DALTON
FULL PAPER

Synthesis and structure of $[M_3(\mu_3\text{-Se})(\mu\text{-SeS})_3]^{4+}$ core compounds (M = Mo, W): a less-common type of linkage isomerism for the μ-SSe ligand

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Received 28th June 2001, Accepted 17th November 2001
First published as an Advance Article on the web 5th February 2002

The $M_3(\mu_3\text{-Se})(\mu\text{-Se})_3^{4+}$ clusters (written also as $M_3Se_4^{4+}$) show a strong tendency to add sulfur to the μ-Se bridges giving new chalcogen-rich clusters with $M_3(\mu_3\text{-Se})(\mu\text{-SeS})_3^{4+}$ cores *i.e.* $Mo_3Se_4S_3^{4+}$. They are isolated as dithiophosphate complexes $[M_3(\mu_3\text{-Se})(\mu\text{-SeS})_3((RO)_2PS_2)_3]Cl$ (**1a**, M = Mo, R = Et; **1b**, R = *i*-Pr; **2a**, M = W, R = Et, **2b**, R = *i*-Pr) upon treatment of solutions of $[M_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl with a large excess of P_4S_{10}/ROH reagent. The structures of **1a** and **2a** have been determined by single crystal X-ray analysis. The sulfur atom forms a part of the μ-SeS ligand, which is asymmetrically coordinated to two metal atoms, so that the sulfurs are almost coplanar with the M_3 triangle (equatorial positions) and the Se atoms are strongly out of the plane (axial positions). This represents a rare kind of linkage isomerism since the opposite bridging mode is observed for the SeS ligand in the clusters $M_3(\mu_3\text{-S})(\mu\text{-SeS})_3^{4+}$ in which the Se is equatorial and the S occupies the axial positions. As an alternative the pure dithiophosphate salts $KS_2P(OR)_2$ (R = Et, *i*-Pr) do not lead to sulfur addition and allow isolation of $[Mo_3Se_4((RO)_2PS_2)_3(\mu\text{-}CH_3COO)(C_5H_5N)]$ (**3**) upon recrystallyzation from a CH_3CN–CH_3COOH–pyridine mixture. Both **3** and its sulfur analogue abstract sulfur from propylene sulfide at room temperature to give $Mo_3Se_4S_3^{4+}$ and $Mo_3S_7^{4+}$ clusters, respectively.

Introduction

The reactivity patterns of the incomplete cuboidal $M_3(\mu_3\text{-Q})(\mu\text{-Q})_3^{4+}$ clusters (M = Mo, W, Re; Q = S, Se), apart from the external ligand substitution on the metal site, are dominated by heterometal addition to the three μ-Q bridges to give a plethora of $M_3M'Q_4$ cuboidal and $M_6M'Q_8$ double cube structures.[1,2] There is also a strong tendency to form $\{M_3Q_4\}_2$ dimers in the solid state through short Q ··· Q interactions.[3–5] However, little effort has been devoted to exploit this reactivity for incorporation of non-metals into the cluster. Among the few examples are a study of reversible sulfur addition/abstraction to $[Mo_3S_4(S_2C_2H_4)_3]^{2-}$ and $[Mo_3S_4(Et_2PS_2)_3](Et_2\ PS_2)$ which allows cycling between the Mo_3S_4 and chalcogen-rich Mo_3S_7 cluster cores,[6,7] and a serendipitous preparation of $[Re_3(\mu\text{-S})(\mu\text{-S})_2(\mu\text{-SO}_2)(PEt_3)_3Cl_6]^-$ through slow oxidation of the Re_3S_4 core.[8] In this work we explore the synthetic potential of chalcogen addition to the $M_3Se_4^{4+}$ (M = Mo, W) clusters. Some related aspects of the reactivity of their sulfur analogues are also addressed.

Results and discussion

Synthesis and reactivity

Our original idea was to prepare complexes of $M_3Se_4^{4+}$ (M = Mo, W) with dithiphosphate ligands $(RO)_2PS_2^-$ (dtp). A rich chemistry comparable to that of the dtp derivatives of $Mo_3S_4^{4+}$ clusters was anticipated.[9] The dtp ligands were prepared *in situ* from P_4S_{10} and ethanol or iso-propanol according to the equation:

$$P_4S_{10} + 8ROH = 4(RO)_2P(S)SH + 2H_2S$$

The reaction proceeds rapidly upon heating and as soon as a clear colourless solution is produced, it is added to a solution of the cluster in 2 M HCl. A brown precipitate appears immediately. If it is separated just after precipitation, it consists of a mixture of a compound soluble in CH_3CN (brown solution), which in the case of Mo is most probably $[Mo_3Se_4(dtp)_4(H_2O)]$, similar to $[Mo_3S_4((EtO)_2PS_2)_4(H_2O)]$[10] (the W derivative also gives an intractable product, which is also soluble in CH_3CN, but it could not be isolated in a pure form), and of another compound, slightly soluble in CH_3CN but very soluble in $CHCl_3$ or CH_2Cl_2 (M = Mo, orange solutions, M = W, red solutions). These latter products exhibit intensive peaks in FAB-MS corresponding to the molecular ions $[M_3(\mu_3\text{-Se})(\mu\text{-SeS})_3((RO)_2PS_2)_3]^+$ (M^+), which result from sulfur addition to the three μ-Se bridges of the starting cluster. The X-ray analysis of **1a** and **2a** confirms the presence of $\mu\text{-}\eta^2\text{:}\eta^2$-SSe ligands in these compounds. If the precipitate is left with its mother liquor for one day, the chalcogen-rich compounds **1a**,**b** and **2a**,**b** are the only products. However, this cluster core transformation is avoided when pure solid $KS_2P(OR)_2$ (R = Et, *i*-Pr) are employed. For Mo the initially formed precipitate (presumably $[Mo_3Se_4(dtp)_3(\mu\text{-dtp})(H_2O)]$) was treated with a CH_3CN–AcOH–py–DMF mixture to give X-ray quality crystals of **3**, according to the equation:

$$[Mo_3Se_4(dtp)_3(\mu\text{-dtp})(H_2O)] + OAc^- + py = [Mo_3Se_4(dtp)_3(\mu\text{-OAc})(py)] + dtp^- + H_2O$$

This approach has been previously used to convert $[W_3S_4(dtp)_3(\mu\text{-dtp})(H_2O)]$ into $[W_3S_4(dtp)_3(\mu\text{-OAc})(py)]$.[11] For W_3Se_4 it does not give identifiable products.

