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ساختار مولکولی و بلوری کمپلکس‌های Zn(II) با لیگاند جدید بیس (تیوسمی‌کابازون)

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چکیده

دو کمپلکس روی بیس(تیوسمی‌کاربازون) از طریق برهمکنش روی استات با لیگاندهای H_3L1 و H_3L2 سنتز شدند و با دیفراکسیون اشعه‌ی ایکس شناسایی شدند. هر دو کمپلکس بصورت خنثی با لیگاند سه آنیونی می‌باشند. این لیگاندها دارای توالی دهنده‌های SNONS هستند و می‌توانند دو یون فلزی را در فاصله‌ی نزدیک به هم نگه دارند. فضای کوئوردیناسیون توسط اتم‌های نیتروژن ایمینی و سولفور تشکیل شده است و موقعیت‌های باقیمانده در یک هندسه‌ی هرم با قاعده‌ی مربعی توسط سه اتم اکسیژن اتری، استات-پل شده و آلکوکسید-پل شده اشغال شده است. ساختار مولکولی $[Zn_2\mathbf{L1}(CH_3COO)].EtOH$ و $[Zn_2\mathbf{L2}(CH_3COO)].MeOH$ مشابه هم می‌باشند در هر دو کمپلکس مراکز روی دارای هندسه‌ی هرم با قاعده‌ی مربعی هستند. پارامترهای سلول واحد برای $[Zn_2\mathbf{L1}(CH_3COO)].EtOH$، a = 10.3511(5) Å، b = 13.1247(9) Å، c = 14.7253(5) Å، α = 81.786(4)°، β= 85.567(4)° و γ = 69.583° و برای کمپلکس $Zn_2\mathbf{L2}(CH_3COO)].MeOH$، a = 10.2695(6) Å، b = 13.4464(7) Å، c=14.3869(7) A°، α = 83.200(4)° ، β =86.968(4)° و γ = 69.620(5)° می‌باشند.

واژه‌های کلیدی: بیس(تیوسمی‌کاربازون)، کمپلکس‌های دوهسته‌ای روی، شیف باز

Molecular and crysal structure of Zn(II) complexes with new bis(thiosemicarbazone) ligand

Abstract

Two new zinc bis(thiosemicarbazone) complexes have been synthesized by the reaction of the metal acetates with $\mathbf{H_3L1}$ and $\mathbf{H_3L2}$ ligands and characterized by single-crystal X-ray diffraction. Both of the complexes have an overall neutral charge with a trianionic ligand. Theses ligands having SNONS donor sequences, capable of holding two metal ions in close proximity, the coordination sphere is formed by the imine nitrogen and sulfur

atom, and the remaining positions, in a square-based pyramid, are occupied by tri oxygen atoms derived of ether, acetate-bridged and alkoxide-bridged groups. The molecular structure of [Zn_2**L1**(CH_3COO)].EtOH is similar to [Zn_2**L2**(CH_3COO)].MeOH, which show both of metal centers are in a square-based pyramid. Unit cell dimensions of [Zn_2**L1**(CH_3COO)].EtOH and [Zn_2**L2**(CH_3COO)].MeOH are a = 10.3511(5) Å, b = 13.1247(9) Å, c = 14.7253(5) Å, α = 81.786(4)°, β= 85.567(4)°, γ = 69.583° and a = 10.2695(6) Å, b = 13.4464(7) Å, c = 14.3869(7) Å, α = 83.200(4)°, β = 86.968(4)°, γ = 69.620(5)°, respectively.

Introduction

The zinc complexes of thiosemicarbazone ligands are excellent alternatives for fluorescent imaging agents [(D. Dayal and et al, 2011), (A. R. Cowley and et al, 2005)]. Zinc complexes not only are readily available, but also they are generally less cytotoxic to cells and are conveniently monitored as well [(E. Bermejo and et al, 2004), (T. S. Lobana and et al, 2009)] The versatile coordinating behavior of bis(thiosemicarbazone) ligands and the structural flexibility of zinc(II) cation leads to the formation of a variety of zinc bis(thiosemicarbazone) complexes with different coordination numbers and geometries. Therefore, formation of monomers, dimers, trimer (D. Dayal and et al, 2011) and polymeric (E. Lopez-Torres and et al, 2004) complexes of zinc bis(thiosemicarbazone) in square pyramidal, tetrahedral and octahedral geometry around zinc have been reported. Structure studies on the zinc complexes derived from pentadentate bis(thiosemicarbazones) have shown that these compounds have mononuclear structure with seven coordinate geometry (N. Chikaraishi and et al, 2003) or dimer structures as [7 + 7] (A. I. Matesanza and et al, 2005), [6 + 6] (C. A. Brown and et al, 2002), [6 + 4] (C. A. Brown and et al, 2002), [5 +5] (R. Pedrido and et al, 2005) and [4 + 4] (G. F. de Sousa and et al, 2000) stereochemistry in the solid state, and the energetic differences between the different crystalline forms should be very small, so the crystalline form of them could be determined by various factors, such as temperature, concentration, crystallization solvent, donor ability, polar or non-polar character, packing forces and synthesis procedure, etc (R. Pedrido and et al, 2005).

