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The Synthesis and Crystal Structure of a Cubane-like Tungsten Copper Sulfur Cluster $[W_3CuS_4]\cdot[S_2P(OC_2H_5)_2]_3\cdot I\cdot\mu_2\text{-}CH_3COO\cdot C_5H_5N$

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Abstract

The title compound crystallizes in the monoclinic space group $P2_1/n$ with the following unit cell dimensions: $a = 14.196(3)$, $b = 17.203(3)$, $c = 18.075(3)$ Å, $\beta = 86.02(2)°$, $Z = 4$, $V = 4404$ Å^3, $D_c = 2.358$ g cm^{-3}. 9235 independent reflections were collected on a CAD-4 four-circle diffractometer with Mo Kα radiation in the range $1° < \theta < 25°$, with 5515 reflections having intensities within the range $I \geqslant 3\sigma(I)$. The structure was determined by direct methods and refined by the least-squares method to a final R index of 0.048. There are some distortions in the cubane-like $[W_3CuS_4]$ core, with three W–W bonds and three weak W–Cu bonds.

Introduction

During recent years, research work on trinuclear clusters has attracted the attention of chemists [1–3]. A series of incomplete cubane-like molybdenum complexes with sulfur bridge(s), $Mo_3O_{4-n}S_n^{4+}$ ($n = 1$–4), are known [4–13]. Some papers have been published on triangular tungsten complexes with sulfur bridge(s): $W_3S_4^{4+}$ aqua ion [14], $[W_3S_4(NCS)_9]^{5-}$ [14], $[W_3(\mu_2\text{-}O)_3(\mu_3\text{-}S)(NCS)_9]^{5-}$ [15], $K_2[W_3OS_3\{N(CH_2COO)_2(CH_2COOH)\}_3]\cdot KCl\cdot 7H_2O$ [16], $[W_3S_4(H_2O)_9](CH_3C_6H_4\cdot SO_3)_4\cdot 7H_2O$ [17]. In particular, people have focused on trinuclear clusters with loose ligands, such as $\{Mo_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$ [18] and $\{W_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$ [19], 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 cubane-like molybdenum iron sulfur cluster $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$ [20] and the cubane-like molybdenum copper sulfur cluster $[Mo_3CuS_4]\cdot[S_2P(OEt)_2]_3\cdot I\cdot\mu_2\text{-}CH_3COO\cdot HCON(CH_3)_2$ [21] have been reported. Now, we report the synthesis and crystal structure of a novel cubane-like cluster with a $[W_3CuS_4]$ cluster core.

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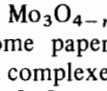
Experimental

Synthesis of the Title Compound

To a solution of $\{W_3S_4[S_2P(OEt)_2]_4\}\cdot CH_3CN$ [19] (0.29 g dissolved in 30 ml of CH_3COOEt) were added 0.038 g of CuI (AR grade), 5 drops of CH_3COOH (AR grade) and 5 drops of C_5H_5N (AR grade). After stirring for 20 min at room temperature and filtering, the resulting solution was evaporated in air for several days. The black crystals were produced and washed with 10 ml of isopropanol and pentane. Finally, 0.25 g of the title compound was obtained. *Anal.* Calc. for $[W_3CuS_4]\cdot[S_2P(OEt)_2]_3\cdot I\cdot\mu_2\text{-}CH_3COO\cdot C_5H_5N$: Cu, 4.06; I, 8.12; S, 20.50; P, 5.94; C, 14.59; H, 2.43; N, 0.90. Found: Cu, 3.89; I, 8.28; S, 20.55; P, 6.08; C, 14.64; H, 2.65; N, 1.10%.

