

Synthesis and Crystal Structure of *N,N'*-Dimethyldithiocarbamate-Copper(I) Polymer $\{[\text{Cu}(\text{Me}_2\text{dtc})]_2\}_n$

ZHANG, Wei(张伟) ZHU, Xiu-Lin*(朱秀林) CHENG, Zhen-Ping(程振平)
 ZHU, Jian(朱健) LANG, Jian-Ping(郎建平) LU, Jian-Mei(路健美)

School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Jiangsu 215006, China

Reactions of CuSCN with tetramethylthiuram disulfide in CH₃CN in the presence of styrene and *N,N,N',N''*-pentamethyldiethylenetriamine gave rise to a new copper(I) complex of *N,N'*-dimethyldithiocarbamate $\{[\text{Cu}(\text{S}_2\text{CNMe}_2)]_2\}_n$. The title compound crystallized in the triclinic *P*-1 space group with lattice parameters $a=0.7610(4)$ nm, $b=0.8911(4)$ nm, $c=0.9268(5)$ nm, $\alpha=68.66(1)^\circ$, $\beta=83.88(2)^\circ$, $\gamma=79.31(2)^\circ$, $V=0.5748(5)$ nm³, $Z=2$. The compound has a unique 1D chain structure composed of CuSCSCuSCS eight-membered rings and a pair of Cu—S bonds, the structure of which has been determined by single-crystal X-ray crystallography. The isolation of this compound may provide some helpful information for the cause of the induction periods of the reverse atom transfer radical polymerization.

Keywords synthesis, crystal structure, *N,N'*-dimethyldithiocarbamate-copper(I), reverse atom transfer radical polymerization

Introduction

In recent years, metal dithiocarbamate complexes remain attractive because of their possible relevance to the nature of the sulfur-metal bond in some bimolecules¹ and their potential biological role in anti-alkylation and cancer disease treatment.² Among them, copper(II) dithiocarbamate complexes have been extensively investigated due to their rich structural magnetic, and electrochemical properties.³ However, the chemistry of copper(I) complexes of dithiocarbamates seems less explored.⁴ For example, the preparation of copper(I) complexes of *N,N'*-diethyldithiocarbamate copper(I) $[\text{Cu}(\text{Et}_2\text{dtc})]$ was reported 30 years ago by reaction of $[\text{Cu}(\text{Et}_2\text{dtc})_2]$ with Cu powder in CS₂,^{4a} however, the structure of this compound has not been reported yet. On the other hand, we are interested in the Cu-mediated reverse atom transfer radical polymerization (ATRP).⁵ During the reverse ATRP of styrene (St) initiated by tetramethylthiuram disulfide (TMTD)/CuSCN/*N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA), the title compound $\{[\text{Cu}(\text{S}_2\text{CNMe}_2)]_2\}_n$ (**1**) was always found in the crystalline form. Considering the facts that there have not been unanimous conclusions⁵ about the mechanism and the causes of induction periods of reverse ATRP or ATRP and the clear elucidation of the structure of **1** may be useful in understanding the role of Cu(I) in the reverse ATRP and ATRP, we characterized **1** by elemental analysis, IR, Raman spectra and single-crystal X-ray crystallography. Herein we

report the synthesis and crystal structure of **1**.

Experimental

Chemical reagents and methods

The IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer as KBr disk (4000—400 cm⁻¹). The Raman spectra were recorded on an FT-Raman 960 spectrometer using Ge detector by fluid nitrogen cooling. The elemental analyses for C, H and N were performed on a LECO-CHNS microanalyzer. Styrene (St) (Chemically Pure, Shanghai Chemical Reagent Co. LTD.) was purified by washing with 5% sodium hydroxide aqueous solution, followed by washing with water and dried with sodium sulfate anhydrous overnight, and finally distilled over CaH₂ under vacuum before use. Tetramethylthiuram disulfide (TMTD) (99.9%, Zhengjiang Zhengdu Chemical Reagent Factory) was recrystallized from mixture of ethanol and chloroform. Copper(I) thiocyanate (CuSCN) (98.0%, Yixing Liaoyuan Chemical Co. LTD.) was purified by washing with acetic acid and acetone, then dried under vacuum. *N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA) was dried with 4 Å molecular sieve and distilled under vacuum. Acetonitrile (CH₃CN) was distilled before use.

