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Complexes of Zinc Dialkyldithiocarbamates.
Part I. Complexes with Bidentate Nitrogen Ligands; Crystal Structure of 1,10-Phenanthroline Zinc Dibutyldithiocarbamate

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Abstract

Reactions of $Zn(S_2CNR_2)_2$ (R = Me, Et, Bu, $PhCH_2$) with an excess of 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline produce crystalline 1:1 complexes which are non-electrolytes. Thermogravimetric studies show that the 2,2′-bipyridyl complexes decompose by loss of ligand whereas the phenanthroline and substituted phenanthroline complexes undergo more complex decomposition. The crystal structure of [(1,10-phenanthroline)$Zn(S_2CNBu_2)_2$] shows the monomeric nature of the complex, octahedral coordination of the metal, approximate planarity of the chelated ZnS_2C unit and confirms infrared evidence for a degree of π-bonding in the C–N bond of the dithiocarbamate moiety.

Introduction

Zinc dialkyldithiocarbamates and their derivatives find wide application in rubber chemistry and technology and as fungicides. 1:1 Complexes of zinc dialkylthiocarbamates with primary and secondary amines and with pyridine have previously been prepared and some of these complexes are very active accelerators for the vulcanisation of rubber by sulphur [1] and the low temperature vulcanisation of latex [2]. Indeed vulcanising mixtures containing $[Zn(S_2CNMe_2)_3]^-$ are extremely fast accelerators, significantly more so than $Zn(S_2CNMe_2)_2$ [3]. Many accelerator mixtures contain stearic acid and it has been suggested [4] that this may form 2:1 adducts with zinc dialkyldithiocarbamates, also enhancing the nucleophilicity of coordinated R_2NCS_2 toward attack on S_8. However, no 2:1 complexes have been reported in the literature nor neutral complexes with bidentate ligands. Herein we report the preparation of 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl- and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes of some zinc dialkyldithiocarbamates and the crystal structure of [(1,10-phenanthroline)Zn-$(S_2CNBu_2)_2$]. The crystal structure of only one neutral complex has previously been reported, namely that of (pyridine)zinc bis(dimethyldithiocarbamate), which has a discrete monomeric structure with the five-coordinate zinc surrounded by 1 nitrogen and 4 sulphur atoms at the corners of a trigonal bipyramid [5]. In contrast zinc dimethyldithiocarbamate [6] and the diethyl analogue [7] have dimeric arrangements, the former containing four-coordinate and the latter five-coordinate zinc atoms. Structures of some anionic zinc dimethyldithiocarbamate complexes have been reported in which both monodentate and bidentate dithiocarbamate ligands are present [3, 8].

Results and Discussion

Zinc dialkyldithiocarbamates, $Zn(S_2CNR_2)_2$ (R = Me, Et, Bu, $PhCH_2$) dissolved in dichloromethane react with 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (DMP) and 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) in methanol in a 1:5 molar ratio, from which crystalline complexes have been isolated. In two cases ($Zn(S_2CN(CH_2Ph)_2)_2$ (DMP) and $Zn(S_2CNMe_2)_2$(TMP)) satisfactory analyses could not be obtained using the above procedure but were obtained when the reaction was carried out in toluene solution. Such complexes are likely to contain six-coordinate zinc, subsequently confirmed from our X-ray crystallographic studies, in contrast to the 1:1 complexes isolated with monodentate amine ligands [1] which all doubtless contain five-coordinate zinc as shown from the crystal structure of (pyridine)$Zn(S_2CNMe_2)_2$ [5]. The possible bonding arrangements of the dithiocarbamate ligand are shown below.

