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Crystal Structures of $Zn(SR)_2$ Complexes: Structural Models for the Proposed $[Zn(cys\text{-}S)_2(his)_2]$ Center in Transcription Factor IIIA and Related Nucleic Acid Binding Proteins

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$[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-methylimidazole})_2]$ (**1**) and $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$ (**2**) were synthesized and structurally characterized by X-ray crystallography. Both **1** and **2** have monomeric structures with distorted-tetrahedral ZnS_2N_2 cores. The metrical parameters of **1** should closely approach those for $[Zn(cys\text{-}S)_2(his)_2]$ centers, which have been postulated in transcription factor IIIA and related nucleic acid binding proteins. The Zn–S and Zn–N distances are 2.300 (2) and 2.047 (10) Å for **1** and 2.256 (3) and 2.099 (10) Å for **2**. The trends in the changes in the M–S and M–N bond distance for the series $[M(SR)_x(\text{imidazole})_{4-x}]$ are discussed. Crystallographic parameters: for **1**, monoclinic space group $P2_1/c$ with a = 15.003 (4) Å, b = 13.786 (4) Å, c = 15.677 (3) Å, β = 114.72 (2)°, V = 2945 (3) Å^3, and Z = 4; for **2**, orthorhombic space group $Pbc2_1$ with a = 12.816 (2) Å, b = 15.581 (2) Å, c = 19.193 (2) Å, V = 3833 (2) Å^3, and Z = 4.

Introduction

Zinc–cysteine coordination is a feature in many important metalloproteins. $Zn(cys\text{-}S)_n$ centers have been proposed or established in a wide range of zinc-containing proteins, including alcohol dehydrogenase,[1] β-lactamase II,[2] aspartate transcarbamylase,[3] 5-aminolevulinate dehydratase,[4] and RNA polymerase from *Escherichia coli*.[5] The number of cysteines coordinated to zinc in these proteins varies from 1 to 4. It has recently been suggested that transcription factor IIIA, from the toad *Xenopus laevis*, is a zinc–cysteine protein.[6-8] TFIIIA, which has a single polypeptide chain of 344 amino acids, activates the transcription of the 5S ribosomal RNA gene by binding to its internal control region. TFIIIA also binds to the transcription product, 5S rRNA, to give a 7S ribonucleoprotein particle. The protein sequence of TFIIIA is made up of 9 repetitive units of ca. 30 amino acids; each unit contains a pair of cysteines and a pair of histidines joined by a chain of ca. 12 residues. Since TFIIIA was known to contain Zn,[9] it has been postulated that $[Zn(cys\text{-}S)_2(his)_2]$ coordination in each of these domains plays a structural role in creating nine binding fingers, which enables the protein to bind to DNA (see Figure 1).[6,7] The occurrence of similar amino acid sequences in a number of other nucleic acid binding proteins has led to the suggestion that "zinc fingers" may be a common feature in many protein–DNA (RNA) interactions.[10-12]

As part of a study to provide structural and spectroscopic models for zinc–cysteine centers in metalloproteins,[13-15] we report the crystal structures of a $[Zn(SR)_2(imid)_2]$[27] and a related bipyridine complex.

Table I. X-ray Crystallographic Parameters

	$[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2\text{-}(1\text{-Me-imid})_2]$ (**1**)	$[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2\text{-}(bpy)]$ (**2**)
formula	$ZnS_2N_4C_{28}H_{38}$	$ZnS_2N_2C_{40}H_{54}$
fw	560	692.4
a, Å	15.003 (4)	12.816 (2)
b, Å	13.786 (4)	15.581 (2)
c, Å	15.677 (3)	19.193 (2)
α, deg	90	90
β, deg	114.72 (2)	90
γ, deg	90	90
V, Å^3	2945 (3)	3833 (2)
Z	4	4
d(calcd), g cm^{-3}	1.263	1.200
space group	$P2_1/c$	$Pbc2_1$
temp	room temp	room temp
radiation (λ, Å)	Mo (0.71073)	Mo (0.71073)
linear abs coeff, cm^{-1}	10.18	7.95
scan mode	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	$0 < 2\theta < 46$	$0 < 2\theta < 50$
reflcns measd	$+h,+k,\pm l$	$+h,+k,+l$
no. of reflcns measd	4504	3792
no. of unique reflcns with $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$	1651	2083
final no. of variables	316	405
$R^a = [\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.0488	0.040
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$	0.0553	0.047
esd of unit wt observn	1.496	1.160

