

Bis-chelates of nickel(II) and copper(II) with an O,S-donor piperazine ligand

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Abstract

A bidentate O,S-donor ligand *N*-(4-benzoyl-piperazine-1-carbothioyl)-benzamide (HL) was synthesized from the reaction of in situ generated benzoylisothiocyanate with piperazine and benzoyl chloride. Reaction of HL with the perchlorate salts of Ni^{II} and Cu^{II} in DMF–MeOH mixture using NEt₃ as base afforded complexes **1** and **2** as crystalline solids in moderate yields. Physico-chemical and spectroscopic studies confirmed the chemical compositions of both the free ligand and its $M(O,S)_2$ type metal complexes. The ligand undergoes keto-thione to keto-thiol tautomerization during metalation which is the driving force for the formation of neutral bis-chelates. The X-ray crystal structure of complex **2** shows bis-chelation with a cis-conformation in an overall square planar environment.

Introduction

The synthesis of thiourea-based O,S donor chelating ligands with substituted secondary amines is a mature field of research [1, 2], which nevertheless continues to draw the attention of synthetic chemists because of diverse applications as synthetic intermediates [3, 4], in organocatalysis [5, 6], alcohol oxidation [7] and enantioselective organic transformations [8, 9]. They are also extensively used as anion transporters [10], anion receptors [11, 12], metal extracting agents [13, 14], and as precursors for the synthesis of nanomaterials and metal sulfide thin films [15, 16]. Moreover, acylthioureas are well known for their in vitro antifungal and antibacterial activities [17–19], activity towards tumors cells [20], urease inhibitory action [21] and antioxidant properties [22].

Bidentate O,S donor ligands can exhibit versatile coordination towards metal centers, including through both O and S in monobasic bidentate fashion [23], only through S in neutral monodentate mode [24], both by O and S in neutral

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bidentate fashion [25] and simultaneously through O,S and N in monobasic bridging fashion [26]. Of these various possibilities, monoanionic bidentate binding through neutral O and anionic S is most common. In general, transition metals with +2 oxidation state stabilize bis-chelates in the cisconformation, whilst metal ions of +3 oxidation state prefer tris-chelates in the fac-arrangement. The interesting phenomenon of wavelength-dependent photoinduced cis-trans isomerization is uncommon [27]. There are various synthetic strategies propounded by different groups, including one pot multicomponent synthesis, metalation of the pure ligand, and photochemical reaction [28].

To date, there have been very limited investigations into the use of cyclic secondary amines like piperazine and morpholine in this context, although morpholine-based O,S ligands and their metal complexes with promising analytical applications have been reported in recent years [17, 29]. Hoyer et al. reported on a piperazine-based bis-bidentate O,S ligand and its metal complexes of general formula M₃L₃ [30]. Monoaryl/acyl-piperazines have been prepared by protecting one of the N-H groups of piperazine, followed by synthesis of the corresponding thiocarbamoyl derivatives [31]. With this in mind, a piperazine-based O,S-donor ligand, N-(4-benzoyl-piperazine-1-carbothioyl)-benzamide (HL) has been synthesized by protecting one of the N–H groups with a benzoyl moiety. Two $M(O,S)_2$ type complexes 1 and 2 were synthesized from this bidentate ligand and characterized by a combination of spectroscopic techniques. In addition, the X-ray crystal structure of complex 2 has

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been determined. The reported compounds may help contribute to various applications in pharmacology and organic reaction catalysis.

Experimental

Materials and methods

Hydrated perchlorate salts of copper(II) and nickel(II) were prepared by treating the corresponding metal carbonates with 1:1 conc. HClO₄-water mixture and crystallized after concentration on a water bath. Other chemicals were obtained from the following sources: triethylamine from S. D. Fine-Chem Ltd., benzoyl chloride from Merck, potassium thiocyanate and piperazine from Aldrich. All other chemicals and solvents were of reagent grade and used as received without further purification. Elemental analysis (C, H, N) was obtained with a Perkin-Elmer model 240 C elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer 883 spectrometer. Solution electrical conductivity measurements were carried out using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} M. Electronic spectra were recorded on a Shimadzu 1601 UV-Vis-NIR spectrophotometer using 1 cm quartz cell pairs. In each measurement, the background was subtracted by taking reference solvent in one of the cells. NMR spectra were recorded on a Bruker 400 MHz instrument in CDCl₃ solvent and the ESI-MS in positive ion mode was recorded on a VG Autospec mass spectrometer using sub-millimolar concentrations in MeCN:H₂O (1:1) mixed solvent. A collision energy of 10 eV, cone voltage of 23-30 V, source temperature of 120 °C, de-solvation temperature of 300 °C, and an average of total 60 scans were routinely used.

