Polyhedron 69 (2014) 181-187

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Divalent transition metal(II) complexes of two heterocyclic ligands with pendant pyridinyl groups: Synthesis, characterization and electrochemistry



^a Department of Chemistry, Nanchang University, Nanchang 330031, China

^b College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, China ^c School of Chemistry, University of East Anglia, Norwich NR4 7TJ, United Kingdom

ARTICLE INFO

Article history: Received 4 September 2013 Accepted 18 November 2013 Available online 1 December 2013

Keywords: Macrocyclic ligands Transition metal ions Crystal structures Pyridinyl derivatives Electrochemistry

ABSTRACT

Treatment of the pentadentate macrocyclic ligand 4-(pyridin-2-ylmethyl)-1,7-dithia-4,10-diazacyclododecane, **L**, and the hexadentate macrocyclic ligand 4,10-bis(pyridin-2-ylmethyl)-1,7-dithia-4,10-diazacyclododecane, **L**', with one equivalent of a M^{2+} metal salt (M = Co, Ni, Cu) in methanol yielded six mononuclear complexes, [CoL(MeCN)](ClO₄)₂ (1), [NiL(H₂O)]Cl₂ (2), [CuL(MeCN)](ClO₄)₂ (3) and [ML'](ClO₄)₂ (4–6). Their solid state crystal structures were determined using X-ray single crystal diffraction analysis. In complexes 1–3, the metal centres exhibit a slightly distorted octahedral geometry, resulting from the coordination of three nitrogen and two sulfur donating atoms in the ligand **L** and one solvent molecule (MeCN for complexes 1 and 3, water for complex 2) whereas in complexes 4–6, the coordination around the metal centres was satisfied by four nitrogen and two sulfur atoms from the ligand **L**'. The electronic spectra and electrochemistry of these complexes are reported.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Busch was the first to show that thioether macrocyclic ligands effectively bind transition metal ions [1]. Since then, the development of macrocyclic ligand assemblies continues to being stimulated in that such ligands form transition metal complexes with tunable physicochemical and functional properties, and thus these complexes have diverse application in pharmaceuticals [2], solar cells as photosensitizers [3], organic transformations as catalysts [4], molecular devices [5], mimics of metalloenzymes [6] and catalytic hydrolysis [7].

Macrocyclic ligands with pendant substituents on the rings have become important since the pendant arms render manoeuvrability to further tune the properties of their transition metal complexes to achieve particular functionalities [8–12]. Although the macrocycle ring size largely controls the coordination chemistry, the pendant substituents on the ring also make contributions [13–16]. For example, macrocycles armed with substituents of a π -accepting nature can enhance the stability of the low oxidation state of a transition metal ion, whereas a moiety of only σ -donating capability can stabilise a transition metal ion of a high oxidation state. The pyridinyl group is both a σ -donor and π -acceptor, with moderate strength in the spectrochemical series [17]. It shows strong binding ability towards transition metal ions and is effective in stabilising low oxidation states of metal ions.

In recent years, we have been interested in synthesizing ligands bearing pyridinyl groups, as well as their transition metal complexes. Of the reported ligands of this type were macrocyclic ligands containing an "NS" donor-set [18-22]. In previous work, novel ligands were designed, synthesized and reacted with transition metal ions; some were found to have potential applications in recognition towards Cu²⁺ and Hg²⁺ ions [23-25]. In this work, as part of our continued efforts in investigating the role of donor atoms in the stability of complexes, we have prepared a macrocyclic ligand possessing an {N₃S₂}-donor set, with one pendant pyridinyl arm, 4-(pyridin-2-ylmethyl)-1,7-dithia-4,10-diazacyclododecane (L), [23] and a macrocyclic ligand possessing an {N₄S₂}-donor set with two pendant pyridinyl arms, 4,10-bis(pyridin-2-ylmethyl)-1,7-dithia-4,10-diazacyclododecane (L'); their Co^{2+} , Ni²⁺ and Cu^{2+} complexes were also synthesized. The structures of these complexes were established using both X-ray crystallographic analysis and microanalysis. The electronic properties of the complexes were investigated using UV-Vis spectroscopic techniques and cyclic voltammetry. Our results revealed that the complexes coordinated with L' exhibited improved reversibility compared to the complexes of the ligand L. This





CrossMark

^{*} Corresponding author at: Department of Chemistry, Nanchang University, Nanchang 330031, China. Tel./fax: +86 0573 83643937.

