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The Synthesis and Crystal Structure of a Novel Cubane-like Molybdenum Copper Sulfur Cluster $[Mo_3CuS_4]\cdot[S_2P(OC_2H_5)_2]_3\cdot I\cdot CH_3COO\cdot HCON(CH_3)_2$

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Abstract

The synthesis and crystal structure of a novel cubane-like cluster with a $[Mo_3CuS_4]$ cluster core is reported herein. This compound was prepared from CuI upon reaction with the trinuclear molybdenum cluster $\{Mo_3S_4[S_2P(OC_2H_5)_2]_4\}\cdot H_2O$. The title compound crystallizes in a triclinic space group $P\bar{1}$ with the following unit cell dimensions: a = 12.639(3); b = 13.722(2); c = 14.644(2); α = 108.78(1); β = 106.36(1); γ = 102.54(1)°; Z = 2; V = 2124 Å^3; D_c = 2.022 g cm^{-3}. 7491 independent reflections were collected on a CAD-4 four-circle diffractometer with Mo Kα radiation in the range $1° < \theta \leqslant 25°$, with only 2434 reflections having intensities within the range $I \geqslant 3\sigma(I)$. The structure was determined by Patterson and Fourier methods and refined by the least-squares method to a final R index of 0.054. There are some distortions in the cubane-like $[Mo_3CuS_4]$ core, with three Mo–Mo bonds and three Mo–Cu bonds.

Introduction

Within recent years, research work on trinuclear clusters has attracted the attention of structural chemists [1]. In particular, people have focussed on trinuclear molybdenum clusters with loose ligands [2], such as $\{Mo_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$, in which the H_2O ligand can be very easily substituted by another ligand; in addition there are three coordinatively unsaturated sulfur atoms in the cluster skeleton. The cluster $[Mo_3CuS_4][S_2P(OEt)_2]_3\cdot I\cdot CH_3COO\cdot HCON(CH_3)_2$ was prepared by allowing CuI to react with $\{Mo_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$ in suitable solvents. It provides an interesting example in investigations of the reaction of trimolybdenum clusters with other transition metals.

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Experimental

Synthesis of the Title Compound

A mixture of 0.30 g of $\{Mo_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$ (prepared according to ref. 2), 0.049 g of CuI (obtained commercially, AR grade) and 5 drops of DMF was added to 30 ml of CH_3COOEt (obtained commercially, CP grade). After stirring for 2 h at room temperature and filtering, the resulting solution was evaporated in air for several days. Finally, 0.28 g of black crystals was obtained.

Elemental Analysis

Found: Mo, 22.35; Cu, 5.08; S, 24.95 P, 6.76; I. 9.64; C, 15.52; H, 3.08; N, 1.32. Calc.: Mo, 22.24 Cu, 4.91; S, 24.77; P, 7.18 I, 9.81; C, 15.78, H, 3.12; N, 1.08%.

IR Spectra

IR spectra were recorded with a Perkin-Elmer 577 spectrophotometer, using KBr pellets.

The IR spectrum of the $S_2P(OEt)_2$ ligand has already been assigned [3]. The wide peak of 410–440 cm^{-1} may be assigned to the overlap of Mo–μ_3S and Cu–μ_3S vibrations [4]. IR (cm^{-1}) 1630(vs), ν(C=O); 1240(m), ν(C=O), ν(C–N); 1416(m), $\nu(-C\overset{O}{\underset{O}{<}})$; 1357(m), ν(H–C–H); 1110(w), δ(H–C=O), δ(N–C–H); 410–440(w), ν(Mo–μ_3S), ν(Cu–μ_3S); 350(w), ν(Mo–μ_3S).

