CUMENTATION PAGE

Form Approved
OMB No. 0704-0188

2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
6 May 1994	Technical Report

4. TITLE AND SUBTITLE
Structure of Di[bis(diethyldithiocarbamato) Zinc (II)] [μ-bis(Diethylphosphino)ethane] • 2 Toluene

5. FUNDING NUMBERS
N00014-91-J-1258
Matlsyn---01

6. AUTHOR(S)
D. Zeng and M. J. Hampden-Smith and
E. M. Larson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Departments of Chemistry and Chemical Engineering
Center for Micro-Engineered Ceramics
University of New Mexico
Albuquerque, NM 87131

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report No. 14

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. H. Guard and Dr. L. Kabikoff
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approval for public release; distribution unlimited

12b. DISTRIBUTION CODE
N00179

13. ABSTRACT *(Maximum 200 words)*

Di[bis(diethyldithiocarbamato)Zinc(II)][μ -bis(Diethylphosphino)ethane] •2 Toluene $(et_2NCSS)_2Zn]_2$ (μ-depe)• $2C_7H_8$ Mr = 1114.4, monoclinic, *P* $2_1/c$, a = 12.960(1), b = 11.311(2), c = 20.129(5), β = 96.46(1)°, V = 2932 Å^3, Z = 2, D_x = 1.254 g cm^{-3}, λ(Mo*K*α) = 0.070930 Å, graphite monochromator, μ = 11.89 cm^{-1}, F(000) = 1180, T = 298 K, final R = 0.055 (Rw = 0.072) for 2531 observed [I > 3σ(I)] reflections. The molecule is positioned symmetrically about an inversion center at the cell origin, which is situated in the center of the bridging diphosphine ligand. Toluene is disordered in this structure such that the rotation between the two positions of the methyl carbon is 36°. The geometry about the zinc can be described as distorted trigonal bipyramid. The Zn- P distance is 2.388 Å and the zinc-sulphur distances range from 2.320 to 2.653 Å .

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

OFFICE OF NAVAL RESEARCH

GRANT N00014-91-J-1258

R&T Code Matlsyn---01

Technical Report #14

Structure of Di[bis(diethyldithiocarbamato)Zinc (II)] [μ-bis(Diethylphosphino)ethane • 2 Toluene

by

D. Zeng, M. J. Hampden-Smith
and E. M. Larson

Department of Chemistry and Center for Micro-Engineered Ceramics

University of New Mexico

Albuquerque, NM 87131.

Structure of Di[bis(diethyldithiocarbamato) Zinc(II)] [μ- bis(Diethylphosphino)ethane] · 2 Toluene

BY D. ZENG and M. J. HAMPDEN- SMITH*

Department of Chemistry and Center for Micro- Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA

AND E. M. LARSON*

Department of Geology, University of New Mexico, Albuquerque, NM 87131, USA

Abstract. Di[bis(diethyldithiocarbamato)Zinc(II)][μ- bis(Diethylphosphino)ethane] ·2 Toluene, $[(Et_2NCSS)_2Zn]_2$ (μ- depe)· $2C_7H_8$) Mr = 1114.4, monoclinic, *P* $2_1/c$, *a*= 12.960(1), *b* = 11.311(2), *c* = 20.129(5), β= 96.46(1)°, V= 2932 Å^3, Z = 2, D_x = 1.254 g cm^{-3}, λ (MoKα) = 0.70930 Å, graphite monochromator, μ = 11.89 cm^{-1}, F(000) = 1180, T = 298 K, final R = 0.055 (Rw = 0.072) for 2531 observed [I > 3σ(I)] reflections. The molecule is positioned symmetrically about an inversion center at the cell origin, which is situated in the center of the bridging diphosphine ligand. Toluene is disordered in this structure such that the rotation between the two positions of the methyl carbon is 36°. The geometry about the zinc can be described as a distorted trigonal bipyramid. The Zn- P distance is 2.388 Å and the zinc- sulphur distances range from 2.320 to 2.653 Å.