Preparation of compound **1**

To a dry glass tube was added a mixture of St,

* E-mail: xlzhu@suda.edu.cn; Fax: 86-512-65111258

Received October 21, 2003; revised February 20, 2004; accepted April 5, 2004.

Project supported by the National Natural Science Foundation of China (No. 20176033) and the Natural Science Foundation of Jiangsu Province (No. Bk2001141).

TMTD, CuSCN, PMDETA and CH₃CN with predetermined ratio (St/TMTD/CuSCN/PMDETA=1000/1/2/6, St/CH₃CN=2.5/1 (V/V)). After the mixture was vibrated into a homogeneous solution, the tube was sealed under nitrogen and placed in an oil bath thermostat at 120 °C for about six hours. During this period, some yellow-green crystals {[Cu(S₂CNMe₂)₂]₂]_n (**1**) were found to form at the bottom of the tube. The formation of **1** in this reaction system is reproducible with ca. 5% yield (based on Cu). Anal. calcd for {[Cu(S₂CNMe₂)₂]₂]_n: C 19.61, H 7.62, N 3.29; found: C 19.26, H 7.67, N 3.26. IR (KBr) ν : 1499 (C—N), 962 (C—S) cm⁻¹. Raman: 362 cm⁻¹ (Cu—S).

X-ray crystallography

A yellow prism crystal of **1** with approximate dimensions of 0.45 mm × 0.05 mm × 0.06 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo K α radiation. Diffraction data were collected at ω mode with a detector to crystal distance of 44.56 mm. Indexing was performed from 6 images, each of which was exposed for 8 s. Cell parameters were refined by using the program Crystalclear (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections between θ of 3.4° and 27.5°. The crystal belongs to triclinic system, space group *P*-1 with cell parameters: *a*=0.7610(4) nm, *b*=0.8911(4) nm, *c*=0.9268(5) nm, α =68.66(1)°, β =83.88(2)°, γ =79.31(2)°, *V*=0.5748(5) nm³, *Z*=2, *D*_{calcd}=2.123 g/cm³, *F*(000)=368, μ =4.386 cm⁻¹. A total of 720 oscillation images were collected in the range of 1.912° < θ < 54.96°. The collected data were reduced by using the program Crystalstructure (Rigaku and MSC, Ver. 3.16, 2003), and an empirical absorption correction was applied, resulting in transmission factors ranging from 0.460 to 0.803. The data were also corrected for Lorentz and polarization effects. Of the 4612 reflections that were collected, 2521 were unique (*R*_{int}=0.026), and equivalent reflections were merged. The structure was solved by direct methods⁶ and expanded using Fourier techniques.⁷ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were put on the calculated positions and included in the final structure-factor refinement. The final cycle of refinement including 139 variable parameters for 1702 reflections with *I*>3.0 σ (*I*) was converged to *R*=0.032, *R*_w=0.050 (*w*=[$\sigma_c^2(F_o) + 0.0012F_o^2$]⁻¹), *S*=1.098, and (Δ/σ)=0.000. The maximum and minimum residual peaks on the final difference Fourier map are 530 and -560 e/nm³, respectively. All calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver. 3.16, 2003).

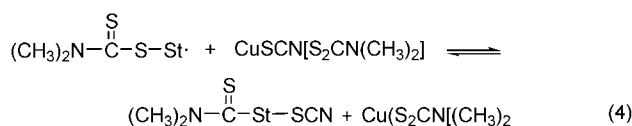
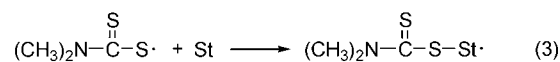
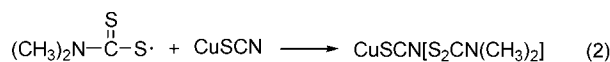
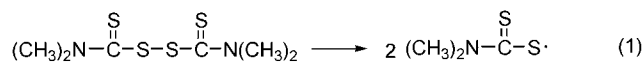
Results and discussion

