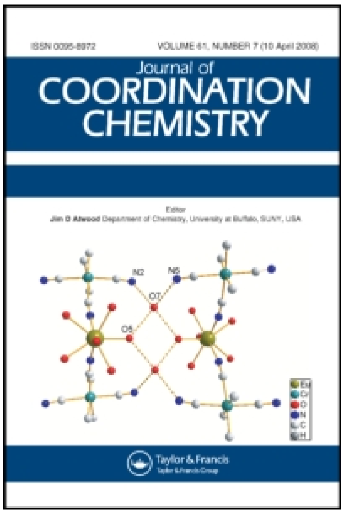

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SYNTHESIS AND CHARACTERIZATION OF TWO NOVEL, NEST-SHAPED Mo-Cu-S CLUSTER COMPOUNDS, $[MoOS_3Cu_3(Py)_5X]$ (X = Br, I), AND THE SUBSTITUTION OF Mo-Cu-S CLUSTERS

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The title compounds $[MoOS_3Cu_3(Py)_5Br]$ (*3*) and $[MoOS_3Cu_3(Py)_5I]$ (*4*) were obtained through the nest-shaped cluster $[(n\text{-}Bu)_4N]_2[MoOS_3Cu_3BrCl_2]$ (*1*) and twin-nest-shaped cluster $[Et_4N]_4[Mo_2Cu_6S_6O_2Br_2I_4]$(*2*) by reacting with pyridine. They show nest-shaped skeletons, and are characterized structurally by single-crystal X-ray analysis. These are the first neutral nest-shaped Mo(W)-Cu(Ag)-S clusters.

KEYWORDS: Mo-Cu-S clusters, synthesis, substitution reaction, X-ray structure

INTRODUCTION

The chemistry of Mo(W)-Cu-S compounds has been of interest for over a century.[1] Many of these compounds have been extensively studied because of their relevance to biological systems and catalytic processes.[2] Recently, we discovered that some Mo(W)-Cu(Ag)-S clusters display very strong nonlinear optical (NLO) effects.[3-6] It was also discovered that all of the cubic cage-shaped Mo(W)-Cu(Ag)-S clusters, $[(n\text{-}Bu)_4N]_3[MS_4M'_3BrX_3]$ (M = Mo, W; M' = Cu, Ag; X = Cl, Br, I)[3], exhibit strong nonlinear absorption and negligibly small nonlinear refraction (self-focusing), while both the nest-shaped clusters $[(n\text{-}Bu)_4N]_2[MoOS_3(CuNCS)_3]$, $[(n\text{-}Bu)_4N]_2[MoOS_3Cu_3BrCl_2]$[5] and the twin-nest-shaped cluster $[Et_4N]_4$ $[Mo_2Cu_6S_6O_2Br_2I_4]$[6] exhibit a strong self-focusing effect. In this article, we report the substitution of compounds (*1*) and (*2*) with pyridine. The substituted compounds (*3*) and (*4*) were analyzed by X-ray diffraction methods.

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EXPERIMENTAL

Infrared spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets. Electronic spectra were measured on a Shimadzu UV-240 instrument. Carbon, hydrogen and nitrogen analyses were performed on a PE 240C Elemental Analyser.

$(NH_4)_2MoO_2S_2$ was prepared according to the literature.[7] The other chemicals were purchased as A.R. grade reagents and used without further purification.

Preparation of compounds

$[(n\text{-}Bu)_4N]_2[MoOS_3Cu_3BrCl_2]$ (*1*)

A well-ground mixture of $(NH_4)_2MoO_2S_2$ (0.23 g, 1 mmol), CuCl (0.20 g, 2 mmol) and $(n\text{-}Bu)_4NBr$ (0.64 g, 2 mmol) was heated at 90°C for 10 h under a nitrogen atmosphere. Extraction of the product with CH_2Cl_2 (20 cm^3) and filtration produced a red clean solution. Dropwise addition of isopropanol (10 cm^3) to the top of the red solution produced a two layer system from which red crystals were obtained after standing for a week.

$[Et_4N]_4[Mo_2Cu_6S_6O_2Br_2I_4]$ (*2*)

A well-ground mixture of $(NH_4)_2MoO_2S_2$ (0.23 g, 1 mmol), CuI (0.40 g, 2 mmol) and Et_4NBr (0.42 g, 2 mmol) was placed in a reaction tube and heated at 100°C for 10 h under a pure nitrogen atmosphere. After extracting the dark red solid product with CH_2Cl_2 (20 cm^3), the deep red extract was filtered and layered with isopropanol (10 cm^3). Deep red, cubic crystals were obtained several days later.

