Sterically Fixed Dithiolate Ligands and Their Zinc Complexes: Derivatives of 1,8-Dimercaptonaphthalene

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The synthesis of two new dithiols, 1,8-dimercapto-2,7-di(*tert*-butyl)naphthalene (H_2L^1) and 1,8-dimercaptonaphthoic anhydride (H_2L^2), is described. They react with diethylzinc to yield the polymeric complexes L^1Zn and L^2Zn. L^1Zn dissolves in the presence of pyridine to form $[L^1Zn{\cdot}py]_x$, which is presumed to be dimeric. Both L^1Zn and L^2Zn react with neocuproin. Structure determinations have confirmed the tetrahedral ZnN_2S_2 coordination in the resulting LZn·neo complexes.

Introduction

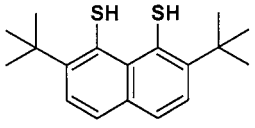
The chemistry of transition metal thiolates is a world of thiolate-bridged oligomers and polymers.[1,2] This extends into biology with the ubiquitous presence of the $Fe_4S_4(SR)_4$ redox unit and the accumulation of copper, zinc or cadmium in the metallothioneins. Yet Nature is able to prevent thiolate bridging and metal aggregation by isolating the cysteine-thiolate donors and limiting the space available to the metals, thereby making the cysteine sulfur one of the prominent monodentate ligands for metals in biology.

Model studies of sulfur-rich metal environments in metalloenzymes invariably suffer from this problem of complex aggregation.[3,4] As a result, far-reaching advances have often only been made in the exceptional situations where thiolate bridging is not preferred, typical examples being the bioinorganic chemistry of octahedral iron[5] or the ZnN_2S_2 coordination motif of the zinc finger proteins.[6]

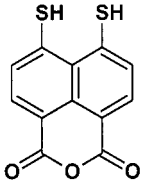
In the bioinorganic chemistry of zinc, model studies of the alcohol dehydrogenases have met with this problem.[7,8] The attachment of the metal to the protein by an NS_2 (histidine, cysteine, cysteine) ligation[9] calls for amine bis-thiolates as model ligands. But to date no such thiolate[10,11] has been found to produce mononuclear $(NS_2)Zn-X$ complexes that are free from thiolate bridging and that bear a ligand X as a substitute for the substrate of the enzyme. The best approximation has been achieved by NS_2 ligands in which the sulfur donors are not of the thiolate type.[12]

The standard procedures for reducing the bridging tendency of thiolate ligands (steric hindrance or increased electronegativity) have been applied successfully to zinc complexes: tris(*tert*-butyl)benzene thiolate has been used to produce a tricoordinate $Zn(SR)_2$·pyridine complex,[13] and we have used pentafluorobenzene thiolate to model the $ZnNS_2O$ ligation pattern of the alcohol dehydrogenase enzyme−substrate complexes.[14]

We are not aware that these principles have been applied to chelating bis-thiolate ligands, and our attempts to do so are reported in this paper. We wanted to synthesize a ligand in which the two thiolate donors have fixed positions in space. This should serve the purpose of preorganization (i.e. good chelating properties) while at the same time the lack of conformational freedom would reduce the oligonucleating tendency. We chose the 1,8-dimercaptonaphthalene framework for our purposes. It strictly defines the locations of the two sulfur atoms, while allowing the attachment of bulky substituents at the 2- and 7-positions or the attachment of electron-withdrawing substituents anywhere on the naphthalene skeleton. The target ligands were H_2L^1 and H_2L^2. This paper describes their synthesis and some preliminary chemistry of their zinc complexes.



