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Structure and characterization of novel zinc(II) and cadmium(II) complexes with 2-(benzoylamino)benzenethiolate and 1-methylimidazole. NH···S Hydrogen bonding in metal complexes with a S_2N_2 binding site

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Neutral four-co-ordinate zinc(II) and cadmium(II) complexes $[M(S\text{-}2\text{-}PhCONHC_6H_4)_2(1\text{-}MeIm)_2]\cdot 0.5H_2O$ (M = Zn **1** or Cd **2**, 1-MeIm = 1-methylimidazole), were synthesized and their structures determined by X-ray crystallography. In both complexes the metal atoms have distorted tetrahedral configurations with S_2N_2 binding sets. The formation of a NH···S hydrogen bond in **1** and **2** was confirmed by IR spectroscopic measurements in the solid state. The solution properties of the complexes were investigated by NMR spectroscopy. In ^1H NMR spectra downfield shifted signals were observed for amide NH protons of complexes **1** and **2** in acetonitrile-d_3 solution. The results indicate that there are also interactions between the NH and sulfur atom in solution. Such non-covalent NH···S interactions are considered to be important in controlling the conformation and properties of complexes with S_2N_2 binding sites.

The sulfur and nitrogen atoms of the side-chain of cysteine and histidine residues are two of the most common donors in biological systems. They can bind to metal ions and form the active centers of metalloenzymes and metalloproteins.[1–8] For example, in the active site of Rieske iron–sulfur proteins there are two cysteine and two histidine residues which bind to the 2Fe2S center.[3,9] Recently, Morris and co-workers[10] reported the synthesis and the properties of $[Fe(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(1\text{-}MeIm)_2]$ (1-MeIm = 1-methylimidazole) as a model of the S_2N_2 binding site. In addition, a copper protein, *Alcaligenes* azurin, has SS^*N_2 binding in the active site (S* refers to the thioether atom of Met-121).[11] It has been proposed that a Asn(47) NH···S Cys(112) hydrogen bond exists in this site.[11] However, the role of this hydrogen bond is unclear. It is also known that two cysteine and two histidine residues bind to the zinc ion in the zinc finger proteins (transcription factor IIIA and related nucleic acid binding proteins).[5–7,12] Up to now, only a few examples of mononuclear zinc complexes with S_2N_2 binding site have been reported. Corwin and Koch[13] have reported the synthesis and structure of $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}MeIm)_2]$ and $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(bipy)]$ (bipy = 2,2′-bipyridine) as structural models of the $Zn(S\text{-}cys)_2(his)_2$ center. Most recently, Wilker and Lippard[14] reported the synthesis and structure of $[Zn(SPh)_2(1\text{-}MeIm)_2]$ and its reaction with $(CH_3O)_3P(O)$ in a modeling study of the DNA methylphosphotriester repair site in *Escherichia coli* Ada. Some other examples of structurally characterized zinc(II) complexes with S_2N_2 binding sites are $[Zn(C_7H_4NS_2)_2(py)_2]$, $[Zn(C_7H_4NS_2)_2(bipy)]$ ($C_7H_4NS_2$ = benzothiazole-2-thiolate anion, py = pyridine)[15] and $[Zn(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2(1\text{-}MeIm)_2]$.[16] Among these reported Zn^{II}–S_2N_2 complexes, only the last one is unstable in solution and lost one N-donor ligand in toluene solution to produce a three-coordinate complex $[Zn(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2(1\text{-}MeIm)]$.[16]

In order to investigate the influence of the NH···S hydrogen bond on the structure and properties of complexes with S_2N_2 binding systems, we synthesized a novel zinc complex and its cadmium analogue with 2-benzoylaminobenzenethiolate and 1-methylimidazole ligands. The formation of an intramolecular NH···S hydrogen bond was investigated by IR and NMR spectroscopic measurements. Such a hydrogen bond has been found to play important roles in regulating the properties of metal–sulfur proteins as well as their model complexes.[17,18] As reported previously, the presence of a NH···S hydrogen bond in the various metal thiolate complexes has been confirmed by X-ray structural analysis, IR, ^2H and ^{19}F NMR spectroscopies, *etc.*[19–22] From these studies the hydrogen bond was demonstrated to be important in controlling the redox potential and stability of the metal thiolate complexes.[18,21,22] However its effect in complexes with S_2N_2 binding systems has not been discussed yet.