$[MoOS_3Cu_3Br(Py)_5]$ (*3*)

Compound (*1*) (0.15 g) was dissolved in pyridine (20 cm^3). After stirring for 1 h, the deep red solution was filtered and isopropanol added dropwise (10 cm^3) to the top of the solution. Black crystals were produced a few days later. Yield 0.12 g, characteristic infrared absorptions at 925 cm^{-1}: $\upsilon(Mo\text{-}O_t)$ and 445 cm^{-1}: $\nu(Mo\text{-}S_b)$. Anal.: calc. for $C_{25}H_{25}N_5BrCu_3MoOS_3$: C, 34.34; H, 2.86; N, 8.01%. Found: C, 34.78; H, 3.04; N, 7.96%.

$[MoOS_3Cu_3I(Py)_5]$ (*4*)

Compound (*4*) was prepared in the same way as (*3*) *using* (*2*) instead of (*1*). Some 0.10 g of black crystals were obtained with characteristic infrared absorptions at 914 cm^{-1}: $\nu(Mo\text{-}O_t)$ and 440 cm^{-1}: $\nu(Mo\text{-}S_b)$. Anal.: calc. for $C_{25}H_{25}N_5ICu_3MoOS_3$: C, 32.59; H, 2.71; N, 7.60%. Found: C, 32.35; H, 3.01; N, 7.31%.

Crystal data and structure determination

Suitable crystals of compounds (*3*) and (*4*) were mounted in random orientation on a glass fibre. Data were collected on a diffractometer using Mo-Kα radiation at

296 K. Details concerning the intensity and data collection are given in Table 1. The data were corrected for Lorentz and polarization factors and for absorption by using empirical scan data and DIFABS.

The structure of (*3*) was solved by direct methods. The structure was refined by full-matrix least-squares methods with isotropic temperature factors for C atoms and anisotropic temperature factors for the remaining non-hydrogen atoms to final $R = 0.069$ and $R_w = 0.078$.

The structure of (*4*) was solved by heavy atom methods, which revealed the position of the Mo amd Cu atoms. The remaining non-hydrogen atoms were located in successive difference Fourier maps. The structure was refined by full-matrix least-squares methods to final $R = 0.054$ and $R_w = 0.067$. The atomic coordinates and thermal parameters are summarized in Table 2.

RESULTS AND DISCUSSION

Description of the structures of (3) and (4)

The skeletons, consisting of one Mo, three μ_3-S and three Cu atoms, show nest-shaped structures. ORTEP diagrams are given in Figures 1 and 2, respectively. Mo is tetrahedrally coordinated by three S atoms and one terminal O atom. The Mo-O bond lengths of 1.69(2) and 1.70(1) Å are typical for an Mo = O double bond. The three longer Mo-S bond lengths are characteristic of single bonds. One Cu atom is coordinated by two μ_3-S atoms, one Br (or I) atom and one pyridine nitrogen

Table 1 Crystal parameters and refinement details

	$[MoOS_3Cu_3(Py)_5Br]$	$[MoOS_3Cu_3(Py)_5I]$
Empirical formula	$C_{25}N_5H_{25}BrCu_3MoOS_3$	$C_{25}N_5H_{25}Cu_3IMoOS_3$
Formula weight	874.17	921.17
Crystal system	Triclinic	monoclinic
Space group	$P\bar{1}$(#2)	*C*2/*c*(#15)
a(Å)	10.314(4)	24.388(6)
b(Å)	12.881(9)	10.043(4)
c(Å)	13.679(8)	26.711(9)
α(°)	113.69(5)	
β(°)	92.79(4)	98.32(3)
γ(°)	108.45(4)	
V(Å^3)	1546(2)	6473(4)
Z	2	8
Dc(gcm^{-3})	1.88	1.89
F(000)	860	3584
Diffractometer	Enraf-nonius CAD4	Rigaku AFC5R
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71069)
2θ max(°)	50.0	50.0
No. observable	with $I > 4\sigma(I)$:1428	with $I > 3\sigma(I)$:2406
No. variables	227	352
R	0.069	0.054
R_w	0.078	0.067
S	1.59	1.52
Δρ max (eA^{-3})	0.79	0.69

