

# Structure and properties of bivalent nickel and copper complexes with pyrazine-amide-thioether coordination: stabilization of trivalent nickel†

Akhilesh Kumar Singh and Rabindranath Mukherjee\*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208 016, India.

E-mail: rnm@iitk.ac.in; Fax: +91-512-2597437

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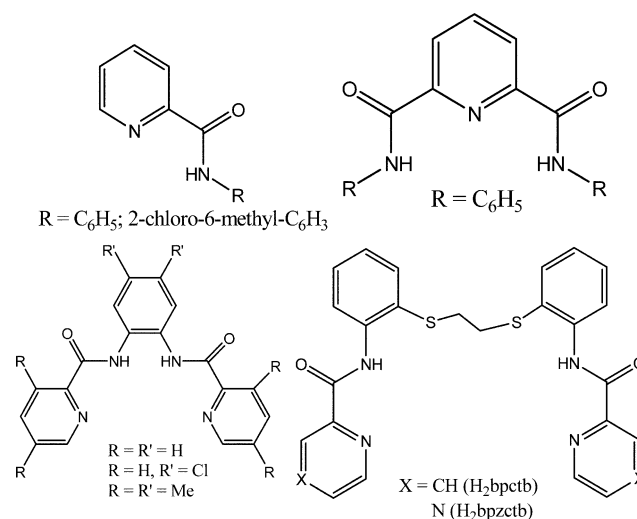
Acyclic pyrazine-2-carboxamide and thioether containing hexadentate ligand 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane ( $H_2$ bpzctb), in its deprotonated form, has afforded light brown  $[Ni^{II}(bpzctb)]$  (**1**) ( $S = 1$ ) and green  $[Cu^{II}(bpzctb)]$  (**2**) ( $S = 1/2$ ) complexes. The crystal structures of **1**·CH<sub>3</sub>OH and **2**·CH<sub>2</sub>Cl<sub>2</sub> revealed that in these complexes the ligand coordinates in a hexadentate mode, affording examples of distorted octahedral  $M^{II}N_2(\text{pyrazine})N'_2(\text{amide})S_2(\text{thioether})$  coordination. Each complex exhibits in CH<sub>2</sub>Cl<sub>2</sub> a reversible to quasireversible cyclic voltammetric response, corresponding to the  $Ni^{III}/Ni^{II}$  (**1**) and  $Cu^{II}/Cu^I$  (**2**) redox process. The  $E_{1/2}$  values reveal that the complexes of bpzctb(2-) are uniformly more anodic by ~0.2 V than those of the corresponding complexes with the analogous pyridine ligand, 1,4-bis[*o*-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane ( $H_2$ bpctb), attesting that compared to pyridine, pyrazine is a better stabilizer of the  $Ni(II)$  or  $Cu(I)$  state. Coulometric oxidation of the previously reported complex  $[Ni^{II}(bpctb)]$  and **1** generates  $[Ni^{III}(bpctb)]^+$  and  $[Ni^{III}(bpzctb)]^+$  species, which exhibit a LMCT transition in the 470–480 nm region and axial EPR spectra corresponding to a tetragonally elongated octahedral geometry. Complex **2** exhibits EPR spectra characteristic of the  $d_{2-2}$  ground state.

## Introduction

There has been continued interest in the design of new peptide ligands containing the pyridine-2-carboxamide functionality and development of coordination chemistry of such ligands, in their deprotonated form, toward transition metal ions.<sup>1–17</sup> Over the past few years, we and others have recognized (i) the strong donor capacity of the deprotonated pyridine-2-carboxamide moiety, attesting their ability to stabilize metal ions in higher oxidation states [chromium(V),<sup>8b</sup> iron(IV),<sup>10a</sup> nickel(III),<sup>3b</sup> nickel(IV),<sup>3b</sup> copper(III)<sup>9g</sup> etc.] and (ii) the  $M^{III}$ -bis-ligand complexes ( $M = Fe,^{3a} Co,^{3a} Ru^{3c}$ ) of the tridentate ligand and *trans*- $\{Fe^{III}(X)_2\}$  ( $X = \text{monodentate anionic and neutral ligands}$ ) complexes of the tetradentate ligand system<sup>7c,e,8c,10a</sup> are *non-innocent* as they exhibit ligand-centred oxidation processes, and in some cases stabilizing ligand  $\pi$ -cation radical complexes to such an appreciable extent that allowed their isolation in the solid-state.<sup>3c,7e,10a</sup>

The coordination behaviour of the ligands *N,N'*-bis(2'-pyrazinecarboxamido)-1,3-propane ( $H_2$ bpzpn) towards copper(II)<sup>18</sup> and *N,N'*-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide ( $H_2$ -bpmpz) in the control of molecular architectures,<sup>19</sup> has been well documented. In pursuit of designing new pyridine/pyrazine amide ligands that will incorporate poorly coordinating thioether donor sites (a weak  $\sigma$ -donor-cum- $\pi$ -acceptor)<sup>20,21</sup> towards transition metal ions two new hexadentate ligands 1,4-bis[*o*-(pyridine-2-carboxamidophenyl)]-1,4-dithiobutane ( $H_2$ -bpctb)<sup>17</sup> and 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane ( $H_2$ bpzctb)<sup>22</sup> have been synthesized. The outcome of our endeavour in  $Fe(II)/Fe(III)$  complexes of bpctb(2-) and bpzctb(2-) providing  $FeN_2(\text{pyridine/pyrazine})-$

