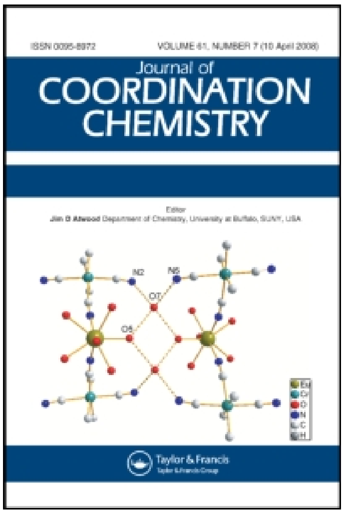

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SYNTHESES AND STRUCTURES OF CLUSTER COMPOUNDS CONTAINING WSe_4Cu_n (n = 3,4) CORES WITH DIALKYLDITHIOCARBAMATE LIGANDS

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SYNTHESES AND STRUCTURES OF CLUSTER COMPOUNDS CONTAINING WSe_4Cu_n ($n = 3, 4$) CORES WITH DIALKYLDITHIOCARBAMATE LIGANDS

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The reactions of $[Et_4N]_2[WSe_4]$ with three equivalents of CuCl in the presence of NaS_2CNR_2 (R = Me, Et) yielded two W–Cu–Se compounds, $[Et_4N]_2[WCu_3Se_4(Et_2NCS_2)_3]$ (**1**) and $[Et_4N]_2[WCu_4Se_4(Me_2NCS_2)_4]$ (**2**). $[Et_4N]_2[MoCu_3Se_4(Et_2NCS_2)_3]$ (**1**) crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 12.976(3)$, $b = 13.336(3)$ and $c = 29.738(6)$ Å, $V = 5153.8(13)$ Å^3, $Z = 4$. Full anisotropic refinement of the structure led to convergence at $R = 0.061$ ($R_w = 0.070$) for 453 variables and 5913 reflections with $F > 4.0\sigma(F)$. The $[WCu_3Se_4(Et_2NCS_2)_3]^{2-}$ anion in **1** comprises three Et_2NCS_2Cu fragments linked by a slightly distorted tetrahedral WSe_4 moiety. Compound **2** crystallizes in the orthorhombic space group *Pbca* with cell constants $a = 14.698(3)$, $b = 18.473(4)$, $c = 37.182(5)$ Å, $V = 10095.6(33)$ Å^3 and $Z = 8$. Anisotropic refinement with 5839 reflections ($F > 6.0\sigma(F)$) and 460 parameters for all non-hydrogen atoms yielded the values $R = 0.061$ and $R_w = 0.073$. The $[WCu_4Se_4(Me_2NCS_2)_4]^{2-}$ anion structure of **2** possesses *pseudo*D_{2d} symmetry for the WSe_4Cu_4 core and a nearly planar WCu_4 array and consists of four Me_2NCS_2Cu fragments coordinated across four edges of the tetrahedral $[WSe_4]^{2-}$ group. IR and electronic spectroscopic data for the two compounds are reported.

Keywords: W–Cu–Se cluster; crystal structure

INTRODUCTION

The chemistry of chalogenometalate anions $[MO_{4-n}E_n]^{2-}$ (M = Mo, W; E = S, Se; $n = 2$–4) and their related compounds have attracted much interest

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owing to their relevance to biological systems, rich structural chemistry and special reactive properties as well as potential applications as nonlinear optical materials.[1-4] Studies on $[MS_4]^{2-}$ (M = Mo, W) synthons have been carried out extensively for more than a decade, whereas work on selenium analogues with $[MSe_4]^{2-}$ (M = Mo, W) synthons began only recently.[5] For instance, Ibers has studied interactions of $[WSe_4]^{2-}$ or $[MoSe_4]^{2-}$ with Cu^+, Ag^+, Au^+, and Ni^{2+} and reported successively a number of coinage-metal/MSe_4^{2-} (M = Mo, W) complexes with linear, cuboidal and planar skeletons.[6]