*Authors to whom correspondence should be addressed.

Experimental. Single crystals of suitable quality for data collection were recrystallized from a toluene solution. The synthesis of this compound is described elsewhere (Zeng & Hampden-Smith). A colorless needle having the dimensions 0.2 x 0.2 x 0.4 mm was mounted in a 0.2 mm diameter sealed capillary tube containing mother liquor to prevent decomposition through loss of solvent. Rapid loss of solvated toluene otherwise occurs in open atmosphere. Cell dimensions were obtained by centering 45 reflections several times ($11 < 2\theta < 27°$). A quadrant of the reciprocal sphere with h= 0 - 14 , k= 0 - 12 , l= ± 0 - 22 , was collected by θ-2θ ($2\theta_{max}$ =45°) scans using a Kuma KM-4 diffractometer. Crystal decay was measured by monitoring 2 reflections every 50 data collected and showed a 40% decline in intensity. Corrections for absorption were made modeling a sphere having a radius of 0.1 mm (min. /max. correction = 0.8375/ 0.8380). Zinc was located using standard Patterson methods and the remaining atoms were found through successive difference fourier calculations. Iterative refinement of atomic positions and anisotropic thermal ellipsoids for all atoms except the disordered toluene, which was modeled with isotropic thermal factors, was performed using (GSAS) General Structure Analysis System (Larson & Von Dreele, 1990). Two toluene rings were modeled as rigid bodies with two positions for each carbon. All ring angles were constrained to be 120° and one methyl C-C and only one ring C-C distance were allowed to refine for both rigid bodies. The rotation angle between the two methyl groups refined to -35.98(0.56) °. The sum of the occupancies for the rings was fixed at 1.0, with final values of 0.454(24) and 0.546(24) for each ring. The function minimized was $Chi = w[Fo - Fc]^2$, with $w = (2Fo/\sigma Fo^2)^2$, where final residuals at convergence were R= 0.055 and wR= 0.072 and the last $\Sigma \Delta/\sigma = 0.0$. There were 232 variables refined for the 2531 observed [$I > 3\sigma(I)$] reflections. Hydrogen atoms were not placed. No correction for extinction was made. The sum of all rho values in a final fourier map was 0.292 electrons. Scattering factors were taken from the *International Tables for X-ray Crystallography* (1974,Vol. IV). Atomic positions and equivalent isotropic thermal factors are listed in Table 1, while selected distances and angles are shown in Table 2. Figure 1 presents an ORTEP (Johnson, 1976) drawing of the zinc compound.* Figure 2 is a packing diagram showing the relationship between the zinc complexes and the associated solvent molecules. Only one toluene ring is shown in this diagram for purposes of clarity.

Related Literature. The structure of the title compound (I) shows some similarity to that of the parent dimer (II), Bis(diethyldithiocarbamato) zinc(II) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). In the latter, one dithiocarbamate ligand bridges both zinc atoms of this dimeric complex, while the other type chelates to each Zn(II). A five coordinate, distorted

trigonal bipyramid environment for zinc results from the long (2.81 Å) sulphur bridge. The inversion center of the monoclinic cell lies in the center of the zinc dimer (II) between the bridging dithiocarbamate ligands. Upon introducing the diphosphine ligand, an expansion of the monoclinic cell is observed with a contraction of the beta angle. However the symmetry of the cell remains the same, P 2_1/c. Both dithiocarbamate ligands become chelating, whereupon the diphosphine bridges the zinc atoms and the inversion center lies between the phosphorous atoms. In the title complex, (I), the zinc coordination geometry remains similar to the parent compound and can be similarly represented by a distorted trigonal bipyramid.

* Lists of structure factors, anisotropic thermal parameters and a complete table of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. . Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference:]

Acknowledgment. MJH-S and DZ thank the office of Naval Research, Chemistry and Materials Research division for funding and the NSF Chemical Instrumentation program for the purchass of a Low-Field NMR spectrometer.