Experimental

Materials

Solvents such as tetrahydrofuran (THF), ethanol, *etc.* were dried and purified by distillation before use. Zinc chloride and cadmium nitrate tetrahydrate were used as commercially obtained. 1-Methylimidazole was distilled just before use. Bis(2-benzoylaminophenyl) disulfide was synthesized by the modified method reported in the literature.[23]

Syntheses

$[Zn(S\text{-}2\text{-}PhCONHC_6H_4)_2(1\text{-}MeIm)_2]\cdot 0.5H_2O$ 1. This complex was prepared by a method similar to that reported for the iron(II) complex with 2,6-diisopropylbenzenethiolate and 1-methylimidazole.[10] An excess of $NaBH_4$ was added in small portions to a THF–ethanol (1 : 1, 10 ml) solution of bis-(2-benzoylaminophenyl) disulfide (117 mg, 0.256 mmol). The mixture was stirred at room temperature for about 1 h to give a clear solution, and then added dropwise to a stirred solution of zinc chloride (35 mg, 0.256 mmol) and 1-methylimidazole (0.041 ml, 0.512 mmol) in THF (10 ml). The stirring was continued for about 1 h after the addition. The solvents were removed by evaporation, then toluene (50 ml) was added to the residue and the mixture stirred overnight at ambient temperature. After filtration, the toluene was removed from the filtrate *in vacuo* to give crude products. Almost colorless crystals were obtained by recrystallization from acetonitrile. Yield: 112 mg (63%) (Found: C, 58.86; H, 4.78; N, 12.06. Calc. for $C_{34}H_{33}N_6O_{2.5}S_2Zn$: C, 58.74; H, 4.78; N, 12.09%).

[Cd(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O 2. Complex **2** was prepared in a manner similar to that of **1** using cadmium nitrate tetrahydrate (158 mg, 0.512 mmol), bis(2-benzoylaminophenyl) disulfide (234 mg, 0.512 mmol) and 1-methylimidazole (0.082 ml, 1.024 mmol). The crude products were recrystallized from toluene and diethyl ether to give colorless crystals in similar yield to that of the zinc analogue (Found: C, 54.98; H, 4.44; N, 11.26. Calc. for $C_{34}H_{33}CdN_6O_{2.5}S_2$: C, 55.02; H, 4.48; N, 11.32%).

Physical measurements

The analyses (C, H and N) were made on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. 500 MHz ^{1}H NMR spectroscopic measurements were carried out on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference. The mixing time used in two-dimensional NOESY spectral measurements was 400 ms. The solid state infrared (IR) spectra were obtained from a Bruker IFS66V vacuum-type FT-IR spectrophotometer by using KBr pellets.

Crystallography

Single crystals of complexes **1** and **2** were grown by slow evaporation from recrystallization solutions. The X-ray diffraction measurements were made on a Siemens P4 automatic four-circle diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 290(2) K. Intensity data were collected in the variable ω-scan mode. Unit-cell parameters were determined from 36 and 32 reflections for complexes **1** and **2**, respectively. Empirical absorption corrections were applied. The crystal structures were solved by the direct method. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms except for those of the water molecule were generated geometrically. Information concerning the crystallographic data collection and structure refinement for complexes **1** and **2** is summarized in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC reference number 186/1293.

See http://www.rsc.org/suppdata/dt/1999/795/ for crystallographic files in .cif format.

