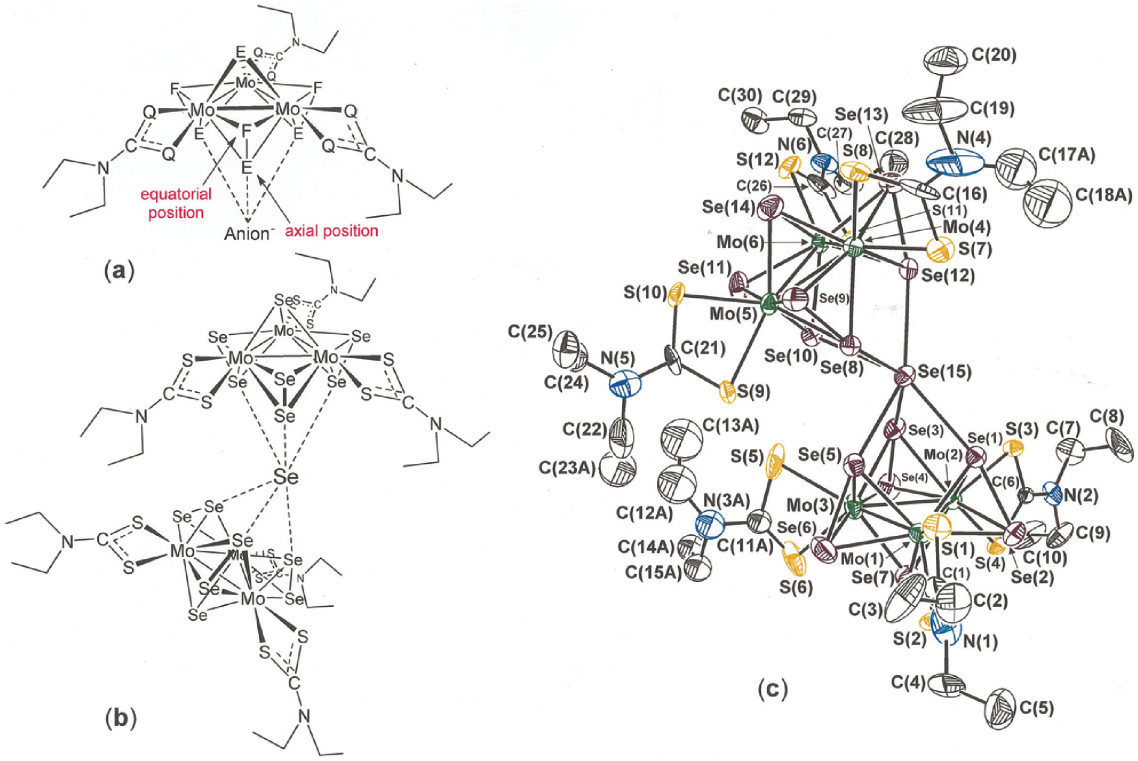
Kyra Brakefield, Justin Barnes and James P. Donahue*

Crystal structure of $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)] \cdot 2(C_6H_4Cl_2)$, $C_{42}H_{68}Cl_4Mo_6N_6S_{12}Se_{15}$



https://doi.org/10.1515/ncrs-2019-0938
Received December 27, 2019; accepted January 31, 2020; available online March 25, 2020

Abstract

$C_{42}H_{68}Cl_4Mo_6N_6S_{12}Se_{15}$, triclinic, $P\bar{1}$ (no. 2), $a = 13.0196(19)$ Å, $b = 18.813(3)$ Å, $c = 19.745(3)$ Å, $\alpha = 117.446(2)°$, $\beta = 99.775(2)°$, $\gamma = 98.233(2)°$, $V = 4091.7(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0557$, $wR_{ref}(F^2) = 0.1618$, $T = 150$ 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%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18161, 6294, 0.049
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4913
$N(param)_{refined}$:	706
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The following procedure is a modification of the original synthesis [4]. A mixture of $[Mo(CO)_6]$ (1.00 g, 3.79 mmol), Se^0 powder (1.20 g, 15.2 mmol), and $Et_2NC(S)SSC(S)NEt_2$ (1.10 g,

Open Access. © 2020 Kyra Brakefield et al., published by De Gruyter. CC BY This work is licensed under the Creative Commons Attribution 4.0 Public License.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{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_{iso}*/U_{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*

[a]Occupancy: 0.561(16), [b]Occupancy: 0.439(16), [c]Occupancy: 0.59(2), [d]Occupancy: 0.41(2), [e]Occupancy: 0.57(2), [f]Occupancy: 0.43(2), [g]Occupancy: 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°/scan), collected at φ = 0.00, 90.00, and 180.00°, and 2 sets of 800 frames in φ (0.45°/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 $C_6H_4Cl_2$ 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 $[Mo_3S_7(S_2CNEt_2)_3]I$ as a precursor to MoS_2 thin films on Cu_2O photocathodes that are both catalytically active for H_2 evolution and protective of the Cu_2O layer against redox deterioration [6]. We have also found that $[Mo_3S_7(S_2CNR_2)_3]I$ complexes (R = Et, ^{i}Bu) function as precursors to homogeneous H_2-evolving catalysts under photolysis in the presence of $[Ru(bipy)_3]^{2+}$ as chromophore and Et_3N as sacrificial electron donor [7]. These observations have motivated us to consider, for effect in the same applications, compounds of the more general formulation $[Mo_3E_4F_3(Q_2CNR_2)_3]^+I^-$ (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 $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]\cdot 2(N,N\text{-DMF})$, 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 $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]$ proceeds from $[Mo(CO)_6]$, Se^0 and $Et_2NC(S)SSC(S)NEt_2$ 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 $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]$ occurs upon a crystallographic C_2 axis in the orthorhombic space group *C2cb* (standard setting: *Aba2*), $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]\cdot 2(C_6H_4Cl_2)$ 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 – $[Mo_3Se_7(S_2CNEt_2)_3]^+$ fragments. As is well documented for the axial sulfur atoms in related $[Mo_3S_7]^{4+}$ clusters [8, 9], the Se_{ax} atoms of the $\mu\text{-}Se_2^{2-}$ ligands have a distinctive electrophilic quality that brings them into close association with a single, soft bridging Se^{2-} counteranion (Fig. (**b**)). The two Mo_3 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 $Se_{ax}\cdots$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 $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]$, the range of Se$\cdots$Se contacts is 2.816(4)–2.905(4) Å, while the Mo_3 planes meet at 46.3°. Isostructural $[[Mo_3S_7(S_2CNEt_2)_3]_2(\mu\text{-}S)]$ shows $S_{ax}\cdots\mu\text{-}S^{2-}$ contacts varying from 2.70(1)–2.72(1) Å but at a somewhat more acute angle of 33° between the Mo_3 planes [11].

In continuing work, we aim to quantitatively compare the H_2-evolving catalytic ability of $[[Mo_3Se_7(S_2CNEt_2)_3]_2(\mu\text{-}Se)]$ against that of $[[Mo_3S_7(S_2CN^iBu_2)_3]I$, which we found would support some 300 turnovers of H_2 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 M_3Se_7 (M = Mo or W) core containing complexes: crystal structure and characterisation of $[M_3(\mu_3\text{-}Se)(\mu\text{-}Se_2)_3(dtc)_3]_2Se$. 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 Mo_2 from $[Mo_3S_7(S_2CNEt_2)_3]I$ for enhancing photoelectrochemical performance and stability of Cu_2O 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.