Structure of (1,10-Phenanthroline)bis(4-toluenethiolato)zinc(II)

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Abstract. $[Zn(C_{12}H_8N_2)(C_7H_7S)_2]$, $[Zn(phen)(4-tol-S)_2]$, monoclinic, $P2_1/c$, $a = 10.009$ (3), $b = 20.12$ (1), $c = 12.140$ (4) Å, $\beta = 107.73$ (1)°, $\rho_{calc} = 1.403$, $\rho_{obs} = 1.396$ Mg m^{-3}, $Z = 4$; $R = 0.058$, $R_w = 0.061$. The coordination geometry of the Zn^{2+} central metal ion is distorted tetrahedral with a S—Zn—S bond angle of 126.2° and a N—Zn—N bond angle of 78.7°. The N—Zn—S bond angles range from 107 to 113°.

Introduction. Complexes of Zn with the general formula $[Zn(SL)_2(N-N)]$ (N—N = substituted 1,10-phenanthroline or 2,2'-bipyridine, SL = substituted benzenethiol) are of spectroscopic interest (Truesdell, 1978; Koester, 1975). Truesdell has synthesized a large number of these complexes (including the title complex) and noted the presence of an unusual, broad, structureless visible absorption band and its corresponding emission. The transitions were unique to the complexes and not present in the uncoordinated ligands. The transition was interpreted by Truesdell as interligand transmetallic charge transfer in nature. To account for this transition, Truesdell then proposed a molecular-orbital model based on C_{2v} coordination geometry of the metal. The structural analysis reported here was undertaken to examine the coordination around the central metal atom.

Bright, yellow chunks of $[Zn(phen)(4-tol-S)_2]$ were prepared by precipitation from an ethanol solution of stoichiometric mixtures of the metal and ligands. A small crystal (0.12 × 0.25 × 0.29 mm) with {010}, {0$\bar{1}$0}, {011}, and {0$\bar{1}\bar{1}$} faces developed was mounted with the c axis collinear with the spindle axis of the goniometer. Systematic absences of the types $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely defined the space group as $P2_1/c$. Intensity data were collected on an automated Picker full-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. A θ–2θ step scan was used with scans of 1.8°, 20 steps deg^{-1} and 3.0 s step^{-1}. Background measurements of 15 s were made before and after each scan. The standard deviation in intensity was calculated by $\sigma^2(I_o) = TC + BC + (0.33)^2 I_o^2$

Table 1. *Final atomic coordinates and isotropic thermal parameters* (Å^2)

Standard deviations in the least significant figures are given in parentheses.

