研究简报

多硫二硫烯铜配合物(n-Bu$_4$N)[Cu(cddt)$_2$]和(Ph$_4$P)[Cu(cddt)$_2$]的合成、表征及其结构

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关键词: 晶体结构 循环伏安 多硫二硫烯铜配合物
分类号: O614.121

Synthesis and Characterization of (n-Bu$_4$N)[Cu(cddt)$_2$] and (Ph$_4$P)[Cu(cddt)$_2$] (cddt = 4a, 6, 7, 7a-5H-cyclopenta[b]-1, 4-dithiin-2, 3-dithiolate); X-ray Crystal Structure of (Ph$_4$P)[Cu(cddt)$_2$]

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Two copper complexes with a new multi-sulfur 1, 2-dithiolene ligand, C[Cu(cddt)$_2$] (C = tetrabutylammonium, n-Bu$_4$N$^+$; tetraphenylphosphonium, Ph$_4$P$^+$; cddt = 4a, 6, 7, 7a-5H-cyclopenta[b]-1, 4-dithiin-2, 3 dithiolate) have been synthesized and characterized by electrochemical studies, IR, EA, etc. The structure of (Ph$_4$P)[Cu(cddt)$_2$] was determined by single crystal X-ray analysis. The complex was crystallized in the triclinic, space group $P\bar{1}$ with the cell dimensions a = 10.460(2) Å, b = 13.000(3) Å, c = 16.270(3) Å, α = 86.68(3)°, β = 71.92(3)°, γ = 66.66(3)° and Z = 2. R_1 = 0.0548, wR_2 = 0.1358 for 6786 independent reflections. The four S atoms surround the Cu atom [CuS$_4$] core is a square-planar environment.

Keywords: crystal structure cyclic voltammetry copper bisdithiolene

0 Introduction

Metal complexes with sulfur-rich dithiolene ligands have received considerable attention in the area of developing new molecular conductors, magnets, non- linear optical devices and other advanced materials[1~3]. Many dithiolene ligands have been synthesized and utilized in preparing metal complexes in order to get better physical properties[4~8]. We report here the synthesis and properties of two new copper complexes based on the multi-sulfur dithiolene ligand. The crystal structure of (Ph$_4$P)[Cu(cddt)$_2$] is described. The electrochemical behavior of Cu(cddt)$_2^-$ is also presented and compared with those of similar complexes, [Cu(pddt)$_2$]$^-$[9] and [Cu(dddt)$_2$]$^-$[10].

收稿日期:2002-04-12。收修改稿日期: 2002-09-12。
海外杰出青年基金资助项目(No. 29929001)。
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1 Experimental

1.1 Chemicals

All solvents were of analytical grade and used without further purification. The ligand precursor, *cis*-4a, 6, 7, 7a-tetrahydro-5H-cyclopenta[b]-1, 3-dithiolo[4, 5-e] [1, 4] dithiin-2-thione was prepared by the (2 + 4) cycloaddition reaction as described in the literature[11].

1.2 Measurements

C H N analyses were performed using a Perkin-Elmer 240C analytical instrument. Cu element analysis was performed on a Jarrell-ash ICP quantimeter. IR spectra were collected on a Shimadzu 440 spectrometer with KBr pellets. Cyclic voltammetry was measured by a model 79-1V-Analyser with an electrochemical cell using a platinum wire as the working electrode, a platinum plate as auxiliary electrode and Ag/AgCl as reference electrode. Measurements were made in CH_2Cl_2 using 0.4mol · L^{-1} tetrabutylammonium perchlorate as the supporting electrolyte and nitrogen was passed for 15 min prior to each measurement.

1.3 Synthesis

All reactions were carried out under N_2.

1.3.1 (n-Bu_4N)[Cu(cddt)$_2$]

Potassium hydroxide (2.0g, 36mmol) and *cis*-4a, 6, 7, 7a-tetrahydro-5H-cyclopenta[b]-1, 3-dithiolo [4, 5-e][1, 4]dithiin-2-thione (1.0g, 3.8mmol) were added to 20mL of ethanol. The reaction mixture was stirred for 1h at 40℃. The resulting pale yellow microcrystals of K_2cddt were isolated by centrifugation. Then it was dissolved instantly in methanol (20mL). A solution of $CuCl_2 \cdot 2H_2O$ (0.32g, 1.9mmol) in 20mL of methanol was added dropwise to this solution. After stirring at room temperature for 30min, the solution was then exposed to air for 15min. After filtration, 1 equiv. of tetrabutylammonium bromide was added to the filtrate, and purple solids were precipitated immediately. The solids were collected by filteration and then recrystallized from acetone. The yield was 0.85g (60%). Anal. Calc. for $C_{30}H_{52}NCuS_8$: C, 48.29; H, 6.98; N, 1.88; Cu, 8.52. Found: C, 47.92; H, 6.85; H, 1.82; Cu, 8.77. Selected IR absorptions (cm^{-1}): 2953(m), 1459(m), 1438(m), 1373(s), 881(m).