In previous studies on the reaction of MS_4^{2-} (M = Mo, W), CuX (X = Cl and Br) and/or $R_2NCS_2^-$ ligands, we have isolated a series of heterometallic sulfide complexes, such as $[MCu_3S_4(R_2NCS_2)_3]^{2-}$,[7] $[S_2M_2Cu_4S_6(R_2NCS_2)_3]^{2-}$,[8] $[S_2M_2Cu_5S_6(R_2NCS_2)_3]^{2-}$[9] and $[MCu_{10}S_4X_{12}]^{4-}$.[10] To extend studies on the chemistry of MS_4 and provide information of relevance to selenium-containing enzymes, we reported a series of heterometallic cluster compounds, such as the linear complex $[MoAu_2Se_4(PPh_3)_2]$,[11] planar complexes $[MoSe_4Cu_3(R_2NCS_2)_3]^{2-}$, $[MoSe_4Cu_4(Me_2NCS_2)_4]^{2-}$ and $[MoSe_4Cu_4(Py)_6X_2]$ (X = Cl, Br, and CN),[12] the defect cubane-like complex $[OMoSe_3Cu_3Cl_3(Py)]^{2-}$,[13] cubane-like complexes $[SeMoSe_3M'_3X(PR_3)_3]$ (M′ = Cu, Ag)[14] and $[SeMoSe_3Fe_3(Et_2NCS_2)_6]$,[15] and polynuclear complexes $[MoSe_4Cu_{10}(SPh)_{12}]^{4-}$.[12] In this paper we report the syntheses and characterizations of two planar W–Se–Cu cluster compounds with dialkyldithiocarbamate ligands, $[Et_4N]_2[WCu_3Se_4(Et_2NCS_2)_3]$ (**1**) and $(Et_4N)_2[WCu_4S_4(S_2CNMe_2)_4]$ (**2**).

EXPERIMENTAL

All syntheses and manipulations were performed under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were purified by conventional methods and degassed prior to use. All elemental analyses were carried out by the Elemental Analysis Laboratory in this Institute. $[Et_4N]_2[WSe_4]$ was prepared according to a literature method.[16]

Preparations of the Compounds

$[Et_4N]_2[WCu_3Se_4(Et_2NCS_2)_3]$ (1)

A mixture of $[Et_4N]_2[WSe_4]$ (0.31 g, 0.4 mmol), CuCl (0.12 g, 1.2 mmol) and Et_2dtcNa (0.22 g, 0.96 mmol) in 10 cm^3 of DMF was stirred for 24 h at 60°C to give a deep-red solution. After cooling to room temperature, the mixture was filtered, 5 cm^3 of THF was added to the filtrate and the filtrate was put in an icebox. After several days, 0.17 g, (31.1%) of dark-red blocky crystals of **1** suitable for X-ray crystallographic analysis were collected and washed with MeOH and Et_2O. *Anal.* Calcd. for $C_{31}H_{70}N_5WCu_3Se_4S_6$(%): C, 25.51; H, 4.83; N, 4.80; S, 17.57; Cu, 13.06. Found: C, 26.59; H, 5.00; N, 4.72; S, 18.29; Cu, 14.12.

$[Et_4N]_2[WCu_4Se_4(Me_2NCS_2)_4]$ (2)

To a mixture of CuCl (0.3 g, 3 mmol), $[Et_4N]_2[WSe_4]$ (0.76 g, 1 mmol) and Me_2dtcNa (0.40 g, 2.8 mmol) was added 10 cm^3 of DMF and 0.5 cm^3 of H_2O. After stirring for 24 h at 60°C, the deep-red solution thus formed was cooled to room temperature and filtered; to the filtrate was added 5 cm^3 of Et_2O and it was placed in a refrigerator. After several days, 0.33 g (30.1%) of dark-red blocky crystals of **2** suitable for X-ray crystallographic analysis were collected and washed with MeOH and Et_2O. *Anal.* Calcd. for $C_{28}H_{64}N_6MoCu_4Se_4S_8$(%): C, 22.49; H, 4.31; N, 5.62; S, 17.15; Cu, 17,00. Found: C, 23.41; H, 4.29; N, 5.90; S, 17.94; Cu, 18.20.

Physical Measurements

Infrared spectra were recorded on an Magna-750 spectrophotometer with the use of pressed KBr pellets. Electronic absorption spectra were obtained in DMF solution on a Shimazu UV-3000 spectrophotometer.

Crystallographic Studies

Single crystals for **1** and **2** were carefully chosen, coated with epoxy resin and mounted on glass fibres. Cell dimension measurements and data collection were performed on a Siemens Smart CCD diffractometer with graphite-monochromatized MoK_α radiation at 23 ± 1°C. Intensity data for all crystals were obtained in the range $3.5 < 2\theta < 50°$ by using an ω scan technique. Data reduction was performed on a silicon graphics computer station with Smart CCD software. Crystallographic data are listed in Table I.