During the reverse atom transfer radical polymerization (ATRP) in a system containing a mixture of styrene, TMTD, CuSCN, PMDETA and CH₃CN, some yellow-

green crystals {[Cu(S₂CNMe₂)₂]₂]_n (**1**) were always found to form at the bottom of the tube with ca. 5% yield (based on Cu). The identity of **1** was finally confirmed by elemental analysis, IR, Raman and single-crystal X-ray diffraction. The formation mechanism of compound **1** is currently not very clear. According to the Eq. (4) of the mechanism of the reverse ATRP in Scheme 1,^{5a} we found that the real catalyst of this system was CuSCN and PMDETA. Moreover, the relatively long induction periods during the polymerization of styrene were also observed. In this period, compound **1** was formed before the polymerization of styrene began. Compound **1** still existed until the polymerization of styrene finished. According to the above information, we thought that the main cause of the induction periods was due to the formation of the compound **1**. The possible mechanism of formation of compound **1** may be that a little Cu(S₂CNMe₂) was changed into compound **1** at relatively high temperature in this system due to the poor solubility of compound **1**.

Scheme 1 Mechanism of the reverse ATRP^{5a}

Initiation



Propagation

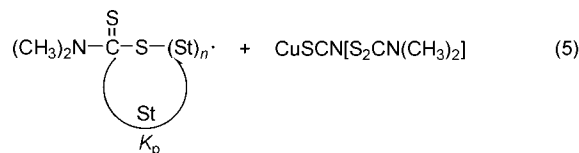
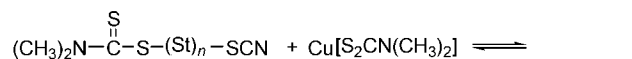


Figure 1 shows the perspective view of a section of the 1D chain of **1** together with the selected bond lengths and angles. An asymmetric unit contains two halves of the [Cu(Me₂dtc)]₂ units. The whole structure consists of [Cu(Me₂dtc)]₂ units linked by two Cu—S bonds. The geometries of two crystallographically independent [Cu(Me₂dtc)]₂ units in the chain are similar, and an inversion center resides in the middle of each unit. Within each unit, two Me₂dtc moieties are interconnected by two Cu atoms, resulting in an eight-membered puckered ring [Cu(1)S(1)C(1)S(2)Cu(1)-S(1)C(1)S(2) or Cu(2)S(3)C(4)S(4)Cu(2)S(4)C(4)S(3)]. The Cu(1) [or Cu(2)] atom bridges two S atoms of two Me₂dtc moieties within the unit and one S atom of one Me₂dtc moiety from the adjacent unit, displaying an

approximate trigonal planar coordination geometry. Interestingly, the Cu(1)—Cu(1) bond length of 2.5887(11) Å is 0.18 Å shorter than that of Cu(2)—Cu(2) bond. This value is not unusual as compared with that structures containing three-coordinated Cu (*e.g.* 2.584 Å in [Cu(*p*-tolCS₂)₄]^{8a} and 2.608 Å in (MepyH)₂[Cu₄(μ-dmit)₃]^{8b} suggesting that dative interactions may exist between the two d¹⁰ Cu(I) centers in the unit. In addition, we noticed a weak interaction between Cu(1) and Cu(2) or between Cu(1) and Cu(2), that is, 2.9081(11) Å for Cu(1)⋯Cu(2) and 2.8436(9) Å for Cu(1)⋯Cu(2). The mean Cu-S length of 2.286 Å is comparable to those found in [Cu(*p*-tolCS₂)₄] (2.273 Å),^{8a} (MepyH)₂[Cu₄(μ-dmit)₃] (2.289 Å),^{8b} [PPh₄]₂[Cu₄(μ-PhS)₆] (2.281 Å)^{9a} and [MoOS₃Cu₂(PyPPh₂)₃] (2.283 Å).^{9b}

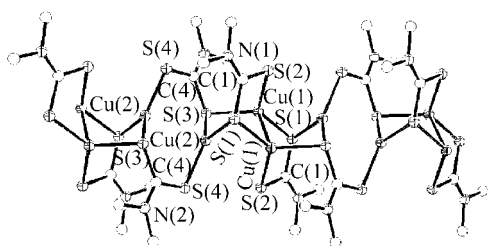


Figure 1 Perspective view of [Cu(S₂CNMe₂)₂]_n showing atom-numbering scheme. Hydrogen atoms were omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°)

