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The Molecular Structure of (N-Salicylidene Ethanolaminato) Zn(II)

Toshio Akimoto, Masako Maeda, Akio Tsuji,[1a] and Yoichi Iitaka[1b]

School of Pharmaceutical Sciences, Showa University[1a] and Faculty of Pharmaceutical Sciences, Tokyo University[1b]

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The crystal structure of (N-sailcylidene ethanolaminato) Zn(II) has been determined by the single crystal X-ray diffraction method. The compound crystallizes in space group $P4_2/n$ with unit cell dimensions of $a=15.004$, $c=8.125$A and $Z=8$. The complex is tetrameric with $\bar{4}$ symmetry. The core unit of the tetrameric structure has a distorted cubic array of four zinc ions and four oxygen atoms of ethanolamine which occupy the eight vertices alternately.

Keywords——zinc-complex; salicylidene; ethanolamine; fluorometric analysis; tetrameric; amino acid; amino-sugar

Introduction

It has been found that α-amino acids and amino sugars with a hydroxy group at its β-position can be detected analytically by the fluorometric method, after they are reacted with Zn(II) ion and pyridoxal (or salicylaldehyde) in pyridine methanol solution.[2] It has been reported that Zn(II) tridentate Schiff base complex is formed by the reaction. The purpose of our study is to determine the structure of fluorescent products. Ethanolamine is the simplest model compound of amino acids and amino sugars. Under the actual condition, Zn(II) ion might be coordinated by water, pyridine, or acetate ion in addition to the ligand of Schiff base. The present paper describes the molecular structure of (N-salicylidene ethanolaminato) Zn(II) complex in the crystalline state.

Experimental

Zinc complex of N-salicylidene ethanolamine was synthesized by the method of Maeda *et al.*[2] The crystals were grown from an absolute methylalcohol solution as prisms elongated along *c*-axis. The specimen used for the data collection had the dimensions of $0.1\times0.1\times0.21$ mm. Twelve strong reflections with 2θ between 24° and 39° by Cu$K\alpha$ radiation were used to obtain precise cell parameters and crystal orientation parameters on a Philips PW 1100 four circle diffractometer.

Results

The crystal data are shown in Table I. Intensity data were collected using Cu$K\alpha$ radiation monochromated by a graphite plate. The θ—2θ scan technique was used with a scan

Table I. Crystal Data

(N-Salicylidene ethanolaminato) Zn(II) complex		
$(C_9H_9NO_2)$ Zn(II)	MW=228.5	
Tetragonal	Space group $P4_2/n$	$Z=8$
$a=15.004$, $c=8.125$ A	$V=1829.1$ A^3	
$D_x=1.66$ gcm^{-3}		

1) Location: *a) 1-5-8 Hatanodai, Shinagawa-ku, Tokyo; b) 7-chome, Hongo, Bunkyo-ku, Tokyo.*

2) M. Maeda, T. Kinoshita, and A. Tsuji, *Analytical Biochemistry*, **38**, 121 (1970); M. Maeda and A. Tsuji, *ibid.* **52**, 555 (1973); M. Maeda, A. Tsuji, S. Ganno, and Y. Oonishi, *J. Chromatogr.*, **77**, 434 (1973).

TABLE II. The List of Atomic Coordinates and Thermal Parameters of (N-Salicylidene ethanolaminato) Zn(II) Complex

Atom	*F*	Mul	*X*	*Y*	*Z*	B11 or B	B22	B33	B12	B13	B23
Zn	5	1.0	0.30766	0.34901	0.13015	0.0027	0.0029	0.0082	0.0000	0.0008	0.0006
C (1)	1	1.0	0.38023	0.16764	0.00026	0.0033	0.0018	0.0071	0.0003	0.0016	−0.0001
C (2)	1	1.0	0.45379	0.23714	−0.00409	0.0022	0.0026	0.0105	0.0003	0.0015	0.0002
C (3)	1	1.0	0.44753	0.38420	−0.11031	0.0022	0.0024	0.0066	−0.0000	0.0000	−0.0001
C (4)	1	1.0	0.41647	0.47443	−0.13415	0.0022	0.0021	0.0076	−0.0004	0.0001	0.0000
C (5)	1	1.0	0.34451	0.51364	−0.04597	0.0028	0.0020	0.0095	−0.0002	0.0007	0.0008
C (6)	1	1.0	0.32160	0.60309	−0.08608	0.0041	0.0024	0.0149	0.0006	0.0011	0.0014
C (7)	1	1.0	0.36616	0.64940	−0.20709	0.0043	0.0022	0.0137	−0.0001	0.0008	0.0012
C (8)	1	1.0	0.43781	0.61051	−0.29292	0.0037	0.0032	0.0124	−0.0011	0.0006	0.0016
C (9)	1	1.0	0.46223	0.52477	−0.25516	0.0025	0.0031	0.0090	−0.0009	0.0005	0.0010
O (1)	3	1.0	0.32045	0.18745	0.13076	0.0019	0.0027	0.0051	0.0002	0.0004	−0.0006
O (2)	3	1.0	0.29977	0.47348	0.06835	0.0044	0.0028	0.0162	0.0011	0.0046	0.0027
N (1)	4	1.0	0.41334	0.32566	−0.01510	0.0023	0.0023	0.0074	0.0001	0.0008	0.0001
H′C 1	2	1.0	0.34615	0.16767	−0.11372	3.6583					
H″C 1	2	1.0	0.40802	0.10001	0.02051	4.0855					
H′C 2	2	1.0	0.49945	0.22817	−0.11071	3.0043					
H″C 2	2	1.0	0.49088	0.23525	0.11636	3.1599					
H C 3	2	1.0	0.50495	0.36699	−0.18131	3.7599					
H C 6	2	1.0	0.26664	0.63415	−0.02488	4.9086					
H C 7	2	1.0	0.34878	0.71761	−0.23465	2.8708					
H C 8	2	1.0	0.47457	0.64595	−0.39187	2.9523					
H C 9	2	1.0	0.51640	0.49394	−0.31769	3.5114					

Estimated standard deviations (*X*, *Y*, *Z* in A, B in A**2, B11 etc by A**2)