$N'_2(\text{amide})S_2(\text{thioether})$  coordination,<sup>22</sup> is a first step towards this goal. Notably, the  $Fe(II)$  compounds have been structurally characterized.<sup>22</sup> This result has subsequently prompted us to synthesize and investigate properties of nickel(II) and copper(II) complexes of bpzctb(2-). As the structures of  $Ni(II)$  and  $Cu(II)$  complexes of bpctb(2-) have already been reported,<sup>17</sup> the present work gives us an opportunity to compare the effect of the heterocyclic ring in going from bpctb(2-) to bpzctb(2-), to investigate the strength and the effect of  $M-S(\text{thioether})$  bonds in the presence of well-documented deprotonated carboxamide N coordination environment. Our present endeavour is set against this background. Specifically, this work undertakes to elucidate the relationship between the structural changes and the redox potential of nickel(II) and copper(II) complexes of bpctb(2-) and bpzctb(2-). Here, we report the syntheses and characterization (structural, magnetic, spectroscopic and redox properties) of two new complexes  $[Ni^{II}(bpzctb)]$  (**1**) and  $[Cu^{II}(bpzctb)]$  (**2**), and EPR spectral properties of coulometrically-generated nickel(III) complexes.



† Electronic supplementary information (ESI) available: UV/VIS spectrum (in CH<sub>2</sub>Cl<sub>2</sub>) of (**2**). Reciprocal molar susceptibility vs. temperature plots for (**1**) and (**2**). EPR spectrum of a polycrystalline sample of (**2**) at 300 K. EPR spectrum of  $[Ni^{III}(bpzctb)]^+$  (coulometrically generated in CH<sub>2</sub>Cl<sub>2</sub>) at 120 K. UV/VIS spectrum of  $[Ni^{III}(bpctb)]^+$  (coulometrically generated in CH<sub>2</sub>Cl<sub>2</sub>). EPR spectra of  $[Ni^{III}(bpctb)]^+$  (coulometrically generated in CH<sub>2</sub>Cl<sub>2</sub>) at 300 and 120 K. See <http://dx.doi.org/10.1039/b504893a>

## Experimental

### Reagents and materials

All reagents were obtained from commercial sources and used as received. Solvents were dried/purified as reported previously.<sup>1,3,7,22</sup> Tetra-*n*-butylammonium perchlorate (TBAP) was prepared as before.<sup>7a</sup> The synthesis of the ligand 1,4-bis[*o*-(pyrazine-2-carboxamide-phenyl)]-1,4-dithiobutane (H<sub>2</sub>bpzctb) was achieved as before.<sup>22</sup>

### Syntheses

**Synthesis of [Ni<sup>II</sup>(bpzctb)] (1).** The ligand H<sub>2</sub>bpzctb (0.200 g, 0.41 mmol) was dissolved in *N,N'*-dimethylformamide (DMF) (10 cm<sup>3</sup>), and to it was added solid NaH (0.020 g, 0.82 mmol), resulting in a light orangish solution. To it solid [Ni(H<sub>2</sub>O)<sub>6</sub>][ClO<sub>4</sub>]<sub>2</sub> (0.150 g, 0.41 mmol) was added pinch by pinch. The resulting reddish brown solution was stirred for 1 h. Removal of the solvent was followed by addition of CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and filtration. Slow evaporation of this solution afforded a crystalline reddish brown precipitate, which was filtered off and washed with diethyl ether. The solid thus collected was air-dried (yield: 0.174 g, ~80%). Anal. Calcd for C<sub>24</sub>H<sub>18</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Ni: C, 54.06; H, 3.38; N, 15.76. Found: C, 54.21; H, 3.74; N, 15.64%. IR (KBr, cm<sup>-1</sup>, selected peak): 1613 (ν(CO)). Absorption spectrum [λ<sub>max</sub>, nm (ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), in CH<sub>2</sub>Cl<sub>2</sub>] 250 sh (30 200), 270 sh (26 500), 308 (18 200), 370 sh (10 000), 834 (80), 940 sh (50). Slow evaporation of a dilute solution of the complex in CH<sub>3</sub>OH gave single crystals of composition 1·CH<sub>3</sub>OH, suitable for X-ray diffraction.

**Synthesis of [Cu<sup>II</sup>(bpzctb)] (2).** A similar procedure to that followed for the synthesis of complex 1 was adopted; however, [Cu(H<sub>2</sub>O)<sub>6</sub>][ClO<sub>4</sub>]<sub>2</sub> was used as the starting material. Layering of *n*-hexane over the CH<sub>2</sub>Cl<sub>2</sub> solution of the complex gave single crystals of composition 2·CH<sub>2</sub>Cl<sub>2</sub>, suitable for X-ray diffraction (yield: 0.182 g, ~81%). Anal. Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Cl<sub>2</sub>Cu: C, 47.28; H, 3.15; N, 13.24%. Found: C, 47.34; H, 3.08; N, 13.52%. IR (KBr, cm<sup>-1</sup>, selected peak): 1616 (ν(CO)). Absorption spectrum [λ<sub>max</sub>, nm (ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), in CH<sub>2</sub>Cl<sub>2</sub>] 268 (34 700), 300 sh (23 200), 350 sh (13 900), 716 (150).

