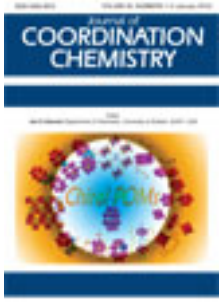
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:40
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Study of copper(I) heteroleptic compounds with 1-phenyl-1, 4-dihydro-tetrazole-5-thione and triphenylphosphine

Saleh Shakhatreh [a], Maria Lalia-Kantouri [b], Maria Gdaniec [c] & Pericles D. Akrivos [b]

[a] Al Huson University College, Al Balqa' Applied University, P.O. Box 50, Al-Huson, Jordan

[b] Department of Chemistry, Laboratory of Inorganic Chemistry, Aristotle University of Thessaloniki, P.O. Box 135, GR-541 24 Thessaloniki, Greece

[c] Faculty of Chemistry, Adam Mickiewicz University, 60 780 Poznań, Poland

Published online: 22 Dec 2011.

To cite this article: Saleh Shakhatreh, Maria Lalia-Kantouri, Maria Gdaniec & Pericles D. Akrivos (2012) Study of copper(I) heteroleptic compounds with 1-phenyl-1, 4-dihydro-tetrazole-5-thione and triphenylphosphine, Journal of Coordination Chemistry, 65:2, 251-261, DOI: 10.1080/00958972.2011.647001

To link to this article: http://dx.doi.org/10.1080/00958972.2011.647001

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 http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [Renmin University of China] at 10:40 13 October 2013

Journal of Coordination Chemistry
Vol. 65, No. 2, 20 January 2012, 251–261

Taylor & Francis
Taylor & Francis Group

Study of copper(I) heteroleptic compounds with 1-phenyl-1, 4-dihydro-tetrazole-5-thione and triphenylphosphine**

SALEH SHAKHATREH†, MARIA LALIA-KANTOURI‡, MARIA GDANIEC§ and PERICLES D. AKRIVOS*‡

†Al Huson University College, Al Balqa' Applied University, P.O. Box 50, Al-Huson, Jordan
‡Department of Chemistry, Laboratory of Inorganic Chemistry, Aristotle University of Thessaloniki, P.O. Box 135, GR-541 24 Thessaloniki, Greece
§Faculty of Chemistry, Adam Mickiewicz University, 60 780 Poznań, Poland

(*Received 3 October 2011; in final form 21 November 2011*)

The synthesis and structural investigation of three mononuclear heteroleptic copper(I) complexes of 1-phenyl-1,4-dihydro-tetrazole-5-thione (HL) with the stoichiometry [CuX(HL)$(PPh_3)_2$], where X represents a halide, are reported. The compounds were studied both in the solid state and in solution by a variety of spectroscopic methods. X-ray crystal structure determination of the three compounds revealed a distorted tetrahedral coordination environment around copper in every case. The thermal behavior of the complexes was investigated with respect to the thione ligand fragmentation. Complexation to copper(I) has a stabilizing effect on the nitrogen-rich thione as the TG studies on the free ligand reveal.

Keywords: Thioamide; Tetrazole thione; Copper(I) complexes; Crystal structure; Thermal behavior

Downloaded by [Renmin University of China] at 10:40 13 October 2013

1. Introduction

Heterocyclic thioamides have versatility of coordination schemes in the synthesis of their coordination compounds where several alterations occur as in color and nature of the reaction mixture [1]. Their homoleptic compounds generally show low solubility, preventing extended spectroscopic studies other than those carried out in the solid state. Their heteroleptic complexes, however, especially when the other ligands are phosphines, provide enhanced solubility and have been studied in detail with a variety of spectroscopic and other physical methods; valuable information has been retrieved by crystal structure determinations [2].

Thioamides may adopt a range of coordination modes as the availability of two lone electron pairs on the thioamide sulfur; this versatility is enhanced in the case of a neighboring heterocyclic nitrogen atom which may also participate in bonding. Besides the normally expected bridges chelate formation also occurs. There are cases in the

*Corresponding author. Email: akrivos@chem.auth.gr
**Dedicated to the memory of Professor Stefan I. Stoyanov.

ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.647001

literature where more than one bonding mode has been detected in the same crystal of a coordination compound [3]. Furthermore, the ability of the ligands to undergo thiol – thione tautomerism allows "thione" or "thiol" complexes. Deprotonation of the ligands in solution may therefore give "thionate" or "thiolate" anionic ligands which have both been observed in coordination compounds [4, 5]. In this case the predominant coordination mode of the heterocyclic thioamides is that of bidentate bridging accompanied by the formation of oligonuclear clusters [6].

