

# Reactions of the Cationic Zinc Thiolate Model Complex $[\text{Zn}(\text{Tab})_4](\text{PF}_6)_2$ with N-Donor Ligands and Cobalt Dichloride

Ai-Xia Zheng,<sup>†,‡</sup> Jing Si,<sup>†</sup> Xiao-Yan Tang,<sup>§</sup> Li-Li Miao,<sup>†</sup> Miao Yu,<sup>†</sup> Kai-Peng Hou,<sup>†</sup> Fan Wang,<sup>†</sup> Hong-Xi Li,<sup>†</sup> and Jian-Ping Lang<sup>\*,†,‡</sup>

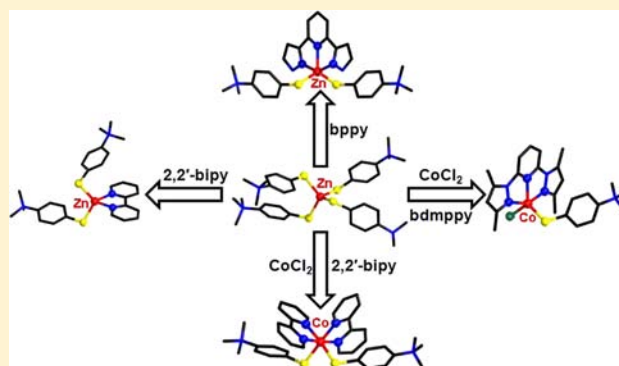
<sup>†</sup>College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China

<sup>‡</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210093, People's Republic of China

<sup>§</sup>Jiangsu Laboratory of Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, People's Republic of China

## S Supporting Information

**ABSTRACT:** Reactions of  $[\text{Zn}(\text{Tab})_4](\text{PF}_6)_2$  (Tab = 4-(trimethylammonio)benzenethiolate) (**1**) with 2,2'-bipyridine (2,2'-bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen), N-methylimidazole (N-Meim), and 2,6-bis(pyrazol-3-yl)pyridine (bppy) or with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  at the presence of N-donor ligands (2,2'-bipy, phen, 4,4'-dimethyl-2,2'-bipyridine (4,4'-dmppy), 2,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (bdmppy)) gave rise to a family of zinc or cobalt thiolate complexes,  $[\text{Zn}(\text{Tab})_2(\text{L})](\text{PF}_6)_2$  (**2**: L = 2,2'-bipy, **3**: L = phen, **4**: L = 2,9-dmphen),  $[\text{Zn}(\text{Tab})_2(\text{N-Meim})_2](\text{PF}_6)_2$  (**5**),  $[\text{Zn}(\text{Tab})_2(\text{bppy})](\text{PF}_6)_2$  (**6**),  $[\text{Co}(\text{Tab})_2(\text{L})_2](\text{PF}_6)_3$  (**7**: L = 2,2'-bipy, **8**: L = phen, **9**: L = 4,4'-dmppy), and  $[\text{Co}(\text{Tab})(\text{bdmppy})\text{Cl}](\text{PF}_6)$  (**10**). These compounds were characterized by elemental analysis, IR spectra, UV-vis spectra, <sup>1</sup>H NMR, electrospray ionization (ESI) mass spectra, and single-crystal X-ray diffraction. The Zn(II) in  $[\text{Zn}(\text{Tab})_2\text{L}_n]^{2+}$  dications of **2-5** is tetrahedrally coordinated by two Tab ligands and one L or two N-Meim ligands. In **6**, the Zn(II) has a distorted trigonal-bipyramidal geometry, coordinated by two Tab ligands and one tridentate bppy ligand. The Co(III) in the  $[\text{Co}(\text{Tab})_2(\text{L})_2]^{3+}$  trications of **7-9** is octahedrally chelated by two bidentate L ligands and two Tab ligands. In **10**, the Co(II) adopts a distorted trigonal-bipyramidal geometry, coordinated by one Cl<sup>-</sup>, one Tab ligand, and one tridentate bdmppy. In the formation of **2-6**, two Tab ligands are removed from the  $[\text{Zn}(\text{Tab})_4]^{2+}$  dication when it is attacked by L ligands, while in the cases of **7-9**, the Zn(II) of the  $[\text{Zn}(\text{Tab})_4]^{2+}$  dication was replaced by Co(III) (derived from oxidation of Co(II) by O<sub>2</sub>) followed by the removal of two Tab ligands via L ligands. In the case of **10**, the central Zn(II) of the  $[\text{Zn}(\text{Tab})_4]^{2+}$  dication was displaced by Co(II) followed by the removal of three Tab ligands via one Cl<sup>-</sup> and one tridentate bdmppy. These ligand and metal replacement reactions may provide some interesting information on the interactions of the  $[\text{Zn}(\text{S-Cys})_4]^{2-}$  unit of Zn-MTs with N-heterocyclic ligands and toxic metal ions encountered in a natural environment.



## INTRODUCTION

Immense interest in the coordination chemistry of zinc(II) thiolate complexes continues to be motivated by the importance of these complexes as active centers of enzymes, such as methionine synthase and metalloproteinase.<sup>1</sup> The most abundant protein sites containing zinc ions are the zinc finger proteins containing a  $[\text{Zn}(\text{S-Cys})_x(\text{N-his})_y]$  unit,<sup>2</sup> which plays a structural role in creating DNA-binding fingers<sup>3</sup> for the transcription of DNA. The most prominent one is the Ada protein of *Escherichia coli* that contains a distorted tetrahedral  $[\text{Zn}(\text{S-Cys})_4]^{2-}$  unit.<sup>4</sup> However, the effective strength of the Zn-S(thiolate) bond (2.35–2.37 Å) is dependent on the nature of the four thiolate ligands in the unit and its structure is relatively unstable in the presence of other donor ligands.<sup>5</sup> For

example, Lippard et al. found that  $[\text{Zn}(\text{SPh})_4]^{2-}$  will dissociate thiolate from the model used for zinc-thiolate alkylation, in which the  $[\text{Zn}(\text{SPh})_4]^{2-}$  anion for representing the  $[\text{Zn}(\text{S-Cys})_4]^{2-}$  unit of Ada is methylated by  $(\text{MeO})_3\text{PO}$ .<sup>6</sup> There are many reports on the  $\text{ZnS}_2\text{N}_2$  model complexes, most of which were prepared by the reaction of zinc salts with thiolates and N-donor ligands.<sup>6a,7</sup> However, reactions of the preformed Zn(II)/thiolate model complexes with N-donor ligands and other transition-metal ions have been less explored. On the other hand, it is known that cobalt(II) has been employed commonly as a probe of zinc metalloenzymes and metalloproteins and such a substitution does

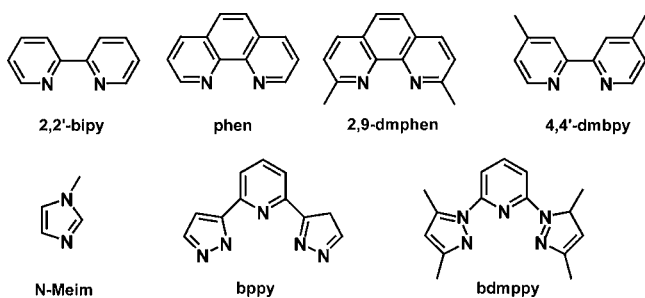
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not measurably alter the overall protein structure.<sup>8</sup> The Zn(II) ions in Zn(II)-MT (MT = metallothionein) were reported to be substituted by Co(II), Ni(II), or Cd(II) ions, to form a set of M(II)-MT.<sup>9</sup> Their electronic, magnetic circular dichroic and electron spin resonance spectra revealed that they have analogous coordination geometry to that of Zn(II)-MT. However, no crystal structures of those M(II)-MTs has been available yet. Co(II)-MT<sup>9a</sup> is very sensitive to air, and exposure results in a light yellow product, a decomposition common to a number of sulfur-containing reconstituted proteins and model compounds.<sup>10</sup> Therefore how to stabilize it and what structure the Co(II) holds remains a challenge. There have been no reports on substitution of Zn(II) ions from the model Zn/thiolate complexes using Co(II), even in the presence of N-donor ligands, though several Co(II)/thiolate/phen complexes (phen = 1,10-phenanthroline)<sup>11a</sup> and one cationic Co(III) complex [Co(SPh)<sub>2</sub>(phen)<sub>2</sub>](ClO<sub>4</sub>) were documented.<sup>11b</sup>

In the past years, we have been engaged in the preparation and property of various metal complexes of the unique zwitterionic 4-(trimethylammonio)benzenethiolate (Tab).<sup>12</sup> One mercury(II)/thiolate model complex [Hg(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was employed to react with various donor ligands (inorganic anions, amines, N-heterocyclic compounds, and carboxylic acids) for mimicking the reactivity of the unsaturated HgS<sub>2</sub> species in Hg-MerR (MerR = metalloregulatory protein)<sup>13a-d</sup> and Hg-MT.<sup>13e-h</sup> In our recent work, we reported the preparation of a mononuclear Zn(II)/Tab complex [Zn(Tab)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> (**1**) and its substitution reactions with Cd<sup>2+</sup> and Hg<sup>2+</sup>.<sup>12k</sup> Could complex **1** be used as a model complex in mimicking the reactivity of the [Zn(S-Cys)<sub>4</sub>]<sup>2-</sup> unit in Zn(II)-MT? Considering that N-heterocyclic compounds like imidazole, pyrimidine, adenine, etc. are always encountered in nature, could they, like carboxylic acids,<sup>14a</sup> react with **1**, and replace some of the Tab ligands from its Zn(II) coordination sphere and even change the geometry of its zinc(II) center? Could other transition-metal ions like cobalt(II) displace the zinc center of **1** to retain the similar coordination geometry? These questions activated us to carry out its reactions with a set of selected N-donor ligands (2,2'-bipyridine (2,2'-bipy), phen, 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen), N-methylimidazole (N-Meim), and 2,6-bis(pyrazol-3-yl)pyridine (bppy)) (Chart 1) or its reactions with cobalt dichloride in the presence