We have also found that, though **3** can be recrystallized repeatedly from the reaction mixture, gradually a second product (thin orange needles, **4**) builds up which is not soluble in acetonitrile. Its FAB-MS shows the presence of the molecular peak $[Mo_3(\mu_3\text{-Se})(\mu\text{-SeS})_3(dtp)_3]^+$, but the other peaks attributable to the whole range of progressively Se substituted species ($[Mo_3(\mu_3\text{-Se})(\mu\text{-SeSe})(\mu\text{-SSe})_2(dtp)_3]^+$, $[Mo_3(\mu_3\text{-Se})(\mu\text{-SeSe})_2(\mu\text{-SSe})(dtp)_3]^+$, $[Mo_3(\mu_3\text{-Se})(\mu\text{-SeSe})_3(dtp)_3]^+$)

DOI: 10.1039/b105682b

Table 1 Selected bond distances (Å) and angles (°) for **1a**

Mo(1)–Mo(2)	2.739(2)	Mo(1)–Mo(3)	2.742(2)
Mo(1)–Se(1)	2.513(3)	Mo(1)–Se(2)	2.529(2)
Mo(1)–Se(4)	2.521(2)	Mo(1)–S(1)	2.520(4)
Mo(1)–S(3)	2.549(3)	Mo(1)–S(4)	2.518(4)
Mo(1)–S(5)	2.569(4)	Mo(2)–Mo(3)	2.732(2)
Mo(2)–Se(1)	2.505(2)	Mo(2)–Se(2)	2.512(2)
Mo(2)–Se(3)	2.528(2)	Mo(2)–S(2)	2.507(4)
Mo(2)–S(1)	2.509(4)	Mo(2)–S(7)	2.548(4)
Mo(2)–S(6)	2.534(6)	Mo(3)–Se(3)	2.533(2)
Mo(3)–Se(1)	2.508(2)	Mo(3)–S(3)	2.555(3)
Mo(3)–Se(4)	2.522(3)	Mo(3)–S(9)	2.555(5)
Mo(3)–S(2)	2.508(4)	Se(3)–S(2)	2.206(5)
Mo(3)–S(8)	2.514(4)	S(4)–P(1)	1.984(7)
Se(2)–S(1)	2.202(4)	S(5)–P(1)	1.983(6)
Se(4)–S(3)	2.270(3)	S(6)–P(2)	1.973(7)
S(7)–P(2)	1.975(8)	S(8)–P(3)	2.005(6)
S(9)–P(3)	1.981(7)		
Se(1)–Mo(1)–Se(2)	112.82(8)	Se(1)–Mo(1)–Se(4)	113.11(8)
Se(1)–Mo(1)–S(1)	84.17(11)	Se(1)–Mo(1)–S(3)	83.55(9)
Se(1)–Mo(1)–S(4)	79.58(11)	Se(1)–Mo(1)–S(5)	156.61(11)
Se(2)–Mo(1)–Se(4)	83.66(7)	Se(2)–Mo(1)–S(1)	51.72(10)
Se(2)–Mo(1)–S(3)	136.49(9)	Se(2)–Mo(1)–S(4)	134.19(12)
Se(2)–Mo(1)–S(5)	84.50(11)	Se(4)–Mo(1)–S(3)	53.19(8)
Se(4)–Mo(1)–S(4)	133.85(12)	Se(4)–Mo(1)–S(5)	83.31(11)
S(1)–Mo(1)–S(3)	167.53(13)	S(1)–Mo(1)–S(4)	88.64(14)
S(1)–Mo(1)–S(5)	95.84(14)	S(3)–Mo(1)–S(4)	87.03(12)
S(3)–Mo(1)–S(5)	94.58(13)	S(4)–Mo(1)–S(5)	77.04(14)
Se(1)–Mo(2)–Se(2)	113.66(8)	Se(1)–Mo(2)–Se(3)	113.84(8)
Se(1)–Mo(2)–S(1)	84.56(10)	Se(1)–Mo(2)–S(2)	85.36(11)
Se(1)–Mo(2)–S(6)	77.82(13)	Se(1)–Mo(2)–S(7)	154.37(14)
Se(2)–Mo(2)–Se(3)	82.17(7)	Se(2)–Mo(2)–S(1)	52.03(11)
Se(2)–Mo(2)–S(2)	133.91(12)	Se(2)–Mo(2)–S(6)	136.10(13)
Se(2)–Mo(2)–S(7)	83.69(13)	Se(3)–Mo(2)–S(1)	133.91(12)
Se(3)–Mo(2)–S(2)	51.96(11)	Se(3)–Mo(2)–S(6)	133.99(13)
Se(3)–Mo(2)–S(7)	86.14(12)	S(1)–Mo(2)–S(2)	169.90(14)
S(1)–Mo(2)–S(6)	89.85(15)	S(1)–Mo(2)–S(7)	92.87(14)
S(2)–Mo(2)–S(6)	87.41(15)	S(2)–Mo(2)–S(7)	95.95(14)
S(6)–Mo(2)–S(7)	76.68(17)	S(1)–Mo(3)–Se(3)	113.58(8)
Se(1)–Mo(3)–Se(4)	113.23(8)	Se(1)–Mo(3)–S(2)	85.30(11)
Se(1)–Mo(3)–S(3)	83.52(9)	Se(1)–Mo(3)–S(8)	77.60(11)
Se(1)–Mo(3)–S(9)	155.09(13)	Se(3)–Mo(3)–Se(4)	82.50(8)
Se(3)–Mo(3)–S(2)	51.90(11)	Se(3)–Mo(3)–S(3)	135.27(10)
Se(3)–Mo(3)–S(8)	134.06(11)	Se(3)–Mo(3)–S(9)	85.02(12)
Se(4)–Mo(3)–S(2)	134.16(12)	Se(4)–Mo(3)–S(3)	53.11(8)
Se(4)–Mo(3)–S(8)	136.21(12)	Se(4)–Mo(3)–S(9)	84.48(12)
S(2)–Mo(3)–S(3)	168.70(13)	S(2)–Mo(3)–S(8)	87.30(14)
S(2)–Mo(3)–S(9)	94.69(15)	S(3)–Mo(3)–S(8)	88.77(12)
S(3)–Mo(3)–S(9)	94.80(13)	S(8)–Mo(3)–S(9)	77.52(15)

