This article was downloaded by: [Universitaetsbibliothek Giessen] On: 24 October 2014, At: 01:39 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

Some DI- and Trinuclear Zinc Complexes: Anion Induced Complex Formation

Orhan Atakol ^a , Hasan Nazir ^a , Mecit Aksu ^a , Cengiz Anci ^b , Filiz Ercan ^b & Burhanettin Çiçek ^c

^a Chemistry Department, Faculty of Sciences, University of Ankara, Tandogan, 06100, Ankara, Turkey

^b Department of Engineering Physics, Hacettepe University, Beytepe, 06532, Ankara, Turkey

^c Chemical Engineering Department, University of Ankara, Tandogan, 06100, Ankara, Turkey Published online: 23 Apr 2008.

To cite this article: Orhan Atakol , Hasan Nazir , Mecit Aksu , Cengiz Anci , Filiz Ercan & Burhanettin Çiçek (2000) Some DI- and Trinuclear Zinc Complexes: Anion Induced Complex Formation, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 30:4, 709-718, DOI: <u>10.1080/00945710009351793</u>

To link to this article: <u>http://dx.doi.org/10.1080/00945710009351793</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views

expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://www.tandfonline.com/page/terms-and-conditions</u>

SOME DI- AND TRINUCLEAR ZINC COMPLEXES: ANION INDUCED COMPLEX FORMATION

Orhan Atakol* Hasan Nazır^a, Mecit Aksu^a, Cengiz Arıcı^b, Filiz Ercan^b, Burhanettin Çiçek^c

^aChemistry Department, Faculty of Sciences, University of Ankara, Tandogan 06100, Ankara, Turkey

^bDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey ^cChemical Engineering Department, University of Ankara, Tandogan 06100 Ankara, Turkey

ABSTRACT

Complexes of N,N'-bis(salicylidene)-1,3-diaminopropane, an ONNO type ligand, with ZnX_2 (X = AcO', NO₃', Cl', Br', l') salts were prepared. Molecular structures of these complexes were identified using elemental analyses, IR spectrometry and X-ray diffraction techniques. It has been observed that the reactions between zinc ions and the said ligand tend to produce polynuclear complexes and depending on the anion present either di- or trinuclear complexes are formed. Thus, it can be deduced from the results presented in this article that trinuclear complexes form when the zinc salt used was the acetate or nitrate and dinuclear complexes form if the anion in the zinc salt is a halogen.

INTRODUCTION

N,N'-Bis(salicylidene)-1,3-diaminopropane (H₂L), a tetradentate ONNO Schiff base (Fig. 1), has been known since 1946^{1} . In those early years, researchers found that two different complexes form from the reactions of this ligand with nickel(II) salts. Of these complexes, one was diamagnetic while the other clearly was paramagnetic. This puzzle remained unresolved until the development of X-ray diffractometers, an invaluable tool of chemists for molecular



Fig 1. N,N'-Bis(salicylidene)-1,3-diaminopropane, H₂L

structure identification. With these developments it has been clearly demonstrated that this ligand forms trinuclear complexes with transition elements²⁻⁵.

Zinc(II) ion is the first in a row of essential rare elements for living beings⁶. It has been recognised to be an activator for more than 120 hydrolytic enzymes. Although its necessity for human life was appreciated in the early times, its uses and accumulation in the human body have yet to be resolved. Zinc in the zinc enzyme complexes whose molecular structures were identified were found to be in tetrahedral and square-pyramidal coordinations^{6,7}. So far, zinc has not been observed to form an octahedral complex with enzymes.

Recently, a comprehensive study for the preparation of trinuclear zinc complexes from a closely similar ligand was reported in the literature⁵. In this present communication, however, we report on five different complexes of H_2L with $Zn(AcO)_2$, $Zn(NO_3)_2$, $ZnCl_2$, $ZnBr_2$ and Znl_2 and on their molecular structures as identified by elemental analyses (halogens, C, H, N and Zn), IR and X-ray diffraction techniques.