[a] Quantity minimized $(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2)$; weight $w = 1/(\sigma^2 + 0.0016F_o^2)$.

Experimental Section

Synthesis of $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-Me-imid})_2]$ (1). LiS-2,3,5,6-Me_4C_6H was generated in ethanol (60 mL) by combining the thiol (0.769 g, 4.62 mmol) with lithium wire (0.036 g, 5.2 mmol). $ZnCl_2$ (0.315 g, 2.31 mmol) was added, and the reaction was stirred for 2 h. Upon the addition of 1-methylimidazole (0.50 mL, 6.3 mmol), the reaction mixture went from a white suspension to a clear solution. The solvent was removed under vacuum and replaced with 75 mL of toluene. The reaction mixture was heated to 100 °C for 2 h and filtered hot. The filtrate stood for 3 days, during which time a large amount of white whiskers crys-

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Table II. Atomic Coordinates for $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$

atom	*x*	*y*	*z*
Zn	0.23277 (7)	0.19524 (8)	0.05981 (6)
S1	0.1877 (2)	0.2460 (2)	−0.0924 (1)
S2	0.3570 (2)	0.0832 (2)	0.0987 (1)
N1	0.2833 (4)	0.3101 (5)	0.1513 (4)
N2	0.1138 (4)	0.1518 (4)	0.0809 (4)
N3	0.3590 (4)	0.3975 (5)	0.2779 (4)
N4	−0.0397 (4)	0.1141 (5)	0.0527 (4)
C11	0.0581 (5)	0.2450 (6)	−0.1516 (5)
C12	0.0021 (5)	0.3120 (6)	−0.1271 (5)
C13	−0.0994 (5)	0.3126 (7)	−0.1759 (5)
C14	−0.1425 (5)	0.2485 (7)	−0.2484 (5)
C15	−0.0884 (6)	0.1818 (7)	−0.2727 (5)
C16	0.0110 (5)	0.1794 (6)	−0.2239 (5)
C17	0.0502 (6)	0.3834 (6)	−0.0491 (6)
C18	−0.1642 (6)	0.3820 (8)	−0.1529 (7)
C19	−0.1433 (7)	0.1170 (8)	−0.3564 (7)
C10	0.0710 (6)	0.1078 (7)	−0.2505 (6)
C21	0.4210 (5)	0.1140 (6)	0.2204 (5)
C22	0.3882 (5)	0.0695 (6)	0.2835 (5)
C23	0.4316 (6)	0.0994 (7)	0.3772 (5)
C24	0.5035 (6)	0.1665 (7)	0.4051 (6)
C25	0.5409 (6)	0.2073 (7)	0.3443 (6)
C26	0.4974 (5)	0.1789 (6)	0.2498 (5)
C27	0.3139 (6)	−0.0073 (7)	0.2575 (6)
C28	0.3963 (7)	0.0597 (9)	0.4455 (6)
C29	0.6226 (7)	0.2775 (8)	0.3831 (8)
C20	0.5307 (7)	0.2257 (7)	0.1805 (6)
C31	0.3115 (5)	0.3142 (6)	0.2431 (5)
C32	0.3629 (6)	0.4483 (6)	0.2061 (6)
C33	0.3156 (6)	0.3943 (6)	0.1285 (5)
C34	0.3981 (7)	0.4251 (7)	0.3766 (6)
C41	0.0264 (5)	0.1294 (6)	0.0175 (5)
C42	0.0109 (6)	0.1289 (7)	0.1471 (5)
C43	0.1024 (5)	0.1515 (7)	0.1635 (5)
C44	−0.1420 (6)	0.0928 (8)	0.0048 (7)