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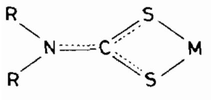
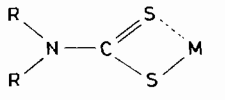
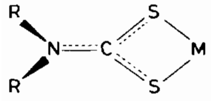


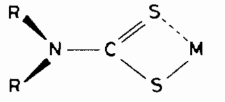
C_{2v}



C_s



C_2



C_1

Assignment of bands in the infrared spectra of dithiocarbamate complexes has been used to establish the mode of coordination of the dithiocarbamate moiety to the metal. Bands in the carbon–nitrogen stretching region 1440–1520 cm^{-1} (Table 1) clearly are indicative of considerable double bond character. Additionally the presence of only one strong band at *ca.* 1000 cm^{-1}, attributed to the carbon–sulphur asymmetric stretching vibration, was earlier believed to be diagnostic of symmetric coordination of dithiocarbamate whereas two closely spaced bands in the 1000 ± 70 cm^{-1} range would be expected in the case of an asymmetrically bonded dithiocarbamate ligand (unidentate or bidentate asymmetric) [3,9–12]. However, more recent studies [13] have shown that the splitting of bands in the 1000 cm^{-1} region is due to interligand coupling of the CS ligand modes and that R–N modes are also present in this region, thus making it unsuitable for the determination of ligand bonding type. Further, comparison of X-ray diffraction data for metal diethyldithiocarbamate complexes has shown that the dithiocarbamate ligand, irrespective of the host complex or the ligand bonding type, is at sites of C_1 symmetry, thus ruling out the possibility of detecting the ligand bonding type from the solid state vibrational spectra.

Although splitting of the bands in the 1000 cm^{-1} region, listed in Table 1, might earlier have been interpreted as showing asymmetry in the dithiocarbamate ligand, we have sought confirmatory evidence by the X-ray structural analysis of one of the complexes.

The structure of $[(phen)Zn(S_2CNBu_2)_2]$ contains four discrete monomeric units per unit cell with each molecule situated on a two-fold rotation axis (Fig. 1). The zinc atom is situated at the centre of a distorted octahedral arrangement of four sulphur atoms from the chelating dithiocarbamate groups and two nitrogen atoms from the chelating phenanthroline ligand. As with other dithiocarbamate complexes the MS_2C ring is almost planar [3, 5–8, 14].

Of particular interest with respect to the dithiocarbamate–zinc bonding are the Zn–S, C–S and C–N distances and the associated angles. Bond distances and angles are listed in Table 2 and comparison of selected molecular parameters with other zinc dialkyldithiocarbamates and their complexes is shown in Table 3. The small bite of the dithiocarbamate group results in a small S–Zn–S angle in all the complexes listed but is particularly small (70.8(1)°) in

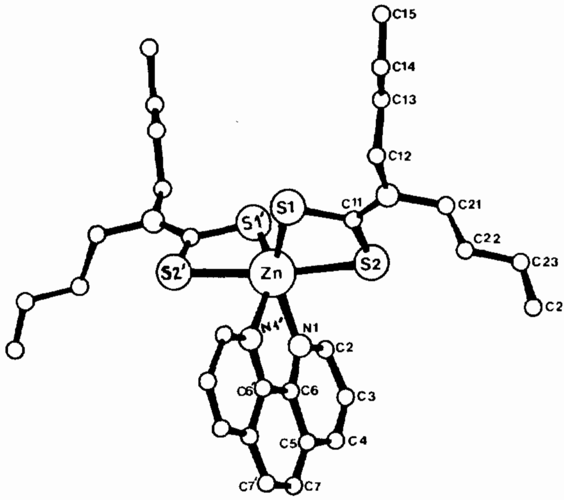


Fig. 1. The structure and atom labelling for $(phen)Zn(S_2CNBu_2)_2$ with H atoms omitted for clarity.

