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Synthesis and structural determinations of zinc(II) complexes containing dithiol and N,N-heterocyclic ligands

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Abstract

Syntheses and single crystal structural determinations of four zinc complexes are presented: a mononuclear species, Zn(bdt)(biq); two binuclear species, $[Zn(bdt)(phen)]_2$ and $[Zn(tdt)(phen)]_2 \cdot$1,4-diphenyl-1,3-butadiene; and an unusual trinuclear species, $Zn_3(tdt)_3(phen)_2$, in which the zinc ions display either a four- or five-coordination geometry in a single molecule. The heterocyclic ligands used are 1,10-phenanthroline (phen) and biquinoline (biq), and the dithiols are 1,2-benzenedithiol (bdt) and 3,4-dimercaptotoluene (tdt). Long range interactions due to overlapping π systems of the heterocycles are also indicated by the structures.

Keywords: Crystal structures; Zinc complexes; Dithiolate complexes; Heterocyclic ligand complexes

1. Introduction

Complexation of zinc(II) with N,N-heterocyclic ligands and benzenethiol ligands on the same metal ion produces highly colored and luminescent materials. Principally two types of emission are observed from both glasses and solids at 77 K; a long-lived structured phosphorescence that emanates from the coordinated heterocycle [1,2] and a broad, diffuse band(s) that appears to be charge transfer in nature. The excited state producing the latter emission has been assigned to a ligand–ligand charge-transfer (LLCT) configuration in which an electron has been promoted from the HOMO of the zinc sulfur moiety to the LUMO of the coordinated heterocycle [3]. Because bis(monothiol) complexes have been shown to exhibit different conformations of the ligands about the zinc ion [4], we turned to the study of analogous complexes containing dithiol ligands in an effort to produce complexes with unique geometries and, hopefully, analogous reproducible spectroscopic behaviors.

Although our usual synthetic methods (vide infra) invariably produced monomeric complexes when monothiols were employed, the attempted syntheses of the dithiol analogs produced polynuclear species. Indeed, both dimeric and trinuclear species have been obtained. In this article, we report the syntheses and crystal structures of several multinuclear zinc species. We also present an interesting trimetallic complex in which the zinc(II) atoms exhibit both four- and five-coordinate geometry.

2. Experimental

2.1. Chemicals

Zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$; Merck and Company, Inc.), 1,10-phenanthroline (phen; Aldrich Gold Label, 99+%), 1,4-diphenyl-1,3-butadiene (Aldrich, 98%) and 2,2′-biquinoline (biq; Aldrich) were used without further purification. 1,2-Benzenedithiol (bdt) and 3,4-dimercaptotoluene (tdt), both purchased from Aldrich, were redistilled under reduced pressure prior to use. Dimethylformamide (DMF; Baker Analyzed Reagent) and Ethanol (USI Chemicals Co; spectroscopic grade), were used as received.

2.2. Zn(bdt)(biq) (I)

$Zn(OAc)_2 \cdot 2H_2O$ (219.5 mg, 1 mmol) was dissolved in 50 ml of hot ethanol. To this solution, bdt (1.43 mg, 1 mmol) dissolved in 25 ml hot ethanol was added dropwise. A white precipitate formed, which was redissolved by addition of a small amount of hot DMF, and the resultant solution brought to reflux. A solution

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containing biq (256.3 mg, 1 mmol) dissolved in 50 ml of hot ethanol was added slowly with vigorous stirring to the aforementioned refluxing solution. The resultant reaction mixture was cooled slowly and allowed to stand for 24 h. A dark purple solid was collected by vacuum filtration, recrystallized from a 1:1 DMF/ethanol solvent, washed twice with cold ethanol, and dried in vacuo. Yield 60–70%.

2.3. *[Zn(bdt)(phen)]$_2$ (II)*

$Zn(OAc)_2 \cdot 2H_2O$ (219.5 mg, 1 mmol) was dissolved in 50 ml of hot ethanol. To this, a solution of bdt (142.3 mg, 1 mmol) dissolved in hot ethanol was added dropwise. The resultant precipitate was redissolved with addition of a small amount of DMF and brought to reflux. To this solution a solution consisting of phen (180.2 mg, 1 mmol) dissolved in 50 ml of hot ethanol was added slowly with vigorous stirring. After the resultant solution stood for 24 h, the solid was collected, then recrystallized from an approximately 2:3 DMF/ethanol solvent mixture, washed with ethanol, and dried in vacuo. Yield 50–65%.

2.4. *Zn$_3$(tdt)$_3$(phen)$_2$ (III)*

This compound was prepared in a manner analogous to the preparation described for **II** except tdt (156.3 mg, 1 mmol) was used. Compound **III** formed even in the presence of a large excess of phenanthroline ligand (up to three-fold molar excess). Recrystallizations were carried out in the same solvent mixture as described above; however, the percentage of DMF required was much higher due to the lower solubility of this complex in ethanol. Yield 40–50%.

2.5. *[Zn(tdt)(phen)]$_2$·1,4-diphenyl-1,3-butadiene (IV)*

Compound **III** (0.04 g, 3.9×10^{-5} mol) was dissolved in 50 ml of DMF along with 1,4-diphenyl-1,3-butadiene (0.021 g, 1.0×10^{-4} mol). The solution was slowly cooled and the DMF was allowed to evaporate off slowly over a period of days. Dark orange crystallographic quality crystals were collected, washed with cold ethanol, and dried in vacuo.