Table 2 Positional parameterse and B(eq) values for (*3*) (former) and (*4*)

Atom	*x*	*y*	*z*	*B*(eq)
Mo	0.4201(2)	0.0991(2)	0.3650(2)	2.57(8)
Br(1)	0.0670(3)	-0.2835(2)	0.1677(2)	3.6(1)
Cu(1)	0.2962(4)	0.2205(3)	0.5147(3)	3.3(1)
Cu(2)	0.1668(3)	-0.0618(3)	0.2446(3)	3.1(1)
Cu(3)	0.4253(4)	0.2357(3)	0.2609(3)	3.4(1)
S(1)	0.3503(7)	0.0292(6)	0.1828(6)	3.5(2)
S(2)	0.4746(8)	0.3045(6)	0.4446(6)	3.3(2)
S(3)	0.2400(8)	0.0156(6)	0.4287(6)	3.4(3)
O(1)	0.557(2)	0.065(2)	0.397(2)	5.6(8)
N(1)	0.128(2)	0.271(2)	0.504(2)	2.3(7)
N(2)	0.373(2)	0.266(2)	0.676(2)	3.4(8)
N(3)	0.612(2)	0.290(2)	0.202(2)	3.3(8)
N(4)	0.000(2)	-0.011(2)	0.215(2)	4.0(8)
N(5)	0.325(2)	0.321(2)	0.208(2)	3.5(8)
C(12)	0.019(3)	0.237(2)	0.552(2)	3.5(6)
C(13)	-0.102(3)	0.255(3)	0.513(3)	4.7(7)
Mo	0.30275(7)	0.4143(2)	0.17718(5)	3.37(7)
I	0.39965(6)	0.2577(1)	0.04564(5)	5.00(6)
Cu(1)	0.36199(9)	0.4465(2)	0.09974(7)	3.6(1)
Cu(2)	0.3624(1)	0.6003(2)	0.23160(8)	4.2(1)
Cu(3)	0.2312(1)	0.6014(2)	0.13796(9)	4.5(1)
S(1)	0.3968(2)	0.4392(5)	0.1852(2)	3.8(2)
S(2)	0.2672(2)	0.4347(5)	0.0943(2)	3.7(2)
S(3)	0.2688(2)	0.5822(5)	0.2205(2)	4.5(2)
O	0.2846(6)	0.265(1)	0.1994(5)	6.2(7)
N(1)	0.3864(6)	0.620(1)	0.0675(6)	4.5(8)
N(2)	0.3906(7)	0.789(2)	0.2259(6)	4.3(8)
N(3)	0.3949(6)	0.572(1)	0.3088(4)	3.8(7)
N(4)	0.1440(7)	0.578(2)	0.1254(6)	4.7(8)
N(5)	0.2341(6)	0.794(1)	0.1093(5)	3.9(7)
C(11)	0.4172(8)	0.624(2)	0.0307(6)	5(1)
C(12)	0.4328(9)	0.736(2)	0.0102(6)	5(1)

atom. Each of the other two Cu atoms binds with two μ_3-S atoms and two pyridine nitrogen atoms. All three Cu atoms adopt distorted tetrahedral geometry. Selected bond lengths and bond angles are listed in Tables 3 and 4 respectively. In reported nest-shaped clusters, every Cu atom is in an approximately triangular planar geometry. Due to differences of Cu coordination, bond lengths and angles of the nest-shaped skeleton show considerable change. Table 5 collects some related bond lengths and angles for compounds *(1)*, *(2)*, *(3)* and *(4)*.

Compared to *(1)* and *(2)*, the Mo-O, Mo-S, Cu-S, Mo-Cu distances and Cu-Mo-Cu angles of the substituted products *(3)* and (4) increase, and the S-Mo-S and O-Mo-S bond angles change slightly. Related bond lengths and angles of *(3)* and *(4)* are very close.