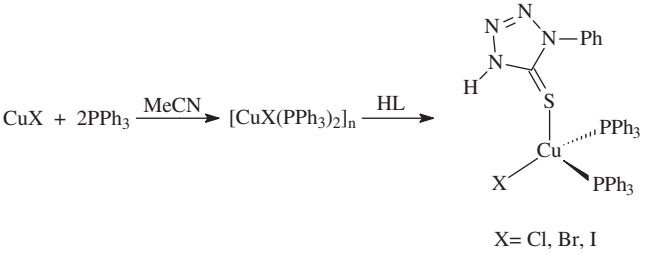
Apart from academic interest in the coordination compounds of thiones, their applications in a variety of aspects related to life and technology adds to their merit. Their close structural resemblance to thioamides, their possession of a mercapto group, which is the most active moiety in the cell, and their redox ability have made them a good starting point for biological studies [7, 8]. Furthermore, the properties of surfaces are notoriously being transformed by adsorption or bonding of thiolate compounds and they are made therefore more appropriate for a variety of applications including molecular-based electronics, chemical sensors, etc. [9].

Among the numerous heterocyclic systems, 5-substituted tetrazoles and especially 5-oxo and 5-thio possess wide applications in biology. For instance many pesticides and herbicides possess such a backbone as well as drugs patented for the treatment of central nervous system disorders, HIV, asthma, obesity, and diabetes. Analogous substructures are also present in many antiviral, antibacterial, analgesic, anesthetic, antihistaminic, antimicrobial, and antiinflammatory drugs [10]. Tetrazoles are a group with high nitrogen content and have therefore been studied as to the extent of thermal decomposition, releasing N_2 or HN_3, provided that they possess relatively high density and decomposition temperature they might be candidates for energetic materials in propellant systems [11]. This study is concerned with the synthesis and structural investigation of heteroleptic copper(I) complexes which incorporate the characteristic moieties of tetrazoles and heterocyclic thioamides. Three complexes with the stoichiometry $[CuX(PPh_3)_2(HL)]$, where X is Cl, Br, or I and HL the title tetrazolinethione, have been crystallized and studied both in the solid state and in solution (scheme 1).

2. Experimental

2.1. *Materials and measurements*

Organic molecules and the copper(I) halides were obtained from Aldrich while the solvents used for the synthesis and spectroscopic measurements were products of Merck and were all used without any purification.



Scheme 1. Synthetic route for **1**–**3**.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

Thermal behavior studies were performed under dinitrogen at a heating rate of $5^{\circ}C\,min^{-1}$ up to 400°C on a SETARAM TG-DSC 15 thermogravimetric analyzer using Al_2O_3 crucible using samples between 5 and 10 mg. Infrared spectra were recorded in KBr discs on a Perkin-Elmer 1600 FTIR spectrometer operating at the mid-infrared following the accumulation of 16 pulses at a resolution of $4\,cm^{-1}$ and electronic excitation spectra were obtained on a Hitachi U-2001 spectrophotometer using 1 cm quartz cuvettes. NMR for ^{1}H and ^{13}C were measured at 300 and 75 MHz, respectively, in $CDCl_3$ solutions on a Bruker 300 spectrometer using TMS as internal standard.

X-ray diffraction studies of **1**, **2**, and **3** were carried out with a KM4CCD diffractometer using graphite-monochromated Mo-Kα radiation. The unit cell determination and data integration were carried out using the CRYSALIS software [12]. Intensity data were corrected for Lorentz-polarization factors and for absorption. The structures were solved by direct methods using the SHELXS-97 program [13] and refined with SHELXL-97 [14] by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms. All hydrogen atoms were located on difference Fourier maps. For the refinement procedure H atoms were placed geometrically (C–H = 0.96 Å, N–H = 0.90 Å) and treated as riding on their parent atoms with $U_{iso} = 1.2 \times U_{eq}$(C,N). Crystal data and some other details of the X-ray structural analyses are given in table 1.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

