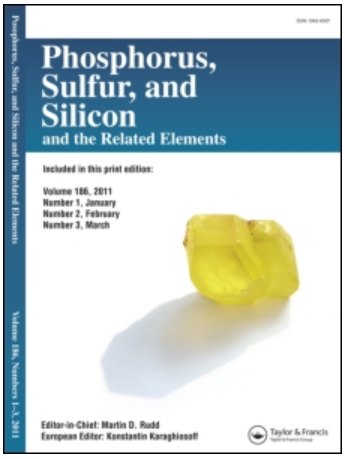

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Synthesis, Infrared Spectroscopic, and Cyclic Voltammetric Studies on 1,10-Phenanthroline and 2,2' -Bipyridine Adducts of Bis(4-morpholinecarbodithioato-S,S')zinc(II) and Single-Crystal Structure Determination of (2,2' -Bipyridine)bis(4-morpholinecarbodithioato-S,S') zinc(II)

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Synthesis, Infrared Spectroscopic, and Cyclic Voltammetric Studies on 1,10-Phenanthroline and 2,2′-Bipyridine Adducts of Bis(4-morpholinecarbodithioato-S,S′)zinc(II) and Single-Crystal Structure Determination of (2,2′-Bipyridine)bis(4-morpholinecarbodithioato-S,S′) zinc(II)

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*(1,10-Phenanthroline)bis(4-morpholinecarbodithioato-S,S′)zinc(II), [Zn(mdtc)$_2$(1,10-phen)] (**1**) and (2,2′-bipyridine)bis(4-morpholinecarbodithioato-S,S′) zinc(II), [Zn(mdtc)$_2$(bipy)] (**2**) adducts were prepared, and the crystal structure of **2** is reported. The Zn-S distances in **2** are longer than those in [Zn(dtc)$_2$](dtc = dithiocarbamate) complexes. The acceptance of an additional neutral ligand by the tetrahedral dithiocarbamato complex of zinc to form an octahedral adduct causes an increase in the Zn-S bond lengths and a consequent lowering of the S-Zn-S bite angle. The cyclic voltammetric study on the complexes shows an increase of electron density on the central metal ion in the adducts compared to Zn(mdtc)$_2$. The use of HMDE as a working electrode in the CV studies indicate the involvement of Hg in complex formation, which is otherwise absent with a platinum working electrode. The thioureide C-N distance of 1.330 (**4**) Å in compound **2** is in line with the ν_{C-N} observed at 1465 cm^{-1}.*

Keywords Crystal structure; cyclic voltammetry; IR spectrum; 1,10-phenanthroline/2,2′-bipyridine/morpholinecarbodithioato complex; Zn(II)

INTRODUCTION

Group XII dithiocarbamates represent a large and interesting class of inorganic compounds.[1,2] The materials are used in a wide number of

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diverse applications, which include their role as additives to pavement asphalt,[3] in analytical determinations,[4,5] and as potent biological pesticides and/or pharmaceuticals, e.g., Ziram.[6–8] Zinc dithiocarbamates are also useful for the design of metal complexes, and for use as selective binding agents for the inclusion of "guest" species.[9–12] In addition, zinc dithiocarbamates (in combination with amines) act as effective radical scavenging agents for high thermal stress industrial lubricants—an additional role of such a complex is to engender high thermal stability characteristics to the resulting lubricant composite.[13,14] As a part of an investigation of dithiocarbamate complexes,[15,16] in this article we describe the synthesis, IR spectroscopic, and cyclic voltammetric studies on [Zn(mdtc)$_2$(1,10-phen)] and [Zn(mdtc)$_2$(bipy)] and the crystal structure of [Zn(mdtc)$_2$(bipy)].

RESULTS AND DISCUSSION

IR Spectroscopic and Thermogravimetric Studies

The C-N stretching bands in the complexes are given in Table I. The ν_{C-N} has been used as a measure of the thioureide form of the ligands to the complexes.[17] IR spectra of the complexes (**1**) and (**2**) show ν_{C-N} bands at 1461 and 1465 cm^{-1}, respectively. The shift in ν_{C-N} bands to lower frequencies compared to the parent dithiocarbamate is due to the change in coordination geometry from tetrahedral to octahedral.[18] The ν_{C-S} bands appear around 1000 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety.[17] However, ring frequencies associated with 1,10-phenanthroline and 2,2′-bipyridine are observed in the range of 1600–1000 cm^{-1}. In the present study, 1,10-phenanthroline adduct shows two bands at 1621 and 1512 cm^{-1}, whereas 2,2′-bipyridine adduct shows a prominent band at 1595 cm^{-1}. Other bands are masked by those due to dithiocarbamate ligands.