Synthesis of N-(4-benzoyl-piperazine-1-carbothioyl)-benzamide

Potassium thiocyanate (2.91 g, 30 mmol) was suspended in dry acetone (80 mL). After stirring for about 15 min, benzoyl chloride (3.5 mL, 30 mmol) was added dropwise with continuous stirring and the mixture was boiled under reflux, whereupon a precipitate of KCl appeared. To the cooled mixture, a solution of piperazine (2.58 g, 30 mmol) in acetone (20 mL) was added slowly and stirring was continued for a further 1 h. A second portion of benzoyl chloride (3.5 mL, 30 mmol) was added, and finally after adding water (250 mL), the mixture was stirred overnight. The solid white precipitate was filtered off and washed several times with water. The crude product was recrystallized from methanol. Yield: 7.95 g (75%). Anal. Calcd. for $C_{19}H_{19}N_3O_2S$ (353.439 g mol⁻¹): C, 64.57; H, 5.42; N, 11.89. Found: C, 64.61; H, 5.44; N, 11.91%. Selected FTIR bands (KBr, cm⁻¹): 3446(br), 3303(s), 1678(vs), 1521(vs), 1458(s), 1273(m), 1191(vs), 1022(m), 710(vs). ¹HNMR (CDCl₃): δ =3.66–4.29 (m, 8H, CH₂), 7.42–7.50 (m, 7H, Ph), 7.59 (t, *J*₁=6.8, *J*₂=7.2 Hz, 1H, Ph), 7.84 (s, 1H, Ph), 8.68 (s, 1H br, NH) ppm. ¹³CNMR (CDCl₃): δ =41.5 (CH₂), 46.5 (CH₂), 51.4 (2CH₂), 127.1 (2C), 127.8 (2C), 128.6 (2C), 129.0 (2C), 130.2 (C), 132.0 (C_q), 133.3 (C), 134.8 (C_q), 163.3 (CO), 170.8 (CO), 179.8 (CS) ppm.

Synthesis of complex 1

A solution of HL (0.35 g, 1 mmol) in DMF (10 mL) was added dropwise to a stirred solution of nickel(II) perchlorate (0.18 g, 0.5 mmol) in methanol (5 mL). NEt₃ (0.13 mL, 1 mmol) was then added to give a brown suspension. Evaporation on a hot water bath gave a solid brown product, characterized as complex **1**. Yield: 0.470 g (62%). Anal. Calcd. for C₃₈H₃₆N₆O₄S₂Ni (763.556 g mol⁻¹): C, 59.77; H, 4.75; N, 11.01. Found: C, 59.73; H, 4.74; N, 11.06%. Selected FTIR bands (KBr, cm⁻¹): 3447(br), 1636(vs), 1507(s), 1424(s), 1284(m), 1214(m), 1003(m), 722(s), 711(s). Molar conductance ($\Lambda_{\rm M}$, MeCN solution at 25°C): 13.3 S m² mol⁻¹. UV–Vis spectra [$\lambda_{\rm max}$, nm (ε , L mol⁻¹ cm⁻¹)]: (MeCN solution) 505 (145), 293 (13,330), 265 (12,903).

