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# Metal(II) complexes with monodentate S and N ligands as structural models for zinc–sulfur DNA-binding proteins

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## Abstract

The reaction of several metal salts with various amounts of the monodentate ligands *N*-(2-thiophenyl)-2,5-dimethylpyrrole (H-tpdp) and *N*-methylimidazole in the presence of a base provided a series of novel complexes. They are of the general formulas  $[M^{II}(tpdp)_4]^{2-}$ ,  $[M^{II}(tpdp)_2(N-MeIm)_2]$  (M = Zn, Co, Cd) and  $[M^{II}(tpdp)_3(N-MeIm)]^-$  (M = Zn, Co). The products were characterized by X-ray structure analyses as well as by elemental analyses and infrared spectroscopy, and for the cobalt complexes by additional UV–Vis spectroscopy. Crystallographic parameters:  $[Et_3NH]_2[Zn(tpdp)_4]\cdot MeCN$  (1),  $[Et_3NH]_2[Co(tpdp)_4]\cdot MeCN$  (2),  $[Zn(tpdp)_2(N-MeIm)_2]$  (6) and  $[Co(tpdp)_2(N-MeIm)_2]$  (7) are monoclinic, space group  $P2_1/c$ , with Z = 4;  $[Cd(tpdp)_2(N-MeIm)_2]$  (8) is monoclinic, space group  $P2_1/n$ , with Z = 4;  $[Ph_4P]_2[Cd(tpdp)_4]$  (3),  $[Me_4N][Zn(tpdp)_3(N-MeIm)]$  (4), and  $[Me_4N][Co(tpdp)_3(N-MeIm)]$  (5) are triclinic, space group  $P\overline{1}$ , with Z = 2. All compounds have tetragonally compressed metal cores. The complexes are significant as models for many zinc-containing DNA-binding proteins.  $\mathbb{C}$  1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Zinc complexes; Cobalt complexes; Cadmium complexes; Sulfur and nitrogen ligand complexes

#### 1. Introduction

Zinc cysteine coordination is a feature in many important DNA-binding proteins. The number of cysteine residues coordinated to zinc in these proteins varies from 2 to 4. Zinc finger proteins contain a Zn(S-cys)<sub>2</sub>(N-his)<sub>2</sub> centre which plays a structural role in creating DNA-binding fingers [1-10] enabling the transcription of DNA. Other zinc-containing transcription factors are steroid receptors which activate the fixation of a steroid hormone to a special gene. These steroid receptors contain two separated Zn(Scys)<sub>4</sub> centres [6,11,12]. The Ada protein of Escherichia coli also employs a Zn(S-cys)<sub>4</sub> site to repair deoxyribonucleic acid alkyl phosphotriester lesions [13-15]. In the last five years there has been an increasing interest in the investigation of retroviral-type zinc finger proteins with a Zn(Scys)<sub>3</sub>(N-his) centre [16,17]. A better understanding of these nucleocapsid proteins may open the path to the development of a new anti-HIV strategy [18-20].

As part of a study to provide structural and spectroscopic models for zinc-cysteine centres in DNA-binding proteins, we report the syntheses and crystal structures of a series of

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new compounds with the ligands *N*-(2-thiophenyl)-2,5dimethylpyrrole (H-tpdp) and *N*-methylimidazole. In order to get further information about the environment of the metal core in zinc-containing proteins, zinc is often replaced by cobalt or cadmium [21], so that other spectroscopic examinations like UV–Vis and <sup>113</sup>Cd NMR spectroscopy are possible. Accordingly, we synthesized not only zinc, but also cobalt and cadmium complexes enabling us to investigate differences and similarities in the direct metal environment. Herein we report the syntheses and crystal structures of the eight new complex compounds  $[M^{II}- (tpdp)_4]^{2-}$ ,  $[M^{II}(tpdp)_2(N-MeIm)_2]$  with M = Zn, Co, Cd, and  $[M^{II}(tpdp)_3(N-MeIm)]^-$  with M = Zn, Co.