H_2L^1



H_2L^2

Results and Discussion

The Ligands

1,8-Dimercaptonaphthalene[15] and 1,8-dimercaptohexachloronaphthalene[16] have been described in the literature, but not investigated extensively as ligands.[16,17] Our approach of generating the 1,8-dithiol functionality in H_2L^1 and H_2L^2 followed the established procedure of introducing sulfur as the naphthalene-1,8-disulfide and then reducing it. Scheme 1 describes this for H_2L^1, using the literature method to prepare naphthalene-1,8-disulfide.[18] The overall yield of H_2L^1 starting from bromonaphthalene was 8%. H_2L^1 is a yellow crystalline solid which is soluble in weakly polar organic solvents. It is easily identified by its simple

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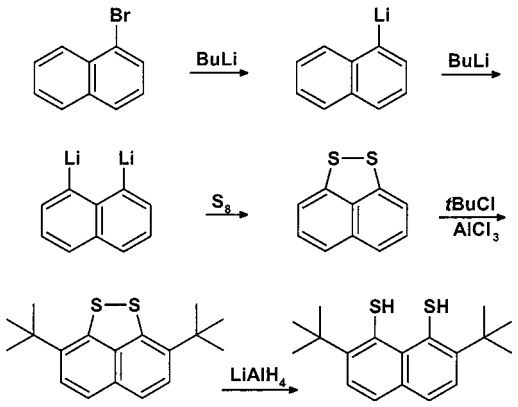
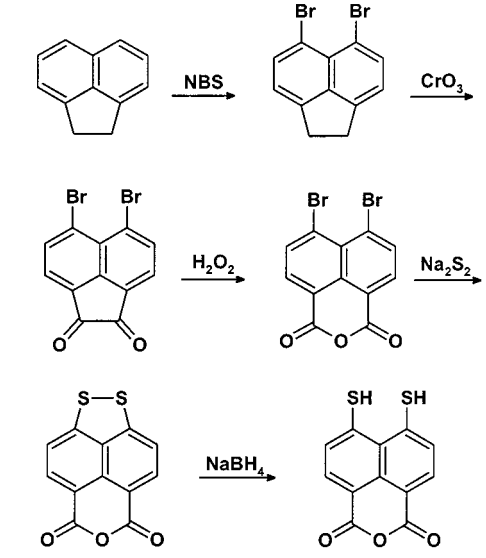
^{1}H NMR spectrum (see Experimental Section). Upon exposure to air, it is oxidized to the disulfide. Upon deprotonation, its colour in solution becomes a deeper yellow.



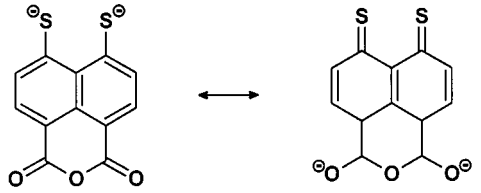
Scheme 1

The synthesis of H_2L^2 was performed according to Scheme 2 starting from acenaphthene, using the literature procedure[19] to generate its 1,8-dibromide. The overall yield of H_2L^2 starting from acenaphthene was again 8%.



Scheme 2

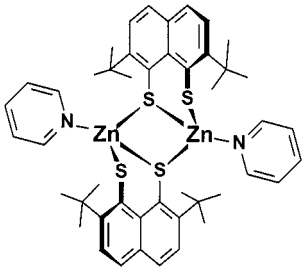
H_2L^2 is a yellow solid of low solubility which again has a simple ^{1}H NMR spectrum (see Experimental Section). Its air sensitivity is similar to that of H_2L^1. Deprotonation greatly enhances its solubility in polar solvents. Its solutions are deep red, indicating the delocalized nature of the anion according to the following valence structures.



Zinc Complexes

Diethyl zinc was found to be the best reagent to convert H_2L^1 and H_2L^2 into the binary zinc complexes ZnL^1 (**1**) and ZnL^2 (**2**), respectively, by hydrolytic cleavage in aprotic media. The resulting compounds **1** and **2** were obtained in very good yields. They dissolve only in very good donor solvents, in agreement with the assumption that they are oligomeric or polymeric. It is likely that they contain zinc in a ZnS_4 environment, i.e. each thiolate sulfur bridges two zinc ions.