E-mail addresses: xiaoming.liu@mail.zjxu.edu.cn, xiaoming.liu@ncu.edu.cn (X. Liu).

^{0277-5387/\$ -} see front matter \circledcirc 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.11.032

ladie I				
Crystallographic da	ta for	complexes	1–2 and	4-6 .

Complexes	1	2	4	5	6
Chemical formula	C ₁₆ H ₂₆ CoN ₄ S ₂ ,2(ClO ₄)	C14H25N3NiOS2,2Cl,5(H2O)	$C_{20}H_{28}CoN_4S_2,2(ClO_4)$	C20H28N4NiS2,2(ClO4)	$C_{20}H_{28}CuN_4S_2,2(ClO_4)$
Formula weight	596.37	535.18	646.41	646.19	651.02
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}2_{1}2_{1}$	C2/m	C2/c	C2/c	C2/c
a (Å)	10.7201(5)	21.229(10)	14.030(7)	13.732(4)	13.9755(14)
b (Å)	12.1620(5)	12.032(6)	17.103(8)	16.939(5)	17.0085(17)
<i>c</i> (Å)	18.3304(8)	9.549(5)	11.264(5)	11.466(4)	11.2534(11)
α (°)	90	90	90	90	90
β(°)	90	100.539(8)	106.250(10)	103.495(4)	104.836(2)
γ (°)	90	90	90	90	90
$V(Å^3)$	2389.88(18)	2398(2)	2595(2)	2593.4(14)	2585.8(4)
Ζ	4	4	4	4	4
F(000)	1228	1070	1332	1336	1340
μ (Mo Ka, mm $^{-1}$)	1.166	1.185	1.081	1.168	1.266
Total No. of reflns.	18129	6679	5910	10644	7195
θ_{\max}	28.26	27.62	24.00	26.83	26.25
No. of unique reflns (R _{int})	5768 (0.0534)	2626 (0.0299)	2041 (0.0352)	2786 (0.0552)	2601 (0.0262)
No. of observed refns	3050	1927	1519	2341	1829
No. of variables	299	155	168	163	190
R_1 , wR_2 (obsd data)	0.0589, 0.1345	0.0483, 0.1434	0.0451, 0.1128	0.0611, 0.1750	0.0359, 0.0923
R_1 , wR_2 (all data)	0.0936, 0.1400	0.0707, 0.1562	0.0668, 0.1212	0.0719, 0.1892	0.0571, 0.0979
GOF, S	1.053	1.044	1.067	1.037	1.077

improvement is attributed to the increase in the number of pendant pyridinyl groups.

2. Experimental

2.1. Instrument and materials

The reactions were performed under an argon atmosphere using standard Schlenk techniques when necessary. Solvents were freshly distilled by using appropriate drying agents prior to use. ¹H and ¹³C NMR spectra were recorded on an AVANCE DRX 400 (Bruker) spectrometer in CDCl₃. UV–Vis spectra were recorded with a Cary 50 COCN (Varian) spectrometer at room temperature. Electrochemical measurements of the complexes were performed on an Echo Chemie Autolab PGESTAT 30 in dry acetonitrile with [NBu₄][BF₄] as the supporting electrolyte; platinum and Ag/AgCl were used as the working and reference electrodes, respectively. The microanalysis service was provided by Nanjing University

(Heraeus CHN-O-Rapid). The macrocycle L and its complex (3) were synthesised as reported in our previous work [23].

Caution! Perchlorate salts are potentially explosive, only small quantities should be used and they should be handled with great care.

2.2. Synthesis

2.2.1. 2-(Chloromethyl)pyridine

Pyridin-2-ylmethanol (3.0 g, 27.5 mmol) in dry CH_2Cl_2 (25 mL) was cooled in an ice bath before thionyl chloride (5.0 g, 37.6 mmol) was dropwise added under rapid stirring. After the addition, the reaction mixture was warmed to room temperature and left standing overnight under continuously stirring. The solvent was removed under vacuum to give an off-white solid which was re-dissolved by adding a solution of sodium hydroxide (10%, 50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were separated and combined



Scheme 1. The synthetic route to the ligand L' and complexes **1–6**.