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 had already been assigned [22]. The wide peak of 415–450 cm may be assigned to the overlap of W-μ_3S vibrations and Cu-μ_3S vibrations [23]. IR (cm^{-1}): 1600(m), ν(); 1435(s), ν(); 760(m), 690(m); δ(–CH=CH– in pyridine); 415–450(w), ν(W–μ_3S), ν(Cu–μ_3S); 360(m), ν(W–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 $1° < \theta < 25°$. Accurate cell dimensions were obtained by least-squares refinement of 25 high-order reflections. The crystal is monoclinic belonging to the space group $P2_1/n$, with the following cell dimensions: $a = 14.196(3)$, $b = 17.203(3)$, $c = 18.075(3)$ Å, $\beta = 86.02(2)$, $V = 4404$ Å^3, $Z = 4$, $D_c = 2.358$ g cm^{-3}. 9235 independent reflections were collected, of which 5515 reflections with $I \geqslant 3\sigma(I)$ were used for structure analysis. Intensities were corrected for Lp factor and empirical absorption.

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Structure Determination

Computations were performed on a VAX computer using SDP/VAX programs pack (B. A. Frenz 1978). The structure was solved by direct methods. The coordinates of three tungsten atoms and the copper atom were determined; the remaining non-hydrogen atoms were located from successive difference Fourier maps. The structure was refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The final R index has a value of 0.048.

The atoms coordinates and thermal parameters are listed in Table 1; the important bond lengths

TABLE 1. Atomic Coordinates and Thermal Parameters

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
W(1)	0.61589(5)	0.20889(4)	0.30941(4)	3.06(1)	O(3)	0.460(1)	−0.1593(8)	0.3322(9)	5.6(4)
W(2)	0.64582(5)	0.05012(4)	0.31471(4)	2.99(1)	O(4)	0.399(1)	−0.061(1)	0.250(1)	8.0(5)
W(3)	0.78783(6)	0.15526(4)	0.33676(5)	3.26(1)	O(5)	1.072(1)	0.077(1)	0.394(1)	7.0(5)
Cu	0.7224(2)	0.1299(1)	0.1867(1)	4.28(5)	O(6)	1.043(1)	0.197(1)	0.449(1)	7.1(4)
I	0.7630(1)	0.12133(9)	0.05181(9)	6.18(4)	C(1)	0.670(2)	−0.037(1)	0.472(1)	4.4(4)
S	0.6509(4)	0.1379(3)	0.4149(3)	3.6(1)	C(2)	0.702(1)	−0.093(1)	0.523(1)	4.3(4)
S(1)	0.8011(3)	0.0448(3)	0.2605(3)	3.6(1)	C(3)	0.760(1)	−0.149(1)	0.497(1)	4.1(4)
S(2)	0.7574(4)	0.2458(3)	0.2443(3)	3.6(1)	C(4)	0.794(2)	−0.151(1)	0.424(1)	4.6(5)
S(3)	0.5643(3)	0.1171(3)	0.2255(3)	3.5(1)	C(5)	0.761(1)	−0.095(1)	0.376(1)	3.3(4)
S(11)	0.5398(4)	0.3143(3)	0.2338(3)	4.2(1)	C(6)	0.730(1)	0.314(1)	0.409(1)	4.3(5)
S(12)	0.4606(4)	0.2292(3)	0.3815(3)	4.5(1)	C(7)	0.749(2)	0.383(1)	0.456(2)	7.1(7)
S(21)	0.4904(4)	0.0048(3)	0.3765(3)	4.5(1)	C(8)	0.516(2)	−0.196(1)	0.388(1)	5.7(6)
S(22)	0.6127(4)	−0.0738(3)	0.2411(3)	4.1(1)	C(9)	0.461(2)	−0.266(1)	0.416(2)	7.9(8)
S(31)	0.9618(4)	0.1854(4)	0.3011(4)	5.3(1)	C(10)	0.474(2)	0.434(2)	0.385(2)	7.0(7)
S(32)	0.8681(4)	0.0999(4)	0.4437(4)	5.2(1)	C(11)	0.445(3)	0.516(1)	0.389(2)	9(1)
O(11)	0.6533(9)	0.3075(6)	0.3802(7)	3.7(3)	C(12)	0.314(2)	0.223(2)	0.233(2)	10(1)
O(31)	0.796(1)	0.2627(7)	0.4035(8)	4.4(3)	C(13)	0.229(2)	0.203(2)	0.237(3)	18(2)
N	0.701(1)	−0.0395(8)	0.3987(9)	3.7(3)	C(14)	0.387(3)	−0.069(3)	0.175(2)	14(1)
P(1)	0.4298(4)	0.3105(3)	0.3076(3)	4.1(1)	C(15)	0.343(4)	−0.018(3)	0.140(3)	18(2)
P(2)	0.4872(4)	−0.0772(3)	0.2983(4)	4.7(1)	C(16)	1.057(2)	0.002(2)	0.360(2)	8.5(8)
P(3)	0.9912(4)	0.1399(4)	0.3975(4)	5.4(1)	C(17)	1.153(2)	−0.034(2)	0.349(2)	8.9(9)
O(1)	0.405(1)	0.3919(7)	0.3431(9)	5.4(4)	C(18)	1.007(2)	0.280(2)	0.466(2)	9.2(9)
O(2)	0.333(1)	0.295(1)	0.274(1)	6.3(4)	C(19)	0.972(3)	0.281(2)	0.540(2)	12(1)