1.3.2 (Ph_4P)[Cu(cddt)$_2$]

This complex was synthesized by mixing (n-Bu_4N)[Cu(cddt)$_2$] with excess Ph_4PBr in CH_3OH, The brown precipitate was collected by filtration and washed with methanol and ether, dried in vacuo. Anal. Calc. for $C_{38}H_{36}CuPS_8$: C, 54.05; H, 4.26; Cu, 7.52 Found: C, 53.75; H, 4.25; Cu, 7.66. Selected IR absorptions (cm^{-1}): 3050(w), 2953(m), 1585(m), 1459(m), 1437(m), 1108(s), 881(m), 688(s).

1.4 X-Ray Structure Determination

Brown crystals of (Ph_4P)[Cu(cddt)$_2$] were obtained upon recrystallization from CH_2Cl_2 and CH_3OH. The intensity data were measured on a Siemens P4 diffractometer equipped with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$Å) radiation. The detail of data collection and structure refinement are summarized in Table 1.

Table 1 Crystal Data and Details of Data Collection and Refinement

empirical formula	$C_{38}H_{36}CuPS_8$
formula weight	843.55
temperature	293(2)K
wavelength	0.71073Å
crystal system	triclinic
space group	$P\bar{1}$
a/Å	10.460(2)
b/Å	13.000(3)
c/Å	16.270(3)
α/(°)	86.68(3)
β/(°)	71.92(3)
γ/(°)	66.66(3)
Z	2
D_c	1.455Mg · m^{-3}
μ(Mo $K\alpha$)	1.070mm^{-1}
F(000)	872
crystal size	0.2 × 0.2 × 0.3mm
θ range for data collection	1.32° ≤ θ ≤ 24.98°
limiting indices	$0 \leq h \leq 12$, $-14 \leq k \leq 15$, $-18 \leq l \leq 19$
reflections collected/unique	7196/6786 [R(int) = 0.0579]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	6786/0/436
goodness-of-fit on F^2	0.903
final R indices [$I > 2.0\sigma(I)$]	R_1 = 0.0548, wR_2 = 0.1358
R indices (all data)	R_1 = 0.2055, wR_2 = 0.1930
largest diff. peak and hole	0.443 and −0.378 e · Å^{-3}

The structure was solved by direct methods using SHELXTL software and refined by full-matrix least-squares methods on F^2 using SHELXTL software[12]. All H atoms were geometrically fixed and allowed to ride on their attached atoms.

2 Result and Discussion

2.1 Structure of (Ph$_4$P)[Cu(cddt)$_2$]

The molecular structure of (Ph$_4$P) [Cu(cddt) $_2$] with the atom numbering scheme is shown in Fig. 1, and selected bond distances and angles are listed in Table 2. The bond distances of C1-C2 is 1.328(9)Å, corresponding to the typical distance of a C = C bond in alkene, and slightly shorter than that in Cu(dddt)$_2^-$ (1.342(3)Å)[11].

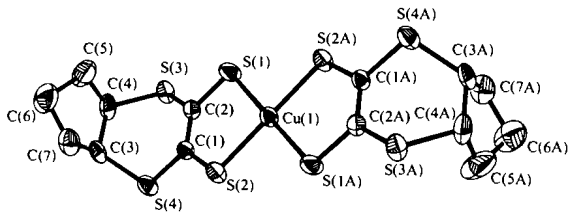

Fig. 1　Ortep view of [Cu(cddt)$_2$]$^-$ with atom numbering scheme
hydrogen atoms are omitted for clarity

The four S atoms surround the Cu atom yielding a square-planar geometry, with nearly equal Cu-S bond lengths and S-Cu-S angles. The Cu atom lies at the origin and hence one half of the anion is inversely related to the other half. The $S_2C = CS_2$ units in cddt ligand are also planar. The gross geometry of [Cu(cddt) $_2$]$^-$ is very similar to that of [N(CH$_3$) $_3$H] [Cu(dddt$_2$)]$^-$[11] . The cyclopentene ring adopts an envelope conformation with the trans orientation.

From the packing diagram of anions ([Cu(cddt) $_2$]$^-$) (Fig. 2), no significant S···S interactions are observed. The closest intermolecular Cu··· Cu and S ··· S distances are 10.46Å and 4.385Å, respectively. They are similar to those in (n-Bu$_4$N) [Cu(dddt)$_2$] (10.34Å and 4.47Å).