### Physical measurements

Elemental analyses were obtained using Thermo Quest EA 1110 CHNS-O, Italy. Conductivity measurements were done with an Elico type CM-82T conductivity bridge (Hyderabad, India). Spectroscopic measurements were made using the following instruments: IR (KBr, 4000–600 cm<sup>-1</sup>), Brüker Vector 22; electronic, Perkin Elmer Lambda 2 and Agilent 8453 diode-array spectrophotometer; X-band EPR, Varian 109 C and Brüker EMX 1444 spectrometers (fitted with a quartz dewar for measurements at 77 K and 120 K respectively). The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH (*g* = 2.0037).

Magnetic susceptibility measurements on solid samples of 1 and 2 were done with a locally-built Faraday balance equipped with an electromagnet with constant-gradient pole caps (Polytronic Corporation, Mumbai, India), Sartorius balance M-25-D/S (Göttingen, Germany), a closed-cycle refrigerator, and a Lake Shore temperature controller (Cryo Industries, USA). All measurements were made at a fixed main field strength of ~6 kG. The calibration of the system and details of measurements are already reported in the literature.<sup>3</sup>

Solution-state magnetic susceptibilities were obtained by the NMR technique of Evans<sup>23</sup> in CH<sub>2</sub>Cl<sub>2</sub> with a PMX-60 JEOL (60 MHz) NMR spectrometer. Corrections underlying diamagnetism were applied with the use of appropriate constants.<sup>24</sup>

Cyclic voltammetric experiments were performed at 298 K by using a PAR model 370 electrochemistry system consisting of a M-174A polarographic analyzer, a M-175 universal programmer, and a RE 0074 X–Y recorder. The cell contained a glassy carbon working electrode (PAR model G0021), a

Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. For constant potential electrolysis experiments a Pt mesh was used as the working electrode. Details of the cell configuration are as described before.<sup>7a</sup> The solutions were ~10<sup>-3</sup> mol dm<sup>-3</sup> in complex and 0.1 mol dm<sup>-3</sup> in supporting electrolyte, TBAP.

### Crystallography

Single crystals of suitable dimensions were used for data collection. Diffracted intensities were collected on a Bruker SMART APEX CCD diffractometer, with graphite-monochromated Mo-K<sub>α</sub> (λ = 0.71073 Å) radiation at 100(2) K. For data reduction the 'Bruker Saint Plus' program was used. Empirical absorption correction (SADABS) was applied to both data sets. The structures were solved by SIR 92, expanded by Fourier-difference syntheses and refined with the SHELXL 97 package incorporated in the WINGX 1.64 crystallographic collective package.<sup>25</sup> The positions of the hydrogen atoms were calculated assuming ideal geometries, but not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedure on *F*<sup>2</sup>. For 2, some disorder was encountered with the methylene carbon atom of dichloromethane, which was refined with a site occupation factor of 0.5. Hydrogens (H1S and H2S) of the solvent molecule were picked up from the Fourier map and were refined with a site occupation factor of 0.5. Pertinent crystallographic parameters are summarized in Table 1.

CCDC reference numbers 267708 (1·CH<sub>3</sub>OH) and 267709 (2·CH<sub>2</sub>Cl<sub>2</sub>).

See <http://dx.doi.org/10.1039/b504893a> for crystallographic data in CIF or other electronic format.

## Results and discussion

### Synthesis and characterization

Our familiarity with pyridyl amide ligands<sup>1,3,7</sup> has prompted us, for viable thioether coordination, to employ a combination of pyrazine amide functionality and dithiaalkyl fragment, -S(CH<sub>2</sub>)<sub>2</sub>S-, in a single ligand system.<sup>22</sup> The reaction of Na<sub>2</sub>bpzctb with [M<sup>II</sup>(H<sub>2</sub>O)<sub>6</sub>][ClO<sub>4</sub>]<sub>2</sub> (M = Ni and Cu) in DMF and usual workup afforded [Ni<sup>II</sup>(bpzctb)] (1) as reddish brown and [Cu<sup>II</sup>(bpzctb)] (2) as green crystalline compounds. The absence of ν(N–H) in the IR spectrum confirms that the ligand is coordinated in the deprotonated form. Elemental analyses, IR, and solution electrical conductivity data (non-electrolyte)<sup>26</sup> are