	x	y	z	U_{eq}		x	y	z	U_{eq}
Zn	0.2130 (1)	0.9935 (1)	0.7678 (1)	0.0461 (5)	C(23)	0.1498 (8)	0.2502 (3)	0.3174 (6)	0.050 (4)
S(1)	0.2746 (2)	0.8855 (1)	0.7957 (2)	0.0564 (12)	C(24)	0.0505 (8)	0.2850 (4)	0.2329 (6)	0.052 (5)
S(2)	0.7225 (2)	0.5650 (1)	0.8507 (2)	0.0667 (14)	C(25)	0.0880 (8)	0.3352 (4)	0.1783 (6)	0.051 (5)
N(1)	0.2254 (5)	0.0454 (3)	0.9226 (4)	0.057 (3)	C(26)	0.1092 (12)	0.1921 (5)	0.3795 (9)	0.079 (7)
N(2)	0.9994 (5)	0.0070 (3)	0.7514 (4)	0.043 (3)	H(1)	0.437 (9)	0.445 (4)	0.501 (6)	0.0583
C(1)	0.3401 (8)	0.0684 (3)	0.0018 (6)	0.051 (5)	H(2)	0.437 (8)	0.367 (4)	0.648 (6)	0.0494
C(2)	0.3319 (9)	0.1100 (4)	0.0019 (6)	0.058 (5)	H(3)	0.191 (8)	0.344 (4)	0.668 (7)	0.0519
C(3)	0.2026 (9)	0.1250 (4)	0.0991 (6)	0.059 (5)	H(5)	0.934 (8)	0.346 (4)	0.578 (7)	0.0608
C(4)	0.0822 (7)	0.1060 (3)	1.0156 (5)	0.046 (4)	H(6)	0.750 (10)	0.382 (5)	0.425 (7)	0.0621
C(5)	0.9437 (9)	0.1234 (4)	0.0165 (7)	0.064 (5)	H(8)	0.628 (9)	0.450 (4)	1.246 (6)	0.0557
C(6)	0.8326 (10)	0.1018 (4)	0.9347 (8)	0.070 (6)	H(9)	0.692 (10)	0.511 (5)	0.107 (8)	0.0684
C(7)	0.8422 (7)	0.0621 (3)	0.8388 (6)	0.049 (4)	H(10)	0.910 (9)	0.526 (5)	1.099 (8)	0.0722
C(8)	0.7297 (8)	0.0401 (4)	0.7475 (7)	0.060 (5)	H(14)	1.448 (8)	0.558 (4)	1.156 (6)	0.0418
C(9)	0.7539 (8)	0.0040 (4)	0.6611 (8)	0.064 (6)	H(15)	0.508 (9)	0.591 (4)	0.012 (6)	0.0507
C(10)	0.8885 (8)	0.5882 (3)	0.6637 (6)	0.050 (5)	H(17)	0.272 (8)	0.754 (4)	0.993 (7)	0.0431
C(11)	0.9765 (6)	0.0433 (3)	0.8374 (5)	0.038 (4)	H(18)	0.197 (9)	0.727 (4)	0.137 (7)	0.0595
C(12)	0.0977 (7)	0.0650 (3)	0.9273 (5)	0.041 (4)	H(19A)	0.579 (8)	0.246 (5)	0.136 (7)	0.0621
C(13)	0.3195 (7)	0.6377 (3)	0.1693 (5)	0.043 (4)	H(19B)	0.486 (10)	0.311 (5)	0.134 (7)	0.0621
C(14)	0.4091 (7)	0.8005 (4)	0.1269 (6)	0.047 (4)	H(19C)	0.626 (9)	0.309 (4)	0.195 (8)	0.0621
C(15)	0.4448 (7)	0.6228 (3)	0.0310 (5)	0.047 (4)	H(21)	0.437 (8)	0.339 (4)	0.316 (6)	0.0570
C(16)	0.3944 (7)	0.8182 (3)	0.4760 (5)	0.042 (4)	H(22)	0.365 (9)	0.250 (4)	0.407 (7)	0.0608
C(17)	0.3072 (8)	0.7183 (4)	0.0197 (6)	0.048 (4)	H(24)	0.940 (9)	0.272 (4)	0.201 (6)	0.0570
C(18)	0.2691 (7)	0.6975 (3)	0.1152 (6)	0.049 (5)	H(25)	0.017 (9)	0.368 (4)	0.123 (7)	0.0570
C(19)	0.4379 (11)	0.7943 (5)	0.3740 (7)	0.075 (6)	H(26A)	0.188 (10)	0.165 (5)	0.409 (8)	0.0760
C(20)	0.2269 (8)	0.3607 (3)	0.2091 (5)	0.050 (4)	H(26B)	0.091 (10)	0.207 (5)	0.449 (8)	0.0760
C(21)	0.3262 (8)	0.3243 (4)	0.2916 (6)	0.057 (5)	H(26C)	0.031 (11)	0.174 (5)	0.333 (8)	0.0760
C(22)	0.2870 (9)	0.2689 (4)	0.3439 (6)	0.057 (5)					

Table 2. *Bond lengths* (Å) *and angles* (°)

Standard deviations in the least significant figures are given in parentheses.