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$

Zn–S1	2.301 (2)	S1–Zn–S2	109.46 (8)
Zn–S2	2.298 (2)	S1–Zn–N1	110.6 (2)
Zn–N1	2.057 (6)	S1–Zn–N2	111.1 (2)
Zn–N2	2.037 (6)	S2–Zn–N1	108.1 (2)
Zn–S1–C11	108.8 (2)	S2–Zn–N2	115.3 (2)
Zn–S2–C22	97.9 (2)	N1–Zn–N2	101.9 (2)

Table IV. Atomic Coordinates for $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$

atom	*x*	*y*	*z*
Zn	−0.19851 (5)	−0.16131 (5)	−0.2500 (0)
S1	−0.1167 (1)	−0.0336 (1)	−0.2392 (1)
S2	−0.2092 (1)	−0.2234 (1)	−0.3557 (1)
N1	−0.3376 (4)	−0.1669 (4)	−0.1915 (3)
N2	−0.1544 (4)	−0.2368 (4)	−0.1651 (3)
C11	−0.0927 (5)	−0.0257 (4)	−0.1477 (3)
C12	−0.1681 (5)	0.0067 (4)	−0.1028 (4)
C13	−0.1458 (7)	0.0117 (5)	−0.0321 (4)
C14	−0.0496 (7)	−0.0123 (5)	−0.0055 (4)
C15	0.0233 (6)	−0.0401 (5)	−0.0515 (4)
C16	0.0059 (6)	−0.0488 (5)	−0.1216 (4)
C11A	−0.2705 (6)	0.0410 (5)	−0.1301 (4)
C11B	−0.2577 (7)	0.1314 (6)	−0.1578 (6)
C11C	−0.3602 (7)	0.0360 (6)	−0.0787 (5)
C12A	−0.0289 (10)	−0.0077 (7)	0.0716 (5)
C12B	−0.0068 (8)	−0.0894 (6)	0.1044 (5)
C12C	−0.0575 (9)	0.0634 (7)	0.1081 (5)
C13A	0.0942 (6)	−0.0762 (5)	−0.1688 (4)
C13B	0.1747 (6)	−0.1346 (6)	−0.1340 (6)
C13C	0.1490 (8)	0.0020 (6)	−0.1997 (5)
C21	−0.3468 (5)	−0.2177 (4)	−0.3686 (3)
C22	−0.3917 (5)	−0.1490 (5)	−0.4053 (3)
C23	−0.4984 (6)	−0.1462 (5)	−0.4131 (4)
C24	−0.5653 (6)	−0.2081 (5)	−0.3855 (4)
C25	−0.5190 (5)	−0.2758 (4)	−0.3518 (4)
C26	−0.4137 (5)	−0.2829 (4)	−0.3422 (4)
C21A	−0.3263 (6)	−0.0758 (5)	−0.4344 (5)
C21B	−0.3205 (7)	−0.0022 (5)	−0.3835 (6)
C21C	−0.3604 (8)	−0.0467 (7)	−0.5059 (6)
C22A	−0.6818 (5)	−0.2010 (5)	−0.3953 (5)
C22B	−0.7204 (6)	−0.2542 (6)	−0.4550 (5)
C22C	−0.7419 (8)	−0.2229 (8)	−0.3303 (6)
C23A	−0.3696 (6)	−0.3619 (5)	−0.3060 (5)
C23B	−0.3530 (8)	−0.4317 (6)	−0.3591 (7)
C23C	−0.4337 (7)	−0.3928 (5)	−0.2468 (7)
C31	−0.4308 (6)	−0.1369 (5)	−0.2105 (4)
C32	−0.5161 (6)	−0.1400 (6)	−0.1685 (5)
C33	−0.5064 (6)	−0.1731 (6)	−0.1042 (5)
C34	−0.4101 (7)	−0.2025 (6)	−0.0819 (4)
C35	−0.3269 (6)	−0.1988 (5)	−0.1277 (4)
C41	−0.0629 (6)	−0.2731 (5)	−0.1552 (4)
C42	−0.0308 (6)	−0.3043 (5)	−0.0918 (5)
C43	−0.0974 (7)	−0.2956 (6)	−0.0372 (4)
C44	−0.1926 (7)	−0.2601 (6)	−0.0468 (5)
C45	−0.2200 (5)	−0.2330 (4)	−0.1116 (4)