**Chart 1. Structures of 2,2'-bipy, phen, 2,9-dmphen, 4,4'-dmbpy, N-Meim, bppy, and bdmppy Ligands**



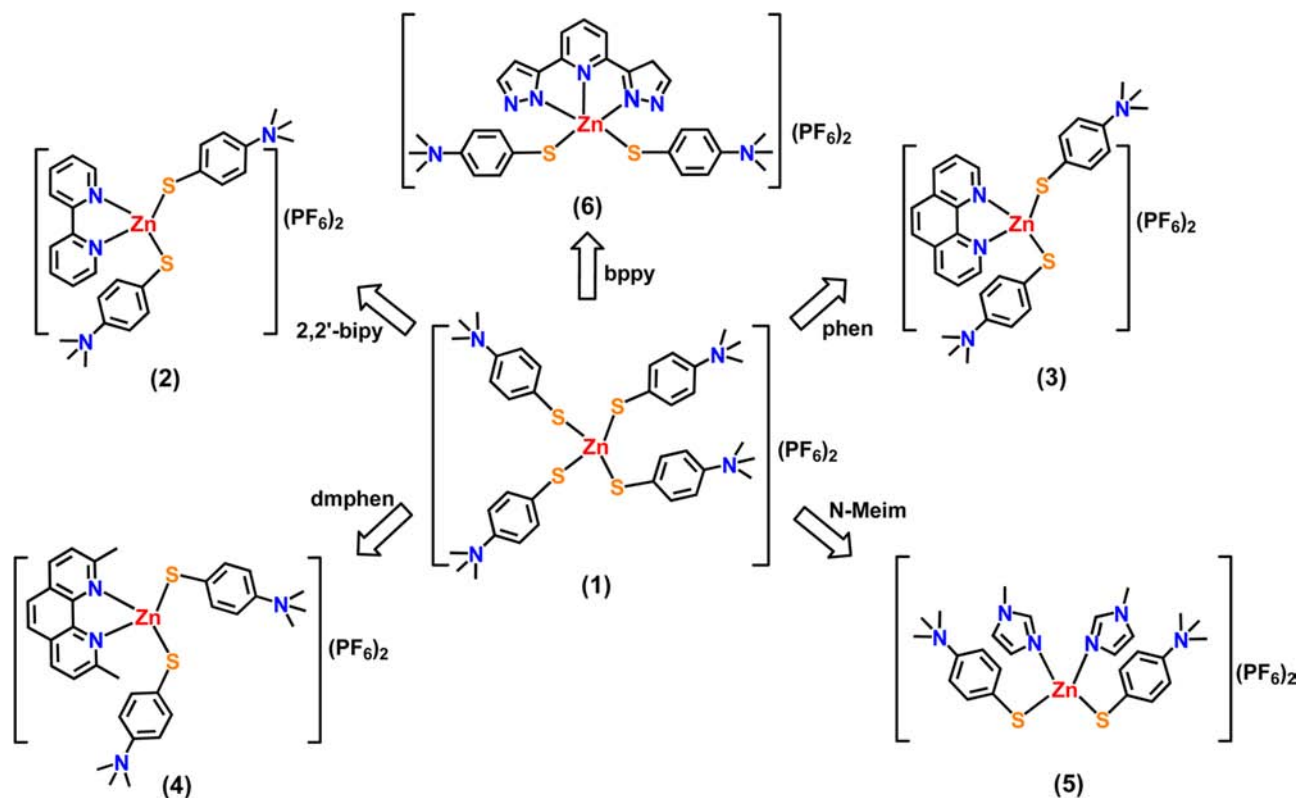
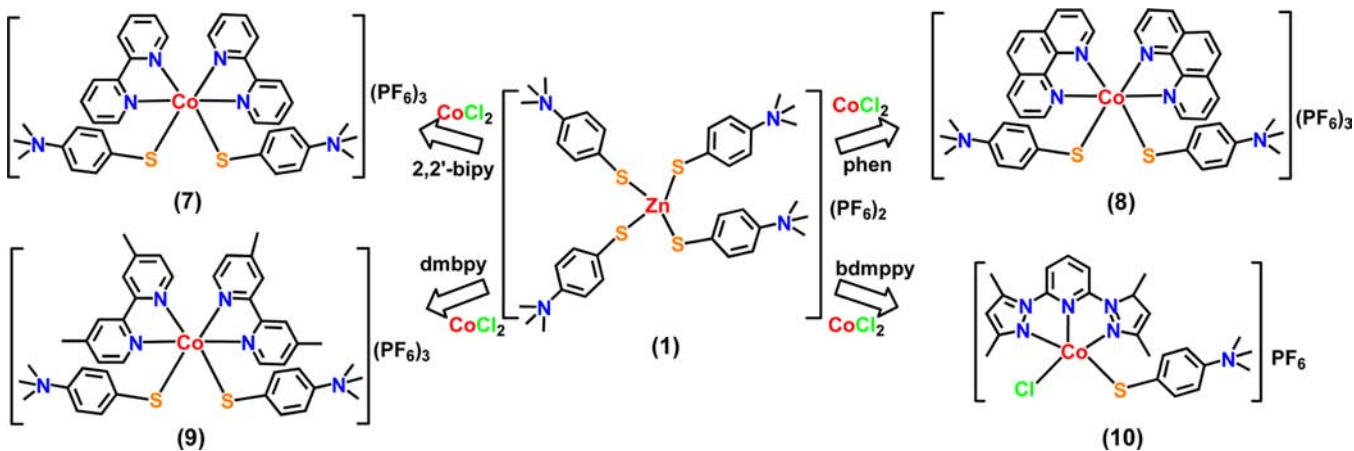
of 2,2'-bipy, phen, 4,4'-dimethyl-2,2'-bipyridine (4,4'-dmbpy), and 2,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)pyridine (bdmppy) (Chart 1). A family of cationic mononuclear complexes [Zn(Tab)<sub>2</sub>L<sub>n</sub>](PF<sub>6</sub>)<sub>2</sub> (**2-6**: L = N-donor ligand, *n* = 1 or 2), [Co(Tab)<sub>2</sub>L<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**7-9**: L = N-donor ligand), and [Co(Tab)(bdmppy)Cl](PF<sub>6</sub>) (**10**) were isolated and structurally

characterized. The results revealed that two of the four Tab ligands of **1** were replaced by the N-donor ligands and the Zn(II) of **1** was displaced by Co(III) or Co(II) in the presence of N-donor ligands, which may present some insights into the possible chemical reactions of the [Zn(S-Cys)<sub>4</sub>]<sup>2-</sup> unit of Zn(II)-containing proteins and enzymes with N-heterocyclic ligands and toxic metal ions existed in nature. Herein we report the replacement reactions along with their isolation and spectral and structural characterization of **2-10**.

## RESULTS AND DISCUSSION

**Synthetic and Spectral Aspects.** Treatment of complex **1** with equimolar 2,2'-bipy, phen, or 2,9-dmphen in MeCN/MeOH gave rise to the mononuclear complexes **2**, **3**, or **4** in an almost quantitative yield (Scheme 1). Reactions with the same components in 1:2 or 1:3 molar ratio did not produce the expected complex [Zn(Tab)<sub>2</sub>(L)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> or cause the replacement of all the four Tab ligands from **1** but still yielded the same product. When **1** was reacted with excess N-Meim, it afforded complex **5** in 94% yield. The elemental analyses of **2-5** were consistent with their chemical formulas. In these reactions, two Tab ligands of the [Zn(Tab)<sub>4</sub>]<sup>2+</sup> dication were replaced by one bidentate N-donor ligand (**2-4**) or two monodentate N-donor ligands (**5**). Although each Zn(II) center in **2-5** remains a tetrahedral geometry, the orientations of the two remaining Tab ligands did get changed due to the different bulkiness of the N-donor ligands, which were described later in this article. It is worth noting that similar reactions of **1** with 1 or 2 equiv of one tridentate ligand, bppy, generated one five-coordinated complex **6** in 95% yield. In this reaction, two Tab ligands of the [Zn(Tab)<sub>4</sub>]<sup>2+</sup> anion were again replaced by bppy. However, the tetrahedral coordination geometry of the Zn(II) center in **1** was changed into a trigonal-bipyramidal one in **6**, which was also confirmed by its UV-vis spectrum. These results imply that the interactions of the Tab ligands with the zinc center in the [Zn(Tab)<sub>4</sub>]<sup>2+</sup> dication are not strong and the coordination geometry of its zinc center could be changed depending on the polydentate N-donor ligands it encountered.

On the other hand, we performed the reactions of **1** with CoCl<sub>2</sub>·6H<sub>2</sub>O, in which a large amount of black precipitate was observed to develop immediately. Such a precipitate was insoluble in common organic solvents, which excluded further identification of its composition. Tuck et al. reported that the electrochemical oxidation of a cobalt anode in an acetonitrile or acetone solution of PhSH and phen produced an insoluble Co(II)/thiolate polymeric complex [Co(SPh)<sub>2</sub>], which further combined with phen to form a neutral adduct Co(II) complex [Co(SPh)<sub>2</sub>(phen)<sub>2</sub>].<sup>11b</sup> In our previous reports, it was found that strong N-donor ligands could stabilize the structure of the metal/Tab complexes.<sup>12h,j</sup> We carried out a one-pot reaction of CoCl<sub>2</sub> with TabHPF<sub>6</sub> and N-donor ligands (2,2'-bipy, phen, etc.) in a molar ratio of 1:2:2. A large amount of insoluble black precipitate was again formed immediately, and we failed to isolate any Co(II) complexes bearing mixed N- and S-donor ligands. Thus we first mixed CoCl<sub>2</sub>·6H<sub>2</sub>O with L ligand (L = 2,2'-bipy, phen, and 4,4'-dmbpy) in MeCN/MeOH to form a homogeneous solution, to which an acetonitrile solution of **1** was added. These reactions did not form the expected substituted product [Co(II)(Tab)<sub>2</sub>(L)](PF<sub>6</sub>)<sub>2</sub> but gave rise to a set of uncommon mononuclear Co(III)/Tab/L complexes **7**, **8**, and **9**, which were isolated as black crystals in 85%, 80%, and 82% yields, respectively (Scheme 2). Intriguingly, analogous reactions of **1** with CoCl<sub>2</sub>·6H<sub>2</sub>O and the tridentate ligand

