THE CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPLEX OF ZINC(II) WITH DI-μ-DIALLYLDITHIOCARBAMATE--BIS(DIALLYLDITHIOCARBAMATE)

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The structure of $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$ was solved by X-ray structural analysis. The heavy atom method was used in interpretation of the structure. The dimeric compound crystallizes in the triclinic system with a space group of $P\bar{1}$ and lattice parameters of $a = 0{\cdot}8218(2)$, $b = 0{\cdot}9462(6)$, $c = 1{\cdot}2942(9)$ nm, $\alpha = 77{\cdot}70(5)$, $\beta = 77{\cdot}46(4)$, $\gamma = 78{\cdot}25(4)°$. The experimentally determined density value for $Z = 2$ is 1·42 Mg m^{-3} and the calculated value is 1·44 Mg m^{-3}. In the dimeric molecule each Zn atom is coordinated by five sulphur atoms at distances of Zn—S_1 0·2346, Zn—S_2 0·2339, Zn—S_3 0·2468, Zn—S_4 0·2846, Zn—S'_4 0·2387 nm in a deformed trigonal bipyramid. The coordination number of Zn can be expressed as 3 + 1 + 1. The distance between two zinc atoms is 0·3580 nm.

The zinc(II) bis(diallyldithiocarbamate) complex can be included among relatively stable binuclear complexes of the $[M(dtc)_2]_2$ type, formed by some transition metals[1-3]. In the framework of a study of the relationship between the preparation, structure and properties of some complex compounds of dithiocarbamic acid, this work deals with the effect of an unsaturated alkyl chain that permits greater conjugation in the structure on the coordination of the central atom and on the inter-atomic distances.

To our knowledge, only the crystal structure of a single representative of the above type of compound, the nickel(II) bis(diallyldithiocarbamate) complex, has been described in the literature[4].

EXPERIMENTAL AND RESULTS

Preparation of the Complex

The zinc(II) bis(diallyldithiocarbamate) complex was prepared by the reaction of an aqueous solution of $ZnCl_2$ with an aqueous solution of Na(I)diallyldithiocarbamate. The precipitate formed was filtered off and dried. The product was dissolved in acetone, CCl_4 or $CHCl_3$ and rectangular,

colourless crystals formed in the solution, crystallizing in the triclinic system with a space group of $P\bar{1}$. The purity of the substance was confirmed by elemental analysis and chelometric determination of zinc.

$\{Zn[S_2CN(C_3H_5)_2]_2\}_2$	(819·9)		m.p. 108–110°C	
	% C	% H	% N	% Zn
calculated	41·02	4·91	6·83	15·94
found	40·94	4·92	6·87	15·91

The crystal density, 1·42(2) Mg m^{-3} was measured by the flotation method (aqueous $ZnSO_4$ solution). The calculated value assuming the presence of 2 formula units in a unit cell is 1·44 Mg m^{-3}.

TABLE I

The atomic parameters (. 10^4) of the nonhydrogen atoms in the crystal structure of $\{Zn[S_2CN.(C_3H_5)_2]_2\}_2$ with standard deviations given in parentheses

Atom	*x/a*	*y/b*	*z/c*
Zn	1 019(1)	0 070(1)	8 623(1)
S1	1 929(3)	7 660(2)	8 304(1)
S2	2 289(3)	1 881(2)	8 965(1)
S3	1 455(3)	0 292(2)	6 652(1)
S4	1 926(3)	9 301(2)	0 697(1)
C1	2 535(9)	1 005(7)	0 228(6)
C2	1 949(10)	8 419(7)	6 987(6)
C3	3 897(11)	3 027(8)	0 426(6)
C4	3 620(12)	0 867(8)	1 920(6)
C5	2 480(14)	4 293(10)	0 559(8)
C6	2 564(13)	1 680(10)	2 768(7)
C7	2 542(18)	5 306(10)	1 117(9)
C8	3 218(15)	2 020(11)	3 526(7)
C9	2 109(13)	8 140(9)	5 091(6)
C10	2 862(12)	5 962(8)	6 487(6)
C11	3 820(15)	7 984(10)	4 343(8)
C12	1 348(17)	5 224(9)	6 740(8)
C13	4 022(19)	7 254(12)	3 491(8)
C14	1 184(22)	4 250(13)	6 150(11)
N1	3 270(8)	1 583(6)	0 840(5)
N2	2 304(9)	7 560(6)	6 215(5)

Structure Solution and Refinement

The approximate lattice parameter values calculated from the rotation and Weissenberg patterns were refined on a Syntex $P2_1$ diffractometer by the least squares method on the basis of 10 reflections.