Results and discussion

Single crystals of [Zn_2**L1**(CH_3COO)].EtOH and [Zn_2**L2**(CH_3COO)].MeOH were grown by slow evaporation of chloroform/ethanol and chloroform/methanol solvent mixture, respectively. ORTEP views of complexes are shown in Figs. 1 and 2. These compounds are the first examples of dinuclear alkoxide-bridged zinc complexes derived from a bis(thiosemicarbazone) ligand. Generally, the dinuclear zinc complexes derived from pentadentate bis(thiosemicarbazones) are as dimer. These structures show both zinc atoms adopt a five-coordinate geometry with a [SNOOO] donor environment, via: the azomethine nitrogen atom, the thiolate sulfur atom, the ether oxygen atom, the bridging alkoxide oxygen atom and the oxygen atom from acetate group. Indeed, alkoxide oxygen atom and acetate group are bridged between two zinc(II) ions. In the both complexes, two oxygen derived from acetate group occupy the axial positions on both the metal center and another donors comprise the basal plane of the square-pyramid. The metal centers have near square pyramidal coordination geometry according to the geometrical parameter τ_5, defined as (β - α)/60, where β and α are the two largest coordination angles around the metal center. The τ_5 values are zero and one for perfect square pyramidal and trigonal bipyramidal geometry, respectively (D. Kovala-Demertzi and et al, 2006). The calculated τ_5 values are 0.04 and 0.05 for Zn1 and Zn2 respectively in [Zn_2**L1**(CH_3COO)].EtOH complex, showing that both of the zinc atoms have near square pyramidal geometry and for [Zn_2**L2**(CH_3COO)].MeOH complex, τ_5 values are 0.06 and 0.31 for Zn1 and Zn2 respectively showing that distortion of square pyramidal for the Zn2 is greater than Zn1. The negative charge of the trianionic ligands are delocalized over both of the bisthiosemicarbazone arms and the S–C bonds distances are consistent with increased single bond character, while the imine C–N distances and both thioamide C–N distances indicate considerable double bond character [(L. Latheef and et al, 2007), (A. castineiras and et al, 2002)]. Zn–O bonds lengths of the oxygen atoms derived from bridged acetate group are 1.976(2) and 1.997(2) Å for [Zn_2**L1**(CH_3COO)].EtOH and 1.972(2) and 1.993(2) Å for [Zn_2**L2**(CH_3COO)].MeOH. They are in good agreement with those dinuclear zinc complexes in which the acetate group is bridged between metal centers [(T. P. Stanojkovic and et al, 2010), (E. Bermejo and et al, 2004)] Furthermore alkoxide oxygen also acts as bridging between zinc centers. The Zn–O_{bridge} bond lengths 1.971(2) and 2.006(2) Å for [Zn_2**L1**(CH_3COO)].EtOH and 1.9760(19) and 1.9939(19) Å for [Zn_2**L2**(CH_3COO)].MeOH. Participation of deprotonated alcohol as a bridge between the zinc centers have not been found for dinuclear zinc complexes of bisthiosemicarbazones. Last oxygens involved in the coordination space, are etheric oxygens with bond lengths longer than the other oxygen bond lengths. Zn1–Zn2 distances for [Zn_2**L1**(CH_3COO)].EtOH and [Zn_2**L2**(CH_3COO)].MeOH complexes are 3.187 and 3.143 Å respectively. These distances are shorter than the distances that have been reported so far for dinuclear zinc complexes of bis(thiosemicarbazones), presumably because they are in dimers form. As you can see, there is little difference between the two complexes with chlorine and bromine substituents.