For the structural analyses, all calculations were performed on a Legend/586 computer with the SHELXL-PC program.[17a] The structures were refined through the use of the SHELXL-93 program.[17b] The positions of the tungsten, selenium and copper atoms were determined by direct methods, and successive difference electron density maps located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride

TABLE I Crystallographic data for $[Et_4N]_2[WCu_3Se_4(Et_2NCS_2)_3]$ (**1**) and $[Et_4N]_2[WCu_4Se_4(Me_2NCS_2)_4]$ (**2**)

	1	**2**
Formula	$C_{31}H_{70}Cu_3N_5S_6Se_4W$	$C_{28}H_{64}Cu_4N_6S_8Se_4W$
fw	1395.6	1495.2
Space group	$P2_12_12_1$	*Pbca*
a, Å	12.976(3)	14.968(3)
b, Å	13.336(3)	18.473(4)
c, Å	29.738(6)	37.182(8)
V, Å	5153.8(13)	10095.6(33)
Z, $Å^3$	4	8
ρ_{calcd}, $g\,cm^{-3}$	1.80	1.93
μ, mm^{-1}	6.54	7.083
T, K	296	296
λ, Å	0.71073	0.71073
R	0.061	0.061
R_w	0.070	0.073

on their respective parent C atoms before the final cycle of least-squares refinement. For **1**, the final refinement based on F_o for 5913 observations ($F > 4.0\sigma(F)$) and 451 variables led to convergence. For **2**, the final anisotropic refinement of all non-hydrogen atoms on F_o for 5893 observations ($F > 6.0\sigma(F)$) and 460 variables led to convergence. Final positional parameters for **1** and **2** are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Syntheses

The reaction of $(Et_4N)_2WSe_4$, CuCl and Et_2NCS_2Na with a mol ratio of 1 : 3 : 3 in DMF at 60°C gave the tetranuclear compound **1**. If the reaction was carried out at room temperature, similar to the synthesis of $(Et_4N)_2[MoSe_4(CuEt_2NCS_2)_3]$,[12] no reaction was observed; this indicates that the chemistry of WSe_4^{2-} is not parallel to that of $MoSe_4^{2-}$ and WSe_4^{2-} is rather inert as compared to $MoSe_4^{2-}$. Similar to the preparation of Mo(W)–Cu–S and Mo–Cu–Se cluster compounds,[7,12] the synthetic reaction of **1** is a self-assembly reaction, in which the $[WSe_4(CuCl)_3]^{2-}$ species was formed first and Cl^- was replaced by $R_2NCS_2^-$ *via* a simple ligand substitution reaction to yield the final product **1**.

$$[WSe_4]^{2-} + 3CuCl \longrightarrow [WSe_4(CuCl)_3]^{2-}$$

$$[WSe_4(CuCl)_3]^{2-} + 3Et_2NCS_2Na \longrightarrow [WSe_4(CuEt_2NCS_2)_3]^{2-}\ (\mathbf{1}) + 3NaCl$$

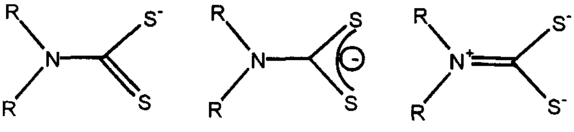
TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 1

