media Cu(II) is fully complexed and $[CuL_2]$ predominates over pH 6, while in water: ethanol $[CuL]^+$ (around pH 7) and $[CuL_2]$ (over pH 8) are predominant.

Table 3 shows the stability constants of the complexes Ln(III)–dpk (Ln = La, Sm, Yb) in water and water: ethanol. Species with 1 : 1 and 1 : 2 stoichiometry are detected in water. The stability constants are almost the same among the Ln ions. In water : ethanol, 2 : 1 species are not detected, while 1 : 1 species exhibit lower stability. Figure 3 compares the chemical speciation of the Sm–dpk system in both solvents. The lanthanide ion is fully complexed in water, predominating as $[SmL]^{2+}$ at pH 4.5, and as $[SmL_2]^+$ over pH 8. In water : ethanol, and under the same conditions, around 10% of Sm(III) remains free at acidic pH values, while $[SmL]^+$ predominates above pH 8.

Table 3. Hydrolysis of lanthanide ions and formation constants for Ln–dpk complexes, 25.0°C, $I = 0.5$ M, in water and water : ethanol (1 : 1, v : v).

	log *K*, water			log *K*, water : ethanol		
Equilibrium	La(III)	Sm(III)	Yb(III)	La(III)	Sm(III)	Yb(III)
$Ln^{3+} + H_2O \leftrightarrow [Ln(OH)]^{2+} + H^+$			−7.5(1)	−7.27(3)	−7.35(5)	−7.14(3)
$Ln^{3+} + HL \leftrightarrow [LnL]^{2+} + H^+$	1.52(4)	1.54(2)	1.99(5)	−0.29(2)	−3.83(4)	−3.82(4)
$Ln^{3+} + HL \leftrightarrow [Ln(HL)]^{3+}$	4.44(5)	4.41(2)	4.92(5)	1.7(1)	2.89(3)	2.26(6)
$Ln^{3+} + 2HL \leftrightarrow [LnL_2]^{+} + 2H^+$	−2.8(2)	−2.8(1)	−1.0(2)			
σ	0.6	0.3	0.7	2.1	1.2	0.3

HL represents the neutral form of the ligand. The σ value obtained for Yb(III) hydrolysis was $\sigma = 0.1$, and for the Ln(III) hydrolysis in water : ethanol (1 : 1, v : v) was $\sigma = 0.9$ in the three cases.

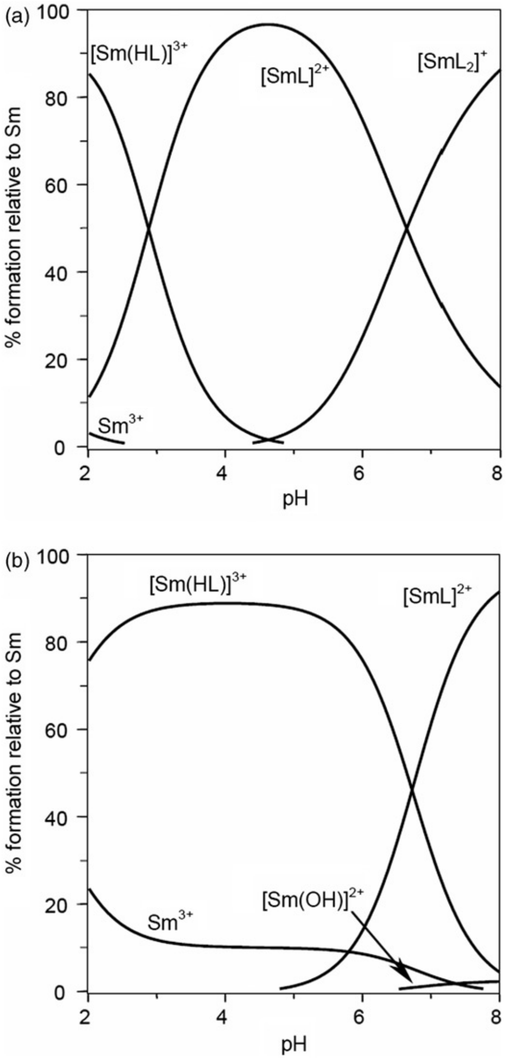

Figure 3. Species distribution diagram for the Sm(III)–dpk system: (a) water (b) water : ethanol (1 : 1, v : v). In all cases, [dpk] = 20 mM, [Sm] = 10 mM, $T = 25.0$°C, and $I = 0.5$ M Me_4NCl.

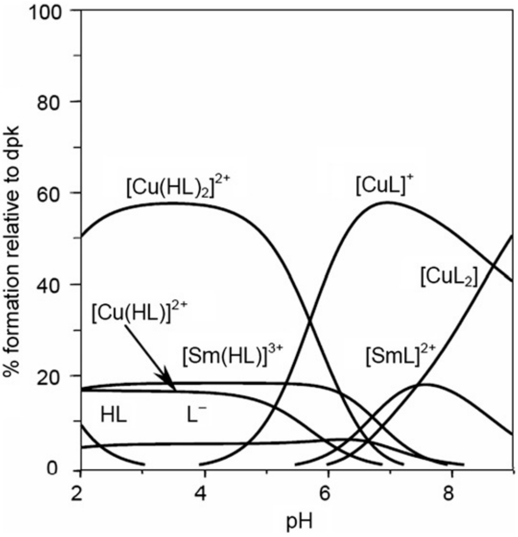

Figure 4. Species distribution diagram for a system containing dpk, Cu(II) and Sm(III) in water : ethanol (1 : 1, v : v). [dpk] = 30 mM, [Cu] = 20 mM, [Sm] = 10 mM, $T = 25.0$°C, and $I = 0.5$ M Me_4NCl.

