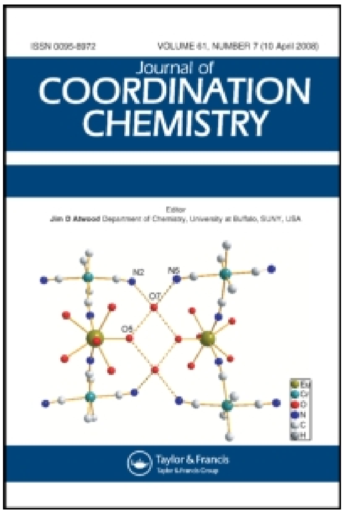

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal structure and thermal behaviour of copper(II) and zinc(II) complexes with *N*-pyrrolidine-*N*′-(2-chloro-benzoyl)thiourea

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To cite this Article Arslan, H. , Flörke, U. , Külcü, N. and Emen, M. F.(2006) 'Crystal structure and thermal behaviour of copper(II) and zinc(II) complexes with *N*-pyrrolidine-*N*′-(2-chloro-benzoyl)thiourea', Journal of Coordination Chemistry, 59: 2, 223 — 228

To link to this Article: DOI: 10.1080/00958970500270992
URL: http://dx.doi.org/10.1080/00958970500270992

Journal of Coordination Chemistry
Vol. 59, No. 2, January 2006, 223–228

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Crystal structure and thermal behaviour of copper(II) and zinc(II) complexes with *N*-pyrrolidine-*N*′-(2-chloro-benzoyl)thiourea

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(*Received in final form 2 June 2005*)

The crystal structures and thermal behaviour of bis(*N*-pyrrolidine-*N*′-(2-chloro-benzoyl) thioureato)zinc(II) (ZnL_2) and its copper(II) analogue (CuL_2) are reported. In both structures, the metal atoms are coordinated by two oxygen and two sulfur atoms to form neutral *trans*-square planar (Cu) and distorted tetrahedral (Zn) species. The thermal decomposition of the complexes was investigated by TG and DTA.

Keywords: Copper(II); Zinc(II); Benzoylthiourea; X-ray structure; Thermal behaviour

1. Introduction

Thioureas have a long history as a ligand in coordination chemistry and coordinate to a metal via both sulfur and oxygen [1]. These hard and soft donor atoms provide a multitude of bonding possibilities [2]. Hydrogen bonding behaviour of some thioureas has been investigated and it is found that intramolecular hydrogen bonds between the carbonyl oxygen and a hydrogen atom on N′ is common. The development of selective extractants for the separation and pre-concentration of transition metals at trace levels reflects an increasing need for these metals to be recovered and analysed. Of extractants containing soft and hard atoms, a novel group of benzoylthioureas has been reported to form complexes with Cu, Fe, Pb, Ni, Zn, Cd, Co, Ag, Pd, Hg and Au [3–5]. The synthesis of new agents able to coordinate these toxic metal ions with a view to obtaining complexes that can be readily eliminated is an important

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500270992

area of research [6]. Recently, our research has focussed on the chemical and physical properties of benzoylthiourea derivatives and their metal complexes [7–14]. In the present work, we report the crystal structures of copper(II) and zinc(II) complexes of *N*-pyrrolidine-*N*′-(2-chlorobenzoyl)thiourea, together with their thermal properties.

2. Experimental

2.1. *Instrumentation*

Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD [15] using monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Semi-empirical absorption corrections from equivalents were applied [15]. The structures were solved by direct and conventional Fourier methods [15]. Full-matrix least-squares refinement [15] was based on F^2, with non-H atoms being refined anisotropically. H atoms were refined isotropically at idealized positions with a riding model. Further details concerning data collection and refinement are given in table 1. DTA and TG curves were obtained simultaneously with a Shimadzu DTG-60H instrument. The heating rate was $10\,\mathrm{K\,min^{-1}}$ with a nitrogen flow rate of furnace atmosphere – $60\,\mathrm{cm^3\,min^{-1}}$. The sample mass was 12 mg and the reference used was α-Al_2O_3. X-ray powder diffraction analyses of the final residues were carried out with a Siemens, F model diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å).

Table 1. Summary of crystallographic data and refinement parameters for CuL_2 and ZnL_2.