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$

Zn–S1	2.259 (2)	S1–Zn–S2	119.32 (8)
Zn–S2	2.251 (2)	S1–Zn–N1	112.3 (2)
Zn–N1	2.109 (6)	S1–Zn–N2	107.4 (2)
Zn–N2	2.088 (6)	S2–Zn–N1	114.2 (2)
Zn–S1–C11	103.3 (2)	S2–Zn–N2	118.5 (2)
Zn–S2–C21	99.4 (2)	N1–Zn–N2	77.9 (2)

tallized (0.52 g). The filtrate was concentrated slightly and cooled to −20 °C to yield a second crop of crystals (0.34 g; 66% total yield). Recrystallization was achieved from hot acetonitrile. ^1H NMR ($CDCl_3$): δ 6.81 (s, 4 H), 6.73 (s, 2 H), 6.57 (s, 2 H), 3.53 (s, 6 H), 2.30 (s, 12 H), 2.10 (s, 12 H).

Synthesis of $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$ (2). $LiS\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$ was generated in situ by the reaction of $HS\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$ (0.79 g, 3.3 mmol) and lithium wire (0.024 g, 3.3 mmol) in EtOH. $ZnCl_2$ (0.229 g, 1.68 mmol) was added with no notable change in the color of the solution. The subsequent addition of 2,2′-bipyridine (0.262 g, 1.68 mmol) resulted immediately in a bright yellow solution, and within seconds, a yellow powder precipitated. The product was filtered and, washed with EtOH, and dried under vacuum (0.93 g; 80% yield). Yellow crystals were obtained from volume reduction of an CH_3CN solution. ^1H NMR ($CDCl_3$): δ 7.9 (complex multiplet, 6 H), 7.2 (m, 2 H), 6.64 (s, 2 H), 3.83 (sept, J = 7 Hz, 4 H), 2.72 (sept, J = 7 Hz, 2 H), 1.16 (d, J = 7 Hz, 12 H), 0.96 (d, J = 7 Hz, 24 H).

X-ray Crystal Structures

Unit cell determinations, data collection, and structure solutions were performed by using standard procedures previously described.[16] Parameters connected with the crystallographic studies are given in Table I.

$[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$. A colorless crystal grown from cooling a hot CH_3CN solution was mounted on a fiber and examined on a CAD4 diffractometer. The unit cell was monoclinic with absences consistent with only the $P2_1/c$ space group and a volume indicating Z = 4. An absorption correction was not applied. The structure was solved by Patterson and Fourier methods. Non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located from a difference map or were calculated. The hydrogen atoms were assigned fixed temperature factors and were included in the structure factor calculations but were not refined. Final refinement gave R (R_w) = 0.0488 (0.0553). Atomic positional parameters are given in Table II, and bond distances and angles are found in Table III.

$[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$. Single crystals were grown by volume reduction of an CH_3CN solution. Unit cell determination and data collection were obtained by using a yellow crystal of dimensions 0.75 × 0.5 × 0.5 mm. The volume of the unit cell was consistent with Z = 4. An absorption correction was not applied. The systematic absences for the orthorhobmic unit cell limited the choice of space groups to $Pbc2_1$ (a nonstandard setting of $Pca2_1$) and $Pbcm$. Attempts to solve the structure in the centric space group, $Pbcm$, were not successful. The structure solution in the noncentric space group was straightforward with the usual Patterson and Fourier techniques. All non-hydrogen atoms were refined anisotropically, and the hydrogen atom positions were calculated, given fixed temperature factors, and included in the structure factor calculations but were not refined. Final least-squares refinement for the preferred enantiomorph gave R (R_w) = 0.040 (0.047). Refine-

