X-ray results. Refinements were carried out by a least-squares procedure [6c], minimizing $\Sigma w(F_o^2 - k^2F_c^2)^2$ using all independent data. Weights were assigned as $w = \sigma^{-2}$, where $\sigma^2 = (\sigma_{exp}^2 + (0.015)F_o^2)^2)$. The structure model included adjustable positional and anisotropic thermal parameters for all 136 atoms, a scale factor k, and a parameter for an isotropic-type I extinction correction with Lorentzian mosaic spread [6c]. The maximum extinction correction was 10%, for the ($\bar{1}$23) reflection. Neutron scattering lengths were taken from a recent compilation by Sears [6b]: $b_C = 0.66484$, $b_H = -0.3741$, $b_N = 0.936$, $b_P = 0.513$, $b_{Re} = 0.920$ (all $\times 10^{-12}$ cm). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation. b) J. DeMeulenaer, H. Tompa, *Acta Crystallogr.* **1965**, *19*, 1014; L. K. Templeton, D. H. Templeton, *Am. Crystallogr. Assoc. Mtg.*, Storrs, CT Abstract E10, **1973**; c) J.-O. Lundgren, *Crystallographic Computer Programs* in Report UUIC-B13-4-05, Institute of Chemistry, University of Uppsala, Sweden, **1982**. d) P. Becker, P. Coppens, *Acta Crystallogr. Sect. A* **1974**, *30*, 129; *ibid.* **1975**, *31*, 417; e) V. F. Sears in *International Tables for Crystallography, Vol. C* (Ed.: A. J. C. Wilson), Kluwer, Academic Publishers, Dordrecht, **1993**.

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Hydrothermal Synthesis of a Novel Se_{12} Ring in $[\{(NH_4)_2[Mo_3S_{11.72}Se_{1.28}]\}_2[Se_{12}]]$**

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Since their discovery,[1] the $[Mo_3S_{13}]^{2-}$ core clusters have spurred researchers on to further study. Electron-poor, trinuclear molybdenum chalcogenides, sulfides in particular, have aroused considerable interest because of their hydrodesulfurization activity.[2] New ventures into trinuclear molybdenum polychalcogenide chemistry have yielded several new "polymeric" materials: $[Mo_9Se_{40}]^{8-}$, $[Mo_3Se_{18}]^{2-}$, $[Mo_{12}Se_{56}]^{12-}$, $[Mo_3S_{15}]^{2-}$, and $[Mo_6Se_{27}]^{6-}$.[3,4] In this paper we report the formation of a novel puckered Se_{12} ring, stabilized by $[Mo_3S_{13}]^{2-}$ clusters through interchalcogen interactions. This new form of selenium fits into the Q_n sequence (Q = chalcogen) of homoatomic sulfur ring structures, S_8, S_{10}, S_{12}, … S_{20}.[5]

Large ring systems of polyselenides and polytellurides have been examined as parts of metal complexes.[6,7] For example, it has been known that selenium and tellurium ions can form complex rings since the isolation of an Se_8^{2+} ring in $[Se_8][AlCl_4]_2$.[8] Kanatzidis has found isolated Se_{11}^{2-} rings in $(Ph_4P)_2[Se_{11}]$. These rings comprise two Se_5^{2-} ions and one Se^{2+} ion and link to form a cluster of corner-sharing "cyclohexane-like" rings of selenium.[9] Very recently, Sheldrick reported that the structure of Cs_3Te_{22} contains a two-dimensional 4^4 network of tellurium Te_6^{3-} ions as well as discrete Te_8 rings.[7]

The synthesis of the above-mentioned polychalcogenides has been achieved through moderate temperature reactions of the elements with oxidizing agents[8]—in the case of polyselenide ions with a mild oxidant[9]—or through methanothermal reactions with the elements.[10] We have had some success in preparing large polysulfide clusters by hydrothermal reactions,[4,11] and we used this synthetic route to prepare the title compound **1**.

$[\{(NH_4)_2[Mo_3S_{11.72}Se_{1.28}]\}_2[Se_{12}]]$ **1**

The hydrothermal reaction of $(NH_4)_2MoS_4$ with A_2S_x (A = Na, K; $x = 2-6$) generally resulted in the formation of a new phase of $(NH_4)_2[Mo_3S_{13}]$.[11] Replacing the polysulfide salt with A_2Se_x (A = Na, K; $x = 2-4$) yielded primarily selenium metal, molybdenum metal, and some soluble polychalcogenides. By preparing a new heteropolychalcogenide salt, $Na_2S_3Se_3$,[12] whose redox potential lies between the polysulfide and polyselenide,[13,14] we were able to tune the chemistry of the redox reaction and isolate compound **1**.

