

Stepwise synthesis of trimetallic dithiophosphinato clusters containing a cubane-type Mo_2WCuS_4 cluster core

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Abstract

Starting from $\text{Mo}(\text{CO})_6$ and disulfanes $\text{R}_2\text{P}(\text{S})\text{--S--S--P}(\text{S})\text{R}_2$ the “trimetallic” tetranuclear clusters $\text{Mo}_2\text{WCuS}_4\text{I}(\text{R}_2\text{PS}_2)_4$ **3** ($\text{R} = \text{Et}$ (**a**), Pr (**b**)) were obtained via the dinuclear compounds $\text{Mo}_2\text{S}_4(\text{R}_2\text{PS}_2)_2$ **1** and the trinuclear complexes $\text{Mo}_2\text{WS}_4(\text{R}_2\text{PS}_2)_4$ **2**. The crystal structure of **3b** shows a cubane-type core Mo_2WCuS_4 . Both Mo atoms and the W atom are chelated by a dithiophosphinato ligand. One Mo and the W atom are bridged by the fourth ligand. The coordination of W and Mo2 is octahedral, of Mo1 trigonal bipyramidal, and of Cu tetrahedral.

Keywords: Molybdenum; Tungsten; Copper; Metal–sulfur-clusters; Dithiophosphinato ligands; Crystal structure

1. Introduction

Heterometal sulfur clusters are of great interest mainly because of their importance with respect to bioinorganic and technical processes [1]. Recently we reported on a series of metal–sulfur clusters containing dithiophosphinato groups R_2PS_2^- as chelating or bridging ligands or as anions [2]. Depending on these different functions they give rise to resonance signals in well separated regions of field strength in their $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra. Thus, ^{31}P -NMR spectroscopy turned out to be very helpful in the structure determination of the clusters and revealed in combination with crystal structure analysis not only isomerism of some compounds [3] but also differences between crystal and solution structure e.g. in case of $[\text{Mo}_3\text{S}_4(\text{Pr}_2\text{PS}_2)_4\text{HgI}_2]$ [4]. Moreover, this method enabled us to elucidate the role of Mo–S clusters in the catalytic sulfidation of tertiary phosphines [5] or unsaturated hydrocarbons [6] and to pursue the stepwise synthesis of the “trimetallic” clusters **3** described below which contain the cubane-type cluster core Mo_2WCuS_4 .

2. Experimental section

2.1. General procedures

All syntheses were carried out under dry argon. Solvents were purified and dried by standard methods. $^{31}\text{P}\{^1\text{H}\}$ -NMR, Bruker HX 90 R; electronic spectra, Perkin-Elmer Lambda 5 (CH_2Cl_2), λ (nm), (ϵ ($\text{M}^{-1}\text{cm}^{-1}$)); IR, Perkin-Elmer 283 (KBr pellets); mass spectra, Varian MAT 311 A, EI-MS: 70 eV, FD-MS: 8 kV, activated tungsten emitters; molecular weights, Knauer osmometer; electric conductivities, Metrohm 518 conductimeter; magnetic measurements, Bruker magnet B-E 10 in combination with a microbalance Sartorius Type 4107 (Faraday-method), Pascal constants: [7]; melting points (uncorrected), Büchi 510 W; microanalyses (C, H), Institut für Pharmazeutische Chemie der Universität Düsseldorf; Mo, W, Cu, atomic absorption spectrometer Perkin-Elmer 3100; P, photometrically as molybdate–vanadate [8]; I, titration with silver nitrate and potentiometric indication [8]; S, gravimetrically as BaSO_4 [8].

2.2. Synthesis of $\text{Mo}_2\text{WS}_4(\text{R}_2\text{PS}_2)_4$ **2**, general procedure

Equimolar amounts of $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ [9] and $[\text{R}_2\text{P}(\text{S})\text{S}]_2$ [10] were added to a solution of 1 mmol **1**

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[11] in 75 ml toluene at 80 °C. The solution was stirred for 3 h at this temperature and the colour turned to deep black with evolution of CO. After adding 100 ml of ligroine (100–140°C) to the hot solution the product began to precipitate, which was repeatedly recrystallized from CH₂Cl₂/toluene (1:1). Black crystals, soluble in acetone, toluene or dichloromethane with deep red color.