Crystal Data

A crystal of the title compound was scanned on an Enraf-Nonius CAD-4 four-circle diffractometer using Mo Kα radiation in the range $1° < \theta \leqslant 25°$. Accurate cell dimensions were obtained by least-squares refinement of 25 high-ordered reflections. The crystal is triclinic belonging to the space group $P\bar{1}$, with the following cell dimensions: a = 12.369(3), b = 13.722(2), c = 14.644(2) Å, α = 108.78(1)°, β = 106.36(1)°, γ = 102.54(1)°, V = 2124 Å^3; Z = 2; D_c = 2.022 g cm^{-3}. 7491 independent

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TABLE I. Positional Parameters (e.s.d.s in parentheses)

Atom	x	y	z	B (Å^2)[a]
Mo(1)	0.0307(1)	−0.2888(1)	−0.2604(1)	2.77(4)
Mo(2)	0.1616(2)	−0.1617(1)	−0.0498(1)	2.82(4)
Mo(3)	0.2390(1)	−0.1171(1)	−0.1901(1)	2.50(4)
Cu	0.2465(2)	−0.3164(2)	−0.1661(2)	4.03(7)
I	0.3440(2)	−0.4531(1)	−0.1591(2)	6.87(6)
S(1)	0.3544(4)	−0.1410(4)	−0.0483(3)	3.0(1)
S(2)	0.1888(4)	−0.2932(4)	−0.3191(3)	2.9(1)
S(3)	0.0605(4)	−0.1051(4)	−0.1722(4)	3.2(1)
S(4)	0.0754(5)	−0.3508(4)	−0.1305(4)	3.7(1)
S(5)	−0.0722(5)	−0.4903(5)	−0.3902(4)	5.0(2)
S(6)	−0.1848(5)	−0.3248(5)	−0.2737(4)	4.5(2)
S(7)	0.1901(5)	−0.0245(4)	−0.3110(4)	4.0(2)
S(8)	0.4355(4)	−0.0619(4)	−0.2167(4)	3.8(1)
S(9)	0.2437(5)	−0.1774(5)	0.1227(4)	4.5(2)
S(10)	0.0079(5)	−0.1297(5)	0.0255(4)	4.5(2)
O(01)	−0.053(1)	−0.2547(9)	−0.3963(8)	3.5(4)
O(02)	0.244(1)	0.0144(9)	0.0430(8)	3.0(3)
O(03)	0.309(1)	0.0515(8)	−0.0741(9)	3.4(4)
C(01)	−0.040(2)	−0.278(2)	−0.481(1)	4.3(6)
N(02)	−0.084(2)	−0.242(2)	−0.552(1)	6.6(6)
C(03)	−0.059(2)	−0.260(2)	−0.646(1)	7.7(8)
C(04)	−0.155(3)	−0.168(2)	−0.529(2)	10(1)*
C(05)	0.296(2)	0.080(1)	0.016(1)	3.3(6)
C(06)	0.353(2)	0.201(1)	0.086(1)	4.4(6)
P(1)	−0.2134(6)	−0.4819(5)	−0.3559(5)	5.3(2)
P(2)	0.1035(5)	−0.1466(5)	0.1501(4)	4.7(2)
P(3)	0.3589(5)	0.0074(4)	−0.3037(4)	4.0(2)
O(1)	−0.233(2)	−0.554(1)	−0.291(1)	9.8(7)
O(2)	−0.334(1)	−0.539(1)	−0.457(1)	7.3(6)
O(3)	0.028(1)	−0.236(1)	0.1767(9)	7.0(5)
O(4)	0.140(1)	−0.046(1)	0.2547(9)	5.2(4)
O(5)	0.428(1)	0.1316(9)	−0.2674(9)	4.8(4)
O(6)	0.366(1)	−0.034(1)	−0.4168(9)	5.8(5)
C(1)	−0.304(4)	−0.532(3)	−0.210(3)	17(2)*
C(2)	−0.384(6)	−0.596(5)	−0.260(5)	30(3)*
C(3)	−0.350(2)	−0.515(2)	−0.549(2)	8.0(8)
C(4)	−0.466(2)	−0.617(2)	−0.632(2)	9(1)
C(5)	−0.008(3)	−0.364(2)	0.111(2)	11(1)
C(6)	−0.129(3)	−0.387(3)	0.051(3)	15(1)*
C(7)	0.214(2)	0.065(2)	0.275(1)	4.9(7)
C(8)	0.336(2)	0.094(2)	0.362(2)	7.0(9)
C(9)	0.464(2)	0.207(2)	−0.159(2)	4.7(6)
C(10)	0.378(2)	0.270(2)	−0.155(2)	7.7(9)
C(11)	0.311(2)	−0.150(2)	−0.486(2)	8.1(8)
C(12)	0.328(3)	−0.161(2)	−0.584(2)	11(1)*