2.6. *Crystallographic data collection and structure determination*

X-ray diffraction data collections were performed on either a Nicolet R3M/E or a Syntex P2$_1$ diffractometer upgraded to Nicolet P3F specifications, and the structures were solved by using direct methods within the Version 5.1 SHELXTL structure solution package [5]. Data for complex **I** were collected by use of graphite monochromated Cu Kα radiation [6]. Accurate unit cell parameters were obtained through centering of 25 reflections with 2θ values between 50° and 60°. Data for complexes **II–IV** were collected by use of graphite monochromated Mo Kα radiation. Accurate unit cell parameters were obtained through centering of 25 reflections with 2θ values between 19° and 29°. Empirical absorption corrections were made by the assumption of an ellipsoidal crystal in all cases. Pertinent crystallographic parameters are included in Table 1.

For all complexes direct methods located the zinc atoms. Subsequent difference maps revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were fixed at calculated positions (r(C–H) = 0.96 Å). The thermal parameters were anisotropic on all non-carbon and non-hydrogen atoms only. The thermal parameters for all hydrogen atoms were fixed at approximately 1.2 times the thermal parameter of the heavier atom directly bonded to it. Selected bond lengths and angles are given in Tables 2 and 3, respectively. Atomic coordinates and thermal parameters are listed in Table 4. See also Section 4.

3. Results and discussion

3.1. *Structure descriptions*

Complex **I** packs as discrete molecules with an elongated tetrahedral geometry around the zinc atoms (Fig. 1(a)). Zn–S bond lengths are 2.244(3) and 2.256(3) Å for Zn–S(1) and Zn–S(2), respectively. The Zn–N bond lengths are 2.041(7) and 2.087(7) Å for Zn–N(1) and Zn–N(2), respectively. The bond angles are 98.2(1)° for S(1)–Zn–S(2), 127.1(2)° for S(1)–Zn–N(1), 109.9(2)° for S(2)–Zn–N(1), 128.5(2)° for S(1)–Zn–N(2), 114.8(2)° for S(2)–Zn–N(2) and 78.4(3)° for N(1)–Zn–N(2). Since the S(1)–Zn–S(2) and N(1)–Zn–N(2) bond angles are less than the value of 109.5° for a regular tetrahedron and the other four bond angles are greater than this value, the complex exhibits an elongated tetrahedral geometry. Both of the ligands are quite planar even though the 2,2′-biquinoline ligand can twist around the 2,2′ bond. There are no abnormal carbon–nitrogen, carbon–sulfur or carbon–carbon bond lengths.

The plane of the 2,2′-biquinoline ligand overlaps with another 2,2′-biquinoline ligand on an adjacent molecule generated through an inversion center (Fig. 2). The distance separating the two ligand planes is 3.39(1) Å. This establishes a pseudo-dimeric arrangement of the molecules in the crystal. Adjacent pseudo-dimers pack perpendicular to each other with an overlap similar to that observed in complex **II** (vide infra, Fig. 2) and a distance of 3.17(1) Å between the pseudo-dimers. This appears to generate a quasi-one-dimensional system with no apparent contact between the chains.

Table 1
Crystallographic data for complexes **I–IV**

	I	**II**	**III**	**IV**
Chemical formula	$ZnC_{24}H_{16}N_2$	$Zn_2C_{48}H_{24}N_4S_4$	$Zn_3C_{45}H_{34}N_4S_6$	$Zn_2C_{70}H_{56}N_4S_4$
Formula weight	461.64	915.22	1018.81	1211.48
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	11.799(3)	10.987(6)	11.454(4)	9.463(4)
b (Å)	11.665(3)	10.7685(4)	20.590(9)	13.421(5)
c (Å)	14.630(3)	13.344(5)	18.548(4)	13.466(5)
α (°)				118.17(3)
β (°)	93.18(2)	101.08(4)	95.20(2)	92.44(3)
γ (°)				102.60(3)
V (Å^3)	2010.4(8)	1549(1)	4356(3)	1450(1)
Z	4	4	4	2
T	ambient	ambient	ambient	ambient
λ (Å)	1.54178	0.71069	0.71069	0.71069
ρ_{calc} (g cm^{-3})	1.53	1.96	1.55	1.39
μ (cm^{-1})	37.2	19.0	19.9	10.4
$R(F_o)$	0.0814	0.0435	0.0913	0.0928
$R_w(F_o^2)$	0.0898	0.0318	0.0792	0.1021