The solid-state structure of **1** is shown in Figures 1 and 2.[15,16] Double layers (AB packing) of trinuclear molybdenum

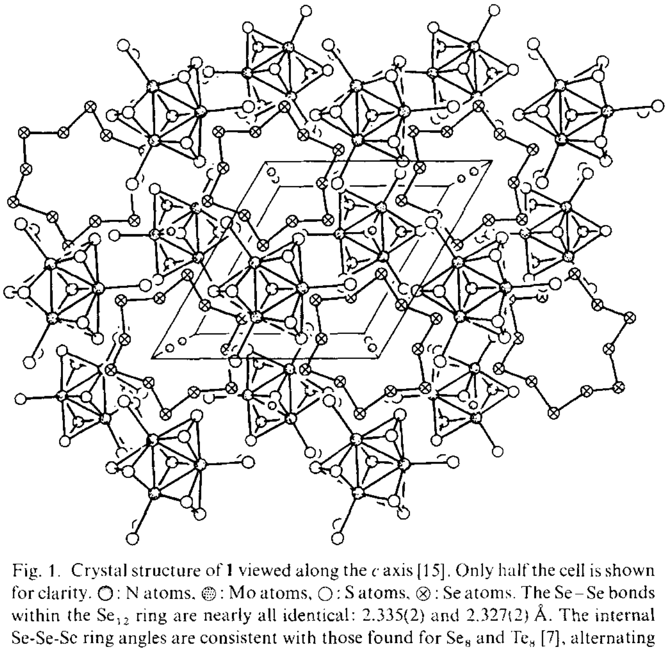

Fig. 1. Crystal structure of **1** viewed along the *c* axis [15]. Only half the cell is shown for clarity. ○: N atoms, ◍: Mo atoms, ○: S atoms, ⊗: Se atoms. The Se–Se bonds within the Se_{12} ring are nearly all identical: 2.335(2) and 2.327(2) Å. The internal Se-Se-Se ring angles are consistent with those found for Se_8 and Te_8 [7], alternating between 105.14(4) and 102.94(7)°. Instead of $[Mo_3S_{11.72}Se_{1.28}]$ the simplified structure of $[Mo_3S_{13}]$ is shown.

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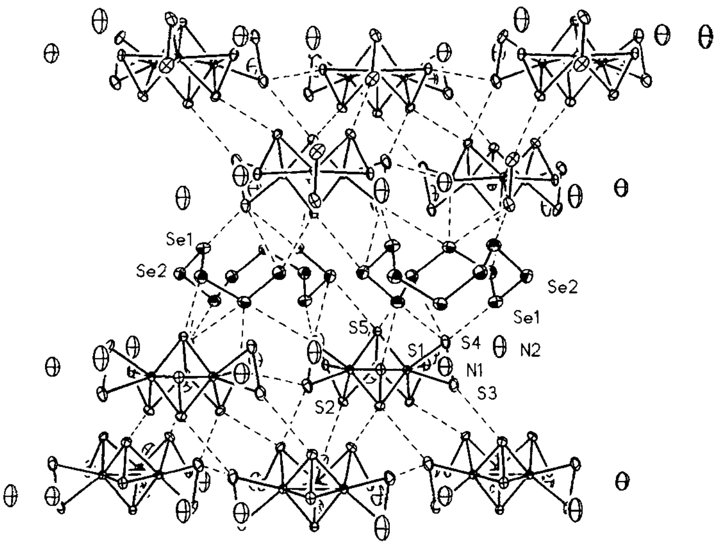

Fig. 2. Crystal structure of **1** viewed along the *a* axis and showing important Se–S intercluster interactions (dashed lines). Anisotropic thermal ellipsoids are shown: Mo and Se atoms are shaded, S and N atoms are principle axis ellipsoids. Selected chalcogen interaction distances [Å]: interactions between clusters from layer A and clusters from layer B: S2–S2, 3.207(3); S2–S3, 3.507(3); interactions between clusters within the same layer: S1–S3, 3.466(3); cluster–ring interactions: S1–Se1, 3.331(3); S4–Se1, 3.754(3) and 3.492(3); S4–Se2, 3.472(3); S5–Se2, 3.544(3). Instead of $[Mo_3S_{11.72}Se_{1.28}]$ the simplified structure of $[Mo_3S_{13}]$ is shown.

clusters of $[Mo_3S_{11.72}Se_{1.28}]^{2-}$ encircle D_{3d} rings of Se_{12}. One type of ammonium cation is located above and below the Se_{12} rings, located within the planes of the molybdenum clusters (N1, Fig. 2). A second ammonium cation (N2) is found centered on the other threefold axis in the cell, above and below the double layers. The packing forms a very intricate network of interactions between anionic clusters and neutral Se_{12} rings (Fig. 2). A summary of atomic coordinates is found in Table 1.