RESULTS AND DISCUSSION

As mentioned above, five different salts of zinc(II) were utilised in the complex preparation When zinc(II) acetate or nitrate were used as the salt, complexes with the molecular formulas shown in Fig. 2 were obtained. In these complexes 3 Zn atoms are connected by 4 μ -oxygen bridges and 2 acetato or nitrato bridges. Zn ions at both edges have square-pyramidal coordination in N₂O₃ donor system while the central Zn ion is in an O₆ octahedral geometry.

On the other hand, when $ZnCl_2$, $ZnBr_2$ or Znl_2 were used as the salt, dinuclear complexes of the compositions $ZnL.ZnCl_2$, $ZnL.ZnBr_2$ and $ZnL.Znl_2$ formed. These complexes contain 2 dinuclear bridging sites, as shown in Fig. 3.



Fig. 2. Molecular Formulas of ZnL.Zn(AcO)2.ZnL and ZnL.Zn(NO3)2.ZnL



L' is a solvent molecule which may be either MeOH or DMF. X = Cl, Br, 1

Fig. 3. Molecular Formula of Dinuclear Complexes

In the dinuclear complexes one of the zinc ion is in a square-pyramidal coordination while the other is connected to halogen atoms and is in tetrahedral geometry. Of these complexes, the crystals of ZnL.ZnCl₂ and ZnL.ZnBr₂ were grown and subjected to X-ray structural analysis.

However, we were not able to obtain crystals of $ZnL.Znl_2$ suitable for X-ray analysis. The molecular structure of $ZnL.ZnCl_2$ was reported in an earlier communication¹¹ and that of $ZnL.ZnBr_2$ is illustrated in Fig. 4. Tables I through III present, respectively, the crystal and experimental data, selected bond distances and bond angles and final atomic coordinates of this complex.

Research is in progress for the structural identification of the trinuclear complexes by X-ray diffraction. The molecular structure of ZnL.Zn(AcO)₂.ZnL, involving an acetate bridge, was



Fig. 4. ORTEP Drawing of ZnL.ZnBr₂

Table I. Crystal and Experimental Data of ZnL.ZnBr2.DMF

Formula: C20H23N3O3Zn2Br2 Formula weight = 643.983 Crystal system: orthorombic Space group: P212121 = 4a = 10.2713(11) Å b = 14.5472(12) Å c = 15.9177(13) Å $V = 2783.4(4) \text{ Å}^3$ $D_{\rm x} = 1.798 \, {\rm g/cm^3}$ $\mu = 5.421 \text{ mm}^{-1}$ *T* = 295 K Colourless $F(0 \ 0 \ 0) = 1272$ Crystal size: 0.40 x 0.35 x 0.30 mm Radiation -- Mo Ka R = 0.058 $R_w = 0.061$ No. of reflection used = 2155No. of parameters = 271 Goodness-of-fit = 1.10 $(\Delta \sigma)_{max} - 0.0009$ $(\Delta \rho)_{max} = 0.55 \text{ e} \dot{A}^3$ $(\Delta \rho)_{min} = -0.37 \text{ eÅ}^{-3}$ Measurements: Enraf-Nonius CAD-4 diffractometer Program system: CAD-4-EXPRESS Software Structure determination: SIR88 and MolEN Treatment of Hydrogen Atoms: Geometric calculation Refinement: Full matrix least-squares (MolEN)