Results and discussion

Synthesis and crystal structure of [M(S-2-PhCONHC$_6$H$_4$)$_2$-(1-MeIm)$_2$]·0.5H$_2$O (M = Zn 1 or Cd 2)

The preparation of $M^{II}S_2N_2$ complexes is readily accomplished by reaction of lithium or sodium thiolate with $M^{II}Cl_2$ and a N-donor ligand. For reported ZnS_2N_2 and CdS_2N_2 complexes LiSR was generally employed.[13,14,24] In our synthesis the sodium thiolate was generated by reduction of bis(2-benzoylaminophenyl) disulfide with $NaBH_4$ *in situ* and then reacts directly with a mixture of M^{2+} and 1-methylimidazole. A similar method has been used for the synthesis of [Fe(S-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$-(1-MeIm)$_2$].[10]

The structures of [Zn(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O **1** and [Cd(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O **2** were determined by X-ray crystallography. From the crystal data as listed in Table 1 it is clear that the two compounds are isomorphous and isostructural. The crystal structure of complex **1** is shown in Fig. 1. The co-ordination environments of zinc(II) and cadmium(II) atoms in the complexes **1** and **2** are both distorted tetrahedral with a S_2N_2 binding set. The largest angle, S(1)–Zn–S(2) in complex **1**, is 118.09(3)°, while the smallest angle, N(3)–Zn–N(5) in **1**, is 103.14(8)° (Table 2). The corresponding angles in complex **2** are 126.11(3) [S(1)–Cd–S(2)] and 99.53(8)° [N(3)–Cd–N(5)]. This indicates that the S(1)–Zn–S(2) and N(3)–Zn–N(5) angles in the zinc complex are closer to the ideal angle (109.5°) of a tetrahedral configuration than the corresponding angles in the cadmium analogue. Similar angles, S(1)–Zn–S(2) and N(1)–Zn–N(2), which are between 101.9(2) and 115.3(2)° have been reported in complex [Zn(S-2,3,5,6-Me$_4$C$_6$H)$_2$(1-MeIm)$_2$],[13] while in the case of [Cd(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$(1-MeIm)$_2$], the corresponding angles are between 94.0(4) and 126.1(1)°;[24] [Zn(S-2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$(1-MeIm)$_2$] also presents similar bond angles [S(1)–Zn–S(2) 115.5(1); N(1)–Zn–N(3) 101.7(4)°].[16] The data show that the distortion from the tetrahedral geometry of the zinc complex is smaller than that of the cadmium analogue in the S_2N_2 binding system. The dihedral angles between the two planes of S(1)–M–S(2) and N(3)–M–N(5) (M = Zn or Cd), which are usually considered as an indication of the degree of distortion of a complex with tetrahedral co-ordination geometry, are 91.1 and 91.6° for **1** and **2**, respectively. The slightly greater dihedral angle (0.5°) of the cadmium complex supports larger distortion. The reported complex [Fe(S-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(1-MeIm)$_2$] is much more distorted from a tetrahedral co-ordination geometry than are **1** and **2** since the dihedral angle between the S(1)–Fe–S(2) and N(1)–Fe–N(2) planes is 86.9°.[10] The bond lengths of **1**, Zn–S$_{av}$ [2.3041(7) Å] and Zn–N$_{av}$ [2.036(2) Å] (Table 2), are quite similar to those of [Zn(S-2,3,5,6-Me$_4$C$_6$H)$_2$(1-MeIm)$_2$], Zn–S$_{av}$ [2.300(2) Å] and Zn–N$_{av}$ [2.047(6) Å],[13] [Zn(S-2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_2$-(1-MeIm)$_2$], Zn–S$_{av}$ [2.315(3) Å] and Zn–N$_{av}$ [2.048(10) Å][16] as well as [Zn(SPh)$_2$(1-MeIm)$_2$], Zn–S [2.2916(7) Å] and Zn–N [2.038(2) Å].[14] The Cd–S$_{av}$ [2.4671(8) Å] and Cd–N$_{av}$ [2.253(2) Å] distances for **2** are also similar to those [2.461(1), 2.264(9) Å] of [Cd(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$(1-MeIm)$_2$].[24]