A crystal with dimensions of 0·20 × 0·15 × 0·30 mm was selected for determination of the basic crystallographic data and for measuring the intensities. The integral intensities were collected on a Syntex $P2_1$ diffractometer. Graphite monochromatic $CuK\alpha_1$ radiation was used for the measurements and the intensities were recorded in the range $0° < 2\theta \leqq 100°$. A total of 1 943 reflections were measured; 1 548 were classified as observed with $I \geqq 1{\cdot}95\sigma(I)$. All the intensities were corrected for the Lorentz and polarization factors and converted to an absolute scale. Absorption was neglected, $\mu = 57{\cdot}4\ cm^{-1}$.

A space group of $P\bar{1}$ or $P1$ followed from the Weissenberg patterns. The position of the zinc atom was found from the three-dimensional Patterson function. The positions of the sulphur atoms and of the other nonhydrogen atoms of the complex were found from the Fourier maps using the method of successive approximations. The R-factor had a value of 0·28.

The structure was refined by the least squares method using a diagonal approximation, employing the minimization function $M = \sum w(|F_o| - |F_c|)^2$ and the Cruickshank weighing

TABLE II

The calculated and found values (. 10^3) of the atomic parameters of the hydrogen atoms in the structure of $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$

Atom	x/a	y/b	z/c
H31	482	309	090
H32	447	308	−041
H41	329	−025	209
H42	493	080	194
H51	140	440	085
H61	172	140	313
H71	131	592	122
H72	340	480	205
H81	424	160	388
H82	222	238	423
H91	128	753	487
H92	154	929	502
H101	375	558	581
H102	348	572	718
H111	424	874	450
H112	087	520	754
H131	290	700	320
H132	330	780	460
H141	000	440	480
H142	190	427	709

scheme[5] $w = (a + |F_o| + b|F_o|^2)^{-1/2}$ (constants a and b were assigned values of 3·0 and 0·0037, respectively). A value of parameter R, defined as $\sum||F_o| - |F_c||/\sum|F_o|$, was 0·179 after 6 refinement cycles with isotropic temperature parameters. In the next 6 refinement cycles, anisotropic vibrations of all the nonhydrogen atoms were assumed, where factor R decreased to a value of 0·057. At this level, the difference Fourier synthesis did not contain maxima greater than 0·61 . 10^3 e nm^{-3}.

In this case, assuming sp^3 hybridization, the positions of the hydrogen atoms were calculated and the positions of the other H atoms were found by difference synthesis. The coordinates of the hydrogen atoms were not refined and their introduction into the structure yielded a final R-factor value of 0·052.

Scattering factors for the neutral atoms were taken from the International Tables[6]. The calculations were performed on a Siemens 4004/150 computer using programs described in ref.[7].

The refined positions of the nonhydrogen atoms are listed in Table I and the coordinates of the hydrogen atoms are given in Table II. The bonding distances and valence angles are

TABLE III

The bonding interatomic distances (nm) in the symmetrically independent part of the $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$ molecule with standard deviations given in parentheses

Bond	Length of the bond
Zn—Zn′	0·3580(3)
Zn—S1	0·2346(2)
Zn—S2	0·2339(3)
Zn—S3	0·2468(3)
Zn—S4	0·2846(3)
Zn—S4′	0·2387(2)
S1—C2	0·1701(7)
S3—C2	0·1717(7)
S2—C1	0·1702(8)
S4—C1	0·1732(7)
C1—N1	0·1348(9)
C2—N2	0·1366(9)
N1—C3	0·1508(10)
N1—C4	0·1479(10)
N2—C9	0·1472(9)
N2—C10	0·1476(9)
C3—C5	0·1501(13)
C5—C7	0·1332(14)
C4—C6	0·1491(12)
C6—C8	0·1337(14)
C9—C11	0·1523(15)
C11—C13	0·1385(14)
C10—C12	0·1490(15)
C12—C14	0·1358(16)

given in Tables III, IV and VII. The values of the coefficients of the $AX + BY + CZ = D$ plane located by the least squares method through selected atoms are listed in Table V. Deviations of some atoms from the 1—4 plane, defined in Table V, are listed in Table VI. Fig. 1

TABLE IV

The valence angles (°) of the dithiocarbamate ligand of the $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$ molecule with standard deviations given in parentheses