# 2. Experimental

All procedures were carried out under an argon or nitrogen atmosphere using standard Schlenk and glovebox techniques. Solvents were dried and degassed. Elemental analyses were carried out at the Institute of Organic Chemistry, University of Münster. <sup>1</sup>H NMR spectra were recorded on a Bruker WH 300 spectrometer. Infrared spectra were measured on a Bruker FTIR IFS 48 instrument. KBr pellets were used. The UV–Vis spectra were recorded on a Hewlett Packard HP-8453 instrument in DMSO.

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# 2.1. Synthesis of the ligand N-(2-thiophenyl)-2,5dimethylpyrrole (H-tpdp)

According to Buu-Hoï et al. [22], 50 g of freshly distilled 2-aminothiophenol (0.4 mol) and 60 g of acetonylacetone (0.52 mol) were dissolved in 250 ml benzene and treated with 1.5 ml acetic acid. The mixture was refluxed for 10 h. The solvent was removed in vacuo. Fractional distillation of the remaining oil yielded 68.8 g (85%) of H-tpdp [b.p. = 74°C (0.1 mm)] as a colourless liquid. NMR: <sup>1</sup>H,  $\delta$  = 7.19–7.39 (m, Ph), 5.95 (s, C=CH), 2.92 (s, SH), 1.95 (s, CH<sub>3</sub>). IR (cm<sup>-1</sup>): 3102m, 3063m, 2977s, 2918vs, 2885s, 2856m, 2550s, 1586s, 1522s, 1481vs, 1440vs, 1398vs, 1321s, 1261m, 1219m, 1091m, 1036m, 766vs, 738vs, 473m. MS (*m/e* (%)): 203 (66) *M*<sup>+</sup>.

# 2.2. Syntheses of the Zn(II), Co(II) and Cd(II) complexes

#### 2.2.1. Synthesis of $[Et_3NH]_2[Zn(tpdp)_4] \cdot MeCN(1)$

0.068 g (0.5 mmol) of dry ZnCl<sub>2</sub> dissolved in 5 ml MeOH was added dropwise to a solution of Et<sub>3</sub>N (0.4 g, 4 mmol) and H-tpdp (0.61 g, 3 mmol) in 15 ml MeOH. After 30 min of stirring, the white precipitate was collected, washed with MeOH and dried in vacuo (88% yield, 492 mg). **1** was recrystallized from hot acetonitrile to yield colourless prisms. M.p. 183°C. *Anal.* Calc. for C<sub>62</sub>H<sub>83</sub>N<sub>7</sub>S<sub>4</sub>Zn: C, 66.5; H, 7.5; N, 8.8. Found: C, 66.4; H, 7.5; N, 8.8%. IR (cm<sup>-1</sup>): 3441m, 3096w, 3048w, 2975m, 2919w, 2669w, 1582s, 1474vs, 759m, 662vs, 487vs, 477vs.

## 2.2.2. Synthesis of $[Et_3NH]_2[Co(tpdp)_4]$ ·MeCN (2)

The synthesis was conducted analogously to **1**. Green prisms were obtained in 85% yield. Decomposition at 98°C. *Anal.* Calc. for C<sub>62</sub>H<sub>83</sub>N<sub>7</sub>S<sub>4</sub>Co: C, 66.9; H, 7.5; N, 8.8. Found: C, 66.5; H, 7.7; N, 8.6%. IR (cm<sup>-1</sup>): 3096w, 3046m, 2975m, 2919m, 1579m, 1474vs, 760s, 664m, 481m. UV–Vis (DMSO),  $\lambda_{max}$  in nm ( $\varepsilon$  in cm<sup>-1</sup> M<sup>-1</sup>): 716 (3875), 701 (862), 681 (930), 613 (421).

#### 2.2.3. Synthesis of $[Ph_4P]_2[Cd(tpdp)_4]$ (3)

0.95 g (4.7 mmol) H-tpdp was dissolved in 5 ml DMF and 45 ml <sup>i</sup>PrOH. Et<sub>3</sub>N (1 ml), Ph<sub>4</sub>PCl (0.74 g, 1.2 mmol) and 0.18 g CdCl<sub>2</sub> (1 mmol) were added to the solution. After stirring overnight, the white precipitate was collected and dried in vacuo (86% yield, 1.37 g). **3** was recrystallized from a DMF/<sup>i</sup>PrOH solution (1/10 vol./vol.) to yield pale yellow crystals after cooling the solution to 0°C for 24 h. M.p. 207°C. *Anal.* Calc. for C<sub>96</sub>H<sub>88</sub>N<sub>4</sub>P<sub>2</sub>S<sub>4</sub>Cd: C, 72.1; H, 5.5; N, 3.5. Found: C, 72.5; H, 5.6; N, 3.6%. IR (cm<sup>-1</sup>): 3040m, 2960m, 2900m, 2880m, 1665m, 1575s, 1510m, 1460s, 1425s, 1390s, 1310m, 1245w, 1220w, 1100s, 1070s, 1030m, 990s, 740s, 660w, 470m.

