Kyra Brakefield, Justin Barnes and James P. Donahue*

Crystal structure of $[[\text{Mo}_3\text{Se}_7(\text{S}_2\text{CNEt}_2)_3]_2(\mu\text{-Se})] \cdot 2(\text{C}_6\text{H}_4\text{Cl}_2)$, $\text{C}_{42}\text{H}_{68}\text{Cl}_4\text{Mo}_6\text{N}_6\text{S}_{12}\text{Se}_{15}$

<https://doi.org/10.1515/ncrs-2019-0938>

Received December 27, 2019; accepted January 31, 2020; available online March 25, 2020

Abstract

$\text{C}_{42}\text{H}_{68}\text{Cl}_4\text{Mo}_6\text{N}_6\text{S}_{12}\text{Se}_{15}$, triclinic, $P\bar{1}$ (no. 2), $a = 13.0196(19)$ Å, $b = 18.813(3)$ Å, $c = 19.745(3)$ Å, $\alpha = 117.446(2)^\circ$, $\beta = 99.775(2)^\circ$, $\gamma = 98.233(2)^\circ$, $V = 4091.7(10)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0557$, $wR_{\text{ref}}(F^2) = 0.1618$, $T = 150$ K.

CCDC no.: 1981099

*Corresponding author: James P. Donahue, Department of Chemistry, Tulane University, 6400 Freret Street, Stern Hall Room 2015, New Orleans, LA 70118-5698, USA, e-mail: donahue@tulane.edu. <https://orcid.org/0000-0001-9768-4813>

Kyra Brakefield: Department of Chemistry, Millersville University, 40 Dilworth Road, Millersville, PA 17551, USA

Justin Barnes: Department of Chemistry, Tulane University, 6400 Freret Street, New Orleans, LA 70118-5698, USA