Atom	S(*X*) FR	S(*Y*) FR	S(*Z*) FR	S(*X*) A	S(*Y*) A	S(*Z*) A	S(B11)	S(B22)	S(B33)	S(B12)	S(B13)	S(*B*23)
Zn	0.00003	0.00003	0.00005	0.00039	0.00042	0.00042	0.00002	0.00002	0.00010	0.00001	0.00002	0.00002
C (1)	0.00022	0.00019	0.00040	0.00329	0.00279	0.00323	0.00013	0.00011	0.00046	0.00011	0.00021	0.00020
C (2)	0.00020	0.00021	0.00045	0.00295	0.00322	0.00367	0.00012	0.00013	0.00053	0.00010	0.00021	0.00023
C (3)	0.00021	0.00022	0.00040	0.00316	0.00327	0.00324	0.00012	0.00013	0.00045	0.00010	0.00019	0.00019
C (4)	0.00021	0.00021	0.00036	0.00311	0.00314	0.00295	0.00013	0.00012	0.00052	0.00010	0.00019	0.00019
C (5)	0.00022	0.00019	0.00043	0.00327	0.00292	0.00346	0.00014	0.00012	0.00050	0.00010	0.00022	0.00020
C (6)	0.00028	0.00023	0.00056	0.00414	0.00350	0.00453	0.00018	0.00015	0.00072	0.00013	0.00028	0.00026
C (7)	0.00026	0.00023	0.00055	0.00390	0.00342	0.00444	0.00018	0.00013	0.00068	0.00012	0.00028	0.00025
C (8)	0.00025	0.00025	0.00051	0.00373	0.00370	0.00413	0.00016	0.00015	0.00065	0.00013	0.00027	0.00027
C (9)	0.00021	0.00023	0.00042	0.00313	0.00342	0.00343	0.00013	0.00014	0.00055	0.00011	0.00022	0.00022
O (1)	0.00017	0.00014	0.00024	0.00252	0.00209	0.00192	0.00009	0.00011	0.00036	0.00007	0.00013	0.00013
O (2)	0.00018	0.00017	0.00040	0.00276	0.00253	0.00326	0.00014	0.00011	0.00049	0.00009	0.00022	0.00021
N (1)	0.00017	0.00016	0.00033	0.00253	0.00240	0.00272	0.00010	0.00010	0.00041	0.00008	0.00017	0.00017
H′C 1	0.00270	0.00354	0.00533	0.04045	0.05319	0.04332	1.07929					
H″C 1	0.00274	0.00281	0.00598	0.04117	0.04212	0.04857	1.00071					
H′C 2	0.00289	0.00279	0.00472	0.04339	0.04184	0.03836	0.86348					
H″C 2	0.00293	0.00289	0.00471	0.04399	0.04341	0.03824	0.92295					
H C 3	0.00298	0.00287	0.00588	0.04468	0.04301	0.04781	0.95110					
H C 6	0.00302	0.00310	0.00602	0.04526	0.04651	0.04889	1.08565					
H C 7	0.00257	0.00281	0.00478	0.03861	0.04221	0.03883	0.81148					
H C 8	0.00293	0.00264	0.00495	0.04396	0.03968	0.04025	0.86671					
H C 9	0.00289	0.00296	0.00601	0.04332	0.04442	0.04880	0.91800					

TABLE III. The List of Observed and Calculated Amplitudes

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
K, L=	0	0	10	23	21	11	7	7	9	60	60	12	13	−13
2	56	−62	12	7	−7	K, L=	14	0	10	20	18	13	25	−24
4	97	−105	14	11	10	2	50	−48	11	28	−28	14	24	23
8	79	−78	16	10	9	4	49	47	12	40	−38	15	14	14
12	6	6	18	42	−45	6	14	13	13	7	−5	17	20	20
14	21	−21	K, L=	7	0	8*	4	−2	14	22	21	18*	3	−4
16*	3	−2	1	14	−15	10	28	27	15	41	40	K, L=	5	1
18	24	−25	3	90	−95	12	14	−14	16	12	−12	1	111	120
K, L=	1	0	7	18	−20	K, L=	15	0	17	32	−32	2	13	12
3	61	−58	9	11	−11	1	18	−16	18	7	7	3	34	−38
8*	4	0	11	40	38	3	53	53	K, L=	2	1	4	41	−41
11	37	36	13	21	−21	5	25	−24	1	27	30	5	37	−31
13	30	−28	15	7	−7	7	16	−15	2	56	−60	6	10	9
15	25	26	17	30	−32	8*	5	0	3	81	83	7	43	45
17	8	−7	K, L=	8	0	9	53	55	4	31	−25	8	21	18
19	12	13	2	79	−78	11	23	−24	5	95	−102	9	35	−36
K, L=	2	0	4	128	138	K, L=	16	0	6	6	6	10	47	46
2	22	25	6	119	−121	2	12	11	7	94	99	11	18	18
4	97	108	8	37	−37	4	27	−27	8*	3	1	12	22	−22
8	110	114	10	46	44	6*	4	−2	9	15	−12	13	50	50
10	50	51	12	41	−57	8	36	37	10	10	−11	14	21	20
12	71	−71	K, L=	9	0	10	24	−24	11	53	−50	15	20	−20
14	24	21	1	54	50	K, L=	17	0	12	9	8	16	27	28
16	6	−6	3	71	70	1	13	−13	13	57	55	17	12	−11
18*	3	3	5	101	−104	3	10	11	14	38	38	18	27	−29
K, L=	3	0	7	66	64	5	12	13	15	10	−9	K, L=	6	1
1	65	61	9	88	90	7	5	−6	16	44	−45	1	69	−67
3	63	62	11	57	−55	K, L=	18	0	17	6	−5	2	95	−97
5	63	−68	13	22	22	2	16	15	18	8	8	3	65	−65
7	123	135	15	25	25	4	10	−11	K, L=	3	1	4	16	−12
9	42	38	K, L=	10	0	6	9	−10	1	49	−53	5	64	64
11	87	−88	2	11	−11	K, L=	19	0	2	29	−27	6	49	47
13	66	64	4	10	−6	1	29	31	3	13	19	7	52	−46
15	15	−15	6	44	42	K, L=	0	1	4	40	−41	8	80	−80
17	30	−31	8	17	−16	1	114	−164	5	40	−37	9	9	−9
K, L=	4	0	10	65	−64	2	36	−34	6	110	116	10	33	30
2	21	19	12	47	46	3	71	69	7	26	−26	11*	4	−3
4	34	28	14*	4	4	4	6	9	8	22	−23	12	15	15
6	24	28	16	33	−35	5	112	120	9	7	7	13	18	17
8	14	−16	K, L=	11	0	6	54	−50	10	43	−42	14	42	−43
10	78	−75	1	18	−19	7	80	−80	11*	4	−3	15	16	18
12	74	74	3	41	41	8	94	−95	12	68	68	16*	4	4
14	27	−26	5	12	−11	9	24	24	13	12	12	17	26	−26
16	34	−35	9	26	−25	10	75	75	14	30	−30	K, L=	7	1
18	21	21	11	28	27	11	14	−12	15	23	−23	1	14	−10
K, L=	5	0	13	7	−5	12	34	−32	16	15	−16	2	8	4
1	6	8	15	24	−26	13	12	−11	17	11	12	3*	5	−3
3	17	19	K, L=	12	0	14	11	−11	18	14	13	4	89	91
5	60	−58	2	55	54	15	8	−7	K, L=	4	1	5	36	32
7	6	5	4	72	−71	16	34	35	1	36	−29	6	97	−96
9	16	−17	6	18	18	17	14	−14	2	55	62	7	53	−52
11	53	51	8	28	28	18	13	−13	3	26	−23	8	20	19
13	22	−22	10	20	20	K, L=	1	1	4	36	−37	9	76	73
15	14	−14	12*	5	−5	1	91	109	5	11	−5	10	47	45
17	18	18	14	7	−7	3	91	−98	6	15	12	11	5	−5
K, L=	6	0	K, L=	13	0	4	103	114	7	58	−54	12	16	−16
2	11	13	1	12	13	5	27	−24	8	46	47	13	46	−44
4	117	−126	3	83	−83	6	121	−136	9	14	−13	14	9	9
6	75	77	5	31	31	7	18	13	10	28	−28	15	31	31
8	65	60	7	34	34	8	99	99	11	56	54	16*	3	−2