TABLE 2. Bond Lengths (Å)

W(1)–W(2)	2.7668(3)	W(3)–S(1)	2.348(2)	P(1)–O(1)	1.572(5)
W(1)–W(3)	2.6872(4)	W(3)–S(2)	2.347(2)	P(1)–O(2)	1.570(6)
W(1)–Cu	2.9308(9)	W(3)–S(31)	2.562(3)	P(2)–O(3)	1.577(5)
W(1)–S	2.346(2)	W(3)–S(32)	2.499(2)	P(2)–O(4)	1.594(7)
W(1)–S(2)	2.344(2)	W(3)–O(31)	2.213(5)	P(3)–O(5)	1.568(6)
W(1)–S(3)	2.341(2)	Cu–I	2.470(1)	P(3)–O(6)	1.577(7)
W(1)–S(11)	2.554(2)	Cu–S(1)	2.320(2)	O(1)–C(10)	1.47(1)
W(1)–S(12)	2.506(2)	Cu–S(2)	2.319(2)	O(2)–C(12)	1.47(1)
W(1)–O(11)	2.211(4)	Cu–S(3)	2.314(2)	O(3)–C(8)	1.47(2)
W(2)–W(3)	2.7579(4)	S(11)–P(1)	1.984(3)	O(4)–C(14)	1.39(2)
W(2)–Cu	2.8406(9)	S(12)–P(1)	2.003(3)	O(5)–C(16)	1.46(1)
W(2)–S	2.363(2)	S(21)–P(2)	2.000(3)	O(6)–C(18)	1.54(1)
W(2)–S(1)	2.351(2)	S(22)–P(2)	1.998(3)	C(1)–C(2)	1.42(2)
W(2)–S(3)	2.350(2)	S(31)–P(3)	1.981(3)	C(2)–C(3)	1.33(1)
W(2)–S(21)	2.526(2)	S(32)–P(3)	2.005(3)	C(3)–C(4)	1.37(2)
W(2)–S(22)	2.573(2)	O(11)–C(6)	1.25(2)	C(4)–C(5)	1.40(1)
W(2)–N	2.334(5)	O(31)–C(6)	1.281(8)	C(6)–C(7)	1.50(1)
W(3)–Cu	2.960(1)	N–C(1)	1.369(9)	$C–C_{ave}$ (in OEt)	1.40 ± 0.10[a]
W(3)–S	2.340(2)	N–C(5)	1.334(8)		

[a]Standard error $\sigma = [(\Sigma x^2 - n\bar{x}^2)/n]^{1/2}$.

