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X-ray Diffraction Analysis of Zn(II) Acetate Complex with 2-Amino-5-ethyl-1,3,4-thiadiazole

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Abstract—Results of a single-crystal X-ray diffraction study of the complex of zinc(II) acetate with 2-amino-5-ethyl-1,3,4-thiadiazole were presented. The coordination polyhedron of the complex has a distorted tetrahedral configuration with nitrogen atoms of the two 2-amino-5-ethyl-1,3,4-thiadiazole molecules and oxygen atoms of the two acetate ions coordinated to the central ion.

We earlier showed [1] that the structure of Zn(II) coordination compounds with unsubstituted 2-amino-1,3,4-thiadiazole depends on the nature of acido ligands in such a way that with halide acido ligands tetrahedral complexes are formed, whereas with the bulky nitrate acido ligand, a trigonal-pyramidal complex with three 2-amino-1,3,4-thiadiazole molecules in the equatorial plane and two nitrate ions in the axial position is formed. More recently we found [2] that the coordination compound of Zn(II) nitrate with the substituted heterocyclic ligand 2-amino-5-ethyl-1,3,4-thiadiazole (AET) is a distorted tetrahedral cationic complex with three 2-amino-5-ethyl-1,3,4-thiadiazole molecules and one water molecule in its inner coordination sphere and two nitrate ions in the outer sphere. In this connection further study of the relationship between of the structure of Zn(II) complexes and the nature of both acido and heterocyclic ligands is of interest.

Here we present the results of a single-crystal X-ray diffraction study of the complex compound $[Zn(CH_3COO)_2(AET)_2]$ formed by zinc(II) acetate with 2-amino-5-ethyl-1,3,4-thiadiazole (Figs. 1 and 2, Tables 1–3).

Crystals of $[Zn(CH_3COO)_2(AET)_2]$ have a molecular structure with the Zn(II) ion coordinating two nitrogen atoms of the thiadiazole rings and two oxygen atoms of the acetate ligands in the apexes of a distorted tetrahedron (Figs. 1 and 2). The lengths of the Zn^1–O^{1d} [1.961(1) Å] and Zn^1–O^{1c} [1.981(3) Å] bonds differ from each other, apparently because of intramolecular hydrogen bonds, such as N^1–H···O, involving coordinated oxygen atoms of an acetate group and hydrogen atoms of an exocyclic amino group (Table 3). The formation of such bonds decreases tetrahedral bond angles up to 100.50(10) ($O^{1c}Zn^1N^{2a}$) and 100.04(11)° ($O^{1d}Zn^1N^{3b}$), leaving the $O^{1c}Zn^1N^{3b}$ [109.24(11)°] and $N^{2a}Zn^1N^{3b}$ [110.34(11)°] angles close to theoretical and increasing the $O^{1d}Zn^1O^{1c}$ [123.24(12)°] and $O^{1d}Zn^1N^{2a}$ [113.43(11)°] angles (Table 2). Unlike noncoordinated 2-amino-5-ethyl-1,3,4-thiadiazole [2], where the N^2–C^2 bond length is 1.289(8) Å, in coordinated 2-amino-5-ethyl-1,3,4-thiadiazole molecules the N^{2a}–C^{1a} and N^{3b}–C^{1b} bond lengths have increased to 1.317(4) and 1.321(4) Å,

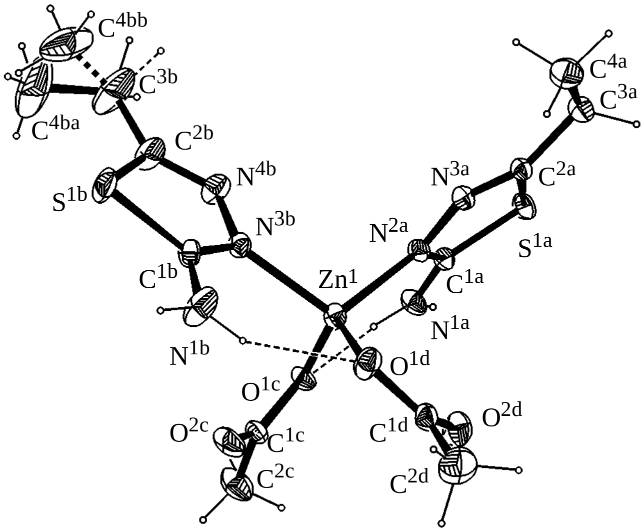

Fig. 1. Molecular geometry of the complex $[Zn(CH_3COO)_2(AET)_2]$.