2.2.1. 1, 2, 3-Tris(diethylthiophosphinato)-1, 2-μ-diethylthiophosphinato-tri-μ-thio-μ₃-thio-triangulo-1-tungsten-2, 3-dimolybdenum 2a

Obtained from 0.63 g (1.0 mmol) **1a**, 0.39 g (1.0 mmol) W(CO)₃(CH₃CN)₃ and 0.31 g (1.0 mmol) [Et₂P(S)S]₂. Yield: 0.25 g (22%). m.p. about 200°C (decomp.); molecular weight: 1112 (CHCl₃, 37°C, 0.002 mol kg⁻¹); EI-MS: *m/z* (%): 964 (100) [M⁺-Et₂PS₂]; FD-MS: 1117 [M⁺]; χM(found.): -580 · 10⁻⁶ cm³ mol⁻¹; χM(calc.): -620 · 10⁻⁶ cm³ mol⁻¹; Anal. Found: C, 17.43; H, 3.57; P, 11.21; S, 34.60. Calc. (for C₁₆H₄₀Mo₂P₄S₁₂W): molecular weight 1116.8; C, 17.21; H, 3.61; P, 11.09; S, 34.45.

2.2.2. 1, 2, 3-Tris(dipropylthiophosphinato)-1, 2-μ-dipropylthiophosphinato-tri-μ-thio-μ₃-thio-triangulo-1-tungsten-2, 3-dimolybdenum 2b

From 0.68 g (1.0 mmol) **1b**, 0.39 g (1.0 mmol) W(CO)₃(CH₃CN)₃ and 0.36 g (1.0 mmol) [Pr₂P(S)S]₂. Yield: 0.25 g (20%). m.p. about 195°C (decomp.); molecular weight: 1180 (CHCl₃, 37°C, 0.002 mol kg⁻¹); EI-MS: *m/z* (%): 1048 (100) [M⁺-Pr₂PS₂]; FD-MS: 1229 [M⁺]; Anal. Found: C, 23.36; H, 4.65; P, 10.01; S, 31.11. Calc. (for C₂₄H₅₆Mo₂P₄S₁₂W): molecular weight 1229.0; C, 23.45; H, 4.59; P, 10.08; S, 31.40.

2.3. Synthesis of Mo₂WCuS₄I(R₂PS₂)₄ 3, general procedure

Approximately equimolar amounts of **2** and CuI were stirred in 20 ml toluene for 48 h at room temperature. Afterwards a red-brown precipitate had formed which was filtered off, dried in vacuo, and dissolved in CH₂Cl₂. The solution was filtered and **3** precipitated with ligroine (60–80°C). The compounds **3** are soluble in chlorinated hydrocarbons, CH₂Br₂, and acetone with dark red color.

2.3.1. 1, 2, 3-Tris(diethylthiophosphinato)-1, 3-μ-diethylthiophosphinato-4-iodo-tetra-μ₃-thio-tetrahedro-1-tungsten-2, 3-dimolybdenum-4-copper 3a

From 1.05 g (0.85 mmol) **2a** and 0.16 g (0.86 mmol) CuI, red brown crystals; yield: 0.8 g (66%). m.p. about 130°C (decomp.); UV/VIS: λ_{max} (ε) = 400 (8200), 484 (4350), 540 (3200); EI-MS: *m/z* (%): 1329–1305 (21) [M⁺], 1203–1178 (34) [M⁺-I], 960–943 (100) [M⁺-CuI-Et₂PS₂]; ¹H-NMR (200 MHz, CD₂Cl₂, TMS) δ_H

= 1.27 (m, c), 1.9 (m, c), 2.27 (m, c); λ_c (CH₂Br₂, 25°C, 10⁻³ M): 0.14 Scm² mol⁻¹; χM(found): -726 · 10⁻⁶ cm³ mol⁻¹; χM(calc.): -758 · 10⁻⁶ cm³ mol⁻¹; Anal. Found: C, 14.81; H, 3.02; Cu, 4.99; Mo, 14.33; I, 9.63; S, 29.23. Calc. (for C₁₆H₄₀CuIMo₂P₄S₁₂W): molecular weight 1307.3; C, 14.70; H, 3.08; Cu, 4.86; Mo, 14.68; I, 9.71; S, 29.43.

