Journal of Organometallic Chemistry 694 (2009) 2085–2091

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Mononuclear zinc(II) and mercury(II) complexes of Schiff bases derived from pyrrolealdehyde and cysteamine containing intramolecular NH···S hydrogen bonds

Kuan-Yi Wu, Chang-Chih Hsieh, Yih-Chern Horng *

Department of Chemistry, National Changhua University of Education, 1 Jin-De Road, Changhua 50058, Taiwan

ARTICLE INFO

Article history:
Received 7 December 2008
Received in revised form 4 February 2009
Accepted 10 February 2009
Available online 21 February 2009

Keywords:
NH···S hydrogen bond
Cysteamine
Schiff base
Pyrrole

ABSTRACT

Two neutral group 12 metal complexes, bis(pyrrol-2-ylmethyleneaminoethylthio)zinc(II) (**1**) and bis(pyrrol-2-ylmethyleneaminoethylthio)mercury(II) (**2**), with the $(N_{imine})_2S_2$ coordination mode were synthesized by using metal-templated Schiff base condensation, and their molecular structures were determined by X-ray diffraction analysis. Complex **1** exhibits a distorted tetrahedral geometry around the metal, whereas the metal center has a bisphenoidal configuration in complex **2**. Both mononuclear complexes possess intramolecular NH···S hydrogen bonds, as evidenced by IR, ^{1}H NMR and X-ray crystallography. The hydrogen-bond donor (H–$N_{pyrrole}$) and acceptor (S atom) are coming from different ligands within a single molecule. Complex **2** represents the first example of a mercury complex in the N_2S_2 coordination mode with intramolecular NH···S hydrogen-bond interactions. An investigation of the effects of the NH···S hydrogen bonding on the stability of **1** and **2**, using an *N*-methyl pyrrolyl analogue, demonstrated that the N–H hydrogen-bond donor from the pyrrolyl moiety probably played a role in the stability of **1**, but not **2**.

1. Introduction

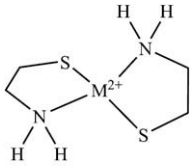
Recently, hydrogen-bond interactions [1] have been attracting a considerable amount of interest because they play an essential role in supramolecular chemistry [2,3], solid-state design [4–6], and biochemical environments [7]. Among these interactions, (amide)NH···S hydrogen-bonding contacts are quite often found in metalloproteins, where the sulfur atoms from the side-chains of cysteines, cofactors, or substrates are coordinated to metals. The functions of these NH···S hydrogen bonds in several metalloproteins have been investigated through mutagenesis, inorganic synthetic modelings, or computational methods. It has been proposed that the catalytic ability of P450 enzymes to perform C–H hydroxylations vs. C=C epoxidations is modulated by the electron-donating power of iron-bound sulfur atoms affected by hydrogen bonding [8–12]. The switch between the on and off state for the NH···S hydrogen bond has been suggested to control the redox potential of the metal center and the reactivity toward O-atom transfer in tungsten and molybdenum enzymes [13–15]. The contribution of the NH···S hydrogen bond on cysteine (Cys) residue to the redox potential of rubredoxins [16] and ferredoxin [17] was found in the model complexes studied by Ueyama et al. This redox control by NH···S hydrogen bonds was also suggested in other electron transfer proteins [18,19]. The presence or absence of hydrogen-bond contacts was thought to be the key regulating the nucleophilicity and specificity of thiolate for the alkyl group transfer in zinc-containing proteins [20–24]. It is also known that NH···S hydrogen bonding has significant effects on the properties of the S–Hg–S bond in $Hg(SAr)_2$ [25] and on the stability of the extra negative charge of $[Hg(SAr)_4]^{2-}$ [26].

It is well-established that the moiety of $Zn(His)_2(Cys)_2$ (His = histidine) is used for structural purpose in zinc finger proteins [27]. The competition of soft heavy-metal ions Cd^{2+} and Hg^{2+} with Zn^{2+} for binding to the Cys and His sites is thought to be in part the origin of the toxicity [28,29]. Thus, the group 12 metal complexes with N_2S_2 coordination environment should be suitable models for these metals in proteins.

Similar to the properties of amide protons, not particularly acidic or basic, pyrrole is generally used to support hydrogen-bond interactions, mostly NH···anion, under different conditions [30]. In addition, the ease of incorporating pyrrole into a variety of cyclic or acyclic structures makes pyrrole-based molecules excellent models for the study of anion complexation [31]. Recently, Fleischer et al. synthesized and characterized the group 12 metal complexes with cysteamines, which possess the same S-containing unit as cysteine, as shown in Scheme 1. Although the molecular structures of those complexes show intermolecular interactions through hydrogen bonds, thiolate bridging, or Hg···S contacts, the major contribution for the formation of a structural network is from the NH···S interactions [32]. In order to synthesize a mononuclear metal complex containing intramolecular NH···S hydrogen bonds without any intermolecular interactions for structural and functional studies, and to investigate the influence of the NH···S hydrogen bonds on

* Corresponding author. Tel.: +886 4 7232105x3551; fax: +886 4 7211190.
E-mail address: ychorng@cc.ncue.edu.tw (Y.-C. Horng).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.02.010



M = Zn, Cd, Hg

Scheme 1.

the structure and properties of complexes in N_2S_2 binding mode, we decided to utilize an extension of cysteamine with the pyrrolyl moiety to prevent the intermolecular NH···S interactions, and to form intramolecular ones instead. By using this strategy, two novel group 12 metal complexes with N_2S_2 coordinational environment were synthesized, and the unprecedented intramolecular NH···S hydrogen bonds formed between the two metal-bound ligands within the same complex were observed.

2. Experimental

2.1. General considerations

Commercially available chemicals were purchased from Aldrich or Acros, and used as received. Pyrrole-2-carboxaldehyde, $Zn(SC_2H_4NH_2)_2$ and $Cd(SC_2H_4NH_2)_2$ were synthesized and identified by following the published procedures [32–34]. ^1H and ^{13}C NMR spectra were collected on a Bruker AC 200 or Avance 300 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were recorded in ppm relative to the residual proton and ^{13}C of $CDCl_3$, D_2O and DMSO-d_6. Infrared spectra were recorded on a Bio-Rad FTS-185 instrument using KBr discs. The ES-MS mass spectra were performed on a LCQ mass spectrometer (Finnigan MAT, Thermo Quest). The *m/z* values reported correspond to those of the most intense peak in the corresponding isotopic patterns. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instruments Center of National Chung Hsing University, Taiwan.