TABLE 1. Infrared Absorption Bands (950–1050, 1450–1530 cm^{-1}) for $Zn(S_2CNR_2)_2 \cdot L$

L	R			
	Me	Et	Bu	$PhCH_2$
Bipy	977vs, 1010m 1480vs	987vs, 1010m 1470vs	982s, 1010s 1465vs	998vs, 978msh 1440vs
Phen	974vs, 1011vw 1485vs	989s, 980sh 1472vs	970m, 1000mw 1470vs	1000vs, 1010s 1460s, 1448vs
DMP	970s, 1010w 1500sbr	990s 1450s, 1475–1500sbr	965ms 1450sbr, 1480s	985ms, 1015m 1475sbr, 1510s
TMP	970s 1470–1510sbr	980m 1470s	970m, 1005m 1485s, 1520m	980s, 1020m 1490s, 1520m

TABLE 2. Bond Lengths (Å) and Angles (°)[a]

Distances (Å)			
Zn–N(1)	2.218(1)	S(1)–C(11)	1.723(15)
Zn–S(1)	2.516(4)	S(2)–C(11)	1.688(13)
Zn–S(2)	2.530(4)	N(2)–C(1)	1.32(2)
N(1)–C(6)	1.36(2)	N(2)–C(12)	1.44(2)
N(1)–C(2)	1.34(2)	N(2)–C(21)	1.49(2)
C(2)–C(3)	1.40(2)	C(12)–C(13)	1.57(3)
C(3)–C(4)	1.33(2)	C(13)–C(14)	1.42(4)
C(4)–C(5)	1.42(2)	C(14)–C(15)	1.47(5)
C(5)–C(6)	1.46(2)	C(21)–C(22)	1.59(2)
C(5)–C(7)	1.44(2)	C(22)–C(23)	1.46(3)
C(6)–C(6′)	1.36(2)	C(23)–C(24)	1.33(4)
C(7)–C(7′)	1.33(3)		
Angles (°)			
N(1)–Zn–S(1)	148.8(3)	Zn–S(1)–C(11)	85.6(4)
N(1)–Zn–S(2)	83.1(3)	Zn–S(2)–C(11)	85.8(5)
S(1)–Zn–S(2)	70.8(1)	S(1)–C(11)–S(2)	117.9(8)
N(1)–Zn–N(1′)	73.9(1)	S(2)–Zn–S(2′)	173.1(6)
N(1)–Zn–S(1)	95.0(2)	S(1)–Zn–S(1′)	107.8(3)
N(1′)–Zn–S(2)	102.5(3)		
C(2)–N(1)–C(6)	119.0(10)	S(1)–C(11)–N(2)	120.4(11)
C(2)–N(1)–Zn	126.5(8)	S(2)–C(11)–N(2)	121.7(12)
C(6)–N(1)–Zn	114.3(7)	C(11)–N(2)–C(12)	126(1)
C(3)–C(2)–N(1)	122.9(13)	C(11)–N(2)–C(21)	122(1)
C(4)–C(3)–C(2)	119.5(13)	C(12)–N(2)–C(21)	111(1)
C(5)–C(4)–C(3)	121.3(14)	N(2)–C(12)–C(13)	110(1)
C(6)–C(5)–C(4)	116.4(12)	C(12)–C(13)–C(14)	103(2)
C(5)–C(6)–N(1)	120.7(10)	C(13)–C(14)–C(15)	104(2)
C(6)–C(5)–C(7)	117.4(11)	N(2)–C(21)–C(22)	114(1)
C(7)–C(5)–C(4)	126.2(12)	C(21)–C(22)–C(23)	109(2)
C(6′)–C(6)–N(1)	118.6(10)	C(22)–C(23)–C(24)	110(2)
C(6′)–C(6)–C(5)	120.6(11)		
C(7′)–C(7)–C(5)	121.8(11)		

[a] e.s.d.s given in parentheses.

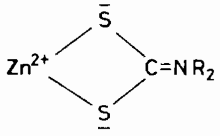
TABLE 3. Comparative Molecular Parameters for Zinc Dialkyldithiocarbamates and their Complexes