2.3.2. 1, 2, 3-tris(dipropylthiophosphinato)-1, 3-μ-dipropylthiophosphinato-4-iodo-tetra-μ₃-thio-tetrahedro-1-tungsten-2, 3-dimolybdenum-4-copper 3b

From 0.58 g (0.52 mmol) **2b** and 0.1 g (0.53 mmol) CuI, brown crystals; yield: 0.4 g (59%). m.p. about 130°C (decomp.); molecular weight: 1428 (CH₂Br₂, 37°C); UV/VIS: λ_{max} (ε) = 400 (8650), 480 (5400), 540 (3050); EI-MS: *m/z* (%): 1433–1412 (6) [M⁺], 1311–1290 (21) [M⁺-I], 1055–1039 (100) [M⁺-CuI-Pr₂PS₂]; λ_c (CH₂Br₂, 25°C, 10⁻³ M): 0.08 Scm² mol⁻¹; χM(found): -885 · 10⁻⁶ cm³ mol⁻¹; χM(calc.): -853 · 10⁻⁶ cm³ mol⁻¹; Anal. Found: C, 20.03; H, 3.90; Cu, 4.52; Mo, 13.75; I, 8.76; S, 27.83. Calc. (for C₂₄H₅₆CuIMo₂P₄S₁₂W): molecular weight 1419.6; C, 20.31; H, 3.98; Cu, 4.48; Mo, 13.52; I, 8.94; S, 27.10.

2.4. Crystal structure determination of 3b

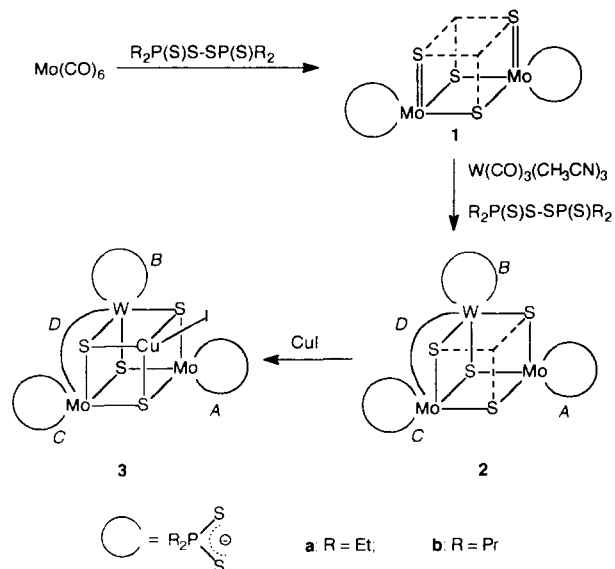
C₂₄H₅₆P₄S₁₂CuMo₂WI, M = 1419.46, monoclinic, space group *P*2₁/*n*, *a* = 1278.3(2), *b* = 2206.0(4), *c* = 1750.8(3) pm, β = 97.10(1)°, *V* = 4.899(1) nm³, *Z* = 4, *D_c* = 1.924 mg mm⁻³, *F*(000) = 2768. Syntex/Siemens diffractometer P2₁/P3 with crystal monochromator, Mo Kα, λ = 71.073 pm, μ = 4.6 mm⁻¹.

The intensities were measured at room temperature using a crystal of approximate size 0.40 × 0.45 × 0.50 mm³ and performing a variable ω:2θ-scan up to 2θ = 50°. The indices ranged from 0 to *h* = 15, *k* = 26 and from *l* = -20 to *l* = 20. All 8609 unique reflections have been used for the structure solution [12] and refinement of 427 parameters by full-matrix least-squares on *F*² [13]. H atoms have been added in calculated fixed positions. The final residuals were *R*(*F*) = 0.034 (0.044) and *wR*(*F*²) = 0.093 (0.099) for the 7065 observed (*I* > 2σ_{*I*}) (all) reflections. Residual electron densities ranged from -0.86 to 0.82 · 10⁻⁶ e pm⁻³. Further details have been deposited as supplementary material [14].

3. Results and discussion

3.1 Syntheses and properties

We obtained the “trimetallic” clusters **3** by systematically completing the “incomplete” cubane framework of the precursor complexes **1** and **2** according to Scheme 1 which shows the schematic structure of **1–3**.