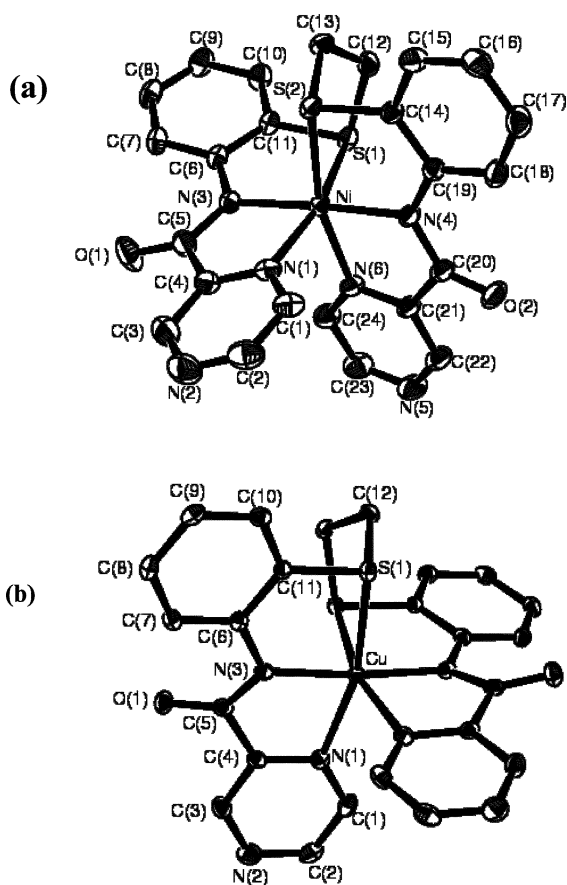
**Table 1** Data collection and structure refinement parameters for [Ni<sup>II</sup>-(bpzctb)]·MeOH (1·CH<sub>3</sub>OH) and [Cu<sup>II</sup>(bpzctb)]·CH<sub>2</sub>Cl<sub>2</sub> (2·CH<sub>2</sub>Cl<sub>2</sub>)

	1·CH <sub>3</sub> OH	2·CH <sub>2</sub> Cl <sub>2</sub>
Chemical formula	C <sub>25</sub> H <sub>22</sub> N <sub>6</sub> O <sub>5</sub> S <sub>2</sub> Ni	C <sub>25</sub> H <sub>20</sub> Cl <sub>2</sub> CuN <sub>6</sub> O <sub>2</sub> S <sub>2</sub>
<i>M</i>	576.7	635.03
Crystal colour, habit	Brown, needle	Green, cube
<i>T</i> /K	100(2)	100(2)
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>Pnna</i> (no. 52)
<i>a</i> /Å	8.937 (7)	11.243 (5)
<i>b</i> /Å	10.803 (8)	13.823 (5)
<i>c</i> /Å	14.305 (11)	16.083 (5)
<i>a</i> /°	106.821(13)	90.0
<i>β</i> /°	100.367(14)	90.0
<i>γ</i> /°	98.199(13)	90.0
<i>V</i> /Å <sup>3</sup>	1272.4 (17)	2499.5 (16)
<i>Z</i>	2	4
<i>d</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.507	1.688
<i>μ</i> /mm <sup>-1</sup>	0.966	1.293
No. refls collected	7450	15686
No. indep refls	5726 ( <i>R</i> <sub>int</sub> = 0.0438)	3088 ( <i>R</i> <sub>int</sub> = 0.0382)
No. refls used [ <i>I</i> > 2σ( <i>I</i> )]	3649	2680
GOF on <i>F</i> <sup>2</sup>	0.952	1.029
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0548 (0.1229)	0.0360(0.0894)
<i>R</i> indices (all data)	0.1180 (0.1400)	0.0428 (0.0928)

in agreement with the above formulations. The complexes are soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN or DMF.

### Crystal structures

A perspective view of [Ni(bpzctb)]·CH<sub>3</sub>OH (**1**·CH<sub>3</sub>OH), without solvent of crystallization, is shown in Fig. 1(a), and the metric parameters associated with metal coordination environment are listed in Table 2. Two pyrazine nitrogen atoms, two deprotonated amide nitrogen atoms, and two thioether sulfur atoms of bpzctb(2-) ligand provide the six coordination sites around a pseudo-octahedral nickel(II) ion. The NiN<sub>2</sub>(pyrazine)N<sub>2</sub>(amide)S<sub>2</sub>(thioether) coordination sphere is, however, severely distorted from ideal octahedral geometry. The angles between *trans* atoms at the metal centre are: N(1)–Ni–S(1) 164.09(9)°, N(3)–Ni–N(4) 175.70(11)°, and N(6)–Ni–S(2) 164.32(9)°. The *cis* angles span a wide range, 79.83(13)–99.73(10)°. The dimethylene bridge of the five-membered NiS<sub>2</sub>C<sub>2</sub> ring has *gauche* conformation. The corresponding angles for [Ni<sup>II</sup>(bpctb)]<sup>17</sup> are closely similar: 80.64(8)–98.06(5)° (*cis*-positioned donor pairs); 164.44(6)–177.16(7)° (*trans*-positioned pairs). Average Ni–N(pyrazine), Ni–N(amide), and Ni–S(thioether) distances are 2.085(3), 2.028(8), and 2.400(3) Å, respectively. The Ni–N<sub>amide</sub> distance is very close to the value observed for [Ni<sup>II</sup>(bpctb)] [2.025(7) Å].<sup>17</sup> The Ni–S<sub>thioether</sub> distance is normal.<sup>17,20,21,27a,d</sup> Compared to the Ni–N<sub>pyridine</sub> distance in [Ni<sup>II</sup>(bpctb)] [2.066(7) Å]<sup>17</sup> the Ni–N<sub>pyrazine</sub> distance in **1**·CH<sub>3</sub>OH is longer by ~0.02 Å. The Ni–S<sub>thioether</sub> distance observed in **1** is shorter by ~0.006 Å than that in [Ni<sup>II</sup>(bpctb)] [2.4058(7) Å].<sup>17</sup> In effect this change in metric parameter is a reflection of the mutual *trans* effect between pyridine/thioether in [Ni<sup>II</sup>(bpctb)] and between pyrazine/thioether in **1**·CH<sub>3</sub>OH.