Synthesis of complex 2

Complex 2 was synthesized by a similar procedure as for 1, except that copper(II) perchlorate (0.37 g, 1 mmol) was used in place of nickel(II) perchlorate. The green powdery product obtained from concentration on a hot water bath was dissolved in DMSO and kept for crystallization a room temperature. After about 25 days, block shaped green crystals were obtained. One of the diffraction quality single crystals was selected for X-ray structure analysis. Yield: 0.420 g (55%). Anal. Calcd. for $C_{38}H_{36}N_6O_4S_2Cu$ (768.408 g mol⁻¹): C, 59.40; H, 4.72; N, 10.94. Found: C, 59.39; H, 4.74; N, 10.97%. Selected FTIR bands (KBr, cm^{-1}): 3446(br), 1625(vs), 1458(m), 1419(m), 1341(s), 1201(s), 1007(s), 712(s). Molar conductance (Λ_M , MeCN solution at 25°C): 9.1 S m² mol⁻¹. UV–Vis spectra [λ_{max} , nm (ε , L mol⁻¹ cm⁻¹)]: (MeCN solution) 505 (145), 293 (13,330), 265 (12,903).

Crystal data collection and refinement

X-ray crystallographic diffraction data for complex **2** were collected using a Bruker SMART APEX-II CCD X-ray diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 20 °C, with increasing ω (width of 0.3° per frame) at a scan speed of 6 s per frame. Information concerning X-ray data collection and structure refinement is summarized in Table 1. The structure of complex

Empirical formula	$C_{38}H_{36}N_6O_4S_2Cu$		
Formula weight (M/g mol ⁻¹)	768.40		
Space group	C2/c		
Crystal system	Monoclinic		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.150(3), 10.2188(17), 21.161(5)		
α, β, γ (°)	90, 108.564(5), 90		
Volume (Å ³)	3515.6(12)		
Temperature (K)	293(2)		
Z/Density (calc.) $(g \text{ cm}^{-3})$	4/1.452		
μ (Mo–K α)/cm ⁻¹	7.91		
<i>F</i> (000)	1596		
Crystal dimension (mm ³)	$0.39 \times 0.25 \times 0.19$		
Reflections collected/unique	$21,791/3548 (R_{int}=0.0723)$		
Data/parameters	2229/231		
Max. and min. transmission	0.789/0.860		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0448; wR_2 = 0.0686$		
Goodness-of-fit on F^2	1.426		
Largest diff. peak and hole (e. $Å^{-3}$)	0.523 and -0.395		
CCDC NO.	1001811		

 Table 1
 Crystal parameters and refinement data for complex 2

2 was solved by direct methods and refined by full-matrix least-squares based on F^2 with a total of 3548 reflections having Miller indices: $h_{\min} = -20$, $h_{\max} = 21$, $k_{\min} = -12$, $k_{\max} = 12$, $l_{\min} = -26$, $l_{\max} = 26$ [32]. In the final cycles of the F^2 method, all non-hydrogen atoms were assigned anisotropically and hydrogen atoms were introduced in calculated positions in fixed geometry with respect to their carrier atoms. The molecular plot was drawn using Diamond V. 2.1e program [33]. CCDC file 1001811 contains the supplementary crystallographic data in CIF format for complex 2. The data can be obtained free of charge either from www. ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center: 12, Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223/336-033; e-mail: deposit@ ccdc.cam.ac.uk).

Results and discussion

The proligand HL was synthesized in good yield by the reaction of in situ generated benzoylisothiocyanate with piperazine and a slight excess of benzoyl chloride (Fig. 1). The reaction proceeds via nucleophilic addition of isothiocyanate to the carbonyl carbon followed by elimination of chloride, followed by an addition reaction with N-benzoylpiperazine. A broad resonance in the ¹H NMR spectrum at 8.68 ppm, assigned to the N–H group, together with the presence of an N–H vibration at 3303 cm⁻¹ in the FTIR, plus the characteristic stretching vibrations of C=O at 1678 cm⁻¹ and C=S



Fig. 1 Synthetic scheme of proligand HL and its complexes 1 and 2

at 1273 cm⁻¹ (vide supra) indicates successful formation of the proligand. Subsequent 2:1 stoichiometric reaction of HL with $M(CIO_4)_2$ (M=Ni^{II} or Cu^{II}) in DMF in the presence of NEt₃ as base afforded bis-chelate square planar complexes **1** and **2** (Fig. 1). Both the complexes were isolated as micro-crystalline solids. Complex **2** was crystallized from a saturated solution of DMSO. The elemental analysis and solution conductivity measurements confirm the chemical compositions and non-ionic natures of both complexes.