Some attempts were made to isolate adducts of ZnL with monodentate donors. They were successful for the combination ZnL^1/pyridine. Upon addition of equimolar amounts of pyridine to a suspension of ZnL^1 in chloroform, the complex dissolved. However, a new precipitate of composition ZnL^1·pyridine (**3**) formed immediately; again, this complex was of rather low solubility. This reaction did not occur with ZnL^2. Assuming the likely $ZnNS_3$ coordination in this species, it follows that one of the two thiolate functions acts as a bridge. Thus a dimeric structure can be proposed for **3**, in analogy with the one described by Kellogg for the zinc complex of a sterically hindered pyridine-bis(thiolate) ligand.[10]



As expected, the highly preferred ZnN_2S_2 coordination with **1** and **2** was readily found in the form of mononuclear complexes. We chose neocuproin (2,9-dimethylphenanthroline, neo) as the bidentate nitrogen co-ligand, as we had previously found it to be most suitable for this purpose.[20] Compounds **1** and **2** dissolve in its presence, and cleanly form the 1:1 complexes (neo)Zn(L^1) (**4**) and (neo)Zn(L^2) (**5**), which are orange crystalline solids suitable for X-ray analysis (see below). In complex **5**, the electron-withdrawing properties of ligand L^2 can be confirmed by the positions of its ν(CO-carboxylate) IR bands: these are shifted by approximately 20 cm^{-1} to lower wavenumbers than those of H_2L^2.

Structures

The structure determinations of **4** and **5** (see Figure 1 and 2) confirmed the identities and compositions of the species described here, and gave some information about the ligating properties of L^1 and L^2. The crystalline structure of compound **4** has an asymmetric unit with two molecules that are quite similar. The overall coordination geometries in **4** and **5** are as expected, with Zn−N and Zn−S distances

in the normal range and with relatively small N−Zn−N and relatively large S−Zn−S angles.

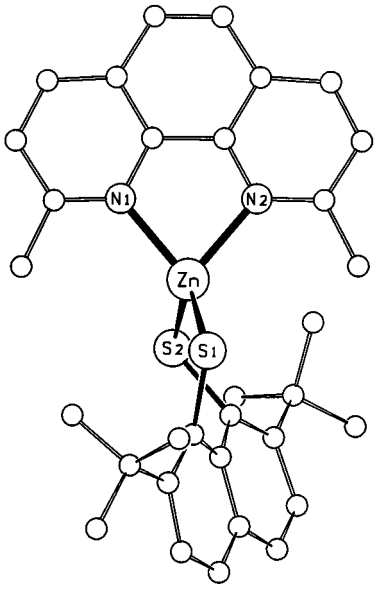


Figure 1. Molecular structure of **4** (one of the two independent molecules); bond lengths [Å]: Zn−S1 2.227(1)/2.222(1), Zn−S2 2.229(1)/2.226(1), Zn−N1 2.086(3)/2.085(3), Zn−N2 2.091(3)/2.092(3); bond angles [°]: S1−Zn−S2 103.06(4)/103.51(4), N1−Zn−N2 80.1(1)/80.5(1), S1−Zn−N1 126.1(1)/126.6(1), S1−Zn−N2 114.5(1)/115.7(1), S2−Zn−N1 113.0(1)/109.0(1), S2−Zn−N2 120.4(1)/122.0(1)

