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Inheritance of the guanidinium chloride structure in two molybdenum (II) chloride salts

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Abstract

Depending on the proticity of the solvent, two different salts may be crystallized from the combination of solutions of guanidinium chloride, $C(NH_2)_3Cl$, and the acidic hydrate of molybdenum dichloride, $[(Mo_6Cl_8)Cl_6](H_{20}O_9)$. From aprotic solvents such as dimethyl sulfoxide (DMSO) or formamide (FA), compound I, $[(Mo_6Cl_8)Cl_6]Cl_6(C(NH_2)_3)_8$, crystallizes, while from protic solvents such as ethanol or water, compound II, $[(Mo_6Cl_8)Cl_6]Cl_3(C(NH_2)_3)_5$, crystallises. In both compounds, the basic motif of the two parent structures, the octahedral $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster and the planar, triangular, $C(NH_2)_3Cl_3$ entity are fairly well preserved. The assembly of the blocks, however, differs distinctly, and while both compounds are rather porous, compound I (s.g. $Fm\bar{3}m$, No. 225) has a volume of 27 Å^3/non-hydrogen atom, compound II (s.g. $C2/c$, No. 15) is somewhat denser, with a volume of 24 Å^3/non-hydrogen atom. ***To cite this article: A. Flemström et al., C. R. Chimie 8 (2005)***.
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Résumé

En fonction du caractère donneur de protons du solvant utilisé, deux sels différents peuvent être cristallisés par interaction de solutions de chlorure de guanidine, $C(NH_2)_3Cl$, et d'hydrate acide de dichlorure de molybdène, $[(Mo_6Cl_8)Cl_6](H_{20}O_9)$. Le composé I $[(Mo_6Cl_8)Cl_6]Cl_6(C(NH_2)_3)_8$ cristallise à partir de solvants aprotiques, tels que le diméthylsulfoxide (DMSO) ou le formamide (FA), tandis que le composé II $[(Mo_6Cl_8)Cl_6]Cl_3(C(NH_2)_3)_5$ cristallise à partir de solvants protiques, tels que l'éthanol ou l'eau. Dans les deux composés, les motifs de base présents dans chacune des deux structures de départ, le cluster octaédrique $[(Mo_6Cl_8)Cl_6]^{2-}$ et l'entité triangulaire plane $C(NH_2)_3Cl_3$ sont bien conservés. Cependant, bien que ces deux composés soient plutôt poreux, l'assemblage de ces blocs diffère significativement et le composé I ($Fm\bar{3}m$, n° 225) a un volume de 27 Å^3/atome non-hydrogène, tandis que le composé II ($C2/c$, n° 15) est plus dense, avec un volume de 24 Å^3/atome non-hydrogène. ***Pour citer cet article : A. Flemström et al., C. R. Chimie 8 (2005)***.
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Keywords: Molybdenum octahedral cluster; Guanidine; Crystal structure; Single-crystal X-ray diffraction

Mots clés : Cluster octaédrique de molybdène ; Guanidine ; Structure cristalline ; Diffraction des rayons X sur monocristal

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1. Introduction

The interest in solid-state organic–inorganic hybrid materials is motivated by their potential applications in such diverse fields as ion exchange [1,2], hydrogen storage [3], magnetism [4,5], luminescence, [6] and catalysis [7]. The attraction lies in combination of vast combinatorial libraries available from the merger of rigid inorganic cluster nuclei with the flexible fine-tunable organic counterparts. What is achieved is a concept that allows for simultaneous predictability and variability. The supramolecular nature of the composites does away with the need for major chemical reactions and this enhances structural predictability. Particular attention has been given to systems based on the octahedral $M_6X_8Y_6$ and M_6X_{12} clusters that are formed by many of the early transition metals with chalcogens and halogens [8–12] while the organic groups may be chosen to tune connectivity and properties alike [13,14].