	x/a	*y/b*	*z/c*	*U(eq)*
W	711(1)	157(1)	1309(1)	43(1)
Cu(1)	5650(2)	−621(2)	745(1)	65(1)
Cu(2)	8408(2)	1075(2)	1903(1)	67(1)
Cu(3)	5969(2)	1887(2)	1277(1)	71(1)
Se(1)	6506(2)	937(2)	642(1)	58(1)
Se(2)	6467(2)	−1461(2)	1358(1)	68(1)
Se(3)	6587(2)	1100(2)	1944(1)	63(1)
Se(4)	8895(1)	84(1)	1274(1)	58(1)
S(2)	3755(4)	−643(7)	834(2)	123(3)
S(1)	5001(4)	−1468(5)	119(2)	76(2)
S(4)	9427(4)	2522(4)	2033(2)	70(2)
S(3)	9237(5)	781(4)	2628(2)	81(2)
S(6)	6193(4)	3684(4)	1207(2)	91(3)
S(5)	4261(4)	2570(4)	1281(3)	93(3)
N(1)	3007(17)	−1788(16)	200(6)	97(8)
N(2)	10437(14)	2341(12)	2803(6)	75(7)
N(3)	4363(19)	4579(16)	1268(11)	146(14)
N(4)	6792(13)	4543(15)	2755(5)	81(8)
N(5)	9491(14)	3003(17)	473(6)	83(8)
C(1)	3826(15)	−1388(18)	363(7)	75(9)
C(2)	9753(16)	1920(15)	2518(6)	62(7)
C(3)	4887(17)	3695(17)	1248(9)	90(10)
C(11)	2984(27)	−2286(24)	−240(10)	124(14)
C(12)	3223(29)	−3368(32)	−157(12)	215(28)
C(13)	2031(25)	−1860(32)	435(14)	202(27)
C(14)	1376(27)	−1025(32)	358(16)	219(32)
C(21)	10738(22)	1880(21)	3228(8)	111(13)
C(22)	10046(27)	2160(25)	3610(9)	160(18)
C(23)	10871(17)	3331(18)	2730(8)	86(10)
C(24)	11890(20)	3309(16)	2475(9)	102(11)
C(31)	4915(30)	5575(27)	1248(18)	216(31)
C(32)	4871(48)	6030(39)	896(16)	453(68)
C(33)	3276(24)	4737(37)	1353(23)	364(53)
C(34)	2669(30)	4872(51)	1200(21)	601(99)
C(41)	5728(22)	4334(24)	2867(10)	132(15)
C(42)	5085(20)	3817(20)	2480(9)	113(12)
C(43)	6885(26)	5200(34)	2315(10)	202(24)
C(44)	6172(28)	6202(26)	2394(12)	179(22)
C(45)	7249(32)	3713(30)	2597(10)	197(23)
C(46)	7337(28)	2921(24)	3011(11)	183(21)
C(47)	7253(23)	5124(21)	3133(9)	131(14)
C(48)	8362(20)	5354(30)	3102(10)	176(20)
C(51)	8857(25)	3283(31)	882(9)	156(20)
C(52)	9015(36)	4316(37)	1002(14)	273(37)
C(53)	9220(25)	1997(30)	384(13)	165(21)
C(54)	9737(31)	1482(29)	−6(12)	187(24)
C(55)	9111(24)	3638(25)	102(10)	143(16)
C(56)	7952(24)	3594(30)	−12(12)	206(24)
C(57)	10546(22)	3219(30)	530(9)	168(20)
C(58)	11081(23)	2477(28)	899(10)	166(19)

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for **2**

	x/*a*	*y*/*b*	*z*/*c*	*U*(*eq*)
W	5098(1)	2046(1)	6218(1)	35(1)
Cu(1)	5235(1)	1749(1)	6917(1)	55(1)
Cu(2)	5241(1)	2544(1)	5539(1)	56(1)
Cu(3)	4342(1)	758(1)	6060(1)	54(1)
Cu(4)	5741(1)	3334(1)	6437(1)	56(1)
Se(1)	4451(1)	2737(1)	6674(1)	61(1)
Se(2)	6394(1)	2609(1)	5985(1)	69(1)
Se(3)	3982(1)	1877(1)	5775(1)	58(1)
Se(4)	5589(1)	943(1)	6443(1)	68(1)
S(11)	5032(3)	1277(2)	7479(1)	60(1)
S(12)	6678(3)	2089(2)	7259(1)	53(1)
S(21)	5695(3)	2417(2)	4949((1)	56(1)
S(22)	4688(3)	3661(2)	5225(1)	56(1)
S(31)	2864(3)	288(2)	6264(1)	60(1)
S(32)	4207(2)	−367(2)	5781(1)	48(1)
S(41)	6787(3)	3855(2)	6851(1)	54(1)
S(42)	5647(3)	4606(2)	6321(1)	59(1)
N(1)	6557(9)	1365(7)	7862(3)	63(5)
N(2)	5161(9)	3516(8)	4549(4)	71(5)
N(3)	2540(7)	−909(6)	5904(3)	49(4)
N(4)	6846(8)	5278(6)	6744(3)	55(5)
N(5)	7964(7)	612(6)	332(3)	49(4)
N(6)	145(9)	1337(7)	2036(3)	64(5)
C(1)	6167(9)	1568(7)	7563(4)	47(5)
C(2)	5174(9)	3210(9)	4872(4)	54(5)
C(3)	3122(8)	−392(7)	5975(3)	38(4)
C(4)	6476(9)	4646(8)	6657(3)	50(5)
C(11)	6113(12)	949(10)	8129(4)	91(8)
C(12)	7464(11)	1567(10)	7952(4)	81(7)
C(21)	5534(14)	3159(12)	4243(5)	117(11)
C(22)	4736(12)	4200(11)	4460(6)	107(10)
C(31)	1603(9)	−922(9)	6051(4)	69(6)
C(32)	2734(10)	−1485(8)	5663(4)	68(6)
C(41)	6626(12)	5939(9)	6577(5)	87(8)
C(42)	7528(11)	5290(9)	7033(5)	85(8)
C(51)	8519(11)	−81(10)	287(4)	78(7)
C(52)	8084(13)	−753(10)	383(6)	103(9)
C(53)	7091(10)	580(9)	112(4)	67(7)
C(54)	7210(12)	485(12)	−258(5)	122(12)
C(55)	8561(9)	1213(9)	209(4)	61(6)
C(56)	8183(11)	1972(10)	236(5)	90(8)
C(57)	7620(10)	723(9)	699(4)	62(6)
C(58)	8339(13)	798(12)	973(4)	105(9)
C(61)	−616(13)	1452(10)	1781(5)	87(8)
C(62)	−1064(14)	2224(10)	1791(6)	126(12)
C(63)	910(13)	1875(9)	1958(5)	91(8)
C(64)	1340(16)	1769(11)	1585(5)	134(12)
C(65)	455(14)	559(9)	1983(5)	89(8)
C(66)	1276(13)	353(12)	2183(5)	111(10)
C(67)	−145(14)	1501(12)	2410(5)	100(9)
C(68)	−929(16)	1036(12)	2536(5)	131(12)