Table 2
Selected bond distances (Å) for complexes **I–IV**

	I	**II**	**III**	**IV**
Zn(1)–S(1)	2.244(3)	2.488(1)		2.451(5)
Zn(1)–S(2)	2.256(3)	2.292(2)		2.306(4)
Zn(1)–S(3)			2.364(5)	
Zn(1)–S(5)			2.459(5)	
Zn(1)–S(6)			2.541(5)	
Zn(1)–S(1A)		2.421(1)		2.410(3)
Zn(2)–S(1)			2.386(5)	
Zn(2)–S(5)			2.511(5)	
Zn(2)–S(6)			2.473(5)	
Zn(3)–S(1)			2.352(5)	
Zn(3)–S(2)			2.280(6)	
Zn(3)–S(3)			2.367(5)	
Zn(3)–S(4)			2.302(5)	
Zn(1)–N(1)	2.041(7)	2.119(4)	2.125(12)	2.198(11)
Zn(1)–N(2)	2.087(7)	2.235(4)	2.113(13)	2.166(12)
Zn(2)–N(3)			2.152(11)	
Zn(2)–N(4)			2.130(12)	
S(1)–C(1)	1.765(10)	1.765(5)	1.815(17)	1.785(15)
S(1)–C(6)	1.771(10)	1.764(5)	1.697(18)	1.741(16)
S(1)–C(8)			1.791(16)	
S(1)–C(13)			1.765(16)	
S(1)–C(15)			1.759(23)	
S(1)–C(20)			1.769(17)	

Complex **II** crystallizes as discrete dimers with five-coordinate zinc metal centers. The geometry around the zinc metal centers is distorted trigonal bipyramidal (Fig. 1(b)). Zinc–sulfur bond lengths are 2.488(1), 2.292(2) and 2.421(1) Å for Zn–S(1), Zn–S(2) and Zn–S(1A), respectively. Zinc–nitrogen bond lengths are 2.119(4) and 2.235(4) Å for Zn–N(1) and Zn–N(2), respectively. For a true trigonal bipyramid the coordination geometry around the central metal would consist of one 180°, three 120° and six 90° angles. In a square pyramid, two 180° and eight 90° angles would be present. To a good approximation the coordination geometry approaches that of the first case (Table 3). The asymmetric unit consists of one half of the dimer molecule related to the other by an inversion center. The Zn–S(1) bond length is longer than the Zn–S(1A) bond length, which is probably best accounted for by the observation that the bond lengths of the benzenedithiol moiety are the same as those of complex **I**. The rigidity in the dithiol ligand and the presence of a second coordination bond at sulfur one (S(1)) forces some asymmetry into the metal–sulfur bond lengths and the Zn–S(1) bond length becomes longer than that of the Zn–S(1A) bond. The bridging zinc–sulfur–zinc angles are 88.2(1)°. There are no apparent carbon–nitrogen, carbon–sulfur or carbon–carbon bond length abnormalities.

The 1,10-phenanthroline ligand defines a plane and is overlapped by adjacent phenanthroline ligands on separate dimers generated through inversion centers. The distance between these ligands is 3.23(1) Å. This creates a quasi-one-dimensional system with no essential contact between the chains. Unlike complex **I**, however, these dimers stack parallel to each other. Overlap of the phenanthroline ligands between dimers is small and located on the periphery of the N,N-heterocyclic ligand (Fig. 2).

Complex **III** crystallizes as discrete trinuclear oligomers (Fig. 1(c)). By comparison with complexes **I** and **II** and a consideration of the values in Table 3 it is possible to assign the coordination geometry around each of the metal centers. Zn(1) and Zn(2) exhibit distorted trigonal bipyramidal geometry with even greater distortion than that observed in complex **II**. Zn(3) exhibits an elongated tetrahedral coordination geometry, thus establishing two different coordination geometries around the zinc atoms in the same molecule.