have comparable intensity. The analysis of this product gave the approximate composition $[Mo_3Se_4(S_{2.28}Se_{0.72})(dtp)_3]Cl$. The chloride obviously comes from HCl, since the original precipitate was subjected to subsequent tranformation while still wet. This result implies that the Mo_3Se_4 core is disrupted under the reaction conditions (slow oxidation in air may be the cause), liberating Se which is reincorporated into the remaining clusters to give more stable chalcogen-rich species. The similar transformation of $Mo_3OS_3^{4+}$ and $Mo_3S_4^{4+}$ clusters into $Mo_3(O)(S_2)_3^{4+}$ and $Mo_3(S)(S_2)_3^{4+}$, respectively, has been reported.[6,7,9,12] What then is the source of sulfur? In the *slow* transformation of **3** into **4** it may be the dtp ligand but we do not think that it plays this role in the *fast* reaction leading to **1a**,**b** and **2a**,**b**, since the use of pure solid samples of Kdtp (even in five-fold excess against the 1 : 4 stoichiometry) does not give any of the chalcogen-rich species. Although $(RO)_2PS_2H$ are the main products of the reaction of phosphorous(V) sulfide with alcohols and are generally obtained in high yields, the reaction sequence leading to them must be complex. Intermediates or side products (unidentified) may be present in sufficient amounts to serve as the sulfur source when a large molar excess of freshly prepared alcoholic solution of P_4S_{10} is employed. The use of the P_4S_{10}/EtOH reagent as sulfur donor for the self assembly of $Mo_3S_7^{4+}$, $Mo_4S_4^{6+}$, $Mo_4OS_3^{6+}$ and $W_4S_4^{6+}$ clusters from mononuclear starting compounds is well documented.[13,14]

Crystal structures

Structures of 1 and 2. The chalcogen rich clusters **1** and **2** belong to the family of triangular high valent M(IV) clusters $M_3(\mu_3\text{-}Q)(\mu\text{-}QQ')_3^{4+}$ (M = Mo, W; μ3-Q = O, S, Se, Te; Q, Q′ = S, Se, Te). Compounds **1a** and **2a** are isostructural (Figs. 1 and 2). The cluster core is rather rigid. For example, the M–μ3-Se average distances are 2.51 Å for **1a** and 2.50 Å for **2a** (Tables 1 and 2), which is practically identical to the value of 2.50 Å encountered in $[M_3Se_7(Et_2NCS_2)_3](Et_2NCS_2)$ (M = Mo, W).[15] This means that the μ3 capping ligand is not sensitive to the changes in other parts of the cluster structure. The M–M bond lengths are, however, influenced by the nature of the bridging ligands and the bulkier Se atom causes its elongation, from 2.72 Å in $[Mo_3S_7(Et_2NCS_2)_3]Cl$[15] to 2.78 Å in $[Mo_3Se_7(Et_2NCS_2)_3](Et_2NCS_2)$,[14] and from 2.74 Å in $[W_3S_7X_6]^{2-}$ (X = Cl, Br)[16,17] to 2.76 Å in $[W_3Se_7(Et_2NCS_2)_3](Et_2NCS_2)$[14] and $[W_3Se_7(EtO)_2PS_2)_3]Br$.[18] The average M–M distances are 2.73 Å for **1a** and 2.74 Å for **2a**. The M–S bond distances to the ligands have their usual values.[18]

The most interesting feature in **1** and **2** is the mode of coordination of the μ-η²:η² S–Se ligands. This Se–S bond distance is about 2.20 Å, which is close to S–Se bond distances

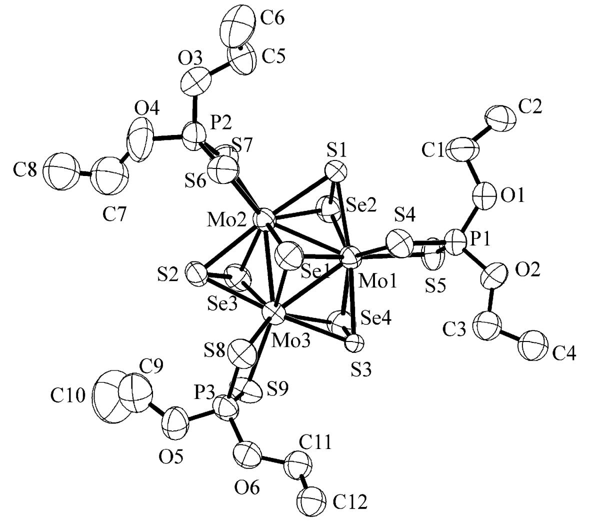

Fig. 1 View of the cation $[Mo_3(\mu_3\text{-}Se)(\mu\text{-}SeS)_3((EtO)_2PS_2)_3]^+$ in **1a** with 50% displacement ellipsoids. The hydrogen atoms are omitted. The disorder in the orientation of ethyl groups is not shown.

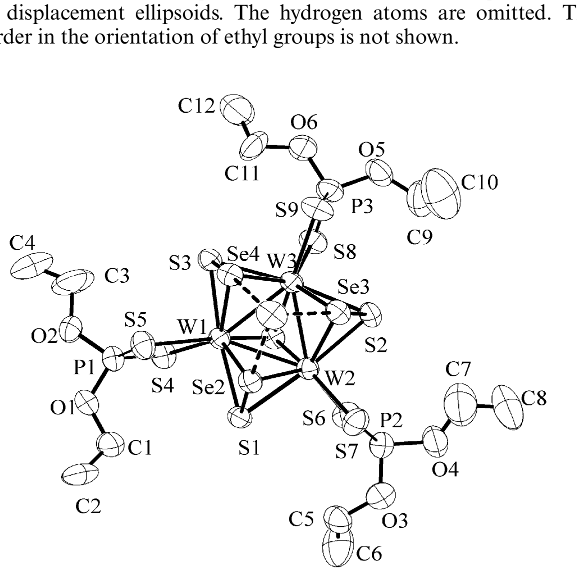

Fig. 2 View of the ionic pair $[W_3(\mu_3\text{-}Se)(\mu\text{-}SeS)_3((EtO)_2PS_2)_3]^+Cl^-$ in **2a** with short Se ··· Cl contacts. 50% displacement ellipsoids; the hydrogens are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for **2a**