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2.2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

reflections were collected, of which only 2434 reflections with $I \geqslant 3\sigma(I)$ were used for structure analysis. Intensities were corrected for Lp factors and empirical absorption.

Structure Determination

Computations were performed using SDP programs provided by Enraf-Nonius. The structure was solved by Patterson and Fourier methods. The coordinates of the three molybdenum atoms and the copper atom were determined; the remaining non-hydrogen atoms were then located from successive difference Fourier maps. The structure was refined by full-matrix least-squares with anisotropic temperature factors for most non-hydrogen atoms except the C atoms in OEt and DMF. The final R index has a value of 0.054.

The atomic coordinates and thermal parameters are listed in Table I; the important bond lengths and bond angles are given in Tables II and III, respectively. See also 'Supplementary Material'.

Results and Discussion

The configuration of the cluster molecule is shown in Fig. 1. The cluster core $[Mo_3CuS_4]$ has a cubane-like structure. Each molybdenum atom is coordinated

TABLE II. Bond Distances (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo(1)	Mo(2)	2.770(2)	S(7)	P(3)	2.002(8)
Mo(1)	Mo(3)	2.749(2)	S(8)	P(3)	1.979(8)
Mo(2)	Mo(3)	2.679(2)	S(9)	P(2)	1.987(9)
Mo(1)	Cu	2.807(3)	S(10)	P(2)	1.989(8)
Mo(2)	Cu	2.856(3)	O(01)	C(01)	1.24(2)
Mo(3)	Cu	2.885(3)	O(02)	C(05)	1.23(2)
Mo(1)	S(2)	2.352(5)	O(03)	C(05)	1.31(2)
Mo(1)	S(3)	2.322(5)	C(01)	N(02)	1.32(3)
Mo(1)	S(4)	2.303(6)	N(02)	C(03)	1.46(3)
Mo(1)	S(5)	2.570(6)	N(02)	C(04)	1.49(3)
Mo(1)	S(6)	2.542(6)	C(05)	C(06)	1.51(3)
Mo(1)	O(01)	2.214(13)	P(1)	O(1)	1.61(2)
Mo(2)	S(1)	2.332(6)	P(1)	O(2)	1.59(2)
Mo(2)	S(3)	2.332(6)	P(2)	O(3)	1.59(2)
Mo(2)	S(4)	2.320(6)	P(2)	O(4)	1.56(2)
Mo(2)	S(9)	2.541(6)	P(3)	O(5)	1.56(1)
Mo(2)	S(10)	2.501(6)	P(3)	O(6)	1.60(2)
Mo(2)	O(02)	2.182(12)	O(1)	C(1)	1.66(6)
Mo(3)	S(1)	2.331(5)	O(2)	C(3)	1.45(3)
Mo(3)	S(2)	2.355(5)	O(3)	C(5)	1.59(3)
Mo(3)	S(3)	2.330(6)	O(4)	C(7)	1.48(2)
Mo(3)	S(7)	2.507(6)	O(5)	C(9)	1.46(2)
Mo(3)	S(8)	2.561(6)	O(6)	C(11)	1.45(3)
Mo(3)	O(03)	2.181(12)	C(1)	C(2)	1.06(9)
Cu	I	2.454(3)	C(3)	C(4)	1.59(4)
Cu	S(1)	2.277(6)	C(5)	C(6)	1.41(5)
Cu	S(2)	2.300(6)	C(7)	C(8)	1.55(3)
Cu	S(4)	2.306(6)	C(9)	C(10)	1.52(3)
S(5)	P(1)	1.966(9)	C(11)	C(12)	1.48(4)
S(6)	P(1)	1.995(9)			