#### 2.2.4. Synthesis of $[Me_4N][Zn(tpdp)_3(N-MeIm)]$ (4)

0.207 g Sodium (9 mmol) was dissolved in 25 ml MeOH and treated with 1.827 g H-tpdp (9 mmol) and 0.409 g dry

ZnCl<sub>2</sub> (3 mmol). The resulting white precipitate was dissolved through further addition of 25 ml MeOH and 1 h of stirring. Next, 0.246 g *N*-methylimidazole (3 mmol) were added. The solution was stirred again for 1 h and Me<sub>4</sub>NCl (0.329 g, 3 mmol) was added. The white precipitate was collected, washed with MeOH and dried in vacuo (79% yield, 1.98 g). Recrystallization with acetone yielded colourless crystals after one day. Decomposition occurs at 210°C. *Anal.* Calc. for C<sub>44</sub>H<sub>54</sub>N<sub>6</sub>S<sub>3</sub>Zn: C, 63.8; H, 6.6; N, 10.1. Found: C, 63.8; H, 6.6; N, 10.2%. IR (cm<sup>-1</sup>): 3043w, 3017w, 2969m, 2917s, 1580vs, 1472vs, 764m, 663vs, 478vs.

#### 2.2.5. Synthesis of $[Me_4N][Co(tpdp)_3(N-MeIm)]$ (5)

The synthesis was conducted analogously to **4**. After recrystallization from acetonitrile green prisms of **5** were obtained at  $-15^{\circ}$ C. 82% yield. Decomposition occurs at 141°C. *Anal.* Calc. for C<sub>44</sub>H<sub>54</sub>N<sub>6</sub>S<sub>3</sub>Co: C, 64.3; H, 6.6; N, 10.2. Found: C, 64.0; H, 6.6; N, 10.4%. IR (cm<sup>-1</sup>): 3050w, 2974m, 2917m, 1579m, 1472vs, 737vs, 662m, 481m. UV–Vis (DMSO),  $\lambda_{max}$  in nm ( $\varepsilon$  in cm<sup>-1</sup> M<sup>-1</sup>): 716 (3834), 698 (981), 681 (1040), 606 (421).

#### 2.2.6. Synthesis of $[Zn(tpdp)_2(N-MeIm)_2]$ (6)

0.2 g Et<sub>3</sub>N (2 mmol), 0.406 g H-tpdp (2 mmol) and 0.164 g *N*-methylimidazole (2 mmol) were dissolved in 35 ml MeOH. Dry ZnCl<sub>2</sub> (0.136 g, 1 mmol) in 10 ml MeOH was added and big colourless crystals were obtained. The crystals were filtered off, washed with MeOH and dried in vacuo (82% yield, 0.52 g). **6** was recrystallized from hot toluene to give colourless needles. M.p. 215°C. *Anal.* Calc. for  $C_{32}H_{36}N_6S_2Zn$ : C, 60.6; H, 5.7; N, 13.2. Found: C, 60.5; H, 5.7; N, 13.3%. IR (cm<sup>-1</sup>): 3131w, 3057w, 2967w, 2928w, 1582s, 1472vs, 763vs, 655vs, 479vs.