Table 1. Atomic coordinates, U(eq) ($Å^2 \times 10^3$), and site-occupancy factors SOF for **1**.

	x	y	z	U(eq)	SOF
N(1)	0.3333	0.6667	0.1236(7)	66(6)	
N(2)	0.0	0.0	0.1467(7)	54(5)	
Mo	0.6606(1)	0.1768(1)	0.1612(1)	15(1)	
S(1)	0.3799(2)	0.0572(2)	0.1570(1)	20(1)	
S(2)	0.8459(2)	0.3247(2)	0.2202(1)	22(1)	
S(3)	0.6386(14)	0.9295(14)	0.1850(4)	34(2)	0.786(7)
S(4)	0.6537(19)	0.9736(21)	0.1123(6)	29(3)	0.789(6)
S(5)	0.6667	0.3333	0.0978(1)	17(1)	
Se(1)	0.9616(1)	0.2332(1)	0.0451(1)	38(1)	
Se(2)	0.7372(1)	0.1506(1)	0.0030(1)	38(1)	
Se(3)	0.6579(19)	0.9417(22)	0.1905(6)	24(3)	0.214(7)
Se(4)	0.6683(29)	0.9788(34)	0.1099(9)	27(5)	0.211(7)

The neutral Se_{12} rings are reminiscent of the S_{12} allotrope of sulfur.[17] Until now, the largest known neutral selenium ring systems were only Se_8 rings[18] and heteropolychalcogenide, n-membered S_xSe_y rings (where $6 \leq n \leq 12$).[19] (Of course, gray selenium exists in the more common, "infinite" chain form.[20])

Unlike with our previous structures,[4, 11] the $[Mo_3Q_{13}]^{2-}$ portion of **1** (Q = S, Se) did not refine well. It was quite possible that both S_2^{2-} and Se_2^{2-} formed during the reaction of MoS_4^{2-} with the heteropolychalcogenide salt in aqueous solution.[14] The S3 and S4 atoms that comprise the "paddles" of the cluster were the only sulfur atoms that did not refine satisfactorily. This is consistent with the relative ease of substitution at this position of the $[Mo_3S_7]^{4+}$ core.[21] Using a correlated site-occupancy model,[22] we refined the site-occupancy factor of two related atoms (S and Se) on two different sites. The resulting refinement yielded a cluster best modeled as formula **2**.

$$[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{\eta_2\text{-}(S_{2-x}Se_x)\}_3]^{2-} \quad \mathbf{2} \quad x = 0.425$$

The reactivity of our new heteropolychalcogenide anion $S_3Se_3^{2-}$ in hydrothermal reactions has proven to be unique. Hydrothermal synthesis has yielded a new form of neutral selenium that is intimately held within a network of molybdenum polychalcogenide clusters and ammonium ions.

Experimental Procedure

The title compound **1** was prepared by combining $(NH_4)_2MoS_4$ (0.131 g, 0.5 mmol) and $Na_2S_3Se_3$ (0.381 g, 1.0 mmol) with 500 µL degassed water in an evacuated, flame-sealed, fused silica ampoule. The reaction was complete under autogenous pressure at 150 °C after 100 h. The resulting solution was filtered, and the solids washed with deionized water until the filtrate was colorless. Since diffraction lines from any other compound were absent from the powder diffraction pattern of the product solids, the yield was nearly quantitative; selenium and molybdenum powders were, however, found. Elemental analysis (EDS) for $H_{16}N_4Mo_6S_{23.44}Se_{14.56}$ [%]: calcd. Mo 22.58, S 29.48, Se 45.11; found Mo 22.53, S 29.77, Se 44.71.

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[12] $Na_2S_3Se_3$ was prepared from the elements in liquid ammonia. Differential scanning calorimetry confirmed that this new salt is a single phase with a congruent melting point of 330 °C. Chemically associated reduction/oxidation waves are seen at −0.74 V and −0.17 V vs. SHE.