W(1)–Se(1)	2.5014(18)	W(1)–Se(2)	2.5322(18)
W(1)–Se(4)	2.5263(19)	W(1)–S(1)	2.505(4)
W(1)–S(3)	2.502(4)	W(1)–S(4)	2.510(4)
W(1)–S(5)	2.564(5)	W(1)–W(3)	2.7366(11)
W(2)–Se(1)	2.4980(18)	W(2)–Se(2)	2.5315(19)
W(2)–Se(3)	2.5315(19)	W(2)–S(1)	2.498(4)
W(2)–S(2)	2.497(4)	W(2)–S(6)	2.512(5)
W(2)–S(7)	2.561(5)	W(3)–Se(1)	2.4982(18)
W(3)–Se(3)	2.5400(18)	W(3)–Se(4)	2.529(2)
W(3)–S(2)	2.501(4)	W(3)–S(3)	2.508(4)
W(3)–S(8)	2.506(4)	W(3)–S(9)	2.548(5)
Se(2)–S(1)	2.195(4)	Se(3)–S(2)	2.197(5)
Se(4)–S(3)	2.201(4)		
Se(1)–W(1)–Se(2)	113.01(6)	Se(1)–W(1)–Se(4)	113.07(6)
Se(1)–W(1)–S(1)	83.97(11)	Se(1)–W(1)–S(3)	83.96(11)
Se(1)–W(1)–S(4)	80.98(11)	Se(1)–W(1)–S(5)	157.44(12)
Se(2)–W(1)–Se(4)	83.89(6)	Se(2)–W(1)–S(1)	51.67(10)
Se(2)–W(1)–S(3)	135.45(10)	Se(2)–W(1)–S(4)	133.38(11)
Se(2)–W(1)–S(5)	83.57(12)	Se(4)–W(1)–S(1)	135.18(10)
Se(4)–W(1)–S(3)	51.93(10)	Se(4)–W(1)–S(4)	133.25(11)
Se(4)–W(1)–S(5)	82.79(12)	S(1)–W(1)–S(3)	167.89(14)
S(1)–W(1)–S(4)	88.81(14)	S(1)–W(1)–S(5)	95.98(14)
S(3)–W(1)–S(4)	88.39(14)	S(3)–W(1)–S(5)	94.80(14)
S(4)–W(1)–S(5)	76.46(15)	Se(1)–W(2)–Se(2)	113.15(6)
Se(1)–W(2)–Se(3)	113.65(6)	Se(1)–W(2)–S(1)	84.20(10)
Se(1)–W(2)–S(2)	85.02(10)	Se(1)–W(2)–S(6)	80.38(12)
Se(1)–W(2)–S(7)	156.14(13)	Se(2)–W(2)–Se(3)	82.85(6)
Se(2)–W(2)–S(1)	51.76(10)	Se(2)–W(2)–S(2)	134.35(1)
Se(2)–W(2)–S(6)	135.24(11)	Se(2)–W(2)–S(7)	82.49(13)
Se(3)–W(2)–S(1)	134.29(11)	Se(3)–W(2)–S(2)	51.80(11)
Se(3)–W(2)–S(6)	132.57(12)	Se(3)–W(2)–S(7)	85.18(12)
S(1)–W(2)–S(2)	169.20(13)	S(1)–W(2)–S(6)	90.37(15)
S(1)–W(2)–S(7)	92.91(14)	S(2)–W(2)–S(6)	87.35(15)
S(2)–W(2)–S(7)	96.77(15)	S(6)–W(2)–S(7)	75.95(17)
Se(1)–W(3)–Se(3)	113.35(6)	Se(1)–W(3)–Se(4)	113.09(6)
Se(1)–W(3)–S(2)	84.94(10)	Se(1)–W(3)–S(3)	83.90(10)
Se(1)–W(3)–S(8)	79.82(10)	Se(1)–W(3)–S(9)	156.41(13)
Se(3)–W(3)–Se(4)	83.16(6)	Se(3)–W(3)–S(2)	51.67(11)
Se(3)–W(3)–S(3)	134.61(11)	Se(3)–W(3)–S(8)	133.14(10)
Se(3)–W(3)–S(9)	84.41(12)	Se(4)–W(3)–S(2)	134.55(11)
Se(4)–W(3)–S(3)	51.83(10)	Se(4)–W(3)–S(8)	134.98(11)
Se(4)–W(3)–S(9)	83.28(13)	S(2)–W(3)–S(3)	168.82(14)
S(2)–W(3)–S(8)	87.67(14)	S(2)–W(3)–S(9)	95.48(15)
S(3)–W(3)–S(8)	89.81(13)	S(3)–W(3)–S(9)	94.53(15)
S(8)–W(3)–S(9)	76.64(15)	W(1)–Se(1)–W(2)	66.62(5)
W(1)–Se(1)–W(3)	66.53(5)	W(2)–Se(1)–W(3)	65.66(5)

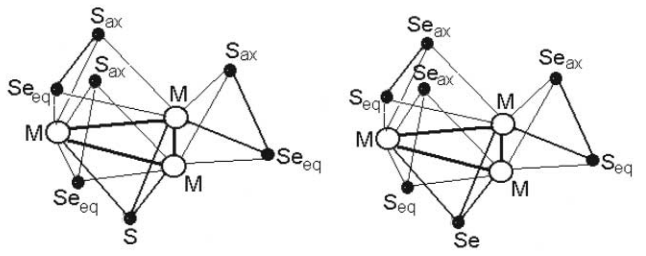

Chart 1 The two known types of (μ-SeS) ligand as found in $[M_3(\mu_3\text{-}S)(\mu\text{-}Se_{eq}\text{–}S_{ax})_3]^{4+}$ (left) and in $[M_3(\mu_3\text{-}Se)(\mu\text{-}Se_{ax}\text{-}S_{eq})_3]^{4+}$ (the present study; right).