# 2.2.7. Syntheses of [Co(tpdp)<sub>2</sub>(N-MeIm)<sub>2</sub>] (7) and of [Cd(tpdp)<sub>2</sub>(N-MeIm)<sub>2</sub>] (8)

The syntheses of **7** and **8** were conducted analogously to **6**. **7** was recrystallized from benzene to give dark green crystals at 4°C within 5 days. 33% yield. M.p. 150°C. *Anal.* Calc. for C<sub>32</sub>H<sub>36</sub>N<sub>6</sub>S<sub>2</sub>Co: C, 61.2; H, 5.8; N, 13.4. Found: C, 61.1; H, 5.6; N, 13.7%. IR (cm<sup>-1</sup>): 3129m, 3048m, 2967m, 2915w, 1581m, 1471vs, 755vs, 654vs, 484vs. UV–Vis (DMSO),  $\lambda_{max}$  in nm ( $\varepsilon$  in cm<sup>-1</sup> M<sup>-1</sup>): 733 (4520), 658 (5360), 565 (5480), 502 (5560).

**8** was recrystallized from hot acetonitrile to yield colourless needles. *Anal.* Calc. for  $C_{32}H_{36}N_6S_2Cd$ : C, 55.5; H, 5.5; N, 12.4. Found: C, 55.9; H, 5.3; N, 12.3%. IR (cm<sup>-1</sup>): 3120m, 3040w, 2950w, 2920m, 2870w, 1575m, 1420m, 1400s, 1310m, 1280m, 1230s, 1035m, 990s, 820s, 735s, 650s, 470m.

## 2.3. Crystal structure determination

Intensity data were collected on a STOE imagingplate diffraction system (3,6,7,8) (Mo K $\alpha$  radiation,

Table 1							
Crystallographic	data	for	1,	2,	4,	5	

	1	2	4	5
Formula	$C_{62}H_{83}N_7S_4Zn$	C <sub>62</sub> H <sub>83</sub> N <sub>7</sub> S <sub>4</sub> Co	$C_{44}H_{54}N_6S_3Zn$	C44H54N6S3C0
Formula weight	1119.96	1113.52	828.48	822.04
Temperature (K)	170(2)	170(2)	150(2)	170(2)
Diffractometer	Siemens P3	Siemens P3	Syntex P2 <sub>1</sub>	Siemens P3
Crystal size (mm)	0.35  imes 0.41  imes 0.32	0.40  imes 0.25  imes 0.18	0.28  imes 0.22  imes 0.35	0.25  imes 0.28  imes 0.20
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P\bar{1}$
a (Å)	22.302(5)	22.306(4)	11.850(2)	11.973(2)
b (Å)	13.631(3)	13.646(3)	13.236(3)	13.283(3)
<i>c</i> (Å)	20.326(4)	20.311(4)	16.102(3)	16.171(3)
$\alpha$ (°)	90	90	89.26(3)	89.35(3)
$\beta$ (°)	91.87(2)	91.91(2)	71.19(3)	71.07(3)
$\gamma$ (°)	90	90	64.81(3)	64.68(3)
$V(Å^3)$	6176(2)	6197(2)	2140(1)	2175(1)
Ζ	4	4	2	2
$D_{\rm c}  ({\rm g}  {\rm cm}^{-3})$	1.205	1.197	1.285	1.256
F(000)	2392	2380	876	870
$\mu  ({\rm cm}^{-1})$	5.76	4.56	7.58	5.76
$2\theta$ Range (°)	$4.00 \le 2\theta \le 54.00$	$4.00 \le 2\theta \le 50.10$	$4.00 \le 2\theta \le 54.04$	$4.02 \le 2\theta \le 50.00$
hkl Range	$-28 \le h \le 18$	$-26 \le h \le 1$	$-10 \le h \le 15$	$0 \le h \le 14$
	$-1 \le k \le 17$	$-16 \le k \le 16$	$-15 \le k \le 16$	$-14 \le k \le 15$
	$-25 \le l \le 25$	$-24 \le l \le 24$	$-19 \le l \le 20$	$-18 \le l \le 19$
No. data collected	13685	11179	9735	7917
No. unique data	13344	10880	9278	7519
R <sub>int</sub>	0.0481	0.0381	0.0201	0.0260
No. unique data with $I \ge 2\sigma(I)$	8773	6774	6880	4710
$R1 \ (I > 2\sigma(I))$	0.0354	0.0391	0.0319	0.0609
wR2 (all data)	0.0815	0.0887	0.0827	0.1812
GOF	0.849	0.835	0.939	0.964
Residual density (e $Å^{-3}$ )	0.680	0.538	0.488	1.680