Electronic spectra

For comparison, the electronic spectra arising from the $MoOS_3^{2-}$ moiety for compounds *(3)* and *(4)* are summarized in Table 6. Because the S → Mo charge

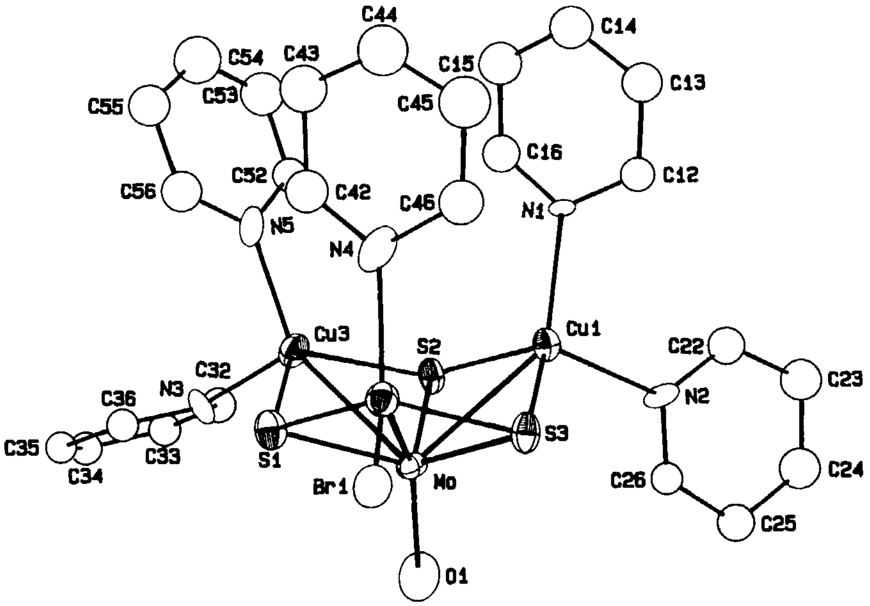

Figure 1 ORTEP diagram of [$MoOS_3Cu_3(Py)_5Br$].

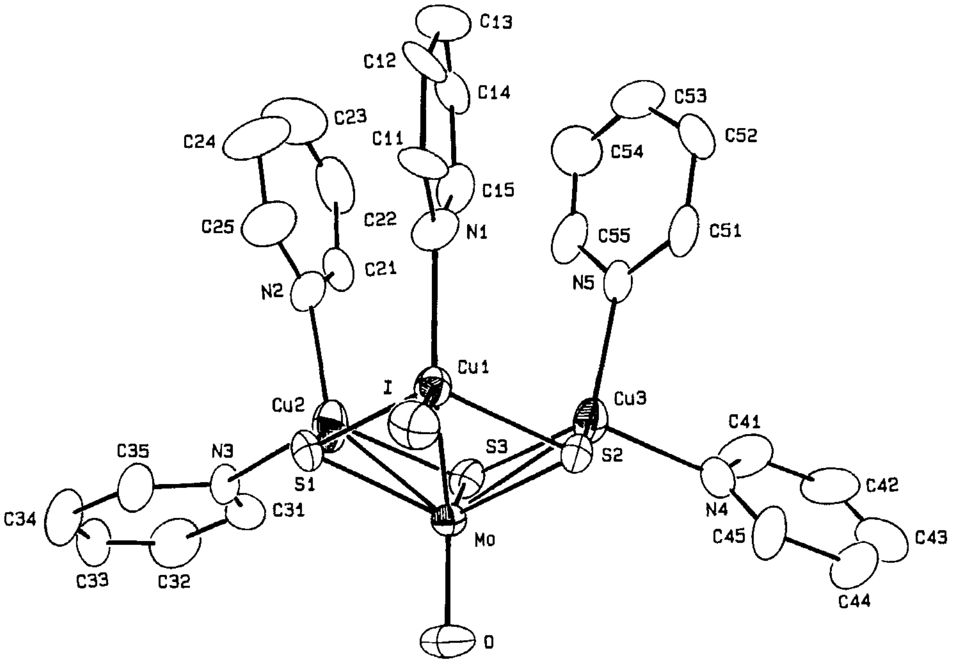

Figure 2 ORTEP diagram of [$MoOS_3Cu_3(Py)_5I$].