Scheme 1. Stepwise synthesis of **3** and schematic structure of the compounds **1**–**3**.

In the first step of the synthesis the metal atom in Mo(CO)_6 is oxidized by disulfanes $\text{R}_2\text{P(S)S-SP(S)R}_2$ which are simultaneously reduced to the lig-

Table 1
 δ_p -values (90 MHz, CH_2Cl_2 , 85% H_3PO_4) of resonances (singlets) in the $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of clusters **2** and **3** (assignments referring to scheme 1)

	δ_p (chelate)			δ_p (bridge)
	A	B	C	D
$\text{Mo}_2\text{WCuS}_4\text{I}(\text{Et}_2\text{PS}_2)_4$ 3a	126.5	125.2	122.8	84.5
$\text{Mo}_2\text{WS}_4(\text{Et}_2\text{PS}_2)_4$ [5] 2a	125.3	122.4	120.3	83.9
$\text{Mo}_2\text{WCuS}_4\text{I}(\text{Pr}_2\text{PS}_2)_4$ 3b	121.4	120.3	118.1	78.8
$\text{Mo}_2\text{WS}_4(\text{Pr}_2\text{PS}_2)_4$ [5] 2b	119.3	117.4	115.3	78.3
assignment	A	B	C	D

ands R_2PS_2^- while CO is evolved. In the second step the dinuclear compounds **1** [11] are converted into the trinuclear clusters **2** [5] which are subsequently transformed into $[\text{Mo}_2\text{WCuS}_4\text{I}(\text{R}_2\text{PS}_2)_4]$ **3** with CuI. “Tri-metallic” clusters with cubane type cluster cores $\text{M}_2\text{M}'\text{M}''\text{S}_4$ have been hitherto prepared by transmetalation reactions i.e. by partial exchange of M' in $\text{M}_2\text{M}'_2$ with M'' [15,16].

Compounds **3** form diamagnetic red-brown crystals which are soluble in chlorinated hydrocarbons or acetone. They are non-electrolytes in CH_2Br_2 . The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **3** show four singlets of nearly equal intensity three of which are in the range of