Fig. 1. Molecular structures of the cations of complex **1** (top) and complex **2** (bottom). In all the crystallographic diagrams, hydrogen atoms have been omitted for clarity and thermal ellipsoids are drawn at the 30% probability level.

before being dried with $MgSO_4$. Removal of the solvent yielded a colourless liquid (3.1 g, 89%). The product was used for the next reaction without further purification.

Table 2

Selected b	ond l	lengths	(Å)	and	angles	(°)	for	complexes	1-3	3.
------------	-------	---------	-----	-----	--------	-----	-----	-----------	-----	----

2.2.2. 4,10-Bis(pyridin-2-ylmethyl)-1,7-dithia-4,10-

diazacyclododecane, L'

A mixture of **L** (1.5 g, 5 mmol) and 2-(chloromethyl)pyridine (0.64 g, 5 mmol) in dry toluene (50 mL) was refluxed under an Ar atmosphere for 48 h in the presence of K₂CO₃ (1.40 g, 10.14 mmol) and KI (0.84 g, 5.05 mmol). Insoluble inorganic solids were filtered off and the solvent was removed under reduced pressure to produce a pale yellow solid. This crude product was further purified by chromatography using ethyl acetate as the eluant to give a pale yellow solid (1.5 g, 79%). ¹H NMR (CDCl₃): 8.455 (d, *J* = 4.52 Hz, Py–*H*), 7.604 (t, *J* = 15.08 Hz, Py–*H*), 7.475 (d, *J* = 7.79 Hz, Py–*H*), 7.097 (t, *J* = 12.18 Hz, Py–H), 3.739 (s, Py–CH₂), 2.802 (t, *J* = 13.08 Hz, NCH₂CH₂), 2.729 (t, *J* = 13.02 Hz, NCH₂CH₂). ¹³C NMR (CDCl₃): 159.26, 149.06, 136.50, 123.05, 122.12, 61.35, 52.54, 26.66.

2.2.3. Complexes **1** and **2**

A solution of ligand L (0.51 g, 1.7 mmol) in methanol (2 mL) was added dropwise to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.62 g, 1.7 mmol) in methanol (2 mL). The reaction mixture was stirred at room temperature for 4 h to give a pink precipitate. The solid (complex 1, 0.81 g, 80%) was collected by filtration, washed with methanol and dried under vacuum. The product was recrystallized by diffusion of diethyl ether into its acetonitrile solution to give crystals suitable for X-ray crystallography. *Anal.* Calc. for complex 1 (C₁₄-H₂₂Cl₂CoN₃O₈S₂·2H₂O, FW = 590.3): C, 28.48; H, 4.44; N, 7.12. Found: C, 27.94; H, 4.09; N, 6.60%.

Complex **2** was prepared similarly using NiCl₂·6H₂O (0.40 g, 1.7 mmol). The reaction was stirred at room temperature for 4 h to give a clear solution before being concentrated. Any insoluble solids were filtered and the filtrate was left in a refrigerator for a few days to produce green crystals (0.75 g, 83%). *Anal.* Calc. for complex **2** ($C_{14}H_{25}N_3OS_2Cl_2Ni\cdot5H_2O$, FW = 535.1): C, 31.40; H, 6.54; N, 7.85. Found: C, 31.93; H, 6.51; N, 7.99%.

2.2.4. Complexes 4-6

A solution of ligand **L**' (63 mg, 0.17 mmol) in methanol (2 mL) was added dropwise to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.62 g, 0.17 mol) in methanol (2 mL). The reaction was stirred at room temperature for 4 h to give a precipitate which was collected by filtration, washed with methanol and dried under vacuum. Recrystallisation by diffusion of diethyl ether into an acetonitrile solution produced crystals of complex **4** suitable for X-ray crystallography (0.82 g, 75%). Anal. Calc. for complex **4** ($C_{20}H_{28}N_4O_8S_2Cl_2Co$,