TABLE III. (continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
17	8	−8	13	35	35	7	9	8	8	7	6	K, L=	6	2
K, L=	8	1	14	6	−6	9	20	−21	9	43	−41	1	41	−39
1	14	12	15	12	−13	10*	3	−4	11*	4	5	2	27	24
2	27	−27	K, L=	12	1	K, L=	17	1	12	29	28	3	61	61
3	93	94	1	34	32	2	5	5	13	14	12	4	25	23
4	20	18	2	18	−17	3	27	28	14	6	5	6	30	−26
5	88	−89	3	54	−54	5	44	−45	15	44	−44	7	103	−105
6*	4	3	4	52	−49	7	13	15	17	31	32	8	41	37
7	23	22	5*	5	3	8	14	−14	18*	4	3	9	97	100
8	43	41	6	24	23	K, L=	18	1	K, L=	3	2	10	22	22
9	31	29	7	20	20	1	26	28	1	20	−18	11	23	23
11	31	−30	8	18	−19	2	14	15	3	7	−6	12	11	9
12	29	−27	9	17	17	3	12	−11	4	41	−45	13	42	−43
13	26	25	10	23	−23	4	27	−28	5	45	38	14	9	9
14	30	29	11*	4	−3	5*	3	−3	6	91	−87	15	45	46
16	17	−17	12	32	34	K, L=	0	2	7	19	17	K, L=	7	2
K, L=	9	1	13	6	7	0	87	87	8	42	42	1	7	−6
1	96	−96	14	18	−19	1	8	5	9	25	21	2	19	−17
2	27	27	K, L=	13	1	2	43	−37	10*	3	2	3	12	−10
3*	3	3	1	14	−13	3	98	104	13	15	−16	4	17	14
4	62	−61	2	51	−48	4	7	5	14	6	7	5	12	−11
5	24	23	3	31	−29	5	59	−58	15	7	7	6	33	−31
6	61	59	4	33	32	6*	5	−3	16	34	35	7	22	20
7	55	−53	5	22	22	7	31	−30	17	9	10	8	67	66
8	19	19	6	29	−29	8	12	−11	18	5	−5	9	28	−26
9	7	−6	7*	4	−1	9	106	110	K, L=	4	2	10	30	−30
10	61	−60	8	24	−24	10	12	11	1	113	128	11	22	−21
11	25	−23	10	18	18	11	85	−86	2	15	12	12	37	−37
12	35	34	11	21	21	12	20	18	3	71	−82	13*	5	3
13	8	8	13	17	−18	13	6	−6	5	9	10	14	54	55
15	15	−15	K, L=	14	1	14	12	−12	6	47	−41	15	9	−9
16	17	−17	1	31	−31	15	58	59	7	89	92	16	27	−28
K, L=	10	1	2	12	−12	17	31	−31	8	5	−3	17	9	−9
1	7	−5	3	37	36	18	9	9	9	68	−68	K, L=	8	2
2	42	41	4	12	12	K, L=	1	2	10	32	−29	1	63	−65
3	6	−6	5	44	−43	1	67	−63	11	17	−16	2	20	−18
4	12	10	6	15	−16	2	59	52	12*	4	−3	3	41	41
5	28	27	7	20	−20	3	99	−101	13	26	24	4*	5	−3
6	58	−55	8	22	22	4	34	30	14	23	23	5	13	−11
8	54	54	9	37	37	5*	3	−3	15	9	8	7	11	10
9	28	−27	10	21	21	6	27	−24	16	8	8	8	7	−7
10	6	−6	12	20	−21	7	10	−9	17	10	−11	9	10	−9
11	44	43	K, L=	15	1	8	52	50	18*	3	−4	10	11	−11
12	7	−6	1	21	−21	9*	4	−2	K, L=	5	2	12	6	−5
13	7	−8	2	27	25	10	89	−89	1	29	−25	13	40	40
14	15	15	3	11	11	11	5	2	2	113	−125	14	7	−6
15	17	−17	4	30	−29	12	20	19	3*	4	−4	15	40	−41
16*	3	3	5	13	12	13	17	18	4	25	28	K, L=	9	2
K, L=	11	1	6	8	−8	14	50	50	5	48	−43	1	21	−19
1	69	68	7	9	9	15*	4	−3	6	39	41	2	84	85
2	16	16	8	20	20	16	55	−55	7	41	−36	3	28	−24
4	20	−19	10	19	−19	18	17	17	8	108	−113	4	7	5
5	49	−47	11	22	−24	K, L=	2	2	9	15	−13	5*	5	−3
6	13	−12	K, L=	16	1	1	65	−68	10	32	31	6	49	−48
7	57	57	1*	5	−6	2	109	−116	11	11	−10	7	20	20
8	17	−17	2*	4	4	3	85	94	12	20	20	8	19	19
9	8	−9	3	17	−17	4	55	−52	13*	5	3	9	17	−15
10	18	17	4	37	37	5	25	−23	14	31	−30	12	13	13
11	13	−13	5	8	8	6	9	9	15	16	18	13	8	8
12	9	−9	6	27	−27	7	21	−19	16	12	11	14	22	−22