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red-orange plate
Size:	0.28 × 0.24 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	8.04 mm ⁻¹
Diffractometer, scan mode:	Bruker Smart APEX, φ and ω
θ_{max} , completeness:	18.8°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18161, 6294, 0.049
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4913
$N(\text{param})_{\text{refined}}$:	706
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The following procedure is a modification of the original synthesis [4]. A mixture of $[\text{Mo}(\text{CO})_6]$ (1.00 g, 3.79 mmol), Se^0 powder (1.20 g, 15.2 mmol), and $\text{Et}_2\text{NC}(\text{S})\text{SSC}(\text{S})\text{NEt}_2$ (1.10 g,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mo1	0.75468(12)	0.67740(10)	0.93010(9)	0.0348(5)
Mo2	0.85658(11)	0.74315(9)	0.85183(9)	0.0297(5)
Mo3	0.90012(12)	0.60346(10)	0.85283(10)	0.0402(5)
Mo4	0.33842(11)	0.31420(9)	0.52657(8)	0.0277(4)
Mo5	0.50872(12)	0.26400(9)	0.58065(8)	0.0296(5)
Mo6	0.51298(12)	0.30370(9)	0.46201(8)	0.0295(5)
Se1	0.65263(13)	0.69400(11)	0.81834(10)	0.0312(5)
Se2	0.73356(14)	0.81721(11)	0.93864(11)	0.0405(6)
Se3	0.82727(13)	0.60523(11)	0.72588(10)	0.0356(5)
Se4	1.00926(14)	0.68011(12)	0.79561(12)	0.0488(6)
Se5	0.70427(13)	0.52705(11)	0.81958(10)	0.0353(5)
Se6	0.82136(16)	0.55888(13)	0.94287(12)	0.0570(7)
Se7	0.95162(16)	0.74387(13)	0.97361(12)	0.0572(7)
Se8	0.44931(12)	0.39015(10)	0.67093(9)	0.0268(5)
Se9	0.33157(14)	0.25924(11)	0.62518(10)	0.0365(5)
Se10	0.65726(13)	0.37801(11)	0.59444(10)	0.0309(5)
Se11	0.65657(16)	0.23851(12)	0.50478(11)	0.0480(6)
Se12	0.45250(12)	0.43587(10)	0.52790(10)	0.0273(5)
Se13	0.33920(14)	0.33450(11)	0.40444(10)	0.0378(5)
Se14	0.38240(17)	0.18137(12)	0.44416(11)	0.0512(6)
Se15	0.60087(13)	0.52841(10)	0.68409(10)	0.0316(5)
S1	0.5738(4)	0.6426(3)	0.9541(3)	0.0421(13)
S2	0.7718(4)	0.7459(3)	1.0766(3)	0.0505(15)
S3	0.8278(3)	0.8077(3)	0.7638(2)	0.0277(11)
S4	0.9862(3)	0.8822(3)	0.9146(2)	0.0279(11)
S5	0.9205(4)	0.4603(3)	0.7643(4)	0.0697(19)
S6	1.0773(4)	0.5864(4)	0.9117(4)	0.0698(19)
S7	0.2101(3)	0.4063(3)	0.5696(3)	0.0463(14)
S8	0.1471(3)	0.2311(3)	0.4566(3)	0.0425(14)
S9	0.6271(3)	0.2803(3)	0.7070(2)	0.0287(12)
S10	0.5031(4)	0.1245(3)	0.5689(2)	0.0439(14)
S11	0.6407(3)	0.3782(3)	0.4175(2)	0.0284(11)
S12	0.5076(4)	0.2095(3)	0.3191(2)	0.0375(13)
N1	0.591(2)	0.7058(14)	1.1089(13)	0.084(7)
N2	0.9779(11)	0.9486(9)	0.8193(8)	0.038(4)
N4	0.0037(3)	0.32781(16)	0.4862(3)	0.113(9)
N5	0.6269(11)	0.1305(11)	0.6932(9)	0.052(5)
N6	0.6295(12)	0.2858(10)	0.2633(9)	0.045(4)
C1	0.6368(19)	0.6969(14)	1.0526(12)	0.067(7)
C2	0.482(3)	0.6707(18)	1.0918(14)	0.095(9)
H2A	0.445965	0.665123	1.040683	0.115*
H2B	0.453243	0.709991	1.132919	0.115*
C3	0.4526(19)	0.5917(14)	1.0867(15)	0.101(9)
H3A	0.510484	0.563645	1.075404	0.152*
H3B	0.386242	0.558010	1.044079	0.152*
H3C	0.440597	0.599542	1.137079	0.152*
C4	0.646(2)	0.7515(16)	1.1970(12)	0.089(8)
H4A	0.615563	0.720291	1.220940	0.107*
H4B	0.723690	0.752430	1.204240	0.107*
C5	0.636(2)	0.8355(16)	1.2389(15)	0.110(10)
H5A	0.679726	0.869884	1.223608	0.165*
H5B	0.662226	0.857417	1.296107	0.165*
H5C	0.560754	0.836242	1.225462	0.165*
C6	0.9382(12)	0.8899(10)	0.8302(9)	0.022(4)*
C7	0.9421(16)	0.9478(13)	0.7461(11)	0.058(6)