Table 3
Selected bond angles (°) for complexes **I–IV**

	I	**II**	**III**	**IV**
S(1)–Zn(1)–S(2)	98.2(1)	89.4(1)		89.2(2)
S(3)–Zn(1)–S(5)			133.0(2)	
S(3)–Zn(1)–S(6)			95.7(2)	
S(5)–Zn(1)–S(6)			79.0(2)	
S(1)–Zn(1)–S(1A)		91.8(1)		98.8(1)
S(2)–Zn(1)–S(1A)		119.5(1)		111.5(2)
S(1)–Zn(2)–S(5)			96.7(2)	
S(1)–Zn(2)–S(6)			128.1(2)	
S(5)–Zn(2)–S(6)			79.3(2)	
S(1)–Zn(3)–S(2)			92.5(2)	
S(1)–Zn(3)–S(3)			122.0(2)	
S(2)–Zn(3)–S(3)			112.0(2)	
S(1)–Zn(3)–S(4)			110.8(2)	
S(2)–Zn(3)–S(4)			131.4(2)	
S(3)–Zn(3)–S(4)			91.4(2)	
Zn(1)–S(1)–Zn(1A)		88.2(1)		81.2(1)
Zn(1)–S(3)–Zn(3)			100.3(2)	
Zn(1)–S(5)–Zn(2)			85.1(2)	
Zn(1)–S(6)–Zn(2)			84.1(2)	
Zn(2)–S(1)–Zn(3)			104.9(2)	
N(1)–Zn(1)–N(2)	78.4(3)	75.9(1)	77.7(5)	75.0(4)
N(1)–Zn(1)–S(1)	127.1(2)	97.0(1)		161.9(3)
N(1)–Zn(1)–S(2)	109.9(2)	120.1(1)		93.7(3)
N(1)–Zn(1)–S(3)			99.3(3)	
N(1)–Zn(1)–S(5)			93.5(3)	
N(1)–Zn(1)–S(6)			164.6(4)	
N(1)–Zn(1)–S(1A)		119.8(1)		96.7(3)
N(2)–Zn(1)–S(1)	128.5(2)	172.9(1)		93.1(3)
N(2)–Zn(1)–S(2)	114.8(2)	94.8(1)		147.5(2)
N(2)–Zn(1)–S(3)			98.1(4)	
N(2)–Zn(1)–S(5)			128.8(4)	
N(2)–Zn(1)–S(6)			96.4(3)	
N(2)–Zn(1)–S(1A)		91.2(1)		100.2(2)
N(3)–Zn(2)–N(4)			77.8(4)	
N(3)–Zn(2)–S(1)			97.0(4)	
N(3)–Zn(2)–S(5)			165.2(4)	
N(3)–Zn(2)–S(6)			96.6(4)	
N(4)–Zn(2)–S(1)			102.0(4)	
N(4)–Zn(2)–S(5)			93.8(3)	
N(4)–Zn(2)–S(6)			129.8(4)	
Zn(1)–S(1)–C(1)	96.4(3)	98.7(2)		98.3(6)
Zn(1)–S(1)–C(1)		108.0(2)		101.4(5)
Zn(1)–S(2)–C(6)	96.8(3)	103.2(2)		102.4(6)
Zn(1)–S(3)–C(8)			104.1(6)	
Zn(1)–S(5)–C(15)			91.4(7)	
Zn(1)–S(6)–C(20)			87.5(5)	
Zn(2)–S(1)–C(1)			106.3(6)	
Zn(2)–S(5)–C(15)			89.6(6)	
Zn(2)–S(6)–C(20)			93.3(6)	
Zn(3)–S(1)–C(1)			98.0(6)	
Zn(3)–S(2)–C(6)			99.9(6)	
Zn(3)–S(3)–C(8)			97.7(6)	
Zn(3)–S(4)–C(13)			99.3(6)	

The observed zinc–sulfur and zinc–nitrogen bond lengths are longer than those present in complexes **I** and **II** (Table 2). The longest zinc–sulfur bond lengths extend to the axial positions of the trigonal bipyramids of Zn(1) and Zn(2) and are 2.541(5) and 2.511(5) Å, respectively. The bridging zinc–sulfur–zinc angles are 104.9(2)°, 100.3(2)°, 85.1(2)° and 84.1(2)° for S(1), S(3), S(5) and S(6), respectively. The methyl group on the bridging toluenedithiol ligand (C(21)) is disordered in the crystal between C(17) and C(18) with site occupancy factors of 0.59 and 0.41, respectively. On the other two toluene dithiol ligands the methyl substituent appears fixed on only one carbon of the aromatic ring. It is not obvious why the methyl groups are fixed *meta* and *para* to the bridging sulfur atoms in these two ligands since there is a pseudo-C_2 axis in the molecule. This is apparently the first example of such a mixed coordination zinc(II) complex. Recently, an analogous trinuclear structure has been observed involving an Ni(II) complex which employs bdt and phosphine rather than N,N-heterocyclic ligands [7]. The remaining carbon–sulfur, carbon–nitrogen and carbon–carbon bond lengths exhibit no noticeable deviation from expected values.

As in complex **II** the 1,10-phenanthroline ligand of complex **III** defines a plane and is observed to overlap to a large degree (Fig. 2) with an adjacent phenanthroline ligand on another trinuclear molecule generated through an inversion center. For the phenanthroline moiety bonded to Zn(1)(phen 1) the distance to the overlapping adjacent phenanthroline ligand is 3.40(1) Å. For the phenanthroline ligand bonded to Zn(2)(phen 2) the distance is 3.51(1) Å. This creates an alternating overlap distance in the quasi-one dimensional system formed by these trinuclear complexes. As in the previously described complexes there is no apparent contact between the quasi-one-dimensional chains.

Complex **IV** is a co-crystallized species that has two discrete 1,4-diphenyl-1,3-butadiene molecules for each discrete dimer in the unit cell (Fig. 1(d)). With the exception of the presence of the co-crystallized molecules, complex **IV** is very similar to complex **II**. As in complex **II**, complex **IV** exhibits distorted trigonal bipyramidal coordination geometry around the zinc(II) atoms (Table 3). Zinc–sulfur bond lengths are 2.451(5), 2.306(4) and 2.410(3) Å for Zn–S(1), Zn–S(2) and Zn–S(1A), respectively. Zinc–nitrogen bond lengths are 2.198(11) and 2.166(12) Å for Zn–N(1) and Zn–N(2), respectively. The bridging zinc–sulfur–zinc angles are 81.2(1)°. As observed in complex **III**, the methyl substituent on the dithiol ligand exhibits disorder in the crystal between the positions *meta* and *para* to the bridging sulfur of the dithiol ligand. The site occupancy factors are 0.66 and 0.34 for the *meta* and *para* positions, respectively. No other bond length abnormalities are observed as noted previously for the other complexes.

