APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 86–87
Main Group Metal Compounds
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.525

Crystallographic report

(2,2′-Bipyridyl)bis(ethanoldithiocarbamato)zinc(II)

M. Saravanan[1], K. Ramalingam[1]*, G. Bocelli[2] and A. Cantoni[2]

[1]Department of Chemistry, Annamalai University, Annamalainagar 608 002, India
[2]IMEM–CNR, Parco area delle Scienze, Parma 43100, Italy

Received 20 June 2003; Revised 23 June 2003; Accepted 24 June 2003

$Zn(meadtc)_2(2,2'\text{-bipy})$ is a ZnS_3N_2 chromophore with a distorted square pyramidal geometry. The IR band at 1002 cm^{-1} and the bond valence sum value of 1.98 confirmed the monodentate dithiocarbamate in coordination. The non-bonding Zn–S distance is 5.004(3) Å. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: dithiocarbamate; monodentate; adduct; thioureide band

COMMENT

Zinc, cadmium and mercury dithiocarbamates and their adducts with nitrogenous bases show interesting structural variations.[1] The zinc ion is in a distorted square pyramidal environment of two nitrogen atoms and three sulfur atoms around it in $Zn(meadtc)_2(2,2'\text{-bipy})$ (Fig. 1). The complex is monomeric in nature with two molecules per unit cell. The thioureide bond distance is 1.315(3) Å. The presence of relatively bulky and strongly coordinating 2,2′-bipyridyl along with dithiocarbamate in the adduct weakens one of the Zn–S bonds of the parent dithiocarbamate leading to the monodentate coordination. The non-bonding Zn(1)–S(23) distance is 5.004(3) Å. The non-bonding nature is well exemplified by the Zn(1)–S(21)–C(22)–S(23) torsion angle equivalent to −166.0°. The contribution of this bond to total valency quenching is only 0.000 38 (bond valence sum[2,3]). The values indicate the correctness of the structure determined and the formal oxidation state of zinc as +2. This report assumes importance in the light of the fact that attempts to crystallize the parent $Zn(meadtc)_2$ and other adducts have not been successful so far. The inter-ring bipyridyl C···C distances vary within the range 3.946–4.245 Å, indicating a near perfect stacking. The IR spectrum of the parent compound shows a strong band at 1540 cm^{-1} corresponding to the thioureide stretching. The adduct shows a very significant reduction in the thioureide stretching band value (1476 cm^{-1}). The observation is a clear indication of the reduced electron density distribution between the $(S_2)C–N$ bands in the adduct.

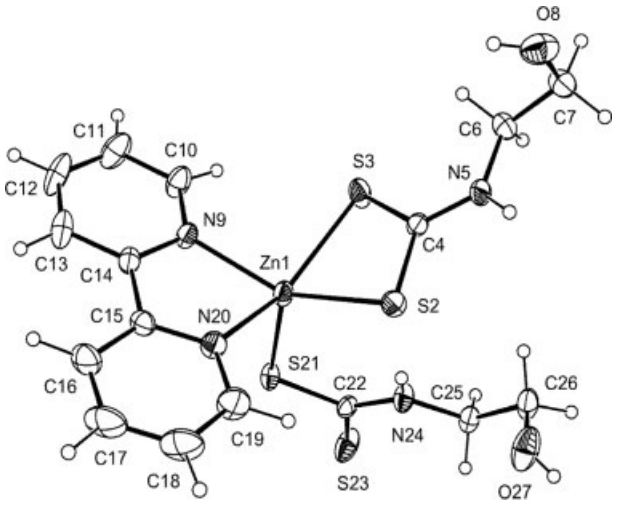

Figure 1. ORTEP view of $Zn(meadtc)_2(2,2'\text{-bipy})$. Key geometric parameters: Zn(1)–S(2) 2.4158(13), Zn(1)–S(3) 2.4982(9), Zn(1)–S(21) 2.3480(10), Zn(1)–S(23) 5.004(3), Zn(1)–N(9) 2.121(2), Zn(1)–N(20) 2.162(2) Å; N(9)–Zn(1)–N(20) 75.61(8), N(9)–Zn(1)–S(21) 100.42(7), N(20)–Zn(1)–S(21) 99.93(7), N(9)–Zn(1)–S(2) 142.90(7)°.

EXPERIMENTAL

A hot solution of 2,2′-bipyridine (2 mmol, 0.31 g) in ethanol was added to a hot solution of $Zn(meadtc)_2$ (2 mmol, 0.625 g) in benzene under constant stirring and the resultant yellow solution was filtered

*Correspondence to: K. Ramalingam, Department of Chemistry, Annamalai University, Annamalainagar 608 002, India.
E-mail: krauchem@yahoo.com

and kept for crystallization. After 2 days, yellow crystals along with some decomposed parent compound were obtained. The yellow crystals were washed with alcohol and were filtered out and dried in air. Anal. Found (calc.): (%)C, 37.90 (38.87); H, 3.55 (4.1); N, 10.80 (11.37). The parent compound shows a fusion temperature of 110 °C and the 2,2′-bipyridyl adduct shows a fusion temperature of 189 °C. The data were collected at room temperature on a programmed Philips PW 1100 single-crystal diffractometer. Crystal dimensions: $0.15 \times 0.22 \times 0.31$ mm^3, $C_{16}H_{20}N_4O_2S_4Zn$, $M = 493.97$, triclinic, $P\bar{1}$, $a = 9.237(2)$, $b = 14.316(2)$, $c = 8.510(3)$ Å, $\alpha = 95.45(3)°$, $\beta = 111.95(3)°$, $\gamma = 82.64(2)°$, V = 1033.8(5) Å^3, $Z = 2$, 2888 unique data ($\theta_{max} = 29.99°$) $R = 0.0304$, $R_w = 0.0653$, $\rho = 1.587$. Programs. SHELX-97;[4] CCDC deposition number: 207 364.

REFERENCES

1. Thirumaran S, Ramalingam K, Bocelli G, Cantoni A. *Polyhedron* 1999; **18**: 925.
2. Summers SP, Abboud KA, Carrah SR, Palanik GJ. *Inorg. Chem.* 1994; **33**: 88.
3. O'Keefe M, Brese NE. *J. Am. Chem. Soc.* 1991; **113**: 3226.
4. Sheldrick GM. SHELX-97 programs for crystal structure analysis (Release 97). University of Güottingen, Germany.