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H7A	0.909788	0.890058	0.702707	0.069*
H7B	1.004353	0.971269	0.733550	0.069*
C8	0.859(2)	0.9984(16)	0.7521(14)	0.112(10)
H8A	0.795222	0.972628	0.760586	0.168*
H8B	0.838636	1.000170	0.702952	0.168*
H8C	0.890079	1.054796	0.796732	0.168*
C9	1.0757(14)	1.0175(11)	0.8813(11)	0.053(6)
H9A	1.071314	1.070418	0.883123	0.063*
H9B	1.076652	1.024375	0.934260	0.063*
C10	1.1760(14)	0.9958(13)	0.8604(12)	0.080(8)
H10A	1.186104	0.948675	0.867324	0.120*
H10B	1.237834	1.043415	0.895076	0.120*
H10C	1.169970	0.981034	0.805128	0.120*
C11A ^a	1.046(3)	0.501(2)	0.848(2)	0.048(8)*
N3A ^a	1.1057(4)	0.4395(3)	0.8406(3)	0.071(7)*
C12A ^a	1.0719(15)	0.3548(2)	0.77169(17)	0.124(14)*
H12A ^a	1.120570	0.324119	0.784339	0.149*
H12B ^a	0.999505	0.330277	0.771979	0.149*
C13A ^a	1.0647(15)	0.3320(8)	0.68986(19)	0.151(17)*
H13A ^a	1.040119	0.271702	0.656411	0.226*
H13B ^a	1.013293	0.357659	0.672683	0.226*
H13C ^a	1.135701	0.351432	0.685180	0.226*
C14A ^a	1.2099(4)	0.4708(14)	0.9008(4)	0.063(8)*
H14A ^a	1.217657	0.435448	0.925211	0.076*
H14B ^a	1.219879	0.528616	0.942833	0.076*
C15A ^a	1.286(3)	0.465(2)	0.850(2)	0.063(9)*
H15A ^a	1.254814	0.415720	0.797682	0.095*
H15B ^a	1.354689	0.459627	0.875037	0.095*
H15C ^a	1.298730	0.514388	0.845385	0.095*
C11B ^b	1.038(4)	0.475(3)	0.808(3)	0.048(8)*
N3B ^b	1.0932(4)	0.4088(2)	0.7987(2)	0.071(7)*
C12B ^b	1.0508(7)	0.3386(2)	0.80933(19)	0.124(14)*
H12C ^b	1.109204	0.319312	0.829564	0.149*
H12D ^b	1.002411	0.352133	0.844696	0.149*
C13B ^b	0.9925(12)	0.2793(10)	0.7277(3)	0.151(17)*
H13D ^b	0.958228	0.227306	0.724073	0.226*
H13E ^b	0.937127	0.301492	0.709446	0.226*
H13F ^b	1.042700	0.269046	0.694487	0.226*
C14B ^b	1.1927(4)	0.4315(8)	0.8606(3)	0.063(8)*
H14C ^b	1.216691	0.380226	0.847917	0.076*
H14D ^b	1.172807	0.449124	0.911116	0.076*
C15B ^b	1.303(4)	0.506(3)	0.878(3)	0.063(9)*
H15D ^b	1.328422	0.489181	0.830431	0.095*
H15E ^b	1.360854	0.513888	0.921797	0.095*
H15F ^b	1.283056	0.558772	0.892780	0.095*
C16	0.1049(15)	0.3189(14)	0.4999(11)	0.061(7)
C17A ^c	−0.0197(4)	0.40794(17)	0.5029(2)	0.106(13)*
H17A ^c	0.045683	0.443157	0.504196	0.127*
H17B ^c	−0.076940	0.397033	0.456796	0.127*
C18A ^c	−0.0525(5)	0.4574(7)	0.5733(2)	0.142(16)*
H18A ^c	−0.064363	0.508013	0.574125	0.212*
H18B ^c	−0.119458	0.425510	0.572786	0.212*
H18C ^c	0.004039	0.471963	0.620524	0.212*
C17B ^d	−0.0442(4)	0.3900(2)	0.54019(16)	0.106(13)*
H17C ^d	−0.000263	0.446198	0.558349	0.127*
H17D ^d	−0.117549	0.384277	0.511135	0.127*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C18B ^d	−0.0501(14)	0.3807(3)	0.60845(18)	0.142(16)*
H18D ^d	−0.082220	0.422888	0.642858	0.212*
H18E ^d	−0.094683	0.325525	0.590711	0.212*
H18F ^d	0.022537	0.387411	0.637898	0.212*
C19	−0.0810(17)	0.2524(19)	0.4294(14)	0.134(13)
H19A	−0.149800	0.257597	0.443877	0.161*
H19B	−0.061972	0.204370	0.431771	0.161*
C20	−0.0953(18)	0.2376(16)	0.3437(14)	0.108(10)
H20A	−0.132569	0.276766	0.337459	0.163*
H20B	−0.137882	0.180838	0.305692	0.163*
H20C	−0.024393	0.245721	0.333861	0.163*
C21	0.5900(14)	0.1759(11)	0.6608(10)	0.040(5)
C22	0.7028(3)	0.1724(3)	0.76875(18)	0.123(11)