TABLE III. (continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
15*	4	3	9	10	11	9	66	−65	K, L=	5	3	14	23	−23
16	7	7	10	16	−16	10	14	−13	1	41	−43	16	8	8
K, L=	10	2	11	22	−23	11	29	28	2	11	10	K, L=	9	3
1	101	105	12	8	−8	12	34	−32	3	68	69	1	72	73
2	8	−8	K, L=	15	2	13	17	16	4	11	−12	2	48	46
3	6	−7	1	11	10	14	26	25	5	32	27	3	21	−22
5	75	−75	4	13	12	15	38	−38	6	14	−10	4	56	−55
6	16	15	6	26	−27	17	19	19	7	84	−84	5	27	−27
7	62	59	7*	3	4	18	12	13	9	55	55	6	34	32
8	6	−6	8*	4	3	K, L=	2	3	10	16	15	7	25	24
9	22	−22	9*	4	−5	1	100	106	11*	5	−4	8	21	19
11	17	−16	10*	4	4	2	77	81	12	25	−24	9	6	6
13	16	17	11	9	−11	3	70	66	13	20	−19	10	40	−39
14*	4	4	K, L=	16	2	4	18	12	14	22	22	11	19	−19
15*	4	4	1	19	19	5	106	−112	15	19	18	12	26	24
K, L=	11	2	2	10	12	6	30	27	16	18	17	13	9	−9
1	7	6	3	21	22	7	74	74	K, L=	6	3	14	8	−8
2	18	−20	4*	3	−3	8	6	5	1	52	−48	15	23	24
3	10	10	5	30	−30	9	9	−9	2	13	15	K, L=	10	3
4	45	−43	7	24	25	10	42	40	3	14	−16	1	18	16
5	30	−28	8	5	−4	11	52	−50	4	45	−40	2	30	−31
6	82	83	9	6	6	12	14	−13	5	70	69	3*	5	−4
7	24	−23	K, L=	17	2	13	55	56	6	67	−64	4	10	−9
8	35	−34	1	12	13	14	22	−23	7	27	−25	5	11	12
9	7	−8	2	8	8	16	23	23	8	63	63	6	57	57
10	23	−22	3	5	−6	17	5	−5	10	12	−12	8	20	−19
11	5	−5	4	41	−43	18*	3	−3	11	17	−17	9	37	−36
12	31	31	5*	3	3	K, L=	3	3	12	25	−23	10	29	−29
13	5	−5	6	34	35	1	110	122	14	37	37	11	21	19
14	11	−11	K, L=	18	2	2	7	5	16	15	−15	12	11	11
15*	4	5	3	28	−29	3	104	−113	17	23	−24	13	13	−14
K, L=	12	2	4*	4	−4	4	56	−55	K, L=	7	3	14	11	12
1	22	−22	5	33	35	5	12	14	1	50	−46	15	16	−16
4	22	−22	K, L=	0	3	6	27	30	2	17	−17	K, L=	11	3
5	32	31	1	100	−108	7	82	81	3	12	8	1	17	−16
6	7	−7	2	60	53	8	39	−37	4	59	58	2	47	45
7	83	−84	3	34	30	9	30	−29	5	19	15	3	19	17
10	6	6	4	68	−68	10	59	−58	6	76	−75	4	7	−8
11	38	39	5	45	48	11	53	−52	7	34	34	5	53	51
13	34	−36	6	13	−11	12	16	14	8	13	12	6	33	−33
14	6	8	7	74	−72	13	9	−8	9	22	−21	7	54	−54
K, L=	13	2	8	61	59	14	27	−28	10	26	25	8	16	−16
1	13	−13	9	21	20	15	15	15	11	14	−14	9	6	6
3	8	8	10	72	−73	17	16	−18	12*	5	−2	10	19	18
4	14	13	11	15	−14	K, L=	4	3	13	42	41	11	23	22
5	24	−24	13*	5	4	1	7	−5	15	26	−27	12	13	−13
6	54	−54	14	39	38	2	77	−82	16	13	−14	13	11	−12
7	11	−11	15*	4	−3	3	44	38	K, L=	8	3	14	5	−5
8	30	30	16	37	−37	4	73	73	1	21	20	K, L=	12	3
9	11	11	17	12	−14	5*	3	1	2	37	37	1	29	27
10	24	25	18*	4	4	6	70	68	3	56	56	2	24	23
11	6	−6	K, L=	1	3	7	64	−62	5	76	−76	3	10	−8
12	38	−39	1	31	−30	8	83	−83	6	8	−8	4	28	28
K, L=	14	2	2	62	61	10	18	16	7	42	40	5	12	11
1	26	−26	3	32	−28	11	39	39	8	14	−14	6	62	−62
2	20	20	4	36	35	12	7	7	9	21	19	7	6	5
3	11	11	5	22	22	13	32	−31	10	7	−4	8	37	36
5	6	−6	6	123	−131	14	5	−5	11	40	−40	10	6	5
6	6	6	7	38	34	15	8	8	12	23	23	11	14	−14
7	14	13	8	56	54	17	23	23	13	17	16	12	40	−40