Comparison of the FTIR spectra (Fig. 2) of the free proligand with those of the metal complexes confirms the generation of monoanionic ligands during metal coordination through keto-thiol tautomerization. The N–H vibration at



Fig. 2 Comparative FTIR spectra of ligand HL with complexes 1 and 2 showing shifts of C=O and C=S bond vibrations

3303 cm⁻¹ for free ligand is absent from the spectra of both complexes, confirming the deprotonation of amine nitrogen [34]. The C=O stretching vibration at 1678 cm⁻¹ and C=S band at 1273 cm⁻¹ for free HL is shifted to lower wave numbers by ca. 42–53 and 59–72 cm⁻¹, respectively, upon complexation, indicative of delocalization of π -electrons within the chelate rings.

Coordination through both carbonyl-O and thiol-S is in accordance with the bathochromic shifts of C=O and C=S bond vibrations compared to the free proligand HL. Sharp and intense bands in the fingerprint region of $1500-1100 \text{ cm}^{-1}$, assigned to partially double bonded CO, CN and CS stretching vibrations in the metal complexes, are absent from the spectrum of free HL. All these observations are consistent with thionyl to thiol transformation during coordination to the metal centers [22, 23].

ESI-MS spectra (Figures S1-S4 in Supporting Information) of both free HL and the complexes in MeCN:H₂O (1:1) mixed solvent provide useful information regarding the stable fragments formed during ionization. A base peak for the free HL at m/z = 354.128 is assigned to the protonated proligand $[H_2L]^+$ (C₁₉H₂₀N₃O₂S). In addition, peaks at m/z = 217.055, 376.111 and 729.230 are attributed to C₁₂H₁₅N₃O, [(HL)Na]⁺ (C₁₉H₁₉N₃O₂SNa) and [(HL)₂Na]⁺ (C₃₈H₃₈N₆O₄S₂Na), respectively. Both complex **1** and the free HL give a major fragment due to [(HL)₂Na]⁺ (m/z = 376.111) while both complexes and HL show a major stable fragment assigned to [H₂L]⁺ (m/z = 354.126). Complex **1** also shows the molecular ion peak at m/z = 763.167for [Ni(L)₂H]⁺. In contrast to this, complex **2** shows a different and distinguishable major fragment at m/z = 416.059for [Cu(L)]⁺ (Table 2).

The electronic spectra (Figures S5 and S6 in the Supporting Information) of both complexes in 10^{-3} M DMSO solution in 10 µM HEPES buffer showed strong absorption bands from charge transfer transitions in the near UV range. For complex 1, the spin forbidden d-d transitions observed at 507 nm ($\varepsilon = 145 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) can be assigned to the $A_{1g} \rightarrow B_{1g}$ transition [35]. In the UV region, bands at 283 nm ($\varepsilon = 14,055$ L mol⁻¹ cm⁻¹) and 250 nm ($\varepsilon = 10,729 \text{ L mol}^{-1} \text{ cm}^{-1}$) for complex **1** and at 275 nm ($\varepsilon = 16,613 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) and 237 nm $(\varepsilon = 13.231 \text{ L mol}^{-1} \text{ cm}^{-1})$ for complex 2 can be assigned to metal-bound intraligand $n-\pi^*$ and $\pi-\pi^*$ charge transfer transitions, overlapped with alternative MLCT transitions. For complex 2, a low energy transition at 511 nm $(\varepsilon = 159 \text{ L mol}^{-1} \text{ cm}^{-1})$ may be assigned to d-d transitions of copper(II). The lower energy intraligand charge transfer band observed for free HL is red shifted in the metal complexes, due to withdrawal of electron density from the coordinated ligands.

