

Design of Trigonal-Bipyramidal ZnN₃S₂ Complexes

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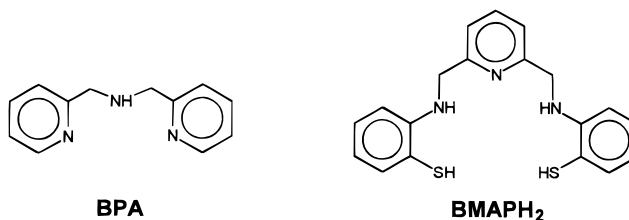
Introduction

The renaissance in the chemistry of metal complexes with chelate ligands containing sulfur and nitrogen donors, due to the work of Sellmann, Schröder, Reedijk, Lindoy, Darensbourg,¹ and many others,² draws its motivation not only from the biological chemistry of the metals but also from the prospect that it may lead to new interconversions of organic substrates in a non-organometallic environment. While this has been demonstrated for complexes of the earlier or more noble transition elements,³ it is still a mere prospect for zinc, despite the importance of this metal for innumerable transformations of polar organic compounds in enzymatic or technical processes.^{4,5}

One reason that this specific type of zinc chemistry lags behind lies in the general disadvantage of all zinc complexes: low thermodynamic stabilities and lack of structurizing d-electron effects. It is still an art to make nontrivial ZnN₃S_y complexes, and there is hardly any chemistry of substrates attached to them. We have experienced this with seemingly simple N,N,S chelate ligands which exert a zinc complex chemistry of puzzling variety.^{6,7} We therefore consider it necessary to learn more about the principles by which N₃S_y ligand systems control the coordination number and geometry as well as the availability and functionality of labile coordination sites in zinc complexes.

This paper reports one result of our attempts in this direction. The aim was to combine a tridentate nitrogen donor of limited conformational freedom with sulfur donors of limited basicity. The former was meant to provide ZnN₃ complex fragments of predictable geometry; the latter was meant to reduce the Zn–S–Zn bridging capacity of the ligands and hence the tendency

of the complexes to oligomerize. Both objectives were realized with the known ligand bis(2-pyridylmethyl)amine (BPA)⁸ and the new ligand 2,6-bis((2-mercaptophenyl)amino)methylpyridine (BMAPH₂). Our observations complement, and put



on a systematic basis, the results of previous structure determinations on the related compounds Zn(terpy)[(*i*-PrO)₂PS₂]₂ with terpy = *sym*-terpyridine⁹ and Zn(BMIP) with BMIP = 2,6-bis((mercaptophenyl)imino)ethylpyridine.¹⁰

Experimental Section

All experimental techniques and the standard IR and NMR equipment were described previously.¹¹ All sulfur-containing compounds were handled in a nitrogen atmosphere. Ligand BPA was prepared according to the published procedure.⁸

The BMAPH₂ Ligand. Freshly distilled 2-aminothiophenol (3.00 mL, 3.51 g, 28.0 mmol) and pyridine-2,6-dicarbaldehyde (1.89 g, 14.0 mmol) in methanol (100 mL) were heated to reflux for 1 h, during which a colorless precipitate formed. After the mixture was cooled to room temperature, NaBH₄ (10.7 g, 283 mmol) was added slowly with vigorous stirring. Then the solvent was removed in a rotary evaporator and the solid residue treated with 100 mL of water. The mixture was neutralized with glacial acetic acid and then extracted four times with 50 mL of diethyl ether. The combined extracts were washed with water (50 mL), dried over Na₂SO₄, and evaporated to dryness in vacuo. Analytically pure BMAPH₂ (4.31 g, 88%) remained as a yellow solid of mp 78 °C. Anal. Calcd for C₁₉H₁₉N₃S₂ (mol wt 353.5): C, 64.55; H, 5.42; N, 11.81. Found: C, 64.80; H, 5.47; N, 11.78. Selected IR bands (KBr, cm⁻¹): 3413w, 3394m, 3371m, 3218w, NH; 2524w, 2504w, SH; 1588vs, 1575s, pyridine. ¹H-NMR (CDCl₃): δ 4.56 [s, 4H, CH₂], 6.61 [dd, ³J = 8.0 Hz, ⁴J = 1.3 Hz, 2H, phenyl H₆], 6.65 [dt, ³J = 7.5 Hz, ⁴J = 1.3 Hz, 2H, phenyl H₄], 7.17 [dt, ³J = 7.5 Hz, ⁴J = 1.3 Hz, 2H, phenyl H₅], 7.22 [d, ³J = 7.5 Hz, 2H, pyridine H_β], 7.44 [dd, ³J = 7.5 Hz, ⁴J = 1.3 Hz, 2H, phenyl H₃], 7.63 [t, ³J = 7.5 Hz, 1H, pyridine H_γ].