Scheme 1. Reactions of **1** with 2,2'-bipy, phen, 2,9-dmphen, N-Meim, and bppy LigandsScheme 2. Reactions of **1** with  $\text{CoCl}_2$  and 2,2'-bipy, phen, 4,4'-dmbpy, and bdmppy Ligands

bdmppy did not produce the expected mononuclear Co(III)/Tab/bdmppy complex  $[\text{Co(III)(bdmppy)(Tab)}_{2-3}](\text{PF}_6)_3$  but afforded a rare mononuclear Co(II)/Tab/bdmppy/Cl complex **10** (in 72% yield). Although we also carried out the reactions of **1** with  $\text{CoCl}_2$  in the presence of L ligands using the standard Schlenk line technique under  $\text{N}_2$  or Ar atmosphere, we could not isolate any Co(II) complexes or Co(III) complexes (7-9) except the Co(II) complex **10**. This result suggested that the presence of  $\text{O}_2$  was quite critical in the formation of the Co(III) complexes 7-9. It is understandable that the formation of **10** was not involved in the oxidation of Co(II). The elemental analyses of 7-10 were consistent with their chemical formulas. As discussed later in this article, the single-crystal X-ray analysis revealed that complexes 7-9 consist of one discrete  $[\text{Co}(\text{Tab})_2(\text{L})_2]^{3+}$  trication with an octahedral configuration and

three  $\text{PF}_6^-$  anions, while complex **10** contains one discrete  $[\text{Co}(\text{Tab})(\text{bdmppy})\text{Cl}]^+$  cation with a trigonal-bipyramidal configuration and one  $\text{PF}_6^-$  anion, which suggests the Co oxidation states in these complexes to be +3 for 7-9 and +2 for **10**, respectively. It was further supported by the Co-N bond distances, which are in the range reported for the Co(III)-N bonds, and significantly shorter than those of the Co(II)-N bonds.<sup>14b,c</sup> The reasons that the aforementioned metal and ligand substitution reactions could be finished may be ascribed to the facts that Co(III) or Co(II) in 7-10 hold the higher thiolate binding ability<sup>15a,b,6b</sup> and the larger coordination number than Zn(II) in **1** and the N-donor ligands (e.g., 2,2'-bipy, phen) in 7-10 are stronger than Tab in **1**. Although the formation mechanism for 7-9 was not clear for the time being, we assumed that these substitution reactions may first form a



**Table 1. Principal Electronic Transitions in Compounds 1-10, Tab and Other Known Zn(II), Co(II), and Co(III) Thiolate Compounds**

compound	$\lambda_{\text{max}}$ nm	ref
Zn-LADH <sup>a</sup>	275	16a,b
[Me <sub>4</sub> N] <sub>2</sub> [Zn(SPh) <sub>4</sub> ]	279	16c,d
[Zn(Tab) <sub>4</sub> ](PF <sub>6</sub> ) <sub>2</sub> (1)	290	12k
[Zn <sub>4</sub> ( $\mu$ -Tab) <sub>6</sub> (Tab) <sub>4</sub> ](PF <sub>6</sub> ) <sub>8</sub>	288, 248	12k
[Zn <sub>2</sub> ( $\mu$ -Tab) <sub>2</sub> (Tab) <sub>4</sub> ](PF <sub>6</sub> ) <sub>4</sub>	286, 246	12k
[Zn(L1)(SPh) <sub>2</sub> ] <sup>b</sup>	296, 306, 332, 348(sh) <sup>c</sup> , 380(sh)	16g
[Zn(BIMKPT)] <sup>d</sup>	301, 349, 391	16h
Co(II)-MT <sup>e</sup>	320, 400(sh)	9a
[Me <sub>4</sub> N] <sub>2</sub> [Co(II)(SPh) <sub>4</sub> ]	417	11a
[Co(III)(SPh) <sub>2</sub> (phen) <sub>2</sub> ](ClO <sub>4</sub> )	395	11b
[Co(II)S <sub>2</sub> <sup>Me2</sup> N <sub>3</sub> (Pr,Pr)] <sup>f</sup>	298, 362, 496, 536	18e
Tab	320, 267(sh)	12c
2	279	this work
3	271, 226	this work
4	276, 230	this work
5	280	this work
6	255, 279(sh), 329(sh)	this work
7	377, 303	this work
8	385, 270	this work
9	374, 299	this work
10	267, 320(sh), 403	this work

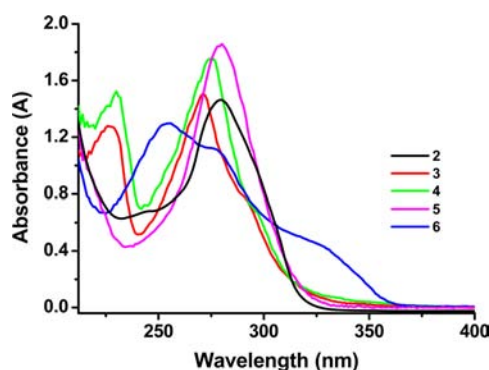
<sup>a</sup>LADH = liver acoholol dehydrogenase. <sup>b</sup>L1 = 4-(1,3,3-trimethylspiro-indolinenaphthoxazine-9'-oxymethyl)-4'-methyl-2,2'-bipyridine. <sup>c</sup>sh = shoulder. <sup>d</sup>BIMKPT = N1,N9-Bis(imino-2-mercapto-2-keto-propane)-1,5,9-triazanonane. <sup>e</sup>MT = metallothionein. <sup>f</sup>S<sub>2</sub><sup>Me2</sup>N<sub>3</sub>(Pr,Pr)<sup>2-</sup> = 2,3,13,14-tetramethyl-4,8,12-triaza-3,12-pentadecadien-2,14-dithiolate.

four-coordinated [Co(II)(Tab)<sub>4</sub>]<sup>2+</sup> species. It may be converted into a six-coordinated [Co(II)(Tab)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> species by substitution of two Tab ligands of the [Co(II)(Tab)<sub>4</sub>]<sup>2+</sup> species via L ligands. The resulting [Co(II)(Tab)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> species was further oxidized into the [Co(III)(Tab)<sub>2</sub>(L)<sub>2</sub>]<sup>3+</sup> species by O<sub>2</sub> in air. This is consistent with the observed result in which a neutral adduct Co(II) complex [Co(SPh)<sub>2</sub>(phen)<sub>2</sub>], when exposed to air, could readily be converted into a cationic Co(III) complex [Co(SPh)<sub>2</sub>(phen)<sub>2</sub>](ClO<sub>4</sub>)<sup>11b</sup>. Similar phenomenon was also observed for the reactions of Cu(I) with Tab in which the resulting Cu(I)/Tab complex underwent a fast oxidation reaction to form Cu(II) species and Tab-Tab.<sup>15c</sup> The conversion of metal/Tab complexes with a low oxidation state (e.g., Cu(I), Co(II)) to those with a higher oxidation state (Cu(II), Co(III)) may be due to the stronger electron-withdrawing ability of the NMe<sub>3</sub><sup>+</sup> unit of the Tab ligand. In the case of **10**, the +2 oxidation state of the central Co was retained which is probably due to the fact that one bdmppy ligand and one Tab and one Cl bind at Co(II) to form a unique trigonal pyramidal geometry, which may make Co(II) be stabilized and not easily be oxidized into Co(III).

Solids **2-10** are relatively stable toward oxygen and moisture and readily soluble in MeCN, DMF, and DMSO but almost insoluble in MeOH, EtOH, CH<sub>2</sub>Cl<sub>2</sub>, benzene, and H<sub>2</sub>O. The IR spectra of **2-10** showed the characteristic P–F stretching vibrations of PF<sub>6</sub><sup>-</sup> at 840 and 559 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of **2-10** in DMSO-*d*<sub>6</sub> at room temperature feature multiplets in the region of 6.98–7.72 ppm for phenyl groups and a singlet at 3.54 ppm for the methyl protons of the NMe<sub>3</sub><sup>+</sup> unit of the Tab ligands. For **2-10**, a set of peaks related to 2,2'-bipy, phen, 2,9-dmphen, N-Meim,

4,4'-dmppy, bppy, and bdmppy are also observed. Other resonances at 2.95 (**4**), 3.66 (**5**), 2.66 and 2.30 (**9**), and 2.52 and 2.23 (**10**) ppm are assigned to the methyl protons of the 2,9-dmphen, N-Meim, 4,4'-dmppy, and bdmppy ligands. The positive ESI mass spectra of **1-10** in MeCN did not show any peaks related to M/Tab/L, M/Tab, or M/L (M = Zn(II), Co(III), Co(II); L = N-donor ligand) cations. Only the peaks related to the TabH<sup>+</sup> and protonated N-donor ligands were exhibited (Figures S1–S10). The results suggested that the cationic species of **1-10** in solutions are not stable under the ESI mass conditions.

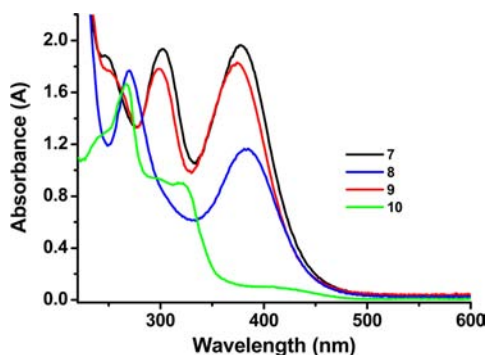
The electronic spectra of **2-5** in MeCN exhibited a strong and broad absorption with maxima values ranging from 226 to 280 nm and a long absorption tail to ca. 400 nm (Figure 1).



**Figure 1.** Electronic spectra of **2** ( $1.0 \times 10^{-5}$  M), **3** ( $2.0 \times 10^{-5}$  M), **4** ( $2.0 \times 10^{-5}$  M), **5** ( $2.0 \times 10^{-5}$  M), and **6** ( $2.0 \times 10^{-5}$  M) in MeCN in a 1-cm-thick glass cell.