1	2	3 [23]
Co(1)-N(2) = 2.142(4)	Ni(1)-N(2) = 2.117(4)	Cu(1)-N(2) = 2.260(3)
Co(1)-N(1) = 2.057(4)	Ni(1)-N(1) = 2.063(4)	Cu(1)-N(1) = 1.992(3)
Co(1)-N(3) = 2.081(4)	Ni(1)-N(3) = 2.098(4)	Cu(1)-N(3) = 2.007(3)
Co(1)-S(1) = 2.479(2)	Ni(1)-S(1) = 2.4293(15)	Cu(1)-S(1) = 2.421(1)
Co(1)-S(2) = 2.481(2)	Ni(1)-O(1) = 2.088(4)	Cu(1)-S(2) = 2.447(1)
Co(1)-N(4) = 2.031(4)	N(1)-Ni(1)-O(1) = 90.68(17)	Cu(1)-N(4) = 2.369(4)
N(4)-Co(1)-N(1) = 92.17(17)	N(1)-Ni(1)-N(3) = 178.59(16)	N(1)-Cu(1)-N(4) = 93.9(1)
N(1)-Co(1)-N(2) = 82.15(15)	O(1) - Ni(1) - N(3) = 90.73(17)	N(1)-Cu(1)-N(2) = 80.5(1)
N(3)-Co(1)-N(2) = 96.19(16)	N(1)-Ni(1)-N(2) = 81.54(16)	N(3)-Cu(1)-N(2) = 98.3(1)
N(4)-Co(1)-S(2) = 94.48(19)	O(1)-Ni(1)-N(2) = 172.22(16)	N(4)-Cu(1)-S(2) = 93.7(1)
N(1)-Co(1)-S(2) = 92.82(16)	N(3)-Ni(1)-N(2) = 97.06(17)	N(1)-Cu(1)-S(2) = 96.88(8)
N(3)-Co(1)-S(2) = 83.97(15)	N(1)-Ni(1)-S(1) = 95.78(3)	N(3)-Cu(1)-S(2) = 85.18(8)
N(2)-Co(1)-S(2) = 86.45(17)	O(1)-Ni(1)-S(1) = 93.35(3)	N(2)-Cu(1)-S(2) = 85.24(8)
N(4)-Co(1)-S(1) = 94.50(19)	N(3)-Ni(1)-S(1) = 84.14(3)	N(4)-Cu(1)-S(1) = 95.5(1)
N(1)-Co(1)-S(1) = 99.59(16)	N(2)-Ni(1)-S(1) = 87.47(3)	N(1)-Cu(1)-S(1) = 92.59(8)
N(3)-Co(1)-S(1) = 83.34(14)	$S(1)^{a}-Ni(1)-S(1) = 166.57(5)$	N(3)-Cu(1)-S(1) = 85.15(8)
N(2)-Co(1)-S(1) = 85.89(17)		N(2)-Cu(1)-S(1) = 86.52(8)
N(4)-Co(1)-N(3) = 89.52(17)		N(3)-Cu(1)-N(4) = 87.3(1)

^a Symmetry code: x, 1 - y, z.

FW = 646.4): C, 37.15; H, 4.37; N, 8.67. Found: C, 37.10; H, 4.32; N, 8.53%.

The corresponding Ni²⁺ and Cu²⁺ complexes were prepared and crystallised in the same manner (complex **5**, 0.89 g, 78%; complex **6**, 0.77 g, 70%). *Anal.* Calc. for complex **5** ($C_{20}H_{28}N_4O_8S_2Cl_2Ni$ -5H₂O, FW = 736.2): C, 32.61; H, 5.16; N, 7.60. Found: C, 32.84; H, 4.94; N, 7.16%. *Anal.* Calc. for complex **6** ($C_{20}H_{28}N_4O_8S_2Cl_2Cu$, FW = 651.0): C, 36.87; H, 4.30; N, 8.60. Found: C, 36.90; H, 4.33; N, 8.48%.

2.2.5. Single-crystal X-ray diffraction analysis

In the crystallographic data collection of complexes **1–6**, standard procedures were used for mounting the crystals on a Bruker Apex-II area-detector diffractometer at *ca* 293 K. The crystals were routinely coated with paraffin oil before being mounted. Intensity data were recorded using MoK α radiation ($\lambda = 0.71073$ Å) using the φ - and ω -scan modes. The structures were solved by the direct method routines in the SHELXS program and refined on F^2 in SHELXL [26].