References

BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, pp. 898- 909.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL- 5138. Oak Ridge National Laboratory, Tennessee, USA

LARSON, A.C. & VON DREELE, R. B. (1990). *GSAS, General Structure Analysis System*, Report LAUR 86- 748. Los Alamos National Laboratory, New Mexico, USA

ZENG, D. & HAMPDEN- SMITH, M. J., *Inorg. Chem.*, In preparation

Table 1. Atomic Positions in Fractional Coordinates

Name	X	Y	Z	Ui/Ue*100
Zn	0.22228(8)	0.00208(10)	0.13061(5)	5.51*
P	0.17153(17)	0.02645(21)	0.01365(11)	5.02*
C1	0.0435(6)	-0.0315(8)	-0.0161(4)	5.09*
C2	0.2550(7)	-0.0581(11)	-0.0388(5)	8.24*
C3	0.3684(8)	-0.0224(14)	-0.0233(6)	11.61*
C4	0.1716(8)	0.1807(9)	-0.0133(5)	8.02*
C5	0.1379(10)	0.2026(11)	-0.0867(6)	11.08*
S1a	0.23159(21)	-0.23105(22)	0.11772(14)	7.11*
S2a	0.10560(20)	-0.08128(21)	0.19647(12)	6.14*
N1a	0.0920(6)	-0.3153(7)	0.1942(4)	7.16*
C1a	0.1387(7)	-0.2208(8)	0.1716(4)	5.85*
C2a	0.1226(10)	-0.4379(10)	0.1746(6)	9.95*
C3a	0.0514(11)	-0.4788(10)	0.1117(8)	12.98*
C4a	0.0120(8)	-0.3035(10)	0.2408(5)	7.85*
C5a	0.0646(9)	-0.3083(12)	0.3132(5)	10.21*
S1b	0.22282(20)	0.22095(22)	0.16682(14)	6.53*
S2b	0.39220(18)	0.04896(22)	0.17197(13)	6.22*
N1b	0.4174(6)	0.2693(7)	0.2147(4)	6.44*
C1b	0.3506(7)	0.1890(8)	0.1871(4)	5.22*
C2b	0.3853(8)	0.3953(8)	0.2228(6)	7.95*
C3b	0.3409(9)	0.4126(10)	0.2896(6)	9.37*
C4b	0.5267(7)	0.2399(9)	0.2422(6)	8.01*
C5b	0.5968(9)	0.2621(10)	0.1909(7)	10.88*
C1t	0.2399(7)	-0.0356(9)	0.4203(10)	15.1(14)
C1't	0.2560(9)	-0.0097(11)	0.3823(6)	12.7(10)
C2t	0.3621(10)	0.0704(12)	0.4995(5)	10.3(10)
C2't	0.3124(9)	0.0192(10)	0.5006(5)	11.3(9)
C3t	0.2801(11)	-0.0105(11)	0.4865(7)	15.4(15)
C3't	0.2465(7)	-0.0358(9)	0.4495(7)	12.2(10)
C4t	0.2817(11)	0.0202(13)	0.3670(6)	12.8(12)
C4't	0.3313(10)	0.0714(11)	0.3660(4)	11.1(9)
C5t	0.4039(7)	0.1262(7)	0.4462(8)	13.8(13)
C5't	0.3877(7)	0.1004(8)	0.4843(5)	9.6(8)
C6t	0.4831(15)	0.2043(16)	0.4587(17)	17.7(20)
C6't	0.4512(15)	0.1535(16)	0.5335(11)	13.4(13)
C7t	0.3637(11)	0.1011(12)	0.3800(6)	12.6(12)
C7't	0.3972(8)	0.1264(8)	0.4170(6)	10.8(9)

* Ue = 1/3 Σ u11+u22+u33

Table 2. Selected Distances (Å) and Angles(°).