TABLE III. (continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
K, L=	13	3	8	63	61	2	15	15	4	103	−106	3	58	59
1	10	−9	9	5	−3	3	24	23	5	10	−8	4*	5	−4
2	24	−24	10	24	−24	4	50	45	6	78	79	5	21	−20
4	37	35	11	9	9	5	23	−19	7	15	15	6	6	−6
5	26	−26	12*	5	−2	6	33	−32	8	10	9	8*	4	4
6	11	−10	13	20	20	7	7	−7	9*	3	3	9	23	23
7	28	29	14	7	−7	8	17	15	10	56	−55	11	10	−10
8	11	−11	15	6	−6	9	23	22	11	9	−9	K, L=	14	4
9	7	−7	16	11	−12	11	11	−11	12	36	35	1*	5	3
10	9	8	K, L=	1	4	12	82	−84	13	12	−13	2	58	59
11	23	−24	1	118	132	13	10	−10	14	10	−10	4	56	−58
K, L=	14	3	2	16	17	14	23	23	15*	4	−3	7	7	7
1	30	−28	3*	5	−4	16	22	22	K, L=	9	4	8	28	28
2*	4	2	5	117	−125	17*	2	−2	3	36	−36	10	20	−20
3	36	35	7	124	131	K, L=	5	4	4	21	−21	K, L=	15	4
4	18	18	8	12	10	1	40	−40	5	73	71	1	29	29
5	34	−34	9	5	−5	2	5	5	6*	4	4	3	37	−37
6	11	10	10	27	−25	3	5	−6	9	54	−52	4	12	−13
7	16	−16	11	41	−39	4	21	18	10	7	−7	5	22	22
9	22	24	12	19	−18	5	27	25	11	53	52	7	18	19
10	9	−10	13	27	25	6	31	−29	13	15	−14	9	29	−29
11	9	−9	14*	4	−3	7	18	−16	15	7	−7	K, L=	16	4
K, L=	15	3	15	13	−13	8	7	6	K, L=	10	4	1*	4	−4
1	26	27	16	7	−6	11	21	−18	1	15	−14	2	5	−5
2	25	24	17	13	14	12	6	−7	2	5	3	4	6	5
3	15	16	K, L=	2	4	13	39	40	3	25	23	5*	4	4
4	15	−15	1*	5	6	14	6	6	4	44	43	6*	4	−4
5	27	−28	2	62	−60	15	8	9	5	8	8	7	8	−8
6	18	19	3	6	−6	K, L=	6	4	6	9	−9	K, L=	17	4
7*	5	5	4	48	−49	1	13	−10	7*	3	−1	1	23	24
8	30	31	5	43	−39	2	10	8	8	24	−22	2	8	8
9	6	−6	8	67	−65	3	10	−8	9	7	7	3	10	−11
10	12	−12	9	28	26	4	72	73	10	51	52	4	10	11
K, L=	16	3	10	49	−45	5	25	−23	12	27	−28	K, L=	0	5
1	7	6	11	9	−9	6	63	−61	13	8	−8	1	107	111
2	5	−5	12	56	56	7	10	9	14	7	−7	2	54	49
3	15	−16	13	12	−12	8	35	35	K, L=	11	4	3	29	−26
4	26	−26	14	53	−54	10	12	−12	1	36	34	4	52	−49
5*	3	2	15*	4	3	12*	4	2	2	22	22	5	91	−91
6	21	23	16	9	−8	13	21	21	3	18	18	6	16	−13
7	13	13	K, L=	3	4	14	9	9	4	9	8	7	62	62
8	6	−6	1	44	−40	16	18	−20	5	13	12	8	68	68
K, L=	17	3	2	14	−16	K, L=	7	4	6	6	−6	9	26	−24
1	6	−6	3	38	32	1	45	41	7*	4	4	10	22	−22
2	10	10	4	15	14	2	16	16	8	17	17	11	31	−30
3	11	−11	5	123	131	3	69	70	9	19	17	13	5	−5
4*	4	5	6	7	−6	4	11	10	11	28	−29	14	10	10
5	12	12	7	69	−69	5	111	−114	12	8	−9	15	10	−10
6*	3	3	8	21	19	6*	4	5	K, L=	12	4	16	23	−23
K, L=	18	3	9	14	13	7	71	69	1	10	−9	K, L=	1	5
1	21	21	10	9	9	9	7	7	2	34	−32	1	48	−44
K, L=	0	4	16	60	60	10*	4	−5	3	8	8	2	49	−48
0	126	−138	12*	4	6	11	24	−23	4	29	26	3	18	−16
1*	5	2	13	75	−77	12	8	7	5	16	−17	4	45	−45
2	93	96	14	12	13	13	20	20	6	13	−13	5*	5	2
3	37	31	15	11	10	15	11	−12	8	11	−11	6	97	99
4	46	43	16*	4	−5	K, L=	8	4	11	5	−5	7	21	17
5	32	30	17	24	24	1	25	23	12*	4	4	8	22	−21
6	98	−100	K, L=	4	4	2	42	39	K, L=	13	4	9	46	−43
7	18	16	1	18	−18	3	7	6	1	41	−40	10	15	15