**Fig. 1** View of the metal coordination environment in the crystals of (a) [Ni<sup>II</sup>(bpzctb)]·CH<sub>3</sub>OH (**1**·CH<sub>3</sub>OH) and (b) [Cu<sup>II</sup>(bpzctb)]·CH<sub>2</sub>Cl<sub>2</sub> (**2**·CH<sub>2</sub>Cl<sub>2</sub>), showing atom-labeling scheme and 50% probability ellipsoids. Hydrogen atoms are omitted for the sake of clarity. In (b) unlabeled atoms are related to labeled atoms by a crystallographic mirror plane.

**Table 2** Selected bond lengths (Å) and angles (°) in [Ni<sup>II</sup>(bpzctb)]·MeOH (**1**·CH<sub>3</sub>OH) and [Cu<sup>II</sup>(bpzctb)]·CH<sub>2</sub>Cl<sub>2</sub> (**2**·CH<sub>2</sub>Cl<sub>2</sub>)

1·CH <sub>3</sub> OH		2·CH <sub>2</sub> Cl <sub>2</sub>	
Ni–N(1)	2.096(3)	Cu–N(1)	2.1797(18)
Ni–N(3)	2.021(3)	Cu–N(3)	1.9754(18)
Ni–N(4)	2.036(3)	Cu–S(1)	2.4934(8)
Ni–N(6)	2.074(3)	N(1)–Cu–S(1)	164.55(5)
Ni–S(1)	2.4046(17)	N(1)–Cu–S(1')	92.16(5)
Ni–S(2)	2.3959(19)	N(1)–Cu–N(1')	91.73(9)
N(1)–Ni–N(3)	79.83(13)	N(1')–Cu–S(1)	92.16(5)
N(1)–Ni–N(4)	95.91(13)	N(3)–Cu–N(1)	80.59(7)
N(1)–Ni–N(6)	88.88(11)	N(3)–Cu–S(1)	83.97(5)
N(1)–Ni–S(1)	164.09(9)	N(3)–Cu–N(1')	102.97(7)
N(1)–Ni–S(2)	96.30(9)	N(3)–Cu–N(3')	174.99(9)
N(3)–Ni–N(4)	175.70(11)	N(3)–Cu–S(1')	92.42(5)
N(3)–Ni–N(6)	98.17(12)	N(3')–Cu–N(1)	102.97(7)
N(3)–Ni–S(1)	84.50(10)	N(3')–Cu–S(1)	92.42(5)
N(3)–Ni–S(2)	97.31(9)	S(1)–Cu–S(1')	88.05(3)
N(4)–Ni–N(6)	81.08(12)		
N(4)–Ni–S(1)	99.73(10)		
N(4)–Ni–S(2)	83.67(9)		
N(6)–Ni–S(1)	90.67(8)		
N(6)–Ni–S(2)	164.32(9)		
S(1)–Ni–S(2)	88.34(4)		

The symmetry operation required to generate N(1'), N(3') and S(1') is  $-x + 1/2, -y, z$ .

The structure of [Cu<sup>II</sup>(bpzctb)]·CH<sub>2</sub>Cl<sub>2</sub> (**2**·CH<sub>2</sub>Cl<sub>2</sub>), without solvent of crystallization, is illustrated in Fig. 1(b), and selected bond distances and bond angles are included in Table 2. This complex has a mirror plane passing through Cu and the midpoint of C(12) and its symmetry related atom. As in **1**·CH<sub>3</sub>OH, the bpzctb(2-) ligand employs two pyrazine nitrogen, two deprotonated amide nitrogen, and two thioether sulfur to bind copper(II) in this pseudo-octahedral complex. The relative orientations within the pairs are *cis*, *trans* and *cis*. As in **1**·CH<sub>3</sub>OH the CuN<sub>2</sub>(pyrazine)N<sub>2</sub>(amide)S<sub>2</sub>(thioether) coordination unit is severely distorted from ideal octahedral geometry. The angles at the metal center between *cis*-positioned donor pairs span the range 80.59(7)–102.97(7)° and those between *trans*-positioned pairs are 164.55(5) and 174.99(9)°. The corresponding angles for [Cu<sup>II</sup>(bpctb)]<sup>17</sup> are closely similar: 80.9(1)–97.8(1)° (*cis*-positioned donor pairs); 164.97(9)° and 177.3(2)° (*trans*-positioned pairs). The dimethylene bridge of the five-membered CuS<sub>2</sub>C<sub>2</sub> ring has *gauche* conformation. Average Cu–N(pyrazine), Cu–N(amide), and Cu–S(thioether) distances are 2.1797(18), 1.9754(18), and 2.4934(8) Å, respectively. The observed Cu–N<sub>amide</sub> distance is comparable to that reported for closely similar complexes.<sup>1,4,11–13,28</sup> The Cu–N<sub>pyrazine</sub> distance is on the higher side to that reported in the literature.<sup>18,19</sup> The Cu–S<sub>thioether</sub> distance is normal.<sup>17,20,21,27e</sup> As for that observed for **1**, the Cu–N<sub>amide</sub> distance is very close to the value noted for [Cu<sup>II</sup>(bpctb)] [1.977(3) Å].<sup>17</sup> Compared to the Cu–N<sub>pyridine</sub> distance in [Cu<sup>II</sup>(bpctb)] [2.155(4) Å]<sup>17</sup> the Cu–N<sub>pyrazine</sub> distance in **2**·CH<sub>2</sub>Cl<sub>2</sub> is longer by ~0.025 Å. The Cu–S<sub>thioether</sub> distance observed in **2**·CH<sub>2</sub>Cl<sub>2</sub> is shorter by ~0.01 Å than that in [Cu<sup>II</sup>(bpctb)].<sup>17</sup> As for that observed in **1**·CH<sub>3</sub>OH, this change in metric parameter is a reflection of the mutual *trans* effect between pyridine/thioether in [Cu<sup>II</sup>(bpctb)] and between pyrazine/thioether in **2**·CH<sub>2</sub>Cl<sub>2</sub>.