The main absorption bands at 279 nm (**2**), 271 nm (**3**), 276 nm (**4**), and 280 nm (**5**) are comparable to those observed in Zn-LADH (275 nm)<sup>16a,b</sup> and [Me<sub>4</sub>N]<sub>2</sub>[Zn(SPh)<sub>4</sub>] (279 nm) (Table 1).<sup>16c,d</sup> These bands are blue-shifted with respect to the absorption band at 314 nm of the Tab ligand,<sup>12c</sup> which might be ascribed to the ligand(Tab)-to-metal charge transfer (LMCT).<sup>16e,f</sup> Such bands are also blue-shifted relative to those of complexes containing tetrahedrally coordinated Zn(II) such as **1** (290 nm), [Zn<sub>4</sub>( $\mu$ -Tab)<sub>6</sub>(Tab)<sub>4</sub>](PF<sub>6</sub>)<sub>8</sub> (288 nm)<sup>12k</sup> and [Zn<sub>2</sub>( $\mu$ -Tab)<sub>2</sub>(Tab)<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub> (286 nm)<sup>12k</sup> and [Zn(L1)(SPh)<sub>2</sub>] (296/306 nm),<sup>16g</sup> suggesting that Zn(II) in **2-5** may have somewhat different tetrahedral coordination environments due to the different bulkiness of its coordinated N- and S-donor ligands. Currently it is difficult to clearly and accurately correlate the UV–vis absorption data (the position and/or intensity of the bands), for example, with structural features like Zn–S (or Zn–N) bond lengths, S–Zn–S (or S–Zn–N and N–Zn–N) angles, or other structural parameters. **6** exhibited a main broad peak at 255 nm and two shoulder peaks at 279 and 329 nm, which remarkably deviated from those of tetrahedrally coordinated complexes **2-5** and implying that Zn(II) in **6** may hold a totally different coordination geometry. Although Zn(II) in **6** is five-coordinated, its absorption bands are also different from those of other five-coordinated Zn(II) complexes like [Zn(BIMKPT)] (Table 1),<sup>16h</sup> which may be due to the different steric and electronic properties of the ligands around Zn(II). In addition, the high-energy bands at 226 nm for **3**, 230 nm for **4**, and 255 nm for **6** are assigned to the intraligand (IL)  $\pi \rightarrow \pi^*$  transitions of the phenanthroline moieties (**3** and **4**) or the pyridine and pyrazole moieties (**6**).<sup>17</sup>

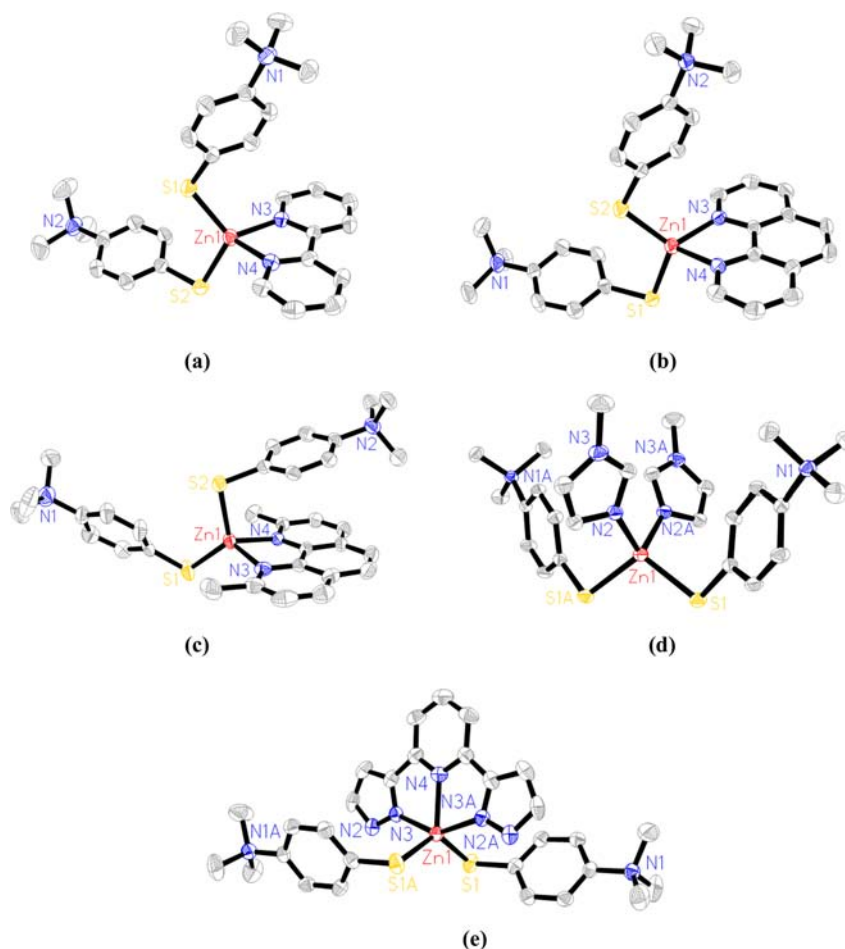
The electronic spectra of 7-9 in MeCN exhibited a strong and broad absorption with maxima values ranging from 267 to 403 nm and a long absorption tail to *ca.* 600 nm (Figure 2).



**Figure 2.** Electronic spectra of 7 ( $2.0 \times 10^{-5}$  M), 8 ( $1.0 \times 10^{-5}$  M), 9 ( $2.0 \times 10^{-5}$  M), and 10 ( $2.0 \times 10^{-5}$  M) in MeCN in a 1-cm-thick glass cell.

The absorption bands at 377 nm for 7, 385 nm for 8, and 374 nm for 9 are different from those of the tetrahedrally coordinated Co(II) complexes such as Co(II)-MT (320 nm)<sup>9a</sup> and  $[\text{Me}_4\text{N}]_2[\text{Co}(\text{SPh})_4]$  (417 nm).<sup>11a</sup> However, these bands are close to the octahedrally coordinated Co(III) complex

$[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$  (395 nm),<sup>11b</sup> suggesting that the coordination environments of Co(III) centers in 7-9 may resemble that of  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$ . These bands might be also ascribed to the ligand(Tab)-to-metal charge transfer (LMCT).<sup>18a-d</sup> The electronic spectrum of 10 showed a strong band at 267 nm, a shoulder peak at 320 nm, and a weak broad peak at 403 nm. These absorptions remarkably differ from those of Co(II)-MT (Table 1), in which Co(II) holds a tetrahedral geometry, and those of octahedrally coordinated Co(III) complexes containing 7-9, implying that Co(II) in 10 may possess a different coordination sphere. These bands are different from those of the five-coordinated Co(II) complexes like  $[\text{Co}(\text{II})\text{S}_2^{\text{Me}_2}\text{N}_3(\text{Pr},\text{Pr})]^{18e}$  (Table 1). Such a difference may be due to the different steric and electronic properties of the ligands around Co(II). The high-energy bands at 303 nm for 7, 270 nm for 8, 299 nm for 9, and 267 nm for 10 are tentatively assigned to be the IL  $\pi \rightarrow \pi^*$  transitions of the bipyridine (7 and 9), phenanthroline moieties (8), or pyridine and pyrazole moieties (10).<sup>9a,18d</sup> It is noted that the main absorption bands for six-coordinated Co(III) complexes 7-9 are red-shifted relative to those of six-coordinated Zn(II) complexes 2-5. Co(III) in 7-9 has the  $d^6$  configuration, while Zn(II) has the  $d^{10}$  configuration in 2-5. Thus Co(III) may produce the smaller transition energy and thus exhibit the longer absorption wavelength than Zn(II). In the case of 6 and 10, both complexes



**Figure 3.** (a) View of the  $[\text{Zn}(\text{Tab})_2(2,2'\text{-bipy})]^{2+}$  dication in 2. (b) View of the  $[\text{Zn}(\text{Tab})_2(\text{phen})]^{2+}$  dication in 3. (c) View of the  $[\text{Zn}(\text{Tab})_2(2,9\text{-dmphen})]^{2+}$  dication in 4. (d) View of the  $[\text{Zn}(\text{Tab})_2(\text{N-Meim})_2]^{2+}$  dication in 5. Symmetry code: A,  $-x + 1, y, -z + 1/2$ . (e) View of the  $[\text{Zn}(\text{Tab})_2(\text{bppy})]^{2+}$  dication in 6. Symmetry code: A,  $-x, 1 + y, 1/2 - z$ . All H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2-10<sup>a</sup>