TABLE I IR Spectral and Cyclic Voltammetric Data

	IR (cm^{-1})		
Compound	ν_{C-N}	ν_{C-S}	Cyclic voltammetric data (V) E_p^{red}
Zn(mdtc)$_2$	1489	995	–1.150[a]
[Zn(mdtc)$_2$(1,10phen)]	1461	999	–1.500[b]
[Zn(mdtc)$_2$(bipy)]	1465	999	–1.625[c]

Other redox couples: [a]0.800/–0.700 and $E_p^{Ox} = 0.350$; [b]1.150/–0.750; [c]1.250/–0.850.

The thermogravimetric studies on the complexes were performed to confirm the stoichiometry of the complexes. The final product of thermal decomposition was ZnS in all the complexes. The 2,2′-bipyridine adduct decomposes by loss of 2,2′-bipyridine ligand followed by decomposition of dithiocarbamate moiety. In the case of 1,10-phenanthroline adduct, the dithiocarbamate moiety also starts to decompose concertedly.

Cyclic Voltammetric Studies

In the case of $Zn(mdtc)_2$, the CV response at –1.150 V corresponds to a two-electron reduction process with the formation of Zn(Hg).

$$Zn(mdtc)_2 + 2e^- \overset{Hg}{\rightarrow} 2mdtc^- + Zn(Hg) \quad (1)$$

The response at –0.350 V for $Zn(mdtc)_2$ complex is due to the oxidation of Zn(Hg)

$$Zn(Hg) \rightarrow Zn^{2+} + 2e^- + Hg \quad (2)$$

The redox couple around –0.800/ –0.700 V is ascribed to the reaction:

$$mdtc - + 1/2Hg \rightleftharpoons 1/2Hg(mdtc)_2 + e^- \quad (3)$$

Such a response is absent when using a platinum electrode. Therefore, the present study completely falls in line with the earlier observations.[19,20]

In the cases of [$Zn(mdtc)_2$(1,10-phen)] and [$Zn(mdtc)_2$(bipy)], the first redox couples are observed at –1.150/–0.750 V and –1.250/–0.850 V, respectively. The redox couple does not appear unless a hanging mercury drop electrode (HMDE) is used for the CV studies. The response is totally absent when a platinum electrode is used. Therefore, the redox couple must be due to an electroactive species produced as a result of the interaction of Hg with other species.

The CV responses at –1.500 and –1.625 V for [$Zn(mdtc)_2$(1,10-phen)] and [$Zn(mdtc)_2$(bipy)] complexes correspond to two electron addition processes.

$$[Zn(mdtc)_2(N, N)] + 2e^- \rightleftharpoons [Zn(mdtc)_2(N, N)]^{2-} \quad [(N, N) = 1, 10 - \text{phen, bipy}] \quad (4)$$

Controlled potential electrolysis could not be carried out because the response was observed very close to the solvent decomposition

potential. But a comparison of the current per-unit concentration of the complex with that of the parent dithiocarbamate indicates the nature of the reduction to be a two-electron process.

The absence of the reduction response around –0.800 V in both the adducts indicates that the exchange of zinc with mercury does not takes place as is observed in the case of parent dithiocarbamate. Also, the absence of the response at –0.350 V in the oxidative scan for both the adducts indicates the absence of Zn(Hg) formation.

The most important outcome of the observations is that in both of the adducts, the electron addition process becomes more difficult compared to the parent bisdithiocarbamate complex. This fact is supported by the very large shift in reduction potential of the adducts compared to the parent bisdithiocarbamate. The observation clearly indicates excess electron density on zinc in the adducts compared to the parent dithiocarbamate, which makes the electron addition more difficult in the former.