2.2. Preparation of compounds

2.2.1. Synthesis of $(HL'S)_2$

This compound was prepared by means of a modified literature procedure [35]. To a stirring solution of cysteamine dihydrochloride (0.30 g, 1.30 mmol) in ethanol (10 mL), a $NaHCO_3$(aq) solution (2 mL, 1.3 M) was added. After the mixed solution was stirred at room temperature for about 1 h, a batch of pyrrole-2-carboxaldehyde (0.25 g, 2.60 mmol) was added, and the solution was stirred overnight. After completion, the solution was dried under vacuum, and extracted with CH_2Cl_2 and water. The portions of CH_2Cl_2 extract were collected and dried using anhydrous $MgSO_4$, and then the solvent was removed under vacuum to afford a pale-brown powder (0.38 g, 95%). IR (KBr): 3190 b (ν_{N-H}), 1641 s ($\nu_{C=N}$) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.06 (s, 2H, NC*H*C_4H_3NH), 6.87 (t, J = 1.2 Hz, 2H, NHC$_4H_3$), 6.50 (dd, J = 4 and 1.2 Hz, 2H, NHC$_4H_3$), 6.22 (dd, J = 4 and 1.2 Hz, 2H, NHC$_4H_3$), 3.77 (t, J = 6 Hz, 4H, NC$_2H_4$S), 2.99 (t, J = 6 Hz, 4H, NC$_2H_4$S). ^1H NMR ($CDCl_3$, 237 K): δ 11.19 (br, 2H, N*H*C$_4H_3$). ^{13}C NMR ($CDCl_3$, 300 K): δ 153.3, 129.9, 122.3, 115.0, 109.8, 59.3, 40.4. Anal. Calc. for $C_{14}H_{18}N_4S_2$: C, 54.87; H, 5.92; N, 18.28. Found: C, 55.12; H, 5.90; N, 17.97%. ESI-MS: *m/z* 307.1, $[M+H]^+$.

2.2.2. Synthesis of 2-(pyrrol-2-yl)tetrahydrothiazole (L″)

To a stirring solution of 2-mercaptoethylammonium chloride (0.24 g, 2.07 mmol) in N_2-purged ethanol (10 mL), a N_2-purged $NaHCO_3$(aq) solution (2 mL, 1.3 M) was added. After the mixed solution was stirred at room temperature for about 1 h, a batch of pyrrole-2-carboxaldehyde (0.20 g, 2.10 mmol) was added, and the solution was stirred at room temperature under N_2 atmosphere for 24 h. After completion, the solution was dried under vacuum, and extracted with CH_2Cl_2 and water. The portions of CH_2Cl_2 extract were collected and dried using anhydrous $MgSO_4$, and then the solvent was removed under vacuum to afford a white powder (0.29 g, 90%). IR (ν_{N-H}): 3248 b, 3418 b (KBr) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, 300 K): δ 8.53 (b, 1H, N*H*C$_4H_3$), 6.71 (dd, J = 4 and 2.5 Hz, 1H, NHC$_4H_3$), 6.22 (m, 1H, NHC$_4H_3$), 6.15 (dd, J = 6 and 4 Hz, 1H, NHC$_4H_3$), 5.63 (s, 1H, C*H*NHC$_2H_4$S), 3.42 (dt, J = 12 and 6 Hz, 1H, CHNHC$_2H_4$S), 3.15 (dt, J = 12 and 6 Hz, 1H, CHNHC$_2H_4$S), 3.03 (d, 1H, J = 6 Hz, CHNHC$_2H_4$S), 3.01 (dd, J = 6 and 2 Hz, 1H, CHNHC$_2H_4$S), 1.96 (br, 1H, CHN*H*C$_2H_4$S). ^{13}C NMR ($CDCl_3$, 300 K): δ 130.0, 117.6, 108.8, 107.3, 66.4, 52.1, 35.7. Anal. Calc. for $C_7H_{10}N_2S_1$: C, 54.51; H, 6.54; N, 18.16. Found: C, 54.20; H, 6.43; N, 18.27%.

2.2.3. Synthesis of $Zn(HL'S)_2$ (**1**)

2-Mercaptoethylammonium chloride (0.87 g, 7.50 mmol) was dissolved in methanol (10 mL) and treated with a NaOH(aq) solution (2 mL, 7.5 M). After stirred at room temperature for 10 min, the mixture was added with a batch of zinc(II) sulfate (1.08 g, 3.75 mmol). After stirred for another 2 h, the solution was added with pyrrole-2-carboxaldehyde (0.70 g, 7.36 mmol) and the resulting mixture was stirred at room temperature overnight. The solvent was evaporated and replaced by $CHCl_3$ (20 mL). The insoluble NaCl was filtered off, and the filtrate was added with diethyl ether (60 mL), which leads to the precipitation of a light-orange solid. Yield: 0.86 g (62%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into $CHCl_3$ solution of **1** at −20 °C. IR ($\nu_{C=N}$): 1628 s (KBr) cm^{-1}. ^1H NMR ($CDCl_3$, 300 K): δ 13.45 (br, 2H, N*H*C$_4H_3$), 8.10 (s, 2H, NC*H*C$_4H_3$NH), 7.18 (d, J = 3 Hz, 2H, NHC$_4H_3$), 6.70 (d, J = 3 Hz, 2H, NHC$_4H_3$), 6.26 (t, J = 3 Hz, 2H, NHC$_4H_3$), 3.66 (t, J = 5 Hz, 4H, NC$_2H_4$S), 2.89 (t, J = 5 Hz, 4H, NC$_2H_4$S). ^1H NMR ($CDCl_3$, 237 K): δ 13.52 (s, 2H, N*H*C$_4H_3$). ^{13}C NMR ($CDCl_3$, 300 K): δ 156.2, 126.8, 122.9, 110.8, 77.2, 65.6, 27.8. Anal. Calc. for $C_{14}H_{18}ZnN_4S_2$: C, 45.22; H, 4.88; N, 15.07. Found: C, 45.28; H, 5.14; N, 15.13%.