Zn1-Zn2	3.1480(7)	01-C1	1.331(3)
Brl-Znl	2.334(2)	02-C17	1,343(4)
Br2-Zn1	2.349(2)	O3-C18	1.232(3)
Zn1-O1	1.983(7)	NI-C7	1.236(2)
Zn1-O2	1.992(7)	N1-C8	1.484(4)
Zn2-O1	2.048(7)	N2-C10	1.488(2)
Zn2-O2	2.051(7)	N2-C11	1.341(4)
Zn2-O3	2.034(7)	N3-C18	1.312(5)
Zn2-N1	2.079(9)	N3-C19	1.487(2)
Zn2-N2	2.002(9)	N3-C20	1.443(2)
Brl-Znl-Br2	118.43(6)	Zn2-O2-C17	127.4(6)
Brl-Znl-Ol	112.2(2)	Zn2-O3-C18	120.3(6)
Br1-Zn1-O2	112.0(2)	Zn2-N1-C7	123.6(7)
Br2-Zn1-O1	114.6(2)	Zn2-NI-C8	117.1(7)
Br2-Zn1-O2	114.4(2)	C7-N1-C8	118.8(9)
Ol-Znl-O2	78.9(3)	Zn2-N2-C10	121.3(7)
O1-Zn2-O2	76.0(3)	Zn2-N2-C11	124,7(7)
01-Zn2-O3	99.5(3)	C10-N2-C11	113.7(9)
OI-Zn2-NI	88.2(3)	C18-N3-C19	121.0(1)
OI-Zn2-N2	152.0(3)	C18-N3-C20	121.0(1)
O2-Zn2-O3	96.9(3)	C19-N3-C20	117.0(1)
02-Zn2-O3	155.9(3)	01-C1-C2	122.0(9)
02-Zn2-N1	88.6(3)	01-C1-C6	118.1(8)
02-Zn2-N2	103.7(3)	NI-C7-C6	129.0(1)
O3-Zn2-N1	105.6(3)	N1-C8-C9	113.0(9)
N1-Zn2-N2	97.7(3)	N2-C10-C9	111.9(9)
Zn1-O1-Zn2	102.7(3)	N2-C11-C12	127.0(1)
Zn1-O1-C1	129.4(6)	02-C17-C12	123.4(9)
Zn2-01-C1	127.4(6)	O2-C17-C16	119.8(9)
Zn1-O2-Zn2	102.3(3)	O3-C18-N3	126.0(1)
Zn1-02-C17	130.3(6)		

Table II. Selected Bond Distances (Å) and Bond Angles (°) of ZnL.ZnBr2.DMF

solved and contains Zn-Zn-Zn atoms in a linear array. Although similar structures, prepared with Zn(II) and other transition metal ions are known in the literature,^{3-5,8,9} few reports of polynuclear complexes are available.¹⁰

There exist 6 μ -bridges in the structures of the trinuclear complexes. These bridges are formed by 4 phenolic oxygen atoms and 2 acetato or nitrato bridges. A linear trimerization was observed to result when a polyatomic anion such as CH₃COO⁻, NO₃⁻ or NO₂⁻ is present.¹¹

As shown in Fig. 2, two of the Zn(II) ions of the trinuclear complexes have square-pyramidal coordinations through N_2O_3 donors while the central Zn(II) ion has an octahedral coordination through the O₆ donor system. In the dinuclear complexes, one of the two Zn(II) ions has a square-pyramidal coordination and the other has a tetrahedral coordination in N_2O_3 and O_2X_2