Zn–N(1)	2·104 (5)	N(1)–Zn–N(2)	78·7 (2)
Zn–N(2)	2·120 (5)	S(1)–Zn–S(2)	126·16 (7)
Zn–S(1)	2·256 (2)	N(1)–Zn–S(1)	113·7 (2)
Zn–S(2)	2·265 (2)	N(1)–Zn–S(2)	107·3 (2)
S(1)–C(13)	1·787 (6)	N(2)–Zn–S(1)	111·2 (2)
S(2)–C(20)	1·799 (6)	N(2)–Zn–S(2)	109·6 (2)
		C(13)–S(1)–Zn	104·6 (2)
		C(20)–S(2)–Zn	95·9 (2)

Phenanthroline ring

N(1)–C(1)	1·337 (8)	C(10)–N(2)–C(11)	118·3 (6)
N(1)–C(12)	1·355 (8)	C(12)–N(1)–C(1)	118·9 (6)
N(2)–C(10)	1·338 (8)	N(1)–C(12)–C(4)	122·1 (6)
N(2)–C(11)	1·349 (7)	N(1)–C(1)–C(2)	121·8 (7)
		N(2)–C(11)–C(7)	123·0 (6)
		N(2)–C(10)–C(9)	121·4 (7)
		N(2)–C(11)–C(12)	116·9 (5)
		N(1)–C(12)–C(11)	118·0 (5)
C(1)–C(2)	1·34 (1)	C(1)–C(2)–C(3)	119·8 (7)
		C(2)–C(3)–C(4)	118·7 (7)
C(2)–C(3)	1·38 (1)	C(3)–C(4)–C(5)	122·5 (7)
C(3)–C(4)	1·40 (1)		
C(4)–C(5)	1·43 (1)	C(3)–C(4)–C(12)	118·7 (7)
C(4)–C(12)	1·398 (9)	C(4)–C(5)–C(6)	120·7 (7)
C(5)–C(6)	1·32 (1)	C(4)–C(12)–C(11)	120·0 (6)
C(6)–C(7)	1·44 (1)	C(5)–C(6)–C(7)	122·9 (8)
C(7)–C(8)	1·39 (1)	C(6)–C(7)–C(8)	125·8 (7)
C(7)–C(11)	1·401 (9)	C(6)–C(7)–C(11)	117·4 (7)
C(8)–C(9)	1·36 (1)	C(7)–C(8)–C(9)	119·7 (7)
		C(8)–C(9)–C(11)	116·8 (7)
C(9)–C(10)	1·38 (1)	C(8)–C(9)–C(10)	120·7 (8)
C(1)–H(1)	1·04 (8)	H(1)–C(1)–N(1)	118 (4)
		H(1)–C(1)–C(2)	120 (4)
C(2)–H(2)	1·16 (8)	H(2)–C(2)–C(1)	116 (4)
		H(2)–C(2)–C(3)	123 (4)
C(3)–H(3)	1·03 (8)	H(3)–C(3)–C(2)	122 (4)
		H(3)–C(3)–C(4)	119 (4)
C(5)–H(5)	1·00 (8)	H(5)–C(5)–C(4)	118 (5)
		H(5)–C(5)–C(6)	121 (5)
C(6)–H(6)	0·87 (9)	H(6)–C(6)–C(5)	122 (6)
		H(6)–C(6)–C(7)	114 (6)
C(8)–H(8)	1·03 (9)	H(8)–C(8)–C(7)	121 (4)
		H(8)–C(8)–C(9)	119 (4)
C(9)–H(9)	0·81 (9)	H(9)–C(9)–C(8)	124 (7)
		H(9)–C(9)–C(10)	116 (7)
C(10)–H(10)	0·93 (9)	H(10)–C(10)–C(9)	122 (6)
		H(10)–C(10)–N(2)	114 (6)