Compound 2				Compound 7			
Zn(1)–S(1)	2.2668(11)	Zn(1)–S(2)	2.2720(12)	N(6)–Co(1)–S(1)	177.16(9)	N(3)–Co(1)–S(2)	94.04(10)
Zn(1)–N(3)	2.080(3)	Zn(1)–N(4)	2.060(3)	N(4)–Co(1)–S(2)	174.21(9)	N(5)–Co(1)–S(2)	88.92(10)
S(1)–Zn(1)–S(2)	112.50(4)	N(4)–Zn(1)–N(3)	79.07(11)	N(6)–Co(1)–S(2)	95.82(9)	N(3)–Co(1)–N(4)	82.53(13)
N(3)–Zn(1)–S(1)	114.36(9)	N(4)–Zn(1)–S(1)	123.74(9)	N(5)–Co(1)–N(4)	94.85(13)	N(3)–Co(1)–N(5)	175.02(14)
N(3)–Zn(1)–S(2)	117.85(9)	N(4)–Zn(1)–S(2)	105.75(9)	N(3)–Co(1)–N(6)	93.36(14)	N(4)–Co(1)–N(6)	89.05(12)
Compound 3				Compound 8			
Zn(1)–S(1)	2.2741(13)	Zn(1)–S(2)	2.2603(12)	Co(1)–S(1)	2.274(2)	Co(1)–S(2)	2.271(2)
Zn(1)–N(3)	2.109(3)	Zn(1)–N(4)	2.071(3)	Co(1)–N(3)	1.978(5)	Co(1)–N(4)	1.960(6)
S(2)–Zn(1)–S(1)	113.12(5)	N(4)–Zn(1)–N(3)	80.18(11)	Co(1)–N(5)	1.946(5)	Co(1)–N(6)	1.980(5)
N(3)–Zn(1)–S(1)	114.51(9)	N(4)–Zn(1)–S(1)	105.83(9)	S(2)–Co(1)–S(1)	80.71(7)	N(3)–Co(1)–S(1)	93.10(16)
N(3)–Zn(1)–S(2)	118.37(9)	N(4)–Zn(1)–S(2)	120.56(9)	N(4)–Co(1)–S(1)	90.86(17)	N(5)–Co(1)–S(1)	94.27(16)
Compound 4				Compound 9			
Zn(1)–S(1)	2.265(2)	Zn(1)–S(2)	2.285(2)	Co(1)–S(1)	2.3005(15)	Co(1)–S(2)	2.2805(16)
Zn(1)–N(3)	2.088(6)	Zn(1)–N(4)	2.085(5)	Co(1)–N(3)	1.974(4)	Co(1)–N(4)	1.942(4)
S(1)–Zn(1)–S(2)	121.95(8)	N(4)–Zn(1)–N(3)	80.5(2)	Co(1)–N(5)	1.933(4)	Co(1)–N(6)	1.982(4)
N(3)–Zn(1)–S(1)	119.82(17)	N(4)–Zn(1)–S(1)	114.47(15)	S(2)–Co(1)–S(1)	81.28(6)	N(3)–Co(1)–S(1)	94.47(13)
N(3)–Zn(1)–S(2)	104.94(15)	N(4)–Zn(1)–S(2)	107.29(15)	N(4)–Co(1)–S(1)	88.54(12)	N(5)–Co(1)–S(1)	95.90(13)
Compound 5				Compound 10			
Zn(1)–S(1)	2.3158(7)	Zn(1)–S(1A)	2.3158(7)	Co(1)–S(1)	2.2811(11)	Co(1)–N(2)	2.1259(18)
Zn(1)–N(2)	2.0393(18)	Zn(1)–N(2A)	2.0393(18)	Co(1)–N(3)	1.974(4)	Co(1)–N(6)	2.1460(19)
S(1A)–Zn(1)–S(1)	109.31(3)	N(2)–Zn(1)–N(2A)	101.27(10)	Co(1)–N(5)	1.933(4)	S(1)–Co(1)–Cl(1)	115.81(4)
N(2)–Zn(1)–S(1)	115.09(6)	N(2A)–Zn(1)–S(1)	108.04(6)	S(2)–Co(1)–S(1)	81.28(6)	N(4)–Co(1)–S(1)	118.00(6)
N(2A)–Zn(1)–S(1A)	115.09(6)			N(4)–Co(1)–S(1)	88.54(12)	N(5)–Co(1)–S(1)	118.00(6)
Compound 6				Compound 10			
Zn(1)–S(1)	2.3267(16)	Zn(1)–S(1A)	2.3267(16)	N(6)–Co(1)–S(1)	174.65(12)	N(3)–Co(1)–S(2)	175.49(12)
Zn(1)–N(3)	2.261(5)	Zn(1)–N(3A)	2.261(5)	N(4)–Co(1)–S(2)	96.25(13)	N(5)–Co(1)–S(2)	89.33(13)
Zn(1)–N(4)	2.113(7)	S(1)–Zn(1)–S(1A)	125.93(11)	N(6)–Co(1)–S(2)	93.71(12)	N(4)–Co(1)–N(3)	82.06(16)
N(3)–Zn(1)–S(1)	91.99(13)	N(3A)–Zn(1)–S(1)	102.66(12)	N(5)–Co(1)–N(3)	92.64(17)	N(5)–Co(1)–N(4)	173.35(16)
N(3)–Zn(1)–S(1A)	102.66(12)	N(3A)–Zn(1)–S(1A)	91.99(13)	N(3)–Co(1)–N(6)	90.59(16)	N(4)–Co(1)–N(6)	93.90(17)
N(4)–Zn(1)–S(1)	117.03(5)	N(4)–Zn(1)–S(1A)	117.03(5)	N(5)–Co(1)–N(6)	82.09(17)		
N(4)–Zn(1)–N(3)	73.79(13)	N(4)–Zn(1)–N(3A)	73.79(13)				
N(3A)–Zn(1)–N(3)	147.6(3)						
Compound 7				Compound 10			
Co(1)–S(1)	2.2820(13)	Co(1)–S(2)	2.2761(13)	Co(1)–S(1)	2.2811(11)	Co(1)–N(2)	2.1259(18)
Co(1)–N(3)	1.951(3)	Co(1)–N(4)	1.964(3)	Co(1)–N(4)	2.0699(19)	Co(1)–N(6)	2.1460(19)
Co(1)–N(5)	1.952(3)	Co(1)–N(6)	1.977(3)	Co(1)–Cl(1)	2.2864(9)	S(1)–Co(1)–Cl(1)	115.81(4)
S(2)–Co(1)–S(1)	82.15(5)	N(3)–Co(1)–S(1)	88.79(11)	N(2)–Co(1)–S(1)	102.69(6)	N(4)–Co(1)–S(1)	118.00(6)
N(4)–Co(1)–S(1)	93.08(9)	N(5)–Co(1)–S(1)	95.60(10)	N(6)–Co(1)–S(1)	95.82(5)	N(4)–Co(1)–N(2)	75.57(7)
				N(2)–Co(1)–N(6)	149.82(7)	N(4)–Co(1)–N(6)	74.73(7)
				N(2)–Co(1)–Cl(1)	98.33(6)	N(4)–Co(1)–Cl(1)	125.87(6)
				N(6)–Co(1)–Cl(1)	94.69(6)		

<sup>a</sup>Symmetry codes for 5: (A)  $-x + 1, y, -z + 1/2$ ; 6: (A)  $-x + 1, y, -z + 1/2$ .

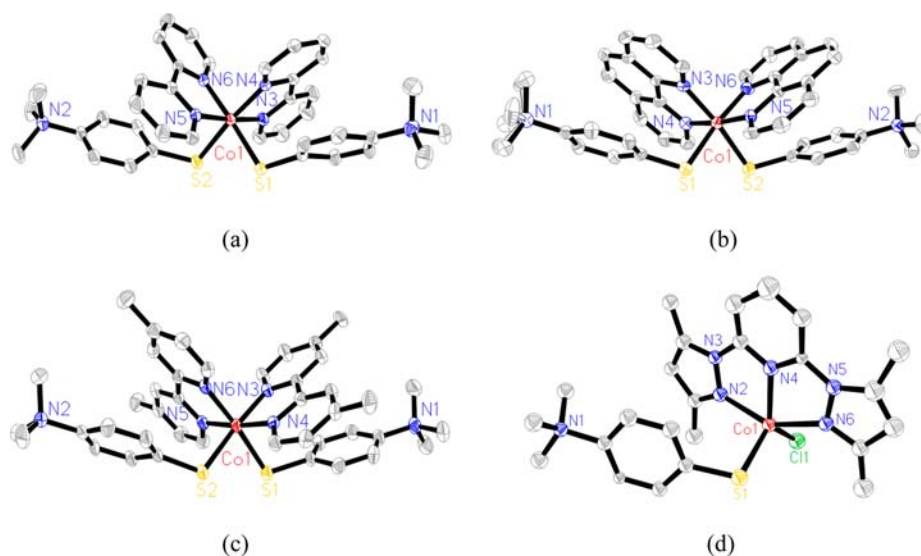
are five-coordinated and have an oxidation state of +2. Their absorption spectra are somewhat similar, but the main bands of **6** are blue-shifted relative to those of **10**, which may be due to the fact that Zn(II) with the  $d^{10}$  configuration may produce the larger transition energy and thus exhibit the shorter absorption wavelength than Co(II) with the  $d^7$  configuration.

**Crystal Structures of 2·MeOH, 3·MeCN, 4·0.5MeCN, 5, and 6.** Compound 2·MeOH and 3·MeCN crystallize in the triclinic space group  $P\bar{1}$ , while 4·0.5MeCN crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit of 2·MeOH, 3·MeCN, or 4·0.5MeCN consists of one  $[\text{Zn}(\text{Tab})_2(\text{L})]^{2+}$  (L = 2,2'-bipy (2), phen (3), 2,9-dmphen (4)) dication, two  $\text{PF}_6^-$  anions, and one MeOH (2), one MeCN (3) or half a MeCN solvent molecule (4). Compounds 5 and 6 crystallize in the monoclinic space group  $C2/c$  and their asymmetric unit contains half a  $[\text{Zn}(\text{Tab})_2(\text{L})]^{2+}$  (5: L = N-Meim; n = 2, 6: L = bpy, n = 1) dication and one  $\text{PF}_6^-$  anion. There is a crystallographic 2-fold axis running through the Zn atom in 5 or through the

Zn1–N4 bond in 6. The central Zn(II) in 2-5 is tetrahedrally coordinated by two S atoms of two Tab ligands and two N atoms from a bidentate N-donor ligand (2,2'-bipy for 2, phen for 3 and 2,9-dmphen for 4) (Figures 3a-3c) or two monodentate N-Meim ligands (5) (Figure 3d). Such a structure is observed in several mononuclear Zn(II)/thiolate complexes such as  $[\text{Zn}(\text{SPh})_2(\text{MeIm})_2]$  (MeIm = 1-methylimidazole),<sup>6a</sup>  $[\text{Zn}(\text{L})(\text{SR})_2]$  (R =  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4$ ; L = 2,9-dimethyl-1,10-phenanthroline),<sup>19a,b</sup>  $[\text{Zn}(\text{S-2,4,6-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2(2,2'\text{-bipy})]$ ,<sup>20</sup> and  $[\text{Zn}(\text{L})(\text{SPh})_2]$  (L = 4-(1,3,3-trimethylspiroindolinaphthoxazine-9'-oxymethyl)-4'-methyl-2,2'-bipyridine).<sup>21</sup>

As indicated in Table 2, the mean Zn–S bond length in 2 (2.2694(12) Å) is comparable to those in 3 (2.2672(13) Å), 4 (2.275(2) Å), and  $[\text{Zn}(\text{L})(\text{SR})_2]$  (2.267(3) Å for R =  $p\text{-CH}_3\text{C}_6\text{H}_4$ , 2.246(3) Å for R =  $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4$ ; L = 2,9-dimethyl-1,10-phenanthroline)<sup>19a,b</sup> but shorter than those found in  $[\text{Zn}(\text{SPh})_2(\text{MeIm})_2]$  (2.2916(7) Å)<sup>6a</sup> and 5 (2.3158(7) Å). The average Zn–N bond distance of 2 (2.070(3) Å), 3 (2.090(3) Å), or





**Figure 4.** (a) View of the  $[\text{Co}(\text{Tab})_2(2,2'\text{-bipy})_2]^{3+}$  trication of **7**. Only one of the two orientations of the disordered methyl groups is shown. (b) View of the  $[\text{Co}(\text{Tab})_2(\text{phen})_2]^{3+}$  trication of **8**. Only one of the two orientations of the disordered methyl groups is shown. (c) View of the  $[\text{Co}(\text{Tab})_2(4,4'\text{-dmbpy})_2]^{3+}$  trication of **9**. (d) View of the  $[\text{Co}(\text{Tab})(\text{bdmppy})\text{Cl}]^+$  cation of **10**. All H atoms have been omitted for clarity.