Structure Analysis

An ORTEP plot of [Zn(mdtc)$_2$(bipy)] is shown in Figure 1. Selected bond distances and angles are given in Table II. The structure of [Zn(mdtc)$_2$(bipy)] contains four discrete monomeric units per unit cell. Zinc is hexa-coordinated with four sulfur atoms from the chelating dithiocarbamate groups and two nitrogen atoms from the chelating bipyridine. Selected molecular parameters for related zinc compounds are given in Table III. The small bite of the dithiocarbamate groups forces a small S-Zn-S angle in all the related complexes. In particular, in the present compound, the bite angle is as low as 71.6(1) degrees, indicating the effect of hexa-coordination around zinc. A reduction in S-Zn-S angle in the present compound has not affected the S-C-S angle and C-S distance when compared with similar compounds listed in Table III. However, there has been only a very significant increase in the Zn-S distance. The Zn-S distances in [Zn(mdtc)$_2$(bipy)] are longer than the other zinc dithiocarbamates. The presence of an additional neutral ligand causes an increase of the Zn-S bond lengths. There is a considerable difference between the pairs of Zn-S bonds [2.490(1) and 2.547(1) Å].

However, the C-S bond distances are symmetric [C(1)-S(1) 1.722(3) and C(1)-S(2) 1.724(3) Å]. The average C-N bond distance is 1.330(4) Å, which clearly indicates the contribution of the thioureide form to the dithiocarbamate ligand. This contrasts well with the adjacent typical single bonded N-C distance [mean 1.475(6) Å]. The Zn-N

TABLE II Selected Bond Distances (Å) and Angles (°) for $[Zn(mdtc)_2(bipy)]$

Zn1–S1	2.490(1)	S1–C1	1.722(3)
Zn1–S2	2.547(1)	S2–C1	1.724(3)
Zn1–N8	2.215(3)	C1–N2	1.327(4)
Zn1–S1′	2.486(1)	S1′–C1′	1.722(3)
Zn1–S2′	2.540(1)	S2′–C1′	1.717(3)
Zn1–N8′	2.205(3)	C1′–N2′	1.333(4)
S1′–Zn1–S2′	71.6(0)	S1′–C1′–S2′	117.5(1)
N8–Zn1–N8′	73.9(1)	S1–C1–S2	117.5(1)
S1–Zn1–S2	71.6(0)		

distance [2.210(3) Å] is longer than that found in a five-coordinate $[Zn(S_2CNMe_2)_2(py]$ complex (2.079(6) Å)[21] due to the increased steric effect of bipyridyl on zinc. The fact that the monodentate pyridine ligand may get closer to zinc compared to the bidentate bipyridine ligand is responsible for the lengthening of Zn-N bond. The bipyridine molecule

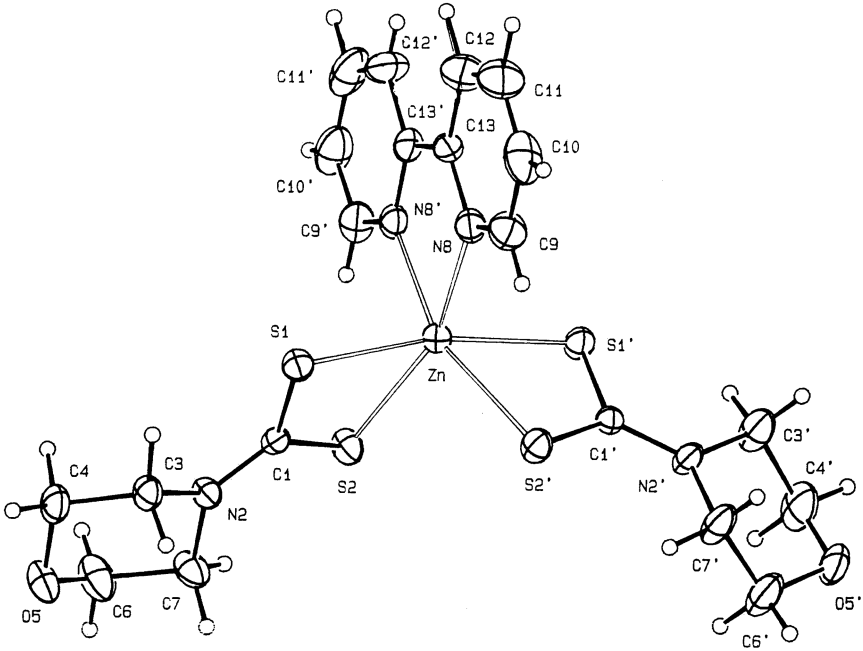

FIGURE 1 ORTEP plot of $[Zn(mdtc)_2(bipy)]$ complex showing the labeling of the non-H atoms.