2.2. *Synthesis of the compounds*

In a typical synthesis, a concentrated acetonitrile solution of 1.0 mmol of the appropriate copper(I) halide was prepared and 2.0 mmol of triphenylphosphine was added. The mixture produced a white solid which was left to stir at room temperature for a few minutes before adding 1.0 mmol of the thione. The solution became transparent instantly and was left to stir at room temperature for an hour. Filtration of small quantities of undissolved material produced clear solutions which were concentrated at the rotary evaporator to about half of the original volume. The amorphous or microcrystalline materials isolated were recrystallized from acetonitrile–dichloromethane solutions and upon slow evaporation at room temperature produced crystals suitable for X-ray determination. Anal. Calcd for **1** (%): C, 64.42; H, 4.53; N, 6.99. Found: C, 64.30; H, 4.41; N, 7.04. Anal. Calcd for **2** (%): C, 61.03; H, 4.29; N, 6.62. Found: C, 61.20; H, 4.14; N, 6.34. Anal. Calcd for **3** (%): C, 57.82; H, 4.06; N, 6.27. Found: C, 57.60; H, 3.99; N, 6.08.

3. Results and discussion

3.1. *Spectroscopic data*

The spectra confirm the existence of the thioamide in its thione tautomeric form [15, 16] on the basis of the observation of N–H stretching frequencies but not the corresponding S–H ones. Furthermore, coordination of the ligand with the exocyclic sulfur is verified by the relative shifts of the characteristic thioamide bands [17, 18] relative to the ones of the free ligand. The first thioamide band observed at $1491\,cm^{-1}$ in the ligand appears at slightly lower wavenumbers. Thioamide II band is observed at $1272\,cm^{-1}$ for the free

Table 1. Crystal data and structure refinement for **1**–**3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{43}H_{36}ClCuN_4P_2S$	$C_{43}H_{36}BrCuN_4P_2S$	$C_{43}H_{36}CuIN_4P_2S$
Formula weight	801.75	846.21	893.20
Temperature (K)	294	110	294
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)			
a	10.1568(5)	16.2320(6)	16.6420(5)
b	12.9649(5)	14.1004(4)	14.2149(4)
c	15.5540(6)	18.2692(7)	18.5211(6)
α	74.053(4)	90	90
β	79.097(4)	112.546(3)	113.535(3)
γ	80.310(4)	90	90
Volume (Å^3), Z, Z'	1919.07(14), 2, 1	3861.8(2), 4, 1	4017.0(2), 4, 1
Absorption coefficient (mm^{-1})	0.813	1.774	1.479
Crystal size (mm^3)	$0.50 \times 0.40 \times 0.30$	$0.5 \times 0.4 \times 0.2$	$0.35 \times 0.30 \times 0.20$
θ range for data collection (°)	3.49–25.03	3.20–26.37	3.57–26.37
Reflections collected	14,336	21,509	21,879
Independent reflection	6724 [R(int) = 0.0199]	7839 [R(int) = 0.0252]	8171 [R(int) = 0.0260]
Completeness to θ (max) (%)	99.2	99.4	99.5
Data/restraints/parameters	6724/0/469	7839/0/469	8171/0/469
Goodness-of-fit on F^2	1.073	1.083	1.127
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$; $wR_2 = 0.0865$	$R_1 = 0.0307$; $wR_2 = 0.0735$	$R_1 = 0.0404$; $wR_2 = 0.1002$
R indices (all data)	$R_1 = 0.0432$; $wR_2 = 0.0914$	$R_1 = 0.0360$; $wR_2 = 0.0764$	$R_1 = 0.0535$; $wR_2 = 0.1083$
Largest difference peak and hole (e Å^{-3})	0.323 and −0.297	0.518 and −0.404	1.091 and −0.545

Downloaded by [Renmin University of China] at 10:40 13 October 2013

ligand while in the complexes studied it is constantly observed at higher wavenumbers. Negligible shifts are observed in the region of the thioamide III band (1050 cm^{-1} in the ligand spectrum) while small shifts to higher wavenumbers are present in the spectra of the complexes relative to the thioamide IV band of the ligand (751 cm^{-1}). Of course no absolute evidence can be deduced from the positions of these bands because, although they are normally correlated with CN (thioamide I and II) and CS (thioamide III and IV) bond stretches they correspond to strongly coupled vibrations [19]. However, the shifts of the bands occurring upon coordination are in line with observations made for related sulfur-coordinating thioamides [20]. The P–C bond stretches are observed in the expected region [21] and are indicative of coordination of phoshpine to the metal centre. These bands appear at 510 and 520 cm^{-1} and do not vary significantly with the halogen present.

