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研究简报

三维混合价态铜配位聚合物$[Cu(Me_2dtc)_2(CuI)_3]_n$的合成与晶体结构

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Synthesis and Crystal Structure of a Three-Dimensional Mixed-Valence Copper Dithiocarbamate-Copper Iodide Coordination Polymer $[Cu(Me_2dtc)_2(CuI)_3]_n$

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Abstract: A new three-dimensional copper dithiocarbamate-copper iodide coordination polymer $[Cu(Me_2dtc)_2(CuI)_3]_n$ (Me_2dtc=*N*,*N*-dimethyldithiocarbamate) was synthesized by reactions of $Cu(OAc)_2$, NaI and $Na(Me_2dtc)$ in DMF solution, characterized by elemental analysis, IR spectrum, and single-crystal X-ray diffraction. The crystal belongs to the monoclinic system, space group *C*2/*c* with *a*=1.293 89(17) nm, *b*=1.077 61(11) nm, *c*=1.456 05(17) nm, β=115.585 (4)°, *V*=1.831 1 (4) nm^3, *Z*=4, D_c=3.175 $g\cdot cm^{-3}$, M_r=875.28, λ (Mo $K\alpha$)=0.071 073 nm, μ=10.082 mm^{-1}, *F*(000)=1 604, the final *R*=0.029 5 and *wR*=0.081 7. A total of 2 083 unique reflections were collected, of which 1 918 with $I>2\sigma(I)$ were observed. The Cu atoms are Cu(Ⅰ)/Cu(Ⅱ) mixed-valence and they have two different coordinate geometries, namely planar square and tetrahedron. This three-dimensional structure consists of individual $Cu(Me_2dtc)_2$ molecules linking together CuI polymeric chains which run parallel to the [001] direction vis Cu-S bonds. CCDC: 739046.

Key words: copper; *N*,*N*-dimethyldithiocarbamate; mixed-valence; crystal structure

During the past few decades, the design and synthesis of inorganic-organic hybrid complexes have attracted much attention due to their structural diversity, as well as their potential applications as functional materials[1-4]. Therefore, all kinds of ligands containing nitrogen, oxygen, sulfur or phosphorus are used to synthesize the hybrid complexes[5-10]. Dialkyldithiocarbamate (R_2dtc) anions, which are typical sulfur ligands, acting as monodentate, bidentate or bridging ligands with many different central metal ions can form considerable structural variety of complexes[11-13]. Among them, the chemistry and structures of the homo- or heterometallic halide dithiocarbamate complexes have been extensively explored, and a series of zero-dimen-

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tional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) homo- or hetrometallic complexes have been obtained[13-17]. However, up to the present, 3D homometallic halide dithiocarbamate complex has not been reported. We report here the synthesis and crystal structure of a new 3D mixed-valence copper dithiocarbamate-copper iodide coordination polymer $[Cu(Me_2dtc)_2(CuI)_3]_n$, (**1**), containing a dimethyldithiocarbamate (Me_2dtc) ligand. As far as we know, this is the first example of 3D homometallic halide dithiocarbamate complex.

1 Experimental

1.1 General procedures

Sodium salt of *N*,*N*-dimethyldithiocarbamate ($Na(Me_2dtc)\cdot 2H_2O$) was prepared by literature methods[18]. All solvents and chemicals required for syntheses were commercially available and employed without further purification. Element analyses of carbon, hydrogen, nitrogen, and sulfur were performed with a Vario EL Ⅲ element analyzer. The solid infrared spectra (IR) were obtained from a Nicolet Nexus 470 FTIR spectrometer between 400 and 4 000 cm^{-1} by using KBr pellets. The crystal structure was determined by a Rigaku Mercury CCD area-detector diffractometer and SHELXL crystallographic software of molecular structure.

1.2 Synthesis of the title complex

A mixture of $Cu(OAc)_2\cdot H_2O$ (0.10 g, 0.5 mmol), $Na(Me_2dtc)\cdot 2H_2O$ (0.04 g, 0.2 mmol), and $NaI\cdot 2H_2O$ (0.26 g, 1.5 mmol) was stirred in dimethylformamide (20 mL) at 60 ℃ in air for about one day. The vapor of 2-PrOH was diffused into the resulting solution, and after about one month black crystals (36 mg) were obtained (yield 32.9% based on $Cu(OAc)_2\cdot H_2O$). Anal. Calcd. (%) for **1** (dried): C, 8.23; H, 1.38; N, 3.20; S, 14.65. Found(%): C, 8.89; H, 1.65; N, 3.63; S, 14.21. Selected IR data (KBr, cm^{-1}), ν: 3 434, 2 914, 1 637, 1 509, 1 374, 1 239, 1 139, 945, 569, 435.