Cu(1)—Cu(1)	2.5887(11)	Cu(1)—S(2)	2.279(2)
Cu(2)—Cu(2)	2.7625(10)	Cu(1)—S(3)	2.324(1)
Cu(1)⋯Cu(2)	2.9081(11)	Cu(2)—S(1)	2.325(2)
Cu(1)⋯Cu(2)	2.8436(9)	Cu(2)—S(3)	2.2802(12)
Cu(1)—S(1)	2.253(2)	Cu(2)—S(4)	2.252(1)
S(1)—Cu(1)—S(2)	127.20(4)	S(1)—Cu(1)—S(2)	127.20(4)
S(2)—Cu(1)—S(3)	111.12(4)	S(3)—Cu(2)—S(4)	129.95(5)
S(3)—Cu(2)—S(1)	117.42(4)	S(1)—Cu(2)—S(4)	112.42(3)

As shown in Figure 2, compound **1** possesses a unique ladder-shaped one-dimensional structure, which runs parallel to the crystallographic *a*-axis. There is no evident interaction between the polymeric chains.

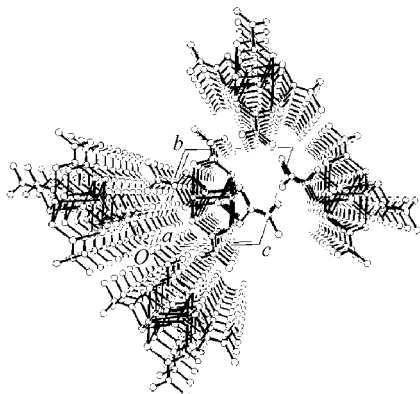


Figure 2 The unit cell packing diagram of **1** looking down the *a*-axis.

Conclusion

In summary, we demonstrated a facile way to synthesize the first copper(I)/dithiocarbamate polymeric complex during the ATRP process and the cause of induction periods was explained. Application of this method to the preparation of related complexes and studying their roles in ATRP system are currently underway in our laboratory.

References

- (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.
(b) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* **1984**, *54*, 23.
- (a) Hersh, E. M.; Brewton, G.; Abrams, D.; Bartlett, J.; Galpin, J.; Gill, P.; Gorter, R.; Gottlieb, M.; Jonikas, J. J.; Landesman, S.; Levine, A.; Marcel, A.; Peterson, E. A.; Whiteside, M.; Zahradnik, J.; Negron, C.; Boutitie, F.; Caraux, J.; Dupuy, J. M.; Saimi, R. *J. Am. Med. Assoc.* **1991**, *265*, 1538.
(b) Stalteri, M. A.; Parrot, S. J.; Griffiths, V. A.; Dilworth, J. R.; Mather, S. J. *Nucl. Med. Commun.* **1997**, *18*, 870.
(c) Scarcia, V.; Furlani, A.; Fregona, D.; Faraglia, G.; Sitran, S. *Polyhedron* **1999**, *18*, 2827.
- (a) Sureshan, C. A.; Bhattacharya, P. K. *Polyhedron* **1997**, *16*, 489.
(b) Jian, F. F.; Wang, Z. X.; Bai, Z. P.; You, X. Z.; Fun, H. K.; Chinnakali, K.; Razak, I. A. *Polyhedron* **1999**, *18*, 3401.
- (a) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1976**, *15*, 2115.
(b) Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 971.
- (a) Zhang, W.; Zhu, X. L.; Cheng, Z. P.; Zhu, J.; Xu, W. J. *J. Macromol. Sci. Part A-Pure Appl. Chem.* **2004**, *A41*, No.1, 49.
(b) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5164.
(c) Yu, B.; Ruckenstein, E. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4191.
(d) Liu, B.; Hu, C. P. *Eur. Polym. J.* **2001**, *37*, 2025.
(e) Li, P.; Qiu, K. Y. *Polymer* **2002**, *43*, 3019.
- Sheldrick, G. M. *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.
- Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF99* The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1999**.
- (a) Camus, A.; Marsich, N.; Manotti, L.; Anna, M.; Ugozzoli, U. *Inorg. Chim. Acta* **1989**, *161*, 87.
(b) Matsubayashi, G.; Yokozawa, A. *J. Chem. Soc., Chem. Commun.* **1991**, 68.
- (a) Baumgartner, M.; Bensch, W.; Hug, P.; Dubler, E. *Inorg. Chim. Acta* **1987**, *136*, 139.
(b) Niu, Y.-Y.; Zheng, H.-G.; Cai, Y.; Xin, X.-Q.; Song, Y.-L. *Acta Chim. Sinica* **2001**, *59*(9), 1435 (in Chinese).