Toluene rings

S(1)–C(13)	1·787 (6)	C(13)–S(1)–Zn	104·6 (2)
C(13)–C(14)	1·383 (9)	S(1)–C(13)–C(14)	122·6 (5)
C(13)–C(18)	1·390 (9)	S(1)–C(13)–C(18)	118·8 (5)
C(14)–C(15)	1·393 (9)	C(13)–C(14)–C(15)	119·8 (6)
C(15)–C(16)	1·380 (9)	C(14)–C(15)–C(16)	122·2 (6)
C(16)–C(17)	1·365 (9)	C(15)–C(16)–C(17)	117·2 (6)
C(16)–C(19)	1·511 (9)	C(15)–C(16)–C(19)	121·1 (6)
C(17)–C(18)	1·389 (9)	C(16)–C(17)–C(18)	122·2 (6)
		C(17)–C(18)–C(13)	120·0 (7)
		C(18)–C(13)–C(14)	*118·5 (6)*
C(14)–H(14)	0·96 (7)	H(14)–C(14)–C(13)	125 (4)
		H(14)–C(14)–C(15)	115 (4)
C(15)–H(15)	0·99 (8)	H(15)–C(15)–C(14)	109 (4)
		H(15)–C(15)–C(16)	128 (4)
C(17)–H(17)	0·83 (8)	H(17)–C(17)–C(16)	125 (6)
		H(17)–C(17)–C(18)	113 (6)
C(18)–H(18)	1·02 (8)	H(18)–C(18)–C(17)	116 (5)
		H(18)–C(18)–C(13)	124 (5)
C(19)–H(19A)	0·99 (9)	H(19A)–C(19)–C(16)	110 (5)
		H(19A)–C(19)–H(19B)	126 (8)
		H(19A)–C(19)–H(19C)	99 (7)
C(19)–H(19B)	0·92 (9)	H(19B)–C(19)–C(16)	113 (5)
		H(19B)–C(19)–H(19C)	97 (8)
C(19)–H(19C)	0·93 (8)	H(19C)–C(19)–C(16)	110 (6)

Table 2 (*cont.*)

S(2)–C(20)	1·799 (6)	C(20)–S(2)–Zn	95·9 (2)
C(20)–C(21)	1·38 (1)	S(2)–C(20)–C(21)	120·2 (6)
C(20)–C(25)	1·39 (1)	S(2)–C(20)–C(25)	121·9 (6)
C(21)–C(22)	1·40 (1)	C(20)–C(21)–C(22)	120·8 (7)
C(22)–C(23)	1·37 (1)	C(21)–C(22)–C(23)	120·9 (7)
C(23)–C(24)	1·38 (1)	C(22)–C(23)–C(24)	118·7 (7)
C(23)–C(26)	1·51 (1)	C(22)–C(23)–C(26)	121·0 (7)
C(24)–C(25)	1·39 (1)	C(23)–C(24)–C(25)	121·0 (7)
		C(24)–C(25)–C(20)	120·6 (7)
		C(24)–C(23)–C(26)	121·4 (8)
		C(25)–C(20)–C(21)	117·8 (6)
C(21)–H(21)	1·09 (8)	H(21)–C(21)–C(20)	120 (4)
		H(21)–C(21)–C(22)	119 (4)
C(22)–H(22)	0·99 (9)	H(22)–C(22)–C(21)	113 (5)
		H(22)–C(22)–C(23)	126 (5)
C(24)–H(24)	1·09 (8)	H(24)–C(24)–C(23)	124 (4)
		H(24)–C(24)–C(25)	115 (4)
C(25)–H(25)	0·98 (8)	H(25)–C(25)–C(20)	118 (5)
		H(25)–C(25)–C(24)	121 (5)
C(26)–H(26A)	0·9 (1)	H(26A)–C(26)–C(23)	108 (6)
		H(26A)–C(26)–H(26B)	102 (8)
		H(26A)–C(26)–H(26C)	118 (9)
C(26)–H(26B)	0·97 (9)	H(26B)–C(26)–C(23)	110 (6)
		H(26B)–C(26)–H(26C)	109 (9)
C(26)–H(26C)	0·9 (1)	H(26C)–C(26)–C(23)	109 (6)

where TC = total count, BC = background count, and I_o = TC − BC. In the range $4° \leq 2\theta \leq 45°$, a total of 3029 unique reflections were collected. Low-angle data $(4° \leq 2\theta \leq 20°)$ consisted of 275 reflections and were collected with a more absorbing Zr filter. The scale factors which related the high-angle and low-angle data were 1·00 to 1·63, respectively. Three standard reflections were monitored after every 41 reflections and showed no systematic deviations from normal counting statistics. Absorption corrections ($\mu = 1·2730$ mm^{-1}) were made with transmission factors ranging from 0·88 to 0·73.