2.2.4. Synthesis of $Hg(HL'S)_2$ (**2**)

This compound was prepared similar to **1** by taking 2-mercaptoethylammonium chloride (0.61 g, 5.3 mmol), NaOH(aq) solution (1.5 mL, 7.5 M), mercury(II) nitrate (0.92 g, 2.6 mmol) and pyrrole-2-carboxaldehyde (0.50 g, 5.3 mmol). Yield: 1.26 g (96%). Colorless crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into THF solution of **2** at -20 °C. IR ($\nu_{C=N}$): 1636 s (KBr) cm^{-1}. ^1H NMR ($CDCl_3$, 300 K): δ 11.35 (br, 2H, N*H*C$_4H_3$), 8.10 (s, 2H, NC*H*C$_4H_3$NH), 7.03 (d, J = 0.7 Hz, 2H, NHC$_4H_3$), 6.50 (t, J = 1.8 Hz, 2H, NHC$_4H_3$), 6.22 (m, 2H, NHC$_4H_3$), 3.65 (t, J = 5.2 Hz, 4H, NC$_2H_4$S), 3.06 (t, J = 5.2 Hz, 4H, NC$_2H_4$S). ^1H NMR ($CDCl_3$, 237 K): δ 11.56 (s, 2H, N*H*C$_4H_3$). ^{13}C NMR ($CDCl_3$, 300 K): δ 153.9, 129.2, 123.2, 117.4, 109.7, 64.1, 30.4. Anal. Calc. for $C_{14}H_{18}HgN_4S_2$: C, 33.16; H, 3.58; N, 11.05; S, 12.65. Found: C, 32.92; H, 3.67; N, 10.95; S, 13.06%. ESI-MS: *m/z* 509.1, $[M+H]^+$.

2.2.5. Synthesis of $Hg(MeL'S)_2$ (**3**)

This compound was prepared similar to **2** by taking 2-mercaptoethylammonium chloride (0.61 g, 5.3 mmol), NaOH(aq) solution (1.5 mL, 7.5 M), mercury(II) nitrate (0.92 g, 2.6 mmol) and *N*-methyl-pyrrole-2-carboxaldehyde (0.58 g, 5.3 mmol). A white powder was obtained by adding hexane (60 mL) into $CHCl_3$ solution (10 mL) of **3**. Yield: 1.15 g (83%). ^1H NMR ($CDCl_3$, 300 K): 8.14 (s, 2H, NC*H*C$_4$H$_3$ N), 6.70 (s, 2H, CH$_3$NC$_4H_3$), 6.63 (s, 2H, CH$_3$NC$_4H_3$), 6.11 (m, 2H, CH$_3$NC$_4H_3$), δ 3.88 (s, 6H, C*H*$_3$NC$_4$H$_3$),

Table 1
The summary of crystallographic data for **1** and **2**.

	1	2
Formula	$C_{14}H_{18}N_4S_2Zn$	$C_{14}H_{18}N_4S_2Hg$
Formula weight	371.81	507.03
T (K)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	17.8005(12)	17.9782(4)
b (Å)	10.0865(7)	10.1531(3)
c (Å)	8.8267(6)	8.9987(2)
α (°)	90	90
β (°)	90.887(2)	90.9570(10)
γ (°)	90	90
V (Å^3/Z)	1584.60(19) /4	1642.34(7)/4
$D_{calc.}$ (Mg/m^3)	1.559	2.051
Absorption coefficient (mm^{-1})	1.811	9.624
Crystal size (mm)	0.35 × 0.32 × 0.28	0.29 × 0.25 × 0.23
θ Range (°)	1.14–28.63	1.13–28.79
Number of reflections collected	21 415	20 715
Number of independent reflections	4037	4262
Maximum and minimum transmission	0.6310 and 0.5697	0.2156 and 0.1668
Number of data/restraints/parameters	4037/0/198	4262/0/198
Goodness-of-fit (GOF) on F^2	0.786	0.674
Final R indices [$I > 2\sigma(I)$], R_1[a], wR_2[b]	0.0300, 0.0914	0.0202, 0.0710
R indices (all data), R_1[a], wR_2[b]	0.0569, 0.1195	0.0232, 0.0792
Largest difference in peak and hole (e Å^{-3})	0.376 and −0.410	1.046 and −1.474

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$.
[b] $wR_2 = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]^{1/2}$.

3.66 (t, J = 5.7 Hz, 4H, NC_2H_4S), 3.15 (t, J = 5.7 Hz, 4H, NC_2H_4S). ^{13}C NMR ($CDCl_3$, 300 K): δ 153.7, 128.7, 127.4, 115.6, 108.0, 64.7, 35.5, 29.4. Anal. Calc. for $C_{16}H_{22}HgN_4S_2$: C, 35.91; H, 4.14; N, 10.47. Found: C, 36.22; H, 3.97; N, 10.72%. ESI-MS: m/z 537.1, $[M+H]^+$.