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Table VI. M–S and (M–N) Bond Distances (Å) in the Series $[M(SR)_x(N)_{4-x}]$

	zinc	cadmium	cobalt
$[M(SR)_4]$	$[Zn(SPh)_4]^{2-}$ 2.353 (16)[23]	$[Cd(SPh)_4]^{2-}$ 2.535 (13)[23]	$[Co(SPh)_4]^{2-}$ 2.328 (11)[23]
$[M(SR)_3(N)]$			$[Co(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3(1\text{-}Me\text{-}imid)]^-$ 2.300 (5), (2.051 (6))[16]
$[M(SR)_2(N)_2]$	$[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$ 2.300 (2), (2.047 (10))	$[Cd(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(1\text{-}Me\text{-}imid)_2]$ 2.462 (10), (2.281 (10))[13]	$[Co(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(py)_2]$ 2.263 (9), (2.038 (11))[13]
$[M(SR)(N)_3]$			$[HB(3,5\text{-}Me_2pz)_3Co(SC_6F_5)]$ 2.26 (1), (1.99 (2))[22]
$[M(imid)_4]$	$[Zn(1,2\text{-}Me_2\text{-}imid)_4]^{2+}$ (2.00 (2))[21]		$[Co(1,2\text{-}Me_2\text{-}imid)_4]^{2+}$ (1.995 (7))[21]

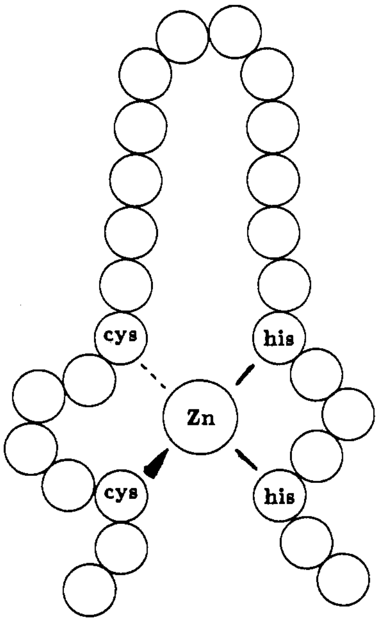

Figure 1. Schematic diagram showing the "zinc finger" structure proposed for transcription factor IIIA and related gene-binding proteins.

ment of the opposite enantiomorph gave higher R values. The final difference map was unremarkable with the highest peak having electron density of 0.48 e/Å^3. Atomic coordinates are given in Table IV; selected bond distances and angles are given in Table V.

Results

$[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$ (**1**) and $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$ (**2**) were prepared by the reaction of $ZnCl_2$ with the appropriate equivalents of the ligands. Bulky aromatic thiolate ligands were used to preserve the monomeric nature of complexes.[17] Compound **2** is bright yellow, an uncommon color for a Zn(II) complex, while **1** is colorless. The color of **2** results from charge-transfer transitions from aromatic thiolate ligands to the bidentate bpy ligand; the spectroscopy of related complexes has been studied in detail.[18]

The X-ray crystal structures of **1** and **2** (Figures 2 and 3) revealed the basic tetrahedral ZnS_2N_2 coordination units in both cases. $Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2$ has Zn–S and Zn–N bonds of 2.300 (2) and 2.047 (10) Å. The L–Zn–L angles show distortions from tetrahedral symmetry with S1–Zn–S2 = 109.46 (8)° and N1–Zn–N2 = 101.9 (2)° and the four S–Zn–N angles in the range of 108–115°. The Zn–S bond distances (2.256 (3) Å) in $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$ are significantly shorter than those in **1**, while the Zn–N bonds (2.099 (10) Å) in **2** are longer than those in **1**. The deviations from 109.5° of the L–Zn–L angles in **2** are larger than those in **1** as a result of the constraint of the chelate ligand. It is interesting to note that the cobalt analogue of **2** binds a solvent molecule to become five-coordinate: $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(bpy)(CH_3CN)]$.[14] Although the zinc complex was also recrystallized from CH_3CN, it did not add a fifth ligand.