1.3 Crystal structure determination

Suitable single crystal of complex **1** was selected and mounted on the end of thin glass fiber using epoxy oil. X-ray diffraction intensity data were collected on a Rigaku Mercury CCD area-detector equipped with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) by using an ω scan mode in the range of $3.10° \leqslant \theta \leqslant 27.47°$ at 293(2) K. A total of 6 864 reflections were measured, of which 2 083 were unique (R_{int}=0.020 7) and 1 918 were observed ($I>2\sigma(I)$). Absorption correction was performed by the CrystalClear program[19]. The structure was solved by direct methods and refined with the aid of SHELX-97 software package of crystallographic software[20]. All non-hydrogen atoms were refined anisotropically. All H atoms were located theoretically and refined as riding atoms, with C-H=0.096 nm and $U_{iso}(H)=1.5U_{eq}(C)$. The final anisotropic refinement converged to R=0.029 5 and wR=0.081 7 ($w=1/[\sigma^2(F_o^2)+(0.052\,6P)^2+1.990\,2P]$, where $P=(F_o^2+2F_c^2)/3$), S=1.097, $(\Delta/\sigma)_{max}$=0.001, $(\Delta\rho)_{max}$=1 322 and $(\Delta\rho)_{min}$=−1 630 e·nm $^{-3}$. Some refinement details and crystal data are gathered in Table 1. Selected bond lengths and angles are listed in Table 2.

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Table 1　Crystallographic data and structure refinement parameters for complex 1

Empirical formula	$C_6H_{12}Cu_4I_3N_2S_4$	μ / mm^{-1}	10.082
Formula weight	875.28	F(000)	1 604
Temperature / K	293(2)	Crystal size / mm	0.20×0.18×0.10
Wavelength / nm	0.071 073	θ range for data collection / (°)	3.10 to 27.47
Crystal system	Monoclinic	Limiting indices	$-15\leqslant h\leqslant 16$, $-13\leqslant k\leqslant 10$, $-18\leqslant l\leqslant 18$
Space group	$C2/c$	Reflections collected / unique (R_{int})	6 864 / 2 083 (0.020 7)
a / nm	1.293 89(17)	Absorption correction	Multi-scan
b / nm	1.077 61(11)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.456 05(17)	Data / restraints / parameters	1 918 / 0 / 93
β / (°)	115.585(4)	Goodness of fit on F^2	1.097

Continued Table 1

V / nm^3	1.831 1(4)	Final R indices [$I>2\sigma(I)$]	R_1=0.029 5, wR_2=0.081 7
Z	4	R indices (all)	R_1=0.033 2, wR_2=0.084 4
D_c / (g·cm^{-3})	3.175	Largest diff. peak and hole / (e·nm^{-3})	1 322 and −1 630

Table 2 Selected bond lengths (nm) and angles (°) for complex 1

Cu(1)-S(1)	0.233 41(11)	Cu(2)-S(2)	0.229 88(18)	Cu(3)-I(1C)	0.262 33(7)
Cu(1)-S(1A)	0.233 41(11)	Cu(2)-S(2B)	0.232 58(17)	Cu(3)-I(1)	0.265 85(8)
Cu(1)-S(2)	0.231 38(11)	Cu(2)-I(2)	0.258 67(13)	Cu(3)-I(2)	0.271 27(8)
Cu(1)-S(2A)	0.231 38(11)	Cu(2)-I(1B)	0.289 64(18)	Cu(3)-Cu(3C)	0.272 98(14)
Cu(2)-Cu(2B)	0.132 5(3)	Cu(3)-S(1A)	0.235 78(13)		
S(2A)-Cu(1)-S(2)	180.0	S(2)-Cu(2)-S(2B)	127.26(8)	S(1A)-Cu(3)-I(1C)	116.57(4)
S(2A)-Cu(1)-S(1A)	77.06(4)	S(2)-Cu(2)-I(2)	105.16(6)	S(1A)-Cu(3)-I(1)	106.06(4)
S(2)-Cu(1)-S(1A)	102.94(4)	S(2B)-Cu(2)-I(2)	104.37(6)	I(1C)-Cu(3)-I(1)	117.76(3)
S(2A)-Cu(1)-S(1)	102.94(4)	S(2)-Cu(2)-I(1B)	108.48(6)	S(1A)-Cu(3)-I(2)	101.93(4)
S(2)-Cu(1)-S(1)	77.06(4)	S(2B)-Cu(2)-I(1B)	105.39(6)	I(1C)-Cu(3)-I(2)	105.77(2)
S(1A)-Cu(1)-S(1)	180.0	I(2)-Cu(2)-I(1B)	103.98(5)	I(1)-Cu(3)-I(2)	107.24(3)

Symmetry transformations used to generate equivalent atoms: A: $-x+3/2$, $-y+3/2$, $-z+1$; B: $-x+1$, y, $-z+1/2$; C: $-x+1$, $-y+2$, $-z+1$.