Electronic excitation spectra in the visible and ultra-violet regions are dominated by bands originating in the ligands and show only minor changes due to solvation. They have been recorded in 1×10^{-4} molL^{-1} solutions in MeCN and CH_2Cl_2. The spectra are dominated by a broad band with a low energy shoulder not further than 285 nm. The spectra are almost identical between the three halide compounds in each solvent and there is only a minor red shift, not exceeding 5 nm, upon dissolving in acetonitrile, indicating that there is no appreciable charge transfer character in the low energy side of the band. The above spectroscopic behavior is identical to analogous triphenylarsine compounds [20].

The ^{1}H and ^{13}C NMR spectra of the compounds reveal signals expected from their stoichiometry. Due to the presence of aromatic protons it was not possible to locate accurately the thione NH in the spectra. The proton spectra are dominated by an extremely complex multiplet ranging between 7.15 and 7.56 ppm which incorporates the 35 aromatic protons of the triphenylphosphine and the 1-phenyl substituent of the thione. However, the range of the multiplet appears to follow the trend observed in the corresponding triphenylarsine compounds where it moves downfield with less electronegative halide [20]. Due to rapid rotation of the phenyl rings in solution a series of 13 close lying signals are observed in all the ^{13}C NMR spectra of the complexes. The most characteristic among them is the resonance of the thione sp^2 carbon at 163.1, 162.5, and 161.9 ppm for **1**, **2**, and **3**, respectively. The ^{31}P NMR spectra reveal a single phosphorus signal in every case, rather broad due to the proximity of the quadrupolar copper nucleus and moving upfield from −3.57 ppm for the chloride to −4.06 ppm for the bromide toward −5.16 ppm for the iodide.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

3.2. *Crystallographic information*

Relevant information about crystal structure determinations of the three compounds are reported in table 1, and the most significant structural parameters in table 2.

Compounds **1**–**3** crystallize in centrosymmetric space groups and consist of discrete molecules (figures 1 and 2). Crystals of the bromido and iodido complexes are isostructural and thus molecular structures of **2** and **3** are very similar. In all studied complexes the environment around copper is distorted tetrahedral as usual, the larger angle being observed between the triphenylphosphine ligands. This angle varies between 123.5 and 125.0° and lies at the higher limit of the observed values in analogous compounds [22]. The arrangement of the thioamide ligand within the complex is dictated by the intramolecular N–H···X hydrogen bond, an interaction observed in all known complexes of formula $[CuX(HL)(PPh_3)_2]$, where X is halogen and HL is a thioamide ligand [23]. A survey of some 40 crystal structures of compounds with the formula $[CuX(thione)(PPh_3)_2]$ reveals that in these compounds the Cu–S distance ranges from 2.33 to 2.46 Å, with the mean value of 2.38 Å, whereas in **1**–**3** the Cu–S bond lengths vary from 2.375 Å in **2** to 2.509 Å in **1**. The ligand is seldom found coordinated in its neutral form; in fact there is only one structure to our knowledge where in a copper(I) cluster of formula $[Cu_4I(L)_3(HL)_3]$ the neutral ligands are monodentate through sulfur with a Cu–S bond distance of 2.267 Å [24], appreciably shorter than the ones in **1**–**3**. The anionic ligands have the expected bridging coordination mode utilizing one of the tetrazole ring nitrogen atoms as in most of the complexes to other metals too. However, there exist several cases where the anion is bonded only through sulfur, for example in $Pd(L)_2(PMe_3)_2$ [25], $Pt(L)_2(PEt_3)_2$ [26], $Hg(L)_2(PPh_3)_2$, $Au(L)(PPh_3)$, $[Au(L)_2]^-$ and $Ag(L)(PPh_3)_2$ [6], or $Cr(L)(CO)_3(Cp)$ [27]. A marked difference between the Cu–S bond lengths in **1** with respect to the other two reflects a slightly different coordination environment of the Cu center. It appears that this represents the longest observed Cu–S bond length in monovalent copper thiolates. A closer inspection of the structure reveals that the tetrazole ring participates in intramolecular π–π stacking, with its double N=N bond placed at 3.66 Å from the centroid of one of the triphenylphosphine phenyl rings. This interaction is not observed

Table 2. Relevant bond lengths (Å) and angles (°) for **1**–**3**.