The molybdenum (II) chloride cluster $([Mo_6Cl_8]Cl_6)^{2-}$ has been known since the pioneering crystallographic work of Brosset [15] in 1945. The compound was however described already by Blomstrand [16] in 1859. It was clear from the very first investigations that although several different hydrates form at different pH, all phases retain the same basic structural entity up till neutral pH values. At higher pH values, Mo is reduced to the metal in aqueous solution. Subsequent investigations [3–5] have unravelled the relationships between the structure of the hydrates and the pH of the mother liquor. The cluster is a strong promoter of hydrogen bonding, and the known hydrates all show remarkable water structures. The work presented here is part of a larger effort to understand how this cluster may be used as a structure-directing agent in various media.

2. Experimental

2.1. Synthesis

As starting materials for the syntheses, the acidic hydrate of molybdenum dichloride, $[(Mo_6Cl_8)Cl_6]$-$(H_{20}O_9)$, henceforth Mo(II)acid, prepared from $MoCl_5$ and elemental Mo as previously decribed [17] was used. All other reagents were from commercial sources used without further purification.

Compound I was synthesised by mixing saturated solutions of Mo(II)acid and guanidinium chloride in DMSO or in FA in the proportions 3:1 by volume. Square platelets of crystallographic quality had precipitated after 24 h at 280 K.

Compound II was prepared by first saturating a solution of 2 parts concentrated HCl and 1 part glacial acetic acid with Mo(II)acid and then mixing this solution in the proportions 3:1 with a saturated solution of $C(NH_2)_3Cl$ in water. From this mixture, needle-shaped crystals precipitated almost immediately. At room temperature, the aspect ratio of the crystals is quite extreme, but if the crystal growth takes place at 280 K, rhombohedral crystals, more suitable for X-ray investigations, form. Replacing either the HCl/HAc solution of Mo(II-)acid or the H_2O solution of $C(NH_2)_3Cl$ or both with the corresponding solutions in EtOH also produced compound II. Replacing $C(NH_2)_3Cl$ by $C(NH_2)_3NO_3$ still yielded compound II, and it appears difficult to reduce the Cl content (and hence enhance the condensation) of the product without introducing further counter-ions.

2.2. Structure determination

Single crystal X-ray data were collected on a STOE IPDS with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. For both compounds, the atomic positions (Mo and Cl) for the Mo(II)cluster were determined using direct methods using the program Shelxs-97 [18]. All other non-hydrogen atoms were located using difference electron density calculations in the software package JANA2000 [19]. Amine hydrogens were added using geometric constraints on angles (H–N–H = H–N–C = $2\pi/3$) and distances (N-H = 0.9 Å). For compound I, the Laue symmetry was cubic, $m\bar{3}m$ and the systematic absences indicated a F-centered lattice. The space group $Fm\bar{3}m$ and a preliminary model from direct methods refined smoothly to a satisfactory result. For compound II, the Laue symmetry was trigonal $\bar{3}m$ and the systematic extinctions indicated rhombohedral centering and a c-glide perpendicular to [100], although there were a few very weak violations of this condition. A solution in the space group $R\bar{3}c$ refined to an acceptable R-value, but there was a region around the rotation triad that displayed relatively large residual densities that could be modelled as a centered tetrahedron with centre-to-vertex distances close to those for the C–N bonds in the $C(NH_2)_3^+$ ion. The most reasonable interpretation was that of a $C(NH_2)_3^+$ disordered over the three orientations given by the rotation triad. Refining the occupancies of the 'CN_4' unit corroborated this, giving full occupancy for the N atom sitting on the triad, and 2/3 occupancy for those off this axis. For the C atom on the axis the thermal parameter was large, indicating either partial occupancy, or a true position slightly displaced from the axis, or both. Such a behaviour may be caused by twinning, and reconsidering the weak violations of the *c*-glides, these may be caused by a lowering of the space group, breaking the three-fold rotational symmetry and preserving the c-glide in one out of three directions. The superposition of the diffraction patterns from individuals with different orientations would then restore the three fold symmetry of the diffraction pattern, and allow for weak violations of the conditions associated with the c-glide extinctions. Transforming the cell, lowering the symmetry to *C*2/*c* and treating the structure as a pseudo merohedral twin reduced the *R*-value and resolved the problem of the strange CN_4 unit. It was not possible to allow a full refinement of the guanidinium C atom that tended to retain the position on the former triad unless constrained. Electron density calculations of the final model however show excellent agreement between model and data, and there were no major residual electron densities in the final refinement. It would appear that the close proximity between the three C positions generated by the pseudo-merohedral twinning in conjunction with the perfectly trigonal data set produces a 'gravity effect', mergir effect, and the refinement is quite stable. In the final model, it was deemed expedient to use a fully rigid modelng the three positions unless hindered. For the N positions that are more clearly separated, there is no simila for the $C(NH_2)_3^+$ unit applicable to both the positions on the former hexad and to the other, crystallographically independent guanidinium ion positions. Pertinent crystallographic data are given in Tables 1a and 1b.