H22A	0.691082	0.134134	0.789829	0.148*
H22B	0.674257	0.219572	0.800511	0.148*
C23A ^e	0.8185(3)	0.2066(12)	0.796(2)	0.098(12)*
H23A ^e	0.854088	0.163083	0.768633	0.148*
H23B ^e	0.842904	0.228748	0.853043	0.148*
H23C ^e	0.836829	0.251209	0.783775	0.148*
C23B ^f	0.7036(18)	0.1643(3)	0.83838(18)	0.098(12)*
H23D ^f	0.768184	0.202616	0.880878	0.148*
H23E ^f	0.639257	0.177343	0.855883	0.148*
H23F ^f	0.703863	0.107370	0.825445	0.148*
C24	0.5947(17)	0.0389(13)	0.6548(12)	0.058(6)
H24A	0.583906	0.014951	0.597002	0.070*
H24B	0.654004	0.019999	0.674613	0.070*
C25	0.4970(16)	0.0077(12)	0.6691(12)	0.060(6)
H25A	0.509786	0.025324	0.725595	0.090*
H25B	0.476076	−0.052920	0.638001	0.090*
H25C	0.439080	0.029588	0.653513	0.090*
C26	0.5932(15)	0.2885(14)	0.3239(11)	0.059(7)
C27	0.7128(17)	0.3555(14)	0.2700(11)	0.062(6)
H27A	0.758206	0.390092	0.325312	0.074*
H27B	0.760006	0.332588	0.235300	0.074*
C28	0.6570(16)	0.4049(13)	0.2465(12)	0.070(6)
H28A	0.604999	0.368860	0.194628	0.105*
H28B	0.709206	0.445450	0.243207	0.105*
H28C	0.618986	0.433895	0.285710	0.105*
C29	0.5876(12)	0.2120(11)	0.1836(10)	0.040(5)
H29A	0.578359	0.229977	0.143488	0.048*
H29B	0.515883	0.181768	0.179324	0.048*
C30	0.6614(14)	0.1540(12)	0.1656(11)	0.058(6)
H30A	0.732902	0.183854	0.170610	0.086*
H30B	0.631589	0.107233	0.111562	0.086*
H30C	0.667401	0.133377	0.203205	0.086*
Cl1	0.3100(6)	0.7537(4)	0.9664(4)	0.096(2)
Cl2	0.5335(5)	0.8744(4)	1.0793(5)	0.116(3)
C31	0.3219(14)	0.8580(7)	1.0239(8)	0.051(5)
C32	0.4198(10)	0.9110(11)	1.0766(10)	0.059(6)
C33	0.4264(13)	0.9940(10)	1.1266(8)	0.069(7)
H33	0.493342	1.030314	1.162627	0.083*
C34	0.3350(19)	1.0239(8)	1.1240(9)	0.076(7)
H34	0.339519	1.080627	1.158201	0.092*
C35	0.2371(14)	0.9708(14)	1.0713(12)	0.089(9)
H35	0.174651	0.991298	1.069540	0.106*
C36	0.2305(9)	0.8879(12)	1.0213(9)	0.087(9)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H36	0.163601	0.851581	0.985297	0.105*
Cl3A ^g	−0.0715(10)	−0.0187(8)	0.3803(7)	0.082(3)*
Cl4A ^g	−0.0730(10)	−0.1869(8)	0.3825(7)	0.090(3)*
C37A ^g	0.0439(15)	−0.0379(15)	0.4163(14)	0.035(7)*
C38A ^g	0.0452(15)	−0.1132(13)	0.4130(13)	0.037(7)*
C39A ^g	0.1415(19)	−0.1266(12)	0.4414(15)	0.056(8)*
H39A ^g	0.142339	−0.178049	0.439133	0.068*
C40A ^g	0.2366(15)	−0.0647(16)	0.4730(14)	0.062(9)*
H40A ^g	0.302418	−0.073895	0.492384	0.074*
C41A ^g	0.2353(15)	0.0105(14)	0.4763(14)	0.055(8)*
H41A ^g	0.300328	0.052830	0.497923	0.065*
C42A ^g	0.139(2)	0.0240(12)	0.4480(15)	0.072(10)*
H42A ^g	0.138171	0.075400	0.450202	0.086*
Cl3B ^g	−0.0957(9)	−0.1062(8)	0.3083(7)	0.082(3)*
Cl4B ^g	−0.1936(10)	0.0503(8)	0.3513(7)	0.090(3)*
C37B ^g	−0.1364(18)	−0.0573(14)	0.3937(11)	0.035(7)*
C38B ^g	−0.1767(17)	0.0120(14)	0.4125(12)	0.037(7)*
C39B ^g	−0.2018(18)	0.0522(12)	0.4844(13)	0.056(8)*
H39B ^g	−0.229448	0.099586	0.497225	0.068*
C40B ^g	−0.1865(19)	0.0230(15)	0.5375(11)	0.062(9)*
H40B ^g	−0.203694	0.050489	0.586671	0.074*
C41B ^g	−0.1462(19)	−0.0463(16)	0.5188(14)	0.055(8)*
H41B ^g	−0.135699	−0.066226	0.555090	0.065*
C42B ^g	−0.1211(19)	−0.0865(13)	0.4469(15)	0.072(10)*
H42B ^g	−0.093455	−0.133844	0.434055	0.086*