Spectral Data for the Ligand BPA. Selected IR bands (film, cm⁻¹): 3311m, NH; 1591s, 1569s, pyridine. ¹H-NMR (DMSO-*d*₆): 3.08 [s, br, 1H, NH], 3.82 [s, 4H, CH₂], 7.26 [m, 2H, pyridine H_β], 7.38 [d, ³J = 6.3 Hz, 2H, pyridine H_δ], 7.71 [m, 2H, pyridine H_γ], 8.49 [d, ³J = 5.1 Hz, 2H, pyridine H_α].

The Zn(BPA)(SPh)₂ Complex. Freshly distilled thiophenol (0.25 mL, 0.27 g, 2.5 mmol) in methanol (30 mL) was treated dropwise under stirring with 10.4 mL (2.5 mmol) of a 0.24 M solution of NaOMe in methanol. A solution of 0.46 g (1.24 mmol) of Zn(ClO₄)₂·6H₂O in methanol (30 mL) and a solution of 0.25 g (1.25 mmol) of BPA in methanol (20 mL) were added with stirring. The clear, orange reaction mixture was reduced in vacuo to 30 mL. The colorless precipitate formed was filtered off, washed with a small amount of methanol, and dried in vacuo. Recrystallization from acetonitrile yielded 0.24 g (40%) of Zn(BPA)(SPh)₂ as colorless crystals of mp 158 °C dec. Anal. Calcd

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Table 1. Crystallographic Details

	Zn(BPA)(SPh) ₂	Zn(BMAP)
formula	C ₂₄ H ₂₃ N ₃ S ₂ Zn	C ₁₉ H ₁₇ N ₃ S ₂ Zn·C ₃ H ₇ NO
mol wt	483.0	416.9 + 73.1
color	colorless	pale red
crystal size (mm)	0.4 × 0.3 × 0.3	0.6 × 0.2 × 0.2
space group	<i>P1</i>	<i>P2₁2₁2₁</i>
<i>Z</i>	2	4
<i>a</i> (Å)	9.951(1)	10.654(2)
<i>b</i> (Å)	11.354(1)	11.035(7)
<i>c</i> (Å)	11.788(1)	19.128(4)
α (deg)	61.800(5)	90
β (deg)	77.000(4)	90
γ (deg)	86.150(4)	90
<i>V</i> (Å ³)	1142.5(2)	2249(2)
<i>d</i> _{calc} (g/cm ³)	1.40	1.45
<i>d</i> _{obs} (g/cm ³)	1.35	1.39
μ (mm ⁻¹)	1.27	1.30
2 θ range	6–52	5–46
<i>hkl</i> ranges	<i>h</i> : –12 to 0 <i>k</i> : –13 to +13 <i>l</i> : –14 to +14	<i>h</i> : –11 to 0 <i>k</i> : –11 to 0 <i>l</i> : –19 to 0
no. of refl measd	4740	1469
no. of indep refl	4471	1469
<i>R</i> (int)	0.025	
no. of refl used (<i>I</i> ≥ 2 σ (<i>I</i>))	3246	833
no. of params	271	211
<i>R</i> (unweighted)	0.037	0.063
res el density (e/Å ³)	+0.6, –0.4	+0.4, –0.5