found in $Mo_3(\mu_3\text{-}S)(\mu\text{-}Se_{eq}\text{–}S_{ax})_3^{4+}$ clusters—the only complexes with Se–S ligand structurally characterized hitherto.[19–21] In all the clusters having the $[M_3(\mu_3\text{-}Q)(\mu\text{-}QQ')_3]^{4+}$ core the μ-QQ′ ligand is coordinated asymmetrically so that one atom is roughly in the M_3 plane (designated as equatorial) and the other is strongly out of the plane (roughly in the same position which is occupied by μ-Q atoms in closely related incomplete cuboidal M_3Q_4 clusters), and is termed axial. The equatorial atom is more loosely bound; for example in $[Mo_3S_7(Et_2NCS_2)_3]Cl$ the $M\text{–}S_{eq}$ bond distance is 0.07 Å longer than the $M\text{–}S_{ax}$,[15] and is more reactive.[22] It is by substituting Se for the S_{eq} that the $M_3(\mu_3\text{-}S)(\mu\text{-}S_{eq}\text{–}S_{ax})_3^{4+}$ core is transformed into the $M_3(\mu_3\text{-}S)(\mu\text{-}Se_{eq}\text{–}S_{ax})_3^{4+}$ core. The reagents employed for the substitution are PPh_3Se and KSeCN.[19–21] The clusters **1** and **2** have exactly the reverse coordination mode of the μ-SSe ligand, with Se atoms occupying the more strongly bound axial position. The relationship between these two known structure types is shown in Chart 1. This leads to the curious phenomenon that, for example in **2a**, the distances $W\text{–}S_{eq}$ (2.50 Å) and $W\text{–}Se_{ax}$ (2.53 Å) are very close despite the 0.15 Å difference in the covalent radii between the two chalcogens.[3] Thus the SeS ligand demonstrates a rare type of linkage isomerism in its coordination as a bridging ligand, if we omit the μ_3-Q cap and consider only the $Mo_3(\mu\text{-}SSe)_3$ part. It is remarkable that the chalcogen substitution gives one isomer, and the chalcogen addition the other, both with an exceptional selectivity. Whether and on what conditions the interconversion between the isomers is possible remains to be seen.

Anion–cation interactions. In both chalcogen-rich cluster cations **1a** and **2a** the axial Se atoms of the (SeS) ligands form short contacts with Cl^-, 2.88–2.91 Å for the Mo derivative **1a** and 2.87–2.89 Å for the W derivative **2**. Similar shortened contacts are observed in $[W_3Se_7((EtO)_2PS_2)_3]Br$[18] and $[Mo_3Se_7((EtO)_2PSe_2)_3]Br$,[23] which are isostructural with **1a** and **2a**. This ability of the axial chalcogen atoms to coordinate various anions is a common feature of the M_3Y_7 clusters (M = Mo, W, Re; Y = S, Se, Te) and has been reviewed[3] and given a theoretical treatment recently.[24] The shortness of the Se ··· Cl contacts in our compounds looks even more impressive if it is compared with the S ··· Cl contacts found in $[Mo_3S_7((EtO)_2PS_2)_3]Cl$ (2.86–2.96 Å)[25] and they are even *shorter* than in $[Mo_3S_7((n\text{-}Pr)_2PS_2)_3]Cl$ [2.936(4) Å].[26] Taking into account the difference of *ca.* 0.15 Å in both covalent and van der Waals radii of S and Se it is evident that the axial Se atoms are stronger acceptors than the sulfur atoms. Theoretical calculations for the $Mo_3S_7^{4+}$ cluster core show that the electron density is less at the axial S atoms (which thus become electrophilic) than at the equatorial atoms. This effect must be even more pronounced for the (SeS) ligand, having S in the equatorial position, due to the greater electronegativity of S compared to Se and this explains the very short Se ··· Cl distance. Indeed, the statistics of Se–Cl bond lengths displays almost a continuum when one starts from $SeCl_2$ [2.157(3) Å] and $SeCl_4^{2-}$ (2.441 Å), and then considers the $Se\text{–}Cl_{br}$ bonds in $Se_2Cl_6^{2-}$ (2.62–2.73 Å), $Se_2Cl_9^-$ (2.58–2.72 Å), $Se_2Cl_{10}^{2-}$ (2.51–2.80 Å) and arrives at 2.851 Å in the rather asymmetrically bridged $[Se(O)_2(\mu\text{-}Cl)_2Cl_4]^{2-}$.[27] The latter value almost attains the 2.87–2.91 Å interval found for **1a** and **2a**. These shortened contacts can be described using a quantitative parameter, the covalency index f_{cov},[24] expressed as $[R_{vdw}(A) + R_{vdw}(B) - d(AB)][R_{vdw}(A) + R_{vdw}(B) - R_{cov}(A) - R_{cov}(B)]^{-1}$, for an A–B interaction, R_{vdw} and R_{cov} being the van der Waals and covalent radii of respective atoms.[28] In our case, considering the $Se_{ax}\text{–}X$ distances, we obtain for f_{cov} the value 0.54 for **2a** (Se ··· Cl), 0.56 for $[W_3Se_7((EtO)_2PS_2)_3]Br$[18] (Se ··· Br) and even 0.71 for the recently prepared $[W_3Se_7(Et_{23}NCS_2)_3]_2Se$[29] (Se ··· Se). The same approach applied to a series of $[Mo_3S_7(Et_2NCS_2)_3]X$ (X = ClO_4, Cl, I, 1/2S) gave lower f_{cov} values, ranging from 0.21 for the perchlorate salt to 0.60 for the sulfide, the value for chloride being 0.40. These values are in turn in good agreement with spectroscopic data and quantum mechanical calculations.[24] Thus a significant release of electron density from the anion to the cation takes place, and this effect is more pronounced for the $Se_{ax}\text{–}X$ interactions. This is in fact what is to be expected from the application of a simple model of electron density donation from the lone pair at the donor atoms X onto σ* orbitals of the dichalcogen ligand. For Se_2 or SeS this orbital has lower energy than for S_2, and thus is more accessible to binding.