In complex **2**, two Cl⁻ ions were disordered and have been split in two fragments, Cl1, Cl2/O5, O6, which were constrained to be identical with occupancy factors of 0.5/0.5. In complex 5, the perchlorate anion exhibited disorder over two positions and the oxygen atoms bonded to the Cl atom were split into two fragments O(1)-O(4)/O(1A)-O(4A) with occupancy factors of 0.69/0.31. In complex 6, the 072–074 atoms in the perchlorate anion and the C3 and C4 atoms in the ethylene group were each disordered over two positions with occupancy factors O(72)-O(74)/O(75)-O(77) of 0.877/0.123 and C2, C3/C2x, C3x of 0.774/0.226. All non-hydrogen atoms were modelled anisotropically. Except for water hydrogen atoms, which were not added, all other hydrogen atoms were positioned geometrically and treaded as riding on their parent atoms with C-H distances of 0.97 (ethyl), 0.96 (methyl) and 0.93 Å (aromatic rings), and with $U_{iso}(H) = 1.2U_{eq}$ (C) (ethyl and aromatic rings), and $U_{iso}(H) = 1.5U_{eq}$ (C) (methyl). Details of the crystallographic and refinement data are given in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The ligand **L** in its copper(II) complex (**3**) was reported previously [23]. As shown in Scheme 1, the ligand **L**' was obtained by further reaction of ligand **L** with 2-(chloromethyl)pyridine in the presence of K₂CO₃ and KI under reflux in toluene. The ligand **L**' was isolated as a yellow solid in a high yield. ¹H and ¹³C NMR confirmed unambiguously its identity. Subsequently, treatment of the ligands **L** and **L**' with the perchlorate salts of cobalt(II), nickel(II) and copper(II) in MeOH led to complexes **1** and **3–6**. These complexes could be easily crystallised in MeCN-Et₂O systems to give single crystals suitable for X-ray diffraction. Crystals of complex **2** were obtained by the direct reaction of the ligand **L** with NiCl₂ in methanol solution. Complexes **1–6** are air and moisture stable in their solid state, and soluble in polar solvents such as MeCN, DMSO and DMF.

3.2. Structural analysis of complexes 1-6

The crystal structure of complex **3** was reported in our previous work [23]. The structures of complexes **1** and **2** are shown in Fig. 1. Selected bond lengths and angles are summarized in Table 2. The structures of these complexes are essentially superimposable. An octahedral coordination geometry was adopted by the central metal ions. In these structures, five ligating atoms from the ligand **L** coordinate to M^{2+} in a nearly perfect square-pyramidal geometry, with one of the amine N atoms as the vertex. The pyridinyl group

dangled from this N atom, and *trans* to this amine N was a loosely bound acetonitrile (**1** and **3**) or water (**2**) molecule. It is interesting to note that there is a crystallographic plane passing through the Ni1, O1, N2 and N3 atoms and the pyridinyl ring in the structure of the cation of complex **2**. Although analogous planes are found in the structures of complexes **1** and **3**, they are not as perfectly symmetrical as that in complex **2**. The M–N bond lengths of the three complexes are as expected, as shown in Table 2. When the bond possesses π -back bonding (the pyridinyl group or acetonitrile), the bond length is shorter than that to the σ -only bond. One exception is Cu–N_{MeCN} (2.369 Å) [23], where the lengthening is attributed to the Jahn Teller effect. The Ni1–O(1) bond length of 2.088(4) Å in complex **2** is similar to the corresponding Ni–O_{water}



Fig. 2. The molecular structures of the cations of complexes **4** (top), **5** (middle) and **6** (bottom).

Table 3		
Selected bond lengths ((Å) and angles (°) for complexes 4-6.

4	5	6
Co-N(22) = 2.113(3)	Ni(1)-N(1) = 2.066(3)	Cu-N(12)=2.003(2)
Co-N(1) = 2.240(3)	Ni(1)-N(2) = 2.156(3)	Cu-N(1) = 2.128(2)
Co-S(4) = 2.491(2)	Ni(1)-S(1) = 2.440(1)	Cu-S(4) = 2.6669(8)
N(22)-Co-N(1) = 76.5(1)	N(1)-Ni(1)-N(2) = 81.0(1)	N(12)-Cu-N(1) = 82.02(9)
$N(1)^{a}$ -Co-N(1) = 120.3(2)	$N(2)^{b}-Ni(1)-N(2) = 105.2(2)$	$N(1)-Cu-N(1)^{a} = 106.0(1)$
$N(22)^{a}-Co-S(4) = 88.22(9)$	$N(1)^{b}-Ni(1)-S(1) = 83.6(1)$	N(12)-Cu-S(4) = 84.22(6)
N(22)-Co-S(4) = 116.83(9)	N(1)-Ni(1)-S(1) = 107.4(1)	$N(12)^{a}-Cu-S(4) = 112.78(6)$
$N(1)^{a}-Co-S(4) = 82.41(9)$	$N(2)^{b}-Ni(1)-S(1) = 86.91(9)$	N(1)-Cu-S(4) = 84.66(6)
N(1)-Co-S(4) = 80.28(9)	N(2)-Ni(1)-S(1) = 83.23(9)	$N(1)^{a}-Cu-S(4) = 80.67(6)$
$N(22)^{a}-Co-N(22) = 91.9(2)$	$N(1)^{b}-Ni(1)-N(1) = 96.2(2)$	$N(12)-Cu-N(12)^{a} = 95.0(1)$

