A Tetranuclear Copper(I)-Diisopropyldithiophosphate Cluster Compound $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ Obtained from Copper(II) as a Starting Material

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(Received 24th March, 2004, revised 20th March, 2005)

Summary: A sulfur coordinated tetranuclear copper(I)-diisopropyldithiophosphate cluster compound $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ was synthesized by the reaction of $Na[S_2P(O\text{-}i\text{-}Pr)_2]$ with $CuCl_2$ and its structure was characterized by X-ray crystallography. The cluster compound crystallizes in the tetragonal system, space group I4(1)/a. The four symmetry-equivalent Cu(I) atoms are arranged in a tetrahedral geometry and two S-atoms of each dithiophosphate ligand are coordinated monodentate and bidentate respectively to triangular Cu_3 units.

Introduction

Transition metal-sulfur cluster chemistry, an important subject in inorganic and metalloprotein chemistry, is currently receiving much attention. The chemistry of trinuclear and cubic Mo and W sulfido clusters has been extensively studied [1], and heterometallic cubic derivatives reported [2]. Biologically relevant Fe/sulfido clusters have been synthesized [3]. In nitrogenase the Fe/Mo/S cofactor is believed to be the site of substrate activation and reduction [4]. As a part of these studies the dithiophosphinate clusters, $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3[\mu_2\text{-}S_2P(OEt)_2][S_2P(OEt)_2]_3(H_2O)$, with three d^2 Mo(IV) forming localized electron-pair Mo-Mo bonds [5], $Cu_8[S_2P(O\text{-}i\text{-}Pr)_2]_6(\mu_8\text{-}S)$, a sulfide-centered Cu_8 cube, and $Cu_6[S_2P(OEt)_2]_6(H_2O)_2$, a distorted octahedron [6], have been prepared. Clusters containing Cu(I) with chalcogenide ligands have taken on renewed interest through their commercial use and their possible antioxidant properties in life systems and their photophysics [7]. The compound CuDDP (DDP = dialkyl dithiophosphate) has been described to be an important antioxidant when added with ZnDDP in the compounding of lubricating oils [8]. Dithiophosphate, having two P-attached sulfur atoms that can coordinate to metal ions by different modes, is an important ligand in promoting the formation of new types of clusters. Lawton *et al.*, [9] obtained the tetranuclear copper (I)-diisopropyldithio-phosphate cluster compound $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ from the reaction of cuprous chloride and ammonium o,o'-diisopropyldi-thiophosphate. In the present paper, another interesting method to synthesis of $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ was reported, and the structures from the different methods were also compared.

Results and Discussion

The crystal structure of the title compound contains four symmetry-related $Cu_4[S_2P(O\text{-}i\text{-}Pr)_2]_4$ molecules each lying on $\bar{4}$ (S_4) axis in a tetragonal unit cell such that the crystallographically independent unit consists of one-quarter molecule. Fig. 1 shows that the resulting four symmetry-equivalent Cu (I) atoms are arranged in a tetrahedral geometry. The structure of the cluster compound is similar to that reported by Lowton *et al.*, [9] where cuprous chloride and ammonium o,o'-diisopropyl-dithiophosphate were used as the starting materials, although two cluster compounds are different in crystal systems, space group and unit cell parameters. The mean distance of the six Cu-Cu bonds is 0.280 nm (0.2738 ~ 0.2928 nm), which is similar to that (0.275 nm) found in tetrameric copper(I) thiolate complexes in which the Cu_4S_6 cores consist of a tetrahedral array of copper atoms inscribed in a distorted nonbonding octahedron of sulfur atoms with each Cu(I) atom exhibiting an approximate trigonal-planar sulfur coordination [10]. The closer Cu(I)-Cu(I) distance of 0.280 nm suggests the occurrence of weakly attractive bonding interaction [11,12]. The four Cu_3 triangles in tetrahedral cluster are each capped by a $\mu_3\text{-}[S_2P(O\text{-}i\text{-}Pr)_2]^-$ ligand in which one S atom is bound to one Cu atom while the other S atom bridges the two other Cu atoms. In addition to interaction with three other Cu atoms in tetrahedral cluster, each of the four Cu atoms has a distorted trigonal planar coordination composed of one mono-coordinated S atom and two μ_2-S atoms from three $[S_2P(O\text{-}i\text{-}Pr)_2]^-$ ligands. The sum of the three S-Cu-S bond angles around one Cu atom is close to 360 °C, e. g. 357.7 °C for Cu (I), and their mean value is 119.23 °C (112.02

