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A Novel Dimeric Zinc Complex: Bis{μ-[(dimercaptomethylene)propanedinitrilato-*S,S′*]}-tetrakis(4-methylpyridine)dizinc(II)−Chloroform

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Introduction

In recent years, zinc complexes containing S_4, S_3N, or S_2N ligand cores have attracted more and more attention due in part to their ability to act as structural models for the immediate ligand environment of zinc in DNA-binding proteins and certain zinc-containing enzymes. For example, it has been suggested recently that Zn(cysteine-*S*)$_2$(histidine)$_2$ is the active center of the transcription factor IIIA.[1] On the other hand, some volatile zinc thiolato and nitrogen-containing ligand complexes are important MOCVD precursors for zinc sulfide semiconducting materials[2] that are widely used as phosphors, long-wavelength windows, and catalysts.[3] A particular dithiolato ligand, 1,1-dicyanoethylene-2,2-dithiolate, commonly called isomaleonitrile dithiolate (i-MNT), has recently received considerable attention in new organic conductor explorations.[4,5] A perusal of the literature has showed that there is an extensive ligand chemistry of i-MNT covering the synthesis and structural investigations of its transition and non-transition metal complexes and their reaction products with a variety of Lewis bases.[6] Like most bidentate complexes containing dithiolates such as dithiocarbamate, dialkyl dithiophosphate, and carbonadithioate, the reaction of M(i-MNT) (M = Zn, Cd, Hg) compounds with Lewis bases often reduces the original polymeric structures to monomeric adducts.[7] Thus far no planar metal(II) complex has been found to contain μ-bridging bidentate dithiolate ligands after the effective formation of nitrogen-base adducts. However, we have found that zinc isomaleonitrile dithiolate reacts with 4-methylpyridine to yield a zinc dimer containing the eight-membered $Zn_2S_4C_2$ ring. The formation of such a novel dimer is attributable to the ability of the dithiolato ligand to maintain the μ-bridging bonding mode even after the adduct is formed. We report here the synthesis and X-ray crystal structure of bis{μ-[(dimercaptomethylene)propanedinitrilato-*S,S′*]}tetrakis(4-methylpyridine)dizinc(II)−chloroform, Zn_2(i-MNT)$_2$(4-mpy)$_4$·$CHCl_3$ (**1**).

Experimental Section

Synthesis of 1. Zinc chloride, 0.20 g (1.47 mmol), was dissolved in 20 mL of absolute ethanol to form a clear solution, which was added dropwise to a 20-mL EtOH and $CHCl_3$ solution containing 0.32 g (1.47 mmol) of [(dimercaptomethylene)propanedinitrilato-*S,S′*]dipotassium (K_2(i-MNT)). A yellow precipitate of Zn(i-MNT) was formed.[7] To the yellow suspension was slowly added 2 mL of 4-methylpyridine (4-mpy). The colorless needle-shaped single crystals suitable for X-ray structure determination were obtained after the solution was evaporated at room temperature for 2 weeks. The product for elemental analysis was filtered off, washed with water and ethanol, and dried in vacuum (0.34 g, 60% yield based on $ZnCl_2$; if the 4-methylpyridine is increased to 10 mL, the yield may reach 85%). Anal. Calcd for $Zn_2S_4N_8C_{32}H_{28}$: C, 49.01; H, 3.57; N, 14.30. Found: C, 48.86; H, 3.60; N, 14.63. IR (KBr, Nujol mull): 3066 (w), 2202 (s), 1508 (m), 1409 (s), 1214 (m), 1031 (s), 941 (s), 867 (m), 808 (s), 759 (s), 356 (s), 309 (w), 277(vs), 234 (m), 200 (s) and 182 (w) cm.$^{-1}$ X-ray photoelectron spectroscopy gave binding energies (eV) for Zn_{2p} (1027.0), S_{2p} (167.2), N_{1s} (404.0), and C_{1s} (289.80).[7] ^{1}H NMR spectral data for **1** (pyridine-d_5, C_5ND_5 solution): 8.61 (s, 2H, *o*-py), 7.04 (s, 2H, *m*-py), and 2.21 (s, 3H, CH_3). The colorless crystals lose a $CHCl_3$ solvent molecule rapidly and turn to an opaque pale-yellow solid which is stable in air.