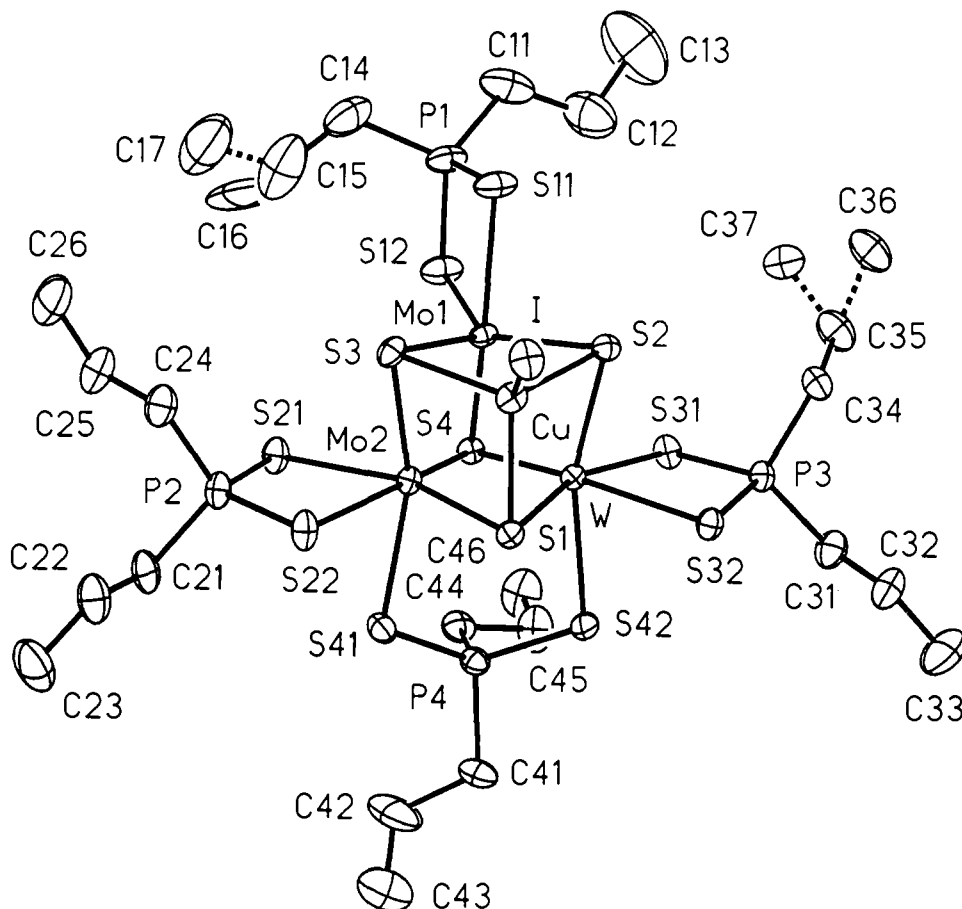


Fig. 1. Molecular structure of **3b** with displacement parameters of 25% probability [12]. For clarity the H atoms have been deleted. A description of the disorder of atoms Mo_2 , W and of terminal C atoms is given in the text.

chelating ligands and one is in the region of a bridging dithiophosphinato group. The corresponding δ_p -values and their assignment with respect to the labels in Scheme 1 for **3** and its precursor clusters **2** are listed in Table 1. There is no indication for the presence of isomeric forms, e.g. bridging of two Mo instead of Mo and W. In this case three additional singlets of relative intensity 2:1:1 should be expected which are, however, not observed as is $^2J(\text{PM})$ -coupling with ^{183}W and ^{95}Mo or ^{97}Mo .

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for **3b** with e.s.d.s in parentheses. U_{eq} is defined by $U_{\text{eq}} = 1/3(U_{11}a^2 + \dots + 2U_{23}b^*c^*bc \cos \alpha)$

	x	y	z	U_{eq}
W	6523(1)	1597(1)	1022(1)	33(1)
I	3041(1)	2144(1)	-713(1)	64(1)
Cu	4529(1)	2114(1)	327(1)	46(1)
Mo(1)	5065(1)	2009(1)	1943(1)	35(1)
Mo(2)	6210(1)	2819(1)	1171(1)	36(1)
S(1)	6187(1)	2290(1)	6(1)	37(1)
S(2)	4797(1)	1235(1)	1062(1)	40(1)
S(3)	4390(1)	2830(1)	1274(1)	46(1)
S(4)	6895(1)	2160(1)	2153(1)	36(1)
S(11)	3205(1)	1748(1)	2223(1)	68(1)
S(12)	5308(1)	2036(1)	3333(1)	61(1)
S(21)	6413(1)	3637(1)	2214(1)	50(1)
S(22)	5831(2)	3786(1)	365(1)	53(1)
S(31)	7241(1)	720(1)	1856(1)	45(1)
S(32)	6673(1)	766(1)	21(1)	44(1)
S(41)	8092(1)	3166(1)	1015(1)	49(1)
S(42)	8460(1)	1668(1)	776(1)	43(1)
P(1)	3729(2)	1914(1)	3329(1)	63(1)
P(2)	5948(1)	4240(1)	1372(1)	49(1)
P(3)	6992(1)	183(1)	911(1)	42(1)
P(4)	9068(1)	2448(1)	1247(1)	44(1)
C(11)	3474(8)	1294(6)	3958(5)	107(4)
C(12)	4008(10)	711(6)	3818(8)	133(5)
C(13)	3707(17)	229(8)	4363(11)	243(10)
C(14)	3151(8)	2572(6)	3686(6)	109(4)
C(15)	3237(26)	3181(13)	3229(17)	194(13)
C(16)	3757(59)	3457(41)	3498(41)	224(49)
C(17)	2836(36)	3719(13)	3394(16)	199(19)
C(21)	6895(6)	4847(3)	1380(4)	65(2)
C(22)	6585(8)	5351(4)	808(5)	87(3)
C(23)	7382(11)	5845(5)	829(7)	127(4)
C(24)	4704(6)	4576(4)	1535(4)	71(2)
C(25)	4713(8)	4896(4)	2300(5)	91(3)
C(26)	3668(9)	5163(5)	2417(8)	132(5)
C(31)	8138(6)	-267(3)	790(4)	64(2)
C(32)	8125(8)	-539(4)	-5(6)	92(3)
C(33)	9153(10)	-898(6)	-62(9)	165(6)
C(34)	5902(5)	-328(3)	989(4)	55(2)
C(35)	5928(7)	-642(4)	1760(5)	80(2)
C(36)	4998(11)	-993(7)	1878(8)	88(6)
C(37)	5188(21)	-379(14)	2205(17)	100(11)
C(41)	10258(5)	2586(4)	809(4)	64(2)
C(42)	10812(9)	3203(6)	1056(9)	143(5)
C(43)	11610(11)	3390(7)	752(10)	173(7)
C(44)	9504(5)	2372(3)	2284(4)	54(2)
C(45)	9989(7)	1753(4)	2515(5)	80(2)
C(46)	10216(8)	1690(4)	3346(5)	92(3)