^a Symmetry codes: a: 1 - x, y, 0.5 - z.

^b Symmetry codes: 1 - x, y, 1.5 - z.

bond lengths in other similar compounds: $[Ni(Batp)(H_2O)](CF_{3-}SO_3)_2$ (2.079 Å) [21] and $[Ni(H_2O)_2(PyNS)](BF_4)_2$ (2.082(2) Å) [27].

The crystals of complexes 4-6 are essentially isostructural and their structures are shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The structures of the three cations adopt an octahedral geometry about each metal centre, but the geometry is severely distorted, due to the presence of the additional pyridinyl group, compared to those of complexes 1–3. The coordination in each structure involves the two pyridinyl nitrogen atoms, two amino nitrogen atoms and two thioether sulfur atoms of the hexadentate ligand L'. In all these structures, the pairs of aromatic nitrogen atoms are *cis* to each other, as are the pairs of amino N atoms, whereas the two thioether sulfur atoms are in the opposing (trans) positions. These structures possess a crystallographic two fold symmetry (C_2) axis that passes through the metal centre. In complexes 4-6, the M-N_{amino} bond lengths are longer than the M- N_{pv} bond lengths, reflecting the existence of the back donating π bond between the metal and the pyridinyl group.

All the complexes are structurally highly similar, adopting an octahedral geometry. In general, the bond lengths of the complexes bearing two pyridinyl groups (4-6) are slightly longer than the analogous bond lengths of the other complexes (1-3) derived from ligand **L**. The lengthening is certainly attributed to the steric hindrance caused by the hexa-coordination of the hexadentate ligand **L**'. However, the length (2.6669 Å) of the Cu–S bond of complex **6** is about 0.2 Å longer than the other M–S bonds (*ca* 2.4 Å). The cause of this lengthening is probably due to the Jahn–Teller effect.

3.3. Electronic absorption spectra

The electronic spectra of these complexes and the ligands, in acetonitrile, are shown in Fig. 3. Since the ligand L' possesses only one more pyridinyl group than ligand L, the two ligands have very similar electronic spectra. The two sets of complexes, 1-3 and 4-6, show three types of transitions, viz ligand-based, ligand-to-metal and d-d transitions. The absorption band of L and L' at about 272 nm is assigned to the π - π ^{*} transition of the pyridinyl moiety. This ligand-based transition is essentially intact in the spectra of the complexes. For the complexes of the ligand L (1-3), additional absorption band(s) shift gradually towards longer wavelengths, at about 290 nm for the Ni²⁺ complex, at 315 nm (a shoulder) for the Co²⁺ complex and at 373 nm (a strong peak) for Cu²⁺, as shown in Fig. 3 (top). Similar absorption bands with moderate intensity and analogous variation trends were also observed for complexes 4-6, Fig. 3 (bottom). These transition bands are assigned to ligandto-metal charge-transfer (LMCT) absorption bands. In the long wavelength range, weak absorption bands are observed for all the complexes which are assigned to d-d transitions, Fig. 3 (inset).



Fig. 3. UV–Vis absorption spectra of the ligand **L** and its complexes **1–3** (top) and the ligand **L**' and its complexes **4–6** (bottom) in MeCN (C = $1.8 \times 10^{-4} \text{ mol L}^{-1}$) (Inset: d–d transitions of complexes **1–6**).