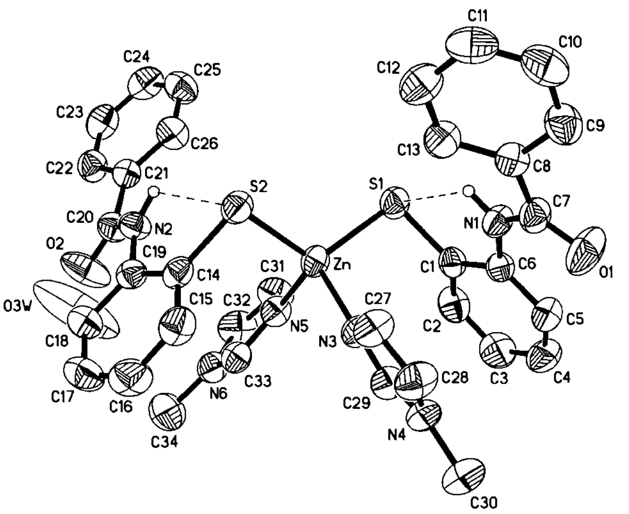

Fig. 1 Crystal structure of [Zn(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O **1** with the numbering scheme and NH · · · S hydrogen bonding. Thermal ellipsoids are drawn at 50% probability. The protons except the amide NH were omitted for clarity.

As shown in Fig. 1, the carbonyl (C=O) group is directed to the outside, as a consequence the amide NH group faces the arenethiolate sulfur atom. Furthermore, the distances between N and S, N(1)–S(1) 2.940, N(2)–S(2) 2.986 Å for complex **1**, N(1)–S(1) 2.947, N(2)–S(2) 2.996 Å for **2** as listed in Table 3, indicate that the amide NH group is quite close to the adjacent thiolate sulfur atom. This implies that a NH · · · S hydrogen bond exists in the S_2N_2 co-ordination complexes as in metal thiolate complexes.[20,25] The distances and angles of the NH · · · S hydrogen bonds for complexes **1** and **2** are summarized in Table 3. The formation of such bonds is also confirmed by infrared spectroscopic measurements as described later. In addition to the intramolecular NH · · · S hydrogen bond, two

Table 1 Summary of crystallographic data for complexes [M(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O (M = Zn **1** or Cd **2**)

	1	**2**
Chemical formula	$C_{34}H_{33}N_6O_{2.5}S_2Zn$	$C_{34}H_{33}CdN_6O_{2.5}S_2$
Formula weight	695.15	742.18
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	49.218(4)	49.911(5)
b/Å	8.1460(10)	8.1660(10)
c/Å	17.1460(10)	17.272(2)
β/°	104.92	105.260(10)
U/Å^3	6642.6(11)	6791.4(13)
Z	8	8
μ/mm^{-1}	0.907	0.807
Reflections collected	7324	7537
Independent reflections	6523 (R_{int} = 0.0136)	6661 (R_{int} = 0.0174)
R (observed data)	0.0329	0.0303
wR (observed data)	0.0701	0.0604
*R*1 (all data)	0.0593	0.0534
wR (all data)	0.0873	0.0645