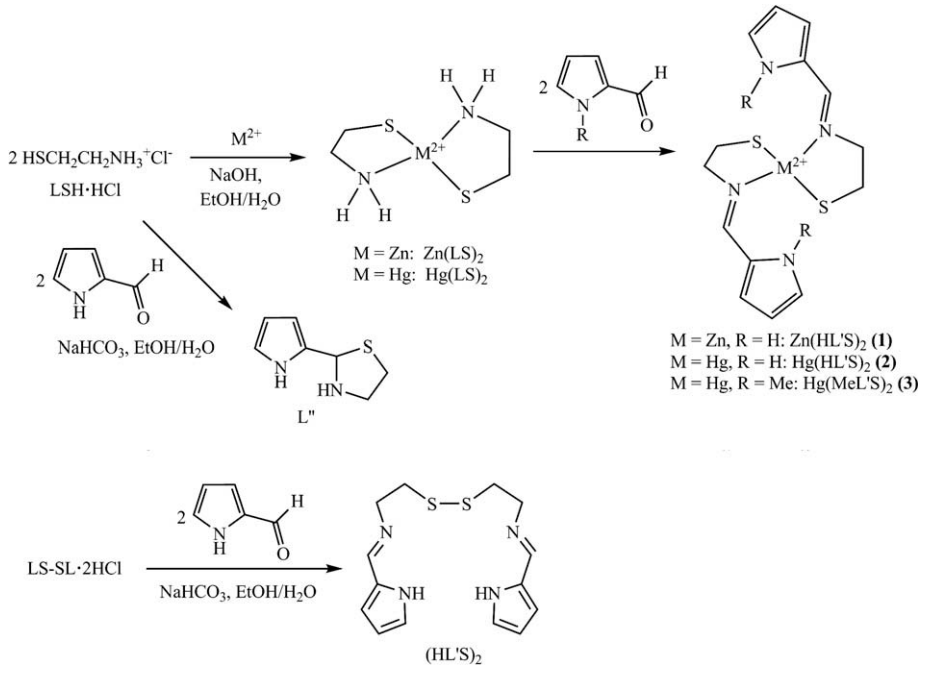
2.3. Structure analyses

The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97 [36]. Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from a standard source [37]. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Crystallographic data collection and refinement parameters were listed in Table 1.

3. Results and discussion

3.1. Syntheses and physical properties

Thus far, in the literature, we have not found any structurally known pyrrol-2-ylmethyleneaminoethanethiol ligand (HL′SH) coordination compounds. This may be due to the difficulty of preparing the Schiff base HL′SH. It has been shown that the direct synthesis of the Schiff base from 2-aminothiophenol and salicylaldehyde yields 2-(2-hydroxyphenyl)benzothiazoline [38]. To synthesize metal complexes containing 2-[(2-mercaptothiophenyl)iminoemthyl]phenol (H_2L), Bastida *et al.* utilized an electrochemical method for the reductive cleavage of the disulfide bond of the Schiff base H_2L_2 [39]. The condensation of 2-mercaptoethylammonium chloride (LSH·HCl) and pyrrole-2-carboxaldehyde under anaerobic conditions only gave 2-(pyrrol-2-yl)tetrahydrothiazole (L″) (Scheme 2). However, in contrast to the electrochemical synthesis of metal complexes, four-coordinate bis(pyrrol-2-ylmethyleneaminoethylthio)zinc(II) (**1**), and bis(pyrrol-2-ylmethyleneaminoethylthio)mercury(II) (**2**) were prepared using a one-pot synthesis involving a metal-templated Schiff base condensation, as illustrated in Scheme 2. For spectroscopic comparisons, di(pyrrol-2-ylmethylenylaminoethyl)disulfide $(HL'S)_2$ was also synthesized with high yield using a modified procedure from the literature [35]. Although the intermediates, $Zn(LS)_2$ and $Hg(LS)_2$, were not spectroscopically or structurally characterized, our synthesis procedures for both intermediates were quite similar to those previously published [32,40].



Scheme 2.

In a typical reaction, 1 equiv. of M^{2+} (M = Zn or Hg) ion was added to a stirred solution of 2 equiv. of LSH·HCl and 4 equiv. of NaOH. After the reaction mixture was stirred for 2 h, 2 equiv. of pyrrole-2-carboxaldehyde was added to give the desired final products.

The elemental analysis agreed that the complexes were in a 1:2 adduct between metal ions and HL′S$^-$. Consistent with the formation of **1** and **2**, the ^{1}H NMR spectra of the complexes in $CDCl_3$ at room temperature showed a chemical shift of the azomethine protons, which is a downfield shift from that of $(HL'S)_2$ (from δ 8.06 to 8.10 ppm). The (pyrrole)N-H chemical shifts of complexes **1** (δ 13.45 ppm) and **2** (δ 11.35 ppm) gave evidence that the pyrrolyl nitrogen was not deprotonated and was free from metal binding. The IR spectra of **1** and **2** in the solid state exhibited C=N stretching at 1628 and 1636 cm^{-1}, respectively, which are slightly lower than the value from $(HL'S)_2$ (1641 cm^{-1}), and promised the formation of the designed complexes. The free disulfide showed a broad NH stretching band at 3190 cm^{-1}, which was absence in **1** and **2**. Instead, several bands over 2750–3050 cm^{-1} were appeared for both complexes, characteristic of NH groups involved in hydrogen bonds [41].

It is well-established that pyrroles are excellent hydrogen-bonding donors and are largely employed for anion bonding [31]. The evidence for the formation of S···H–$N_{pyrrole}$ hydrogen bonds in complexes **1** and **2** also came from X-ray diffraction analysis (see the following section) and ^{1}H NMR measurements. We were not able to detect the pyrrolyl NH signal of $(HL'S)_2$ from the ^{1}H NMR spectroscopies (Fig. 1a), mostly due to the fast exchange rate of the pyrrole NH protons at room temperature. The appearance of the (pyrrole)N–H chemical shifts of **1** and **2** at room temperature provided the first indication that those slowly exchanged protons are engaged in hydrogen-bond interactions [42]. Moreover, the ^{1}H NMR experiments conducted at a lower temperature (237 K) to measure the chemical shifts of pyrrolyl NH for $(HL'S)_2$, **1**, and **2** showed a downfield shifting of the pyrrolyl N-H signals for **1** and **2** ($\Delta\delta$ = 2.33 ppm for **1**; 0.37 ppm for **2**) compared to $(HL'S)_2$ in chloroform solution (Fig. 1b). The results gave the second evidence for the formation of the NH···S hydrogen bonds. The order of the $\Delta\delta$(NH) values for the two complexes with the same ligands suggested that the strength of the intramolecular NH···S hydrogen bonding of **1** was stronger than **2** in a solution state.