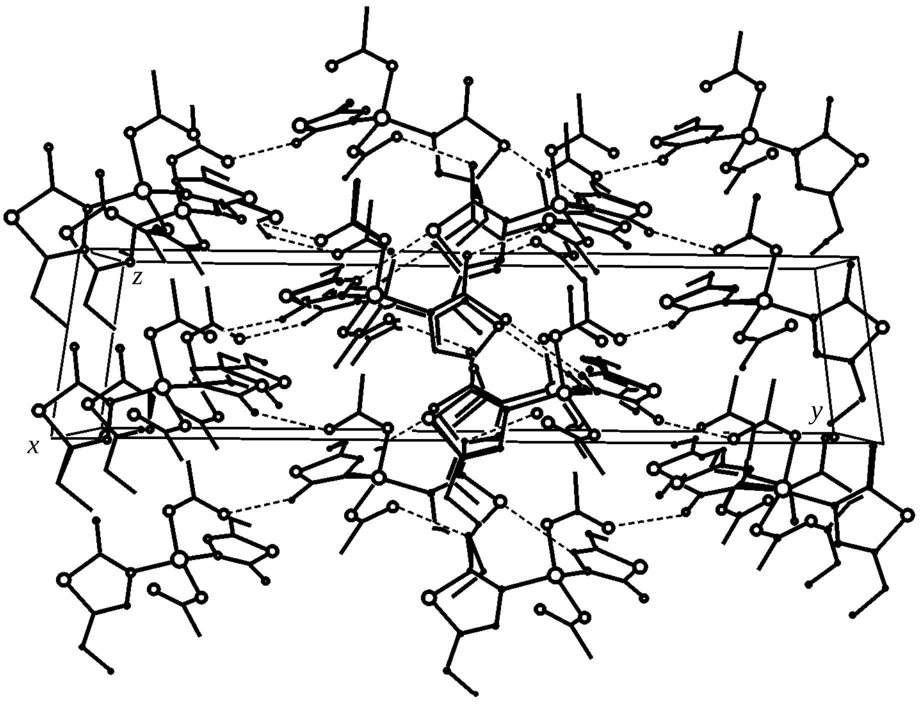

Fig. 2. Projection of the crystal structure of the $[Zn(CH_3COO)_2(AET)_2]$ complex on the *yz* plane.

respectively, whereas the lengths of the other endocyclic bonds N^1–C^1 [1.324(8) Å] and N^1–N^2 [1.403(7) Å] have decreased to 1.297(5) (N^{3a}–C^{2a}), 1.278(6) (N^{4b}–C^{2b}), 1.383(4) (N^{3a}–N^{2a}), and 1.378(4) Å (N^{3b}–N^{4b}). The length of the N^3–C^2 bond with the exocyclic amino group has decreased from 1.34(2) Å in the free ligand to 1.321(5) Å (N^{1b}–C^{1b}), implying conjugation of the amino group with the ring and overall electron density displacement from the ring to the coordination center. The endocyclic $N^2N^1C^1$ angles have decreased from 113(2)° in the free molecule to 112.1(3) ($C^{2a}N^{3a}N^{2a}$) and 112.8(3)° ($C^{2b}N^{4b}N^{3b}$) in coordinated 2-amino-5-ethyl-1,3,4-thiadiazole, while the $N^1N^2C^2$ angles have increased from 112(2) to 114.0(3) ($C^{1a}N^{2a}N^{3a}$) and 113.8(3)° ($C^{1b}N^{3b}N^{4b}$) (Table 2).