for C₂₄H₂₃N₃S₂Zn (mol wt 483.0): C, 59.68; H, 4.80; N, 8.70. Found: C, 59.76; H, 4.73; N, 8.70. Selected IR bands (KBr, cm⁻¹): 3174m, NH; 1599s, 1575s, pyridine. ¹H-NMR (DMSO-*d*₆): 4.08 [s, 4H, CH₂], 4.89 [s, br, 1H, NH], 6.78 [m, 6H, phenyl H₂, H₃, H₄], 7.21 [d, ³*J* = 6.9 Hz, 4H, phenyl H₁, H₅], 7.25 [m, 2H, pyridine H_β], 7.31 [d, ³*J* = 6.3 Hz, 2H, pyridine H_β], 7.84 [m, 2H, pyridine H_γ], 8.41 [d, ³*J* = 5.3 Hz, 2H, pyridine H_α].

The Zn(BMAP) Complex. Ligand BMAPH₂ (56 mg, 0.16 mmol) dissolved in 6 mL of dichloromethane/methanol (2:1) was added to a solution of NaOH (13 mg, 33 mmol) in 4 mL of water/methanol (1:1). To this solution was added dropwise with stirring a solution of Zn(ClO₄)₂·6H₂O (59 mg, 0.16 mmol) in 4 mL of water/methanol (1:1). After 1 h of stirring and pumping-off of the dichloromethane, the mixture was filtered and the remaining reddish precipitate washed with water and dried in vacuo. Recrystallization from hot acetone/dimethylformamide (10:3) yielded 60 mg (77%) of Zn(BMAP)·DMF as pale-red crystals of mp 245 °C dec. Anal. Calcd for C₁₉H₁₇N₃S₂Zn·C₃H₇NO (mol wt 416.9 + 73.1): C, 53.93; H, 4.94; N, 11.44. Found: C, 53.71; H, 4.80; N, 10.89. Selected IR bands (KBr, cm⁻¹): 3296s, NH; 1604m, 1581m, pyridine. ¹H-NMR (DMSO-*d*₆): 4.02 [s, br, 2H, CHH], 4.37 [s, br, 2H, CHH], 6.61 [t, ³*J* = 7.5 Hz, 2H, NH], 6.83 [dt, ³*J* = 7.2 Hz, ⁴*J* = 1.7 Hz, 2H, phenyl H₄], 6.89 [dt, ³*J* = 7.3 Hz, ⁴*J* = 1.7 Hz, 2H, phenyl H₅], 7.19 [dd, ³*J* = 7.2 Hz, ⁴*J* = 2.1 Hz, 2H, phenyl H₆], 7.30 [dd, ³*J* = 7.3 Hz, ⁴*J* = 2.0 Hz, 2H, phenyl H₃], 7.52 [d, ³*J* = 7.7 Hz, 2H, pyridine H_β], 8.06 [t, ³*J* = 7.7 Hz, 1H, pyridine H_γ].

X-ray Crystallography. Crystals of both complexes were obtained from the above mentioned recrystallizations. The poor quality of the structure determination of Zn(BMAP) is due to the fact that crystals of sufficient quality could not be obtained. Data were taken on a Nonius CAD4 diffractometer utilizing graphite-monochromatized Mo K α radiation and the $\omega/2\theta$ technique and were used without an absorption correction. All crystallographic details are listed in Table 1. Both structures were solved with direct methods using the SHELX program system¹² and refined anisotropically. No attempt was made to determine the absolute configuration of Zn(BMAP). Hydrogen atoms were included at fixed positions (C–H = 0.96 Å). Their isotropic temperature factors were fixed at 1.2 times the value for the C atoms attached

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (pm² × 10⁻¹) for Zn(BPA)(SPh)₂