The attempts to synthesize the cadmium analogue were unsuccessful. The preparation of $Cd(HL'S)_2$, using a method similar to the syntheses of **1** and **2**, resulted in $Cd(LS)_2$ and a trace amount of $(HL'S)_2$, regardless of whether $CdCl_2$ or $Cd(O_2CCH_3)_2$ was used. In addition, no reaction was found between purified $Cd(LS)_2$ [32] and pyrrole-2-carboxaldehyde in methanol at room temperature under either aerobic or anaerobic conditions. It should be noticed that the complexation product of cysteamine with Cd^{2+} is a chain-like polymer, in which each Cd atom is in a N_2S_3 coordination mode. Thus, the synthesis of a Cd^{2+} analogue may come from other preparative procedures.

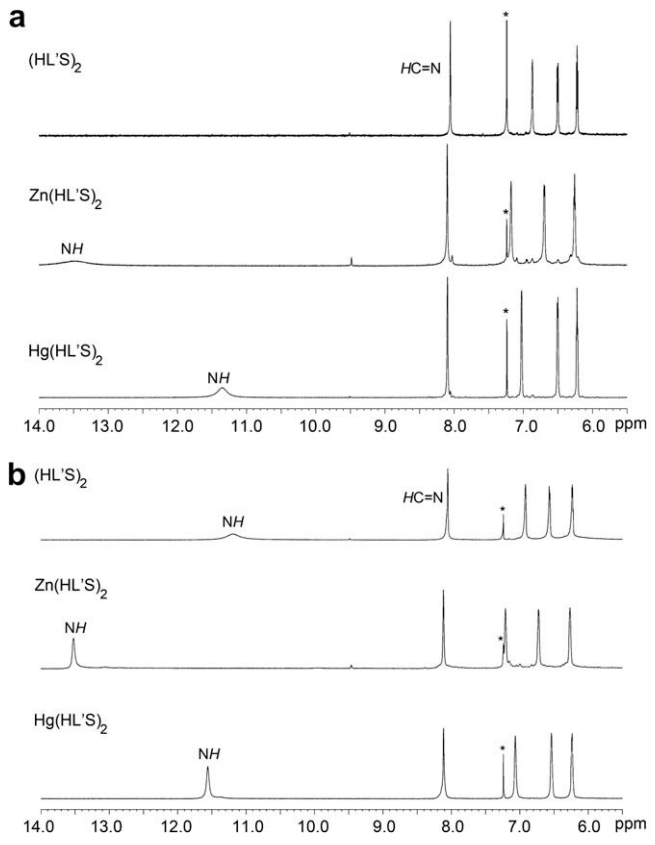


Fig. 1. Partial ^{1}H NMR spectra (300 MHz) of $(HL'S)_2$, $Zn(HL'S)_2$ and $Hg(HL'S)_2$ at (a) 300 K and (b) 237 K. Spectra were obtained from $CDCl_3$(∗) solution.

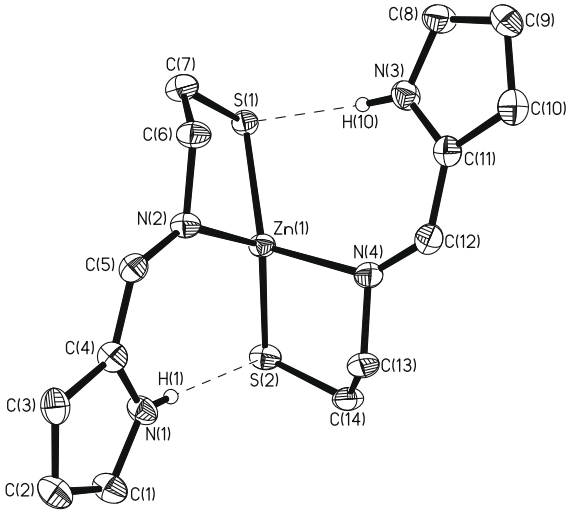


Fig. 2. The molecular diagram for **1**. The thermal ellipsoids were drawn at 50% probability level with dash lines showing the NH···S hydrogen-bond interactions. Hydrogen atoms bound to carbon atoms were omitted for clarity.

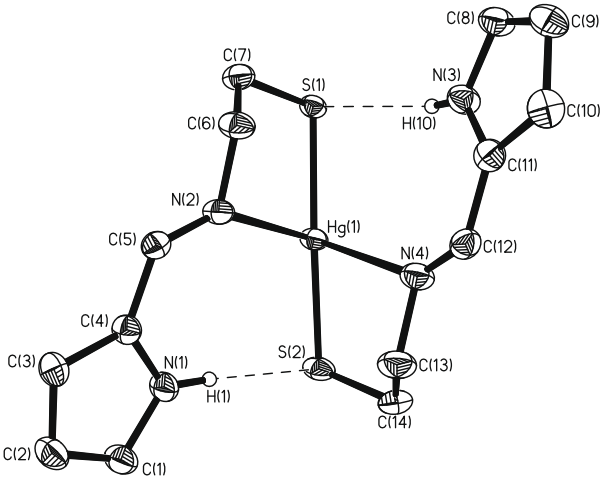


Fig. 3. The molecular structure of **2**. The thermal ellipsoids were drawn at 50% probability level with dash lines showing the NH···S hydrogen-bond interactions. Hydrogen atoms bound to carbon atoms were omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Zn(1)–N(2)	2.077(2)	Hg(1)–N(2)	2.615(2)
Zn(1)–N(4)	2.134(2)	Hg(1)–N(4)	2.724(3)
Zn(1)–S(2)	2.2500(7)	Hg(1)–S(2)	2.3376(8)
Zn(1)–S(1)	2.2857(7)	Hg(1)–S(1)	2.3518(6)
C(5)–N(2)	1.286(3)	C(5)–N(2)	1.288(3)
N(4)–C(12)	1.283(3)	N(4)–C(12)	1.275(4)
N(2)–Zn(1)–N(4)	96.20(9)	N(2)–Hg(1)–N(4)	79.00(8)
N(2)–Zn(1)–S(2)	121.58(6)	N(2)–Hg(1)–S(2)	107.33(5)
N(4)–Zn(1)–S(2)	91.28(6)	N(4)–Hg(1)–S(2)	81.89(6)
N(2)–Zn(1)–S(1)	91.02(6)	N(2)–Hg(1)–S(1)	82.27(5)
N(4)–Zn(1)–S(1)	119.02(6)	N(4)–Hg(1)–S(1)	105.31(6)
S(2)–Zn(1)–S(1)	133.71(3)	S(2)–Hg(1)–S(1)	169.17(3)
C(14)–S(2)–Zn(1)	94.84(9)	C(14)–S(2)–Hg(1)	100.88(11)
C(5)–N(2)–Zn(1)	138.49(18)	C(5)–N(2)–Hg(1)	141.6(2)
C(6)–N(2)–Zn(1)	105.56(16)	C(6)–N(2)–Hg(1)	102.45(16)
C(7)–S(1)–Zn(1)	94.05(9)	C(7)–S(1)–Hg(1)	100.37(9)
C(12)–N(4)–Zn(1)	139.11(19)	C(12)–N(4)–Hg(1)	142.41(23)
C(13)–N(4)–Zn(1)	103.06(16)	C(13)–N(4)–Hg(1)	98.78(20)