Atom	x	y	Z	$B_{eq}/Å^2$	
Brl	0.2851(1)	0.12751(9)	0.13302(9)	3.93	
Br2	0.2013(1)	-0.14147(8)	0.11006(9)	4.40	
Znl	0.1294(1)	0.01121(8)	0.12229(7)	2.12	
Zn2	-0.1651(1)	0.07103(7)	0.12585(7)	1.85	
01	-0.0145(6)	0.0448(5)	0.0451(4)	2.2	
02	-0.0167(7)	0.0289(5)	0.2030(4)	2.4	
03	-0.2593(6)	-0.0518(4)	0.1197(5)	2.6	
NI	-0.2516(9)	0.1482(6)	0.0311(5)	2.3	
N2	-0.2435(8)	0.1372(6)	0.2239(6)	2.4	
N3	-0.246(1)	-0.2071(6)	-0.1210(7)	3.8	
CI	-0.019(1)	0.0405(6)	-0.0385(6)	1.9	
C2	-0.069(1)	-0.0054(8)	-0.0831(7)	3.0	
C3	-0.073(1)	-0.0120(8)	-0.1682(7)	3.0	
C4	-0.033(1)	0.0336(7)	-0.2135(7)	2.7	
C5	-0.113(1)	0.0772(8)	-0.1699(7)	2.6	
C6	-0.1283(9)	0.0869(7)	-0.0816(6)	1.7	
C7	-0.224(1)	0.1402(7)	-0.0438(6)	2.1	
C8	-0.364(1)	0.2063(9)	0.0549(8)	3.7	
C9	-0.342(1)	0.2577(7)	0.1345(9)	4.0	
C10	-0.355(1)	0.2003(8)	0.2131(7)	3.1	
СП	-0.210(1)	0.1233(7)	0.3041(7)	2.7	
C12	-0.1039(9)	0.0667(6)	0.3359(6)	1.5	
C13	-0.107(1)	0.0598(9)	0.4247(7)	4.2	
C14	-0.003(1)	0.0084(9)	0.4621(7)	3.2	
C15	-0.081(1)	-0.0402(9)	0.4134(7)	3.9	
C16	-0.079(1)	-0.0314(8)	0.3289(7)	2.7	
C17	-0.019(1)	0.0212(7)	0.2868(6)	1.9	
C18	-0.197(1)	-0.1242(6)	0.1226(7)	3.0	
C19	-0.162(2)	-0.2892(8)	0.119(1)	7.2	
C20	-0.385(1)	-0.2218(9)	0.1155(9)	4.9	

Table III. Final Atomic Coordinates of ZnL.ZnBr2.DMF

 $B_{eq} = (8\pi^2/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

(X=Cl, Br, I) donors systems, respectively. It can be further concluded from Fig. 4 and Table II that coordinations are not ideal but are better described as distorted square-pyramidal and distorted octahedral structures. Tetrahedral and square-pyramidal coordinations are the most common structural arrangements for Zn(II) ions¹².

In five-coordinate compounds, the observed structures can be distorted square-pyramidal or distorted trigonal bipyramidal. A parameter, τ , has been defined,

$$\tau = (\beta - \alpha) / 60$$

where, α and β are the two largest angles around the metal ion. The coordination is then assumed to be an ideal square pyramid when τ is zero and is an ideal trigonal bi-pyramid when τ is 1.

For ZnL.ZnBr₂, the two largest angles around Zn2 are, 152.0 (3)° and 155.9 (3)° for O1-Zn2-N2 and O2-Zn2-N1 angles, respectively. Therefore, τ may be calculated as¹³,

$$\tau = (155.9 - 152.0)/60 = 0.065$$

This value is closer to that of a square pyramid. The value of τ for ZnL.ZnCl₂ was also found to be closer to that of the square pyramid as it was 0.1866^{11} .

Elemental analysis data for the complexes are presented in Table IV. These results support the proposed stoichiometries. IR spectroscopy was employed to identify functional groups and to monitor the progress of the reactions. Table V shows some of the important stretching frequencies obtained from IR spectra in KBr pellets.

EXPERIMENTAL

Apparatus

Melting points were determined with a Gallenkamp apparatus without correction. IR spectra were run on a Mattson-1000 FTIR spectrometer using KBr pellets. Thermogravimetric analyses were performed on a temperature controlled vacuum oven with 10° C increaments under 4 mm Hg pressure. Carbon, hydrogen, and nitrogen analyses were carried out on a LECO 1000 analyser. Halogen analyses were performed gravimetrically as silver halide and zinc analyses were executed by a Hitachi 8200 atomic absorption spectrophotometer.

Chemicals

Salicylaldehyde (99%), 1,3-diaminopropane (for synthesis), zinc(11) chloride (anhydrous), zinc(11) iodide, dioxan, MeCN, MeOH and DMF were purchased from Merck AG and used without further purification. Zinc(11) bromide was prepared in our laboratory from zinc(11) oxide and hydrobromic acid¹⁴.