3. Discussion

3.1. Fractional atomic parameters are given in Tables 2 and 3a,3b

For a discussion of the structures it is instructive first to consider the structure of guanidinium chloride, $C(NH_2)_3Cl$ itself. Here, each guanidinium ion forms

Table 1a
$[(Mo_6Cl_8)Cl_6]Cl_6(C(NH_2)_3)_8$ (I)

Crystal data		***Refinement***	
Formula weight (g/mol)	1764.81	Refinement on	F^2
$\rho_{\text{X-ray}}$ (g/cm^3)	1.8879	*R*, *Rw*	0.0387; 0.028
ρ_{measured} (g/cm^3)	1.9396	Weighting scheme	$1/\sigma^2$
Crystal system	Cubic	No of refls used	536
Space group	$Fm\bar{3}m$ (no.225)	No of parameters used	27
a (Å)	18.380(2)	Residual electron density (e Å^{-1})	–1.5; 1.0
Z	4		
2θ range	3.8–52.0		
Crystal size (mm)	0.16x 0.15x 0.15		
μ (mm^{-1})	2.07		
Data collection			
Diffractometer	STOE IPDS		
Collection method	Φ-scan		
Adsorption correction	Numerical f shape		
Radiation type	Mo-Kα		
Wavelenght	0.71073		
$T_{\min}$; $T_{\max}$	0.734; 0.836		
No of measured relfs.	12303		
No of independent refls.	536		
Criterion of obs refls.	$F^2>3\sigma(F^2)$		
R_{int}	0.1151		
h, k, l range	22; -22		

Table 1b
$[(Mo_6Cl_8)Cl_6]Cl_3(C(NH_2)_3)_5$ (II)

Crystal data		***Refinement***	
Formula weight (g/mol)	1478.45	Refinement on	F^2
$\rho_{\text{X-ray}}$ (g/cm^3)	2.414	*R*, *R*w	0.0299; 0.0295
Crystal system	Monoclinic	Weighting scheme	$1/\sigma^2$
Space group	*C*2/c (no. 15)	No of refls used	4389
a (Å)	10.890(1)	No of parameters used	123
b (Å)	40.113(1)	Residual electron density (e Å^{-1})	–2.7; 1.6
c (Å)	23.463(8)		
β (°)	156.61		
Z	4		
2θ range	4.1—52.0		
Crystal size (mm)	0.22x 0.27x 0.29		
μ (mm^{-1})	2.94		
Data collection			
Diffractometer	STOE IPDS		
Collection method	Φ-scan		
Adsorption correction	Numerical f shape		
Radiation type	Mo Kα		
Wavelenght	0.71073		
T_{min}; T_{max}	0.4956; 0.6326		
No of measured relfs.	15928		
No of independent refls.	4389		
Criterion of obs refls.	$F^2>3\sigma(F^2)$		
R_{int}	0.0104		
h range	–13; 12		
k range	–12; 13		
l range	–72; 72		

Table 2
Atomic coordinates and isotropic displacement parameters (in Å^2) For (I)
$[(Mo_6Cl_8)Cl_6]Cl_6(C(NH_2)_3)_8$