Table 3
Distances (Å) and angles (°) of NH···S hydrogen bonds for **1** and **2**.

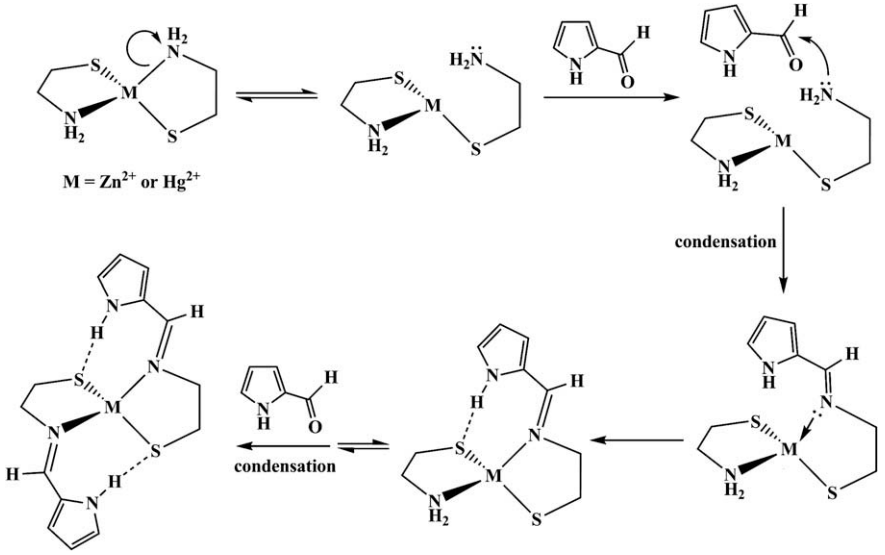
	1	**2**
S(1)···N(3)	3.210(2)	3.311(3)
S(1)···H(10)	2.33(3)	2.52(5)
S(2)···N(1)	3.260(3)	3.343(3)
S(2)···H(1)	2.49(3)	2.40(4)
S(1)···H(10)–N(3)	170.1(27)	160.6(44)
S(2)···H(1)–N(1)	173.2(33)	176.4(31)

3.2. Descriptions of structures

The molecular structures of **1** and **2** were determined by X-ray crystallography and the ORTEP drawings of both complexes, including their atomic numbering schemes, are shown in Figs. 2 and 3. The selected bond distances and angles, and the structural parameters for weak interactions, are listed in Tables 2 and 3, respectively. Similarly, both mononuclear complexes are built up of one metal ion and two HL′S$^-$ ligands. The N(2)–C(5) and N(4)–C(12) bond lengths of both complexes are within the value of 1.29 Å, which is consistent with the assignment of the C=N bonds [43]. The central metal atom is coordinated by the sulfur and the imino nitrogen atoms of the HL′S$^-$ in an N_2S_2 binding mode. The pyrrolyl nitrogen atoms are free from binding to the metal ions.

The structure of complex **1** exhibits a highly distorted tetrahedral geometry around the zinc center, with the largest binding angle being 133.71(3)° [S(2)–Zn(1)–S(1)] and the smallest one being 91.02(6)° [N(2)–Zn(1)–S(1)]. The dihedral angle of 69.33(6)° between the ZnS_2 and ZnN_2 planes, and the bond distances of the Zn–S (average 2.2679(7) Å) and Zn–N (average 2.1055(2) Å), are very similar to those of [Zn(MPIMP)$_2$] (MPIMP = 2-[(2-mercaptophenyl)iminomethyl]pyrrole) with a similar skeleton (72.6°, 2.263(1) Å, and 2.057(3) Å, respectively) [35] and those of other zinc complexes with an N_2S_2 coordination set [44]. In contrast, the geometry around the mercury atom in the molecular structure of **2** is best described as bisphenoidal with S–Hg–S and N–Hg–N bond angles of 169.17(3) and 79.00(8)°, respectively. In contrast to the structure of Hg(LS)$_2$, there is no intermolecular Hg···S contacts present in the structure of **2**. The dihedral angle of 71.12(8)° between the HgS_2 and HgN_2 planes, and the bond distances of the Hg–S (average 2.3447(7) Å), are very similar to those of other Hg(N_2S_2) complexes, but the Hg–N distances (2.615(2), and 2.724(3) Å) are slightly deviated from the range between 2.314 and 2.608 Å [44]. Nevertheless, the lengths between the mercury and nitrogen atoms in **2** are still shorter than those of other reported mercury thiolate complexes with weak intramolecular Hg···N interactions (2.786–2.980 Å) [45–48]. It is worthwhile to notice that the Hg-S bonds in **2** are slightly shorter than those in Hg(LS)$_2$ (2.357(2) and 2.364(2) Å), where a similar bisphenoidal N_2S_2 coordination mode around Hg atom is present. Thus, it is reasonable that the Hg–N bonds in **2** are slightly longer than those in Hg(LS)$_2$ (2.531(6) and 2.650(6) Å) [32].