Apart from the above-mentioned intramolecular hydrogen bonds, in the crystal structure of $[Zn(CH_3COO)_2(AET)_2]$ there are also intermolecular hydrogen bonds (Table 3) formed by the amino hydrogen atom of 2-amino-5-ethyl-1,3,4-thiadiazole and the carbonyl oxygen atom of the acido ligand. Each molecular complex $[Zn(CH_3COO)_2 \cdot (AET)_2]$ is linked by such intermolecular hydrogen bonds to four adjacent molecules, thus forming tetrahedron-like structures. Therewith, the presence in the systems of such a symmetry element as a glide reflection plane results in formation of a carcass structure with hydrogen bonds.

Table 1. Coordinates of non-hydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$, Å^2) in $[Zn(CH_3COO)_2(AET)_2]$

Atom	*x*	*y*	*z*	U^a
Zn^1	12463(1)	6144(1)	12524(1)	35(1)
S^{1b}	9489(1)	7305(1)	12563(2)	61(1)
S^{1a}	11199(1)	4553(1)	11185(1)	48(1)
O^{1c}	14419(3)	6021(1)	15362(4)	44(1)
O^{2c}	14914(4)	6780(1)	15229(5)	64(1)
O^{1d}	12491(4)	6484(1)	10514(4)	51(1)
O^{2d}	14208(4)	5923(1)	11154(6)	68(1)
N^{1a}	13531(4)	5031(1)	14628(5)	49(1)
N^{2a}	11548(3)	5466(1)	11651(4)	36(1)
N^{3a}	10185(3)	5400(1)	9650(4)	40(1)
C^{1a}	12213(4)	5060(1)	12670(5)	36(1)
C^{2a}	9849(4)	4946(1)	9183(5)	43(1)
C^{3a}	8426(5)	4763(2)	131(7)	59(1)
C^{4a}	7323(6)	5154(3)	5665(8)	77(2)
N^{1b}	11173(6)	7287(1)	11208(8)	73(1)
N^{3b}	10953(3)	6581(1)	12557(4)	37(1)
N^{4b}	10263(4)	6412(1)	13377(6)	53(1)
C^{1b}	10664(4)	7043(1)	12045(6)	43(1)
C^{2b}	9479(6)	6738(2)	13489(8)	65(1)
C^{3b}	8572(12)	6643(3)	14294(16)	123(3)
C^{4ba}	8530(60)	6992(6)	15400(70)	181(17)
C^{4bb}	7500(40)	6920(20)	13800(80)	140(19)
C^{1c}	15318(4)	6391(1)	16130(5)	42(1)
C^{2c}	16925(6)	6335(2)	18203(8)	77(2)
C^{1d}	13448(5)	6298(1)	10265(6)	44(1)
C^{2d}	13610(9)	6550(2)	8837(11)	79(2)

[a] $U = (\Sigma\Sigma U_{ij} a_i^* a_j^* a_i a_j)/3$.