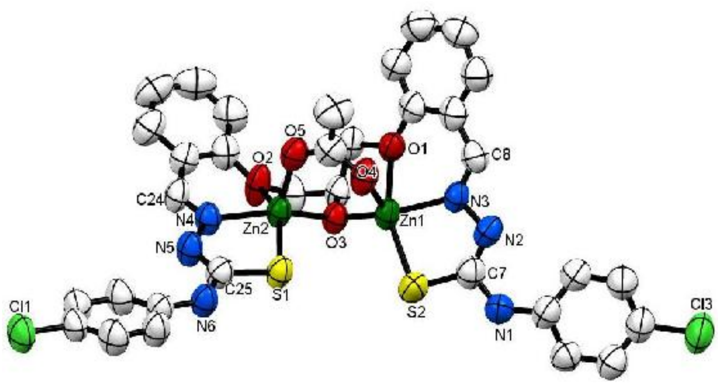

Fig. 7. Molecular structure of complex [Zn_2L1(CH_3COO)].EtOH

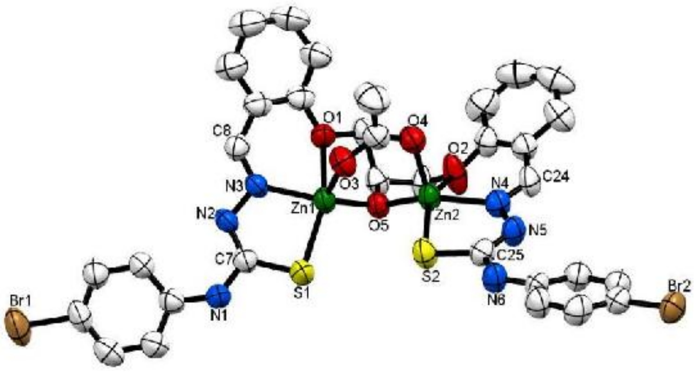

Fig. 6. Molecular structure of complex [Zn_2L2(CH_3COO)].MeOH

Table 1. Selected bond distances (Å) and angles (°) for [Zn_2L2(CH_3COO)].EtOH (1) and [Zn_2L4(CH_3COO)].MeOH (2)

bond distances	Complex 1	Bond angles	Complex 1	Bond distances	Complex 2	Bond angles	Complex 2
N3–Zn1	2.084 (3)	O3–Zn1–N3	142.76 (9)	C25–N5	1.311(4)	O1–Zn1–S1	147.40(6)
N4–Zn2	2.097 (3)	O4–Zn1–N3	100.39 (10)	C7–N2	1.315(4)	N3–Zn1–S1	85.27(7)
O1–Zn1	2.382 (2)	O3–Zn1–S2	105.44 (7)	C25–S2	1.757(3)	N3–Zn1–O5	140.79(8)
O2–Zn2	2.277 (2)	O4–Zn1–S2	123.57 (7)	C7–S1	1.744(3)	N3–Zn1–O3	101.42(9)
O3–Zn1	1.971 (2)	N3–Zn1–S2	84.36 (7)	O1–Zn1	2.3603(19)	S1–Zn1–O5	104.20(6)
O3–Zn2	2.006 (2)	O4–Zn1–O1	88.84 (9)	O3–Zn1	1.972(2)	S1–Zn1–O3	122.09(7)
O4–Zn1	1.976 (2)	S2–Zn1–O1	145.18 (6)	O5–Zn1	1.9760(19)	O5–Zn1–O3	104.88(8)
O5–Zn2	1.997 (2)	O5–Zn2–O3	99.69 (9)	N3–Zn1	2.084(2)	O4–Zn2–O5	100.60(8)
Zn1–S2	2.3063 (9)	O5–Zn2–N4	107.57 (10)	S1–Zn1	2.2999(8)	O4–Zn2–O2	102.31(9)
Zn2–S1	2.3038 (8)	O3–Zn2–N4	144.22 (10)	O5–Zn2	1.9939(19)	O4–Zn2–S2	109.00(6)
C25–S1	1.763 (3)	O5–Zn2–O2	101.50 (10)	O2–Zn2	2.303(2)	O4–Zn2–N4	106.91(9)
C7–S2	1.743 (3)	N4–Zn2–O2	77.03 (9)	O4–Zn2	1.993(2)	O2–Zn2–O5	74.76(8)
N2–C7	1.311 (4)	O5–Zn2–S1	110.39 (7)	S2–Zn2	2.3059(8)	O2–Zn2–S2	147.63(7)
N5–C25	1.314 (4)	O3–Zn2–S1	106.49 (6)	N4–Zn2	2.079(2)	N4–Zn2–O5	144.10(9)

Conclusion

In this paper, we report the synthesis of new zinc complexes of N(4)-substituted bis(thiosemicarbazone) ligands and showed the influence of different substitution on the phenyl ring of the thiosemicarbazone part and the role of hanging hydroxyl group on the structural of resulting zinc complexes. The interaction of the zinc(II) acetate salt with N(4)-substituted bis(thiosemicarbazone) ligands involving hanging hydroxyl group created dinuclear complexes. In fact, the presence of alkoxide oxygen provides the potential to form the dinuclear zinc complexes. The complex involving Cl substituent have C-S bond lengths longer than its analogue involving Br substituent on average.

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