Crystallographic Analysis. A colorless needle-shaped single crystal with the approximate dimensions of 0.20 × 0.20 × 0.18 mm was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at room temperature using the $\omega-2\theta$ scan technique. Cell parameters and an orientation matrix for data collection were obtained from the least-squares refinement using the setting angles of 25 reflections in the range of $27.16° \le 2\theta \le 29.86°$. A total of 3924 independent reflections ($R_{int} = 0.027$) were measured in the range of $0° \le 2\theta \le 50°$ ($h = 0-15$, $k = -10$ to 0, $l = -20$ to $+20$), of which 2842 with $I > 3\sigma(I)$ were used in the refinement of the structure. No significant intensity decay of three standard reflections recorded after every 300 reflections was observed. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on a series of ψ-scans with minimum and maximum correction coefficients 0.9173 and 1.000, respectively, was applied.[8]

The structure was solved by direct methods using MITHRIL.[8] The heavy atom Zn was located in an *E* map, and the remaining non-H atoms were located using DIRDIF.[9] H atoms were placed in geometrically calculated positions (C−H = 0.95 Å) and were included in the structure factor calculations but not refined. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all atoms. All calculations were performed on a VAX3100 computer using the TEXSAN program package.[10] The maximum and minimum peak values in the final difference Fourier map are 0.70 and −0.80 e/Å^3, respectively. Crystal data and data collection parameters are summarized in Table 1, while selected bond distances and angles are listed in Table 2.

Results and Discussion

The elemental analyses, IR, XPS, and ^{1}HNMR indicated that the reaction of Zn(i-MNT) with 4-methylpyridine gave a new

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Table 1. Summary of Crystallographic Data for $[Zn_2(i\text{-}NMT)_2(4\text{-}mpy)_4\cdot CHCl_3]$

formula	$C_{33}Cl_3H_{29}N_8S_4Zn_2$	Z	2
fw	903.00	μ(Mo Kα), cm^{-1}	16.10
space group	$P2/c$	ρ(calcd), gcm^{-3}	1.45
a, Å	13.372(2)	F(000)	916
b, Å	9.198(3)	T, K	296
c, Å	16.872(2)	GOF	1.56
β, deg	93.93(1)	R,^{a} %	4.5
V, Å^3	2070.4(7)	R_w,^{b} %	6.0

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Zn_2(i\text{-}NMT)_2(4\text{-}mpy)_4\cdot CHCl_3]^a$

Distances (Å)			
Zn−N(3)	2.077(3)	Zn−N(4)	2.035(4)
Zn−S(1)	2.317(1)	Zn−S(2)*	2.321(1)
S(1)−C(1)	1.746(4)	S(2)−C(1)	1.724(4)
N(1)−C(3)	1.131(6)	N(2)−C(4)	1.133(7)
Angles (deg)			
N(3)−Zn−N(4)	103.8(1)	S(1)−Zn−S(2)*	110.80(5)
S(2)*−Zn−N(3)	96.7(1)	S(2)*−Zn−N(4)	122.6(1)
S(1)−Zn−N(3)	106.7(1)	S(1)−Zn−N(4)	113.3(1)
C(1)−S(1)−Zn	102.8(1)	C(1)*−S(2)*−Zn	104.3(2)
S(1)−C(1)−S(2)	119.5(3)	S(1)−C(1)−C(2)	120.5(3)
S(2)−C(1)−C(2)	119.8(3)	C(3)−C(2)−C(4)	115.7(4)

^{a} An asterisk indicates the symmetry code $-x, y, -z$.

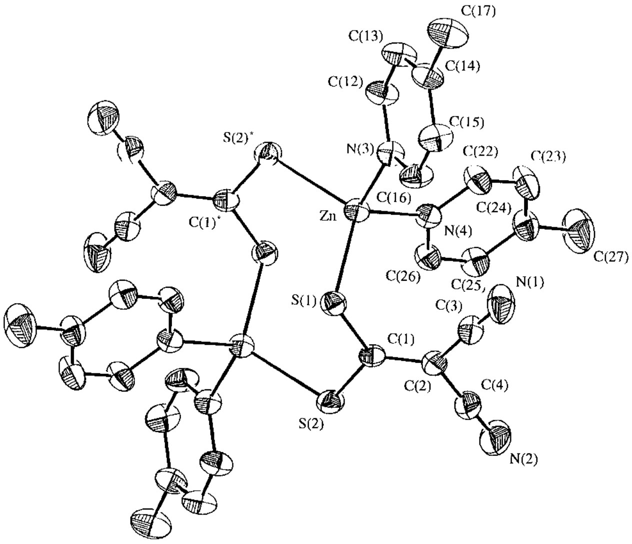

Figure 1. ORTEP representation (30% probability thermal ellipsoids) of $[Zn_2(i\text{-}NMT)_2(4\text{-}mpy)_4\cdot CHCl_3]$ with the numbering scheme. Symbols on the figure correspond to the symmetry code $-x, y, -z$.