TABLE III. Bond Angles (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo(2)	Mo(1)	Mo(3)	58.07(6)	Mo(2)	S(3)	Mo(3)	70.2(2)
Mo(1)	Mo(2)	Mo(3)	60.58(6)	Mo(1)	S(4)	Mo(2)	73.6(2)
Mo(1)	Mo(3)	Mo(2)	61.35(6)	Mo(1)	S(4)	Cu	75.0(2)
Mo(2)	Mo(1)	Cu	61.61(7)	Mo(2)	S(4)	Cu	76.3(2)
Mo(1)	Mo(2)	Cu	59.83(7)	Mo(1)	O(01)	C(01)	130.0(1)
Mo(1)	Cu	Mo(2)	58.56(7)	O(01)	C(01)	N(02)	125.0(2)
Mo(3)	Mo(1)	Cu	62.56(7)	C(01)	N(02)	C(03)	124.0(2)
Mo(1)	Mo(3)	Cu	59.69(7)	C(01)	N(02)	C(04)	118.0(2)
Mo(1)	Cu	Mo(3)	57.74(7)	C(03)	N(02)	C(04)	117.0(2)
Mo(3)	Mo(2)	Cu	62.75(7)	Mo(2)	O(02)	C(05)	125.0(1)
Mo(2)	Mo(3)	Cu	61.63(7)	Mo(3)	O(03)	C(05)	123.0(1)
Mo(2)	Cu	Mo(3)	55.62(7)	O(02)	C(05)	O(03)	123.0(2)
S(2)	Mo(1)	S(3)	106.0(2)	O(02)	C(05)	C(06)	122.0(2)
S(2)	Mo(1)	S(4)	103.3(2)	O(03)	C(05)	C(06)	115.0(2)
S(3)	Mo(1)	S(4)	104.2(2)	S(5)	P(1)	S(6)	107.7(4)
S(3)	Mo(1)	S(5)	160.5(2)	S(9)	P(2)	S(10)	105.8(4)
S(2)	Mo(1)	S(6)	157.4(2)	S(7)	P(3)	S(8)	106.3(3)
S(4)	Mo(1)	O(01)	167.2(4)	S(5)	P(1)	O(1)	109.0(1)
S(1)	Mo(2)	S(3)	108.9(2)	S(5)	P(1)	O(2)	112.0(7)
S(1)	Mo(2)	S(4)	100.3(2)	S(6)	P(1)	O(1)	111.6(8)
S(1)	Mo(2)	S(10)	155.9(2)	S(6)	P(1)	O(2)	113.2(8)
S(3)	Mo(2)	S(4)	103.3(2)	S(9)	P(2)	O(3)	113.7(9)
S(3)	Mo(2)	S(9)	159.4(2)	S(9)	P(2)	O(4)	112.8(7)
S(4)	Mo(2)	O(02)	173.4(4)	S(10)	P(2)	O(3)	113.5(7)
S(1)	Mo(3)	S(2)	98.1(2)	S(10)	P(2)	O(4)	113.5(7)
S(1)	Mo(3)	S(3)	109.0(2)	S(7)	P(3)	O(5)	113.7(7)
S(1)	Mo(3)	S(7)	156.6(2)	S(7)	P(3)	O(6)	112.7(6)
S(2)	Mo(3)	S(3)	105.7(2)	S(8)	P(3)	O(5)	114.7(6)
S(2)	Mo(3)	O(03)	172.0(4)	S(8)	P(3)	O(6)	112.4(7)
S(3)	Mo(3)	S(8)	158.1(2)	O(1)	P(1)	O(2)	103.0(1)
Mo(1)	Cu	I	143.8(1)	O(3)	P(2)	O(4)	97.8(9)
I	Cu	S(1)	116.3(2)	O(5)	P(3)	O(6)	97.1(8)
I	Cu	S(2)	117.9(2)	P(1)	O(1)	C(1)	123.0(2)
I	Cu	S(4)	112.2(2)	P(1)	O(1)	C(2)	124.0(3)
S(1)	Cu	S(2)	101.3(2)	P(1)	O(2)	C(3)	124.0(2)
S(1)	Cu	S(4)	102.4(2)	P(2)	O(3)	C(5)	123.0(2)
S(2)	Cu	S(4)	104.8(2)	P(2)	O(4)	C(7)	122.0(1)
Mo(2)	S(1)	Mo(3)	70.1(2)	P(3)	O(5)	C(9)	120.0(1)
Mo(2)	S(1)	Cu	76.6(2)	P(3)	O(6)	C(11)	119.0(1)
Mo(3)	S(1)	Cu	77.5(2)	O(1)	C(1)	C(2)	95.0(7)
Mo(1)	S(2)	Mo(3)	71.5(2)	O(2)	C(3)	C(4)	101.0(2)
Mo(1)	S(2)	Cu	74.2(2)	O(3)	C(5)	C(6)	99.0(4)
Mo(3)	S(2)	Cu	76.6(2)	O(4)	C(7)	C(8)	106.0(2)
Mo(1)	S(3)	Mo(2)	73.0(2)	O(5)	C(9)	C(10)	108.0(2)
Mo(1)	S(3)	Mo(3)	72.5(2)	O(6)	C(11)	C(12)	107.0(2)