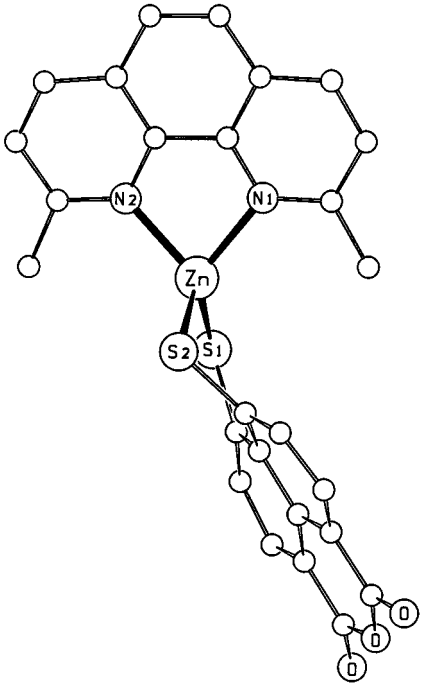


Figure 2. Molecular structure of **5**; bond lengths [Å]: Zn−S1 2.230(2), Zn−S2 2.260(2), Zn−N1 2.058(5),Zn−N2 2.050(4); bond angles [°]: S1−Zn−S2 103.04(7),N1−Zn−N2 81.6(2), S1−Zn−N1 125.1(1), S1−Zn−N2 122.7(1), S2−Zn−N1 111.8(1), S2−Zn−N2 112.0(1)

However, both complexes are severely distorted from their ideal C_{2v} symmetry. The reason for this lies in the conformational requirements of the sulfur atoms which do not allow for the zinc ions to reside together with them in the planes of the naphthalene rings. The necessity for small Zn−S−C angles (101−108°) together with the given Zn−S bond lengths enforces an out-of-plane motion of the zinc ions and/or both sulfur atoms. This geometry is highlighted in Figure 1 and 2. In these figures, the bisector of the S−Zn−S angle is in the plane of the paper with a viewing direction normal to the plane of the neocuproin ligand. The naphthalene rings are bent away from the bisector, and partly rotated with respect to their expected orientation perpendicular to the plane of the paper. This relieves the torsional strain at the sulfur atoms and the intramolecular repulsive forces.

More specifically, in both independent molecules of **4**, the sulfur atoms are bent away in opposite directions from the naphthalene plane by approximately 1.0 and 1.2 Å. The carbon atoms attached to them follow this movement to a lesser degree. The out-of-plane displacement of the sulfur atoms is reversed for the zinc ion which is roughly in the naphthalene plane again. Concomitantly, the naphthalene plane is tilted by only 8° with respect to the bisector of the S−Zn−S angle. In **5**, the sulfur atoms are also bent away from the naphthalene plane in opposite directions, but this time by only 0.75 Å on average. Contrary to the case in compound **4**, both S−Zn bonds in **5** are tilted in the same direction, thereby causing the observed tilt of 30° of the naphthalene ring with respect to the bisector of the S−Zn−S angle. The reason for this difference between **4** and **5** may lie in the *tert*-butyl substituents of **4**, which prevent the pronounced tilting owing to their van der Waals interactions with the methyl groups of the neocuproin ligand. Generally, the observed asymmetry of **4** and **5** seems to effect the necessary relief from the inherent steric strain, thereby making ligand L^1 and L^2 suitable for their intended purpose.

The ZnN_2S_2 ligation in complexes **4** and **5** is also the most common one in zinc finger motifs.[6] The geometric features of the ZnN_2S_2 units in these complexes and in the zinc fingers compare reasonably well but, as was discussed in detail for zinc-neocuproin complexes of bis(cysteinyl)-peptides,[20] the geometric constraints induced by the small bite angle of the neocuproin ligand make the N−Zn−N angles smaller and concomitantly the S−Zn−S angles larger than the situation in the proteins.

Conclusions

The ligands H_2L^1 and H_2L^2 were accessible. They are two new members of a hitherto unexplored group of sterically fixed dithiolate ligands that are geometrically similar to the dithiolene ligands. The ligand H_2L^1 is sterically crowded owing to the favourable positioning of its *tert*-butyl substituents, whereas the Ligand H_2L^2 is electron poor. At the same time, the dianion L^2 should have ligating properties for hard metal ions at its carboxylate oxygen atoms, as in-

dicated by its resonance structures and the IR spectroscopic data of its zinc complex **5**.