adduct. In the IR spectra of **1** the diagnostic absorption band of $\nu_{C\equiv N}$ (2202 cm^{-1}) was observed in good agreement with that of M(i-MNT) (M = Zn, Cd, and Hg).[7] Similarly, a band at 941 cm^{-1} with a very weak shoulder at 976 cm^{-1} also appeared in **1**, suggesting that the bidentate dithiolate may adapt a μ-bridging mode which is commonly found in the polymeric structure of Zn(i-MNT). This was confirmed later in the crystal structure determination. Moreover, the ν_{Zn-N} (356 and 309 cm^{-1}) and ν_{Zn-S} (277 and 234 cm^{-1}) modes were found in **1** in accord with those in Zn(en)(i-NMT).[7] In the ^{1}H NMR of **1**, three group signals at 8.61, 7.04, and 2.12 ppm were observed in agreement with the structure of **1**. The crystal lattice of **1** consists of dimeric $(Zn_2(i\text{-}MNT)_2(4\text{-}mpy)_4$ units and solvent $CHCl_3$ molecules. In $(Zn_2(i\text{-}MNT)_2(4\text{-}mpy)_4$, two dimercaptopropanedinitrilato ligands each bridge two zinc atoms to form an eight-membered $Zn_2S_4C_2$ ring, while two 4-mpy molecules coordinate to a zinc atom to complete the local tetrahedral geometry for the metal ion. Figure 1 shows an ORTEP representation of **1**. In contrast, the adduct formation of $Zn_2(SCNEt_2)_4$,[7] $Zn_2[(CH_3)S_2C_2Ph_2)_4$,[7] and $Ni_2[S_2P(OEt)_2]_4$[7] destroys the original dimeric structures and the dithiolate μ-bridging mode disappears to yield a monomeric adduct.[7,11] Moreover, the two-dimensional $Zn_2(S_2COEt)_2$ network also reacts with pyridine to give a monomeric adduct.[12] It is worth noting that, in all the M(II) metal complexes formed with the divalent anionic bidentate ligands such as 4,5-dimercapto-1,3-dithiole-2-thionate, 6,7-dihydro-5*H*-1,4-dithiepin-2,3-dithiolate, and dithiooxoalate, as well as (i-NMT)$^{2-}$, the two sulfur atoms from each ligand are chelated to only one metal atom to form nearly planar structures.[13] It is therefore surprising that the i-NMT ligand in **1** maintains the μ-bridging mode and coordinates to two metal atoms to form a dimeric structure. To the best of our knowledge, this is the first metal(II) μ-bridging dithiolato structure with the effective formation of a base adduct. The Zn−N bond lengths are comparable with those of 2.064(3), 2.045(4), and 2.057(6)−2.037(6) Å found in other zinc complexes with tetrahedral coordination such as $Zn(S_6)(py)_2$,[14] $Zn(S_6)(N\text{-}Melm)_2$,[15] and $Zn(s\text{-}2,3,5,6\text{-}Me_4C_6H_2)_2(1\text{-}Me\text{-}imid)_2$,[1] respectively. Similarly, no significant difference of the Zn−S bond distances is observed compared with $Zn(S_6)(py)_2$,[14] (2.286(1) Å), $Zn(S_6)(N\text{-}Melm)_2$[15] (2.317) Å), and $Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H_2)_2(1\text{-}Me\text{-}imid)_2$[1] (2.301(2)−2.298(2) Å). However, the Zn−N bond lengths are slightly shorter than those found in $C_{40}H_{34}N_2S_4Zn\cdot 0.5CH_2Cl_2$ (2.090(7)−2.104(8) Å)[7] and $(phen)Zn(S_2CNBu_2)_2$ (2.218(1) Å),[11] probably due to the zinc atom in the latter being in a distorted square pyramidal and octahedral environment, while the Zn−S bond distances in **1** are also shorter in comparison with those in $(phen)Zn(S_2CNBu_2)_2$[11] (2.516(4)−2.530(4) Å). It is noteworthy that the dimeric structure of **1** is quite different from those of $[MeZnSCNEt_2]_2$[16] and $[Zn(S_2CNEt_2)_2]_2$[7] in which each dithiocarbamate chelates one zinc atom and bridges the next. The structure of **1** is reminiscent of that of the $Ni_2[S_2P(OEt)_2]_4$, which also exhibits a dimeric structure containing an eight-membered ring.[7] It should be pointed out that the $CHCl_3$ solvent molecule exhibits disorder and the atoms C(5), Cl(1), and Cl(2) have the fractional site occupancy factor of 0.5, respectively, while Cl(3) is equal to 0.3Cl(3) + 0.2Cl(3′) and the position of C(5) is located in the *f* site; i.e., equavalent points are ($^1/_2$, *y*, $^1/_4$) and ($^1/_2$, *y*, $^3/_4$).

In conclusion, unlike most of the planar metal(II) complexes formed as the reaction products with Lewis bases to yield the monomeric adducts with chelating dithiolato ligands, **1** forms an unprecedented dimer containing the eight-membered $Zn_2S_4C_2$ ring in which each of two (dimercaptomethylene)propanedinitrilato S atoms bridges two bis(4-methylpyridine)dizinc moieties even though an adduct has effectively been formed.

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Supporting Information Available: ^{1}H NMR and IR spectra for **1** (2 pages). An X-ray crystallographic file, in CIF format, for **1**·$CHCl_3$ is available. Access and ordering information is given on any current masthead page.

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