Atom	Wyck.	*x*	*y*	*z*	*U*	
Mo1	24*e*	1/2	0.09994(6)	0		
Cl1	32*f*	0.4050 (1)	0.4050	0.4050		
Cl2	24*e*	1/2	0.2312	0		
Cl3	24*d*	1/4	1/4	0		
C1	32*f*	0.1583(1)	0.1583	0.1583		
N1	96*j*	0.130 (2)	0.131 (1)	0.218(1)	0.5	
H1	96*j*	0.15027	0.09410	0.23838		
Anisotropic displacement parameters (in Å^2)						
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.0282(6)	0.0227(6)	0.0282	-	-	-
Cl1	0.0368(9)	0.0368	0.0368	0.0070(8)	0.0070	0.0070
Cl2	0.0652(1)	0.0259(1)	0.0652	-	-	-
Cl3	0.083(2)	0.083	0.041(3)	-0.023)(3)	-	-
C1	0.071(6)	0.071	0.071	0.020(7)	0.020	0.020
N1	0.17(3)	0.059(1)	0.117(1)	0.046(8)	0.09258(2)	0.042(1)

strong hydrogen bonds (2.4–2.6 Å) to three surrounding Cl-ions, forming large triangular assemblies. Each Cl-ion, is likewise surrounded by three guanidinium ions and the whole structure is composed of two mutually interpenetrating (10,3) networks (Fig. 1a–1b) separated by a gyroid type surface. Such arrangements have recently been discussed by Lee et al. [20]. A second set of more weakly coordinated Cl-ions may be identified

Table 3a
Atomic coordinates and isotropic displacement parameters (in Å^2) for (II) [$(Mo_6Cl_8)Cl_6$]$Cl_3(C(NH_2)_3)_5$

Atom	Wyck	*x*	*y*	*z*	*U*
Mo1	8f	0.5575 (1)	–0.3919(1)	–0.8377(2)	
Mo2	8f	–0.9208 (1)	–0.0296 (1)	–0.1134(2)	
Mo3	8f	0.3626 (1)	0.5288 (1)	0.0047(2)	
Cl1	8f	0.5023(7)	–0.3977(4)	–0.9478(8)	
Cl2	8f	0.6146(6)	–0.3982(4)	–0.7436(6)	
Cl3	8f	–0.8493(5)	–0.1572(4)	–0.2634(6)	
Cl4	8f	0.2417(4)	0.4507(3)	0.9535(6)	
Cl5	8f	–0.3252(5)	0.0653(5)	0.0105(9)	
Cl6	8f	–0.3629(9)	0.7489(5)	0.3747(8)	
Cl7	8f	0.6925(5)	0.4308(4)	0.7391(7)	
Cl8	4e	0.5042(9)	0	–1/4	
Cl9	8f	0.4984(7)	–0.2787(5)	–0.8897(9)	
C2a	4e	0.346(1)	1/2	3/4	0.0396(7)
N21a	8f	0.286(1)	0.5701	0.8495	0.0570(6)
N23a	4e	0.468(1)	1/2	3/4	
H21a	8f	0.323(1)	0.6125	0.9097	0.110(7)
H23a	8f	0.504 (1)	0.5421	0.8098	
H25a	8f	0.212 (1)	0.5701	0.8495	
C2b	8f	–0.1705(9)	0.3220(5)	0.3973(8)	
N21b	8f	–0.0671(9)	0.3509(5)	0.4207(8)	
N22b	8f	–0.2182(9)	0.3578(5)	0.4991(8)	
N23b	8f	–0.2262(9)	0.2573(5)	0.2719(8)	
H21b	8f	–0.0382(9)	0.3292(5)	0.3591(8)	
H22b	8f	–0.2808(9)	0.3403(5)	0.4849(8)	
H23b	8f	–0.1976(9)	0.2358(5)	0.2107(8)	
H24b	8f	–0.2884(9)	0.2399(5)	0.2578(8)	
H25b	8f	–0.0333(9)	0.3901(5)	0.4967(8)	
H26b	8f	–0.1844(9)	0.3970(5)	0.5751(8)	
C2c	8f	0.0171(3)	0.3391(2)	0.1546(4)	
N21c	8f	0.0294(3)	0.4009(2)	0.2144(4)	
N22c	8f	0.1105(3)	0.2886(2)	0.0859(4)	
N23c	8f	–0.0885(3)	0.3279(2)	0.1635(4)	
H21c	8f	–0.0271(3)	0.4315(2)	0.2560(4)	
H22c	8f	0.1030(3)	0.2512(2)	0.0497(4)	
H23c	8f	–0.1446(3)	0.3583(2)	0.2048(4)	
H24c	8f	–0.0959(3)	0.2908(2)	0.1276(4)	
H25c	8f	0.0935(3)	0.4076(2)	0.2089(4)	
H26c	8f	0.1745(3)	0.2954(2)	0.0805(4)	