TABLE III. (continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
11	23	21	8	18	17	7	23	23	9	24	−24	6	21	20
12	41	41	9	20	19	9	25	25	K, L=	15	5	8*	4	3
13	17	17	10	22	−22	10	39	38	1	20	21	10	9	10
14*	5	−3	11	9	−10	12	32	−33	2	17	−17	11	19	−19
15	23	−23	12	26	26	13	12	−12	3	7	7	13	8	−8
16	8	8	13*	5	−4	14*	4	−4	7*	2	−1	K, L=	4	6
K, L=	2	5	14*	5	−3	K, L=	10	5	K, L=	16	5	1	88	−89
1	81	−80	15	17	19	1	7	−6	1	7	7	3	69	69
2	48	48	K, L=	6	5	2	13	−13	3	18	17	4*	4	5
4	20	−20	1	34	31	3	5	5	4	11	−12	5	9	8
5	73	73	2	16	15	4*	5	4	K, L=	0	6	7	44	−43
6*	4	−4	3	56	54	5	31	−31	0	27	26	8	12	11
7	71	−71	4	22	−21	6	29	28	1	9	9	9	23	21
8	26	26	5	64	−62	7	12	12	2	27	−25	10	19	−19
9	26	25	6	19	−18	8	11	−10	3	34	−33	11	12	−13
10	42	41	7	33	31	9	29	30	4	26	−24	12	9	9
11	38	37	8	34	34	10	13	−14	5	19	18	13	16	−17
12	19	−19	9	11	10	11	27	−28	6	6	5	K, L=	5	6
13	37	−36	10	14	−13	13	9	8	7	26	24	1	24	23
14	13	−13	11*	4	−3	K, L=	11	5	8	8	−8	2	78	80
15*	3	3	12*	4	−2	1	27	−26	9	38	−37	3	19	17
16	20	21	13*	3	−4	2	26	−25	10	7	−8	4	24	−23
K, L=	3	5	14	18	19	3*	4	5	11	47	48	5	30	−28
1	63	60	15	7	−7	4	10	10	12	16	16	6	31	−30
3	36	−38	K, L=	7	5	5	29	30	13	12	12	7	14	−12
4	42	41	1	7	6	7	37	−38	K, L=	1	6	8	82	85
5	13	14	2	33	32	8	8	7	1	41	−39	9	14	−14
6	65	−65	3	10	−9	9	5	3	2	19	19	10	29	−28
7	29	28	4	79	−80	10	19	−19	3	7	−6	11	15	15
8	51	50	5	7	−6	12	9	10	4	8	−7	12	30	−31
9	14	−14	6	52	52	K, L=	12	5	5	13	13	13*	3	2
10	37	35	7	34	34	1	21	−20	6	34	−32	K, L=	6	6
11	13	−13	8	9	10	2*	5	4	7	13	−12	1	16	16
12	55	−55	9	18	−15	3	45	46	8	36	−36	2*	4	2
14	17	17	10	29	−27	4	11	11	9	18	16	3	17	−16
15*	3	4	11	13	−13	5	20	−20	10	45	44	4	43	−42
16*	2	1	12	13	13	6	38	−37	11	11	11	5	21	−22
K, L=	4	5	13	20	20	7*	3	3	12	14	−14	6*	4	0
1	40	−37	14	6	−6	8	20	19	14	29	−30	7	59	57
2	57	−57	15	18	−19	8	6	5	K, L=	2	6	8	11	11
3	8	6	K, L=	8	5	11*	3	3	1	35	34	9	50	−49
4	38	37	1	38	−35	K, L=	13	5	2	5	−3	10	8	−7
5	26	−25	2	24	25	1	10	9	3	52	−51	11	10	−10
6	34	32	3	62	−62	2	43	42	4	21	19	12	7	8
7	39	38	5	58	55	3	7	−7	5	6	−4	14*	2	3
8	72	−71	6*	5	−5	4	39	−39	6	23	−23	K, L=	7	6
9	34	33	7	19	−19	5	21	−22	7	5	5	1	6	−6
10	7	−7	8	15	−13	6*	3	3	8	14	13	2	8	7
11	47	−46	9	25	−24	7	20	20	9	19	18	3	28	−28
12	7	7	11	43	44	8	16	16	10	19	19	4	7	−7
13	32	33	12	11	10	9	9	−10	11	13	−13	6	21	21
16*	4	−4	13	10	−9	10	8	−7	12*	3	4	7	14	13
K, L=	5	5	14	20	−20	K, L=	14	5	14*	3	−3	8	33	−33
1	25	−25	K, L=	9	5	1	14	13	K, L=	3	6	9	18	−18
2	6	4	1	39	38	3	34	−34	1	23	−19	10	22	21
3	36	35	3	21	−20	4	6	6	2	72	−73	11	12	12
4	35	35	4	55	54	5	13	13	3	11	11	12	20	21
6	14	−13	5	17	−15	6	6	6	4	35	35	K, L=	8	6
7	58	−57	6	29	−27	8	14	−13	5	14	−12	1	53	51

TABLE III. (continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
2*	4	5	8	36	−35	9	36	−36	4	23	−21	3	33	−33
3	7	−4	9	14	−15	10	22	−23	6	40	41	4	6	−5
5	13	−12	10	41	41	11	7	8	7	12	−12	5	56	60
6	8	−9	11	8	−9	K, L=	6	7	8	30	−32	6	13	−15
7*	4	−4	12	13	−13	1	37	38	9	8	9	K, L=	8	8
9	20	20	K, L=	1	7	2	10	−10	10*	4	−4	1	9	−9
10	14	15	1	20	19	3	32	32	K, L=	1	8	2	9	−9
13	27	−28	2	27	−27	4	5	−6	1	75	−77	3	8	9
K, L=	9	6	3*	4	2	5	29	−29	2*	5	−4	4	48	51
1	6	−7	4	23	−22	6	34	33	3	5	−6	6	34	−36
2	56	−56	5	26	−24	7	7	7	4	12	−13	K, L=	9	8
3*	5	−4	6	33	32	8	31	−30	5	51	52	1	6	7
4	16	−17	7	14	−14	9*	4	−3	6*	3	−2	2	11	11
5	22	−22	8	32	−32	10	34	36	7	60	−62	3	20	20
6	20	18	9	29	29	K, L=	7	7	8	10	10	K, L=	10	8
7*	4	2	10*	4	4	2	18	18	9	11	11	2	10	−11
8	12	−12	11	22	−23	4	34	−34	10	13	−14	K, L=	0	9
9	6	−6	12	16	18	5	9	8	K, L=	2	8	1	40	−41
K, L=	10	6	K, L=	2	7	6	21	19	2	30	30	2	11	12
1	66	−67	1	33	−32	7	35	−36	3	13	12	3	14	15
2	9	−9	2	43	−42	8*	4	−4	4	40	40	4	13	14
3	9	8	3	14	−12	9	21	21	6	64	−68	5	32	33
5	37	37	4	13	12	10	16	−17	8	37	39	6	10	−11
6	12	12	5	26	25	K, L=	8	7	10	21	21	K, L=	1	9
7	34	−32	7	30	−30	2	25	−24	K, L=	3	8	2	29	29
9	12	11	9	22	22	3	26	−25	1	6	−6	3	8	−9
10*	4	−2	10	13	−14	4	6	−6	2	6	6	4	32	33
K, L=	11	6	11	14	13	5	21	21	4	15	−14	5	17	−19
2	37	38	12	5	5	7	21	−22	5	46	−45	6	39	−40
3	19	20	K, L=	3	7	8	8	8	7	34	34	K, L=	2	9
4	27	27	1	21	−19	9	13	−12	8	17	19	1	31	33
5	7	−8	3	46	44	K, L=	9	7	K, L=	4	8	2	13	−13
6	47	−48	4	10	10	1	44	−43	1	21	21	3*	3	−3
7	8	−8	5*	4	−1	2	10	−10	2	13	13	4*	5	−6
8	30	31	6	35	−34	3	11	10	3	10	−10	5	50	−53
K, L=	12	6	7	9	9	4	26	26	5	7	−7	6	5	−5
1	21	21	8	14	14	5	14	14	6	14	15	K, L=	3	9
2	19	19	9	22	21	6	19	−19	7	17	18	1	6	−5
3	7	7	10	9	7	7	19	−19	8*	4	−3	2*	5	6
4	15	−16	12	22	−23	K, L=	10	7	9	9	−8	3	18	18
5	33	−35	K, L=	4	7	1*	5	4	K, L=	5	8	4	13	−14
7	40	41	2	61	62	2	33	33	1	28	29	5	6	−6
K, L=	13	6	3	11	11	3	16	16	2*	5	3	6	36	39
1	12	−12	4	28	−26	4	16	15	3	26	26	K, L=	4	9
2	11	12	5*	5	−6	5	12	−12	4	10	10	1	6	5
3	21	−23	6	24	−23	6	29	−30	5	17	−17	2	11	10
4	10	−11	7	33	33	7	5	6	6	7	7	4	13	−13
8	19	−19	8	20	19	K, L=	11	7	7	6	5	5	10	10
K, L=	14	6	9	11	12	1	36	38	8	18	−19	K, L=	5	9
1	23	24	10	17	−16	2	12	−12	K, L=	6	8	1	16	16
2	7	7	11	27	−28	4*	5	3	1	7	8	2	10	11
K, L=	0	7	K, L=	5	7	5	28	−29	2	12	12	3	11	−12
1	51	49	1	31	30	K, L=	12	7	3*	4	4	4	12	−12
2	15	14	3	49	−48	2	11	−11	4	47	−47	K, L=	6	9
3	15	−16	4*	3	1	3	22	23	6	16	16	1	17	−19
4	28	27	5	15	−15	K, L=	0	8	7*	4	−5	2	13	−14
5	38	−38	6	8	−8	0	101	106	8*	4	−4	3	19	−19
6	27	−26	7	38	38	2	35	−35	K, L=	7	8			
7	26	25	8*	5	−4	3	15	15	1	10	−10			