In a manner similar to that of complex **II**, the phenanthroline ligands form planes that overlap adjacent phenanthroline ligands on separate dimers, but the distance between these overlapping ligands is slightly longer (3.34(1) Å) than in complex **II**. Furthermore, the degree of overlap in complex **IV** is considerably

Table 4
Atomic positional parameters ($\times 10^4$) for complexes **I–IV**

	I				**II**			
	x	*y*	*z*	*U* [a]	*x*	*y*	*z*	*U* [a]
Zn	1625(1)	6627(1)	6129(1)	63(1)*	3866(1)	4156(1)	5401(1)	33(1)*
S(1)	2494(3)	7890(2)	5246(2)	78(1)*	5928(1)	4981(1)	6234(1)	31(1)*
S(2)	2546(3)	7059(2)	7478(2)	71(1)*	2961(1)	5321(1)	6496(1)	50(1)*
N(1)	−75(6)	6493(5)	6298(5)	53(3)*	4262(4)	2254(4)	5713(3)	29(2)*
N(2)	1350(7)	4880(6)	5904(5)	60(3)*	2116(4)	3181(4)	4691(3)	35(2)*
C(1)	3354(8)	8520(8)	6136(6)	62(3)	5423(4)	6178(4)	6961(3)	29(2)*
C(2)	4055(8)	9437(8)	5909(7)	72(3)	6296(5)	7021(4)	7464(4)	34(2)*
C(3)	4765(9)	9988(9)	6541(7)	75(3)	6002(5)	7910(4)	8123(4)	40(2)*
C(4)	4185(9)	9631(9)	7436(7)	75(3)	4807(5)	7980(4)	8285(4)	41(2)*
C(5)	4146(8)	8718(9)	7695(7)	71(3)	3908(5)	7185(5)	7776(4)	37(2)*
C(6)	3405(8)	8166(8)	7060(6)	61(3)	4182(4)	6283(4)	7102(4)	31(2)*
C(7)	−811(8)	7373(8)	6489(6)	63(3)				
C(8)	−452(9)	8514(9)	6311(7)	74(3)				
C(9)	−1210(10)	9401(11)	6455(8)	89(4)				
C(10)	−2270(10)	9174(11)	6811(7)	86(3)				
C(11)	−2612(11)	8131(10)	6997(8)	84(3)				
C(12)	−1882(9)	7164(9)	6833(7)	71(3)				
C(13)	−2215(10)	6038(10)	6998(7)	81(3)				
C(14)	−1502(9)	5158(10)	6790(7)	75(3)				
C(15)	−450(8)	5420(8)	6437(6)	60(3)				
C(16)	341(8)	4515(8)	6168(6)	60(3)				
C(17)	82(9)	3333(8)	6189(6)	68(3)				
C(18)	879(9)	2566(10)	5950(7)	75(3)				
C(19)	1927(8)	2910(8)	5684(6)	65(3)				
C(20)	2789(10)	2126(10)	5432(10)	85(3)				
C(21)	3770(10)	2518(11)	5172(7)	91(3)	5306(5)	1805(5)	6248(4)	40(2)*
C(22)	4012(10)	3723(10)	5092(8)	89(4)	5475(5)	540(4)	6480(4)	38(2)*
C(23)	3180(9)	4490(10)	5349(7)	80(3)	4553(5)	−278(5)	6150(4)	42(2)*
C(24)	2157(8)	4101(9)	5647(6)	65(3)	3420(5)	155(4)	5571(4)	35(2)*
C(25)					2410(5)	−639(5)	5145(4)	42(2)*
C(26)					1374(5)	−182(5)	4553(4)	45(2)*
C(27)					1222(5)	1125(5)	4362(4)	34(2)*
C(28)					162(5)	1676(6)	3779(4)	43(2)*
C(29)					72(5)	2933(5)	3706(4)	46(2)*
C(30)					1076(5)	3654(5)	4164(4)	45(2)*
C(31)					2191(4)	1930(4)	4791(4)	31(2)*
C(32)					3324(4)	1437(4)	5381(3)	31(2)*

	III				**IV**			
	x	*y*	*z*	*U* [a]	*x*	*y*	*z*	*U* [a]
Zn					8405(2)	4381(1)	5060(1)	55(1)
Zn(1)	7430(2)	819(1)	3534(1)	57(1)*				
Zn(2)	5495(2)	521(1)	2100(1)	60(1)*				
Zn(3)	4662(2)	1680(1)	3533(1)	64(1)*				
S(1)	3899(4)	847(2)	2760(2)	73(2)*	9460(4)	4469(3)	3463(3)	69(2)*
S(2)	3746(5)	2469(2)	2828(3)	110(3)*	8258(4)	2404(3)	4185(4)	76(2)*
S(3)	6701(4)	1869(2)	3748(3)	69(2)*				
S(4)	4538(4)	1404(2)	4727(2)	75(2)*				
S(5)	6492(4)	−190(2)	3069(2)	75(2)*				
S(6)	7505(4)	969(2)	2179(2)	72(2)*				
N(1)	7655(11)	475(6)	4618(6)	52(6)*	6833(10)	4278(8)	6187(9)	57(6)
N(2)	9225(11)	1005(6)	3826(6)	65(6)*	7310(10)	5726(8)	5337(8)	55(6)*
N(3)	4886(11)	976(6)	1091(6)	55(6)*				
N(4)	4670(11)	−277(5)	1486(6)	52(5)*				
C(1)	2950(15)	1343(8)	2147(9)	76(6)	9797(14)	3056(11)	2795(11)	67(4)
C(2)	2193(18)	959(11)	1634(10)	107(7)	10684(16)	2833(13)	1926(12)	89(5)