### Absorption spectra

The brown nickel(II) and green copper(II) complexes **1** and **2** display a crystal field transition at 834 nm and 716 nm, respectively.<sup>29,30</sup> For **1** this absorption could be assigned as the  $\nu_1$  band ( $^3A_{2g} \rightarrow ^3T_{2g}$  in octahedral parentage).<sup>29</sup> The spectrum of **1** showing the distinctive features of the complex is displayed in Fig. 2. The spectral signature of **2** is displayed in the ESI.† For

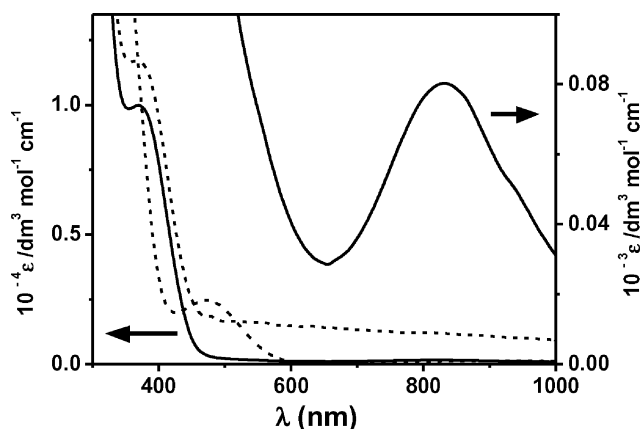


Fig. 2 UV/VIS spectra (in  $\text{CH}_2\text{Cl}_2$ ) of (a)  $[\text{Ni}(\text{bpzctb})]$  (**1**) (solid line) and (b) electrogenerated  $[\text{Ni}(\text{bpzctb})]^+$  (dotted line).

both **1** and **2** the intense higher energy transitions are charge-transfer in origin.

### Magnetism and EPR spectra

As expected, the nickel(II) and copper(II) complexes **1** and **2** are paramagnetic, with respect to two- ( $S = 1$ ) and one-unpaired electron ( $S = 1/2$ ), respectively.<sup>29,30</sup> Temperature-dependent (81–300 K) magnetic susceptibility measurements (ESI†) on solid samples of **1** [ $\mu_{\text{eff}}$  (300 K) =  $2.99 \mu_{\text{B}}$ ] and **2** [ $\mu_{\text{eff}}$  (300 K) =  $2.00 \mu_{\text{B}}$ ] confirmed their spin-state behaviour. Each complex obeys the Curie–Weiss law. The  $\mu_{\text{eff}}$  values for **1** and **2** in  $\text{CH}_2\text{Cl}_2$  solution are  $3.03$  and  $1.97 \mu_{\text{B}}$ , respectively, in good agreement with their solid-state values. The EPR spectra for powder samples of compound **2** at 300 K as well as at 77 K are typical of an axial pattern (ESI†). The spectrum recorded at 77 K is displayed in Fig. 3. The  $g_{\perp}$  and  $g_{\parallel}$  values are:  $2.152$  and  $2.024$  (300 K);  $2.156$  and  $2.022$  (77 K), implying that the unpaired electron lies on the  $d_{z^2}$  orbital.<sup>30</sup> A similar EPR spectral pattern was observed for  $[\text{Cu}(\text{bpctb})]$ .<sup>17</sup> This observation is in line with their solid-state structures.

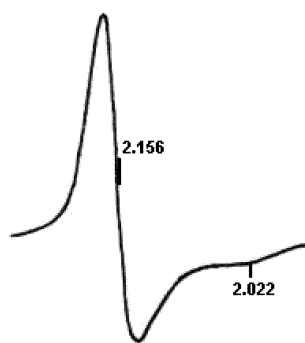


Fig. 3 EPR spectrum (77 K) of solid  $[\text{Cu}^{\text{II}}(\text{bpzctb})]$  (**2**).