The synthesis of **4** starting from **2** (see further) can be foreseen through a simulation including both ions. This is shown in figure 4 for [dpk] = 30 mmol, $[Cu^{2+}] = 20$ mM, $[Sm^{3+}] = 10$ mM, $T = 25.0$°C, and $I = 0.5$ M Me_4NCl in water : ethanol (1 : 1, v : v). The ligand is predominantly bound to Cu(II) in the whole pH range, with only a modest contribution (less than 20%) of Sm(III) species.

3.2. *Synthesis*

Complexes **1**–**3** with formula $[Ln(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ (Ln = Pr, Sm, Gd) were prepared by the direct reaction of the preformed $[Ln(NCS)_3]$ core and dpk. The reaction in ethanol produces the addition of the solvent to dpk and the formation of the ligand $[(py)_2C(OEt)(OH)]$. The IR spectra of these Ln complexes present the ν(OH) vibrations of the alcoholated dpk at 3424 (**1**), 3435 (**2**) and 3449 (**3**) cm^{-1}. The deformation bands of the OH groups could not be unambiguously assigned. The ν(CN) mode of the thiocyanate ligand appears at 2043 (**1**), 2052 (**2**) and 2054 (**3**) cm^{-1}, indicating that the anion is coordinated through the nitrogen [42]. These ν(CN) bands are split into two components, as previously reported in other complexes containing the $[Ln(NCS)_3]$ core [43]. Slight differences in the three NCS anions (see below) would account for this splitting. Although it is difficult to assign ν(CS) in these complexes because of the presence of the pyridyl deformations, a careful comparison of IR spectra of the ligand and the complexes reveals that a sharp band around 802 cm^{-1} is present in the complexes. It could be assigned to ν(CS), also suggesting an N-bonded isothiocyanate [42].

The complexes do not exhibit the characteristic ν(C=O) vibration of dpk (1684 cm^{-1} in the free ligand) due to solvolysis. In the same region a strong band around 1600 cm^{-1} is present, being assigned as a 2-pyridyl coordinated stretching mode (1582 cm^{-1} in the free ligand) [22, 44]. Prominent bands at ca. 1050, 760 and 640 cm^{-1} can be assigned to pyridyl ring breathing, pyridyl C–H out-of-plane bending and in-plane pyridyl ring deformation vibrations, respectively [17, 24].

The green complex **4** can be obtained from a stoichiometric mixture of Cu^{2+}, dpk and SCN^- in ethanol. The IR spectrum shows a split ν(CN) band at 2118 and 2094 cm^{-1} (N-coordination), ν(OH) vibration of the alcoholated dpk at 3405 cm^{-1} and the ν(CO) vibration of dpk at 1608 cm^{-1}. The presence of two well-defined bands in the ν(CN) region is a consequence of the presence of bridging (2118 cm^{-1}) and terminal (2094 cm^{-1}) NCS groups [42], in line with the crystal structure discussed subsequently.

A comparison of the IR spectra of **1**–**4** suggests similar coordination mode of dpk and NCS^-. With this in mind and taking into account the chemical speciation of figure 4, we have prepared **4** starting from **2**. The same green compound with identical composition and IR spectrum was obtained.

3.3. *Description of the structures*

The three compounds **1**–**3** are isostructural with the previously reported $[Er(NCS)_3\{(py)_2C(OEt)(OH)\}_3]\cdot 0.3EtOH\cdot 0.4H_2O$ [24]. They will be described together using **1** as a model compound. Figure 5 shows the atomic disposition, as well as the labeling scheme. Selected interatomic distances and angles are listed in table 4. The crystal structure consists of discrete $[Pr(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ units. The ligand dpk appears as the neutral $[(py)_2C(OEt)(OH)]$, forming a 5-membered chelating ring using one 2-pyridyl N atom and the hydroxyl O atom as donor atoms. The ethoxy O atoms and the other 2-pyridyl N atom remain unbonded.