	1	**2**	**3**
Cu–X	2.3415(7)	2.5266(3)	2.7045(4)
Cu–P	2.2725(6)	2.2548(5)	2.2742(9)
	2.2941(6)	2.2812(6)	2.2996(9)
Cu–S	2.5085(7)	2.3752 (6)	2.3895(9)
S–C	1.674(2)	1.679(2)	1.680(3)
X–Cu–P	110.60(2)	107.097(16)	107.02(2)
	109.11(2)	101.311(17)	100.41(2)
X–Cu–S	99.07(2)	109.336(16)	109.88(3)
S–Cu–P	102.85(2)	110.96(2)	111.06(3)
	106.59(2)	103.99(2)	104.51(3)
P–Cu–P	125.13(2)	123.65(2)	123.50(3)

Downloaded by [Renmin University of China] at 10:40 13 October 2013

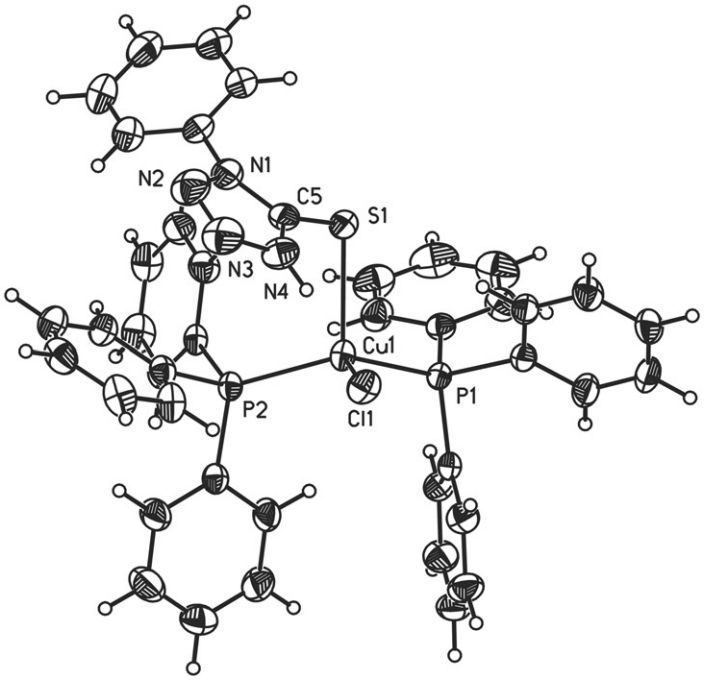


Figure 1. Molecular structure of **1**. The proximity of one of the phenyl rings of triphenylphosphine to the N=N bond of the thioamides ligand is evident. The intramolecular N–H · · · Cl hydrogen bond is shown with a dashed line.

in the other two compounds, where the distance between the center of the N=N double bond and the nearest phenyl ring centroid is increased to 3.99 Å.

In all three cases, the N2–N3 bond of the coordinated thioamide is close to a double N=N bond (1.276 Å), something that would give rise to interesting reactivity especially in cycloaddition reactions or in the thermal behavior where it would be expected to release dinitrogen more promptly than to undergo other pathways of decomposition.

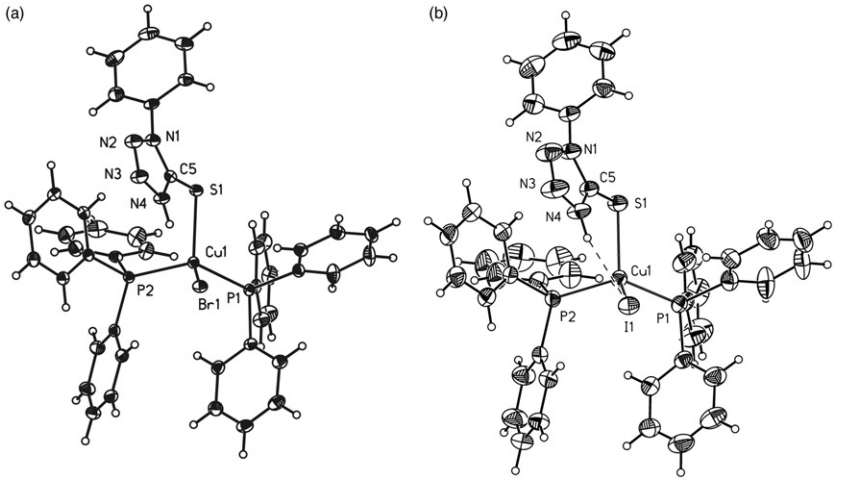


Figure 2. Molecular structures for **2** (a) and **3** (b). The intramolecular hydrogen bonds N–H $\cdots$ X are shown with dashed lines.

Our results, however, reveal that in solution there must take place some reorganization of the molecules with an effect on the specific bond which did not function as an asymmetric dienophile in several attempts to perform typical cycloaddition reactions with benzyl, anthracene, and tetraphenylcyclopentadienone even after prolonged reactions for over 72 h.