2 Results and discussion

2.1 Synthesis

The formation of the complex **1** was under solution condition at 60 ℃ in air for about 24 h. If the reactive temperature and time were reduced, the final product was complex $Cu(Me_2dtc)_2$, not the complex **1**. Series of experiments using other sodium salt of R_2dtc with larger alkyl (R=ethly or propyl) in place of $Na(Me_2dtc)$ under the same condition have also been carried out to prepare 3D homometallic halide dithiocarbamate complex, but unfortunately, no crystal was suitable for X-ray single-crystal analysis. This maybe results from that the steric hindrance effects of the ethyl and propyl are larger than that of methyl. In general, syntheses of the complexes are not only closely related to the geometry and the number of coordination sites provided by metal ions or ligands, but also controlled by the environment conditions (such as: temperature, reactants, metal-to-ligand ratio, countercations, solvents, pH value etc.). Thus, this preparation may mainly depend on the choices of both reactants and the $Cu(OAc)_2$/NaI/$Na(Me_2dtc)$ stoichiometry.

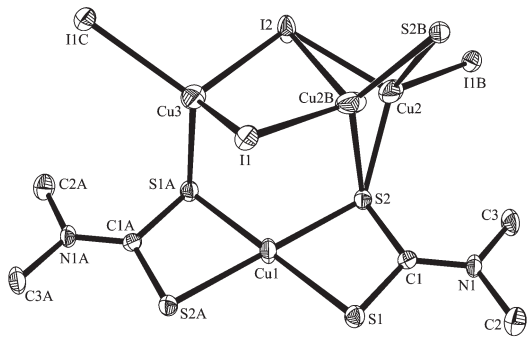
2.2 IR spectrum of complex 1

IR spectrum of complex **1** shows characteristic bands arising from $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$ (partial double bond) at 1 139 and 945 cm^{-1}, respectively, with the $\Delta\nu$ value ($\nu(CS_2)_{asym}-\nu(CS_2)_{sym}$) of 194 cm^{-1}, indicating that the Me_2dtc ligand coordinates to the Cu atom in a bidentate fashion[21-22]. The band at 1 509 cm^{-1} is attributable to t he ν(C-N) (partial double bond) stretching vibration. This position corresponds to a partial double bond character, and is recorded in the range previously reported for similar complexes[21].

2.3 Description of the structure

The structure of **1** is a 3D copper neutral structure which consists of individual Cu $(Me_2dtc)_2$ molecules linking together CuI polymeric chains which run parallel to the [001] direction vis Cu-S bonds (Fig.1, Fig.2 and Fig.3). All the S atoms and I atoms are acting as μ_2 and μ_3 bridges, respectively.

According to the bond valence sum (BVS) calculations[23], valence states are assigned on the basis of $\sum V_i$ values, in which the $\sum V_i$ is the bond strength derived from the Brown equation, $V_i=\exp[(R_0-R_i)/b]$ (R_0(CuS)= 0.202 4 nm, R_0(CuI)=0.210 8 nm and b=0.37). The values of $\sum$Cu(1), $\sum$Cu(2) and $\sum$Cu(3) are 1.92, 1.33 and 1.09, respectively. So Cu (1) and Cu (3) atoms are assigned as bivalent and univalent, respectively. On the other hand, based on the valence equivalence in this



Symmetry codes: A: $-x+3/2$, $-y+3/2$, $-z+1$; B: $-x+1$, y, $-z+1/2$; C: $-x+1$, $-y+2$, $-z+1$

Shown with ellipsoids at the 30% probability level, H atoms have been omitted for clarity