The preliminary complexation reactions with zinc have outlined the coordinating potential of both ligands. While the binary ZnL compounds **1** and **2** could be expected to be polymeric, addition of one pyridine ligand to **1** is sufficient to break up its polymeric structure. The excellent coligand neocuproin ensured the formation of the 1:1:1 complexes **4** and **5**, with a ZnN_2S_2 coordination. Their structure determinations have revealed the basic ligation properties of the naphthalene-1,8-dithiolates. The conformational requirements of the sulfur atoms do not allow for a planar arrangement of the naphthalene rings, the sulfur atoms and the zinc ion. However, the two complex geometries that were observed show that a strain-free and strong metal-dithiolate coordination is present.

Experimental Section

For general preparative and measuring procedures, see ref.[21] All reactions were carried out under a nitrogen atmosphere. Starting materials were obtained commercially or prepared according to the references given.

Ligand H_2L^1: a) 2,7-Di(*tert*-butyl)naphthalene-1,8-disulfide: Naphthalene-1,8-disulfide[18] (3.00 g, 15.8 mmol) was dissolved at 50 °C in a mixture of nitromethane (37 mL) and *tert*-butyl chloride (4.38 g, 47.3 mmol). Anhydrous $AlCl_3$ (400 mg, 3.00 mmol) was added and the mixture was stirred at 50 °C for 20 min. After cooling to room temp. the product precipitated. Washing with nitromethane and recrystallization from acetone yielded 2,7-di(*tert*-butyl)-naphthalene-1,8-disulfide (1.82 g, 38%) as orange crystals, m.p. 129 °C. − $C_{18}H_{22}S_2$ (302.5): calcd. C 71.47, H 7.33; found C 71.55, H 7.37. − ^{1}H NMR ($CDCl_3$): δ = 1.50 (s, 18 H, *t*Bu), 7.36 (d, *J* = 8.0 Hz, 2 H, $H^{5,6}$), 7.42 (d, *J* = 8.0 Hz, 2 H, $H^{4,7}$).

b) H_2L^1: A solution of 2,7-di(*tert*-butyl)naphthalene-1,8-disulfide (5.43 g, 28.5 mmol) in THF (50 mL) was treated with $LiAlH_4$ (1.08 g, 28.5 mmol) and heated at reflux for 1 h. After cooling to room temp., water (1 mL) and 10 M HCl (15 mL) were added dropwise to the stirred solution. After extraction with dichloromethane (100 mL), the organic layer was separated, washed with water (3 × 30 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was recrystallized from cyclohexane/THF (5:1). H_2L^1 was obtained as a yellow powder (8.25 g, 95%), m.p. 137 °C. − $C_{18}H_{24}S_2{\cdot}C_6H_{12}$ (304.5 + 84.2): calcd. C 74.16, H 9.34; found C 75.40, H 9.31. − IR (KBr): $\tilde{\nu}$ = 2544 (SH) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.50 (s, 12 H, C_6H_{12}), 1.64 (s, 18 H, *t*Bu), 4.41 (s, 2 H, SH), 7.48 (d, *J* = 8.6 Hz, 2 H, $H^{4,5}$), 7.50 (d, *J* = 8.6 Hz, 2 H, $H^{3,6}$).

Ligand H_2L^2: a) 1,8-Dibromoacenaphthenedione: 1,8-Dibromoacenaphthene[19] (8.51 g, 27.3 mmol) was dissolved in acetic anhydride (1 L) at 110 °C. CrO_3 (21.1 g, 211 mmol) was added carefully to the stirred solution over a period of 2 h. The resulting green suspension was stirred at 160 °C for 30 min., and then poured while hot onto crushed ice (1 kg). Conc. HCl (20 mL) was added and the mixture was filtered. The brownish precipitate was washed with water, dried in vacuo and recrystallized from acetic anhydride (2 L). 1,8-Dibromoacenaphthenedione (6.23 g, 67%) was obtained as a light brown solid, m.p. 239 °C. − $C_{12}H_4Br_2O_2$ (340.0): calcd. C 42.40, H 1.19; found C 42.22, H 1.19. − ^{1}H NMR ($CDCl_3$): δ = 7.93 (d, *J* = 7.6 Hz, 2 H, $H^{4,7}$), 8.27 (d, *J* = 7.6 Hz, 2 H, $H^{3,8}$).