TABLE 3. Bond Angles (°)

W(2)–W(1)–W(3)	60.73(1)	I–Cu–S(3)	116.67(6)
W(2)–W(1)–Cu	59.73(2)	S(1)–Cu–S(2)	99.08(8)
W(3)–W(1)–Cu	63.42(3)	S(1)–Cu–S(3)	105.14(6)
S–W(1)–S(2)	109.04(6)	S(2)–Cu–S(3)	100.29(3)
S–W(1)–S(3)	105.60(6)	W(1)–S–W(2)	71.98(5)
S–W(1)–S(11)	157.73(6)	W(1)–S–W(3)	69.99(5)
S–W(1)–S(12)	83.04(6)	W(2)–S–W(3)	71.80(5)
S–W(1)–O(11)	81.7(1)	W(2)–S(1)–W(3)	71.87(5)
S(2)–W(1)–S(3)	98.79(6)	W(2)–S(1)–Cu	74.92(5)
S(2)–W(1)–S(11)	85.32(6)	W(3)–S(1)–Cu	78.73(5)
S(2)–W(1)–S(12)	156.27(6)	W(1)–S(2)–W(3)	69.90(5)
S(2)–W(1)–O(11)	81.4(1)	W(1)–S(2)–Cu	77.87(5)
S(3)–W(1)–S(11)	88.25(6)	W(3)–S(2)–Cu	78.75(5)
S(3)–W(1)–S(12)	97.33(6)	W(1)–S(3)–W(2)	72.28(5)
S(3)–W(1)–O(11)	172.0(1)	W(1)–S(3)–Cu	78.03(6)
S(11)–W(1)–S(12)	77.86(6)	W(2)–S(3)–Cu	75.02(6)
S(11)–W(1)–O(11)	83.9(1)	W(1)–S(11)–P(1)	87.69(9)
S(12)–W(1)–O(11)	80.2(1)	W(1)–S(12)–P(1)	88.62(9)
W(1)–W(2)–W(3)	58.21(1)	W(2)–S(21)–P(2)	88.10(9)
W(1)–W(2)–Cu	63.01(2)	W(2)–S(22)–P(2)	86.84(9)
W(3)–W(2)–Cu	63.82(3)	W(3)–S(31)–P(3)	87.5(1)
S–W(2)–S(1)	105.46(7)	W(3)–S(32)–P(3)	88.8(2)
S–W(2)–S(3)	104.76(6)	W(1)–O(11)–C(6)	124.3(4)
S–W(2)–S(21)	86.04(6)	W(3)–O(31)–C(6)	123.8(5)
S–W(2)–S(22)	160.43(6)	W(2)–N–C(1)	120.8(5)
S–W(2)–N	84.0(1)	W(2)–N–C(5)	120.7(4)
S(1)–W(2)–S(3)	103.02(6)	C(1)–N–C(5)	118.5(5)
S(1)–W(2)–S(21)	159.56(6)	S(11)–P(1)–S(12)	105.8(1)
S(1)–W(2)–S(22)	87.23(6)	S(11)–P(1)–O(1)	113.1(2)
S(1)–W(2)–N	84.3(1)	S(11)–P(1)–O(2)	114.6(3)
S(3)–W(2)–S(21)	89.90(6)	S(12)–P(1)–O(1)	113.9(2)
S(3)–W(2)–S(22)	86.28(6)	S(12)–P(1)–O(2)	112.4(2)
S(3)–W(2)–N	166.4(1)	O(1)–P(1)–O(2)	97.5(3)
S(21)–W(2)–S(22)	77.74(7)	S(21)–P(2)–S(22)	106.5(1)
S(21)–W(2)–N	80.1(1)	S(21)–P(2)–O(3)	112.4(2)
S(22)–W(2)–N	82.6(1)	S(21)–P(2)–O(4)	108.5(3)
W(1)–W(3)–W(2)	61.06(1)	S(22)–P(2)–O(3)	114.3(2)
W(1)–W(3)–Cu	62.31(2)	S(22)–P(2)–O(4)	114.6(3)
W(2)–W(3)–Cu	59.45(2)	O(3)–P(2)–O(4)	101.1(4)
S–W(3)–S(1)	106.28(6)	S(31)–P(3)–S(32)	105.7(1)
S–W(3)–S(2)	109.14(6)	S(31)–P(3)–O(5)	115.5(3)
S–W(3)–S(31)	157.39(7)	S(31)–P(3)–O(6)	114.1(3)
S–W(3)–S(32)	83.65(7)	S(32)–P(3)–O(5)	113.4(3)
S–W(3)–O(31)	81.3(1)	S(32)–P(3)–O(6)	113.1(3)
S(1)–W(3)–S(2)	97.48(7)	O(5)–P(3)–O(6)	95.2(3)
S(1)–W(3)–S(31)	88.84(6)	P(1)–O(1)–C(10)	120.6(5)
S(1)–W(3)–S(32)	97.08(7)	P(1)–O(2)–C(12)	122.1(6)
S(1)–W(3)–O(31)	172.3(1)	P(2)–O(3)–C(8)	121.7(5)
S(2)–W(3)–S(31)	84.75(7)	P(2)–O(4)–C(14)	132.2(8)
S(2)–W(3)–S(32)	156.95(7)	P(3)–O(5)–C(16)	120.4(5)
S(2)–W(3)–O(31)	81.5(1)	P(3)–O(6)–C(18)	122.7(6)
S(31)–W(3)–S(32)	77.77(7)	N–C(1)–C(2)	120.8(6)
S(31)–W(3)–O(31)	83.4(1)	C(1)–C(2)–C(3)	118.8(7)
S(32)–W(3)–O(31)	81.6(1)	C(2)–C(3)–C(4)	121.1(7)
W(1)–Cu–W(2)	57.27(2)	C(3)–C(4)–C(5)	118.7(6)
W(1)–Cu–W(3)	54.27(2)	N–C(5)–C(4)	122.2(6)
W(2)–Cu–W(3)	56.74(2)	O(11)–C(6)–O(31)	123.9(6)
I–Cu–S(1)	116.20(6)	O(11)–C(6)–C(7)	120.4(6)
I–Cu–S(2)	116.83(6)	O(31)–C(6)–C(7)	115.7(8)
		O–C–C_{ave} (in OEt)	110.6 ± 6.3[a]