**4** (2.087(5) Å) is in-between those of  $[\text{Zn}(\text{SPh})_2(\text{MeIm})_2]$  (2.038(2) Å)<sup>6a</sup> and **5** (2.0393(18) Å) and those of  $[\text{Zn}(\text{L})(\text{SR})_2]$  (2.120(3) Å for R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 2.117(3) Å for R = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; L = 2,9-dimethyl-1,10-phenanthroline).<sup>19a,b</sup> The steric hindrance among the Tab and N-donor ligands may exert a great impact on the structures of these complexes such as the N–Zn–N angles. For example, the N–Zn–N bite angle of **4** (80.5(2)°) is close to those found in **3** (80.18(11)°) but slightly larger than those in **2** (79.07(11)°) and  $[\text{Zn}(\text{L})(\text{SR})_2]$  (78.84(3)° for R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 79.47(2)° for R = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; L = 2,9-dimethyl-1,10-phenanthroline) and  $[\text{Zn}(\text{S-2,4,6-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2(2,2'\text{-bipy})]$  (77.88(3)°).<sup>20</sup> Because of the rigidity of the phen or 2,2'-bipy or 2,9-dmphen ligand in **2-4**, their N–Zn–N bite angles are remarkably smaller than the N–Zn–N angle of **5** (101.27(10)°) or  $[\text{Zn}(\text{SPh})_2(\text{MeIm})_2]$  (109.8(1)°).<sup>6a</sup> For **6**, its central Zn(II) is coordinated by two S atoms of two Tab ligands and three N atoms from a tridentate ligand bpy to form a trigonal-bipyramidal coordination geometry (Figure 3e). The mean Zn–S bond length in **6** (2.3267(16) Å) is slightly shorter than those containing a similar ZnN<sub>3</sub>S<sub>2</sub> coordination geometry such as  $[\text{Zn}(\text{L})]$  (2.332(2) Å for L = bis(2-thiobenzaldimino)-2,6-diacetylpyridine);<sup>22</sup> 2.347(2) Å for L = 3,7,11-triazatrideca-2,11-diene-2,12-bis(thiocarboxylate)<sup>16h</sup>) and  $[\text{Zn}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_2(\text{L})]$  (2.337(3) Å, L = diisopropyl-dithiophosphate).<sup>23</sup> The average Zn–N bond distance in **6** (2.187(7) Å) is slightly longer than those found in  $[\text{Zn}(\text{L})]$  (2.165(2) Å for L = bis(2-thiobenzaldimino)-2,6-diacetylpyridine);<sup>22</sup> 2.138(2) Å for L = 3,7,11-triazatrideca-2,11-diene-2,12-bis(thiocarboxylate)<sup>16h</sup>) and  $[\text{Zn}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_2(\text{L})]$  (2.164(3) Å, L = diisopropyl-dithiophosphate).<sup>23</sup> Because of such a steric hindrance, the dihedral angles between the phenyl groups of the Tab ligands in **2-6** are also different, amounting to 96.8°(**2**), 91.3°(**3**), 69.3°(**4**), 17.6°(**5**), and 61.4°(**6**), respectively. There exist  $\pi\cdots\pi$  interactions (3.611 Å for **2**, 3.577 Å for **3**, 3.622 Å for **4**, 3.662 Å for **6**) between the phenyl group of each Tab ligand and the pyridyl group of 2,2'-bipy, phen, or dmphen in **2-4** or the imidazolyl group of bpy in **6**.

#### Crystal Structures of **7**, **8**·MeCN, and **9**·MeCN·0.5H<sub>2</sub>O.

Compounds **7**, **8**·MeCN, and **9**·MeCN·0.5H<sub>2</sub>O crystallize in the monoclinic space groups *C*2/*c*, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, and *P* $\bar{1}$ , respectively, and their asymmetric units contain one  $[\text{Co}(\text{Tab})_2(\text{L})_2]^{3+}$

(L = 2,2'-bipy (**7**), phen (**8**·MeCN), 4,4'-dmbpy (**9**·MeCN·0.5H<sub>2</sub>O)) trication, three PF<sub>6</sub><sup>−</sup> anions, and one MeCN (**8**·MeCN and **9**·MeCN·0.5H<sub>2</sub>O) and half a water solvent molecule (**9**·MeCN·0.5H<sub>2</sub>O). Each Co atom is octahedrally coordinated by two S atoms of two Tab ligands and four N atoms from two bidentate N-donor ligands (2,2'-bipy for **7**, phen for **8**, and 4,4'-dmbpy for **9**) (Figures 4a–4c). Such a rare Co(III)S<sub>2</sub>N<sub>4</sub> structure was only found to exist in  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$ .<sup>11b</sup> As presented in Table 2, the mean Co–S bond distance (2.2905(16) Å) in **9** is comparable to that of  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$  (2.297(4) Å)<sup>11b</sup> but slightly longer than those observed in **7** (2.2791(13) Å) and **8** (2.273(2) Å). The average Co–N lengths (1.957(4) Å) of **9** is comparable to those found in  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$  (1.97(1) Å), **7** (1.961(3) Å), and **8** (1.966(6) Å). The mean N–Co–N bite angle of **7** (82.33(13)°), **8** (83.3(2)°), or **9** (82.58(16)°) is close to that of  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$  (82.95(3)°). The S–Co–S angle in **8** (80.71(7)°) is smaller than those in  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$  (83.1(1)°), **7** (82.15(5)°) and **9** (81.28(6)°), which may be due to the fact that the hindrance between Tab and phen in **8** is larger than those observed in **7**, **9**, and  $[\text{Co}(\text{SPh})_2(\text{phen})_2](\text{ClO}_4)$ . The two Tab ligands in **7-9** take a *trans* configuration with a dihedral angle between its two phenyl groups being 57.4°(**7**), 41.7°(**8**), and 128.2°(**9**), respectively. In addition, there exist  $\pi\cdots\pi$  interactions (3.558 Å for **7**, 3.596 Å for **8**, 3.722 Å for **9**) between the phenyl group of each Tab ligand and the pyridyl group of 2,2'-bipy, phen, or 4,4'-dmbpy in **7-9**.

**Crystal Structure of 10.** Complex **10** crystallizes in the triclinic space group *P* $\bar{1}$ , and its asymmetric unit contains one  $[\text{Co}(\text{Tab})(\text{bdmppy})\text{Cl}]^+$  cation and one PF<sub>6</sub><sup>−</sup> anion. The Co(II) in  $[\text{Co}(\text{Tab})(\text{bdmppy})\text{Cl}]^+$  cation is coordinated by one Cl atom, one S atom from Tab ligand, and three N atoms from bdmppy, forming a Co(II)N<sub>3</sub>ClS trigonal-bipyramidal coordination geometry (Figure 4d). The Co–Cl bond length (2.2864(9) Å) is close to that in the five-coordinated Co(II) complex  $[\text{Co}(\text{II})(\text{L})\text{Cl}_2]$  (2.284(3) Å; L = 2,2-diphenyl-4,4,6,6-tetrakis(3,5-dimethylpyrazol-1-yl)-cyclotriphosphazene)<sup>24</sup> but slightly shorter than that of  $[\text{Co}(\text{II})(\text{L})\text{Cl}_2]$  2.315(2) Å; L = bis(2-dimethylaminoethyl)methylamine).<sup>25</sup> The Co–S bond distance (2.2811(11) Å) is comparable to that in  $[\text{Co}(\text{II})(\text{L})]$

(2.287(3) Å, L = 2,3,13,14-tetramethyl-4,8,12-triazapentadeca-3,12-diene-2,14-dithiolate)<sup>18</sup> but shorter than that in [Co(II)-(S<sub>2</sub>SiMe<sub>2</sub>)(L)] (2.380(3) Å, L = N,N,N',N',N''-pentamethyldiethylenetriamine).<sup>26</sup> The average Co–N bond distance (2.1139(19) Å) is in good agreement with those in [Co(II)-(L)Cl<sub>2</sub>] (2.148(3) Å; L = 2,2-diphenyl-4,4,6,6-tetrakis(3,5-dimethylpyrazol-1-yl)-cyclotriphosphazene)<sup>24</sup> and [Co(II)(L)] (2.126(3) Å, L = 2,3,13,14-tetramethyl-4,8,12-triazapentadeca-3,12-diene-2,14-dithiolate).<sup>18</sup> There exist  $\pi\cdots\pi$  interactions (3.754 Å) between the phenyl group of each Tab ligand and the pyrazol group of bdmppy in **10**.

## CONCLUSIONS

In this paper, we have demonstrated the reactivity of the model complex **1** toward N-donor ligands L (2,2'-bipy, phen, 2,9-dmphen, N-Meim, and bppy) and successful isolation of five new Zn(II)/Tab/L complexes (**2–6**). When **1** reacted with CoCl<sub>2</sub> in the presence of N-donor ligands L (2,2'-bipy, phen, 4,4'-dmbpy, bdmppy), three uncommon Co(III)/Tab/L compounds (**7–9**) and one rare Co(II)/Tab/bdmppy complex (**10**) were produced. For **2–6**, two Tab ligands of the [Zn(Tab)<sub>4</sub>]<sup>2+</sup> dication were replaced by one bidentate ligand (2,2'-bipy, phen, 2,9-dmphen) (**2–4**) or two monodentate N-Meim ligands (**5**) or one tridentate ligand bppy (**6**). Although each Zn(II) in **2–5** remains a tetrahedral geometry, the orientations of the two remaining Tab ligands are changed due to the different bulkiness of the N-donor ligands. It is noted that the tetrahedral geometry of Zn(II) in **1** was converted in a trigonal-bipyramidal one in **6** due to the bulky tridentate ligand bdmppy. For those Co complexes, the original tetrahedrally coordinated Zn(II) in **1** was replaced by an octahedrally coordinated Co(III) in **7–9** or a square-pyramidally coordinated Co(II) in **10**. Although the mechanism for the formation of **7–9** was not clear, we proposed that these substitution reactions may yield a four-coordinated Co(II) dication [Co(Tab)<sub>4</sub>]<sup>2+</sup>. Substituting two Tab ligands from the [Co(Tab)<sub>4</sub>]<sup>2+</sup> dication *via* L ligands may afford an octahedrally coordinated Co(II) dication [Co(Tab)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup>, which may be further oxidized into another octahedrally coordinated [Co(III)(Tab)<sub>2</sub>(L)<sub>2</sub>]<sup>3+</sup> trication by O<sub>2</sub>. For **10**, Co(II) was not oxidized into Co(III). It displaced the Zn(II) of **1**, while one Cl and one bdmppy ligand replaced three Tab ligands from the [Zn(Tab)<sub>4</sub>]<sup>2+</sup> of **1**. It is worth noting that Co(III) or Co(II) in **7–10** possesses the higher thiolate binding ability and the larger coordination number than Zn(II) in **1**, while all N-heterocyclic ligands in **7–10** are stronger donor ability than Tab in **1**, which causes the above four interesting metal and ligand substitution reactions to proceed successfully. The results may be useful for our understanding the changes of the physical and chemical properties of Zn(II)-MT when the S-Cys ligands or Zn(II) in its zinc(II) sites are replaced by N-donor ligands or other transition and main-group metal ions existing in natural surroundings.