b) 1,8-Dibromonaphthoic Anhydride: 1,8-Dibromoacenaphthenedione (6.23 g, 18.3 mmol) was dissolved in a mixture of 1,4-dioxane (400 mL) and NaOH (2 M, 400 mL) and heated to 100 °C. A solution of H_2O_2 (10%, 400 mL) was added slowly to the stirred solution. After stirring for a further 30 min. at 100 °C, the mixture was cooled to room temp. and filtered. The filtrate was acidified with conc. HCl producing a voluminous precipitate. This was separated by centrifugation, washed twice with water and dried in vacuo. Recrystallization from acetic anhydride (2.5 L) yielded 1,8-dibromonaphthoic anhydride (4.84 g, 74%) as a light brown powder, m.p. 260 °C. − $C_{12}H_4Br_2O_3$ (356.0): calcd. C 40.49, H 1,13; found C 40.45, H 1.11. − ^{1}H NMR ([D_6]acetone): δ = 7.95 (d, *J* = 7.5 Hz, 2 H, $H^{5,8}$), 8.17 (d, *J* = 7.5 Hz, 2 H, $H^{4,9}$).

c) Naphthoic Anhydride-1,8-disulfide: Na (1.56 g, 67.9 mmol) and sulfur (2.18 g, 68.0 mmol) were suspended in DMF (40 mL). The mixture was stirred at 100 °C until the vigorous reaction had produced a voluminous precipitate. A suspension of 1,8-dibromonaphthoic anhydride in DMF (20 mL) was quickly added, upon which the mixture turned deep purple. After heating at 140 °C for 10 min, it was poured while hot into water (300 mL). The resulting orange suspension was acidified with conc. HCl, and the precipitate was isolated by centrifugation, washed twice with water and dried in vacuo. Recrystallization from 1,4-dioxane (1.6 L) in the presence of activated charcoal (1 g) yielded naphthoic anhydride-1,8-disulfide (2.41 g, 68%) as a red solid, m.p. 330 °C (dec.). − $C_{12}H_4O_3S_2$ (356.0): calcd. C 55.37, H 1.55; found C 55.32, H 1.59. − ^{1}H NMR ([D_6]acetone): δ = 7.83 (d, *J* = 8.0 Hz, 2 H, $H^{3,9}$), 8.37 (d, *J* = 8.0 Hz, 2 H, $H^{4,8}$).

d) HL^2: Naphthoic anhydride-1,8-disulfide (0.32 g, 1.20 mmol) was suspended in methanol (10 mL). After the addition of $NaBH_4$ (94 mg, 2.50 mmol) the mixture turned purple. After stirring for 2 h, the mixture was filtered and the filtrate treated with conc. HCl (1 mL) and stirred for 1 h. The resulting yellow precipitate was washed with water and methanol and dried in vacuo to afford H_2L^2 as a yellow powder (0.23 g, 73%), m.p. 280 °C (dec.). − $C_{12}H_6O_3S_2$ (262.3): calcd. C 54.95, H 2.31; found C 54.18, H 2.59. − IR (KBr): $\tilde{\nu}$ = 2537 (SH) cm^{-1}. − ^{1}H NMR ([D_6]acetone): δ = 5.51 (s, 2 H, SH), 7.80 (d, *J* = 8.2 Hz, 2 H, $H^{5,8}$), 8.42 (d, *J* = 8.2 Hz, 2 H, $H^{4,9}$).