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Zn1	1561(1)	8921(1)	3711(1)	42(1)
S1	439(1)	7138(1)	5650(1)	51(1)
S2	3619(1)	8915(1)	2328(1)	51(1)
N1	-72(3)	8991(3)	2662(3)	47(1)
N2	1041(3)	11010(3)	2776(2)	44(1)
N3	2535(3)	9964(3)	4615(3)	47(1)
C1	597(4)	11333(3)	1563(3)	53(1)
C2	-295(3)	10208(3)	1750(3)	45(1)
C3	-1257(3)	10422(4)	994(3)	55(1)
C4	-2007(4)	9357(4)	1187(4)	62(1)
C5	-1790(4)	8102(4)	2113(4)	64(1)
C6	-815(4)	7952(4)	2834(4)	57(1)
C7	2264(3)	11815(3)	2560(3)	49(1)
C8	2763(3)	11279(3)	3820(3)	46(1)
C9	3431(4)	12077(4)	4134(4)	59(1)
C10	3873(4)	11498(4)	5295(4)	61(1)
C11	3634(3)	10155(4)	6123(4)	58(1)
C12	2965(3)	9422(4)	5751(3)	54(1)
C13	1699(4)	6175(3)	6514(3)	51(1)
C14	3009(4)	6039(4)	5883(4)	65(1)
C15	3949(5)	5274(5)	6605(6)	92(2)
C16	3621(8)	4638(5)	7938(8)	114(2)
C17	2306(8)	4729(5)	8580(5)	101(2)
C18	1347(5)	5498(4)	7880(4)	72(1)
C19	3354(3)	7803(3)	1727(3)	41(1)
C20	2446(4)	6688(3)	2455(4)	53(1)
C21	2284(4)	5832(4)	1967(4)	68(1)
C22	3022(5)	6076(5)	737(5)	75(1)
C23	3924(4)	7173(4)	-3(4)	65(1)
C24	4094(3)	8025(4)	487(3)	52(1)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized tensor *U*_{*ij*}.

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (pm² × 10⁻¹) for Zn(BMAP)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Zn1	9142(3)	540(2)	8297(1)	48(1)
S1	8408(6)	-898(5)	7531(3)	52(2)
S2	10912(6)	298(5)	8978(3)	52(2)
N1	9530(15)	1604(14)	7328(8)	39(5)
N2	8123(17)	2039(18)	8442(12)	49(5)
N3	8090(16)	214(14)	9339(8)	42(5)
C1	9181(21)	-400(17)	6791(10)	39(5)
C2	9310(21)	-1128(19)	6204(10)	48(6)
C3	9900(20)	-762(22)	5603(12)	60(7)
C4	10389(20)	395(22)	5573(12)	66(7)
C5	10302(21)	1179(22)	6145(12)	61(8)
C6	9694(16)	822(16)	6736(11)	35(5)
C7	8421(24)	2380(20)	7225(12)	59(8)
C8	7931(22)	2824(22)	7918(14)	50(7)
C9	7255(24)	3891(22)	7998(14)	65(8)
C10	6777(25)	4166(21)	8643(15)	69(8)
C11	7008(20)	3376(24)	9200(12)	56(7)
C12	7666(21)	2323(24)	9074(17)	62(8)
C13	8016(22)	1426(20)	9638(12)	57(7)
C14	8894(21)	-542(24)	9738(11)	54(6)
C15	8361(25)	-1270(22)	10272(12)	68(8)
C16	9099(24)	-2066(20)	10651(11)	63(7)
C17	10392(21)	-2104(21)	10537(12)	60(7)
C18	10929(25)	-1378(20)	10036(10)	56(6)
C19	10189(20)	-590(24)	9633(11)	52(6)
O1	5473(23)	73(22)	8813(12)	118(10)
N4	4613(22)	1356(26)	8110(11)	79(8)
C20	5353(28)	466(29)	8195(24)	117(16)
C21	3892(27)	2006(26)	8606(14)	99(11)
C22	4584(33)	1848(32)	7382(16)	144(16)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized tensor *U*_{*ij*}.