	Coordination number	S–Zn–S (°)	S–C–S (°)	Zn–S (Å)	C–S (Å)	S_2C–N (Å)	Reference
$[Zn(S_2CNMe_2)_2]_2$	4[a]	76.37(19)[d]	117.29(108)	2.362	1.722	1.347	6
$[Zn(S_2CNMe_2)(C_7H_4NS_2)_2]^-$	4	75.10(8)	117.5(5)	2.408	1.716	1.342	8
$[Zn(S_2CNEt_2)_2]_2$	4[b]	75.78(22)[d]	117.8(8)	2.378	1.727	1.33	7
$[Zn(S_2CNMe_2)_3]^-$	4[c]	73.71(7)[d]	116.8(4)	2.372	1.722	1.340	8
$[Zn(S_2CNMe_2)_2(py)]$	5	72.9(3)	118.3(3)	2.466	1.718	1.337	5
$[\{Zn(S_2CNMe_2)_2\}(\mu\text{-}OCOMe)]^-$	5	72.5(1) 72.8(1)	116.8(6) 116.8(6)	2.459	1.711	1.335	3
$[Zn(S_2CNMe_2)_2(C_7H_4NS_2)]^-$	5	71.60(11) 71.15(10)	116.8(5) 118.1(6)	2.502	1.710	1.332	8
$[(phen)Zn(S_2CNBu_2)_2]$	6	70.8(1)	117.9(8)	2.523	1.705	1.324	this work

[a] It has been suggested that the coordination number is essentially 5 due to the additional presence of a very long (3.306 Å) Zn–S bond in the dimer [8] but the comparison presented here both in terms of the SZnS angles and Zn–S distances suggest that four-coordination is the better description. [b] Additional long Zn–S bond at 2.815 Å. [c] Two additional long Zn–S bonds at 3.115 and 3.151 A.Thus in both [b] and [c] a coordination number >4 could be envisaged but the comparison of parameters leads these authors to believe four-coordination is an adequate description. [d] Bond angle for bidentately bonded ligands only.

this six-coordinate complex and this follows the decreasing trend in size of this angle as the coordination number increases. As the S–C–S angle remained essentially the same in all four neutral compounds listed the reduction in the S–Zn–S angle necessitates either longer Zn–S or shorter C–S bonds or both and it is clear from Table 3 that both parameters are affected. There are considerable differences between both the pairs of Zn–S and also the S–C bonds and it is interesting to note that the shorter of the Zn–S bonds (2.516(4) compared to 2.530(4) Å) is associated with the longer S–C distance (1.723(15) *versus* 1.688(13) Å). The indication is that the dithiocarbamate ligand is asymmetrically linked to zinc. However, some caution has to be taken with such an interpretation for the sets of Zn–S and S–C bonds are not in fact significantly different due to the large errors associated with the atomic positions. The Zn–S distances in [(phen)Zn($S_2CNBu_2)_2$] are longer than those of the other zinc dithiocarbamates compared in Table 3 also reflecting the increasing coordination number of the metal.

The C–N distances as in the other dialkyldithiocarbamate complexes confirm a considerable double bond character, in keeping with the infrared spectroscopic data. This would reflect a significant contribution made by the canonical form below as discussed by Bonamico *et al.* [15].



The Zn–N distance (2.218(10) Å is longer than in five-coordinate (py)Zn($S_2CNMe_2)_2$ (2.079(6) Å) [5] and in (phen)$ZnCl_2$ (2.050(7), 2.072(7) Å) [16] and the N–Zn–N′ angle (73.9(1)°) is smaller than in the chloride analogue (80.4(3)°) [16] reflecting the higher coordination number of the metal, the larger

TABLE 4. Thermal Characteristics (20–600 ℃) for [Zn($S_2CNR_2)_2$L] (R = Me, Et, Bu, $PhCH_2$)