As predicted by IR and ^{1}H NMR analysis, the solid-state structures of both complexes contain intramolecular hydrogen bonds. The pyrrolyl NH moiety of the ligand is used as a hydrogen-bond donor and each sulfur atom is an acceptor. The pyrrolyl N–H groups are directly pointed to the S atoms with N–H···S av. angles of 171.7° and 168.5° for **1** and **2**, respectively (Table 3). The mean S···N contact distances of 3.24 Å (complex **1**) and 3.33 Å (complex **2**), which are shorter than the sum of the van der Waals radii (3.35 Å) [49], are comparable to those of other complexes with hydrogen-bond interactions [21,23,24,26,32,50–52]. With the av. N–H···S angle closer to 180° and the shorter S···N contact distances of **1** comparing to **2**, it is obvious that the NH···S hydrogen bonding is stronger in **1** than **2** in the solid state, which agrees with



Scheme 3.

the results of the NMR analysis in solution. A survey of molecular structures exhibiting the $Zn(N_2S_2)$ coordination environment with intramolecular NH···S hydrogen bonds using the Cambridge Structural Database (CSD) only found two complexes. The complex $[(L4)Zn(S\text{-}2\text{-}CH_3CONHC_6H_4)]$ (L4 designates a N_2S tripodal scorpionate ligand), synthesized by Carrano et al., contains one intramolecular NH···S hydrogen bond [20,21]. The other complex is $[Zn(S\text{-}2\text{-}PhCONHC_6H_4)_2(MeImH)_2]$ (MeImH = 1-methylimidazole), which possesses two intramolecular NH···S hydrogen-bond interactions [53]. Our complex **1** represents the third example. Furthermore, the uniqueness of complex **1** is that the hydrogen-bond donor for interacting with S atom is coming from the other ligand within the same molecule, instead of from the *ortho* position on a phenyl ring. Although several Hg(II) complexes in the N_2S_2 coordination mode were found in the CSD search, we were not able to locate one with S···H intramolecular hydrogen-bond contacts. Nevertheless, a few Hg(II) complexes with different coordination modes, containing NH···S hydrogen-bond interactions, have been reported in the literature [25,26,32,50,54].

3.3. The importance of the intramolecular hydrogen bonds of *1*

To understand the effects of the NH···S hydrogen bonds on the formation and stability of **1** and **2**, *N*-methyl-pyrrole-2-carboxaldehyde, as opposed to pyrrole-2-carboxaldehyde, was used during the condensation process (Scheme 2). Although the one-pot reaction using Hg^{2+} ions gave the desired product (**3**) with an 83% yield, the reaction using Zn^{2+} ions only afforded $Zn(LS)_2$ and un-reacted *N*-methyl-pyrrole-2-carboxaldehyde. It is expected that the nucleophilic thiolate is well-protected by M^{2+} ion (M = Zn and Hg), and the M–N bonds are in the equilibrium between binding and dissociation. Temporary Schiff base formed is stabilized by the subsequent coordination by metal ion (Scheme 3). The prevention of the formation of *N*-methyl derivative of **1** was probably caused by steric hindrance of methyl group close to S atom of the ligand. In the case of **3**, the hindrance was probably avoided by the adjustable weak Hg–N bonds. Thus, the N–H hydrogen-bond donor from the pyrrolyl moiety probably plays a role in stabilizing the final complexes, especially for **1**.

4. Conclusions

We successfully made an extension of cysteamine with the pyrrolyl moiety, which contains an NH hydrogen-bond donor, to prevent the formation of intermolecular S···H contacts, and to form intramolecular ones in metal complexes. Such a strategy may be applied to other complexes with extensive intermolecular hydrogen-bond interactions. Using this strategy, two group 12 metal complexes with the N_2S_2 binding mode were synthesized using metal-templated Schiff base condensation. The intramolecular NH···S hydrogen-bond interactions of both complexes were evidenced by X-ray crystallographic analysis, IR and NMR spectroscopies. Complex **1** adopts a tetrahedral geometry. In contrast, an almost linear S–M–S angle and a smaller N–M–N angle were seen in **2**. The observations suggest that the Zn^{2+} in zinc finger proteins [27], which offer a rigid coordination environment, is better protected against substitution by Hg^{2+} ions. The NH···SZn hydrogen bonding in proteins may provide a further contribution to the stability of the $Zn(N_2S_2)$ core.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Council (Taiwan). We thank Professor Ching-Han Hu for helpful discussions.

Appendix A. Supplementary material

CCDC 698806 and 698807 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.010.