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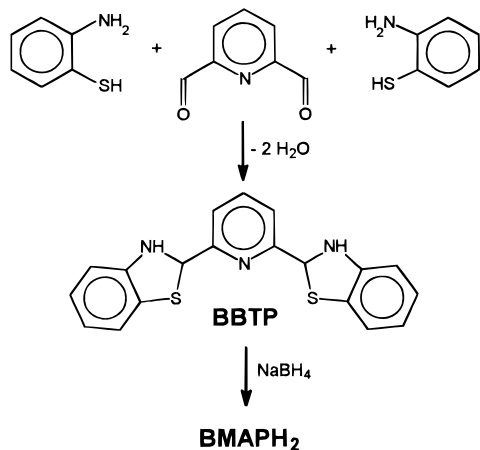
to them. Tables 2 and 3 list the atomic parameters. Drawings were produced with SCHAKAL.¹³

Results and Discussion

The most common coordination found for zinc in a sulfur and nitrogen environment is the tetrahedral ZnN_2S_2 motif,⁴ which also occurs in many zinc fingers.¹⁴ We encountered the problem, however, that chelating N,S ligands which are more than bidentate have a pronounced tendency to realize other coordination numbers or geometries, sometimes using only one or two of their donor atoms or producing oligomeric complexes due to thiolate bridging.^{6,7} In our opinion, one reason for this lies in the geometrical constraints in the ligands which cause them to prefer to occupy three ligand positions meridionally which in turn is impossible in a tetrahedral complex. We found this in tridentate N,N,S⁶ and N,N,N¹⁵ as well as in tripodal tetradentate N(N,N,O)¹⁶ ligands, specifically when they contained pyridyl groups as part of the donor set. These ligands therefore lend themselves to the formation of trigonal-bipyramidal or octahedral zinc complexes, the latter being rather untypical for sulfur-containing ligands.

In order to test the idea of geometrical ligand predisposition, we looked for complexes of the ZnN_3S_2 type in which the nitrogen donors reliably occupy one equatorial and both axial positions of a trigonal bipyramid, which would then force the thiolate donors to fill the two remaining equatorial positions. We knew that the N,N,N ligand BPA has such properties, e.g. in the complex $Zn(BPA)Cl_2$.¹⁵ We hoped that the new ligand BMAPH₂, which has the two thiol functions added to its N,N,N backbone, would follow suit.

Ligand BMAPH₂ has the combined advantages of being pentadentate and easily accessible. It could be prepared in a one-pot synthesis from pyridine-2,6-dicarbaldehyde and 2-aminothiophenol. The condensation reaction yielded 2,6-bis-(2-benzothiazolynyl)pyridine (BBTP) as an intermediate, which



was reductively opened with a large excess of NaBH₄ to form BMAPH₂ in excellent yield, which could then be used without a purification step. The intermediate BBTP has already been used by Tasker et al.¹⁷ for reactions with zinc salts but has not been opened yet to BMAPH₂ or complexes thereof. The thiolate donors in the complexes described here were deliberately chosen to be of the thiophenolate type. As these are less basic than

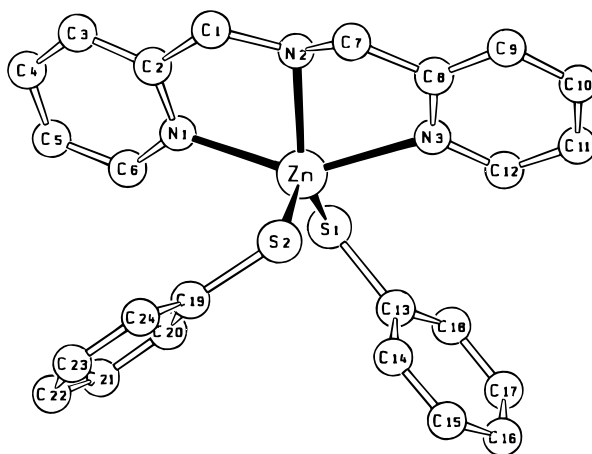


Figure 1. Molecular structure of $Zn(BPA)(SPh)_2$.