3.4. Electrochemical investigation

The cyclic voltammograms of the complexes are shown in Fig. 4. The potentials of the redox processes and their assignments are tabulated in Table 4. The copper complexes (**3** and **6**) exhibit two reduction processes, assigned to Cu^{2+}/Cu^+ and Cu^+/Cu^0 , whereas the complexes of Co^{2+} and Ni^{2+} show both one reduction and one oxidation process. The two redox processes (for Co and Ni) are assigned to M^{2+}/M^+ and M^{3+}/M^{2+} . The assignment for the copper complexes is supported by the observation of the sharp stripping peak at about -0.14 V for both complexes during reverse scanning, Fig. 4 (bottom). The electrochemistry of these complexes



Fig. 4. The CVs of complexes **1** and **4** (top), **2** and **5** (middle), **3–6** (bottom, the coloured lines are CVs without going through the second reduction) in 0.1 mol L^{-1} MeCN solution at a scanning rate of 0.1 V s⁻¹ (298 K).

Table	4
-------	---

Redox	potentials	(V) and	assignme	nts

M ²⁺	Entry	${ m M^{1+}/M^0}$ ${ m E_a/E_c}$	M^{2+}/M^{1+} E_a/E_c , $E_{1/2}$	M^{3+}/M^{2+} E_a/E_c , $E_{1/2}$
Co ²⁺	1 4	1	-1.0, -1.57 ^a -0.91/-0.98, -0.95	0.69/0.47, 0.58 0.82/0.60, 0.71
Ni ²⁺	2 5	 	$-1.47, -1.77^{ m b}$ -1.07/-1.13, -1.10	1.23, 1.41 ^b 1.76
Cu ²⁺	3 6	-0.13 -0.17	0.20/0.09, 0.15 0.15/0.07, 0.11	

^a This is the reduction process of the product from the reaction related to the process of Co^{2+}/Co^{1+} and more likely a process involving Co^{1+}/Co^{0} rather than Co^{2+}/Co^{1+} .

^b As indicated above (note a), their assignment is not straightforward.

demonstrated well how the additional pyridinyl group, both a σ donor and π -acceptor, stabilises the reduced species. The improvement in stability is particularly significant for both the cobalt and nickel ions. For the copper ion, the improvement is exhibited by the cleaner electrochemistry after the first reduction. Although the influence of the additional pyridinyl group on the oxidation process is not as obvious as that on the reduction, improvement in the reversibility of the oxidation of the cobalt complex is still observable, Fig. 4 (top).

4. Conclusions

In summary, the ligand L' was synthesised by the further functionalisation of the ligand **L**, which was reported in our previous work [23]. Compared to the ligand L, the ligand L' possesses an extra pyridinyl group. Reaction of the ligands with three transition metal ions formed complexes $[MLSol]^{2+}$ (1–3, Sol = MeCN (1 and 3) or H₂O (2)) and $[ML']^{2+}$ (4–6) (M = Co²⁺, Ni²⁺, Cu²⁺), respectively. These complexes adopt an octahedral geometry and the additional pyridinyl ligand in the ligand L' led to severely distorted octahedral structures. Their UV-Vis spectra suggest that the electronic structures are similar and the MLCT bands of complexes 4-6 shift towards long wavelengths, probably due to the additional pyridinyl group lowering the energy of the LUMOs of the complexes. The electrochemistry of these complexes reveals that the presence of an additional pyridinyl group in the ligand L' improves the reversibility of the redox processes by stabilising the redox products through the σ -donor and π -acceptor properties of this ligand. The improvement is particularly significant in the reduction of these complexes.

Acknowledgements

The authors thank NSF of China (Grant No.: 20871064, 21171073), the Government of Zhejiang Province (Qianjiang Professorship, XL) for financial support, and the Education Department of Jiangxi Province (Grant No.: GJJ13106).