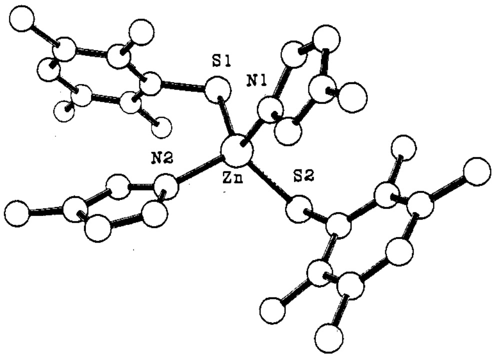

Figure 2. Computer-drawn structural diagram of $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2(1\text{-}Me\text{-}imid)_2]$.

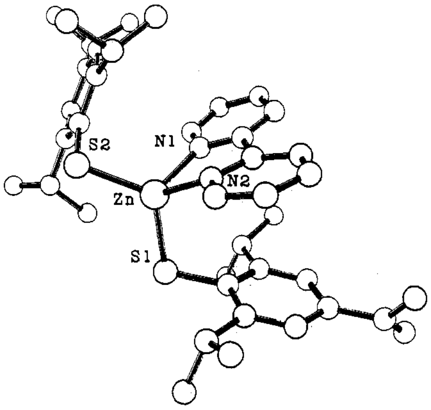

Figure 3. Computer-drawn structural diagram of $[Zn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(bpy)]$.

Discussion

Only a few zinc thiolate complexes have been previously synthesized and structurally characterized.[19] Most of these contain bridging thiolate ligands. A comparison of the structures of **1** and **2** reveals an interesting change in the Zn–S and Zn–N bond distances. The Zn–S distance in **1** is 0.04 Å longer than that in **2**. The Zn–N bonds in **1** are 0.05 Å shorter than the corresponding distances in **2**. The close similarities, of the distances in **2** and the previously characterized $[Zn(S\text{-}p\text{-}tolyl)_2(phen)]$[20] (Zn–S = 2.261 (5) Å, Zn–N = 2.112 (8) Å) provide further evidence for the accuracy of the Zn–L distances reported here. This comparison also indicates that the presence of the ortho substituents on the thiolate ligand of **2** does not have an effect on the Zn–S

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bond distance. $[Zn(S\text{-}p\text{-tolyl})_2(phen)]$ was used as a model compound for a recent EXAFS study of the Zn center in TFIIIA.[6c] It is to be expected that the metal–ligand distances in a $Zn(cys\text{-}S)_2(his)_2$ protein center will more closely approach those found in **1**. The bond distances in **1** are also similar to those reported for bis(2-amino-1,1-dimethylethanethiolato)zinc(II) (Zn–S = 2.297 Å, Zn–N = 2.06 Å).[25a]

A similar trend in bond distances is seen in related Co(II) complexes. The Co–S and Co–N distances in $[Co(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2(py)_2]$ are 2.263 (9) and 2.038 (11) Å.[13] In comparison, the Co–S bond distances (2.244 (2) Å) in $[Co(S\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(2,9\text{-}Me_2phen)]$[14] are 0.02 Å shorter and the Co–N distances (2.055 (5) Å) are 0.02 Å longer. It is worthwhile to compare the M–L distances observed in the series of mixed-ligand complexes $[M(SR)_x(imid)_{4-x}]$ with the homoleptic compounds $[M(SR)_4]^{2-}$ and $[M(imid)_4]^{2-}$ (Table VI). The entries in the tables were limited to complexes with monodentate thiolate and aromatic nitrogen ligands or polydentate ligands that do not severely distort the L–M–L angles from tetrahedral. For each metal ion, the M–S and M–N distances depend on the number of N and S donors. Increasing the number of nitrogen donors in the MS_xN_{4-x} center results in a shortening of the M–S bonds. Increasing the number of sulfurs leads to a lengthening of the M–N bond distances. The structural data support the idea that steric repulsions between the donor atoms can perturb the M–L bond distances in tetrahedral ML_4 complexes.