## EXPERIMENTAL SECTION

**General Procedures.** Compound **1**, bppy, and bdmppy were prepared according to the literature methods.<sup>27</sup> Other chemicals and reagents were obtained from commercial sources and used as received. All solvents were predried over activated molecular sieves and refluxed over appropriate drying agents and freshly distilled prior to use. IR spectra were recorded on a Varian Scamiter-1000 spectrometer (4000–400 cm<sup>-1</sup>) as the KBr disk. UV–vis spectra were measured on a Varian 50 UV–visible spectrophotometer. The elemental analyses for C, H, N, and S were performed on a Carlo-Erba CHNO-S

microanalyzer. <sup>1</sup>H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to the DMSO-*d*<sub>6</sub> signal. ESI mass spectra were performed on a DECAX-30000 LCQ Deca XP mass spectrometer using MeCN as mobile phase.

**Synthesis. [Zn(Tab)<sub>2</sub>(2,2'-bipy)](PF<sub>6</sub>)<sub>2</sub>·MeOH (**2**·MeOH).** To a solution containing **1** (106 mg, 0.1 mmol) in MeCN (3 mL) was added a solution of 2,2'-bipy (16 mg, 0.1 mmol) in MeOH (3 mL). The resulting mixture was stirred for 1 h to form a colorless solution and filtered. Diethyl ether (20 mL) was layered onto the filtrate to form colorless prisms of **2**·MeOH in several days, which were collected by filtration, and washed with Et<sub>2</sub>O and dried *in vacuo*. Yield: 73 mg (87% based on Zn). Anal. Calcd. for C<sub>28</sub>H<sub>34</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>S<sub>2</sub>Zn: C, 39.75; H, 4.05; N, 6.62; S, 7.58. Found: C, 39.62; H, 4.37; N, 4.28; S, 7.26. IR (KBr disk): 1608 (w), 1488 (m), 1445 (w), 1126 (w), 1010 (w), 959 (m), 846 (s), 773 (w), 558 (m) cm<sup>-1</sup>. UV–vis [MeCN; λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 279 (146300)]. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.65 (d, 2H, 2,2'-bipy), 8.34 (d, 2H, 2,2'-bipy), 7.98 (t, 2H, 2,2'-bipy), 7.59–7.72 (m, 8H, Ph), 7.43 (t, 2H, 2,2'-bipy), 3.54 (s, 18H, NMe<sub>3</sub>).

**[Zn(Tab)<sub>2</sub>(phen)](PF<sub>6</sub>)<sub>2</sub>·MeCN (**3**·MeCN).** Compound **3**·MeCN was isolated as colorless prisms in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and phen (19 mg, 0.1 mmol). Yield: 80 mg (92% based on Zn). Anal. Calcd. for C<sub>30</sub>H<sub>34</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>S<sub>2</sub>Zn: C, 41.41; H, 3.94; N, 6.44; S, 7.37. Found: C, 41.72; H, 5.42; N, 6.53; S 14.38. IR (KBr disk): 1627 (w), 1521 (w), 1489 (m), 1427 (w), 1126 (w), 1009 (w), 958 (m), 840 (s), 725 (w), 558 (m) cm<sup>-1</sup>. UV–vis [MeCN; λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 226 (127800), 271 (150600)]. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.89 (d, 2H, phen), 8.76 (d, 2H, phen), 8.12 (brs, 2H, phen), 7.33–7.42 (m, 8H, Ph), 7.04 (t, 2H, phen), 3.38 (s, 18H, NMe<sub>3</sub>).

**[Zn(Tab)<sub>2</sub>(2,9-dmphen)](PF<sub>6</sub>)<sub>2</sub>·MeCN (**4**·0.5MeCN).** Compound **4**·0.5MeCN was isolated as colorless prisms in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and 2,9-dmphen (19 mg, 0.1 mmol). Yield: 81 mg (90% based on Zn). Anal. Calcd. for C<sub>32</sub>H<sub>38</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>S<sub>2</sub>Zn: C, 42.79; H, 4.26; N, 6.24; S, 7.14. Found: C, 42.56; H, 4.48; N, 6.12; S 7.61. IR (KBr disk): 1593 (w), 1490 (m), 1420 (w), 1223 (w), 1125 (w), 1014 (w), 841 (s), 725 (w), 558 (m) cm<sup>-1</sup>. UV–vis [MeCN; λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 230 (152300), 276 (175200)]. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.73 (m, 2H, 2,9-dmphen), 8.11 (m, 2H, 2,9-dmphen), 7.96 (m, 2H, 2,9-dmphen), 7.09–7.25 (m, 8H, Ph), 3.53 (s, 18H, NMe<sub>3</sub>), 2.95 (s, 6H, 2,9-dmphen, Me).

**[Zn(Tab)<sub>2</sub>(N-Meim)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**5**).** Compound **5** was isolated as colorless blocks in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and N-Meim (33 mg, 0.4 mmol). Yield: 80 mg (94% based on Zn). Anal. Calcd. for C<sub>26</sub>H<sub>38</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Zn: C, 36.56; H, 4.48; N, 9.84; S, 7.51. Found: C, 36.27; H, 4.16; N, 9.59; S, 7.28. IR (KBr disk, cm<sup>-1</sup>): 1649 (w), 1586 (w), 1489 (s), 1414 (m), 1284 (w), 1230 (w), 1126 (w), 1010 (w), 960 (m), 839 (s), 754 (w), 559 (m). UV–vis [MeCN; λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 280 (185900)]. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.58–7.70 (m, 4H, Ph), 7.58 (s, 2H, N-Meim NMe), 7.12 (br, 2H, N-Meim CH), 6.88 (d, 2H, N-Meim CH), 3.66 (s, 6H, N-Meim NMe), 3.53 (s, 9H, NMe<sub>3</sub>).

**[Zn(Tab)<sub>2</sub>(bppy)](PF<sub>6</sub>)<sub>2</sub> (**6**).** Compound **6** was isolated as colorless blocks in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and bppy (21 mg, 0.1 mmol). Yield: 85 mg (95% based on Zn). Anal. Calcd. for C<sub>29</sub>H<sub>35</sub>F<sub>12</sub>N<sub>7</sub>P<sub>2</sub>S<sub>2</sub>Zn: C, 38.65; H, 3.91; N, 10.88; S, 7.12. Found: C, 38.93; H, 3.64; N, 10.52; S 7.28. IR (KBr disk): 1614 (w), 1488 (m), 1435 (w), 1125 (w), 1094 (w), 958 (m), 841 (s), 778 (w), 559 (m) cm<sup>-1</sup>. UV–vis [MeCN; λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>): 255 (129700), 279 (sh), 329 (sh)]. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 7.84 (m, 5H, bppy), 7.31–7.62 (m, 8H, Ph), 6.98 (m, 2H, bppy), 3.54 (s, 18H, NMe<sub>3</sub>).

**[Co(Tab)<sub>2</sub>(2,2'-bipy)](PF<sub>6</sub>)<sub>3</sub> (**7**).** A solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (24 mg, 0.1 mmol) in MeOH was treated with a solution containing 2,2'-bipy (32 mg, 0.2 mmol) in MeOH (2 mL) solution. The mixture was stirred at ambient temperature for 1 h. To this mixture was further added a solution of **1** (106 mg, 0.1 mmol) in MeCN (3 mL). A workup similar to that used in the isolation of **2** afforded black crystals of **7**. Yield: 97 mg (85% based on Co). Anal. Calcd. for



Table 3. Crystal Data and Structure Refinement Parameters for 2·MeOH, 3·MeCN, 4·0.5MeCN, 5-7, 8·MeCN, 9·MeCN·0.5H<sub>2</sub>O, and 10

	2·MeOH	3·MeCN	4·0.5MeCN
chemical formula	C <sub>29</sub> H <sub>38</sub> F <sub>12</sub> N <sub>4</sub> OP <sub>2</sub> S <sub>2</sub> Zn	C <sub>32</sub> H <sub>37</sub> F <sub>12</sub> N <sub>5</sub> P <sub>2</sub> S <sub>2</sub> Zn	C <sub>66</sub> H <sub>79</sub> F <sub>24</sub> N <sub>9</sub> P <sub>4</sub> S <sub>4</sub> Zn <sub>2</sub>
formula weight	878.06	911.10	1837.24
crystal system	triclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P2/c
a (Å)	6.2715(13)	6.2296(12)	14.977(3)
b (Å)	15.055(3)	15.480(3)	10.515(2)
c (Å)	19.748(4)	20.076(4)	27.182(5)
$\alpha$ (deg)	96.31(3)	80.93(3)	
$\beta$ (deg)	95.38(3)	82.28(3)	103.19(3)
$\gamma$ (deg)	92.78(3)	88.58(3)	
V (Å <sup>3</sup> )	1841.8(6)	1894.5(6)	4167.6(14)
D <sub>c</sub> (g cm <sup>-3</sup> )	1.583	1.597	1.464
Z	2	2	2
$\mu$ (mm <sup>-1</sup> )	0.959	0.934	0.850
F(000)	896	928	1876
no. of reflns collected	17771	18261	20332
no. of unique reflns	8274 (R <sub>int</sub> = 0.0403)	8513 (R <sub>int</sub> = 0.0468)	7322 (R <sub>int</sub> = 0.0594)
no. of obsd. reflns	6199 (I > 2.00 $\sigma$ (I))	6296 (I > 2.00 $\sigma$ (I))	5244 (I > 2.00 $\sigma$ (I))
no. of variables	450	488	615
R <sup>a</sup>	0.0597	0.0612	0.0995
wR <sup>b</sup>	0.1651	0.1378	0.2415
GOF <sup>c</sup>	1.060	1.082	1.166
	<b>5</b>	<b>6</b>	<b>7</b>
	C <sub>26</sub> H <sub>38</sub> F <sub>12</sub> N <sub>6</sub> P <sub>2</sub> S <sub>2</sub> Zn	C <sub>29</sub> H <sub>35</sub> F <sub>12</sub> N <sub>7</sub> P <sub>2</sub> S <sub>2</sub> Zn	C <sub>38</sub> H <sub>42</sub> CoF <sub>18</sub> N <sub>6</sub> P <sub>3</sub> S <sub>2</sub>
	854.05	901.07	1140.74
	monoclinic	monoclinic	monoclinic
	C2/c	C2/c	C2/c
	23.134(5)	35.349(7)	27.304(6)
	12.825(3)	10.044(2)	10.628(2)
	16.590(3)	10.502(2)	34.147(7)
	133.00(3)	106.03(3)	110.69(3)
	3600(2)	3583.8(12)	9270(3)
	1.576	1.670	1.635
	4	4	8
	0.978	0.988	0.674
	1744	1832	4624
	9860	16366	41307
	4081 (R <sub>int</sub> = 0.0227)	10814 (R <sub>int</sub> = 0.0947)	10541 (R <sub>int</sub> = 0.0559)
	3276 (I > 2.00 $\sigma$ (I))	1765 (I > 2.00 $\sigma$ (I))	8920 (I > 2.00 $\sigma$ (I))
	222	243	750
	0.0395	0.0818	0.0803
	0.1062	0.2325	0.1781
	1.036	0.868	1.195
	<b>8·MeCN</b>	<b>9·MeCN·0.5H<sub>2</sub>O</b>	<b>10</b>
	C <sub>44</sub> H <sub>45</sub> CoF <sub>18</sub> N <sub>7</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>88</sub> H <sub>108</sub> Co <sub>2</sub> F <sub>36</sub> N <sub>14</sub> OP <sub>6</sub> S <sub>4</sub>	C <sub>24</sub> H <sub>30</sub> ClCoF <sub>6</sub> N <sub>6</sub> PS
	1229.83	2493.80	673.95
	orthorhombic	triclinic	triclinic
	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P $\bar{1}$	P $\bar{1}$
	10.432(2)	10.841(2)	8.7041(17)
	15.746(3)	15.231(3)	11.955(2)
	31.076(6)	18.674(4)	15.116(3)
	111.61(3)	70.07(3)	
	100.66(3)	74.73(3)	
	94.32(3)	84.35(3)	
	5104.6(18)	2782.3(10)	1426.6(5)
	1.600	1.488	1.569
	4	1	2
	0.619	0.570	0.890
	2496	1274	690
	15384	21893	15173