The lanthanide ion is 9-coordinated, surrounded by three N atoms from three NCS^- ligands, three 2-pyridyl N atoms from three $[(py)_2C(OEt)(OH)]$ ligands, and three O atoms from the hydroxyl group also belonging to $[(py)_2C(OEt)(OH)]$. Geometry around the central atom can be described as a tricapped trigonal prism. The trigonal faces are determined by the N atoms of the NCS^- ligands

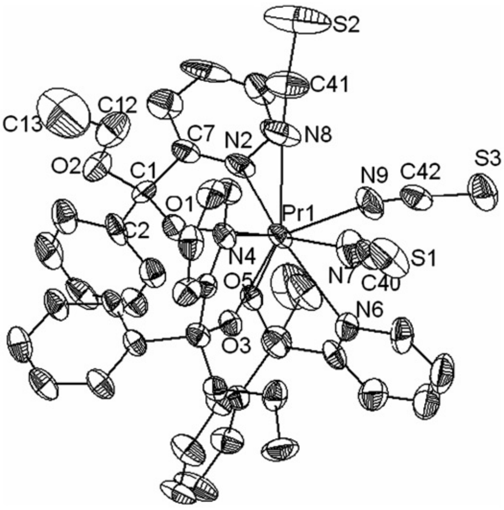

Figure 5. The structure of the mononuclear $[Pr(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability.

Table 4. Selected bond distances (Å) and angles (°) for **1**–**3**.

	1	**2**	**3**
Ln–O1	2.527(9)	2.449(2)	2.436(5)
Ln–O3	2.498(8)	2.438(3)	2.423(3)
Ln–O5	2.515(9)	2.457(3)	2.416(5)
Ln–N2	2.767(9)	2.726(4)	2.696(6)
Ln–N4	2.802(10)	2.706(4)	2.726(6)
Ln–N6	2.783(12)	2.690(4)	2.707(6)
Ln–N7	2.533(15)	2.465(4)	2.457(7)
Ln–N8	2.541(13)	2.454(4)	2.439(6)
Ln–N9	2.521(12)	2.34(2)	2.412(7)
N2–Ln–O1	60.1(2)	60.1(9)	60.5(2)
N4–Ln–O3	59.6(3)	59.8(1)	60.4(2)
N6–Ln–O5	57.8(3)	60.2(9)	59.7(2)
N8–Ln–N9	80.4(5)	76.7(6)	79.8(3)
N8–Ln–N7	82.1(4)	80.18(15)	83.0(3)
N9–Ln–N7	80.6(5)	75.9(7)	80.8(3)
N8–C41–S2	174.6(2)	178.8(5)	173.2(1)
N9–C42–S3	178.0(1)	168(3)	178.7(9)
N7–C40–S1	175.6(1)	179.8(6)	178.7(8)

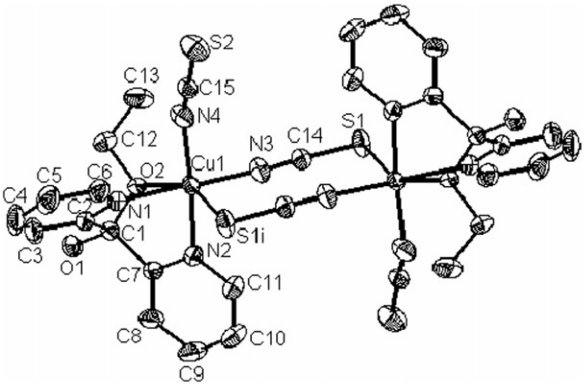

Figure 6. Coordination environment of Cu(II) ions in the dinuclear unit $[Cu(SCN)_2\{(py)_2C(OEt)(OH)\}]_2$. Uncoordinated solvent EtOH and hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability.

(average distance 2.532 Å) and the three O atoms (average distance 2.513 Å). The other three N capping atoms are located at longer distances (average 2.784 Å) and belong to the alcoholated dpk.

The structure of **4** consists of copper(II) dimers connected through di-μ(1,3)-NCS bridges (figure 6 and table 5). Each Cu is hexa-coordinated. The alcoholated dpk is tridentate, bonded to Cu(II) through the two N atoms (average distance 2.027 Å) and the ethoxy O atom (at 2.575 Å). Two nitrogen atoms (average distance 1.950 Å) and one sulphur atom (at 2.925 Å) belonging to three NCS^- ligands complete the coordination sphere. The terdentate chelation of $[(py)_2C(OEt)(OH)]$ together with Jahn–Teller distortion provoke a large deviation of the ideal octahedral geometry. The axial distances Cu–S1 and Cu–O2 are remarkably longer than the equatorial ones.

Table 5. Selected bond distances (Å) and angles (°) for **4**.

Cu1–N1	2.0332(16)	Cu1–S1i	2.9250(9)
Cu1–N2	2.0204(16)	N3–C14	1.158(3)
Cu1–N3	1.9448(17)	C14–S1	1.637(2)
Cu1–N4	1.9547(19)	N4–C15	1.154(3)
Cu1–O2	2.5755(17)	C15–S2	1.621(2)
N3–C14–S1	179.8(3)	N4–Cu1–N2	174.87(8)
N4–C15–S2	179.9(2)	N4–Cu1–N1	89.37(8)
N4–Cu1–N3	91.86(8)	N4–Cu1–O2	105.12(7)
N4–Cu1–S1i	91.21(6)	N3–Cu1–S1i	94.46(6)

Symmetry transformation: (i) $0.5 + x$, $0.5 - y$, $-0.5 + z$.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 689525–689528. A copy of this information may be obtained via http://www.ccdc.cam.ac.uk or from The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44)1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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