Complex	Temperature (℃)	Mass Loss (%)	
Zn($S_2CNMe_2)_2$(bipy)	144–242	35.6	required for bipy, 33.8%
	242–326	60.4	required for Zn($S_2CNMe_2)_2$, 66.2%
Zn($S_2CNEt_2)_2$(bipy)	120–235	34.2	required for bipy, 30.2%
	235–348	64.6	required for Zn($S_2CNEt_2)_2$, 69.8%
Zn($S_2CNBu_2)_2$(bipy)	127–224	25.3	required for bipy, 24.8%
	224–340	74.5	required for Zn(S_2CNBu_2), 75.2%
Zn($S_2CN(CH_2Ph)_2)_2$(bipy)	179–283	21.1%	required for bipy, 20.4%
	283–370	63.6	residue at 500 °C, 15.3% (required for ZnS, 16.0%)
Zn($S_2CNMe_2)_2$(phen)	157–434	70.6	
Zn($S_2CNEt_2)_2$(phen)	247–339	88.0	
Zn($S_2CNBu_2)_2$(phen)	206–420	85.6	residue 14.4% (required for ZnS, 14.9%)
Zn($S_2CN(CH_2Ph)_2)_2$(phen)	207–413	75.5	
Zn($S_2CNMe_2)_2$(DMP)	200–258	44.2	
	381–476	3.4	
	519–600	25.8	
Zn($S_2CNEt_2)_2$(DMP)	195–503	56.4	
Zn($S_2CNBu_2)_2$(DMP)	190–303	53.9	
	303–381	8.0	
Zn($S_2CN(CH_2Ph)_2)_2$(DMP)	220–347	64.0	
	349–403	2.6	
Zn($S_2CNMe_2)_2$(TMP)	100–173	12.1	
	250–465	34.7	
Zn($S_2CNEt_2)_2$(TMP)	240–373	43.9	
Zn($S_2CNBu_2)_2$(TMP)	200–320	52.6	
Zn($S_2CN(CH_2Ph)_2)_2$(TMP)	220–303	39.3	

size of the dithiocarbamate ligand compared to chloride and the fact that the monodentate pyridine ligand may get close to zinc whereas to enable the rigid bidentate phenanthroline ligand to coordinate to zinc longer bonds are needed.

The molecular parameters for the alkyl groups and the phenanthroline ligand are unexceptional. The thermal behaviour of the sixteen complexes are detailed in Table 4. The 2,2′-bipyridyl complexes decompose with one exception by loss of ligand followed closely by evaporation of the zinc dialkyldithiocarbamate. For the benzyl compound 2,2′-bipyridyl is lost between 179 and 283 °C followed by a second mass loss of 63.6% between 283 and 370 °C to leave a residue of 15.3% at 500 °C which corresponds closely to that required for zinc sulphide (16.0%). This intermediate mass loss could correspond to loss of the tetra-alkylthiuram monosulphide $R_2NC(S)SC(S)NR_2$ ($R = PhCH_2$) similar to that proposed for the decomposition of $Sn(S_2CNR_2)_4$ [17]. Alternatively, loss of $R_2NC(S)NR_2 + CS_2$ or $RSNR_2 + RNCS$ may take place and these have been found as two competing reactions in the decomposition of $Sn(S_2CNR_2)_2$ ($R = Et$) [18]. The 1,10-phenanthroline complexes are slightly more stable as evidenced by the temperatures at which onset of decomposition commences. The complexes decomposed in a single step leaving a significant residue at 500 °C. Only in the case of the butyl complex did the mass of residue (14.6%) correspond closely to that required for zinc sulphide (14.9%).

For the substituted phenanthroline complexes decomposition was more complex and well-defined decomposition steps were not obtained as the thermograms tended to drift towards increasing mass loss over quite considerable temperature ranges.

Experimental

Microanalyses were carried out by Elemental Microanalysis Limited. Thermal measurements were recorded using a Mettler TA 3000 thermal analyser. Samples were heated at a rate of 10 °C min^{-1} under a dynamic flow of nitrogen of 0.2 dm^3 min^{-1}. Infrared spectra were recorded as KBr discs using a Pye Unicam SP1000 spectrophotometer. Conductance measurements were carried out on dichloromethane solutions of the complexes using a Wayne Kerr bridge at 25 °C.

Reagents

$Zn(S_2CNR_2)_2$, R = Me (melting point (m.p.) 250 °C, lit. [19] 240–246 °C); R = Et (m.p. 178–179 °C, lit. [19] 177 °C); $R = Bu^n$ (m.p. 108 °C, lit. [19] (100 °C); $R = PhCH_2$ (m.p. 187–192 °C) were commercially available and were recrystallised from chloroform prior to usage. The ligands were commercially available and were used without further purification.

