



مطالعه‌ی ساختار بلوری کمپلکس Cu(II) با لیگاند نامتقارن بیس (تیوسمی کاربازون)

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چکیده

لیگاند نامتقارن چهاردندانه $H_2L1.2MeOH$ از تراکم متعاقب ۴-کلروفنیل تیوسمی کاربازید و ۴-بروموفنیل تیوسمی کاربازید با ۲-۳-۲ (فورمیل فنوکسی) پروپوکسی [بنزآلدئید سنتز شد. ساختار بلوری بیس (تیوسمی کاربازون) نامتقارن و کمپلکس مس آن با کریستالوگرافی اشعه‌ی ایکس شناسایی شدند. لیگاند بر اثر کوئوردیناسیون اتم‌های هیدروژن هیدرازینی را از دست می‌دهد و بعنوان چهاردندانه دوآنیونی عمل می‌کند. در کمپلکس $[CuL1].MeOH$ مرکز فلزی توسط دو اتم نیتروژن ایمینی و دو اتم تیولات کوئوردینه شده است و هندسه‌ی مسطح مربعی انحراف یافته را ایجاد نموده است. پارامترهای سلول واحد برای $[CuL1].MeOH$ ، $a = 19.107(4) \text{ \AA}$ ، $b = 9.110(2) \text{ \AA}$ ، $c = 19.966(4) \text{ \AA}$ ، $\alpha = 90^\circ$ ، $\beta = 106.93(2)^\circ$ ، $\gamma = 90^\circ$ و برای لیگاند $H_2L1.2MeOH$ ، $a = 9.2206(6) \text{ \AA}$ ، $b = 12.2704(5) \text{ \AA}$ ، $c = 30.985(2) \text{ \AA}$ ، $\alpha = 90^\circ$ ، $\beta = 90^\circ$ ، $\gamma = 90^\circ$ می‌باشند.

واژه‌های کلیدی: شیف باز، بیس (تیوسمی کاربازون‌های) نامتقارن، کمپلکس‌های مس

X-ray crystal structural studies of copper(II) complex of asymmetric bis(thiosemicarbazone) ligand

Abstract

Asymmetric, potentially tetradentate ligand $H_2L1.2MeOH$ is formed by subsequent condensation a 4-chlorophenyl thiosemicarbazide and 4-bromophenyl thiosemicarbazide on 2-[3-(2-formyl phenoxy)propoxy]benzaldehyde. The mixed bis(thiosemicarbazone) and its copper(II) complex have been characterized with X-ray crystallography. Ligand loses hydrazinic hydrogen atoms upon coordination and act as dianionic tetradentate donors. In $[CuL1].MeOH$ complex metal center is coordinated by two imine nitrogen atoms and two sulfur atoms with a distorted square planar coordination geometry. Unit cell dimensions of $[CuL1].MeOH$ and $H_2L1.2MeOH$ are $a = 19.107(4) \text{ \AA}$ ، $b = 9.110(2) \text{ \AA}$ ، $c = 19.966(4) \text{ \AA}$ ، $\alpha = 90^\circ$ ، $\beta = 106.93(2)^\circ$ ، $\gamma = 90^\circ$ and $a = 9.2206(6) \text{ \AA}$ ، $b = 12.2704(5) \text{ \AA}$ ، $c = 30.985(2) \text{ \AA}$ ، $\alpha = 90^\circ$ ، $\beta = 90^\circ$ ، $\gamma = 90^\circ$ ، respectively.



بیست و سومین همایش بلورشناسی و کانی‌شناسی ایران



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Introduction

The functionalization of bis(thiosemicarbazones) is used to improve the selectivity of hypoxic cells [(A. R. Cowley and et al, 2006), (P. D. Bonnitcha and et al, 2008), (J. L. J. Dearling and et al. 2002)] But the synthesis of mixed bis(thiosemicarbazones) and their purification is often accompanied by problems, some literatures referred to these problems [(J. P. Holland and et al, 2007), (M. Christlieb and J. R. Dilworth, 2006)]. In general, such compounds are produced by two different thiosemicarbazone moieties in several ways, in some of these molecules, two different arms of bis(thiosemicarbazone) been achieved through incorporation different substituent on part derived from aldehyde or ketone (E. A. Coats and et al, 1976) and in other molecules, by incorporation different N(4)-substituents [(P. D. Bonnitcha and et al, 2008), (S. R. Bayly and et al, 2006)]. Also in some compounds, both of the mentioned structural modification are accessed simultaneously [(J. L. J. Dearling and et al. 2002), (J. K. Lim and et al, 1997), (L. J. Ackerman and et al, 1999)]. Since biological activity has dependence on the thiosemicarbazone's N(4)-substituent, hence two different substituents may provide two modes of activity, as well as additional specificity, in inhibiting growth of human and animal tumors, fungi, bacteria or viruses, against which thiosemicarbazones have shown substantial inhibitory activity [(A. R. Cowley and et al, 2006), (L. J. Ackerman and et al, 1999), (L. J. Ackerman and et al, 1999)].