^aOccupancy: 0.561(16), ^bOccupancy: 0.439(16), ^cOccupancy: 0.59(2), ^dOccupancy: 0.41(2), ^eOccupancy: 0.57(2), ^fOccupancy: 0.43(2), ^gOccupancy: 0.500(5).

3.71 mmol) was refluxed in 50 mL of 1,2-dichlorobenzene for 1.5 hours. The reaction mixture was cooled to room temperature and then vacuum filtered to remove unreacted Se. The filtrate was reduced to a dark red solid residue (1.05 g) under a steady stream of air overnight. This residual solid was washed with CH_2Cl_2 followed by Et_2O and then was allowed to air dry overnight. Red, plate crystals were obtained by diffusion of THF vapor into a concentrated, filtered 1,2-dichlorobenzene solution of this red solid.

Experimental details

Diffraction data were collected with a Bruker Smart APEX diffractometer equipped with an Oxford cryosystem. The full data set was comprised of 400 frames in ω ($0.5^\circ/\text{scan}$), collected at $\varphi = 0.00, 90.00, \text{ and } 180.00^\circ$, and 2 sets of 800 frames in φ ($0.45^\circ/\text{scan}$) collected with ω constant at -30.00 and 210.00° . Data were collected under control of the APEX3 software package [1]. Raw data were reduced to F^2 values using the SAINT software [1], and a global refinement of unit cell parameters was performed using 8654 selected reflections from the full data set. Data were corrected for absorption on the basis of multiple measurements of symmetry

equivalent reflections with the use of SADABS [1], as described by Krause [5]. The structure solution was obtained using SHELXT [2], while refinement was accomplished by a full-matrix least-squares procedure using SHELXL [3]. Several of the diethyldithiocarbamate ligands were disordered over two positions, either in whole or in part, and were therefore refined using a split atom model that permitted a best-fit distribution between sites (see Table 2). Disordered atoms were treated with isotropic refinement. One of the two interstitial C₆H₄Cl₂ solvent molecules was disordered over two positions and refined as a best-fit distribution between the two orientations in conjunction with the AFIX 66 restraint. Hydrogen atoms were added in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the carbon atoms to which they were attached.

Comment

In recent work, we have reported the usefulness of [Mo₃S₇(S₂CNEt₂)₃]I as a precursor to MoS₂ thin films on Cu₂O photocathodes that are both catalytically active for H₂ evolution and protective of the Cu₂O layer against redox deterioration [6]. We have also found that [Mo₃S₇(S₂CNR₂)₃]I complexes (R = Et, ⁱBu) function as precursors to homogeneous H₂-evolving catalysts under photolysis in the presence of [Ru(bipy)₃]²⁺ as chromophore and Et₃N as sacrificial electron donor [7]. These observations have motivated us to consider, for effect in the same applications, compounds of the more general formulation [Mo₃E₄F₃(Q₂CNR₂)₃]⁺I[−] (E = S or Se; F = S or Se in equatorial positions; Q = S or Se on supporting ligand; Fig. (a)). With these objectives in mind, our attention was drawn to a report of [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)]·2(N,N-DMF), the synthesis and structure of which were originally reported by Almond *et al.* [4]. That first structural determination was of rather limited quality. In our work with the compound, we have obtained a differently solvated crystal form and have collected diffraction data providing for somewhat improved resolution.

The preparation of [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)] proceeds from [Mo(CO)₆], Se⁰ and Et₂NC(S)SSC(S)NEt₂ in refluxing 1,2-dichlorobenzene, and crystallization was accomplished by diffusion of THF vapor into a concentrated extract of the compound in 1,2-dichlorobenzene. In contrast to the crystal structure reported by Almond *et al.*, in which [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)] occurs upon a crystallographic C₂ axis in the orthorhombic space group C2cb (standard setting: Aba2), [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)]·2(C₆H₄Cl₂) crystallizes in triclinic P $\bar{1}$. The bridged assembly resides on a general position such that it is comprised of two chemically identical – but crystallographically distinct – [Mo₃Se₇(S₂CNEt₂)₃]⁺ fragments. As is well documented for the axial sulfur atoms in related [Mo₃S₇]⁴⁺ clusters [8, 9], the Se_{ax} atoms of the