Fig.1　A section of the crystal structure of **1**

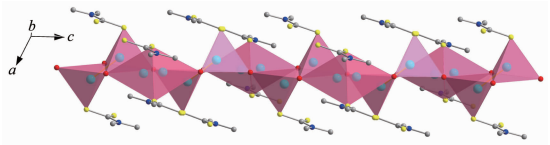
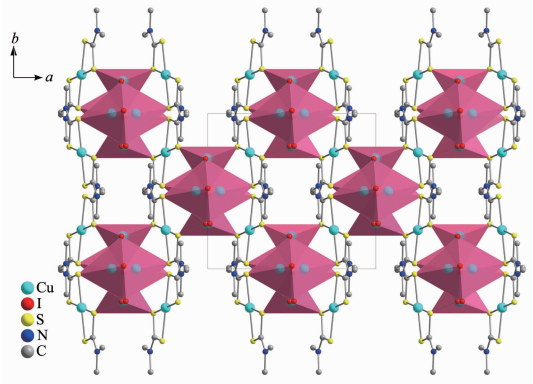


Fig.2　A view showing the 1D chain constructed by Cu(2)S_2I_2 and Cu(3)I_3S units which are shown by polyhedra



All H atoms have been omitted for clarity

Fig.3　A polyhedral representation of the 3D structure of **1**, viewed down *c* axis

complex, Cu(2) atoms is assigned as univalent.

It is interesting that these three mixed-valence Cu(Ⅰ)/Cu(Ⅱ) atoms have two different coordinate configurations. The atom $Cu^{Ⅱ}(1)$ has four-coordinate $Cu(1)S_4$ square-planar environment and is bonded to four S atoms from two different Me_2dtc ligands with the $Cu^{Ⅱ}$-S distances of 0.233 41(11) and 0.231 38(11) nm and the S-$Cu^{Ⅱ}$-S bite angle of 77.06 (4)°, all consistent with those reported previously in Cu(Ⅱ) dithiocarbamate complex CuI(prdtc)(phen) (prdtc=*N*-pyrrolidinyldithiocarbamate, phen=1,10-phenanthroline) with the corresponding values of 0.231 81(15)~0.234 42(15) nm and 76.24(5)° (Table 1)[24]. The atom $Cu^{Ⅰ}(2)$ is of interest, being splitted into two symmetry sites, Cu (2) and Cu (2B) [symmetry code: B:$-x+1$, y, $-z+1/2$] with occupancies of 0.5 and 0.5 and the distance between Cu(2) and Cu(2B) being 0.132 5(3) nm. Cu(2) atom is four-coordinated in a distorted $Cu(2)S_2I_2$ tetrahedral geometry by two I atoms and two S from two different Me_2dtc ligands with the $Cu^{Ⅰ}$-I distances of 0.258 67(13) and 0.289 64(18) nm, and $Cu^{Ⅰ}$-S distances of 0.229 88(18) and 0.232 58(17) nm, respectively. They compare well to those in Cu(Ⅰ) complex $[(Ph_3P)Cu(\mu\text{-}I)_2(\mu\text{-S-Haptsc})Cu(PPh_3)]$ (Haptsc =acetophenone thiosemicarbazone) with the corresponding values of 0.263 79(7) to 0.274 72(7) nm and 0.239 31(12) to 0.241 86(13) nm[25]. The atom $Cu^{Ⅰ}(3)$ is surrounded by three I atoms and one S atom from Me_2dtc ligand in a distorted tetrahedral coordinate sphere $[Cu(3)I_3S]$ with the $Cu^{Ⅰ}$-I distances ranging from 0.262 33(7) to 0.271 27(8) nm and the $Cu^{Ⅰ}$-S distance being 0.235 78(13) nm, which are also similar to that in Cu(Ⅰ) complex $[(Ph_3P)Cu(\mu\text{-}I)_2(\mu\text{-S-Haptsc})Cu(PPh_3)]$[25]. Two $[Cu(3)I_3S]$ tetrahedra are connected by common edge (I(1)-I(1)) to form a dimer, in which there is Cu-Cu interaction with the Cu-Cu distance of 0.272 98(14) nm[26], adjacent dimers are joined by $Cu(2)S_2I_2$ tetrahedra with common edges (I(1)-I(2)) to form 1D chain extending along [001] direction (Fig.2), and then the chains are linked by surrounding $Cu(1)S_4$ planar square via shared vertices (S(1) and S(2)) to give 3D structure (Fig.3).

2D homometallic halide dialkyldithiocarbamate complex $[Cu(pipdtc)_2(CuBr)_6]_n$ (pipdtc=piperidyldithiocarbamate) also built up of individual $Cu(pipdtc)_2$ molecules linked to CuBr polymeric chains vis Cu-S bonds was reported previously[15]. Compared structurally with 2D complex $Cu(pipdtc)_2(CuBr)_n$, it is concluded that, the 3D complex **1** benefits mainly from the steric hinerance effect of Me_2dtc ligand is smaller than that of pipdtc ligand.

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