[a]Standard error $\sigma = [(\Sigma x^2 - n\bar{x}^2)/n]^{1/2}$.

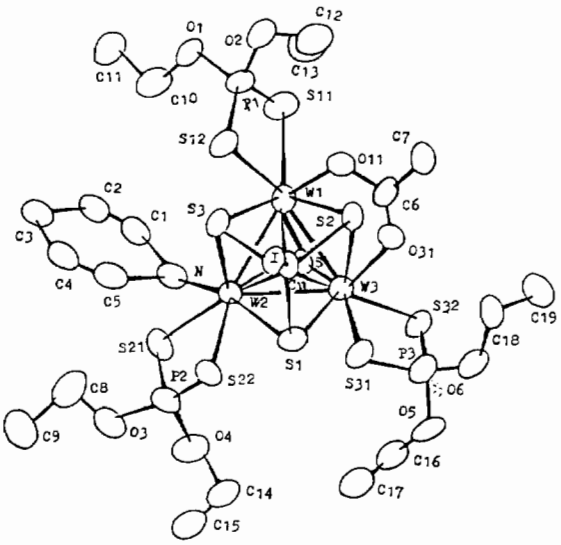

Fig. 1. The molecular configuration of $[W_3CuS_4]\cdot[S_2P(OC_2H_5)_2]_3\cdot I\cdot CH_3COO\cdot C_5H_5N$.

and bond angles are given in Tables 2 and 3, respectively.

Results and Discussion

The configuration of the cluster molecule is shown in Fig. 1. The cluster core $[W_3CuS_4]$ has a cubane-like structure. Each tungsten atom is coordinated by three μ_3-S and a $S_2P(OEt)_2$ chelating terminal ligand. In addition, W(1) and W(3) atoms are coordinated by a CH_3COO bridge ligand, while the W(2) atom is coordinated to a C_5H_5N molecule through a W–N bond of length 2.34(2) Å, which is somewhat longer than a normal single W–N bond. The tungsten atoms are all octahedrally coordinated. 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 $[W_3CuS_4]$ with the following mean bond lengths: W–W 2.74 Å, W–Cu 2.91 Å. Upon application of the extended Wade rule [24] 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.