μ-Se₂^{2−} ligands have a distinctive electrophilic quality that brings them into close association with a single, soft bridging Se^{2−} counteranion (Fig. (b)). The two Mo₃ planes meet at an angle 36.52(9)° instead of being parallel planar, a feature suggesting that the bridging Se^{2−} anion exerts some amount of directionalized covalent bonding (Fig. (c)). The Se_{ax}⋯Se₁₅ interatomic distances range from 2.797(2)–2.909(2) Å, which are well below twice the 1.90 Å van der Waals radius of selenium [10] and also strongly indicative of considerable covalency to the character of the interactions of Se₁₅ with its neighboring Se atoms. In the earlier structural report of [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)], the range of Se⋯Se contacts is 2.816(4)–2.905(4) Å, while the Mo₃ planes meet at 46.3°. Isostructural [[Mo₃S₇(S₂CNEt₂)₃]₂(μ-S)] shows S_{ax}⋯μ-S^{2−} contacts varying from 2.70(1)–2.72(1) Å but at a somewhat more acute angle of 33° between the Mo₃ planes [11].

In continuing work, we aim to quantitatively compare the H₂-evolving catalytic ability of [[Mo₃Se₇(S₂CNEt₂)₃]₂(μ-Se)] against that of [[Mo₃S₇(S₂CN^{*i*}Bu₂)₃]I], which we found would support some 300 turnovers of H₂ over 3 h.

Acknowledgements: This work has been funded in part by support from the NSF (DMR 1460637). The Louisiana Board of Regents is thanked for enhancement grant LEQSF-(2002–03)–ENH–TR–67 with which the Tulane X-ray diffractometer was purchased, and Tulane University is acknowledged for its ongoing support with operational costs for the diffraction facility.

References

1. Bruker. APEX3, SADABS, SAINT and SHELXTL. Bruker AXS Inc., Madison, WI (2016).
2. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
4. Almond, M. J.; Drew, M. G. B.; Redman, H.; Rice, D. A.: A new simple synthetic route to M₃Se₇ (M = Mo or W) core containing complexes: crystal structure and characterisation of [M₃(μ₃-Se)(μ-Se)₃(dtc)₃]₂Se. *Polyhedron* **19** (2000) 2127–2133.
5. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D.: Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **48** (2015) 3–10.
6. Shinde, P. S.; Fontenot, P. R.; Donahue, J. P.; Waters, J. L.; Kung, P.; McNamara, L. E.; Hammer, N. I.; Gupta, A.; Pan, S.: Synthesis of Mo₂ from [Mo₃S₇(S₂CNEt₂)₃]I for enhancing photoelectrochemical performance and stability of Cu₂O photocathode toward efficient solar splitting. *J. Mater. Chem. A* **6** (2018) 9569–9582.
7. Fontenot, P. R.; Shan, B.; Wang, B.; Simpson, S.; Ragunathan, G.; Greene, A. F.; Obanda, A.; Hunt, L. A.; Hammer, N. I.; Webster, C. E.; Mague, J. T.; Schmehl, R. H.; Donahue, J. P.:

- Photocatalytic H_2 -evolution by homogeneous molybdenum sulfide clusters supported by dithiocarbamate ligands. *Inorg. Chem.* **58** (2019) 16458–16474.
8. Llusar, R.; Vicent, C.: Trinuclear molybdenum cluster sulfides coordinated to dithiolene ligands and their use in the development of molecular conductors. *Coord. Chem. Rev.* **254** (2010) 1534–1548.
9. Virovets, A. V.; Podberezskaya, N. V.: Specific nonbonded interactions in the structures of $M_3X_7^{4+}$ and $M_3X_4^{4+}$ ($M = Mo, W$; $X = O, S, Se$) clusters. *J. Struct. Chem.* **34** (1993) 306–322.
10. Bondi, A.: Van der Waals volumes and radii. *J. Phys. Chem.* **68** (1964) 442–451.
11. Meienberger, M. D.; Hegetschweiler, K.; Rüegger, H.; Gramlich, V.: The reactivity of complexes containing the $[Mo_3(\mu_3)(\mu S_2)_3]^{4+}$ core. Ligand substitution, sulfur elimination and sulfide binding. *Inorg. Chim. Acta* **213** (1993) 157–169.