(continued)

Table 4 (*continued*)

	III				**IV**			
	x	y	z	U[a]	x	y	z	U[a]
C(3)	1530(17)	1414(11)	1138(10)	91(7)	11065(17)	1788(14)	1430(13)	92(5)
C(4)	1483(22)	2023(13)	1074(13)	148(10)	10618(19)	979(15)	1709(14)	108(6)
C(5)	2205(19)	2345(11)	1635(11)	133(9)	9735(17)	1181(15)	2556(13)	100(5)
C(6)	2968(16)	2000(9)	2203(9)	90(6)	9305(15)	2229(12)	3111(11)	72(4)
C(7)	669(28)	1179(16)	525(16)	245(15)	12047(28)	1393(22)	538(21)	117(10)
C(8)	6772(16)	1927(8)	4714(8)	62(5)	11383(42)	218(33)	1228(32)	73(14)
C(9)	7860(17)	2199(8)	5058(10)	88(6)				
C(10)	7958(18)	2239(9)	5809(11)	95(7)				
C(11)	7122(19)	2010(9)	6174(10)	85(6)				
C(12)	6011(16)	1757(8)	5872(9)	78(6)				
C(13)	5890(14)	1720(7)	5104(8)	565(5)				
C(14)	7325(22)	2062(10)	7001(8)	200(12)				
C(15)	7631	−333	2513	60(5)				
C(16)	8030	−969	2413	84(6)				
C(17)	8977(16)	−1045(9)	2041(9)	86(6)				
C(18)	9550(18)	−564(10)	1753(10)	96(7)				
C(19)	9194(17)	71(9)	1798(10)	89(6)				
C(20)	8163(16)	193(8)	2165(8)	68(5)				
C(21)	10619(41)	−794(23)	1442(25)	113(23)	6611(14)	3538(11)	6604(11)	66(4)
C(21′)	9540(36)	−1639(19)	1804(22)	172(23)				
C(22)	4939(14)	1576(9)	937(8)	70(6)	5654(14)	3598(11)	7383(11)	69(4)
C(23)	4331(15)	1844(9)	306(9)	88(6)	4952(14)	4430(11)	7748(11)	69(4)
C(24)	3722(15)	1443(8)	−158(9)	75(6)	5164(13)	5235(10)	7328(10)	55(3)
C(25)	3610(13)	792(7)	−7(7)	50(5)	4446(15)	6159(12)	7655(11)	75(4)
C(26)	2949(14)	319(8)	−431(9)	70(5)	4706(15)	6883(12)	7234(11)	69(4)
C(27)	2877(14)	−295(8)	−246(8)	59(5)	5662(14)	6792(11)	6444(11)	63(4)
C(28)	3448(14)	−542(7)	410(8)	62(5)	5989(15)	7538(12)	5983(11)	71(4)
C(29)	3417(15)	−1179(8)	664(8)	75(6)	6918(15)	7359(12)	5258(11)	71(4)
C(30)	4015(15)	−1360(9)	1301(9)	84(6)	7577(14)	6453(11)	4901(11)	63(4)
C(31)	4674(15)	−875(9)	1697(9)	75(6)	6368(12)	5881(10)	6081(9)	46(3)
C(32)	4146(14)	−115(7)	855(7)	48(5)	6101(12)	5115(10)	6556(9)	46(3)
C(33)	4523(14)	553(7)	661(8)	56(5)				
C(34)	6840(15)	205(7)	4971(9)	71(5)				
C(35)	7022(17)	83(8)	5724(10)	87(6)				
C(36)	8064(17)	262(8)	6068(10)	75(6)				
C(37)	8951(17)	527(8)	5741(8)	65(5)				
C(38)	10100(17)	720(8)	6011(10)	82(6)				
C(39)	10859(16)	987(8)	5642(9)	77(6)				
C(40)	10713(16)	1131(9)	4881(10)	78(6)				
C(41)	11361(18)	1417(9)	4436(11)	97(7)	2163(11)	2468(8)	8375(10)	100(5)
C(42)	11118(17)	1528(9)	3713(11)	108(7)	2412	3543	9379	103(5)
C(43)	9957(15)	1296(8)	3430(9)	85(6)	1786	4402	9404	109(6)
C(44)	9518(14)	914(7)	4551(8)	56(5)	910	4187	8427	105
C(45)	8727(16)	639(7)	4947(8)	51(5)	661	3112	7423	91(5)
C(46)					1288	2253	7397	85(5)
C(47)					1067(21)	1066(15)	6428(15)	58(7)
C(47′)					246(58)	1557(46)	6096(41)	108(22)
C(48)					184(16)	593(11)	5552(11)	85(5)
C(51)					5005(9)	629(9)	8384(10)	99(5)
C(52)					5674	1143	9520	113(6)
C(53)					7124	1841	9875	132(7)
C(54)					7904	2026	9093	145(7)
C(55)					7235	1511	7957	107(6)
C(56)					5786	813	7603	76(4)
C(57)					4930(20)	268(16)	6453(15)	62(7)
C(57′)					6119(65)	640(49)	6333(45)	123(24)
C(58)					5358(16)	253(13)	5628(11)	84(5)