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From Porphyrin Isomers to Octapyrrolic "Figure Eight" Macrocycles

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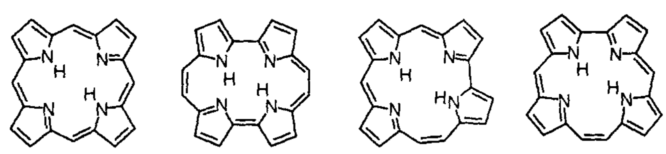
Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday

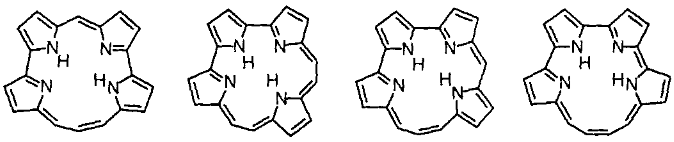
The synthesis of porphycene **2**[1] marks the beginning of a promising new direction of research in porphyrin chemistry: the investigation of porphyrin isomers.[2] The formally simple construction principle of **2** involved the reorganization of the structural elements of porphyrin **1**—four pyrrole and four methine units—while maintaining the N_4 coordination site. This principle also led to the assembly of no less than six additional structural isomers, which contain one or two (as in **2**) (*Z*)-configured C=CH–CH=C units (arene fragments).

The structural isomers of [18]porphyrin-(1.1.1.1) resulting from this operation are depicted in order of increasing energy in Figure 1.[3] Presumably, there are even more candidates than shown, since the structural isomers of **1** might also occur as (*E*) forms due to the presence of the C=CH–CH=C group(s). While the existence of an (*E*) form of **2** can be safely excluded because of geometrical constraints, (*E*) forms are conceivable in the cases of the other isomers **3**–**8**. It should be noted that nonplanar isomers, regardless of their configuration (*E* or *Z*), may adopt chiral conformations, thus offering the possibility of separation of enantiomers.

For the synthesis of the porphyrin isomers **3**–**8**, it is useful to know their energies relative to that of **1**. These energies, calculated by the UHF/PM3 and BLYP/6-31G**//3-21G methods,[4] are given in Figure 1 (in kcal mol^{-1}) for the most stable NH tautomer. In each case, this particular tautomer has a diagonal ("trans") arrangement of the imino protons as shown in the formulas.[5] It is interesting to find that the stability of porphycene compares favorably with that of porphyrin; depending on the computational method employed, either **1** or **2** is predicted to be the more stable isomer. Evidently, the slightly strained porphycene is stabilized by the presence of strong NH ⋯ N hydrogen bonds. [18]Porphyrin-(2.1.1.0) (**3**, hemiporphycene) and [18]porphyrin-(2.1.0.1) (**4**, corrphycene) are predicted to be only moderately higher in energy. This prognosis is in accord with the observation that the hemiporphycenes[6] and corrphycenes[7] that have been synthesized recently have properties similar to porphyrins. The energies of the porphyrin isomers **6**–**8** relative to those of **1**–**5** increase so drastically that it is doubtful whether these species will be stable molecules.



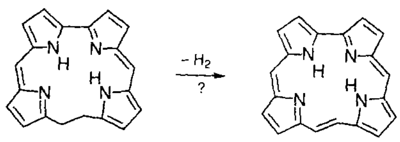
	-(1.1.1.1) **1**	-(2.0.2.0) **2**	-(2.1.1.0) **3**	-(2.1.0.1) **4**
PM3	0.0	1.7	8.6	16.0
BLYP/6-31G**//3-21G	0.0	-1.5	5.1	12.0



	-(3.0.1.0) **5**	-(2.2.0.0) **6**	-(3.1.0.0) **7**	-(4.0.0.0) **8**
PM3	23.6	33.3	39.7	53.9
BLYP/6-31G**//3-21G	19.0	30.6	38.7	70.6

Fig. 1. Porphyrin and its isomers with an N_4 coordination site: [18]porphyrin-(*n.m.p.q*) (**1**–**8**). Data below the structural formulas: values of the relative energies (in kcal mol^{-1}) calculated by PM3 and BLYP/6-31G**//3-21G.

These considerations turned our interests to (*E*)-corrphycene (**10**, Scheme 1). Inspection of the Briegleb–Stuart model indicated that **10** is nearly unstrained but rigid, having the formal double bond in an orthogonal arrangement with respect to the tetrapyrrolic π system. Semiempirical UHF/PM3 calculations predict a similar geometry for **10** and an energy 8 kcal mol^{-1} above that of the (*Z*)-isomer **4**.[8] Consequently, **10** is likely to be a chiral, C_2 symmetric, and nonaromatic porphyrinoid. Porphyrinoid **10** can possibly be synthesized by dehydrogenation of dihydrocorrphycene **9**. According to models, the dihydro compound **9** has a conformation similar to that of **10** with the CH_2CH_2 group in a position conducive to the generation of an (*E*) double bond.



9 **10**

Scheme 1. The 3,4-diethyl substituents of the pyrrole rings are omitted for clarity.

This synthetic strategy fell short of the original goal, since compound **9** never materialized. However, the search was success-

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