Structure of 3. The cluster molecule **3** is shown in Fig. 3 and its geometrical parameters are given in Table 3. The cluster core Mo_3Se_4 has a very distorted incomplete cubane structure with

Table 3 Selected bond distances (Å) and angles (°) for **3**

Mo(1)–Mo(2)	2.8147(15)	Mo(1)–Mo(3)	2.7322(14)
Mo(1)–Se(1)	2.4658(14)	Mo(1)–Se(2)	2.4165(15)
Mo(1)–Se(4)	2.4255(14)	Mo(1)–S(1)	2.527(3)
Mo(1)–S(2)	2.576(3)	Mo(1)–O(7)	2.237(6)
Mo(2)–Mo(3)	2.8503(15)	Mo(2)–Se(1)	2.4621(15)
Mo(2)–Se(2)	2.4190(15)	Mo(2)–Se(3)	2.4205(14)
Mo(2)–S(3)	2.587(3)	Mo(2)–S(4)	2.545(3)
Mo(2)–N(1)	2.377(7)	Mo(3)–Se(1)	2.4598(14)
Mo(3)–Se(3)	2.4181(14)	Mo(3)–Se(4)	2.4123(14)
Mo(3)–S(5)	2.535(3)	Mo(3)–S(6)	2.561(3)
Mo(3)–O(8)	2.218(6)	S(1)–P(1)	1.995(4)
S(2)–P(1)	1.989(4)	S(3)–P(2)	1.986(4)
S(4)–P(2)	1.994(4)	S(5)–P(3)	1.999(4)
S(6)–P(3)	1.986(4)		
Mo(2)–Mo(1)–Mo(3)	61.82(3)	Se(1)–Mo(1)–Se(2)	108.03(4)
Se(1)–Mo(1)–Se(4)	110.97(4)	Se(1)–Mo(1)–S(1)	83.72(7)
Se(1)–Mo(1)–S(2)	157.16(7)	Se(1)–Mo(1)–O(7)	81.44(15)
Se(2)–Mo(1)–Se(4)	91.65(4)	Se(2)–Mo(1)–S(1)	99.66(7)
Se(2)–Mo(1)–S(2)	88.05(7)	Se(2)–Mo(1)–O(7)	170.38(15)
Se(4)–Mo(1)–S(1)	157.80(7)	Se(4)–Mo(1)–S(2)	83.90(7)
Se(4)–Mo(1)–O(7)	83.15(15)	S(1)–Mo(1)–S(2)	77.51(9)
S(1)–Mo(1)–O(7)	82.75(16)	S(2)–Mo(1)–O(7)	83.37(16)
Mo(1)–Mo(2)–Mo(3)	57.67(2)	Se(1)–Mo(2)–Se(2)	108.07(4)
Se(1)–Mo(2)–Se(3)	106.59(4)	Se(1)–Mo(2)–S(3)	157.75(7)
Se(1)–Mo(2)–S(4)	84.09(6)	Se(1)–Mo(2)–N(1)	84.05(18)
Se(2)–Mo(2)–Se(3)	94.39(4)	Se(2)–Mo(2)–S(3)	87.85(6)
Se(2)–Mo(2)–S(4)	161.31(7)	Se(2)–Mo(2)–N(1)	85.50(17)
Se(3)–Mo(2)–S(3)	86.97(6)	Se(3)–Mo(2)–S(4)	95.59(6)
Se(3)–Mo(2)–N(1)	168.76(18)	S(3)–Mo(2)–S(4)	76.96(8)
S(3)–Mo(2)–N(1)	81.79(18)	S(4)–Mo(2)–N(1)	81.65(18)
Mo(1)–Mo(3)–Mo(2)	60.51(3)	Se(1)–Mo(3)–Se(3)	106.73(4)
Se(1)–Mo(3)–Se(4)	111.63(4)	Se(1)–Mo(3)–S(5)	83.33(7)
Se(1)–Mo(3)–S(6)	157.30(7)	Se(1)–Mo(3)–O(8)	81.34(15)
Se(3)–Mo(3)–Se(4)	91.82(4)	Se(3)–Mo(3)–S(5)	99.15(7)
Se(3)–Mo(3)–S(6)	88.86(7)	Se(3)–Mo(3)–O(8)	171.81(16)
Se(4)–Mo(3)–S(5)	158.15(7)	Se(4)–Mo(3)–S(6)	83.56(6)
Se(4)–Mo(3)–O(8)	83.72(15)	S(5)–Mo(3)–S(6)	77.86(8)
S(5)–Mo(3)–O(8)	82.95(16)	S(6)–Mo(3)–O(8)	83.83(16)

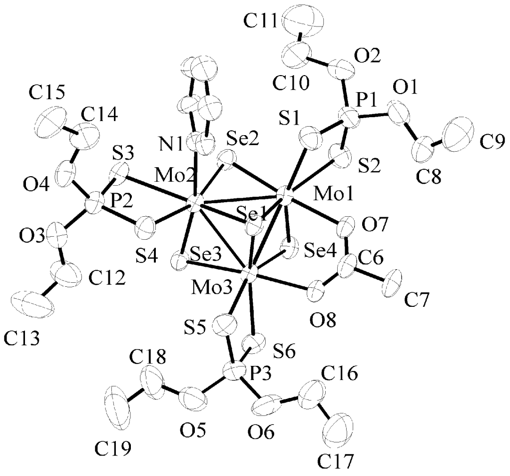

Fig. 3 Molecule of $[Mo_3Se_4((EtO)_2PS_2)_3(\mu\text{-}CH_3COO)(C_5H_5N)]$ in **3** with 50% displacement ellipsoids. The hydrogen atoms and the carbons inside the py ring are omitted for clarity.