 $\lambda = 0.71073$  Å, graphite monochromator) with a sample-toplate distance of 60 mm (3,6,8) and 70 mm (7), respectively. A scan range from 0 to  $180^{\circ}$  with an exposure time of 2 min per 2° increment was used. Intensity data for compounds 1, 2, 4 and 5 were collected on four-circle diffractometers (same radiation, etc.) using the  $\omega$ -scan technique. Further details on the data collections are summarized in Tables 1 and 2. The structures were solved using the Patterson method (program XS) [23]. A series of full-matrix leastsquares refinement cycles on  $F^2$  (program SHELXL 93) [24] followed by Fourier syntheses gave all the remaining atoms. The hydrogen atoms were included at fixed positions with a common isotropic temperature factor, except for the four triethylammonium protons of structures 1 and 2. All nonhydrogen atoms of the complexes 1-8 were refined anisotropically.

## 3. Results and discussion

The ligand H-tpdp is similar to the often used ligand thiophenol [25,26]. The bulky substituent 2,5-dimethylpyrrole in *ortho*-position should prevent the formation of higher condensate aggregates as known from pure zinc thiophenolates [27–29]. The main goal was to produce tetrahedral

metal complexes with monodentate ligands modelling the environment of zinc in N,S-coordinated active centres of enzymes. The reaction of several metal salts with various amounts of the ligands H-tpdp and *N*-MeIm in the presence of a base provided the series of complexes,  $[M^{II}(tpdp)_4]^{2-}$ ,  $[M^{II}(tpdp)_2(N-MeIm)_2]$  (M = Zn, Co, Cd) and  $[M^{II}(tpdp)_3-(N-MeIm)]^-$  (M = Zn, Co). All these compounds were characterized by X-ray structure analyses, elemental analyses and IR absorption spectroscopy. In addition the Co compounds were characterized by UV–Vis spectroscopy. The attempt to synthesize the missing  $[Cd(tpdp)_3(N-MeIm)]^-$  complex was not successful. Here we obtained the dinuclear complex  $[Cd_2(tpdp)_6]^{2-}$ , which will be published later.

# 3.1. Crystal structures of [Et<sub>3</sub>NH]<sub>2</sub>[Zn(tpdp)<sub>4</sub>]·MeCN (1), [Et<sub>3</sub>NH]<sub>2</sub>[Co(tpdp)<sub>4</sub>]·MeCN (2) and [Ph<sub>4</sub>P]<sub>2</sub>[Cd(tpdp)<sub>4</sub>] (3)

A projection of the  $[Zn(tpdp)_4]^{2-}$  anion is depicted in Fig. 1 as an example for this series. Relevant bond length and bond angle information for the three complexes is given in Table 3. In all of these complexes the metal ion is in a distorted tetrahedral environment. Compounds 1 and 2 are isomorphous and isostructural. The average M–S bond

Table 2						
Crytallographic	data	for	3,	6,	7,	8

	3	6	7	8
Formula	C <sub>96</sub> H <sub>88</sub> N <sub>4</sub> P <sub>2</sub> S <sub>4</sub> Cd	C32H36N6S2Zn	C32H36N6S2C0	C32H36N6S2Cd
Formula weight	1600.28	634.16	627.72	681.19
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Diffractometer	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
Crystal size (mm)	0.31  imes 0.20  imes 0.25	0.27  imes 0.30  imes 0.17	0.38  imes 0.31  imes 0.23	0.21  imes 0.25  imes 0.19
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
<i>a</i> (Å)	13.087(1)	15.030(3)	15.186(3)	7.510(1)
<i>b</i> (Å)	13.475(1)	15.818(3)	15.925(3)	15.090(1)
<i>c</i> (Å)	26.821(3)	14.210(3)	13.947(3)	28.488(3)
$\alpha$ (°)	95.92(1)	90	90	90
$\beta$ (°)	93.14(1)	90.73(3)	90.88(3)	95.68(1)
$\gamma$ (°)	116.13(1)	90	90	90
$V(\dot{A}^3)$	4197(1)	3378(1)	3373(1)	3213(1)
Ζ	2	4	4	4
$D_{\rm c}  ({\rm g}  {\rm cm}^{-3})$	1.266	1.247	1.236	1.408
F(000)	1668	1328	1316	1400
$\mu (\mathrm{cm}^{-1})$	4.46	8.80	6.62	8.41
$2\theta$ Range (°)	$10.20 \le 2\theta \le 56.10$	$10.22 \le 2\theta \le 56.04$	$9.14 \le 2\theta \le 51.88$	$10.42 \le 2\theta \le 56.10$
hkl Range	$-17 \le h \le 17$	$-19 \le h \le 18$	$-18 \le h \le 18$	$-9 \le h \le 9$
	$-17 \le k \le 17$	$-20 \le k \le 20$	$-19 \le k \le 19$	$-19 \le k \le 18$
	$-35 \le l \le 35$	$-18 \le l \le 18$	$-17 \leq l \leq 17$	$-37 \le l \le 37$
No. data collected	33928	27873	22486	22 934
No. unique data	18179	7682	6373	7598
R <sub>int</sub>	0.0537	0.0671	0.0794	0.0905
No. unique data with $I > 2\sigma(I)$	12917	5025	4878	5496
$R1 \ (I > 2\sigma(I))$	0.0513	0.0509	0.0438	0.0515
wR2 (all data)	0.1348	0.1337	0.1159	0.1528
GOF	1.113	1.110	1.071	1.054
Residual density (e $Å^{-3}$ )	0.606	0.345	0.238	0.907