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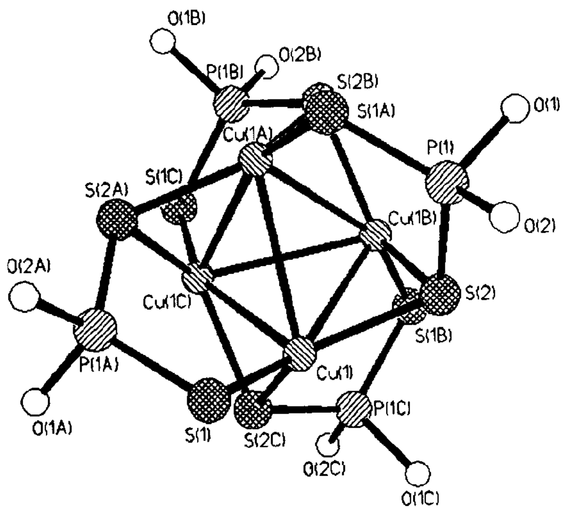

Fig. 1. ORTEP drawing of $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ which possesses crystallographic $\bar{4}$ (S_4) site symmetry. Thermal ellipsoids are shown at 50% probability, and all hydrogen and carbon atoms are omitted for clarity.

~ 123.37 °C). Of the six Cu-Cu bonds comprising the edges of the tetrahedron, two are not bridged by sulfur atom, so the distances of those (0.293 nm) not bridged are longer than of those (0.274 nm) bridged by sulfur. The distances of 12 Cu-S bonds fall into two categories: four 0.229 nm, from μ_2-S atoms, and eight 0.226 nm, of which half from μ_2-S atoms, and the other half from mono-coordinated S atoms. The distances are similar to that, 0.225-0.229 nm, in the tetrameric molecule $Cu_4[S_2CN(C_2H_5)_2]_4$ [13], but shorter than the 0.239 nm sum of the covalent radii of copper (0.135 nm) and sulfur (0.104 nm) [14].

Trigonal-planar, digonal, and tetrahedral ligand coordination are common for Cu (I)-sulfur complexes where each Cu(I) conforms to a closed-shell $3d^{10}$ electronic configuration. Examples include ones with Cu_4S_6, Cu_5S_7 and Cu_8S_{12} cores, the latter class being stabilized only with bidentate sulfur chelates. However, Cu_4S_8 core composed of Cu_3S_2 units is uncommon in Cu(I)-sulfur clusters [9]. The resulting localized sulfur coordination about each Cu (I) is approximately trigonal planar corresponding to the formation of three electron-pair Cu-S bonds.

In conclusion, the tetranuclear cluster compound formally arises from each monoanionic dithiophosphinate $[\mu_3\text{-}S_2P(OR)_2]^-$ ligand effectively functioning as a six-electron tridentate donor in capping a triangular Cu_3 face with one S atom terminally coordinated to one Cu (I) and the other S atom edge-bridging the other two Cu (I) atoms. In addition, the reaction of Cu (II) with dipropyldithiophosphate in an aqueous solution at room temperature gave reduced Cu (I) tetranuclear cluster. This is of significance in spite of not knowing the exact composition and structure of oxidation product. The result shows that Cu (I) ion is easier to the formation of cluster compound than Cu (II) ion. This will be a focus of future attention.

Experimental

Materials and methods

$Na[S_2P(OR)_2]$ (R = i-Pr or Et) was synthesized according to a method previously described [15]. All commercially available chemicals were of analytical reagent grade and used directly without further purification. The C and H contents were determined by using an Elementar Vario EL analyzer. Infrared spectra were recorded from KBr pellets on a Midac Prospet IR spectrometer. All operations were carried out under ambient conditions.