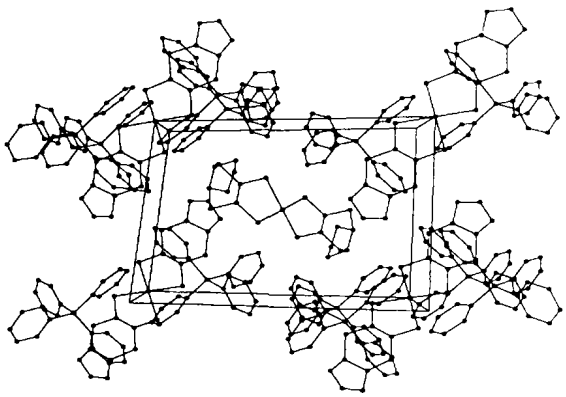

Fig. 2　Packing diagram of the unit cell of (Ph$_4$P)[Cu(cddt)$_2$] looking down the a axis

2.2 Cyclic Voltammetry

The electrochemical data of the complex [Cu(cddt)$_2$]$^-$ together with other related copper dithiolene complexes are given in Table 3. As expected,

Table 2　Selected Bond Distances(Å) and Angles(°) in (Ph$_4$P)[Cu(cddt)$_2$]

Cu(1)-S(2)	2.188(2)	Cu(1)-S(2)#2	2.188(2)	Cu(1)-S(1)	2.190(2)
Cu(1)-S(1)#2	2.190(2)	S(1)-C(2)	1.747(7)	S(2)-C(1)	1.741(7)
S(3)-C(2)	1.748(7)	S(3)-C(4)	1.818(8)	S(4)-C(1)	1.762(7)
S(4)-C(3)	1.809(8)	C(1)-C(2)	1.328(9)	C(3)-C(7)	1.513(10)
C(3)-C(4)	1.548(10)	C(4)-C(5)	1.531(14)	C(5)-C(6)	1.474(12)
C(6)-C(7)	1.488(12)				
S(2)-Cu(1)-S(2)#2	180.00(10)	S(2)-Cu(1)-S(1)	92.22(8)	S(2)#2-Cu(1)-S(1)	87.78(8)
S(2)-Cu(1)-S(1)#2	87.78(8)	S(2)#2-Cu(1)-S(1)#2	92.22(8)	S(1)-Cu(1)-S(1)#2	180.00(8)
C(2)-S(1)-Cu(1)	101.5(3)	C(1)-S(2)-Cu(1)	100.9(2)	C(2)-S(3)-C(4)	101.8(3)
C(1)-S(4)-C(3)	101.6(3)	C(2)-C(1)-S(2)	122.7(5)	C(2)-C(1)-S(4)	120.3(5)
S(2)-C(1)-S(4)	117.0(4)	C(1)-C(2)-S(1)	120.5(5)	C(1)-C(2)-S(3)	122.3(6)
S(1)-C(2)-S(3)	117.2(4)	C(7)-C(3)-C(4)	103.5(7)	C(7)-C(3)-S(4)	114.8(6)
C(4)-C(3)-S(4)	115.3(5)	C(5)-C(4)-C(3)	105.1(7)	C(5)-C(4)-S(3)	109.5(7)
C(3)-C(4)-S(3)	117.0(6)	C(6)-C(5)-C(4)	105.1(10)	C(5)-C(6)-C(7)	101.9(8)
C(6)-C(7)-C(3)	106.2(8)				

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y+1, -z+1$

Table 3 Electrochemical Results of Some Copper Bisdithiolene Complexes

ligand	$E_{1/2}(-1/-2)$/V	$E_{1/2}(0/-1)$/V
dddt	-0.49	0.38
pddt	-0.69	0.32
cddt	-0.55	0.39

the cyclic voltammograms reveals two waves. The mono- to dianion couple for $[Cu(cddt)_2]^-$ exhibits a classic one electron reversible behavior [$E_{1/2}(-1/-2) = -0.55$V] and monoanion to neutral couple presents a one electron irreversible process [$E_{1/2}(0/-1) = 0.39$V]. The corresponding values for $[Cu(dddt)_2]^-$[10] are -0.48V and 0.38V, and for $[Cu(pddt)_2]^-$[9] are -0.69V and 0.32V, respectively. $[Cu(cddt)_2]^{2-}$ is less stable than $[Cu(dddt)_2]^{2-}$ and it is due to the effect of the large external unit of ligand and its electron-pushing ability.

3 Conclusion

Two copper complexes with a new multi-sulfur 1, 2-dithiolene ligand have been prepared. The crystal structure of $(Ph_4P)[Cu(cddt)_2]$ shows that there is no significant inter or intra molecular interactions. This is due to the effect of the large cation and the outer bulky groups in the dithiolene ligand. For the same reason, $[Cu(cddt)_2]^{2-}$ is less stable than $[Cu(dddt)_2]^{2-}$.

Acknowledgements: This work was supported by the Distinguished Overseas Young Fund from The NSFC (No. 29929001). We thank the State Science and Technology Commission and the National nature Science Foundation of China, the support from The University of HongKong.

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