It is obvious that on account of the presence of three coordinatively unsaturated μ_2-S atoms in the trinuclear tungsten cluster $\{W_3S_4[S_2P(OEt)_2]_4\}\cdot H_2O$, 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 different loosely coordinated ligands and the cubane-like skeleton with the different bridge ligands is in progress.

Supplementary Material

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

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References

1 F. A. Cotton, *Polyhedron, 5* (1986) 3.
2 A. Müller, R. Jostes and F. A. Cotton, *Angew. Chem., Int. Ed. Engl., 19* (1980) 875.
3 J.-L. Huang, J.-Q. Huang, M.-Y. Shang, S.-F. Lu, H.-H. Zhuang, X.-T. Lin and D.-M. Wu, *Proceedings of the Molecular Structure, Chemical Reactivity and Biological Activity Symposium*, Beijing, China, 1986, L10, p. 25.
4 T. Shibahar, M. Miyake, K. Kobayashi and H. Kuroya, *Chem. Lett.*, (1986) 139.
5 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan and A. G. Sykes, *Inorg. Chim. Acta, 113* (1986) L19.
6 F. A. Cotton, Z. Dori, R. Llusar and W. Schwotzer, *J. Am. Chem. Soc., 107* (1985) 6734.
7 (a) T. Shibahara and H. Kuroya, *Abstracts of Papers, 5th International Conference on the Chemistry and Use of Molybdenum*, Newcastle-upon-Tyne, U.K., July 1985; (b) *Polyhedron, 5* (1986) 357.
8 F. A. Cotton, R. Llusar, D. O. Marlar, W. Schwotzer and Z. Dori, *Inorg. Chim. Acta, 102* (1985) L25.
9 (a) P. Kathirgamanathan, M. Martinez and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, (1985) 953; (b) 1437.
10 A. Müller, R. Jostes, W. Eltzer, C.-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem., 24* (1985) 2872.
11 T. Shibahara, H. Hattori and H. Kuroya, *J. Am. Chem. Soc., 106* (1984) 2710.
12 T. R. Halbert, K. McGauley, W.-H. Pan, R. S. Czernuszewicz and E. I. Stiefel, *J. Am. Chem. Soc., 106* (1984) 1849.
13 N. C. Howlader, G. P. Haight, Jr., T. W. Hambley, G. A. Lawrance, K. M. Rohmoeller and M. R. Snow, *Aust. J. Chem., 36* (1983) 377.
14 T. Shibahara, K. Kohda, A. Ohtsuji, K. Yasuda and H. Kuroya, *J. Am. Chem. Soc., 108* (1986) 2757.
15 Z. Dori, F. A. Cotton, R. Llusar and W. Schwotzer, *Polyhedron, 5* (1986) 907.
16 T. Shibahara, A. Takeuchi and H. Kuroya, *Inorg. Chim. Acta, 127* (1987) L39.
17 T. Shibahara, A. Takeuchi, A. Ohtsuji, K. Kohda and H. Kuroya, *Inorg. Chim. Acta, 127* (1987) L45.
18 X.-T. Lin, Y.-H. Lin, J.-L. Huang and J.-Q. Huang, *Kexue Tongbao (Science Bulletin), 7* (1986) 509.
19 Zhan Huqiang, *Master Thesis*, to be published.
20 T. Shibahara, H. Akashi and H. Kuroya, *J. Am. Chem. Soc., 108* (1986) 1342.
21 Wu Xintao, Lu Shaofang, Zu Lianyong, Wu Qiangjin and Lu Jiaxi, *Inorg. Chim. Acta, 133* (1987) 39.
22 Y. Zheng, M.-Y. Shang, J.-L. Huang and J.-X. Lu, *Spectrosc. Anal., 2* (1973) 72 (in Chinese).
23 (a) S. Sarkar and S. B. S. Mishra, *Coord. Chem. Rev., 59* (1984) 239; (b) H. Bögge, *Ph.D. Thesis*, Universität Bielefeld, 1980.
24 J.-X. Lu, *Comm. Fujian Inst. Res. Struct. Matter., 1* (1979) 1 (in Chinese).