When similar methods were applied to the reaction of $[Et_4N]_2[WSe_4]$, CuCl and Me_2NCS_2Na in DMF, a pentanuclear cluster compound **2** was isolated, and the mol ratio $WSe_4^{2-}/CuCl$ slightly influences the product. As we know, the chemical properties of dithiocarbamate complexes are susceptible to the nature of subtituents on the ligands because of the existence of resonance forms[18] as follows.



I II III

Increase in the electron-donating ability of R groups favours resonance form III and induces an increase in electron density on the sulfur atoms bound to the copper atom. When the substituent is a methyl group, the strong electron-donating ability, the small size of methyl group, together with the super-conjugation effect from the methyl H atoms to N=C double bond[19] may result in the formation of cluster compounds with different structures. Therefore, the structures obtained are dominated by the special characters of the Me_2dtc ligand.

Similar to the reaction of $MoSe_4^{2-}$, for the formation of **1** and **2** the use of relatively less R_2NCS_2Na is necessary. Otherwise excess $R_2NCS_2^-$ ligands result in the formation of by-products such as $Cu(R_2NCS_2)_2$ and $Cu_3(R_2NCS_2)_3$.[20]

Structures

The crystal structures of both **1** and **2** consist of discrete $[Et_4N]^+$ cations and W–Cu–Se cluster anions; the $[Et_4N]^+$ cation has its expected structure as well as normal distances and angles and will not be discussed further. Selected bond distances and angles for **1** and **2** are given in Tables IV and V respectively.

The structure of the anion $[WCu_3Se_4(Et_2NCS_2)_3]^{2-}$ in **1**, as shown in Figure 1, is the isomorph of the molybdenum–sulfur(selenium) and tungsten–sulfur analogues[7,12] and possesses a two-fold axis through W and Cu(3) atoms. The $[WSe_4]^{2-}$ tetrahedral unit chelates to three Et_2NCS_2Cu species from three of the six tetrahedral Se–Se edges. $[WSe_4]^{2-}$ retains tetrahedral geometry and only slight distortion is observed. The four metal atoms W, Cu(1), Cu(2) and Cu(3) are nearly coplanar with a largest deviation of 0.043 Å from the ideal WCu_3 plane. There are two types of Se