Table 3 Selected bond lengths (Å) for (*3*) (former) and (*4*)

Mo-Cu(3)	2.662(4)	Mo-Cu(1)	2.687(5)	Mo-Cu(2)	2.692(4)
Mo-S(3)	2.239(7)	Mo-S(1)	2.270(8)	Mo-S(2)	2.277(8)
Mo-O	1.69(2)	Br(1)-Cu(2)	2.437(5)	Cu(1)-N(1)	2.06(2)
Cu(1)-N(2)	2.08(2)	Cu(1)-S(3)	2.270(9)	Cu(1)-S(2)	2.285(8)
Cu(2)-S(1)	2.285(8)	Cu(2)-S(3)	2.286(8)	Cu(3)-S(1)	2.270(8)
Cu(3)-S(2)	2.272(8)				
Mo-Cu(3)	2.673(3)	Mo-Cu(1)	2.708(2)	Mo-Cu(2)	2.666(3)
Mo-S(3)	2.268(5)	Mo-S(1)	2.287(5)	Mo-S(2)	2.266(5)
Mo-O	1.70(1)	I-Cu(1)	2.629(3)	Cu(1)-N(1)	2.07(1)
Cu(2)-N(2)	2.03(1)	Cu(1)-S(1)	2.319(5)	Cu(1)-S(2)	2.298(5)
Cu(2)-S(1)	2.272(5)	Cu(2)-S(3)	2.265(5)	Cu(3)-S(3)	2.270(5)
Cu(3)-S(2)	2.286(5)				

Table 4 Selected bond angles (°) for (*3*) (former) and (*4*)

Cu(3)-Mo-Cu(1)	91.6(1)	Cu(3)-Mo-Cu(2)	91.2(1)
Cu(1)-Mo-Cu(2)	89.4(1)	O-Mo-S(3)	108.9(8)
O-Mo-S(1)	113.0(8)	O-Mo-S(2)	110.5(8)
S(3)-Mo-S(1)	108.3(3)	S(3)-Mo-S(2)	108.0(3)
S(2)-Mo-S(1)	107.9(3)	S(3)-Cu(1)-S(2)	106.6(3)
S(1)-Cu(2)-S(3)	106.2(3)	S(1)-Cu(2)-Br	119.4(3)
S(3)-Cu(2)-Br	108.8(2)	Mo-S(1)-Cu(3)	71.8(2)
Mo-S(1)-Cu(2)	72.5(2)	Mo-S(2)-Cu(1)	72.2(2)
Mo-S(3)-Cu(1)	73.1(2)	Cu(3)-S(2)-Cu(2)	114.6(3)
Cu(1)-S(3)-Cu(2)	112.2(3)		
Cu(3)-Mo-Cu(1)	90.38(8)	Cu(3)-Mo-Cu(2)	89.68(9)
Cu(1)-Mo-Cu(2)	91.36(8)	O-Mo-S(3)	110.3(4)
O-Mo-S(1)	111.9(5)	O-Mo-S(2)	109.9(5)
S(3)-Mo-S(1)	107.8(2)	S(3)-Mo-S(2)	108.3(2)
S(2)-Mo-S(1)	108.6(2)	S(1)-Cu(1)-S(2)	106.4(2)
S(1)-Cu(2)-S(3)	108.4(2)	S(1)-Cu(1)-I	114.3(1)
S(2)-Cu(1)-I	110.9(1)	Mo-S(3)-Cu(3)	72.2(1)
Mo-S(1)-Cu(1)	72.0(1)	Mo-S(2)-Cu(3)	71.9(1)
Mo-S(1)-Cu(2)	71.6(1)	Mo-Cu(3)-S(3)	53.9(1)
Mo-Cu(3)-S(2)	53.7(1)	Cu(3)-S(2)-Cu(1)	112.8(2)
Cu(3)-S(3)-Cu(2)	112.2(2)		

Table 5 Some related bond lengths and angles for *(1)*, *(2)*, *(3)* and *(4)*; data given in Å and degrees.

	(1)	*(2)*	*(3)*	*(4)*
Mo-O	1.66	1.69	1.68	1.70
Mo-S	2.262 2.265	2.239 2.270	2.250 2.261	2.266 2.268
	2.266	2.277	2.272	2.287
Cu-S	2.234 2.238	2.270 2.272	2.244 2.250	2.265 2.298
	2.239	2.285	2.280	2.319
Mo-Cu	2.621 2.628	2.662 2.687	2.625 2.646	2.666 2.673
	2.638	2.692	2.703	2.708
S-Mo-S	107.48 107.77	107.9 108.0	107.2 107.9	107.8 108.3
	107.48	108.3	108.1	108.6
O-Mo-S	110.0 111.9	108.9 110.5	111.1 111.2	109.9 110.3
	112.0	113.0	111.3	111.9
Cu-Mo-Cu	86.39 87.14	89.4 91.2	81.73 82.99	89.68 90.38
	87.85	91.6	87.52	91.36