three very different Mo–Mo bond distances. The shortest [2.7322(14) Å] corresponds to the Mo(1)–Mo(3) bond with the acetate bridge and reflects its short bite; the longest is Mo(2)–Mo(3) with 2.8503(15) Å and only Mo(1)–Mo(2) [2.8147(15) Å] has a length similar to those found other known Mo_3Se_4 clusters (2.817 Å in $(Me_4N)_5[Mo_3Se_4(NCS)_9]$,[30] 2.793 and 2.817 Å in cucurbituril adducts $[Mo_3Se_4Cl(H_2O)_8]_2(C_{36}H_{36}N_{24}O_{12})Cl_6{\cdot}16H_2O$ and $(H_3O)_2[Mo_3Se_4Cl_5(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})Cl_6{\cdot}15H_2O$,[5] respectively). In the $[W_3S_4(dtp)_3(\mu\text{-}OAc)(py)]{\cdot}0.5DMF$[11] the W–W bond bridged by acetate is again the shortest, however, the other two bonds have almost the same length. This asymmetry in the core does not affect the Mo–μ-Se distances—they vary only slightly in the 2.41–2.42 Å range. The Mo–N (pyridine) bond is rather long, 2.377(7) Å.[11,31] The acetate is coordinated slightly asymmetrically with the distances Mo(1)–O(7) 2.237(6) Å and Mo(3)–O(8) 2.218(6) Å. The coordination polyhedron around Mo can be described (discounting the M–M bonding) as an octahedron. Both acetate oxygens and the nitrogen from pyridine occupy position *trans* with respect to the μ-Se atoms, but *cis* to the μ_3-Se. The three diethyldithiophosphate ligands form four-membered chelate rings with two non-equivalent sulfur atoms: those in the *trans*-position to the μ_3-Se are located at about 0.03–0.04 Å further from Mo than those in the *cis*-position. The same ligand arrangement is also found in $[W_3S_4(dtp)_3(\mu\text{-}OAc)(py)]$.[11] These distances are also significantly longer than in the chalcogen-rich clusters **1a** and **2a**. The molecules of **3** form centrosymmetrical dimers in the crystal lattice (Fig. 4). The intermolecular Se ··· Se distances in the dimer are shorter than 4.0 Å (twice the Se van der Waals radius): Se(3) ··· Se(3′) 3.22, Se(3) ··· Se(4′) 3.41, Se(3) ··· Se(2′) 3.49 Å. All the known M_3Se_4 clusters form similar dimers in the solid state[3–5,30,32,33] and in one case the Se ··· Se distance is even below 3.0 Å (for $[Mo_3Se_4Cl(H_2O)_8]_2(C_{36}H_{36}N_{24}O_{12})Cl_6{\cdot}16H_2O$).[5] The nature of such interactions merits more detailed study.

The ability of the μ-chalcogen atoms in the Mo_3S_4 and Mo_3Se_4 clusters to abstract sulfur from other sources was also tested in the reaction of $[Mo_3S_4(dtp)_4(H_2O)]$[10] and **3** with propylene sulfide in acetonitrile. Reaction was found to be fast and efficient, leading to the corresponding chalcogen-rich species, $[Mo_3S_7(dtp)_3]^+$ and $[Mo_3S_4Se_3(dtp)_3]^+$, isolated in high yield as chlorides and identified by elemental analysis and FAB-MS. Thus **3** and related M_3Q_4 clusters (M = Mo, W; Q = S, Se) may be of interest as desulfurization agents, *e.g.*, in organic synthesis.

Table 4 Crystallographic data for **1a**, **2a** and **3**

Compound	**1a**	**2a**	**3**
Formula	$C_{12}H_{30}O_6Mo_3P_3S_9Se_4Cl$	$C_{12}H_{30}O_6P_3S_9Se_4W_3Cl$	$C_{21}HMo_3N_3O_8P_3S_6Se_4$
Formula weight	1290.77	1554.71	1335.25
Space system, group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
a/Å	13.146(3)	13.146(3)	13.332(5)
b/Å	22.466(4)	22.466(4)	13.709(5)
c/Å	13.916(2)	13.916(2)	15.347(5)
a/°	90	90	108.660(5)
β/°	114.244(15)	114.244(15)	107.910(5)
γ/°	90	90	102.110(5)
V/Å^3	3747.4(13)	3747.4(13)	2376.4(15)
Z	4	4	2
D_{calc}/g cm^{-3}	2.235	2.756	1.866
μ/mm^{-1}	5.601	13.800	4.246
Crystal size/mm	0.20 × 0.30 × 0.80	0.15 × 0.20 × 0.40	0.20 × 0.30 × 0.50
F(000)	2472	2856	1252
θ_{min}–θ_{max}/°	2.4; 30.4	2.4; 30.6	2.8; 30.4
Total/Unique reflections; R_{int}	11775/11339; 0.068	11814/11399; 0.075	14908/14361; 0.053
Observed reflections [$I \geq 2.0\sigma(I)$]	3648	4756	6380
N_{ref}, N_{par}	11339, 340	11399, 345	14361, 455
R, wR, GooF	0.0772, 0.2119, 0.980	0.0597, 0.1874, 0.90	0.0553, 0.1550, 1.05
w	$1/[s^2(F_o)^2 + (0.1252P)^2]^a$	$1/[s^2(F_o)^2 + (0.0964P)^2]^a$	$1/[s^2(F_o)^2 + (0.0597P)^2]^a$
Min./max. residual density/e Å^{-3}	−1.97/1.94	−1.51/1.86	−0.83/0.91

[a] $P = (F_o^2 + 2F_c^2)/3$.

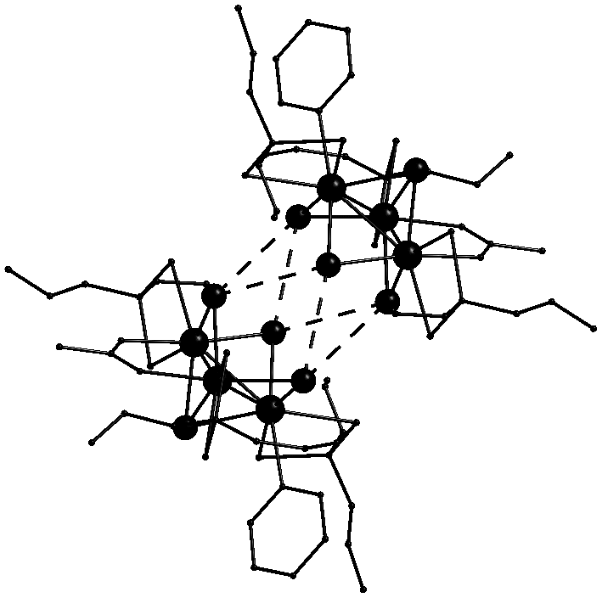

Fig. 4 The $\{[Mo_3Se_4((EtO)_2PS_2)_3(\mu\text{-}CH_3COO)(C_5H_5N)]\}_2$ dimer in the structure of **3**, with short Se ··· Se contacts shown as dashed lines.