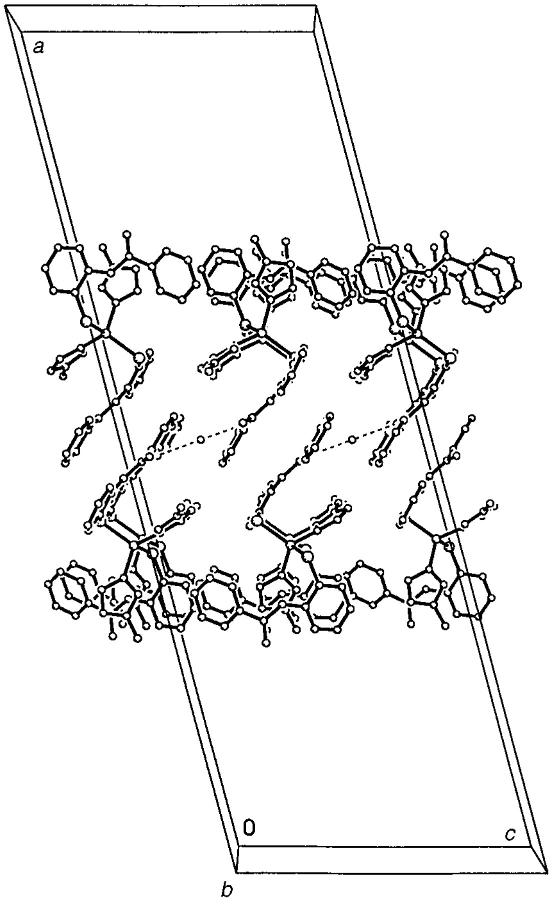

Fig. 2 Crystal packing diagram of [Zn(S-2-PhCONHC$_6$H$_4$)$_2$-(1-MeIm)$_2$]·0.5H$_2$O **1** with intermolecular O(2)···H–O(3w)-H···O(2′) hydrogen bonds.

Table 2 Selected bond lengths (Å) and angles (°) for complexes [M(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O (M = Zn **1** or Cd **2**)

Complex **1**		Complex **2**	
Zn–S(1)	2.3203(7)	Cd–S(1)	2.4806(8)
Zn–S(2)	2.2879(6)	Cd–S(2)	2.4536(8)
Zn–N(3)	2.039(2)	Cd–N(3)	2.261(2)
Zn–N(5)	2.034(2)	Cd–N(5)	2.245(2)
N(5)–Zn–N(3)	103.14(8)	N(5)–Cd–N(3)	99.53(8)
N(5)–Zn–S(2)	111.36(6)	N(5)–Cd–S(2)	110.63(6)
N(3)–Zn–S(2)	107.92(5)	N(3)–Cd–S(2)	105.62(6)
N(5)–Zn–S(1)	107.65(6)	N(5)–Cd–S(1)	106.04(6)
N(3)–Zn–S(1)	107.59(6)	N(3)–Cd–S(1)	105.65(6)
S(1)–Zn–S(2)	118.09(3)	S(1)–Cd–S(2)	126.11(3)
C(1)–S(1)–Zn	96.84(8)	C(1)–S(1)–Cd	96.52(9)
C(14)–S(2)–Zn	95.71(7)	C(14)–S(2)–Cd	95.49(9)
C(29)–N(3)–Zn	127.1(2)	C(29)–N(3)–Cd	126.8(2)
C(27)–N(3)–Zn	126.4(2)	C(27)–N(3)–Cd	126.2(2)
C(33)–N(5)–Zn	127.8(2)	C(33)–N(5)–Cd	127.6(2)
C(31)–N(5)–Zn	125.1(2)	C(31)–N(5)–Cd	125.3(2)

Table 3 Distances (Å) and angles (°) of NH···S hydrogen bonds for complexes [M(S-2-PhCONHC$_6$H$_4$)$_2$(1-MeIm)$_2$]·0.5H$_2$O (M = Zn **1** or Cd **2**)

	Complex **1**	Complex **2**
S(1)–N(1)	2.940	2.947
S(1)–H(1)	2.423	2.435
S(2)–N(2)	2.986	2.996
S(2)–H(2)	2.548	2.556
S(1)–H(1)–N(1)	119.1	118.8
S(2)–H(2)–N(2)	112.7	112.8

molecules of complex **1** as well as **2** share one water molecule in the crystalline state and the distances, O(3w)···O(2) 2.767 Å for complex **1** and 2.790 Å for **2**, show the presence of a O(2)···H–O(3w)-H···O(2′) hydrogen bond. Fig. 2 shows the packing of complex **1** with intermolecular hydrogen bonds and almost the same packing was found for **2**.