Table 6 Electronic spectroscopic data for (*3*) and (*4*)

	vl(nm)	v2(nm)	v3(nm)	v4(nm)
$MoOS^{2-}_3$	465	392	313	260
Compound (3)	488	402	280	244
Compound (4)	480	402	284	240

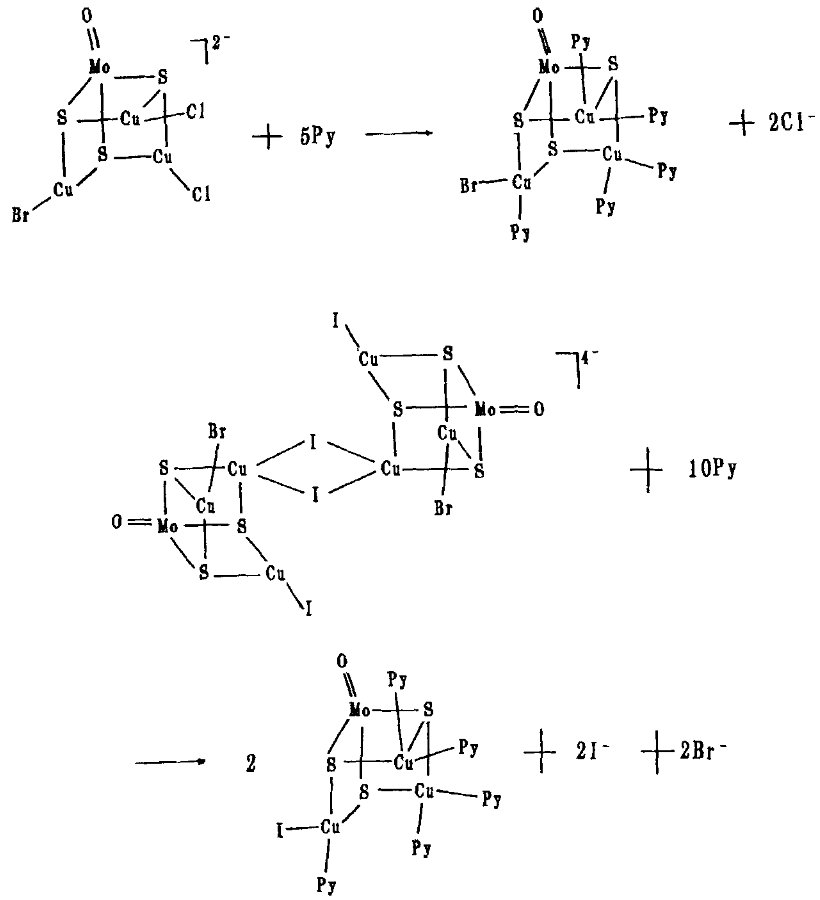

Figure 3 a: The substitution of $[(n\text{-Bu})_4N]_2[MoOS_3Cu_3BrCl_2]$ with Py; b: the substitution of $[Et_4N]_4[Mo_2Cu_6S_6O_2Br_2I_4]$ with Py.

transfer bands are significantly affected by the coordination of $MoOS^{2-}_3$ to Cu $(Cu(S)_2Mo)$, shifts of the electronic transition bands of compounds *(3)* and *(4)* are observed to bc comparable with the $MoOS^{2-}_2$ moiety. Because *(3)* and *(4)* are the same structural clusters, they have similar electronic transition bands.

Reactions of compounds (1) and (2)

In Mo(W)-Cu-S cluster compounds, terminal ligands such as Cl^-, Br^- and I^- have been proposed to be loose and of some activity, and can be substituted by strong ligands such as PPh_3 or Py[8] to produce related compounds. The substitution reactions are classified into the two types:

1. both reacting substances and products have the same structure.
2. the skeletons of products are different from the reactants and the nuclearity of the products is lower.

Reaction of compound *(1)* with Py is represented in Figure 3a. Only two Cl^- ions are substituted by Py; Br^- is not removed. The three Cu atoms are also coordinated by three Py molecules. This reaction belongs to the first type described above. Figure 3b illustrates the reaction of compound *(2)* with Py. The two bridging I atoms are substituted by four Py molecules making the product a monocubic-like cluster. The skeleton of this reaction product changes during reaction and is quite different to the case(s) described previously.

Acknowledgements

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SUPPLEMENTARY DATA

Full lists of atomic positions bond lengths and angles, thermal parameters and observed and calculated structure factors are available from the authors upon request.

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