Zn- P	2.388(2)		
		Zn- P- C1	115.01(27)
		Zn- P- C2	112.77(35)
		Zn- P- C4	113.16(33)
P- C1	1.822(8)	C1- P- C2	101.2(4)
C1- C1^{i}	1.537(16)		
P- C2	1.859(10)	C1- P- C4	106.1(4)
C2- C3	1.522(14)		
P- C4	1.827(10)	C2- P- C4	107.6(5)
C4- C5	1.514(14)		
Zn- S1a	2.653(2)	P- Zn- S1a	91.65(9)
Zn- S2a	2.320(2)	P- Zn_S2a	119.03(9)
		S1a- Zn- S2a	72.05(8)
		S1a- Zn- S1b	169.17(10)
		S1a- Zn- S2b	102.11(9)
S1a- C1a	1.712(9)	Zn- S1a- C1a	80.07(33)
S2a- C1a	1.724(9)	Zn- S2a- C1a	90.36(31)
C1a- N1a	1.334(10)	S1a- C1a- N1a	122.7(7)
S1a- S2a	2.937(3)	S2a- C1a- N1a	119.8(8)
		S1a- C1a- S2a	117.5(5)
N1a- C2a	1.506(13)		
C2a- C3a	1.551(17)		
N1a- C4a	1.480(12)		
C4a- C5a	1.538(14)		
Zn- S1b	2.580(2)	P- Zn- S1b	99.17(9)
Zn- S2b	2.326(2)	P- Zn- S2b	118.11(9)
		S1b- Zn- S2b	73.01(9)
		S2a- Zn- S1b	102.10(9)
		S2a- Zn- S2b	122.66(10)
S1b- C1b	1.699(9)	Zn- S1b- C1b	80.54(31)
S2b- C1b	1.712(9)	Zn- S2b- C1b	88.29(30)
C1b- N1b	1.332(10)	S1b- C1b- N1b	121.7(7)
S1b- S2b	2.926(3)	S2b- C1b- N1b	120.1(7)
		S1b- C1b- S2b	118.2(5)
N1b- C2b	1.498(11)		
C2b- C3b	1.533(14)		
N1b- C4b	1.499(11)		
C4b- C5b	1.472(15)		