Table 3b
Anisotropic displacement parameters (in Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.033(1)	0.027(1)	0.033 (1)	–0.0025	–0.0023(8)	0.0281(1)
Mo2	0.034 (1)	0.0384(1)	0.041(1)	0.0062(9)	0.0075(9)	0.0375(1)
Mo3	0.0289(12)	0.037 (1)	0.043(1)	0.0035(9)	0.0024(9)	0.0377(1)
Cl1	0.050(3)	0.033(3)	0.050(3)	0.006(3)	0.004(3)	0.039(3)
Cl2	0.069(4)	0.038(3)	0.039(3)	–0.019(3)	–0.025(3)	0.035(3)
Cl3	0.044(3)	0.054(3)	0.067(3)	0.023(2)	0.024(2)	0.057(3)
Cl4	0.033(2)	0.044(3)	0.050(3)	0.008(2)	0.015(2)	0.044(3)
Cl5	0.036(3)	0.096(5)	0.129(6)	0.005(3)	–0.005(3)	0.107(5)
Cl6	0.114(6)	0.033(3)	0.045(4)	–0.027(4)	–0.021(4)	0.032(3)
Cl7	0.045(2)	0.073(3)	0.065(3)	–0.001(2)	0.002(2)	0.066(3)
Cl8	0.043(4)	0.060(6)	0.056(4)	–	–	0.055(5)
Cl9	0.048(3)	0.056(4)	0.063(4)	–0.006(4)	–0.005(4)	0.056(4)

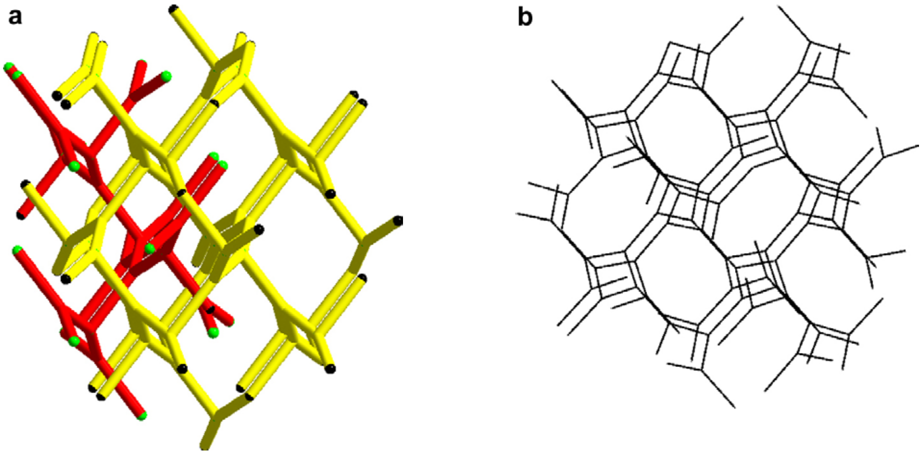

Fig. 1. **(a)** The two interpenetrating (10,3) networks in the guanidinium chloride viewed slightly off the (0 0 1) direction. **(b)** The single network in the $SrSi_2$ type structure slightly off the (1 0 0) direction.