speed of 4° in θ per minute and a scan width in θ of $(1+0.35\tan\theta)°$. For the weak reflections less than 5000 counts per single scan, the scans were repeated twice to obtain better intensity data. Equivalent reflections of the type hkl and $\bar{h}kl$ were both measured and averaged. No extinction and absorption corrections were applied. 1695 non zero reflections were obtained within $\theta=78°$.

Structure Determination and Refinement

The structure was solved by the heavy atom method. The position of the zinc ion was determined from the Patterson map, and subsequent two cycles of difference Fourier syntheses gave all the atomic positional parameters except those of the hydrogen atoms. The structure was then refined by several cycles of block diagonal least-square calculation with anisotropic thermal parameters. After that, peaks of all the hydrogen atoms came out on the difference electron-density map. As the strongest 10 reflections with amplitude more than 134 suffered from severe extinction, these were omitted together with very weak (less than $3\sigma(I)$) reflections. Using 1630 reflections, the structure was finally refined by a few cycles of block-diagonal least-squares calculations in which the following weighting scheme was employed: when $Fo<5.0$, $\sqrt{w}=0.20$ and when $Fo>5.0$, $\sqrt{w}=5.0/Fo$. Isotropic thermal parameters were assumed for hydrogen atoms. Atomic scattering factors used for the refinement were: SX-6, 7, 8 for C, N, O respectively and SX-30 for Zn^{+2} which are cited from International Tables for X ray Crystallography (1962) and for H, those of Stewart, Davidson and Simpson (1965). The final conventional R-factor was 0.048. The atomic parameters are listed in Table II. The atomic numbering scheme is given in Fig. 3.

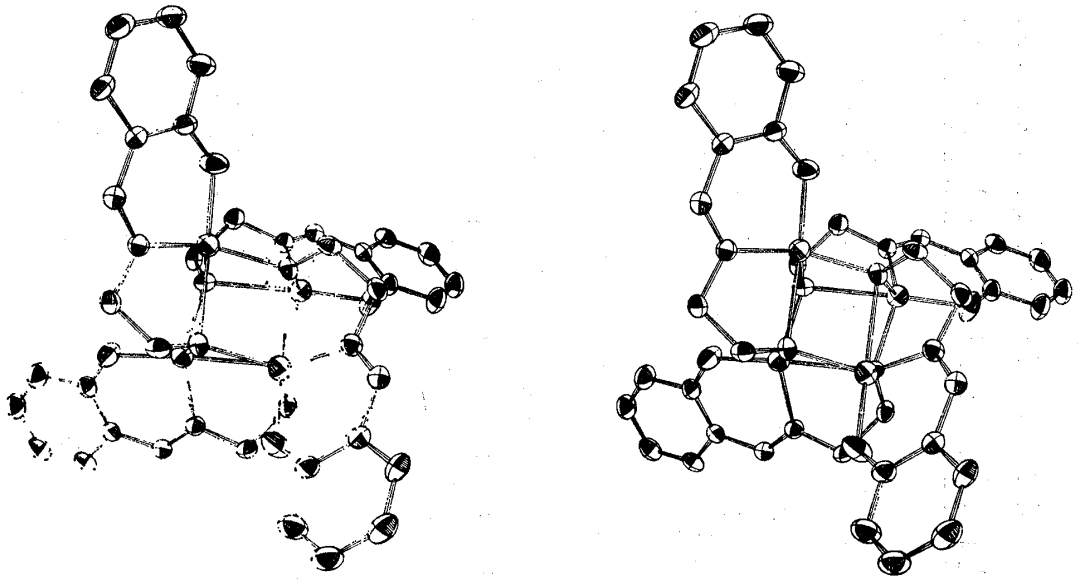

Fig. 1. The Stereoscopic View of (N-salicylidene ethanolaminato) Zn(II) Complex

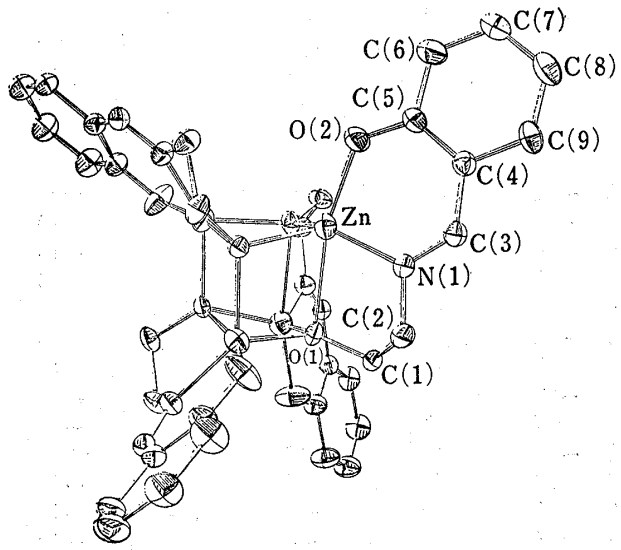

Fig. 2. Another View of (N-Salicylidene ethanolaminato) Zn(II) Complex with Atomic Numbering Scheme

Description and Discussion of the Structure

As shown in Figs. 1 and 2, the complex molecule has the tetrameric structure. The four zinc ions and the four oxygen atoms, each of them belongs to the ethanolamine moiety, occupy alternately the eight corners of a parallelpiped constituting the tetranuclear core unit of the complex molecule.