Toluene Rings

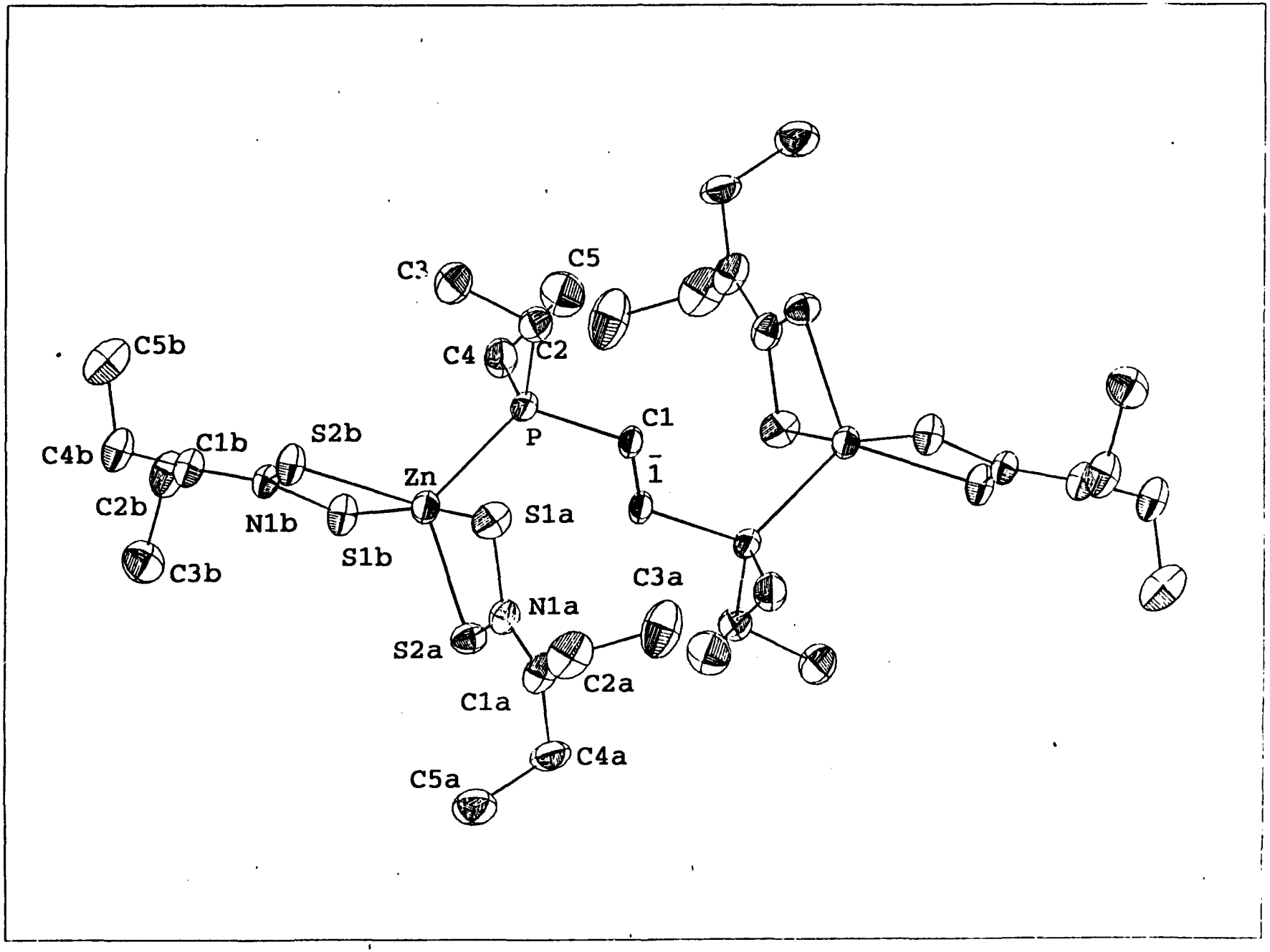
C ring- C methyl	1.35(2)
C ring- C ring	1.404(4)

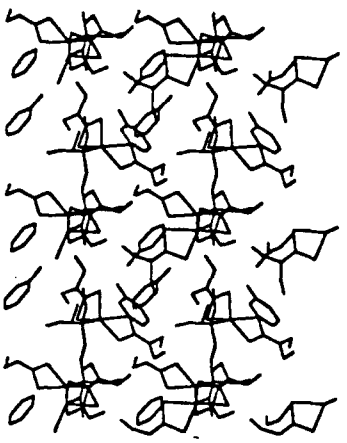
All angles constrained to 120°

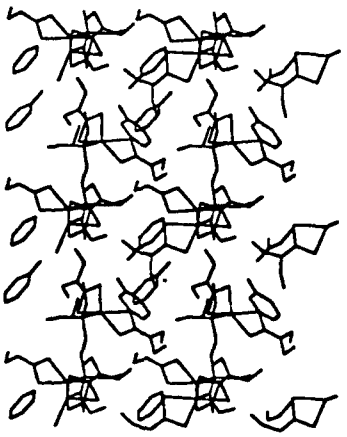
Figure Captions

Figure 1. An ORTEP representation of the zinc dimer. Each half of the molecule is related to the other by the inversion center.

Figure 2. A stereo diagram of the packing arrangement in the crystal structure.


C3
C5
C5b
C4
C2
C4b
C1b
S2b
P
C1
Zn
1̄
C2b
N1b
S1a
S1b
C3b
C3a
N1a
S2a
C2a
C1a
C4a
C5a





Supplimentary Information

1. Anisotropic Thermal Parameters

2. Full Listing of Distances and Angles.

3. Listing of Calculated and Observed Structure Factors.