[a] Isotropic thermal parameters ($Å^2 \times 10^3$) with anisotropic atoms marked with an asterisk. Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

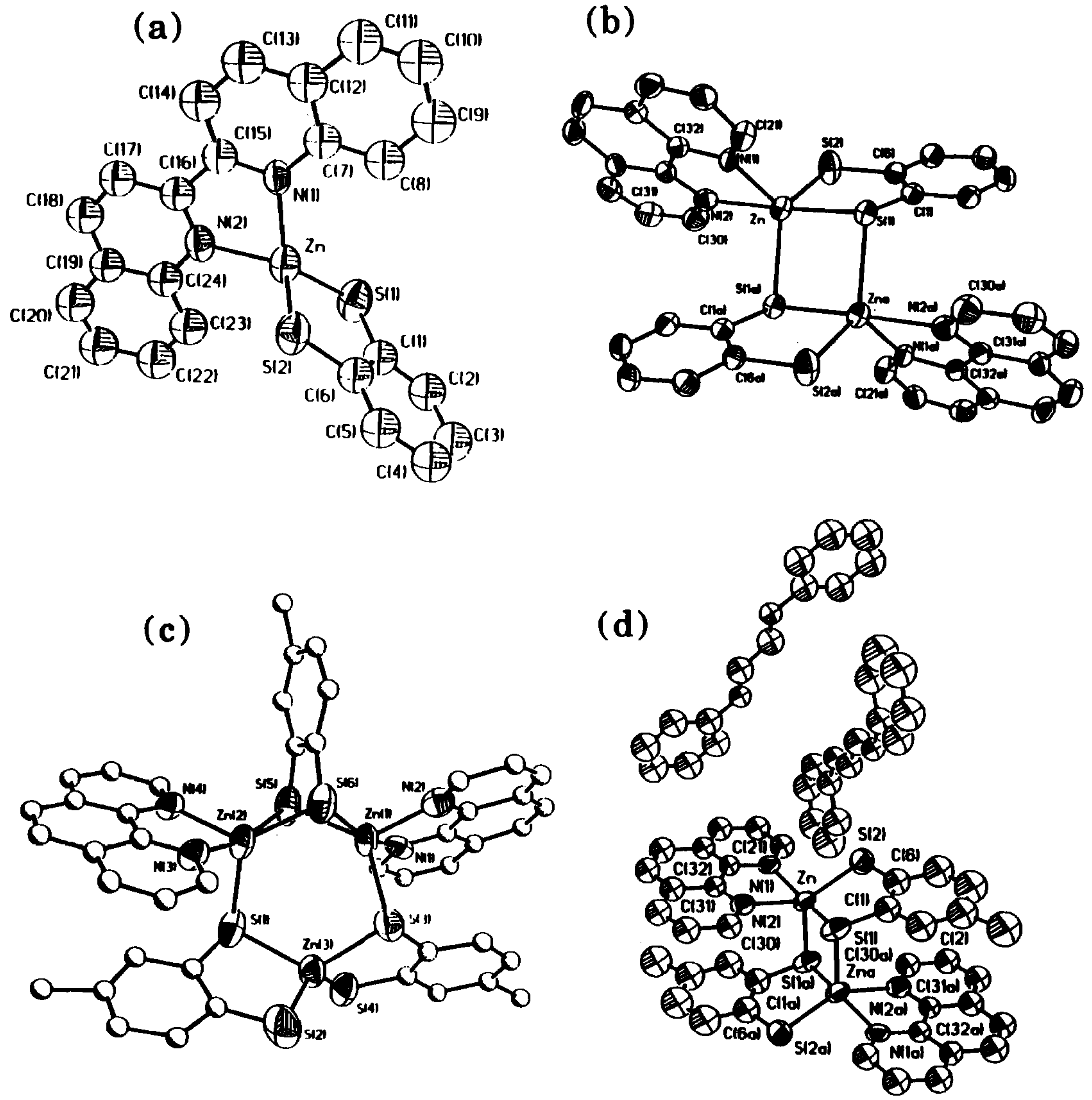
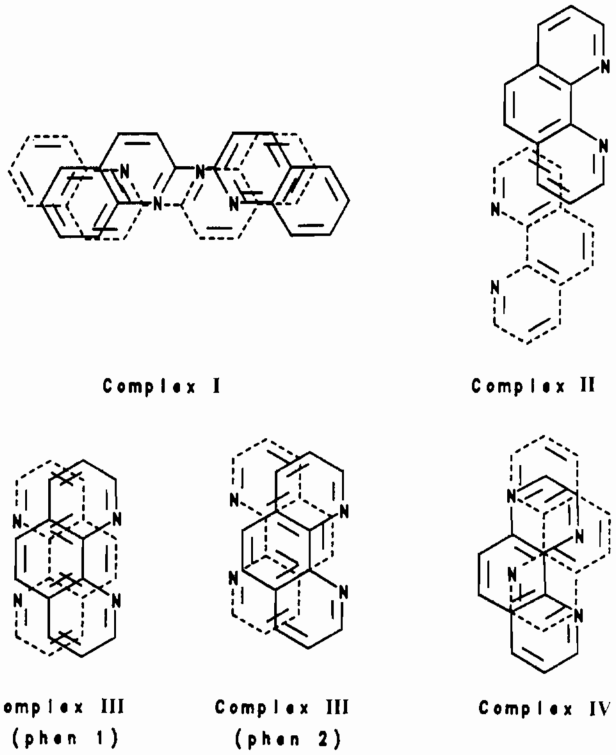