Unlike the cationic complex of Zn(II) nitrate with

Table 2. Bond lengths and bond angles in $[Zn(CH_3COO)_2(AET)_2]$

Bond	*d*, Å	Bond	*d*, Å
$Zn^1–O^{1d}$	1.961(3)	$N^{2a}–N^{3a}$	1.383(4)
$Zn^1–O^{1c}$	1.981(3)	$N^{3a}–C^{2a}$	1.297(5)
$Zn^1–N^{2a}$	2.028(3)	$C^{2a}–C^{3a}$	1.502(5)
$Zn^1–N^{3b}$	2.039(3)	$C^{3a}–C^{4a}$	1.502(8)
$S^{1b}–C^{1b}$	1.735(4)	$N^{1b}–C^{1b}$	1.321(5)
$S^{1b}–C^{2b}$	1.756(5)	$N^{3b}–C^{1b}$	1.321(4)
$S^{1a}–C^{1a}$	1.733(3)	$N^{3b}–N^{4b}$	1.378(4)
$S^{1a}–C^{2a}$	1.747(4)	$N^{4b}–C^{2b}$	1.278(6)
$O^{1c}–C^{1c}$	1.270(4)	$C^{2b}–C^{3b}$	1.524(7)
$O^{2c}–C^{1c}$	1.229(5)	$C^{3b}–C^{4bb}$	1.21(4)
$O^{1d}–C^{1d}$	1.281(4)	$C^{3b}–C^{4ba}$	1.36(2)
$O^{2d}–C^{1d}$	1.239(5)	$C^{1c}–C^{2c}$	1.502(6)
$N^{1a}–C^{1a}$	1.339(5)	$C^{1d}–C^{2d}$	1.497(6)
$N^{2a}–C^{1a}$	1.317(4)		
Angle	ω, deg	Angle	ω, deg
$O^{1d}Zn^1O^{1c}$	123.24(12)	$C^{3a}C^{4a}H^{4ac}$	108(5)
$O^{1d}Zn^1N^{2a}$	113.43(11)	$C^{4ba}C^{3b}C^{2b}$	119.2(11)
$O^{1c}Zn^1N^{2a}$	100.50(10)	$C^{1b}N^{3b}N^{4b}$	113.8(3)
$O^{1d}Zn^1N^{3b}$	100.04(11)	$N^{3a}C^{2a}S^{1a}$	113.9(3)
$O^{1c}Zn^1N^{3b}$	109.24(11)	$C^{3a}C^{2a}S^{1a}$	121.8(3)
$N^{2a}Zn^1N^{3b}$	110.34(11)	$C^{2a}C^{3a}C^{4a}$	114.0(4)
$C^{1b}S^{1b}C^{2b}$	87.17(19)	$C^{1a}N^{2a}N^{3a}$	114.0(3)
$C^{1a}S^{1a}C^{2a}$	87.51(16)	$C^{1a}N^{2a}Zn^1$	127.7(2)
$C^{1c}O^{1c}Zn^1$	111.3(2)	$N^{2a}C^{1a}N^{1a}$	125.1(3)
$C^{1d}O^{1d}Zn^1$	113.8(2)	$N^{2a}C^{1a}S^{1a}$	112.4(2)
$N^{1a}C^{1a}S^{1a}$	122.5(2)	$N^{4b}C^{2b}C^{3b}$	123.3(5)
$N^{3a}C^{2a}C^{3a}$	124.3(4)	$N^{4b}C^{2b}S^{1b}$	114.0(3)
$C^{2b}N^{4b}N^{3b}$	112.8(3)	$C^{3b}C^{2b}S^{1b}$	122.6(4)
$N^{1b}C^{1b}N^{3b}$	125.4(3)	$C^{4bb}C^{3b}C^{4ba}$	50.1(19)
$N^{1b}C^{1b}S^{1b}$	122.4(2)	$C^{4bb}C^{3b}C^{2b}$	118(2)
$N^{3b}C^{1b}S^{1b}$	112.2(3)	$O^{2c}C^{1c}C^{2c}$	120.6(4)
$O^{1d}C^{1d}C^{2d}$	117.4(4)	$O^{1c}C^{1c}C^{2c}$	117.2(4)
$O^{2d}C^{1d}O^{1d}$	121.8(3)	$O^{2d}C^{1d}C^{2d}$	120.8(4)

2-amino-5-ethyl-1,3,4-thiadiazole [2], where the nitrate acido ligand is displaced into the outer sphere, in the $[Zn(CH_3COO)_2(AET)_2]$ complex the coordination power of the acetate ion seems to be comparable to that of the heterocyclic ligand 2-amino-5-ethyl-1,3,4-thiadiazole. As a result, a distorted tetrahedral mixed-ligand complex containing both the acido and heterocyclic ligands in its inner coordination sphere is formed.