Structure of complex 2

The crystal structure of complex **2** is depicted in Fig. 3 with the partial atom numbering scheme. The monoclinic complex with C2/c space group bears a C_2 -symmetry along the midpoint of the metal center in a square planar S_2O_2 coordination environment. Each of the deprotonated HL ligands provides thiolate S and carbonyl O atoms towards Cu^{II}-coordination. Binding of two such bidentate O,S

Bond lengths (Å)			
Cu1–O1	1.9196(17)	N1–C7	1.326(3)
Cu1–S1	2.2313(8)	N1–C8	1.332(3)
O1–C7	1.261(3)	S1–C8	1.729(2)
Bond angles (°)			
01–Cu1–O1*	86.13(10)	S1-Cu1-S1*	89.53(4)
O1-Cu1-S1	94.30(5)	C7-N1-C8	126.1(2)
01-Cu1-S1*	164.27(6)		

Table 2 Selected bond lengths (Å) and bond angles (°) for complex 2

Fig. 3 Molecular structure of complex 2 with partial atom numbering scheme



ligands around each Cu^{II}-center gives a neutral Cu(O,S)₂ chromophore, with a distorted cis-square planar geometry. The six-membered chelate rings (NC₂OS-Cu) are twisted about the central N atom (N1) in order to attain an O...S bite distance of 3.05 Å. The Cu-S distance of 2.231 Å, Cu-O distance of 1.92 Å. C–O distance of 1.261 Å. C–S distance of 1.729 Å and C-N distances of 1.32-1.332 Å are indicative of charge delocalization over the six-membered chelate ring, although the relatively long C-S bond distances suggest that the negative charge is mainly on sulfur. These results are in good agreement with the FTIR data. The cis angles (86.13-94.30°) around the metal are close to the ideal value of 90°, whereas the trans angle of 164.27° deviates significantly from the ideal angle of 180°. The six-membered chelate ring deviates somewhat from planarity, as indicated from the O-C-N-C and C-N-C-S torsion angles of 9.24°. The dihedral angle between the two O-Cu-S planes is 21.37° which is significantly higher than a comparable value from the literature (6.97°) [36].

The crystal of complex **2** has a one-dimensional supramolecular network structure (Fig. 4), in which discrete monomeric units are linked by intermolecular C–H···O hydrogen bonds. Atoms C3 and C3* of the phenyl ring from the ligand backbone serve as hydrogen bond donors via H3 and H3* to the benzoyl oxygens O2 and O2*, respectively, with C–H···O hydrogen bonding parameters: C3···O2=1.208 Å, H3···O2=2.608 Å and C–H···O angles of 120.68°.

The degree of distortion around a tetracoordinate metal center can be quantitatively estimated by dihedral angle

measurements (θ), being 90° for a tetrahedral geometry and 0° for a perfectly square planar arrangement. The dihedral angle (θ) between the O1-Cu1-S1 and O1*-Cu1-S1* planes of complex **2** is 21.37°, which implies the distorted tetracoordinate copper(II) is closer to a square planar arrangement [37]. Using another method as described by Houser [38], the tetracoordinate geometry index was calculated with the formula:

$\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$

where α and β are the two largest angles in the four-coordination species. The τ_4 value is expected to be 1 for tetrahedral geometry and zero for a perfectly square planar geometry. The τ_4 value obtained for complex **2** is 0.22, again indicating a distorted square-planar structure.

Conclusion

A benzoylthiourea-based proligand HL has been synthesized from piperazine as a secondary amine and examined for its coordination potential towards Ni^{II} and Cu^{II}. This anionic unsymmetrical O,S donor ligand binds to both metal ions in a cis-fashion giving distorted square planar geometries. The spectroscopic signatures both in solution and the solid state and the X-ray crystal structure of the copper complex confirm keto-thiol tautomerization during metal binding, as well as delocalization of negative charge over the six-membered chelate rings.



Fig. 4 Formation of 1D supramolecular network through C–H…O hydrogen bonding interactions. Color code: Cu, brown; N, blue; O, red; S, yellow; C, ash and H, green. (Color figure online)

Supporting information

CCDC 1001811 contains the supplementary crystallographic data in CIF format for complex **2**. The data can be obtained free of charge from www.ccdc.cam.ac.uk/conts /retrieving.html, or from the Cambridge Crystallographic Data Center: 12, Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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