Another possible explanation for the data is as follows: as one considers the series $[M(imid)_4]^{2+}$ to $[M(SR)_4]^{2-}$, the M–N and M–S bonds increase in length due to the change in the overall charge on the metal complex. This hypothesis does not account for the changes in the M–L distances in **1** and **2**. Also, the Co–S bonds (2.305 (13) Å) in $[Co(Me_3AsS)_4]^{2+}$ are only slightly shorter than those in $[Co(SPh)_4]^{2-}$.[23,24] There is a further question of the possible effect of alkyl versus aromatic thiolate ligands on M–S bond distances. Monomeric tetrahedral complexes of Zn, Cd, and Co with alkanethiolate ligands are scarce.[25] A comparison of the series of bis(1,2-ethanedithiolate) complexes, $[M(edt)_2]^{2-}$, with the $[M(SPh)_4]^{2-}$ complexes reveals no differences in the Zn–S and Cd–S distances but a shorter Co–S bond distance (2.284 (6) Å) in $[Co(edt)_2]^{2-}$.[23,26] Further examples of structurally characterized alkanethiolate complexes are necessary since they provide the best structural models for metal–cysteine coordination.

Although the differences in the Zn–S distances in the various $[Zn(SR)_x(N)_{4-x}]$ centers are small, the differences are within the accuracy of EXAFS measurements on metalloproteins. It may be possible to estimate the number of cysteines bonded to a zinc center in a metalloprotein by measuring the Zn–S distance.

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Registry No. **1**, 112043-95-5; **2**, 112043-96-6.

Supplementary Material Available: Tables of thermal and hydrogen atom positional parameters and tables of bond distances and angles for **1** and **2** (10 pages); tables of structure factors for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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(27) $HS\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$ = 2,4,6-triisopropylbenzenethiol, $HS\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ = 2,6-diisopropylbenzenethiol, $HS\text{-}2,3,5,6\text{-}Me_4C_6H$ = 2,3,5,6-tetramethylbenzenethiol, imid = imidazole, 1-Me-imid = 1-methylimidazole, $2,9\text{-}Me_2phen$ = 2,9-dimethyl-1,10-phenanthroline, and bpy = 2,2′-bipyridine.

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Copper(II), Nickel(II), and Cobalt(III) Complexes with New Macrocyclic Ligands. 6,14-Dimethyl-1,5,9,13-tetraazacyclohexadeca-5,13-diene ($Me_2[16]diene$) and *C-meso*- and *C-rac*-6,14-Dimethyl-1,5,9,13-tetraazacyclohexadecane (*C-meso*- and *C-rac*-$Me_2[16]ane$)

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The new macrocyclic ligand 6,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,13-diene, $Me_2[16]diene$, can be synthesized by the nontemplate condensation of 1,3-propanediamine monohydroperchlorate and methyl vinyl ketone at −10 °C under anhydrous conditions. $Me_2[16]diene$ on reduction with sodium borohydride gives *C-meso-* and *C-rac-*$Me_2[16]ane$. The macrocycles undergo facile complexation with copper(II), nickel(II), and cobalt(III). The cobalt complexes $[CoLCl_2]^+$ undergo rapid thermal aquation. The high rates of aquation have been discussed in terms of the ability of the macrocycle to fold.

Introduction

The nontemplate synthesis of $Me_6[14]diene$ (I, Chart I) from ethylenediamine monohydroperchlorate and acetone was first reported by Curtis and Hay.[1] By similar procedures, a variety of other tetraaza macrocycles with 13, 14, and 15 members have been prepared by the reaction of polyamines with carbonyl compounds.[2-7] Reactions of 1,4-butanediamine and 1,6-hexanedi-

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