The positions of the Zn, S, N, and all phenanthroline ring C atoms except C(9) [C(1)–C(8), C(10)–C(12)] were determined by the program *MULTAN* (Germain, Main & Woolfson, 1971). The remaining C atoms were located from subsequent electron density maps. The ideal positions of the phenanthroline and toluene ring H atoms were calculated. Electron density difference maps were employed to locate the methyl-group H atoms. Anisotropic temperature factors were used in the refinement of the Zn, S, N, and C positions. The H isotropic temperature factors were fixed at 1 Å^2 plus the isotropic temperature factor of the C to which the H atom is bonded. Maximum parameter shifts for the Zn, S, N, and C atoms after the final least-squares refinement were less than 25% of the parameter errors. For the H atoms, the shift of the parameters was approximately the same as the parameter error. The largest peak on the final electron density difference map corresponded to 0·13 e Å^{-3}. Full-matrix refinement proceeded smoothly to a final R value of 0·96. When reflections with $F > 3·00\sigma$ were omitted, the R value was 0·058 and the weighted R value was 0·061 [$w_{hkl} = (1/\sigma^2)F$]. The standard error of an observation of unit
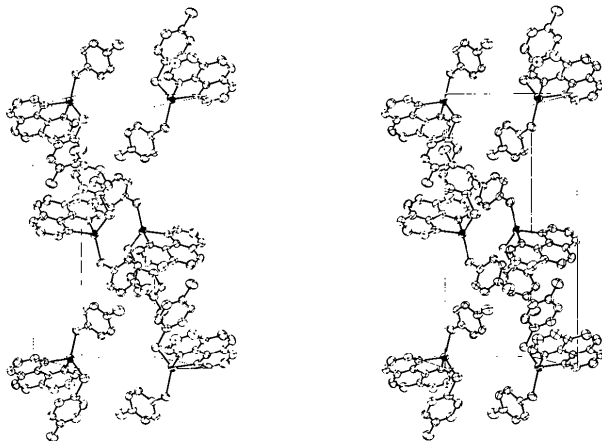
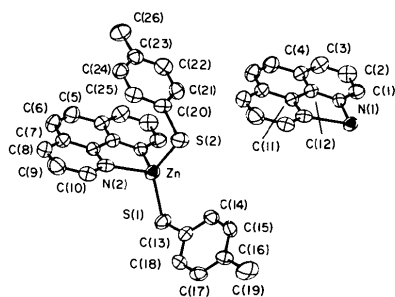Fig. 1. Stereoscopic drawing of the unit-cell structure of [Zn(phen)-(4-tol-S)₂].

Fig. 2. Labelling scheme for [Zn(phen)(4-tol-S)₂]. The phenanthroline ring is shown to the right of the molecular unit to permit labelling of all atoms.

weight was 1·23. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters are given in Table 1 and pertinent distances and angles in Table 2.* Computer programs used were part of a local library which includes modified versions of the following: Busing, Martin & Levy's (1962) *ORFLS* least-squares

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35436 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

program; *ORFFE* (Busing, Martin & Levy, 1964); Johnson's (1965) *ORTEP* program for crystallographic illustrations; the absorption-correction subroutine *ORABS* (Wehe, Busing & Levy, 1962); and *MULTAN*. A unit-cell drawing of the structure is presented in Fig. 1 and a drawing of a molecular unit with all atoms labelled is in Fig. 2. H atoms (not shown on the figures) are labelled to correspond to the C atoms to which they are attached, *i.e.* H(1) is bonded to C(1).

Discussion. The coordination geometry of the Zn^{2+} central metal ion is distorted from tetrahedral. The N—Zn—N bond angle is significantly smaller than the 109° expected for ideal tetrahedral coordination. The S—Zn—S angle is slightly larger than expected for tetrahedral geometry (Table 2 and Fig. 2).

One toluene ring is bent back over the phenanthroline moiety and is coplanar with it (Fig. 2). The second toluene thiol is directed away from the phenanthroline ring and is not coplanar with either the phenanthroline or the first toluene ring. Thus, although the Zn, N, and S geometry has C_{2v} symmetry the overall symmetry of the molecule is reduced.

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