Compound 1: A solution of H_2L^1 (0.20 g, 0.66 mmol) in chloroform (10 mL) was treated dropwise with a solution of diethyl zinc (81 mg, 0.66 mmol) in *n*-hexane (2.0 mL). The resulting precipitate was filtered off, washed with chloroform and dried in vacuo, leaving behind compound **1** (0.23 g, 95%) as a yellow powder, m.p. 160 °C (dec.). − $C_{18}H_{22}S_2Zn$ (367.9): calcd. C 58.77, H 6.03, Zn 17.77; found C 57.38, H 5.97, Zn 17.32. − ^{1}H NMR ([D_6]DMSO): δ = 1.68 (s, 18 H, *t*Bu), 7.06 (d, *J* = 8.5 Hz, 2 H, $H^{4,5}$), 7.25 (d, *J* = 8.5 Hz, 2 H, $H^{3,6}$).

Compound 2: Prepared in the same manner as **1** from H_2L^2 (0.10 g, 0.38 mmol) in toluene (15 mL) and diethyl zinc (47 mg, 0.38 mmol). Compound **2** was obtained as a pale orange powder (0.12 g, 97%), m.p. 175 °C (dec.). − $C_{12}H_4O_3S_2Zn$ (325.7): calcd. C 44.26, H 1.24, Zn 20.08; found C 44.07, H 1.16, Zn 19.89. − ^{1}H NMR ([D_6]DMSO): δ = 7.84 (d, *J* = 8.2 Hz, 2 H, $H^{5,8}$), 8.37 (d, *J* = 8.2 Hz, 2 H, $H^{4,9}$).

Compound 3: A suspension of **1** (0.20 g, 0.54 mmol) in chloroform (10 mL) was treated with a solution of pyridine (44 mg, 0.55 mmol) in chloroform (2 mL). A clear solution was formed from which a yellow solid precipitated after a few seconds. The precipitate was

filtered off, washed with chloroform and dried in vacuo, leaving behind compound **3** as a yellow powder (0.21 g, 85%), m.p. 105 °C (dec.). − $C_{23}H_{27}NS_2Zn$ (447.0): calcd. C 61.80, H 6.09, N 3.13, Zn 14.63; found C 59.48, H 5.97, N 3.05, Zn 14.50. − IR (KBr): $\tilde{\nu}$ = 1609 (C=N) cm^{-1}. − ^1H NMR ([D$_6$]DMSO): δ = 1.68 (s, 18 H, *t*Bu), 7.06 (d, *J* = 8.5 Hz, 2 H, H^{4,5}), 7.25 (d, *J* = 8.5 Hz, 2 H, H^{3,6}), 7.41 (m, 2 H, py), 7.82 (m, 1 H, py), 8.58 (m, 2 H, py).

Compound 4: A solution of H_2L^1 (0.20 g, 0.66 mmol) and neocuproin hydrate (0.14 g, 0.67 mmol) in chloroform (10 mL) was treated with diethyl zinc (81 mg, 0.66 mmol) in *n*-hexane (2.0 mL). After stirring for 20 min. the volume was reduced to 2 mL in vacuo. Addition of petroleum ether (4 mL) produced a precipitate which was filtered off and washed with petroleum ether. Recrystallization from dichloromethane/hexane (1:1) yielded **4** as orange crystals (0.36 g, 95%), m.p. 115 °C (dec.). − $C_{32}H_{34}N_2S_2Zn{\cdot}CH_2Cl_2$ (576.2 + 84.9): calcd. C 59.96, H 5.49, N 4.24, Zn 9.89; found C 59.82, H 5.54, N 3.98, Zn 10.03. − IR (KBr): $\tilde{\nu}$ = 1621 and 1591 (C=N) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.77 (s, 18 H, *t*Bu), 3.19 (s, 6 H, CH_3), 5.35 (s, 2 H, CH_2Cl_2), 7.27 (d, *J* = 8.6 Hz, 2 H, H^{4,5}), 7.45 (d, *J* = 8.6 Hz, 2 H, H^{3,6}), 7.74 (d, *J* = 8.4 Hz, 2 H, neo-H^{3,8}), 7.94 (s, 2 H, neo-H^{5,6}), 8.44 (d, *J* = 8.4 Hz, 2 H, neo-H^{4,7}).