Appendix A. Supplementary data

CCDC 918653–918657 contains the supplementary crystallographic data for complexes **1–2** and **4–6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] D.H. Busch, Acc. Chem. Res. 11 (1978) 392.
- [2] D.Y. Kong, L.H. Meng, J. Ding, Y.Y. Xie, X.Y. Huang, Polyhedron 19 (2000) 217.
- [3] S. Majumder, L. Mandal, S. Mohanta, Inorg. Chem. 51 (2012) 8739.
- [4] S.L.F. Chan, Y.H. Kan, K.L. Yip, J.S. Huang, C.M. Che, Coord. Chem. Rev. 255
- (2011) 899. [5] M.R. Kember, F. Jutz, A. Buchard, A.J.P. White, C.K. Williams, Chem. Sci. 3 (2012)
- 1245.
 [6] B. Korybut-Daszkiewicz, R. Bilewicz, K. Woźniak, Coord. Chem. Rev. 254 (2010) 1637.
- [7] C. Panda, M. Ghosh, T. Panda, R. Banerjee, S. Sen Gupta, Chem. Commun. 47 (2011) 8016.
- [8] P.A. Vigato, V. Peruzzo, S. Tamburini, Coord. Chem. Rev. 256 (2012) 953.
- [9] S.W.A. Bligh, N. Choi, C. Geraldes, S. Knoke, M. McPartlin, M.J. Sanganee, T.M. Woodroffe, J. Chem. Soc., Dalton Trans. (1997) 4119.
- [10] M. Rossignoli, P.V. Bernhardt, G.A. Lawrance, M. Maeder, J. Chem. Soc., Dalton Trans. (1997) 323.
- [11] A.J. Blake, I.A. Fallis, R.O. Gould, S. Parsons, S.A. Ross, M. Schroder, J. Chem. Soc., Dalton Trans. (1996) 4379.
- [12] P. Comba, J. Ensling, P. Gutlich, A. Kuhner, A. Peters, H. Pritzkow, Inorg. Chem. 38 (1999) 3316.

- [13] F.H. Fry, B. Graham, L. Spiccia, D.C.R. Hockless, E.R.T. Tiekink, J. Chem. Soc., Dalton Trans. (1997) 827.
- [14] G. Aullon, P.V. Bernhardt, F. Bozoglian, M. Font-Bardia, B.P. Macpherson, M. Martinez, C. Rodriguez, X. Solans, Inorg. Chem. 45 (2006) 8551.
- [15] M. Costas, R. Xifra, A. Llobet, M. Sola, J. Robles, T. Parella, H. Stoeckli-Evans, M. Neuburger, Inorg. Chem. 42 (2003) 4456.
- [16] H. Kim, S.G. Kang, C.H. Kwak, Inorg. Chim. Acta 387 (2012) 346.
- [17] X.-Y. Xu, Q.-H. Luo, M.-C. Shen, X.-Y. Huang, Q.-J. Wu, Polyhedron 16 (1997) 915.
- [18] A. Tamayo, C. Lodeiro, L. Escriche, J. Casabo, B. Covelo, P. Gonzalez, Inorg. Chem. 44 (2005) 8105.
- [19] S.K. Chatterjee, S. Roy, S.K. Barman, R.C. Maji, M.M. Olmstead, A.K. Patra, Inorg. Chem. 51 (2012) 7625.
- [20] A. Tamayo, J. Casabo, L.S. Escriche, P. Gonzalez, C. Lodeiro, A.C. Rizzi, C.D. Brondino, M.C.G. Passeggi, R. Kivekas, R. Sillanpaa, Inorg. Chem. 46 (2007) 5665.
- [21] A. Tamayo, B. Pedras, C. Lodeiro, L. Escriche, J. Casabo, J.L. Capelo, B. Covelo, R. Kivekas, R. Sillanpaa, Inorg. Chem. 46 (2007) 7818.
- [22] J.G. Gilbert, A.W. Addison, R.J. Butcher, Inorg. Chim. Acta 308 (2000) 22.
- [23] Z.H. Wei, X. Xie, J. Zhao, L.M. Huang, X.M. Liu, Inorg. Chim. Acta 387 (2012) 277.
 [24] Y. Peng, Z.M. Li, Z.G. Niu, Y.Q. Liu, X.R. Zeng, Q.Y. Luo, D.L. Hughes, X.M. Liu,
- Inorg. Chim. Acta 362 (2009) 3975.
 [25] L.M. Huang, Y. Peng, Z.M. Li, Z.H. Wei, D.L. Hughes, X.R. Zeng, Q.Y. Luo, X.M. Liu, Inorg. Chim. Acta 363 (2010) 2664.
- [26] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [27] A. Tamayo, J. Casabo, L. Escriche, C. Lodeiro, B. Covelo, C.D. Brondino, R. Kivekas, R. Sillampaa, Inorg. Chem. 45 (2006) 1140.