3.3. *Thermal studies*

Since tetrazoles follow a complex pattern of decomposition involving release of several products, the main interest focusing on release of dinitrogen [28, 29], the thermal behavior study of the compounds was limited to a range of temperatures not exceeding 400°C. Preliminary studies of the compounds revealed that they undergo several decomposition steps and therefore no true melting point was recorded. The above observations prompted thermal studies on the bis(triphenylphosphine) compounds for which there is sufficient knowledge of their molecular structure.

All thermodiagrams present an exothermal procedure corresponding to dinitrogen loss from the coordinated thioamides. The temperatures where this loss is detected are 180, 193, and 176°C for **1**, **2**, and **3**, respectively. At 200–220°C a slightly exothermal phenomenon is observed which may be attributed to some reorganization of the molecule. Such reorganization is expected since elimination of part of the ligand leads to the formation of a small ring which readily undergoes ring opening and consequently further polymerization reactions. Recent studies have shown that thermal decomposition of 5-substituted tetrazoles proceeds through two possible pathways, involving evolution of dinitrogen or hydrazoic acid both occurring around 200°C [30, 31]. The relative weight of these two routes is dictated by the stability of the residue to which the ring substituents contribute significantly as quantum chemical calculations have revealed [29].

Downloaded by [Renmin University of China] at 10:40 13 October 2013

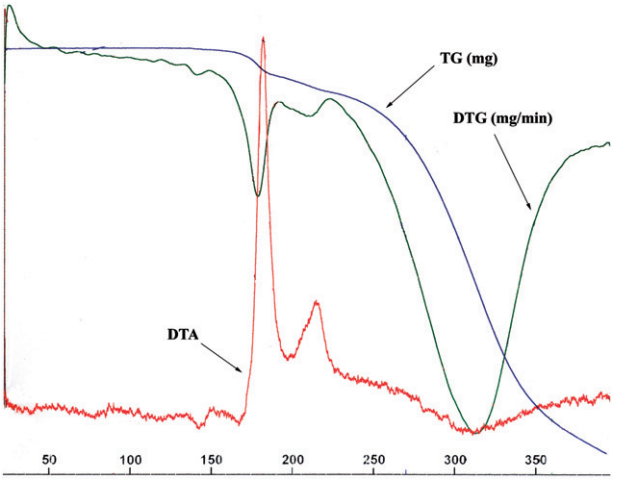


Figure 3. Thermal behavior of **1** up to 400°C.

In a further step, the coordinated phosphines are removed and the process is completed in the 320–330°C regions. A representative diagram for **1** is shown in figure 3.

A thermal study was undertaken for the ligand itself under identical experimental conditions. The decomposition of the compound is indicated by an extensive exothermal phenomenon at 160°C accompanied by a loss of 41% of its total mass, followed by two successive steps up to 300°C whereupon a total loss of 60% of weight is recorded. A Pfeiffer/Vacuum Thermostar quadrupole mass spectrometer coupled to the thermobalance (TG-MS) was employed to record the gas evolution profiles. Secondary reactions were minimized by placing the probe close to the sample crucible of the thermobalance in the direction of the gas flow. The gas line between the TG and the MS was heated to 180°C in order to avoid cold points and subsequent condensation of the gaseous products. During the procedure the mass spectrometer was set to checking specific m/z values corresponding to the possible fragmentation products of the compound, i.e. 43 (N_3H), 58 ($M-N_3Ph$), 77 (Ph), 135 ($M-N_3H$), and 150 ($M-N_2$). Among these the only one that could not be detected since the carrier gas is dinitrogen, is dinitrogen itself; however, one would expect the complementary products of this decomposition to give the appropriate signals. Indeed, the mass elimination occurring at 160°C is accompanied by the detection of two signals at the mass spectrum of the gaseous products, those with $m/z = 77$ and 135, respectively. This is indicative of the rupture of the C–NH rather than the C–NPh bond of the ligand which would provide an alternate route to decomposition. Consequently, hydrazoic acid should be observed, however the instability of the compound as well as the execution of the experiment in a Pt crucible may have led to immediate auto-decomposition to dinitrogen and ammonia [32]. On the other hand, the low concentration of the acid in the reaction chamber and the absence of any organic solvent vapor have precluded any undesired detonation due to violent decomposition of the acid [33]. Indeed in the mass spectrum recording the ionic current corresponding to HN_3 is barely distinguished from the background.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