the aliphatic thiolates, it could be expected that they would have little tendency for bridging and hence support the formation of mononuclear complexes; cf. refs 7 and 18. For ligand BPA, thiophenolate was used as a coligand; ligand BMAPH₂ has two thiophenol units built in. Thus the ligand combinations were designed to lead to trigonal-bipyramidal ZnN_3S_2 complexes in which both sulfur donors occupy equatorial ligand positions.

The designing hypothesis was verified by the complex formations. Complex $Zn(BPA)(SPh)_2$ was obtained from $Zn(ClO_4)_2$, BPA, and NaSPh. Complex $Zn(BMAP)$ seems to result from every molecular or ionic ZnX_2 compound and BMAPH₂ in high yield. The formation from $Zn(ClO_4)_2$, which was most convenient is described in the Experimental Section. Both complexes show a reasonably good solubility in organic solvents, thereby indicating their molecular and possibly mononuclear nature. Their NMR spectra (see Experimental Section) show the presence of the intact ligands. Their IR spectra, due to the absence of SH bands and the typical high-frequency shifts of the pyridine bands near 1600 cm^{-1} , indicate the coordination of the thiolate and pyridyl building blocks. As the spectroscopic information is inconclusive with respect to the bonding of the aliphatic nitrogen donors, it does not allow statements on the coordination number of zinc in the complexes. Proof for this in the solid state was obtained from the two structure determinations (for details, see Experimental Section). Both complexes are trigonal-bipyramidal, albeit seriously distorted, and both contain a comparable disposition of the N_3S_2 donor sets. Figures 1 and 2 show the molecular structures; Tables 4 and 5 allow a side-by-side comparison of the bond distances and angles about the zinc atoms. The crystals of $Zn(BMAP)$ contain one molecule of solvent DMF per molecule of complex which is linked to N3 by a hydrogen bridge (3.00 \AA) to its oxygen atom. Two molecules each of $Zn(BMAP)$ are linked by a hydrogen bridge (3.52 \AA) from N1 to S1. There seem to be no hydrogen bridges in the solid state structure of $Zn(BPA)(SPh)_2$. In both compounds the distortion of the trigonal bipyramid is due to the five-membered chelate rings of the N,N,N ligands causing cis angles around 75° and a trans angle near 150° . Another common feature of both structures is the large difference between the short equatorial and long axial Zn–N bond lengths. Both these structural properties are characteristic for the bis-chelating N,N,N ligands and have been observed in (BPA)- $ZnCl_2$ ¹⁵ and (terpyridine) $ZnCl_2$ ¹⁹ as well. The zinc–sulfur distances in both complexes are normal^{4,18} and virtually constant,

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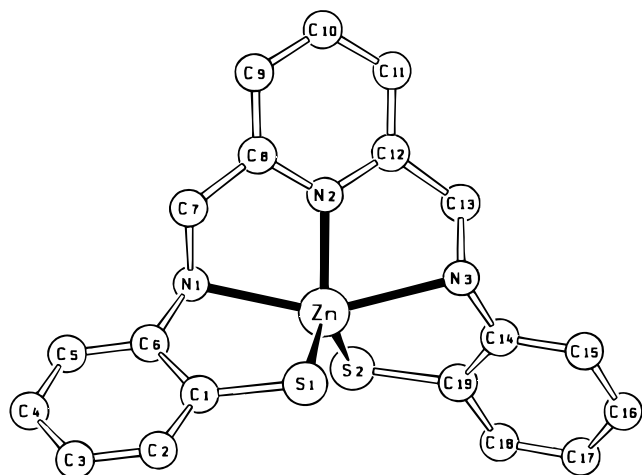


Figure 2. Molecular structure of Zn(BMAP).