Infrared spectroscopy: evidence for the formation of a NH···S hydrogen bond

In order to detect the formation of a NH···S hydrogen bond the IR spectra of complexes **1** and **2** and bis(2-benzoylaminophenyl) disulfide were measured in the solid state. The free disulfide exhibits NH stretching and C=O bands at 3374 and 1679 cm^{-1}, respectively. The corresponding NH and C=O vibration bands were observed at 3232 and 1662 cm^{-1} for complex **1**, 3244 and 1662 cm^{-1} for **2**. The large low wavenumber shifts of NH (Δ*ν* 142 cm^{-1} for **1** and 130 cm^{-1} for **2**) and C=O (Δ*ν* 17 cm^{-1} for **1** and **2**) bands observed indicate the formation of a NH···S hydrogen bond as demonstrated for metal thiolate complexes.[20,23,25,26] For example, $\Delta\nu_{NH}$ (108 cm^{-1}) and $\Delta\nu_{CO}$ (12 cm^{-1}) have been reported for the complex [Co^{II}(S-2-*t*-BuCONHC$_6$H$_4$)$_4$]$^{2-}$ in the solid state.[25] Smaller shifts have been observed for the complexes [Fe$_4$S$_4$(S-2-*t*-BuCONHC$_6$H$_4$)$_4$]$^{2-}$ ($\Delta\nu_{NH}$ = 75 cm^{-1})[23] and [Mo^{IV}O(S-2-CH$_3$CONHC$_6$H$_4$)$_4$]$^{2-}$ ($\Delta\nu_{NH}$ = 59 cm^{-1}).[20] The IR results are consistent with the X-ray structural analysis and confirm the formation of a NH···S hydrogen bond in the S$_2$N$_2$ co-ordination complexes **1** and **2**.

The solution structure: ^{1}H NMR spectra

The solution behaviors of complexes **1** and **2** were investigated by ^{1}H NMR spectroscopy. The peak assignments were carried out by two-dimensional NMR techniques. Fig. 3 illustrates the COSY and NOESY spectra of complex **1** in acetonitrile-d$_3$ at 298 K. The chemical shifts and assignments are in Table 4 together with the data for the ligands (disulfide and 1-methylimidazole). Both upfield and downfield shifted signals were observed for the complexes **1** and **2** compared with the corresponding disulfide and 1-methylimidazole ligands, especially for the signals due to the protons around the zinc and cadmium ions. This implies strong interaction between the metal ions and S, N-donor ligands in acetonitrile solution. In addition, it is noted that the amide NH signal presents the largest downfield shift (1.25 ppm for **1** and 1.22 ppm for **2**). This is interpreted by the formation of a NH···S hydrogen bond in the solution as in the solid state. The large downfield shift of amide NH is considered to originate from the deshielding effect of the sulfur atom due to the formation of the NH · · · S hydrogen bond.

In conclusion, from this study it is clear that an intramolecular NH · · · S hydrogen bond is present in the S_2N_2 binding system as evidenced by X-ray crystallographic analysis, IR and NMR spectroscopies. This work is thought to be the first research dealing with the NH · · · S hydrogen bond in the S_2N_2 binding system. Such non-covalent NH · · · S interactions are considered to be important in regulating the conformation and properties of complexes with S, N-donor ligands as well as of the metalloproteins and metalloenzymes with $(cys)_2(his)_2$ binding centers.