Compound 5: A suspension of **2** (0.10 g, 0.31 mmol) in chloroform (3 mL) was treated with neocuproin hydrate (70 mg, 0.31 mmol). The resulting clear solution formed a precipitate upon addition of hexane (6 mL), which was filtered off, washed with hexane and dried in vacuo, leaving behind compound **5** as orange crystals (0.13 g, 77%), m.p. 140 °C (dec.). − $C_{26}H_{16}N_2O_3S_2Zn{\cdot}C_6H_{14}$ (533.9 + 86.2): calcd. C 61.98, H 4.88, N 4.52, Zn 10.54; found C 62.52, H 5.55, N 4.33, Zn 10.11. − IR (KBr): $\tilde{\nu}$ = 1734 and 1700 (C=O), 1617 and 1590 (C=N) cm^{-1}. − ^1H NMR ([D$_6$]acetone): δ = 0.88 (m, 6 H, hexane-CH_3), 1.27 (m, 8 H, hexane-CH_2), 2.76 (s, 6 H, CH_3), 7.99 (d, *J* = 8.2 Hz, 2 H, H^{5,8}), 8.09 (d, *J* = 8.2 Hz, 2 H, H^{4,9}), 8.11 (d, *J* = 8.3 Hz, 2 H, neo-H^{3,8}), 8.27 (s, 2 H, neo-H^{5,6}), 8.90 (d, *J* = 8.3 Hz, 2 H, neo-H^{4,7}).

Table 1. Crystallographic details

	4	**5**
Formula	$C_{32}H_{34}N_2S_2Zn$	$C_{26}H_{16}N_2O_3S_2Zn{\cdot}CHCl_3$
Mol. wt	576.2	533.9 + 119.4
Crystal size [mm]	1.2 × 0.9 × 0.8	0.7 × 0.5 × 0.4
Space group	$P2_1/c$	$P\bar{1}$
Z	8	2
a [Å]	26.231(5)	9.737(2)
b [Å]	10.400(2)	11.834(2)
c [Å]	22.065(4)	13.847(3)
α [°]	90	67.95(3)
β [°]	108.29(3)	84.66(3)
γ [°]	90	66.48(3)
V [Å^3]	5715(2)	1353.9(5)
d (calc.) [g·cm^{-3}]	1.34	1.60
Temp. [K]	273	183
μ (Mo-K_α) [mm^{-1}]	1.03	1.39
hkl range	*h*: −31 to 32	*h*: −10 to 10
	k: 0 to 12	*k*: −13 to 12
	l: −27 to 0	*l*: −15 to 15
Refl. measd.	11909	6312
Indep. refl.	11588	3892
Obs. refl. [$I > 2\sigma(I)$]	6693	2463
Parameters	667	381
Refl. refined	11588	3892
R_1 (obs. refl.)	0.042	0.060
wR_2 (all refl.)	0.127	0.150
Residual el. density [e/Å^{-3}]	+0.6	+0.6
	−0.5	−0.5

Structure Determinations:[22] Crystals of **4** were obtained by layering a dichloromethane solution with hexane, and crystals of **5** were obtained by layering a chloroform solution with hexane. Diffraction data were recorded with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (Mo-K_α, λ = 0.7107 Å) and a graphite monochromator. No absorption corrections were applied. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[23] Hydrogen atoms were included with fixed distances and isotropic temperature factors which were 1.5 times the value of those of their attached atoms. Parameters were refined against F^2. The *R* values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]]^{1/2}$. Drawings were produced with SCHAKAL.[24] Table 1 lists the crystallographic data.

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[22] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150527 (for **4**) and -150528 (for **5**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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