TABLE III Comparative Molecular Parameters for Zinc Dialkyldithiocarbamates and Their Adducts

Compound	Coordination number	S-Zn-S	S-C-S	Zn-S	C-S	S_2C-N	Ref.
$[Zn(S_2CNMe_2)_2]_2$	4[a]	76.34 (2)	117.29 (1.08)	2.362	1.722	1.347	22
$[Zn(S_2CNEt_2)_2]_2$	4[a]	75.8 (2)	117.8 (8)	2.378	1.727	1.330	23
$[Zn(S_2CNMe_2)\ (C_7H_4NS_2)_2]^-$	4	75.10 (8)	117.5 (5)	2.408	1.716	1.342	24
$[Zn(S_2CNMe_2)py]$	5	72.9 (3)	118.3 (3)	2.466	1.718	1.337	25
$[Zn(S_2CNMe_2)_2$	5	72.5 (1)	116.8 (6)	2.459	1.711	1.335	26
$(\mu\text{-OCOMe})]^-$		72.8 (1)	116.8 (6)				
$[Zn(mdtc)_2(bipy)]$	6	71.6 (1)	117.5 (1)	2.516	1.721	1.330	This work

[a]It has been suggested that the coordination number is essentially 5 due to the presence of very long Zn-S bond in the dimer but the comparison presented here both in terms of the S-Zn-S angles and Zn-S distances suggest that four coordination is a better description.

is almost perfectly planar. The C-C and C-N bond distances associated with the morpholine ring are normal. The morpholine rings are in the regular chair form.

EXPERIMENTAL

Synthesis of the Complex 1 and 2

The bis(4-morpholinecarbodithioato-S,S′)zinc(II) was prepared using an established procedure.[26] A suspension of [Zn(mdtc)$_2$] (1 mmol) in chloroform was added to a hot solution of 1,10-phenanthroline (2 mmol) or 2,2′-bipyridine (2 mmol) in ethanol. The resulting yellow solution was left to evaporate at room temperature. After two days yellow crystals of the adducts separated out. The compounds were analyzed to the proposed formulas.

Physical Measurements

IR spectra were recorded on a JASCO IR-700 spectrophotometer (range 4000–400 cm^{-1}) as KBr pellets. STA 1500 PL thermal sciences instrument was used for thermogravimetric analysis. The heating rate of the furnace was fixed at 10°C per minute.

A bioanalytical system 100 electrochemical analyzer was used for all measurements, platinum and HMDE were used as working electrodes, the counter electrode was platinum wire, and the reference electrode was Ag/AgCl. The supporting electrolyte was tetrabutylammonium perchlorate. The experimental solution was thermostated at 28 ± 1°C in an oxygen-free atmosphere provided by bubbling nitrogen through the solution.

X-Ray Crystallography

Data was collected at 293 (2) K, using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71069 Å), with Philips PW 1100 diffractometer. Cell parameters were obtained from 42 reflections. The structure was solved by direct methods with the SIR 92 program[27] and refined by full matrix least squares with SHELX 93.[28] All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. Crystal data, collection procedures, and refinement results are summarized in Table IV.

Tables containing complete information on atomic coordinates and equivalent isotropic parameters, full intramolecular bond distances and angles, anisotropic thermal parameters, and fractional coordinates

TABLE IV Crystallographic and Structural Parameters for [Zn(mdtc)$_2$(bipy)]

Empirical formula	$C_{20}H_{24}N_4O_2S_4Zn$
Formula weight	546.05
Crystal dimensions (mm^3)	$0.19 \times 0.21 \times 0.32$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å, °)	$a = 12.181(2)$, $b = 11.862(3)$, $c = 16.373(2)$, $\alpha = \beta = \gamma = 90$
Cell volume (Å^3)	2365.7
Z	4
Calculated density (g cm^{-3})	1.5331
Absorption coefficient, μ (cm^{-1})	1.42
$F(000)$	1128
2θ range, deg	3-28
Index ranges	$-16 \leq h \leq 16$, $0 \leq k \leq 15$, $0 \leq l \leq 21$
Reflections collected	6162
Observed reflections	3497
Weighting scheme	$W = A/(\sigma^2F^2 + BF^2)$; $A = 1$, $B = 0.0321$
Number of parameters refined	377
R	0.029
Rw	0.059
GOF	0.883
Largest feature final diff. map (eÅ^{-3})	0.33

of hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDC 634475. Copies of the data can be obtained free of charge upon application to The Director CCDC, 12 Union Road, Cambridge CB2 IEZ, UK.

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