Preparation of the Ligand, H₂L

A quantity of 0.04 mole (4.88 g) of salicylaldehyde was dissolved in 50 mL hot MeOH and mixed with 0.02 mole (1.48 g) of 1,3-diaminopropane. The mixture was then heated with stirring for ten minutes and left unattended for about an hour at room temperature. After this period, the formed yellow crystals were filtered from the solution and dried in ambient air; yield, 5.08 g; m p. 59° C.

Downloaded by [Universitaetsbibliothek Giessen] at 01:39 24 October 2014

Table IV. Elemental Analyses.

								Ē	mental /	Analyses.	%			
										.,	ŕ		Z1	
Comp.	Empirical	Formula	Yield	M.p.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
	Formula	Weight	(%)	(°C)										
H ₂ L	C ₁ -H ₃₈ N ₂ O ₂	282.142	06	59										
ZnL	C ₁ -H ₁₆ N ₂ O ₂ Zn	345.710	92	260*	58.81	59.06	4.78	4.66	7.96	8.10			18.56	18.91
ZnL.Zn(AcO) ₂ .ZnL	C ₃₈ H ₃₈ N ₄ O ₈ Zn ₃	874.422	17	320*	51.93	52.14	4.47	4.38	6.68	6.40			21.96	22.43
ZnL.Zn(NO ₃) ₂ .ZnL	C ₃₄ H ₃₂ N ₆ O ₁₀ Zn ₁	880.422	11	240*	46.49	46.34	10.4	3.63	6.44	6.54			22.11	22.28
ZnL.ZnCl. McOH	C:9H24N2O2Cl2Zh2	545.877	58	+84	41.54	41.76	4.37	4.43	5.67	5.13	13.04	12.98	25.86	23.95
ZnL.ZnBr.,DMF	C ₂₀ H ₂₃ N ₃ O ₃ Br ₂ Zn ₂	643.770	Lt	*651	37.39	37.28	3.59	3.60	7.00	6.52	24.99	24.82	20.13	20.31
ZnL.Znl. DMF	C2cH23N3O3L2I12	737.770	65	158*	32.65	32.53	3.44	3.14	5.86	5.69	33.46	34.40	17.50	17.72

* decomposition

KBr Discs.
.≘
Obtained
Data
Spectroscopic
¥
>
Table

Comp.	v(C-H _x)	v(C-H _{aliph})	v(C=N)	v(C=O _{DMF-Acctate})	v(N=O _{Nitrate})
H ₂ L	3061 w	2948-2877 m	1645 s		
ZnL	3051 w	2927-2852 m	1628 s		
ZnL.Zn(AcO) ₂ .ZnL	3055 w	2917-2885 m	1631 s		
ZnL.Zn(NO ₃) ₂ .ZnL	3027 w	2948-2864 m	1625 s		1414 s
ZnL.ZnCl ₂ .MeOH	3049 w	2925-2880 m	1636 s		
ZnL. ZnBr ₂ . DMF	3050 w	2909-2870 m	1627 s	1651 s	
ZnL Znl ₂ DMF	3046 w	2910-2865 m	1625 s	1651 s	
-	-				

s: sharp, m: medium, w: weak

Preparation of ZnL.Zn(AcO)2.ZnL

A quantity of 0.001 mole (0.282 g) of the ligand was dissolved in 50 mL MeOH by warming and stirring, and mixed with 30 mL hot MeOH containing 0.0015 mole (0.330 g) of $Zn(AcO)_2.2H_2O$. The resulting mixture was set aside for 6-7 hours. The formed colorless crystals were filtered, washed with MeOH and dried in ambient air; yield, 0.07 g; m.p. 320° C (decomposition).

Preparation of ZnL.Zn(NO3)2.ZnL

Step 1 (Preparation of ZnL): 10 mL of ammonia solution (20 %) was added to 50 mL of hot ethanol containing 0.001 mole (0.282 g) of N,N'-bis(salicylidene)-1,3-diaminopropane. The mixture was heated to its boiling point and mixed with 20 mL of hot methanol containing 0.001 mole (0.219 g) of ZnCl₂.2H₂O. After setting aside the mixture for two hours, colourless crystals were obtained which were filtered and oven dried at 107-112° C, yield 0.32 g.