Fig. 1. Molecular anion of complex 1 with vibrational ellipsoids at the 50% probability level.

lengths are 2.337(1) Å for 1, 2.304(1) Å for 2 and 2.537(1) Å for 3. They show no significant differences to the distances in other known metal–sulfur complexes [30,31], but the bond angles deviate significantly from the ideal  $T_d$  symmetry. The angles vary from 97.40(2) to 119.38(2)° for 1, from 94.19(3) to 118.83(3)° for 2 and from 87.61(3) to 124.79(4)° for 3. In 1 and 2 there are strong

Table 3

Selected interatomic distances (Å) and angles (°) for the series  $[M^{II}(tpdp)_4]^{2-}$ 

	M = Zn (1)	M = Co (2)	M = Cd (3)
M-S(1)	2.328(1)	2.296(1)	2.536(1)
M-S(2)	2.332(1)	2.304(1)	2.537(1)
M-S(3)	2.338(1)	2.297(1)	2.551(2)
M-S(4)	2.350(1)	2.318(1)	2.523(1)
S(1)-M-S(2)	115.13(2)	114.38(3)	119.50(4)
S(1)-M-S(3)	115.93(3)	116.65(3)	92.32(4)
S(1)-M-S(4)	97.40(2)	96.68(3)	124.40(4)
S(2)-M-S(3)	94.66(2)	94.19(3)	124.79(4)
S(2)-M-S(4)	119.38(2)	118.83(3)	87.61(3)
S(3)–M–S(4)	115.82(2)	117.70(3)	111.36(4)

interactions between two sulfur atoms of the ligand and the proton of one triethylammonium as shown in Fig. 2. The  $H \cdots S$  distances are 2.44  $(H \cdots S(2))$ , 2.61  $(H \cdots S(1))$ , 2.89  $(H \cdots S(4))$  and 3.34 Å  $(H \cdots S(3))$  for 1 and 2.41  $(H \cdots S(2))$ , 2.65  $(H \cdots S(1))$ , 2.83  $(H \cdots S(4))$  and 3.32 Å  $(H \cdots S(3))$  for 2. In the literature N-H  $\cdots$  S hydrogen bonds are listed for  $H \cdots S$  distances as being significantly shorter than 3 Å [32,33]. Thus, for the complexes 1 and 2, three of these interactions can be described as hydrogen bonds. In both cases the sulfur atoms S(1) and S(4) form a tricentric hydrogen bond with the proton. These strong interactions



Fig. 2. Orientation of the cations in 1 towards the anion (metal donor set) with  $H \cdots S$  distances (Å).

might be one reason for the decrease of the corresponding S–M–S angles.

To our knowledge the distortion of the tetrahedron in complex **3** is the largest one observed for related compounds with monodentate sulfur ligands. This rather large deviation from the ideal  $T_d$  symmetry cannot be explained with packing effects caused by the bulky counterion  $Ph_4P^+$ . In similar complexes like  $[Ph_4P]_2[Cd(SPh)_4]$  the tetrahedral angles vary only from 98.7(2) to 120.0(2)° [26].