Atoms	Angle
C1—N1—C3	120·9(6)
C2—N2—C10	120·7(6)
C3—N1—C4	114·1(6)
C9—N2—C10	116·3(6)
C1—N1—C4	124·9(6)
C2—N2—C9	123·0(6)
S4—C1—N1	119·9(5)
S4—C1—S2	118·9(4)
S2—C1—N1	121·0(5)
S3—C2—S1	118·4(4)
S1—C2—N2	120·9(5)
S3—C2—N2	120·6(5)
N1—C3—C5	111·1(7)
N1—C4—C6	111·4(7)
C3—C5—C7	121·3(10)
C4—C6—C8	122·3(10)
N2—C9—C11	110·5(8)
N2—C10—C12	108·5(8)
C9—C11—C13	118·5(10)
C10—C12—C14	121·6(11)

TABLE V

The values of the coefficients of the $AX + BY + CZ = D$ plane located by the least squares method through selected atoms

Plane	Atoms	*A*	*B*	*C*	*D*
1	S1S3C2N2C9C10	0·9484	0·2707	−0·1651	1·7650
2	S2S4C1N1C3C4	0·8406	−0·3736	−0·3923	−2·8385
3	S1S3C2N2	0·9617	0·2450	−0·1229	2·1581
4	S2S4C1N1	0·8503	−0·3620	−0·3821	−2·6263

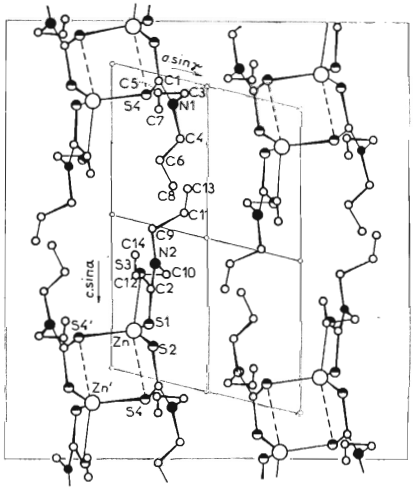

FIG. 1

Projection of the structure of $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$ into the (010) plane. ○ Zn, ● N, ◓ S, ○ C

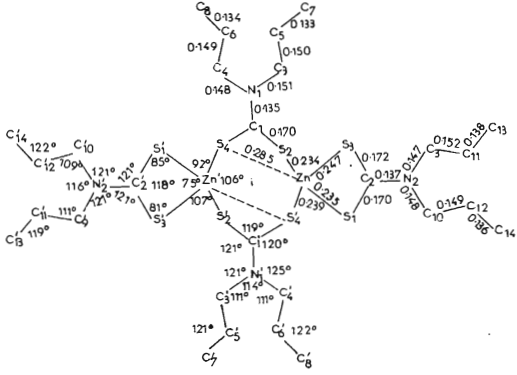

FIG. 2

Interatomic distances and angles in $\{Zn[S_2CN(C_3H_5)_2]_2\}_2$

depicts projection of the structure into the (010) plane. Fig. 2 gives the molecule with designation of the atoms, interatomic distances and angles.

Description of the Structure and Discussion

In the dimeric zinc(II) bis(diallyldithiocarbamate) complex, the two zinc atoms are connected by a bridge consisting of two dithiocarbamate ligands (*A*). This coordination produces an eight-membered chelate ring consisting of 2 zinc atoms, 2 carbon atoms and 4 sulphur atoms. A further two dithiocarbamate ligands (*B*) are bonded bidentally to the zinc atom to form a four-membered chelate ring (typical for zinc(II) dithiocarbamate complexes[8-11]). The four Zn–S distances in the complexes are in sufficiently good agreement with the tetrahedral covalent radii. The fifth distance is somewhat longer and does not have the character of a covalent bond. In all the systems described so far, the coordination around the central Zn atom forms a transition between a deformed tetragonal pyramid and a deformed trigonal bipyramid, except for $[Zn(Medtc)_2]_2$, where the coordination is tetrahedral[8].

In the studied complex, the zinc atoms are coordinated by 5 sulphur atoms with approximately identical Zn–S distances (0·2346, 0·2339 and 0·2387 nm), one significantly longer (0·2468 nm) and one much longer (0·2846 nm). The geometry around the central atom can be considered as a strongly deformed trigonal bipyramid as the deviation of the Zn atom from the plane of a basic trigonal bipyramid $S_1S_2S_4'$ is 0·023 nm, whereas that from the tetragonal plane is 0·069 nm.