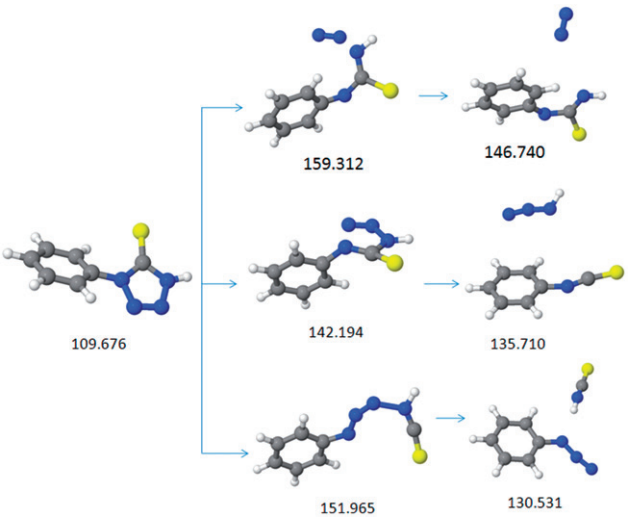


Figure 4. Schematic representation of the ligand fragmentation processes. Heat of formation of the species is reported in kcal mol^{-1}.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

A computational study was carried out in order to verify the above observations. The starting ligand geometry, the proposed final products as well as the transition states connecting reactant and products were approximated by applying the PM6 Hamiltonian [34] as implemented within the MOPAC2009 program [35]. Full geometry optimization was performed in every case using UHF wave-functions in order to account better for the expected transition between closed shell end-points and open shell mid-points during the investigated process. A pictorial representation of the three possible fragmentation mechanisms of the ligand, including the computed heat of formation values of the individual species in kcal mol^{-1}, is presented in figure 4.

Considering that the reactions presented can only be assumed as the initial stages of fragmentation, the compounds termed as "final products" are in fact transition points toward secondary interactions which will lead to more stable products. In this respect the computations are not quantitative but represent the tendency of the studied system to move along the path of various bond dissociation processes. Furthermore the structures of the considered initial fragmentation products were optimized by assuming a safe non-interacting distance of 4 Å between the two fragments kept constant throughout the otherwise full geometry optimization, and therefore do not necessarily correspond to a true state for the system studied. The above semi-empirical computations performed appear to support the possibility of either HN_3 or PhN_3 initial dissociation giving a slight favor to the first one as the lower transition energy dictates (see figure 4). The energy content of the ligand is computed to be 109.70 kcal mol^{-1}, which is slightly higher than 102.80 kcal mol^{-1} calculated within the same approximation for *4H*-tetrazole and 95.30 kcal mol^{-1} for its *1H*-isomer, both of which have been considered as energetic materials in propellants [11].

4. Conclusion

The cyclic thioamide 1-phenyl-1,4-dihydro-tetrazole-5-thione coordinates readily to cuprous halides and forms a variety of heteroleptic complexes. The complexes with the stoichiometry $[CuX(HL)(PPh_3)_2]$ where X is Cl, Br, or I are crystalline and their X-ray structure determination reveals distorted tetrahedral environment around copper and a double N=N bond in positions 4 and 5 of the ligand ring and monodentate coordination to copper through sulfur. The coordination to copper appears to stabilize the nitrogen-rich ligand as TG studies reveal a relative shift to higher temperatures for the first thermal decomposition relative to the free thioamide. However, the density of compounds ranging from 1.38 to 1.48 $g\,cm^{-3}$ and the decomposition temperatures of 176–193°C are too low to allow their use as energetic materials in propellant systems.

Downloaded by [Renmin University of China] at 10:40 13 October 2013

Supplementary material

CCDC reference numbers 703655–703657 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk].