TABLE IV Selected bond lengths (Å) and angles (°) for **1**

W-Se(1)	2.372(2)	Cu(2)-Se(4)	2.376(3)
W-Se(2)	2.322(2)	Cu(3)-Se(1)	2.379(3)
W-Se(3)	2.370(2)	Cu(3)-Se(3)	2.384(3)
W-Se(4)	2.319(2)	Cu(1)-S(1)	2.336(6)
W-Cu(1)	2.735(2)	Cu(1)-S(2)	2.437(6)
W-Cu(2)	2.731(3)	Cu(2)-S(3)	2.442(6)
W-Cu(3)	2.746(2)	Cu(2)-S(4)	2.373(6)
Cu(1)-Se(1)	2.378(3)	Cu(3)-S(5)	2.398(6)
Cu(1)-Se(2)	2.387(3)	Cu(3)-S(6)	2.427(6)
Cu(2)-Se(3)	2.366(3)		
Se(1)-W-Se(2)	110.0(1)	Se(2)-Cu(1)-S(2)	110.8(2)
Se(1)-W-Se(3)	109.7(1)	Se(1)-Cu(1)-S(1)	119.3(2)
Se(1)-W-Se(4)	108.2(1)	Se(2)-Cu(1)-S(1)	122.7(2)
Se(2)-W-Se(3)	109.9(1)	S(2)-Cu(1)-S(1)	73.8(2)
Se(2)-W-Se(4)	108.8(1)	Se(3)-Cu(2)-Se(4)	108.3(1)
Se(3)-W-Se(4)	110.1(1)	Se(3)-Cu(2)-S(4)	122.4(2)
Cu(1)-W-Cu(2)	173.7(1)	Se(4)-Cu(2)-S(4)	115.7(2)
Cu(1)-W-Cu(3)	85.7(1)	Se(3)-Cu(2)-S(3)	113.3(2)
Cu(2)-W-Cu(3)	88.7(1)	Se(4)-Cu(2)-S(3)	119.2(2)
W-Se(1)-Cu(1)	70.3(1)	S(4)-Cu(2)-S(3)	75.0(2)
W-Se(1)-Cu(3)	70.6(1)	Se(1)-Cu(3)-Se(3)	109.1(1)
W-Se(2)-Cu(1)	71.0(1)	Se(1)-Cu(3)-S(6)	115.1(2)
W-Se(3)-Cu(2)	70.4(1)	Se(3)-Cu(3)-S(6)	117.9(2)
W-Se(3)-Cu(3)	70.6(1)	Se(1)-Cu(3)-S(5)	118.5(2)
W-Se(4)-Cu(2)	71.1(1)	Se(3)-Cu(3)-S(5)	118.4(2)
Se(1)-Cu(1)-Se(2)	107.6(1)	S(6)-Cu(3)-S(5)	74.6(2)
Se(1)-Cu(1)-S(2)	119.3(3)		

atoms, μ_2-Se and μ_3-Se, in the complex. The W–μ_3-Se bonds (average 2.371(2) Å) are longer than W–μ_2-Se (average 2.326(2) Å), almost the same as those observed in [$MoSe_4Cu_3(Et_2NCS_2)_3$] (2.373 and 2.318 Å, respectively).[12] Each Cu atom adopts highly disorted tetrahedral geometry consisting of two Se atoms from $[WSe_4]^{2-}$ and two S atoms from one $Et_2NCS_2^-$ ligand with average bite angle of 74.5° in the four-membered chelate ring. The coordination modes of Se atoms slightly influences the Cu–Se distances (2.366–2.387 Å), which are comparable with those found in [$MoSe_4Cu_3(Et_2NCS_2)_3$] (2.365–2.470 Å).[12]

The structure of $[WCu_4Se_4(Me_2NCS_2)_4]^{2-}$ in **2** is depicted in Figure 2 and is the isomorph of the molybdenum–sulfur(selenium) analogues.[12] The structure comprises four Me_2NCS_2Cu fragments ligating through four of the six edges of the tetrahedral $[WSe_4]^{2-}$ group with Se–W–Se angles ranging from 106.4(1)° to 110.9(1)°. In the WCu_4 core, both Mo and Cu atoms are tetrahedrally coordinated, and the five metal atoms are nearly coplanar with deviations of not more than 0.11 Å from the least-squares plane. An interesting feature of **2** is its W–Se and W–Cu distances. Distances from W to the four Se atoms range from 2.335(2) to 2.349(2) Å