Compound	CuL_2	ZnL_2
Empirical formula	$C_{24}H_{24}Cl_2CuN_4O_2S_2$	$C_{24}H_{24}Cl_2ZnN_4O_2S_2$
Formula weight	599.03	600.86
Temperature (K)	173(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	13.1595(11)	11.5476(13)
b (Å)	11.1280(9)	11.9313(13)
c (Å)	8.6052(7)	18.784(2)
β (°)	97.817(2)	105.453(1)
V (Å^3)	1248.43(18)	2494(5)
Z	2	4
D_c (Mg m^{-3})	1.594	1.600
μ (mm^{-1})	1.287	1.397
F(000)	614	1232
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.10$	$0.30 \times 0.20 \times 0.18$
Index ranges	$-17 \leq h \leq 14$, $-14 \leq k \leq 14$, $-5 \leq l \leq 11$	$-15 \leq h \leq 15$, $-15 \leq k \leq 14$, $-24 \leq l \leq 25$
Reflections collected	7747	25544
Independent reflections (R_{int})	2914 (0.0248)	6214 (0.0949)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	2914/160	6215/316
Goodness-of-fit on F^2	1.081	0.830
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0354$, $wR2 = 0.0831$	$R1 = 0.0402$, $wR2 = 0.0512$
R indices (all data)	$R1 = 0.0435$, $wR2 = 0.0869$	$R1 = 0.0926$, $wR2 = 0.0580$
Largest diff. peak and hole	0.375 and -0.250 e Å^{-3}	0.615 and -0.399 e Å^{-3}

2.2. *Synthesis*

The ligand and its complexes were prepared by a procedure similar to that reported in the literature [7, 16]. The complexes were recrystallized from ethanol : dichloromethane mixture (1 : 1).

3. Results and discussion

The molecular structures of the copper and zinc complexes are depicted in figures 1 and 2, respectively. Selected bond lengths and angles are listed in table 2. The complexes are four-coordinate, involving two oxygen and two sulfur atoms [S1–Cu1–S1A = 180° and O1–Cu1–O1A = 180° for CuL_2 with Cu lying on a crystallographic inversion centre; S1–Zn1–S2 = 124.85(4)° and O1–Zn1–O2 = 99.19(9)° for ZnL_2]. The S_2O_2 coordination in CuL_2 is essentially planar whereas the Zn complex has distorted tetrahedral geometry.

The bond lengths of the carbonyl and thiocarbonyl groups [C7–O1 = 1.271(3), C8–S1 = 1.733(3) Å for the zinc complex and C7–O1 = 1.270(2), C8–S1 = 1.725(2) Å for the copper complex] lie between those corresponding to double and single bonds, a feature known in related structures [7, 17, 18]. This is due to strong delocalization in the chelate rings. As expected, Cu–O [Cu1–O1 = 1.9078(15) Å] bond lengths are shorter than Zn–O distances [Zn1–O1 = 1.964(2), Zn1–O2 = 1.959(2) Å]. Similar differences are observed for the metal–sulfur bond lengths [Cu–S = 2.2417(6) Å, Zn–S averages 2.2687(9) Å].

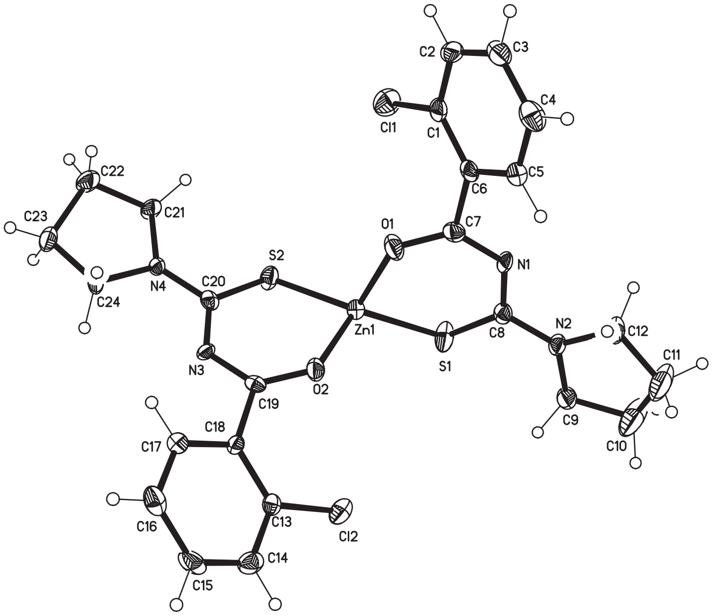

Figure 1. Molecular structure of bis(*N*-pyrrolidine-*N*′-(2-chloro-benzoyl)thioureato)zinc(II) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