Coucouvanis et al. [30] published some structural principles of  $[M^{II}(SPh)_4]^{2-}$  complexes. Therein the phenyl ring approaches coplanarity with its M–S–C plane; this orientation allows the overlap of the  $3p_{\pi}$  sulfur orbital with the aromatic ring. The interaction of the coplanar MSPh groups with the MS<sub>4</sub> core results in the overall distortion of the MS<sub>4</sub> tetrahedron in a systematic manner [26,30]. With respect to this interaction there are only two possible different conformations for the M(SPh)<sub>4</sub> unit, both of which have idealized  $D_{2d}$  symmetry: a  $S_4$  and a  $D_{2d}$  isomer [34,35]. The  $S_4$ isomer is predicted to have a tetragonally compressed MS<sub>4</sub> core while the  $D_{2d}$  isomer is predicted to have a tetragonally elongated MS<sub>4</sub> core [26,30,34,35].

A series of  $[M^{II}(S-2-Ph-C_6H_4)_4]^{2-}$  compounds, published by Silver et al. [31], appear to follow the same rules in spite of the fact that there were slight deviations  $(14-16^{\circ})$  from coplanarity. Although the H-tpdp ligand is quite similar to 2phenylbenzenethiole, complexes **1**, **2** and **3** show even larger deviations from coplanarity between the phenyl rings and the M–S–C planes. The average torsion angles are 26.1° for **1**, 24.8° for **2** and 20.5° for **3**. The two S–M–S angles in **1** bisected by the pseudo  $S_4$  axis are 94.66(2) and 97.40(2)° while the average of the remaining four angles is 116.57°. The S–M–S angles of complexes **2** and **3** are in the same range, as shown in Table 3. Accordingly, the  $D_{2d}$  conformational isomer has been observed in all cases, the symmetry is only approximate.<sup>1</sup>



Fig. 3. Molecular anion of complex **4** with vibrational ellipsoids at the 50% probability level.

# 3.2. Crystal structures of [Me<sub>4</sub>N][Zn(tpdp)<sub>3</sub>(N-MeIm)] (4) and [Me<sub>4</sub>N][Zn(tpdp)<sub>3</sub>(N-MeIm)] (5)

4 and 5 are isomorphous and isostructural. As an example the thermal ellipsoid plot of complex **4** is depicted in Fig. 3. Compounds 4 and 5 crystallize with two  $[M^{II}(tpdp)_3(N-$ MeIm)]<sup>-</sup> anions and two tetramethylammonium ions per unit cell. The counterions are systematically disordered, but will not be discussed in detail here. Selected interatomic distances and angles of both complexes are given in Table 4. The geometry of the metal coordination is approximately tetrahedral. The average bond lengths are 2.328(1) Å (4) and 2.295(2) Å (5) for the M-S bonds and 2.082(2) Å (4) and 2.065(4) Å (5) for the M–N bonds. The angles show only slight deviations from ideal  $T_d$  symmetry. The smallest angles are the S(2)– $M^{II}$ –S(3) angles with 105.23(3)° (4) and 103.8 (1) $^{\circ}$  (5) and the largest angles are the S(2)–M<sup>II</sup>– N(4) angles with  $114.41(5)^{\circ}$  (4) and  $115.2(1)^{\circ}$  (5), respectively. Only very few model complexes for Zn(S-cys)<sub>3</sub>(Nhis) centre have been published so far. To our knowledge there are only two other ZnS<sub>3</sub>N and CoS<sub>3</sub>N crystal structures each reported with monodentate ligands [36-39]. It is

Table 4

Selected interatomic distances (Å) and angles (°) for the series  $[Me_4N][M^{II}(tpdp)_3(N-MeIm)]$ 

	M = Zn (4)	M = Co ( <b>5</b> )
M-S(1)	2.342(1)	2.311(2)
M-S(2)	2.327(1)	2.294(1)
M-S(3)	2.314(1)	2.281(2)
M-N(4)	2.082(2)	2.065(4)
S(1)-M-S(2)	108.25(3)	107.8(1)
S(1)-M-S(3)	114.14(3)	113.0(1)
S(1)-M-N(4)	106.46(5)	106.9(1)
S(2)-M-S(3)	105.23(3)	103.8(1)
S(2)-M-N(4)	114.41(5)	115.2(1)
S(3)-M-N(4)	108.57(5)	110.3(1)