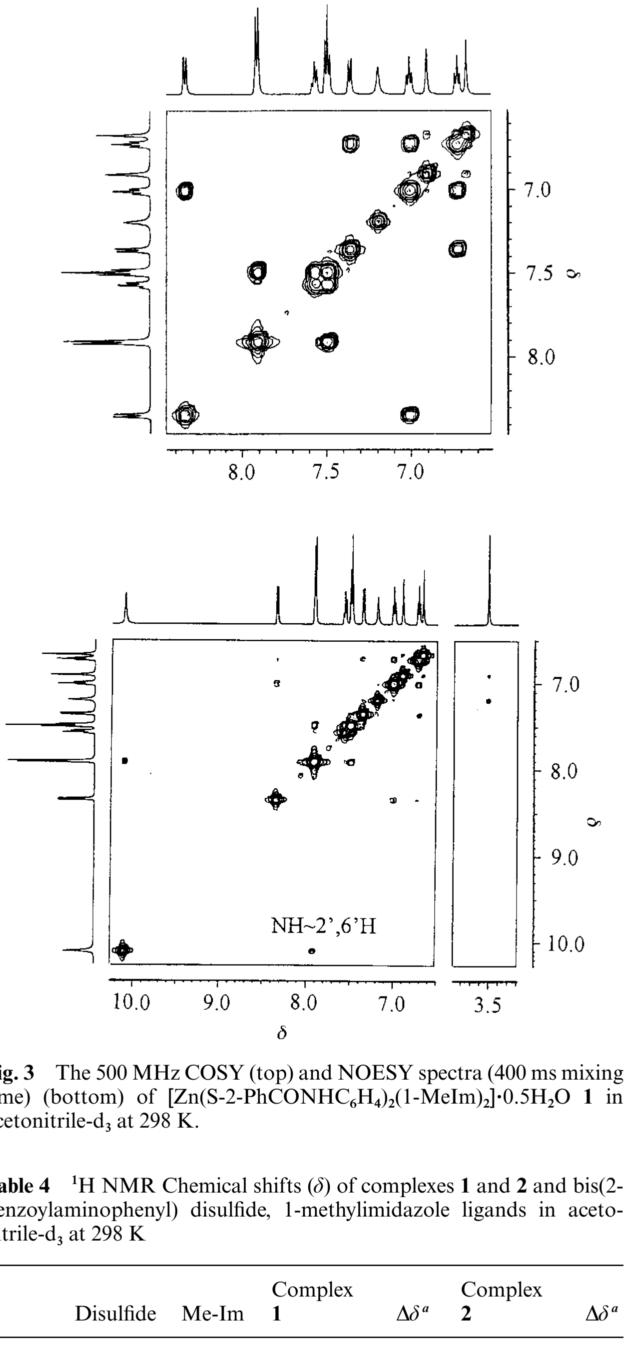

Fig. 3 The 500 MHz COSY (top) and NOESY spectra (400 ms mixing time) (bottom) of $[Zn(S\text{-}2\text{-}PhCONHC_6H_4)_2(1\text{-}MeIm)_2]\cdot 0.5H_2O$ **1** in acetonitrile-d_3 at 298 K.

Table 4 ^1H NMR Chemical shifts (δ) of complexes **1** and **2** and bis(2-benzoylaminophenyl) disulfide, 1-methylimidazole ligands in acetonitrile-d_3 at 298 K

	Disulfide	Me-Im	Complex 1	$\Delta\delta^a$	Complex 2	$\Delta\delta^a$
NH	8.85		10.10	1.25	10.07	1.22
3H	8.06		8.34	0.28	8.33	0.27
4H	7.31		7.00	−0.31	7.00	−0.31
5H	7.07		6.72	−0.35	6.70	−0.37
6H	7.62		7.36	−0.26	7.39	−0.23
2′,6′H	7.71		7.90	0.19	7.89	0.18
3′,5′H	7.49		7.49	0	7.46	−0.03
4′H	7.60		7.56	−0.04	7.55	−0.05
1-CH_3		3.66	3.50	−0.16	3.48	−0.18
2H		7.44	7.19	−0.25	7.02	−0.42
4H		6.91	6.66	−0.25	6.57	−0.34
5H		6.98	6.90	−0.08	6.88	−0.10

[a] $\Delta\delta = \delta_{complex} - \delta_{ligand}$.

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