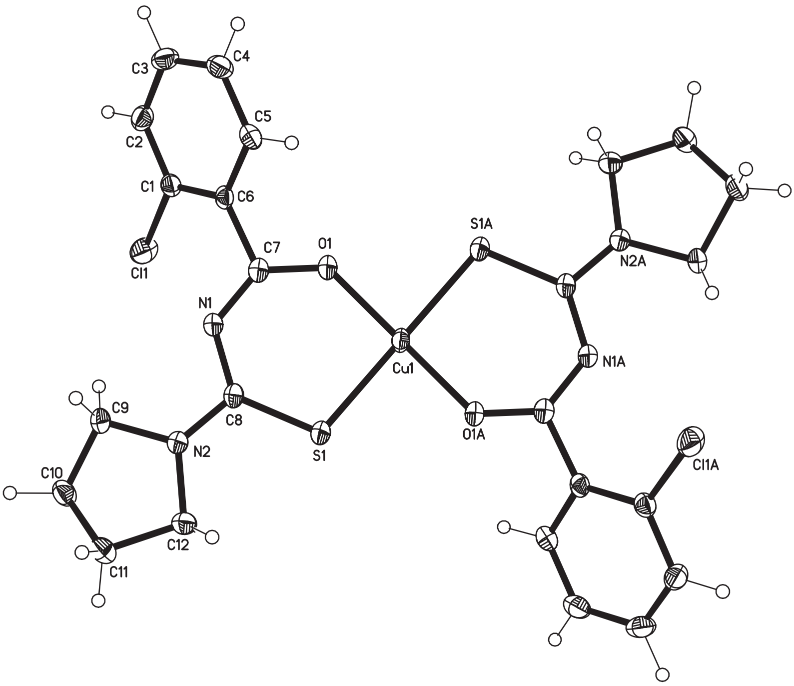

Figure 2. Molecular structure of bis(*N*-pyrrolidine-*N′*-(2-chloro-benzoyl)thioureato)copper(II) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes.

ZnL₂			
Zn1–S1	2.2653(9)	Zn1–S2	2.2722(9)
Zn1–O1	1.964(2)	Zn1–O2	1.959(2)
C8–N1	1.356(3)	C8–N2	1.328(3)
N1–C7	1.304(3)	C6–C7	1.502(4)
C7–O1	1.271(3)	S1–C8	1.733(3)
O1–Zn1–O2	99.19(9)	O1–C7–N1	130.5(3)
S1–Zn1–S2	124.85(4)	C7–N1–C8	125.7(3)
O1–Zn1–S2	115.75(7)	N1–C8–S1	129.2(2)
O2–Zn1–S1	119.58(7)	C8–S1–Zn1	101.52(11)
O1-Zn1–S1	97.14(7)	O1–C7–C6	114.7(3)
O2–Zn1–S2	98.35(6)	S1–C8–N2	116.3(2)
Zn1–O1–C7	127.4(2)		
CuL₂			
Cu1–S1	2.2417(6)	Cu1–O1	1.9078(15)
N1–C7	1.305(3)	C7–O1	1.270(2)
S1–C8	1.725(2)	C6–C7	1.499(3)
C8–N1	1.361(3)	C8–N1A	1.324(3)
O1–Cu1–O1A	180	C7–N1–C8	124.64(18)
S1–Cu1–S1A	180	N1–C8–S1	129.67(15)
O1–Cu1–S1A	85.56(5)	C8–S1–Cu1	107.52(7)
O1–Cu1–S1	94.44(5)	O1–C7–C6	112.91(17)
Cu1–O1–C7	132.5(14)	S1–C8–N1A	116.59(15)
O1–C7–N1	131.21(19)		

The complexes were studied by thermogravimetry from ambient temperature to 1500 K in a nitrogen atmosphere. From the TG curve of CuL_2, it appears that the sample decomposes in two stages over the temperature range 400–1482 K. The first decomposition step occurs between 400 and 551 K with a mass loss of 22.4%; the second starts at 551 K and ends at 1482 K with a 62.1% mass loss. In the corresponding DTA profile, exothermic and endothermic peaks are noted, the first between 394 and 507 K with a maximum at 437 K and the second between 554 and 656 K with a maximum at 599 K, respectively. The first exothermic effect is associated with decomposition of the complex. We could not observe an endothermic effect for the melting of the copper complex, because decomposition and melting occur simultaneously, even though we tried to separate both effects by varying the heating rate. The ultimate product is $Cu_{1.96}S$ (JPDF File No. 29-0578). The TG curve of ZnL_2 complex shows an initial mass loss in the temperature range 517–620 K, corresponding to decomposition of the complex to $Zn(SCN)_2$ (theoretical mass loss: 69.8%, experimental: 70.3%) [19]. The last decomposition step occurs in the temperature range 620–1277 K and corresponds to the formation of ZnS (theoretical mass loss: 83.8%, experimental: 82.7%), also confirmed by XRD. The DTA curve shows two endothermic peak maxima at 507 and 556 K, the former corresponding to melting and the latter to decomposition to $Zn(SCN)_2$.

Supplementary material

Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with numbers CCDC 271221 for CuL_2 and CCDC 271222 for ZnL_2. Copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336-033, email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Mersin University Research Fund (Projects BAP.ECZ.TB.HA. 2004-3 and BAP.FEF.KB.NK.2004.2). We would like to thank Mr T. Yesilkaynak for measuring the DTA/TG diagrams.

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