by three μ_3-S atoms and a $S_2P(OEt)_2$ chelating terminal ligand. In addition, Mo(2) and Mo(3) atoms are coordinated by a CH_3COO bridging ligand, while the Mo(1) atom is coordinated to a DMF molecule through a Mo–O bond of length 2.21(1) Å, which is somewhat longer than a normal single Mo–O bond. The molybdenum atoms are all ocathedrally coordinated. On the other hand, the copper atom is only tetrahedrally coordinated by 3 μ_3-S atoms and an I atom. There are 6 metal–metal bonds in the cluster core $[Mo_3CuS_4]$ with the following bond lengths: Mo–Mo 2.74 Å, Mo–Cu 2.85 Å. Upon application of the extended Wade rule [5] for the skeletal bonding electron pairs, a value of 6 is obtained for the Wade index I_w, indicating that there are 6 metal–metal bonds in the cluster core, consistent with the experimental result.

As far as we are aware, this title compound is the first successful attempt in the synthesis of a [3Mo + 1Cu] cubane-like cluster. It is obvious that

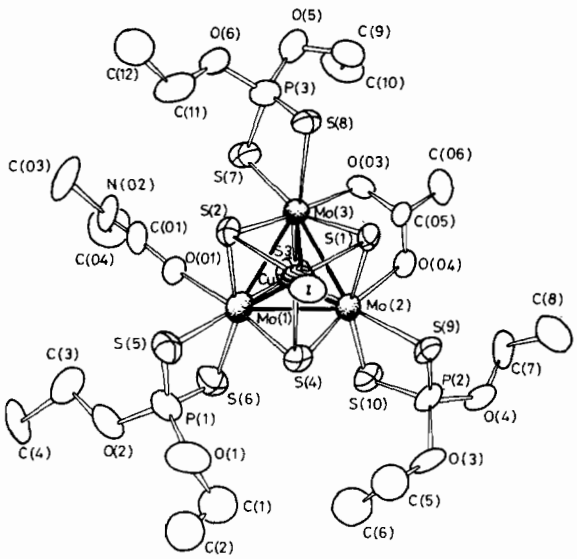

Fig. 1. The molecular configuration of $[Mo_3CuS_4][S_2P(OEt)_2]_3 \cdot I \cdot CH_3COO \cdot HCON(CH_3)_2$.

on account of the presence of three coordinatively unsaturated μ_2-S atoms in the trinuclear molybdenum cluster $\{Mo_3S_4[S_2P(OEt)_2]_4\} \cdot H_2O$, a copper atom (or some other metal atoms) can easily react with these sulfur atoms to form the cubane-like cluster. Further investigation into the relation between the loosely coordinated ligand and the cubane-like skeleton is in progress.

Supplementary Material

A list of the observed and calculated structure factors may be obtained from the authors.

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