References

[1] M.J. Calhorda, J. Chem. Soc., Chem. Commun. (2000) 801–809.
[2] H.-J. Schneider, A.K. Yatsimirsky, Chem. Soc. Rev. 37 (2008) 263–277.
[3] G. Cooke, V.M. Rotello, Chem. Soc. Rev. 31 (2002) 275–286.
[4] J.D. Dunitz, A. Gavezzotti, Angew. Chem., Int. Ed. 44 (2005) 1766–1787.
[5] D. Braga, F. Grepioni, Acc. Chem. Res. 33 (2000) 601–608.
[6] T. Steiner, Angew. Chem., Int. Ed. 41 (2002) 48–76.
[7] J. Cerny, P. Hobza, Phys. Chem. Chem. Phys. 9 (2007) 5291–5303.
[8] N. Suzuki, T. Higuchi, Y. Urano, K. Kikuchi, H. Uekusa, Y. Ohashi, T. Uchida, T. Kitagawa, T. Nagano, J. Am. Chem. Soc. 121 (1999) 11571–11572.
[9] S. Yoshioka, S. Takahashi, K. Ishimori, I. Morishima, J. Inorg. Biochem. 81 (2000) 141–151.
[10] S.P. de Visser, F. Ogliaro, P.K. Sharma, S. Shaik, J. Am. Chem. Soc. 124 (2002) 11809–11826.
[11] A. Dey, T. Okamura, N. Ueyama, B. Hedman, K.O. Hodgson, E.I. Solomon, J. Am. Chem. Soc. 127 (2005) 12046–12053.
[12] F. Paulat, N. Lehnert, Inorg. Chem. 46 (2007) 1547–1549.
[13] K. Baba, T. Okamura, C. Suzuki, H. Yamamoto, T. Yamamoto, M. Ohama, N. Ueyama, Inorg. Chem. 45 (2006) 894–901.
[14] K. Baba, T. Okamura, H. Yamamoto, T. Yamamoto, M. Ohama, N. Ueyama, Inorg. Chem. 45 (2006) 8365–8371.
[15] R.S. Sengar, J.J. Miller, P. Basu, J. Chem. Soc., Dalton Trans. (2008) 2569–2577.
[16] N. Ueyama, M. Nakata, M. Fuji, T. Terakawa, A. Nakamura, Inorg. Chem. 24 (1985) 2190–2196.
[17] N. Ueyama, T. Terakawa, M. Nakata, A. Nakamura, J. Am. Chem. Soc. 105 (1983) 7098–7102.
[18] D.W. Low, M.G. Hill, J. Am. Chem. Soc. 122 (2000) 11039–11040.
[19] A. Donaire, B. Jimenez, C.O. Fernandez, R. Pierattelli, T. Niizeki, J.-M. Moratal, J.F. Hall, T. Kohzuma, S.S. Hasnain, A.J. Vila, J. Am. Chem. Soc. 124 (2002) 13698–13708.
[20] J.N. Smith, Z. Shirin, C.J. Carrano, J. Am. Chem. Soc. 125 (2003) 868–869.
[21] J.N. Smith, J.T. Hoffman, Z. Shirin, C.J. Carrano, Inorg. Chem. 44 (2005) 2012–2017.
[22] S.-J. Chiou, C.G. Riordan, A.L. Rheingold, Proc. Natl. Acad. Sci. USA 100 (2003) 3695–3700.
[23] M.M. Morlok, K.E. Janak, G. Zhu, D.A. Quarless, G. Parkin, J. Am. Chem. Soc. 127 (2005) 14039–14050.
[24] M.M. Ibrahim, J. Seebacher, G. Steinfeld, H. Vahrenkamp, Inorg. Chem. 44 (2005) 8531–8538.
[25] N. Ueyama, K. Taniuchi, T. Okamura, A. Nakamura, H. Maeda, S. Emura, Inorg. Chem. 35 (1996) 1945–1951.
[26] M. Kato, K. Kojima, T. Okamura, H. Yamamoto, T. Yamamura, N. Ueyama, Inorg. Chem. 44 (2005) 4037–4044.
[27] B.L. Vallee, D.S. Auld, Acc. Chem. Res. 26 (1993) 543–551.
[28] R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239–2314.
[29] W.N. Lipscomb, N. Strater, Chem. Rev. 96 (1996) 2375–2434.
[30] H. Maeda, Eur. J. Org. Chem. 2007 (2007) 5313–5325.
[31] J.L. Sessler, S. Camiolo, P.A. Gale, Coord. Chem. Rev. 240 (2003) 17–55.
[32] H. Fleischer, Y. Dienes, B. Mathiasch, V. Schmitt, D. Schollmeyer, Inorg. Chem. 44 (2005) 8087–8096.
[33] R.M. Silverstein, E.E. Ryskiewicz, C. Willard, R.C. Koehler, J. Org. Chem. 20 (1955) 668–672.
[34] D.C. Martyn, A.J. Vernall, B.M. Clark, A.D. Abell, Org. Biomol. Chem. 1 (2003) 2103–2110.
[35] J. Castro, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, A. Castineiras, A. Sousa, D.E. Fenton, J. Chem. Soc., Dalton Trans. (1990) 3255–3258.
[36] G.M. Sheldrick, SHELXTL, Version 5.1, Bruker AXS Inc., Madison, WI, 1998.
[37] L.E. Sutton, Tables of Interatomic Distances and Configurations in Molecules and Ions, Chemical Society Publications, UK, 1965.
[38] R.G. Charles, H. Freiser, J. Org. Chem. 18 (1953) 422–425.
[39] R. Bastida, M.R. Bermejo, M.S. Louro, J. Romero, A. Sousa, Inorg. Chim. Acta 145 (1988) 167–169.
[40] R.T. Wragg, J. Chem. Soc. C (1969) 2087–2092.
[41] J.A. Castro, J. Romero, J.A. Garcia-Vazquez, A. Macias, A. Sousa, U. Englert, Polyhedron 12 (1993) 1391–1397.
[42] J. Habazettl, L.C. Myers, F. Yuan, G.L. Verdine, G. Wagner, Biochemistry 35 (1996) 9335–9348.
[43] H. Jadamus, Q. Fernando, H. Freiser, J. Am. Chem. Soc. 86 (1964) 3056–3059.
[44] H. Fleischer, Coord. Chem. Rev. 249 (2005) 799–827.
[45] J.L. Atwood, D.E. Berry, S.R. Stobart, M.J. Zaworotko, Inorg. Chem. 22 (1983) 3480–3482.
[46] A. Castiñiras, W. Hiller, J. Strähle, J. Bravo, J.S. Casas, M. Gayoso, J. Sordo, J. Chem. Soc., Dalton Trans. (1986) 1945–1948.

[47] D.S. Black, G.B. Deacon, G.L. Edwards, B.M. Gatehouse, Aust. J. Chem. 46 (1993) 1323–1336.
[48] A. Sousa-Pedrares, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, I. Casanova, A. Sousa, J. Chem. Soc., Dalton Trans. (2003) 1379–1388.
[49] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
[50] C.-H. Kim, S. Parkin, M. Bharara, D. Atwood, Polyhedron 21 (2002) 225–228.
[51] H. Fleischer, D. Schollmeyer, Inorg. Chem. 43 (2004) 5529–5536.
[52] T. Okamura, T. Iwamura, H. Yamamoto, N. Ueyama, J. Organomet. Chem. 692 (2007) 248–256.
[53] W.-Y. Sun, L. Zhang, K.-B. Yu, J. Chem. Soc., Dalton Trans. (1999) 795–798.
[54] K. Baba, T. Okamura, H. Yamamoto, T. Yamamoto, N. Ueyama, Inorg. Chem. 47 (2008) 2837–2848.