References

[1] S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama, H. Masuda. *J. Chem. Soc., Dalton Trans*., 2105 (1990).
[2] E.S. Raper. *Coord. Chem. Rev*., **61**, 115 (1985), and references therein.
[3] J. Bravo, M.B. Cordero, J.S. Casas, M.V. Castaño, A. Sánchez, J. Sordo. *J. Organomet. Chem*., **513**, 63 (1996).
[4] E.S. Raper. *Coord. Chem. Rev*., **129**, 91 (1994).
[5] P.D. Akrivos, H.J. Katsikis, A. Koumoutsi. *Coord. Chem. Rev*., **167**, 95 (1997).
[6] H. Nöth, W. Beck, K. Burger. *Eur. J. Inorg. Chem*., 93 (1998).
[7] W.E. Antholine, B. Kalyanaraman, D.H. Petering. *Health Perpsect*., **64**, 19 (1985).
[8] W.A. Denny. *Eur. J. Med. Chem*., **36**, 577 (2001), and references therein.
[9] F. Schreiber. *Progr. Surf. Sci*., **65**, 151 (2000), and references therein.
[10] A.S. Gundugola, K.L. Chandra, E.M. Perchellet, A.M. Waters, J.-P.H. Perchellet, S. Rayat. *Bioorg. Med. Chem. Lett*., **20**, 3920 (2010).
[11] T.M. Klapötke, M. Stein, J. Stierstorfer. *Z. Anorg. Allg. Chem*., **634**, 1711 (2008).
[12] Oxford Diffraction. *Crysalis CCD and RED, Ver. 1.168*, Oxford Diffraction, Abingdon, Oxfordshire, UK (2002).
[13] G.M. Sheldrick. *SHELXS-97: Program for a Crystal Structure Solution*, University of Göttingen, Germany (1997).
[14] G.M. Sheldrick. *SHELXL-97: Program for the Refinement of a Crystal Structure from Diffraction Data*, University of Göttingen, Germany (1997).
[15] S. Stoyanov, I. Petkov, L. Antonov, T. Stoyanova, P. Karagiannidis, P. Aslanidis. *Can. J. Chem*., **68**, 1482 (1990).
[16] S. Stoyanov, T. Stoyanova, P.D. Akrivos. *Research Trends*, **2**, 89 (1998).
[17] I.P. Khullar, U. Agarwala. *Can. J. Chem*., **53**, 1165 (1975).
[18] H.O. Desseyn, B.J. van der Veken, M.A. Herman. *Appl. Spectrosc*., **32**, 101 (1978).
[19] U. Agarwala, B.P. Rao. *Ind. J. Pure Appl. Phys*., **7**, 229 (1969).
[20] R. Singh, S.K. Dikshit. *Polyhedron*, **12**, 759 (1993), and references therein.
[21] M. Ferrari, G. Fava, C. Pelizzi, P. Tarasconi. *Inorg. Chim. Acta*, **7**, 99 (1985).
[22] T.S. Lobana, R. Sultana, G. Hundal. *Polyhedron*, **27**, 1008 (2008), and references therein.

[23] P.D. Akrivos. *Coord. Chem. Rev.*, **213**, 181 (2001), and references therein.
[24] W. Wei, M. Wu, Q. Gao, Q. Zhang, Y. Huang, F. Jiang, M. Hong. *Inorg. Chem.*, **48**, 420 (2009).
[25] Y.-J. Kim, J.-T. Han, S. Kang, W.S. Han, S.W. Lee. *Dalton Trans.*, 3357 (2003).
[26] X. Chang, K.-E. Lee, Y.-J. Kim, S.W. Lee. *Inorg. Chim. Acta*, **359**, 4436 (2006).
[27] V.W. Lin Ng, Z. Weng, J.J. Vittal, L.L. Koh, G.K. Tan, L.Y. Goh. *J. Organomet. Chem.*, **690**, 1157 (2005).
[28] D.J. Whelan, R.J. Spear, R.W. Read. *Thermochim. Acta*, **80**, 149 (1984).
[29] J. Wang, J. Gu, A. Tian. *Chem. Phys. Lett.*, **351**, 459 (2002).
[30] V.P. Sinditskii, V.Y. Egorshev, A.E. Fogelzang, V.V. Serushkin, V.I. Kolesov. *Chem. Phys. Rep.*, **18**, 1569 (2000).
[31] A.I. Lesnikovich, O.A. Ivashkevich, S.V. Levchik, A.I. Balabanovich, P.N. Gaponik, A.A. Kulak. *Thermochim. Acta*, **388**, 233 (2002).
[32] A.V. Ananiev, V.P. Shilov, P. Brossard. *Appl. Catal.*, **A257**, 151 (2004).
[33] J. Wiss, C. Fleury, C. Heuberger, U. Onken, M. Glor. *Org. Process Res. Dev.*, **11**, 1096 (2007).
[34] J.J.P. Stewart. *J. Mol. Model.*, **13**, 1173 (2007).
[35] MOPAC2009, J.J.P. Stewart. *Stewart Computational Chemistry*, Colorado Springs, CO, USA (2009). Available online at: http://OpenMOPAC.net (accessed 16 December 2011).

Downloaded by [Renmin University of China] at 10:40 13 October 2013