Preparation of Complexes

The complexes were prepared by adding a hot solution of the amine (0.05 mol) in methanol to a hot solution of zinc dialkyldithiocarbamate (0.01 mol) in dichloromethane except for $Zn(S_2CN(CH_2Ph)_2)_2(DMP)$ and $Zn(S_2CNMe_2)_2(TMP)$ which were prepared *in toluene* solutions. The resulting solution was cooled and then added to petroleum ether (boiling point 40–60 °C) to produce yellow precipitates which were filtered off and recrystallised from dichloromethane (bipyridyl complexes), methanol (phenanthroline complexes) or chloroform (substituted phenanthroline complexes). Analytical data, melting points, appearance and conductivity data are reported in Table 5.

Crystallographic Studies

A crystal of size 0.12 × 0.20 × 0.64 mm, suitable for X-ray work was mounted with the unique axis *c* coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using the background-ω scan-background technique with graphite monochromated Mo Kα radiation. Data were corrected for Lorentz and polarisation effects and 1891 unique reflections having $I/\sigma(I) \geqslant 3.0$ were used for subsequent analysis. The structure was solved via the heavy atom method and refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms other than C14, C15 and C24. Hydrogen atoms were included in ideal positions (C–H, 1.08 Å) and common isotropic temperature factors were applied to the aromatic and the CH_2 and CH_3 hydrogen atoms and were refined to final values of 0.093(4), 0.198(4) and 0.192(4) $Å^2$ respectively. Complex neutral-atom scattering factors [20] were employed throughout the refinement and a non-unit weighting scheme of the form $w = 1.2132/[\sigma^2(F_o) + 0.0032(F_o)^2]$ was adopted in the final stages of refinement. The final *R* values were $R = 0.069$ and $R' = 0.076$. All calculations were performed on a IBM 4341 computer using SHELX [21].

Crystal data

$C_{30}H_{44}N_4S_4Zn$, $M = 654.3$, orthorhombic, $a = 15.386(9)$, $b = 22.487(18)$, $c = 9.923(6)$ Å, $U = 3433.5$ $Å^3$, $F(000) = 1384$, space group *Pbcn* from systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h + k = 2n + 1$, $D_m = 1.26$, $D_c = 1.27$ g cm^{-3}, $Z = 4$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) 9.25 cm^{-1}.

Final atomic parameters are listed in Table 6.

TABLE 5. Appearance, Melting Points, Conductance and Analytical Data for Zinc Dialkyldithiocarbamate Complexes