Fig. 1. Thermal ellipsoid plots of the structures of zinc complexes: (a) Zn(bdt)(biq) (I); (b) [Zn(bdt)(phen)]$_2$ (II); (c) Zn$_3$(tdt)$_3$(phen)$_2$ (III); (d) [Zn(tdt)(phen)]$_2$·1,4-diphenyl-1,3-butadiene (IV).

greater than that observed in complex **II** (Fig. 2) since the two rings are partially eclipsed. This arrangement creates a quasi-one-dimensional system with no essential contact between the linear chains analogous to the structure of complex **II**.

The co-crystallizing species, 1,4-diphenyl-1,3-butadiene in complex **IV** exhibits a normal fully extended conjugated conformation. This species is, however, disordered in the crystal. The 1,4 positions of butadiene exhibit the largest disorder, most likely due to the possibility of rotation around the 1,2 and 3,4 carbon–carbon bonds. Subsequent disorder created in the phenyl ring due to this behavior led to the aromatic ring being fixed as a rigid body. The long axis of 1,4-diphenyl-1,3-butadiene packs perpendicular to the one-dimensional chain formed by the dimer. Adjacent 1,4-diphenyl-1,3-butadiene molecules have their phenyl groups arranged perpendicularly. Their disposition isolates the one-dimensional chains of the complex **IV** dimers to a much greater degree than that observed for complex **II**. For stereopacking diagrams for these complexes, see Section 4.

Our interest in zinc complexes stems from a desire to understand the origin of the absorption and luminescence properties from molecules with (nd)^{10} ions coordinated with both electron-withdrawing and electron-donating ligands. Such systems are weakly luminescent in glasses at 77 K, but the crystalline samples often emit visible radiation at room temperature, although the intensity is enhanced considerably (5×) when the temperature is lowered to 4.5 K. Moreover, the emissions are singularly devoid of structure, broad, and exhibit multiple decay times. Because bis(benzenethiol)(1,10-phenanthroline)zinc(II) complexes often exhibit several phases and phase-dependent emissions [4], due to varying conformations of the



Complex I

Complex II

Complex III (phen 1)

Complex III (phen 2)

Complex IV

Fig. 2. Projection diagrams illustrating π-overlap of rings of adjacent molecules in the crystal.

monothiol ligands, we turned to dithiol systems in the hope of avoiding these multiple conformations of the sulfur ligands. Our synthetic methods, modeled after those involving monothiol ligands, failed to produce the desired mononuclear species, but rather, almost invariably produced polynuclear complexes when the N,N-heterocyclic ligand used was phenanthroline. Recently, similar behavior was observed when the N,N-heterocycle employed was 2,2′-bipyrimidine [8].

That intermolecular forces play dominant roles in the crystal is supported by the relationship between complexes **III** and **IV**. The former was obtained from the normal synthesis; the latter was the result of adding 1,4-diphenyl-1,3-butadiene to the reaction mixture. One observes that the presence of the non-coordinating hydrocarbon forces the trinuclear species into a dimeric one. Our intent was to produce a species that had the butadiene rings flat on the surface of the heterocycle, but this obviously did not occur. Our conclusion is that crystal packing energies are comparable to intramolecular conformational energies. In retrospect this is not a surprising result, since the zinc(II) ion is a closed-shell species and only weakly prefers tetrahedral coordination and any specific conformation. One can probably generalize these results to corresponding cadmium(II) complexes, but not to those of isoelectronic copper(I). In complexes of the latter ion there are prominent low-lying metal-to-ligand charge-transfer bands and, correspondingly, some charge transfer mixed into the ground state [9]. Undoubtedly, such admixture would confer additional directionality on coordinating bonds in copper(I) systems and the likelihood of finding such low barriers to conformational changes as we find for zinc species is remote.

Finally, we comment on the unusual features of complex **III**. This molecule contains both four- and five-coordinate zinc(II) and, in preliminary studies, appears to be stable in solution. Such an entity appears to be novel. Moreover, although there is a pseudo-C_2 axis in the molecule, one of the dithiols has the methyl group of the tdt *para* to the bridging sulfur, whereas the other is *meta* to it. This is difficult to understand, for there are no obvious structural features in the molecule or the crystal dictating this positional specificity. Further studies into this phenomenon and the solution chemistry of the unusual species is in progress.

4. Supplementary material

Tables of X-ray data collection parameters, anisotropic thermal parameters, interatomic distances, and bond angles for all four complexes (10 pages); stereoscopic views of compounds **I** and **III** (3 pages); and spacial representations of compounds **II**, **III** and **IV** (3 pages) are available from the Cambridge Crystallographic Data Centre (CCDC). Tabulation of the $|F_o|$ and $|F_c|$ values are available from the authors.

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