Synthesis of $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$

Reaction of an aqueous solution of $Na[S_2P(O\text{-}i\text{-}Pr)_2]$ with an aqueous solution of $CuCl_2$ gave a yellow-green precipitate. The precipitate was redissolved in ethanol and after two weeks the filtered solution afforded a tetranuclear cluster $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ (yield 44.8 %) as a yellow crystalline material. Anal. data for $C_{24}H_{56}O_8P_4S_8Cu_4$, Calcd: C, 26.03; H, 5.10. Found: C, 26.14 %; H, 5.07 %. Main IR absorption bands (KBr, cm^{-1}): 2977(s), 1383(s), 1373(s) ($-CH_3$); 2871(w) (≡CH); 1465 (m), 1178(s), 1140(m), 1102(s), 975(vs), 888(s), 651(s), 519(s) ($[S_2P(O\text{-}i\text{-}Pr)_2]^-$); 484(w), 453(m), 436(m) (Cu-S).

X-ray crystallography

Single-crystal X-ray diffraction data for $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ was collected on a Nonius CAD4 diffractometer using MoKα radiation (λ = 0.071073 nm) with a graphite monochromator at 293(2) K. The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by full-matrix least-squares procedures based on F^2 by using the SHELXTL software package [16]. All non-hydrogen atoms were refined

Table 1: Summary of Crystallographic information for compound $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$

Formula	$C_{24}H_{56}O_8P_4S_8Cu_4$ (I)
Formula weight	1107.2
Temperature (K)	293 (2)
Crystal system	tetragonal
Space group	I4(1)/a
Unit cell dimensions	
a (nm)	10.9422(15)
b (nm)	10.9422(15)
c (nm)	39.4869(8)
α (°)	90
β (°)	90
γ (°)	90
V (nm^3)	4.72781(13)
Z	10
D_{calcd} ($g.cm^{-3}$)	1.556
Absorption coefficient (mm^{-1})	2.30
F (000)	2272.0
Crystal size (mm)	0.2×0.2×0.4
θ ranges (°)	1.93-19.89
Reflections collected	4540
Independent reflections	1093 (R_{int} = 0.0878)
Restrains/parameters	0/109
GOF	1.134
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0554
	wR_2 = 0.1430 [a]
R indices(all data)	R_1 = 0.0586
	wR_2 = 0.1490 [a]

[a] $w = 1/[\sigma^2(F^2_o)+(0.0909P)^2+11.5645P]$, $P=(F^2_o+2(F^2_c))/3$

Table-2: Selected bond distances (nm) and bond angles (°)of $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$

Cu(1)-Cu(1A)	0.29285(16)	S(1)-Cu(1)-S(2)	122.29(8)
Cu(1)-Cu(1B)	0.27377(14)	S(1)-Cu(1)-S(2C)	112.02(8)
Cu(1)-Cu(1C)	0.27377(14)	S(2)-Cu(1)-S(2C)	123.37(5)
Cu(1)-S(1)	0.22595(20)	S(1)-Cu(1)-Cu(1C)	107.83(5)
Cu(1)-S(2)	0.22623(19)	S(1)-Cu(1)-Cu(1A)	96.81(6)
Cu(1)-S(2C)	0.22946(18)	S(2)-Cu(1)-Cu(1B)	53.61(5)
Cu(1B)-S(2)	0.22946(19)	S(1)-Cu(1)-Cu(1B)	153.99(7)
Cu(1C)-S(2C)	0.22623(19)	Cu(1A)-Cu(1)-Cu(1B)	57.67(2)
P(1)-S(1A)	0.19790 (27)	Cu(1A)-Cu(1)-Cu(1C)	57.67(2)
P(1)-S(2)	0.20555 (25)	Cu(1B)-Cu(1)-Cu(1C)	64.66(3)

anisotropically. All calculations were performed with the program SHELXL-97. The molecular graphics were created by SHELXTL. Atomic scattering factors and anomalous dispersion correction were taken from International Table for X-Ray Crystallography [17]. A summary of the key crystallographic data and structural refinements is presented in Table-1. Figure 1 shows the perspective view of $Cu_4[\mu_3\text{-}S_2P(O\text{-}i\text{-}Pr)_2]_4$ with atomic numbering scheme. Selected bond lengths and angles are presented in Table-2.

Acknowledgements

The work was supported by the Natural Science Foundation of Shandong Province (Z2006B01, Y2006B07), the Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences (No. O4B0021400), and the Outstanding Adult-young Scientific Research Encouraging Foundation of Shandong Province (No. 2005BS04007).

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