### Metal-centred redox activity

To investigate the extent of stabilization of the metal(II) state towards oxidation/reduction cyclic voltammetric (CV) studies were performed. Light brown  $\text{CH}_2\text{Cl}_2$  solutions of complex **1** display a quasireversible ( $\Delta E_{\text{p}} = 120 \text{ mV}$ ) one-electron oxidation process (Fig. 4) at  $E_{1/2} = 1.04 \text{ V vs. SCE}$ . The brown coulometrically generated oxidized  $\text{CH}_2\text{Cl}_2$  solutions (electrolysis at  $1.4 \text{ V vs. SCE}$ ) display the same CV response as **1**, attesting the stability of the oxidized species. The species  $[\text{Ni}(\text{bpzctb})]^+$  [absorption and EPR (see below) spectra at 300 K were recorded immediately after the electrolysis and EPR spectra at 120 K were recorded after freezing such solutions;  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ); 250 sh (32 300), 270 sh (28 800), 310 sh (20 000), 370 sh (12 000), 470 (2500)] is characterized (Fig. 2) by its ligand-to-metal charge-

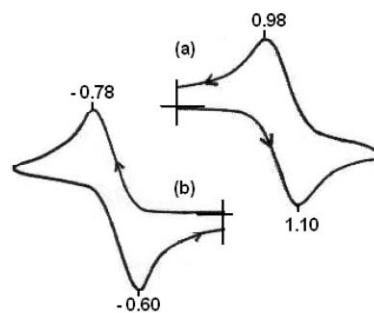


Fig. 4 Cyclic voltammograms ( $100 \text{ mV s}^{-1}$ ) of (a)  $[\text{Ni}^{\text{III}}(\text{bpzctb})]$  (**1**) and (b)  $[\text{Cu}^{\text{II}}(\text{bpzctb})]$  (**2**) at a glassy carbon electrode in  $\text{CH}_2\text{Cl}_2$  ( $\sim 0.1 \text{ dm}^3 \text{ mol}^{-1}$  in TBAP). Indicated potentials (in V) are vs. SCE.

transfer (LMCT) transition<sup>3b</sup> at 470 nm. It is worth noting here that unlike  $[\text{Ni}(\text{bpzctb})]^+$  compound **2** does not display any intense transition in the visible region. To clarify the ambiguous situation between nickel(II)-stabilized ligand radicals<sup>31</sup> and authentic nickel(III)<sup>3b,32</sup> complexes the EPR spectral behaviour of such solutions was investigated. At 300 K such solutions display an axial spectrum with  $g_{\perp} = 2.091$  and  $g_{\parallel} = 2.000$  ( $g_{\text{av}} = 2.046$ ) (Fig. 5). The observed five-line splittings of the  $g_{\perp}$  component indicates coordination of two axial nitrogen donors.<sup>32b</sup> However, at 120 K the spectrum (ESI†) is clearly rhombic with three principal  $g$  values of  $2.140$ ,  $2.070$  and  $2.000$  ( $g_{\text{av}} = 2.071$ ). For the sake of comparison of the relative stability of the nickel(III) species, we generated (coulometric oxidation of  $[\text{Ni}(\text{bpctb})]$  at  $1.1 \text{ V vs. SCE}$ ) brown  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{Ni}(\text{bpctb})]^+$  and examined their CV behaviour and spectral (absorption [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ); 250 sh (34 900), 330 (17 900), 475 (2900)] and EPR) properties (ESI†), under the conditions used for  $[\text{Ni}(\text{bzctb})]^+$  species. Such solutions display the same CV response as  $[\text{Ni}(\text{bpctb})]$ <sup>17</sup> [ $E_{1/2} = 0.84 \text{ V vs. SCE}$ ;  $\Delta E_{\text{p}} = 200 \text{ mV}$ ], attesting the stability of the oxidized species. EPR spectra of such solutions (300 K) exhibit closely similar patterns to that observed for **1**, with  $g_{\perp} = 2.091$  and  $g_{\parallel} = 2.018$  ( $g_{\text{av}} = 2.055$ ). At 120 K the spectrum is clearly rhombic:  $2.145$ ,  $2.071$  and  $1.991$  ( $g_{\text{av}} = 2.070$ ).

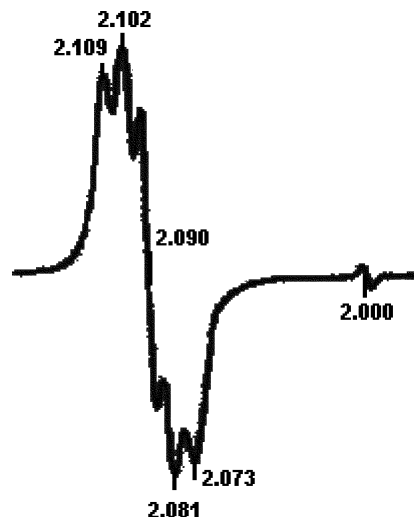


Fig. 5 EPR spectrum in  $\text{CH}_2\text{Cl}_2$  of  $[\text{Ni}^{\text{III}}(\text{bpzctb})]^+$  (coulometrically generated from **1**) at 300 K.