TABLE V Selected bond lengths (Å) and angles (°) for **2**

W-Se(1)	2.341(2)	Cu(3)-Se(3)	2.403(2)
W-Se(2)	2.334(2)	Cu(3)-Se(4)	2.346(3)
W-Se(3)	2.349(2)	Cu(4)-Se(1)	2.361(2)
W-Se(4)	2.336(2)	Cu(4)-Se(2)	2.372(3)
W-Cu(1)	2.691(2)	Cu(1)-S(11)	2.303(4)
W-Cu(2)	2.722(2)	Cu(1)-S(12)	2.546(4)
W-Cu(3)	2.710(2)	Cu(2)-S(21)	2.328(4)
W-Cu(4)	2.706(2)	Cu(2)-S(22)	2.526(4)
Cu(1)-Se(1)	2.352(3)	Cu(3)-S(31)	2.452(4)
Cu(1)-Se(4)	2.386(3)	Cu(3)-S(32)	2.353(4)
Cu(2)-Se(2)	2.378(3)	Cu(4)-S(41)	2.385(4)
Cu(2)-Se(3)	2.389(2)	Cu(4)-S(42)	2.415(4)
Se(1)-W-Se(2)	110.8(1)	Se(3)-Cu(2)-S(21)	121.3(1)
Se(1)-W-Se(3)	108.2(1)	Se(2)-Cu(2)-S(22)	120.9(1)
Se(2)-W-Se(3)	110.9(1)	Se(3)-Cu(2)-S(22)	110.9(1)
Se(1)-W-Se(4)	110.1(1)	S(21)-Cu(2)-S(22)	74.3(1)
Se(2)-W-Se(4)	106.4(1)	Se(3)-Cu(3)-Se(4)	108.3(1)
Se(3)-W-Se(4)	110.5(1)	Se(3)-Cu(3)-S(31)	104.9(1)
Cu(1)-W-Cu(2)	168.2(1)	Se(4)-Cu(3)-S(31)	122.9(1)
Cu(1)-W-Cu(3)	93.5(1)	Se(3)-Cu(3)-S(32)	123.9(1)
Cu(2)-W-Cu(3)	97.3(1)	Se(4)-Cu(3)-S(32)	118.0(1)
Cu(1)-W-Cu(4)	82.0(1)	S(31)-Cu(3)-S(32)	75.4(1)
Cu(2)-W-Cu(4)	87.5(1)	Se(1)-Cu(4)-Se(2)	108.8(1)
Cu(3)-W-Cu(4)	174.1(1)	Se(1)-Cu(4)-S(41)	117.2(1)
Se(1)-Cu(1)-Se(4)	108.0(1)	Se(2)-Cu(4)-S(41)	116.2(1)
Se(1)-Cu(1)-S(11)	126.3(1)	Se(1)-Cu(4)-S(42)	119.1(1)
Se(4)-Cu(1)-S(11)	118.1(1)	Se(2)-Cu(4)-S(42)	117.0(1)
Se(1)-Cu(1)-S(12)	113.7(1)	S(41)-Cu(4)-S(42)	75.8(1)
Se(4)-Cu(1)-S(12)	110.7(1)	Cu(2)-Se(2)-Cu(4)	104.4(1)
S(11)-Cu(1)-S(12)	75.0(1)	Cu(2)-Se(3)-Cu(3)	116.7(1)
Se(2)-Cu(2)-Se(3)	108.0(1)	Cu(1)-Se(4)-Cu(3)	112.5(1)
Se(2)-Cu(2)-S(21)	118.3(1)		

with an average value of 2.340 Å and are significantly shorter than in $[MoCu_4Se_4(Me_2NCS_2)_4]^{2-}$ (av. 2.365 Å).[12] The W–Cu distances with an average value of 2.707(2) Å is also significantly shorter than in **1** (av. 2.737(2) Å) and in $[MoCu_4Se_4(Me_2NCS_2)_4]^{2-}$ (av. 2.724 Å),[12] indicating that there are possible W–Cu bonding interactions in **2**. The Cu–Se bond lengths (2.348(3)–2.403(3) Å) in **2** agree well with those in **1** (2.366(2)–2.387(2) Å), which suggests that Cu–Se distances are not affected by the coordination geometries of the Cu atoms and dialkyldithiocarbamate ligands. Cu(1)–W–Cu(2) and Cu(3)–W–Cu(4) angles are 168.2(1)° and 174.(1)°, respectively, and thus the anion structure has $pseudoD_{2d}$ symmetry.

Electronic and IR Spectra

Electronic absorption spectra for both **1** and **2** show one high energy absorption at about 270 nm with a shoulder at about 283 nm, and one