<sup>&</sup>lt;sup>1</sup>A general remark (for which we are indebted to one of the referees) concerning the possible causes for distortions of tetrahedral  $ML_4$  complexes such as  $M(SR)_4$  thiolates and especially of tetrahedral  $M(S-Cys)_4$  sites in proteins should be added in this context. Tetrahedral complexes are very easily distorted with little or no change of energy; generally it is not necessary to find electronic explanations for these distortions. Very often it is not adequate to make a big and incorrect point of such electronic reasons in the interpretation of crystallographic results. This is especially true for such, sometimes, inadequate discussions for  $MS_4$  distortions in protein structures



Fig. 4. Complex 6 with vibrational ellipsoids at the 30% probability level.

remarkable that only few model compounds for retroviraltype zinc finger proteins are known although they are of increasing interest due to their potential connection to a new HIV-therapy [18–20].

 3.3. Crystal structures of [Zn(tpdp)<sub>2</sub>(N-MeIm)<sub>2</sub>] (6), [Co(tpdp)<sub>2</sub>(N-MeIm)<sub>2</sub>] (7) and [Cd(tpdp)<sub>2</sub>(N-MeIm)<sub>2</sub>] (8)

A thermal ellipsoid plot of complex **6** as an example for this series of neutral complexes is given in Fig. 4. Again the zinc (**6**) and cobalt (**7**) complexes are isomorphous and isostructural. Relevant bond lengths and bond angles for the three complexes are given in Table 5. With average M–S bond lengths of 2.291(1) Å (**6**), 2.275(1) Å (**7**) and 2.467(1) Å (**8**) and M–N bond lengths of 2.074(3) Å (**6**), 2.014(2) Å (**7**) and 2.286(4) Å (**8**) the M-ligand bond lengths are shorter than the ones in the structures described before. This could be caused by the lower steric demand of the two *N*-methylimidazole ligands. Concomitantly, the N–M–N angles are the smallest, while the S–M–S angles are the largest. The bond angles vary from 99.5(1) to 128.75(4)° for **6**, from 102.6(1) to 123.66(3)° for **7** and from 93.3(2) to

Table 5

Selected interatomic distances (Å) and angles (°) for the series  $[M^{II}(tpdp)_2(\textit{N-MeIm})_2]$ 

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	$M = Zn \ (6)$	M = Co (7)	M = Cd (8)			
M-S(1)	2.298(1)	2.286(1)	2.466(1)			
M-S(2)	2.284(1)	2.264(1)	2.467(1)			
M-N(3)	2.054(3)	2.015(2)	2.275(4)			
M-N(5)	2.093(3)	2.013(2)	2.296(4)			
S(1)-M-S(2)	128.75(4)	123.66(3)	136.84(4)			
S(1)-M-N(3)	106.23(8)	105.61(7)	106.3(1)			
S(1)-M-N(5)	104.65(9)	107.61(7)	100.1(1)			
S(2)-M-N(3)	106.23(9)	109.96(7)	96.0(1)			
S(2)-M-N(5)	107.78(8)	105.50(7)	115.2(1)			
N(3)–M–N(5)	99.5(1)	102.6(1)	93.3(2)			

136.84(4)° for **8**. Consequently, in all these complexes the tetrahedron is significantly distorted. The causes of the variation in bond lengths and angles of **6**, **7** and **8** are the different ion radii of the three metal ions. Several  $MS_2N_2$  structures with substituted thiophenol and *N*-methylimida-zole are known in recent literature [40–43].

## 4. Conclusion

The present study shows that the metal centres of the three reported zinc model complexes are similar to the metal centre of zinc-containing DNA-binding proteins [1–17]. Furthermore we report that all cobalt complexes described herein are isomorphous and isostructural to the analogous zinc complexes. The cadmium complexes show slight differences in the crystal systems, but the direct metal environments are quite similar to those in the zinc or cobalt analogues. Thus, the present investigation clearly supports results that there should be only minor changes in the direct metal environment in proteins after replacing zinc by cobalt or cadmium.

## 5. Supplementary material

Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the full journal citation.

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