Results and discussions

Crystals of **H₂L1.2MeOH** (needle, colourless), were grown by slow evaporation of dichloromethane/methanol and crystals of [CuL1].MeOH (plate, brown) were grown chloroform/methanol solvent mixture. Figures 1-2 shows the molecular structures of **H₂L1.2MeOH** and [CuL1].MeOH. Table 1 reports selected bond distances and angles for the determined structures. Crystallographic data of complex show that the ligand act as tetradentate in a planar disposition with τ_4 index = 0.36. We include here the various structural parameters of **H₂L1.2MeOH** for comparison with the structures of the complex. As shown in Fig. 1, two bis(thiosemicarbazone) moieties have a trans orientation relative to each other, indicating that the complexation occurs after a 180° rotation around the carbon backbone of dialdehyde moiety. The C7–S1 and C25–S2 bond lengths of 1.673 and 1.683 Å, respectively, are within the range of C=S double bonds, also the C25–N5, C7–N2 and N5–N4, N3–N2 bond lengths are within the range of the normal single bonds indicating that the ligand exists in thione form in its solid state. In addition, the presence of H5A and H2A on the N5 and N2 atoms confirm obtained result, because thiol tautomeric form occurs after deprotonation at N5 and N2 atoms. The C–S bond distances increase on average from 1.678 Å in the free ligand **H₂L1.2MeOH** to 1.757 Å in the [CuL1].MeOH complex in agreement with formation of a thiolato bond, also the C–N_{thioamide} bond distances reduce from 1.355 Å to 1.299 Å due to deprotonation at N2 and N5 atoms and formation of new predominantly double bonds which refers to an extensive electron delocalization over the molecular skeleton. By comparing bond distances around the metal center and intra-ligand bonds such as C–N, N–N and C–S in the three complexes, it is clear that there is little difference between them. Therefore, based on crystallographic data can be said that both ligands have lost two proton from their tautomeric thiol forms and act as double negatively charged tetradentate ligands coordinating to the

copper(II) ion via two imine nitrogen atoms and two sulfur atoms. The bond lengths and bond angles are in good agreement with the reported data on related Cu(II) thiosemicarbazone complexes [(A. R. Cowley and et al, 2004), (L. Alsop and et al, 2005)].

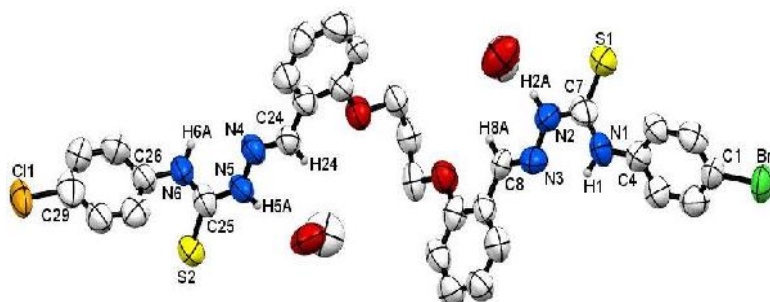


Fig. 1. Molecular structure of complex $H_2L1.2MeOH$

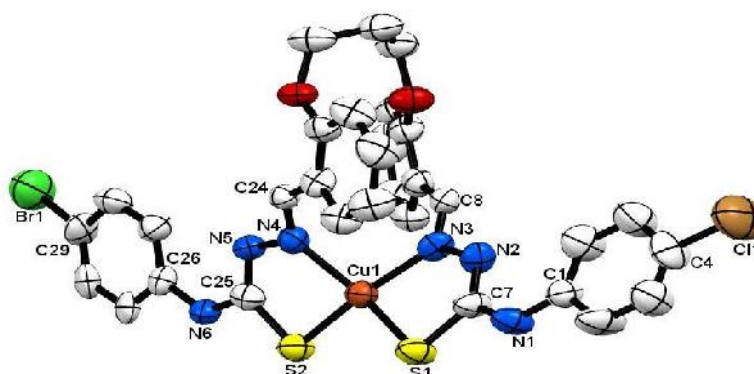


Fig. 2. Molecular structure of complex $[CuL1].MeOH$

Table 1. Selected bond distances (Å) and angles (°) for $[CuL1].MeOH$ and $H_2L1.2MeOH$

Bond distances	$[CuL1].MeOH$	Bond angles	$[CuL1].MeOH$	bond distances	$H_2L1.2MeOH$
Cu1–N4	2.001(6)	N3–Cu1–N4	98.9(2)	N3–N2	1.393(10)
Cu1–N3	1.993(5)	N4–Cu1–S2	85.26(16)	N4–N5	1.382(9)
Cu1–S2	2.2399(18)	N3–Cu1–S1	86.24(17)	N2–C7	1.357(12)
Cu1–S1	2.240(2)	N4–Cu1–S1	152.90(17)	C7–S1	1.673(10)
C25–S2	1.750(7)	N3–Cu1–S2	156.13(16)	N5–C25	1.354(11)
C25–N5	1.316(9)	S2–Cu1–S1	100.82(8)	C25–S2	1.683(10)
N5–N4	1.400(7)				
N3–N2	1.407(7)				
N2–C7	1.282(9)				
C7–S1	1.764(7)				

Conclusion

New unsymmetrical bis(thiosemicarbazone) ligand has been synthesized via incorporation different substituent on N(4)-phenyl, then its copper(II) complex has been synthesized and characterized using X-ray crystallography. In this complex, both ligands lose hydrazinic hydrogen atoms upon



coordination and act as doubly negative anions and coordinate the metal center by two imine nitrogen atoms and two sulfur atoms with a distorted square planar coordination geometry. C-S bond lengths in arm of bis(thiosemicarbazone) involving chlorine substituent are longer than the other arm containing bromine substituent, which refers to an extensive electron delocalization over the molecular skeleton in the presence of chlorine substituent.

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