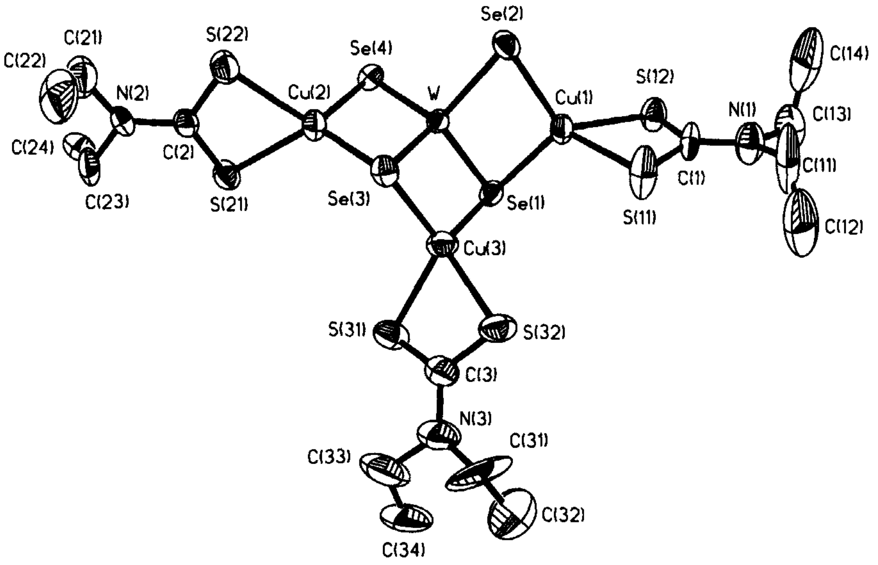


FIGURE 1 Ortep plot of the $[WCu_3Se_4(Et_2NCS_2)_3]^{2-}$ anion in **1** with ellipsoids drawn at the 30% probability level.

strong broad peak at about 430 nm. The first absorption may be attributed to an intraligand transition and the shoulder is from charge-transfer [LMCT $(S \rightarrow Cu)$] in accordance with a similar assignment in $[MoSe_4Cu_n(R_2NCS_2)_n]^{2-}$ ($n = 3, R_2 = Et_2$, C_4H_8; $n = 4, R_2 = Me_2$).[12] The strong broad peak at 430 nm may be assigned to a charge-transfer band of the type $(\pi)Se \rightarrow (d)W$ arising from the WSe_4 moiety,[6a] red-shifted compared to the free $[WSe_4]^{2-}$ anion (470 nm).[20,21]

In IR spectra, ligands R_2dtc give $\nu(C-N)$ absorptions at 1481 and 1484 cm^{-1} for **1** and **2**, respectively, which are blue-shifted compared to those for free R_2dtc ligands ($< 1400\,cm^{-1}$), indicating that the C–N bonds in the two compounds show some C–N double bond character ($> 1500\,cm^{-1}$). $Cu-S_{dtc}$ vibrations show typical absorptions at 351 and 362 cm^{-1} for **1** and **2**, respectively. The $\nu(W-Se)$ frequencies for the two compounds in the 293–306 cm^{-1} region are red-shifted compared to $[WSe_4]^{2-}$ ($341\,cm^{-1}$)[20] owing to the coordination of Cu atoms. For **1**, two W–Se absorptions are observed, one at 306 cm^{-1} assigned to $W-\mu_2$-Se bond vibrations and the other at 293 cm^{-1} to $W-\mu_3$-Se bond vibrations. For **2**, only $W-\mu_3$-Se vibrations 306 cm^{-1} are observed.

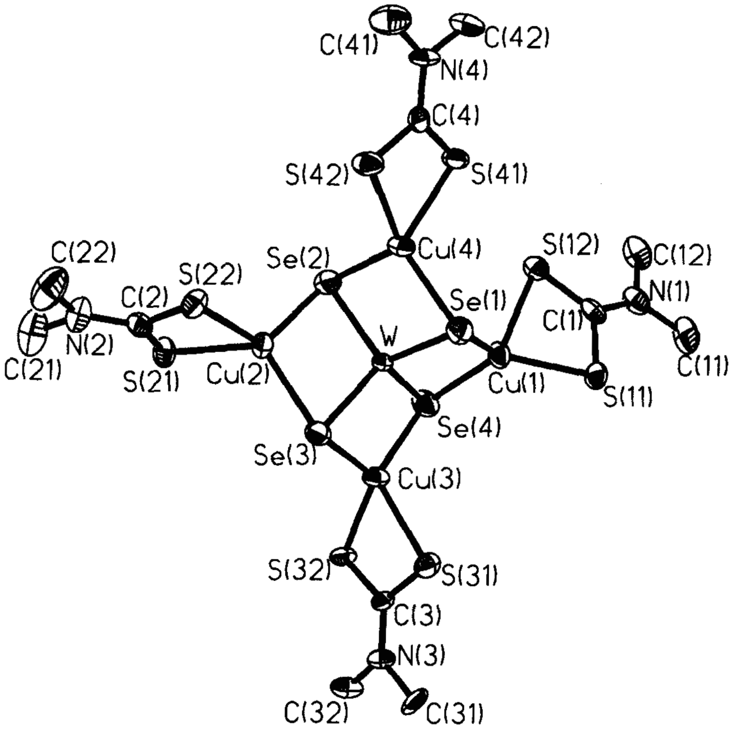


FIGURE 2 Ortep plot of the $[WCu_4Se_4(Me_2NCS_2)_4]^{2-}$ anion in **2** with ellipsoids drawn at the 30% probability level.

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