Table 4. Zinc–Ligand Bond Distances (Å) for Both Complexes

	Zn(BPA)- (SPh) ₂	Zn(BMAP)	Zn(BPA)- (SPh) ₂	Zn(BMAP)
Zn–N1	2.229(3)	2.23(2)	Zn–S1	2.313(1)
Zn–N2	2.175(3)	2.00(2)	Zn–S2	2.315(1)
Zn–N3	2.299(3)	2.32(2)		2.30(1)
				2.31(1)

Table 5. Bond Angles at Zinc (deg) for Both Complexes

	Zn(BPA)- (SPh) ₂	Zn- (BMAP)	Zn(BPA)- (SPh) ₂	Zn- (BMAP)
N1–Zn–N2	75.1(1)	77.3(6)	N2–Zn–S1	129.9(1)
N1–Zn–N3	145.7(1)	152.4(6)	N2–Zn–S2	102.6(1)
N1–Zn–S1	92.3(1)	84.1(4)	N3–Zn–S1	98.4(1)
N1–Zn–S2	104.9(1)	112.2(4)	N3–Zn–S2	94.1(1)
N2–Zn–N3	73.1(1)	75.3(8)	S1–Zn–S2	127.50(3)
				118.4(6)
				117.4(6)
				106.1(4)
				83.7(5)
				123.9(2)

and the S–Zn–S angles are only slightly larger than the ideal value of 120°

There are also noticeable differences between the two complex geometries which can be related to the fact that the thiolate ligands in Zn(BPA)(SPh)₂ are independent whereas in Zn(BMAP) they are part of a chelate ring themselves. This causes small *intra*-chelate and large *extra*-chelate N–Zn–S angles in Zn(BMAP), while the corresponding N–Zn–S angles in Zn(BPA)(SPh)₂ are all closer to the ideal value of 90°. Unexpectedly, though, despite the constraints, the equatorial N–Zn–S angles in Zn(BMAP) are close to 120°, while despite the lack of constraints, they differ by 27° in Zn(BPA)(SPh)₂.

This is in accord with Zn(BMAP) being close to having C₂ symmetry about the Zn–N2 axis while in Zn(BPA)(SPh)₂ the N,N,N ligand is folded such that N1 and N3 bend towards S1 while N2 bends toward S2.

As mentioned in the Introduction, a review of the literature has shown that the structures of two other ZnN₃S₂ complexes, namely Zn(terpy)[(i-PrO)₂PS₂]₂⁹ and Zn(BMIP),¹⁰ have been reported in which a similar disposition of the donor atoms in the ligands results in the same type of trigonal-bipyramidal complex geometry as observed here. Conversely, given a different kind of geometric predisposition in the ligands, different coordination polyhedra result for the ZnN₃S₂ arrangement, as exemplified by Zn[biacetyl bis(*N*-(methylthio)thiocarbonyl)hydrazonato]](*N,N*-diethylnicotinamide)²⁰ or oligomeric Zn(4,6-dimethylpyrimidine-2-thiolate)₂.²¹ This seems to give some justification to the design principle outlined above.

In conclusion, we have found an easily accessible N₃S₂ ligand which may be of use for other transition metals as well and we have shown that, with a suitable choice of the donor atom sequence and geometry, a certain control over the stoichiometry and structure of Zn(N,S chelate) complexes can be gained. The pentadentate ligand BMAPH₂ offering four five-membered chelate rings lends itself to the generation of complexes in which a substrate molecule to be interconverted is attached to a sixth (i.e. octahedral) coordination position. The complex Zn(BMAP) would contain this possibility as a “hidden coordination site”. While it would be untypical to obtain an octahedral zinc bis-(thiolate) complex, it would still be a challenge to synthesize one, and the realization of this possibility should be not so difficult for other transition metals.

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Supporting Information Available: Tables containing the details of data acquisition and refinement, full listings of all interatomic distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated parameters of hydrogen atoms for both structures (9 pages). Ordering information is given on any current masthead page.

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