Complex	Appearance	Analysis: found (calc.) (%)			Melting point (°C)	Molar conductance $\times 10^3$ ($sm^2\ mol^{-1}$)
		C	H	N		
$Zn(S_2CNMe_2)_2(bipy)$	pale yellow needles	41.32 (41.59)	4.24 (4.37)	11.64 (12.13)	230–232	0.56
$Zn(S_2CNEt_2)_2(bipy)$	pale yellow needles	47.39 (46.36)	5.35 (5.46)	10.86 (10.83)	175–176	0.59
$Zn(S_2CNBu_2)_2(bipy)$	pale yellow needles	53.16 (53.35)	7.10 (6.98)	8.71 (8.88)	136–137	0.46
$Zn(S_2CN(CH_2Ph)_2)_2(bipy)$	pale yellow needles	62.53 (62.70)	4.69 (4.77)	7.21 (7.30)	228–230	0.44
$Zn(S_2CNMe_2)_2(phen)$	pale yellow needles	45.20 (44.47)	4.07 (4.16)	11.34 (11.53)	262–263	1.88
$Zn(S_2CNEt_2)_2(phen)$	yellow needles	51.00 (48.73)	5.16 (5.21)	10.63 (10.34)	210–211	1.98
$Zn(S_2CNBu_2)_2(phen)$	bright yellow needles	55.07 (55.06)	6.65 (6.79)	8.56 (8.56)	185–186	1.28
$Zn(S_2CN(CH_2Ph)_2)_2(phen)$	pale yellow needles	62.84 (63.82)	4.57 (4.59)	6.90 (7.08)	230–231	[a]
$Zn(S_2CNMe_2)_2(DMP)$	yellow needles	46.32 (46.73)	4.67 (4.71)	10.54 (10.90)	210–212	0.007
$Zn(S_2CNEt_2)_2(DMP)$	yellow needles	50.22 (50.55)	5.73 (5.66)	9.77 (9.82)	199–202	0.011
$Zn(S_2CNBu_2)_2(DMP)$	yellow needles	55.61 (56.32)	7.19 (7.09)	8.09 (8.20)	130–132	0.026
$Zn(S_2CN(CH_2Ph)_2)_2DMP$	yellow needles	64.43 (64.57)	4.93 (4.93)	6.15 (6.84)	216–217	0.033
$Zn(S_2CNMe_2)_2(TMP)$	pale yellow needles	48.76 (48.75)	5.13 (5.21)	10.14 (10.33)	236–239	0.16
$Zn(S_2CNEt_2)_2(TMP)$	pale yellow needles	52.32 (52.20)	6.20 (6.07)	9.32 (9.36)	220–223	0.23
$Zn(S_2CNBu_2)_2(TMP)$	pale yellow needles	57.61 (57.49)	7.47 (7.38)	7.84 (7.88)	170–174	0.29
$Zn(S_2CN(CH_2Ph)_2(TMP)$	pale yellow needles	63.96 (65.28)	5.15 (5.24)	6.46 (6.62)	126–130	0.24

[a] Too insoluble for measurement of conductance.

TABLE 6. Final Fractional Coordinates ($\times 10^4$)[a]

Atom	x	y	z
Zn	0	1612(1)	2500
N(1)	548(7)	824(4)	1459(10)
C(2)	1126(9)	828(6)	445(13)
C(3)	1504(10)	308(7)	−73(13)
C(4)	1236(10)	−218(7)	369(14)
C(5)	625(9)	−265(6)	1442(13)
C(6)	299(7)	293(5)	1995(11)
C(7)	292(10)	−810(5)	2009(13)
S(1)	−37(3)	2272(2)	4548(4)

(continued)

TABLE 6 *(continued)*

Atom	x	y	z
S(2)	1511(2)	1680(2)	3494(4)
C(11)	1059(10)	2127(6)	4669(12)
N(2)	1526(9)	2363(5)	5655(11)
C(12)	1213(11)	2761(9)	6685(16)
C(13)	1366(14)	3421(8)	6235(21)
C(14)	1220(22)	3746(16)	7437(27)
C(15)	1326(23)	4371(16)	7020(26)
C(21)	2460(10)	2216(7)	5858(16)
C(22)	2617(13)	1668(7)	6847(19)

(continued)

TABLE 6 *(continued)*

Atom	*x*	*y*	*z*
C(23)	3539(15)	1509(13)	6827(27)
C(24)	3651(15)	979(9)	7403(19)
H(2)	1293	1249	−7
H(3)	2017	332	−814
H(4)	1481	−622	−81
H(7)	562	−1220	1613
H(121)	527	2684	6836
H(122)	1557	2682	7617
H(131)	902	3548	5471
H(132)	2017	3487	5857
H(141)	584	3655	7847
H(142)	1710	3636	8175
H(151)	1230	4650	7892
H(152)	837	4471	6273
H(153)	1963	4452	6602
H(211)	2744	2111	4892
H(212)	2779	2602	6277
H(221)	2223	1298	6522
H(222)	2432	1795	7857
H(231)	3910	1852	7325
H(232)	3749	1471	5792
H(241)	4339	885	7349
H(242)	3294	627	6913
H(243)	3455	1008	8446

[a]e.s.d.s given in parentheses.

Supplementary Material

Thermal parameters, and observed and calculated structure factors are available from the authors on request.

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