Table 3

Main bond lengths (pm) and bond angles ($^\circ$) of **3a**. The e.s.d.s are 0.1–0.2 pm and 0.1 $^\circ$, respectively

W–S1	234.5	W–S2	235.5
W–S4	233.6	W–S31	252.9
W–S32	256.0	W–S42	257.0
Mo1–S2	229.7	Mo1–S3	226.9
Mo1–S4	234.7	Mo1–S11	255.1
Mo1–S12	241.5	Mo2–S1	234.8
Mo2–S3	235.6	Mo2–S4	233.8
Mo2–S21	255.7	Mo2–S22	257.0
Mo2–S41	257.2	Cu–S1	229.3
Cu–S2	232.8	Cu–S3	231.3
Cu–I	246.6		
S1–W–S2	99.2	S1–Mo2–S3	99.5
–S4	107.2	–S4	107.1
–S31	163.1	–S21	163.8
–S32	88.3	–S22	87.4
–S42	85.6	–S41	88.1
S2–W–S4	104.4	S3–Mo2–S4	103.5
–S31	89.9	–S21	87.3
–S32	85.8	–S22	85.0
–S42	162.0	–S41	162.0
S4–W–S31	84.0	S4–Mo2–S21	85.3
–S32	159.4	–S22	161.4
–S42	90.6	–S41	89.6
S31–W–S32	78.1	S21–Mo2–S22	78.6
–S42	81.6	–S41	81.5
S32–W–S42	76.9	S22–Mo2–S41	79.1
S2–Mo1–S3	103.4	S1–Cu–S2	101.5
–S4	105.9	–S3	102.4
–S11	84.1	–I	117.8
–S12	133.2	S2–Cu–S3	101.0
S3–Mo1–S4	106.0	–I	118.5
–S11	88.6	S3–Cu–I	113.0
–S12	119.6		
S4–Mo1–S11	159.4		
–S12	80.6		
S11–Mo1–S12	79.6		

3.2. Crystal structure of **3b**

The solution structure postulated for **3** on account of the spectral data corresponds to the crystal structure of **3b** shown in Fig. 1. Atomic coordinates are given in Table 2, selected bond lengths and bond angles are displayed in Table 3.

The cluster contains a cubane like core Mo_2WCuS_4 , the Mo and W atoms being chelated by three bidentate and one bridging dithiophosphinato ligands. The coordination of the Cu atom is completed by the I atom only. The atoms Mo2 and W are disordered with a distribution of $\text{Mo}_x\text{W}_{1-x}$ versus $\text{Mo}_{1-x}\text{W}_x$ ($x = 0.582(2)$). The metal–metal distances can be separated into three short (Mo,W–Mo average 275.7(1)) and three long ones (Mo,W–Cu average 286.6(1) pm). The coordination of the metal atoms is distorted octahedral (W, Mo2) or trigonal bipyramidal (Mo1) by S atoms only and distorted tetrahedral (Cu) by three S and the I atom with deviations from idealized angles of up to 21, 19, 17, and 9 $^\circ$, respectively. Several of the terminal C

atoms show enlarged displacements parameters. However, two groups could be treated with split atom positions only.

4. Conclusion

“Trimetallic” dithiophosphinato clusters with cubane-type Mo_2WCuS_4 cores are readily accessible by systematically completing the “incomplete” framework of suitable precursor clusters via the route shown in Scheme 1. At present we are investigating the extension of this procedure to other metals.

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