Given the controversy associated with the assessment of EPR signals of one-electron oxidized species of Ni(II) complexes the following comments are in order. In general, low-spin Ni(III) ( $S = 1/2$ ) complexes show anisotropic signals at around  $g_{\perp} = 2.2$  and  $g_{\parallel} = 2.0$ .<sup>31</sup> The average  $g$  values observed here indicate that the unpaired electron is associated primarily with the Ni(III) ion. Like other nickel(III) peptide complexes the observation of  $g_{\perp} > g_{\parallel}$  is indicative of a tetragonally distorted octahedral

geometry with elongation of the axial bonds.<sup>32,33</sup> The unpaired electron resides in an orbital which has a large amount of  $d_{z^2}$  character. The predicted  $g$  values are given by the approximate expressions, yielding the condition  $g_{xx}, g_{yy} > g_{zz}$ .<sup>32</sup> A similar situation, as that observed here, was encountered by us with the tridentate pyridine amide ligand.<sup>3b</sup> If ligand oxidation had occurred, the paramagnetic product would be a nitrogen- or carbon-centred radical complex of Ni(II). Such species would be expected to exhibit all three  $g$  values close to the spin-only value of 2.002.<sup>3b,31</sup> The large contribution to paramagnetism actually observed suggests that the unpaired electron is located primarily on the metal ion consistent with the trivalent oxidation state.<sup>3b,32,33</sup> Given the results at hand we assign the oxidative process for **1** and [Ni(bpctb)]<sup>+</sup> as being due to the Ni<sup>III</sup>/Ni<sup>II</sup> couple. In essence, the description of [Ni(bpctb)]<sup>+</sup> and [Ni(bpzctb)]<sup>+</sup> as a nickel(III) species is corroborated by the EPR spectra of the electrooxidized solutions.

It is worth noting that in going from tetramide (tridentate ligand system; Ni<sup>III</sup>/Ni<sup>II</sup> couple: 0.05 V vs. SCE)<sup>3b</sup> to bis-amide [bpctb(2<sup>-</sup>) or bpzctb(2<sup>-</sup>) with two thioether donor site] the stability of the nickel(III) state decreases appreciably (0.8–1.0 V), as expected.<sup>21</sup> Moreover, the present study reveals that the pyrazine carboxamide ligand bpzctb(2<sup>-</sup>) better stabilizes the nickel(II) state by ~200 mV towards oxidation than that of its pyridine analogue bpctb(2<sup>-</sup>).

In CH<sub>2</sub>Cl<sub>2</sub> solution complex **2** displays a well-defined quasireversible ( $\Delta E_p = 180$  mV) Cu<sup>II</sup>/Cu<sup>I</sup> response at  $E_{1/2} = -0.69$  V vs. SCE (Fig. 4). Under our experimental conditions, the complex [Cu(bpctb)]<sup>+</sup> displays in CH<sub>2</sub>Cl<sub>2</sub> a well-behaved CV response at  $E_{1/2} = -0.87$  V vs. SCE. The reported CV response of this complex was measured in DMSO.<sup>17</sup> Like the trend observed for **1**, in going from bpctb(2<sup>-</sup>) to bpzctb(2<sup>-</sup>) the copper(I) state is better stabilized by 180 mV.

Although for Cu(II) compounds of the tetradentate ligand system the observation of the Cu<sup>III</sup>/Cu<sup>II</sup> redox process has been claimed,<sup>9g</sup> compound **2** does not display any oxidative response within the potential window scanned (-1.6 to 1.8 V vs. SCE), under our experimental conditions. The reason behind this lack of oxidative response for **2** is not clear to us.

## Conclusions

The coordinating ability of the hexadentate ligand H<sub>2</sub>bpzctb, in its deprotonated form, incorporating a pyrazine-2-carboxamide unit connected by thioether -SCH<sub>2</sub>CH<sub>2</sub>S- functions, has been expanded to successfully employ thioether binding of nickel(II) ( $S = 1$ ), nickel(III) ( $S = 1/2$ ) and copper(II) ( $S = 1/2$ ). The complexes have a MN<sub>2</sub>(pyrazine)N<sub>2</sub>(amide)-S<sub>2</sub>(thioether) coordination environment, which has been authenticated by the structural characterization of the metal(II) complexes and comparison of the bonding parameters with that of corresponding complexes with the pyridine amide ligand H<sub>2</sub>bpctb. Successful isolation and characterization of these complexes suggest that the presence of the strongly coordinating deprotonated pyridine/pyrazine-2-carboxamide functionality as a part of the hexadentate ligand system adds strength to the weakly coordinating thioether sulfur enabling it to bind to metal ions efficiently. Notably, thioether sulfur binds metal ions uniformly more strongly when they are part of bpzctb(2<sup>-</sup>) rather than that of bpctb(2<sup>-</sup>). The complexes display reversible to quasireversible metal-centred one-electron redox process and the electrogenerated Ni(III) species are stable enough for their redox and spectral characterization to be obtained. Comparison of  $E_{1/2}$  values of complexes of bpctb(2<sup>-</sup>) and bpzctb(2<sup>-</sup>) for Ni<sup>III</sup>/Ni<sup>II</sup> and Cu<sup>II</sup>/Cu<sup>I</sup> redox processes indicate that the pyrazine ring nitrogen confers extra stabilization to the reduced state of the metal center. The nickel(III) complexes of bpctb(2<sup>-</sup>) and bpzctb(2<sup>-</sup>) could not be isolated in the solid state, however, oxidation of nickel(II) to the nickel(III) state [Ni(bpctb)]<sup>+</sup>/[Ni(bpzctb)]<sup>+</sup> is electrochemically achievable. The EPR spectral pattern of

[Ni(bpctb)]<sup>+</sup> and [Ni(bpzctb)]<sup>+</sup> is axial, with the ground state ( $d_{z^2}$ ).<sup>1</sup> The present complexes add to the list of mononuclear complexes that contain dicarboxamido coordination in a [N<sub>4</sub>S<sub>2</sub>] environment.

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