Experimental

Preparation

All the manipulations were done in air. The stock solutions of $[M_3Se_4(H_2O)_9]^{4+}$ were prepared according to the published procedure.[34] P_4S_{10} (Aldrich, 99%) was used as purchased. Propylene sulfide (96%+) was from Aldrich. All the other reagents and solvents were of commercial grade and were used without further purification. Elemental analyses were performed on an EA 1108 CHNS-O microanalytical analyzer. FAB mass spectra were recorded in a VG AutoSpec High resolution Micromass. Only the peaks resulting from the most abundant isotopes are given. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 instrument. Chemical shifts were measured relative to external 85% H_3PO_4; chloroform was used in all cases.

$[Mo_3Se_4S_3((EtO)_2PS_2)_3]Cl$ (1a). To a 20 ml solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl (10 mM) a solution of 2 g P_4S_{10} in 10 ml EtOH, prepared immediately before the reaction, was added. A copious red–brown precipitate appeared which was filtered the next day, washed with water, EtOH, CH_3CN and recrystallized from chloroform to give orange crystals by slow evaporation of the solvent. Yield 70%. Analysis: Found C, 11.00; H, 2.17; S, 21.71. Calc. for $C_{12}H_{30}ClMo_3O_6P_3S_9Se_4$: C, 11.16; H, 2.35; S, 22.35%. ^{31}P NMR: δ −0.88. ^1H NMR: δ 4.22, 4.20, 4.17, 4.15, 4.12 (12H, m); 1.41, 1.39, 1.37 (18H, t). FAB-MS m/e 1256 ($[M]^+$, 100%).

The other compounds $[M_3(\mu_3\text{-}Se)(\mu\text{-}SeS)_3((RO)_2PS_2)_3]Cl$ (**1b**, orange, R = i-Pr; **2a**, M = W, R = Et; **2b**, M = W, R = i-Pr) were prepared by the same protocol with necessary changes in the reagents.

1b. Yield 75%. Analysis: Found C, 15.80; H, 3.12; S, 20.98. Calc. for $C_{18}H_{42}ClMo_3O_6P_3S_9Se_4$: C, 15.72; H, 3.09; S, 20.91%. FAB-MS m/e 1340 (50%, $[M]^+$), 1276 (100%, $[M - 2S]^+$). ^{31}P NMR: δ −7.79. ^1H NMR: δ 4.90, 4.88, 4.86, 4.84, 4.82, 4.81, 4.79, 4.76, 4.74, 4.72 (6H, m); 1.42, 1.41, 1.39, 1.38, 1.36, 1.33, 1.32 (36H, m).

2a. Yield 81%. Analysis: Found C, 9.27; H, 1.89. Calc. for $C_{12}H_{30}ClO_6P_3S_9Se_4W_3$: C, 9.27; H, 1.95; S, 13.56%. ^{31}P NMR: δ 12.83. ^1H NMR: δ 4.34, 4.31, 4.29, 4.27 (6H, quartet); 4.30, 4.28, 4.26, 4.23 (6H, quartet); 1.45, 1.43, 1.41 (18H, t).

2b. Yield 73%. Analysis: Found C, 13.11; H, 2.51; S, 17.91. Calc. for $C_{18}H_{42}ClO_6P_3S_9Se_4W_3$: C, 13.19; H, 2.16; S, 17.61%. ^{31}P NMR: δ 9.28. ^1H NMR: δ 4.93 (6H, septet), 1.43, 1.41 (36H, d). FAB-MS m/e 1602 (100%, $[M]^+$).

$[Mo_3Se_4((EtO)_2PS_2)_3(\mu\text{-}CH_3COO)(C_5H_5N)]\cdot 2CH_3CN$ (3). To a 25 ml solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl (1.15 mM, 0.0287 mmol) 26 mg (0.115 mmol) of $KS_2P(OEt)_2$ was added. A brown precipitate appeared immediately, leaving a colourless solution. The precipitate was collected by filtration and dissolved in 20 ml of CH_3CN to which acetic acid, pyridine and DMF were added (10 drops of each reagent). Slow evaporation of the resulting brown solution produced black crystals of X-ray quality. Yield 30 mg (80%).

Reactions with propylene sulfide

To a dark-brown solution of **3** in acetonitrile three drops of propylene sulfide were added. A light-brown precipitate separated in 30 minutes. It was collected by filtration, dissolved in $CHCl_3$ giving a red solution and stirred with an equal volume of 4 M HCl. The organic layer was then separated and allowed to evaporate slowly. Red crystals were identified as $[Mo_3Se_4S_3((EtO)_2PS_2)_3]Cl$ (**1a**) by FAB-MS and elemental analysis. Yield was quantitative. By an analogous procedure, brown $[Mo_3S_4(dtp)_4(H_2O)]$ was quantitatively converted (reaction time 5 hours in this case) into yellow–orange $[Mo_3S_7((EtO)_2PS_2)_3]Cl$, previously reported in ref. 25.

Crystallography

Single crystals of **1a** and **2a** were obtained by slow evaporation of chloroform solutions. The data collection for all samples was performed at room temperature on an Enraf-Nonius CAD4 diffractometer. Because single crystals of **3** disintegrated rapidly once removed from the mother liquor (due to solvent molecule loss) the data were collected from a crystal sealed into a glass capillary with a drop of the mother liquor. Graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) was employed. No decay was observed for any sample. The structures were solved by direct methods (SIR97)[35] and expanded by Fourier synthesis (SHELX-97).[36] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atom positions were calculated using a riding model and a global isotropic thermal parameter was refined. In the case of **1a** a disorder was observed in the orientation of the ethyl groups in the dtp ligands, in particular for C(7) and C(8) carbon atoms, which is responsible for the large isotropic thermal parameter of O(4). Several disorder models were tried, but the data quality did not allow us to improve the refinement. In this case the hydrogen atoms were not included in the refinement. The crystallographic details are summarized in Table 4.

CCDC reference numbers 175188–175190.

See http://www.rsc.org/suppdata/dt/b1/b105682b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

M. S. is very grateful to the Spanish Ministerio de Educación y Cultura for a research grant with the Program "Estancia de jóvenes científicos y tecnólogos en España". We also thank the Ministerio de Educación y Cultura for a research grant (PM-98-0148). Thanks are also due to Consejería de Educación, Cultura y Deportes del Gobierno de Canarias for financial support through grant COFI2000/11 and to the C.I.C.Y.T. for grant FDI-1427.

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