EXPERIMENTAL

The elemental analysis of the complex for C, H, N, and S was performed a Carlo-Erba EA-1108 analyzer; Zn was determined on a Perkin–iElmer-3030B instrument.

The ligand 2-amino-5-ethyl-1,3,4-thiadiazole was synthesized by the known procedure [3]. To prepare the complex $[Zn(CH_3COO)_2(AET)_2]$, a hot solution of 1.64 g of zinc(II) acetate dihydrate in 20 ml of ethanol was added with stirring to a hot solution of 2.31 g of 2-amino-5-ethyl-1,3,4-thiadiazole in 25 ml of ethanol. The reaction mixture was heated under reflux for 1.5 h, filtered, and left for crystallization. Two days later, the light yellow crystals were separated, washed with water, and dried in air. Yield 68%, mp 173°C. Found, %: C 32.95; H 4.87; N 18.24; S 13.93; Zn 12.93. $C_{12}H_{20}N_6O_4S_2Zn$. Calculated, %: C 32.65; H 4.53; N 19.05; S 14.51; Zn 14.73.

Single crystals of $[Zn(CH_3COO)_2(AET)_2]$ for X-ray diffraction analysis were obtained by recrystallization of powdered complex from hot ethanol.

Crystallographic parameters of the single crystal were determined and refined by 6336 reflections on a Siemens SMART/CCD diffractometer: $C_{12}H_{20}N_6O_4 \cdot S_2Zn$, *a* 10.7454(1), *b* 27.6671(3), *c* 8.4608(1) Å; β 129.159(1)°, *V* 1950.39 Å^3, *Z* 4, *M* 441.83, d_{calc} 1.505 g/cm^3, space group *Cc*.

The data collection (7021 reflections, MoK_α radia-

Table 3. Geometry of hydrogen bonds in $[Zn(CH_3COO)_2(AET)_2]$

D–H···A bond	Position of atom A	Distance, Å			AHD angle, deg
		D···A	D···H	H···A	
		Intramolecular hydrogen bond			
$N^{1a}H···O^{1c}$		2.837(4)	0.89	2.00	156
$N^{1b}H···O^{1d}$		2.887(7)	0.84	2.15	145
		Intermolecular hydrogen bond			
$N^{1a}H···O^{2d}$	*x*; 1 – *y*; 0.5 + *z*	2.823(4)	0.91	1.94	162
$N^{1b}H···O^{2c}$	*x* – 0.5; 1.5 – *y*; *z* – 0.5	2.786(5)	0.88	1.92	165

tion, sharp-focused tube, graphite monochromator) covered a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different angle φ (0.88 and 180°); the exposure time was 30 s, step 0.3° in ω. The crystal-detector distance was 4 cm; the detector vibration angle was 35°. The scope of each set was 99%. The crystal stability was controlled by repeating 30 reflections at the beginning and end of data collection which was carried out at 293 ± 2 K. The crystal dimensions were $0.46 \times 0.40 \times 0.32$ mm, absorption factor μ 1.502 mm^{-1}, $F(000)$ 912. Range of θ: $2.94 \le \theta \le 28.25°$; ranges of indices: $-11 \le h\ 7 < 14$, $-36 \le k \le 29$, and $-11 \le l \le 8$. Analysis of double reflections and sorting empirically unsuitable reflections were carried out using SADABS 87 [4]. After omittig weak reflections with $I < 2\sigma(I)$ (3614 unique reflections), the working array included 3518 reflections.

The structure was solved by Peterson's method using SHELXS 86 [2] adapted for IBM, and refined by the full-matrix least-squares method using SHELXS 93 [5]. Hydrogen atoms of ligands were located by Fourier difference syntheses. The structure involves a disordered methyl group of the ethyl radical of one 2-amino-5-ethyl-1,3,4-thiadiazole molecule (0.72 Å for C^{4ba} and 0.28 Å for C^{4bb} atom). The divergence factors after the final refinement of positional and anisotropic thermal parameters were R 0.0334 and R_W 0.0357. The drawings were obtained using the program complex [6].

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