Step 2 (Preparation of ZnL.Zn(NO₃)₂.ZnL): The complex ZnL (0.001 mole, 0.345 g) was dissolved in 30 mL hot N,N-dimethylformamide and the temperature of the solution was raised to $107-117^{\circ}$ C. Zn(NO₃)₂.6H₂O (0.0005 mole, 0.146 g) was dissolved in 20 mL hot MeOH and gradually added to the former solution. The resulting mixture was set aside for 3-4 days. The formed precipitate was filtered and dried in ambient air; yield, 0.05 g; m.p. 240° C (decomposition).

Preparation of ZnL.ZnCl2.MeOH

A quantity of 0.001 mole (0.282 g) of the ligand was dissolved in 50 mL hot MeOH by warming and mixed with 30 mL of a MeOH solution containing 0.002 mole (0.272 g) of anhydrous ZnCl₂. The mixture was set aside for 15-20 hours. The formed yellow crystals were filtered, washed with MeOH and then dried in ambient air; yield, 0.32 g; m p. 78° C (decomposition).

Preparation of ZnL.ZnBr2.DMF and ZnL.ZnI2.DMF

A quantity of 0.001 mole (0.282 g) of the ligand was dissolved in 30 mL hot DMF by warming and mixed with 30 mL hot MeOH containing either 0.002 mole (0.450 g) of anhydrous ZnBr₂ or 0.002 mole (0.639 g) of ZnI₂. The mixtures were set aside for one day. The resulting yellow precipitated crystals were filtered with a Büchner funnel and

dried in ambient air. ZnL.ZnBr₂: yield, 0.30 g; m.p. 159° C (decomposition). ZnL.Znl₂: yield, 0.48 g; m.p. 158° C (decomposition).

REFERENCES

- A. Martell and M. Calvin, "Die Chemie der Metallchelat-Verbindungen", Verlag Chemie, Weinheim, pp. 135-198 (1958).
- 2. D. Ülkü, M. N. Tahir, O. Atakol and H. Nazır, Acta Cryst., C53, 872 (1997).
- 3. D. Ülkü, F. Ercan, O. Atakol and F. N. Dincer, Acta Cryst., C53, 1056 (1997).
- 4. A. Gerli, K. S. Hagen and L. Marzilli, Inorg. Chem., 30, 4673 (1991).
- S. Uhlenbrock, R. Wegner and B. Krebs, J. Chem. Soc. Dalton Trans., 3731 (1996).
- I. Bertini, H. B. Gray, S. J. Lippard and J. S. Valentine, "Bioinorganic Chemistry", University Science Books, Mill Valley, p. 37 (1994).
- S. J. Lippard and J. M. Berg, "Principles of Bioinorganic Chemistry", University Science Books, Mill Valley, pp. 213-229 (1994).
- 8. F. Ercan and O. Atakol, Acta Cryst., <u>C54</u>, 1268 (1998).
- 9. M. N. Tahir, D. Ülkü, O. Atakol and O. Çakırer, Acta Cryst., C54, 468 (1998).
- C. C. Wang, W. C. Lo, C. C. Chou, H. G. Lee, Chen M. J. and M. S. Peng, Inorg. Chem., <u>37</u>, 4058 (1998).
- O. Atakol, L. Tatar, M. A. Akay and D. Ülkü, Analytical Sciences, 15, 101 (1999).
- 12. N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements", Pergamon Press, pp. 1395-1422 (1994).
- A. W. Addison, T. Rao, J. Reedijk, T. Van Rijn and G. C. Verschoor, J. Chem. Soc. Dalton Trans., 1349 (1984).

Received:	25 May 1999	Referee II:	P. Rabinovich
Accepted:	9 December 1999	Referee III:	T. J. McNeese