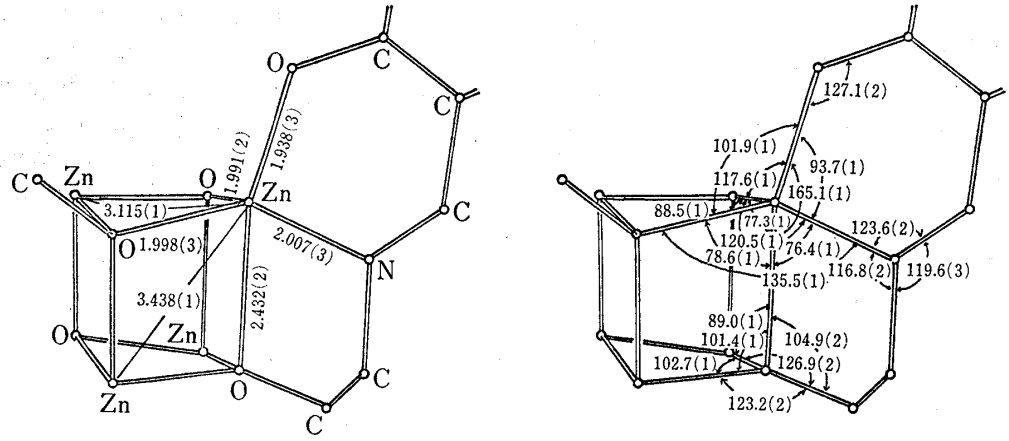

Fig. 3. Bond Lengths and Angles of Core Unit of (N-Salicylidene ethanolaminato) Zn(II) Complex

Within the core unit, every pair of zinc ion is intervened by the two bridging oxygen atoms. Each zinc ion is coordinated by the five ligand atoms; three of them are the bridging oxygen atoms of ethanolamine, the fourth is the phenolic oxygen of salicylidene and fifth is the imino nitrogen atom of ethanolamine moiety.

The structure of the core unit is depicted in Fig. 3 with the bond lengths and angles. As shown in the figure, the zinc ions are located at the acute corners of the cube.

The structure of a ligand group is depicted in Fig. 4 together with bond lengths and angles. Except the oxygen atom and α-methylene carbon atom C (1) of ethanolamine, all the atoms are almost in a plane. The deviation of these atoms from the plane is less than 0.05 A. Oxygen and α-methylene carbon is deviated 0.77 and 1.04 A from the plane respectively.

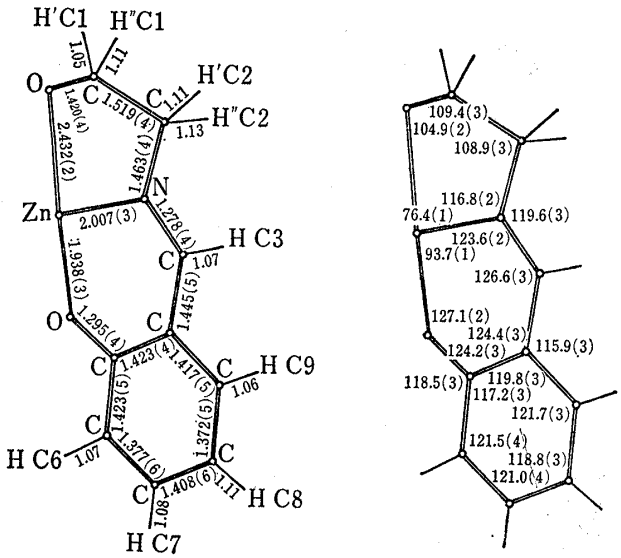

Fig. 4. Bond Lengths and Angles of a Ligand Group

Although this sort of the structure has not been found in Zn(II) complexes, two similar structure has been reported in copper complexes. One is the copper complex of the Schiff base of acetylacetone and ethanolamine, (Cu(EIA)),[3] and the other one is that of the chloride ion and 2-diethylaminoethanol.[4] In the former case, a crystallographic $\bar{4}$ axis is passing through the top and bottom faces like the Zn-complex. On the other hand, in the latter,

3) J.A. Bertrand and J.A. Kelly *Inorganic Chimica Acta*, **4**, 203 (1970).
4) E.D. Estes and D.J. Hodgson *Inorg. Chem.*, **14**, 334 (1975).

only crystallographic two fold axis is passing through the top and bottom faces of the cube. In both crystals, the lengths and angles of the coordination bonds are similar and the copper ion is located on the acute corner of the cube. The coordination to the metal is rather bipyramidal and the axis of the bipyramid is perpendicular to 4 and 2 in each case.

In the present Zn(II) complex, the axis of the bipyramid is parallel to 4. In all cases, the coordination around the bridging oxygen is tetrahedral.

In the case of the structure of $[Zn(OMe)_2(Et\ Zn\ OMe)_6]$,[5] the cubes are linked by a single zinc atom which occupies the center of symmetry. Although the array of zinc and oxygen atoms, and dimensions of a cube are rather similar to the present (N-salicylidene ethanolaminato) Zn(II) complex, the coordination number around Zn(II) atoms of $[Zn(OMe)_2(Et\ Zn\ OMe)_6]$ is four except the zinc atom on the center of symmetry, for which the coordination number is six. As mentioned earlier, in the present (N-salicylidene ethanolaminato) Zn(II) complex, it is five.

Acknowledgement We are grateful to Dr. Y. Kai and coworkers for kindly sending the crystal coordinates of $[Zn(OMe)_2(Et\ Zn\ OMe)_6]$.

5) M. Isimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn*, **49**, 1165 (1976).