Table 3. continued

2-MeOH	3-MeCN	4-0.5MeCN
8437 ( $R_{\text{int}} = 0.0515$ )	9723 ( $R_{\text{int}} = 0.0555$ )	6423 ( $R_{\text{int}} = 0.0352$ )
6508 ( $I > 2.00\sigma(I)$ )	6127 ( $I > 2.00\sigma(I)$ )	5108 ( $I > 2.00\sigma(I)$ )
801	790	361
0.0671	0.0806	0.0398
0.1459	0.2525	0.1049
1.087	1.000	1.018

$^a R = \sum \|F_o - F_c\| / \sum F_o$ .  $^b wR = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)\}^{1/2}$ .  $^c \text{GOF} = \{\sum w((F_o^2 - F_c^2)^2) / (n-p)\}^{1/2}$ , where  $n$  = number of reflections and  $p$  = total number of parameters refined.

$\text{C}_{38}\text{H}_{42}\text{CoF}_{18}\text{N}_6\text{P}_3\text{S}_2$ : C, 40.01; H, 3.71; N, 7.37; S, 5.62. Found: C, 40.38; H, 3.96; N, 7.15; S, 5.32. IR (KBr disk): 1606 (w), 1488 (m), 1448 (w), 1312 (w), 1120 (w), 1012 (w), 959 (w), 837 (s), 765 (w), 558 (m)  $\text{cm}^{-1}$ . UV-vis [MeCN;  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 303 (96700), 377 (98200).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.62 (d, 2H, 2,2'-bipy), 8.38 (d, 2H, 2,2'-bipy), 8.02 (t, 2H, 2,2'-bipy), 7.58–7.70 (m, 4H, Ph), 7.41 (t, 2H, 2,2'-bipy), 3.54 (s, 9H,  $\text{NMe}_3$ ).

**[Co(Tab)<sub>2</sub>(phen)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·MeCN (8·MeCN)**. Compound 8·MeCN was isolated as black blocks in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and phen (38 mg, 0.2 mmol). Yield: 95 mg (80% based on Co). Anal. Calcd. for  $\text{C}_{42}\text{H}_{42}\text{CoF}_{18}\text{N}_6\text{P}_3\text{S}_2$ : C, 42.43; H, 3.56; N, 7.07; S, 5.39. Found: C, 42.17; H, 3.25; N, 7.43; S, 5.06. IR (KBr disk): 1624 (w), 1489 (m), 1427 (w), 1120 (w), 1016 (w), 958 (m), 839 (s), 727 (w), 558 (m)  $\text{cm}^{-1}$ . UV-vis [MeCN;  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 270 (176800), 385 (116500).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.87 (d, 2H, phen), 8.74 (d, 2H, phen), 8.15 (brs, 2H, phen), 7.38–7.50 (m, 4H, Ph), 6.98 (t, 2H, phen), 3.42 (s, 9H,  $\text{NMe}_3$ ).

**[Co(Tab)<sub>2</sub>(4,4'-dmbpy)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·MeCN·0.5H<sub>2</sub>O (9·MeCN·0.5·H<sub>2</sub>O)**. Compound 9·MeCN·0.5H<sub>2</sub>O was isolated as black blocks in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and 4,4'-dmbpy (36 mg, 0.2 mmol). Yield: 102 mg (82% based on Co). Anal. Calcd. for  $\text{C}_{42}\text{H}_{50}\text{CoF}_{18}\text{N}_6\text{P}_3\text{S}_2$ : C, 42.15; H, 4.21; N, 7.02; S, 5.36. Found: C, 42.39; H, 3.96; N, 7.28; S, 5.51. IR (KBr disk): 1623 (w), 1488 (w), 1413 (w), 1261 (w), 1098 (m), 1028 (m), 842 (s), 558 (m)  $\text{cm}^{-1}$ . UV-vis [MeCN;  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 299 (89100), 374 (91500).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.96–8.24 (m, 4H, 4,4'-dmbpy), 6.98–7.22 (m, 4H, Ph), 6.51 (d, 2H, 4,4'-dmbpy), 3.55 (s, 9H,  $\text{NMe}_3$ ), 2.66 (s, 3H, 4,4'-dmbpy, Me), 2.30 (s, 3H, 4,4'-dmbpy, Me).

**[Co(Tab)(bdmppy)Cl](PF<sub>6</sub>) (10)**. Compound **10** was isolated as black blocks in a manner similar to that used for the preparation of **2**, using **1** (106 mg, 0.1 mmol) and bdmppy (36 mg, 0.2 mmol). Yield: 48 mg (72% based on Co). Anal. Calcd. for  $\text{C}_{24}\text{H}_{30}\text{ClCoF}_6\text{N}_6\text{P}_3\text{S}$ : C, 42.77; H, 4.48; N, 12.47; S, 4.76. Found: C, 42.53; H, 4.27; N, 12.81; S, 4.49. IR (KBr disk): 1612 (m), 1563 (w), 1482 (w), 1418 (w), 1394 (w), 1311 (w), 1185 (w), 1138 (w), 1045 (w), 845 (s), 735 (w), 558 (m)  $\text{cm}^{-1}$ . UV-vis [MeCN;  $\lambda_{\text{max}}$  nm ( $\epsilon$ , The following use of keep-together tags is outside the context of a table.  $\text{M}^{-1} \text{cm}^{-1}$ ): 267 (83200), 320 (sh), 403 (5180).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.05 (m, 1H, bdmppy), 7.62 (m, 2H, bdmppy), 7.38–7.56 (m, 4H, Ph), 6.13 (s, 2H, bdmppy), 3.53 (s, 9H,  $\text{NMe}_3$ ), 2.52 (s, 6H, bdmppy CMe), 2.23 (s, 6H, bdmppy CMe).

**X-ray Structure Determinations.** Single crystals of 2·MeOH, 3·MeCN, 4-0.5MeCN, 5-7, 8·MeCN, 9·MeCN·0.5H<sub>2</sub>O, and **10** suitable for X-ray analysis were obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Each single crystal was mounted with grease at the top of a glass fiber and cooled at 223 K in a liquid nitrogen stream. Diffraction data were collected at  $\omega$  mode with a detector-to-crystal distance of 35 mm. Cell parameters were refined by using the program *CrystalClear* (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections. The collected data were reduced by using the program *CrystalClear* (Rigaku and MSc, version 3.6, 2004), and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of 2·MeOH, 3·MeCN, 4-0.5MeCN, 5-7, 8·MeCN, 9·MeCN·0.5H<sub>2</sub>O, and **10** were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms.<sup>28</sup> Two PF<sub>6</sub><sup>−</sup> anions in 4-0.5MeCN were found to be disordered over two positions with an occupancy factor of 0.51/0.49 for F1–F6/F1'–F6' and 0.39/0.61 for F7–F12/F7'–F12'. Three methyl groups of the Tab ligands and two PF<sub>6</sub><sup>−</sup> anions in **7** were split into two sites with an occupancy ratio of 0.54/0.46 for C7–C9/C7'–C9' and F7–F18/F7'–F18'. For 8·MeCN, three methyl groups of the Tab ligands and two PF<sub>6</sub><sup>−</sup> anions were split into two sites with an occupancy ratio of 0.30/0.70 for C7–C9/C7'–C9' and 0.60/0.40 for F7–F18/F7'–F18'. Two PF<sub>6</sub><sup>−</sup> anions in 9·MeCN·0.5H<sub>2</sub>O were found to be disordered over two positions with an occupancy ratio of 0.59/0.41 for F7–F18/F7'–F18'. Because of the partial evaporation of the solvent molecules, the site occupation factors for the MeCN solvent molecules in 4-0.5MeCN and the water molecules in 9·MeCN·0.5H<sub>2</sub>O were fixed at 0.5. All non-hydrogen atoms, except for those of MeOH solvent molecules (C29, O1) in 2·MeOH and the disordered methyl groups of the Tab ligands (C7–C9) in 8·MeCN were refined anisotropically. The hydrogen atoms of the MeOH solvent molecules in 2·MeOH, the MeCN solvent molecules in 4-0.5MeCN, and the water molecules in 9·MeCN·0.5·H<sub>2</sub>O were not located. All other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups; C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for phenyl groups. Important crystal data and collection and refinement parameters for 2·MeOH, 3·MeCN, 4-0.5MeCN, 5-7, 8·MeCN, 9·MeCN·0.5H<sub>2</sub>O, and **10** are given in Table 3.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Crystallographic data of 2·MeOH, 3·MeCN, 4-0.5MeCN, 5-7, 8·MeCN, 9·MeCN·0.5H<sub>2</sub>O, and **10** (CIF) in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jlplang@suda.edu.cn](mailto:jlplang@suda.edu.cn).

### Notes

The authors declare no competing financial interest.

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