The Zn—S bonds in chelate ligand *B* are not completely identical and the $S_1—C_2—S_3$ angle (118°) corresponds to about 120°, as expected for sp^2 hybridization. The magnitudes of the $C_2—S_1—Zn$ and $C_2—S_3—Zn$ angles are in good agreement with the corresponding angles in conjugated  systems of dimethyl,

TABLE VI

Deviations (nm . 10^4) of some atoms from planes 1 to 4, defined in Table V. Designation of atoms and planes as in Table V and Fig. 1

Plane	Zn	S1	S2	S3	S4	C1	C2	C3	C4	C9	C10	N2	N1
1	−171·8	−81·4		67·5			14·4			−92·2	79·5	14·0	
2	9·9		13·2		13·6	−28·5		13·3	13·4				−25·1
3	−142·7	− 3·2		−3·2			10·5					−4·1	
4	− 35·6		6·0		6·0	−20·0							' 8·0

diethyl, diisopropyl and dihexamethylene-dtc complexes[5-8]. Here the S_2CNC_2 fragment is planar, as follows from the deviations of the individual atoms from the $S_1S_3C_2N_2$ resp. $S_2S_4C_1N_1$ planes, given in Table VI.

In ligand *A*, forming a bridge, the lengths of the Zn--S bonds are not equal. The S_4—C_1 bond is somewhat longer than the S_2—C_1 bond, which may be a result of the bridge function of the S_4 atom. The zinc atoms lie at a distance of 0·358 nm, excluding the possibility that this could be a Zn—Zn bond.

It can be seen from Table VII that neither allyl part of the ligand contains bond or angle anomalies, as follows from the given bonding distances and angles of the studied zinc(II) dtc complexes. The values given in the table indicate that the double

TABLE VII

Interatomic distances (nm) and bond angles (°) in dimeric zinc(II) bis(dialkyldithiocarbamate) complexes, $\{Zn[S_2CN(R)_2]_2\}_2$

Bond	R = allyl	= hexamethyl[a]	= isopropyl[b]	= ethyl[b]	= methyl[b]
Zn—S4	0·2846(3)	0·2957(7)	0·2815(1)	0·2815(2)	0·3036(6)
Zn—S4′	0·2387(2)	0·2343(7)	0·2377(1)	0·2383(3)	0·2373(6)
Zn—S3	0·2468(3)	0·2445(7)	0·2454(1)	0·2443(3)	0·2429(6)
Zn—S2	0·2339(3)	0·2340(7)	0·2335(1)	0·2331(3)	0·2312(6)
Zn—S1	0·2346(2)	0·2335(7)	0·2342(1)	0·2355(3)	0·2333(6)
Zn...Zn′	0·2580(3)	0·3630(7)	0·3545(1)	0·3545(4)	0·3973(6)
S4—Zn—S2	68·1(1)	67·5(2)	68·89(3)	69·6	—
S4—Zn—S1	91·9(1)	95·8(2)	91·78(3)	93·6	—
S4—Zn—S3	156·6(1)	153·2(2)	155·31(2)	160·0	—
S4—Zn—S4′	94·1(1)	94·3(2)	94·33(2)	94·4	—
S2—Zn—S1	135·6(1)	127·5(2)	136·40(3)	137·7	136·5(2)
S2—Zn—S3	107·0(1)	108·6(2)	106·41(3)	106·9	108·4(2)
S2—Zn—S4′	105·5(1)	104·0(2)	103·98(3)	107·8	110·7(2)
S1—Zn—S3	75·1(1)	76·1(2)	75·00(3)	75·8(2)	76·4(2)
S1—Zn—S4′	115·8(1)	123·0(2)	116·55(3)	112·1	113·7(2)
S3—Zn—S4′	109·0(1)	111·9(2)	110·18(3)	105·2	105·8(2)
Zn—S4—C1	77·5(3)	75·8(1)	79·4(1)	78·3	—
Zn′—S4—C1	102·3(3)	—	100·6(1)	102·3(3)	96·5(6)
Zn—S2—C1	94·6(3)	98·0(1)	95·8(1)	93·9(6)	96·5(6)
Zn—S1—C2	85·2(3)	85·0(1)	86·4(1)	84·5(6)	84·0(6)
Zn—S3—C2	81·1(2)	82·5(1)	83·2(1)	81·9(6)	82·0(7)
Zn—S4—Zn′	85·9(1)	—	85·70(1)	85·6	—

[a] Ref.[9], [b] ref.[10].

bonds in the allyl chain have no marked effect on the coordination of the central atom. All the C—C bonds have an average length of 0·15 nm and C=C equals 0·135 nm. The angles correspond to sp^3 and sp^2 hybridization.

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