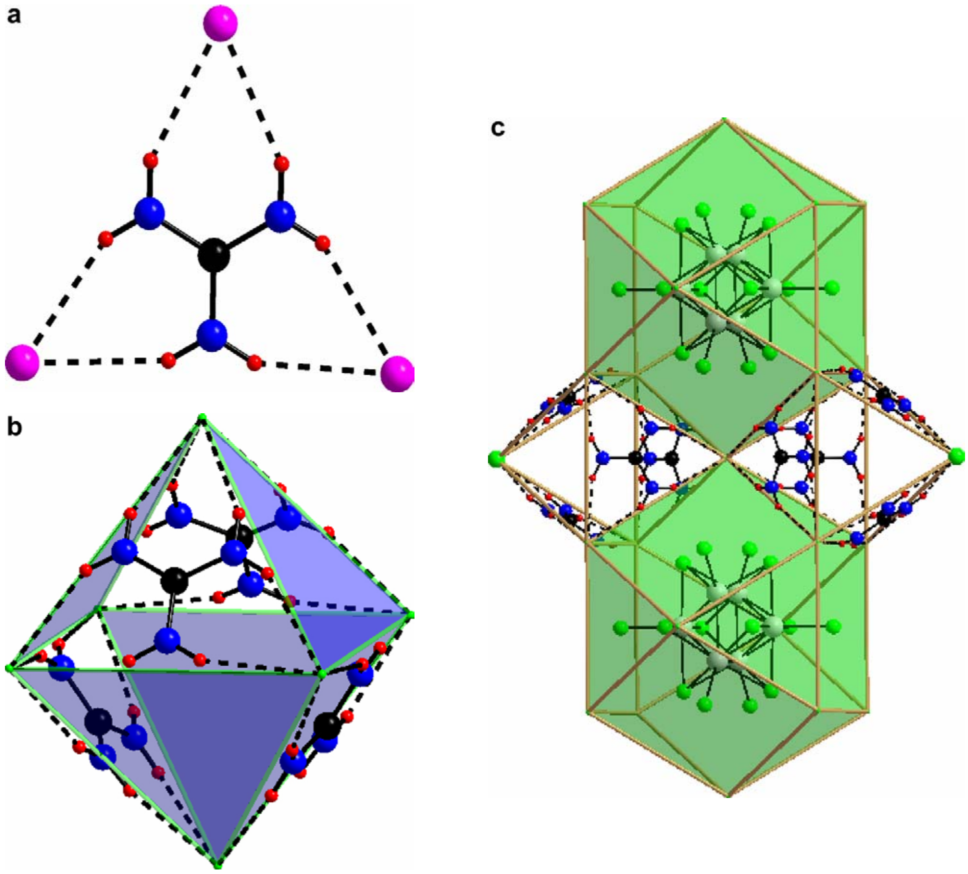

Fig. 2. **(a)** The triangular $C(NH_2)_3^+$ with its chlorine surrounding in compound I. **(b)** The guanidinium chloride octahedron, for clarity the triangles without any guanidinium molecules are light blue. **c)** The triangles in a) form a network via vertex sharing *à la* ReO_3. The Mo(II)-clusters sit in half of the cube-octahedron cavities.

with Cl–H distances ranging from 3.25 Å and up. In structure I, the local arrangement around the guanidinium molecule is identical to that in $C(NH_2)_3Cl$, but the connectivity is different, and the triangular units form closed cages that clathrate the octahedral $[Mo_6Cl_{14}]^{2-}$ (Fig. 2a–2c) cluster. Again the Cl-H distance is around 2.5 Å. There is no strong direct hydrogen bonding between the $C(NH_2)_3^+$ ion and the Cl of the cluster unit, the typical closest distances between terminal cluster Cl-ions and guanidinium H start at 3.25 Å. In compound II there are two distinct local geometries for the guanidinium ion. (Fig. 3). Two out of the three symmetrically independent ions adopt the typical configuration of the $C(NH_2)_3Cl$ structure, form-

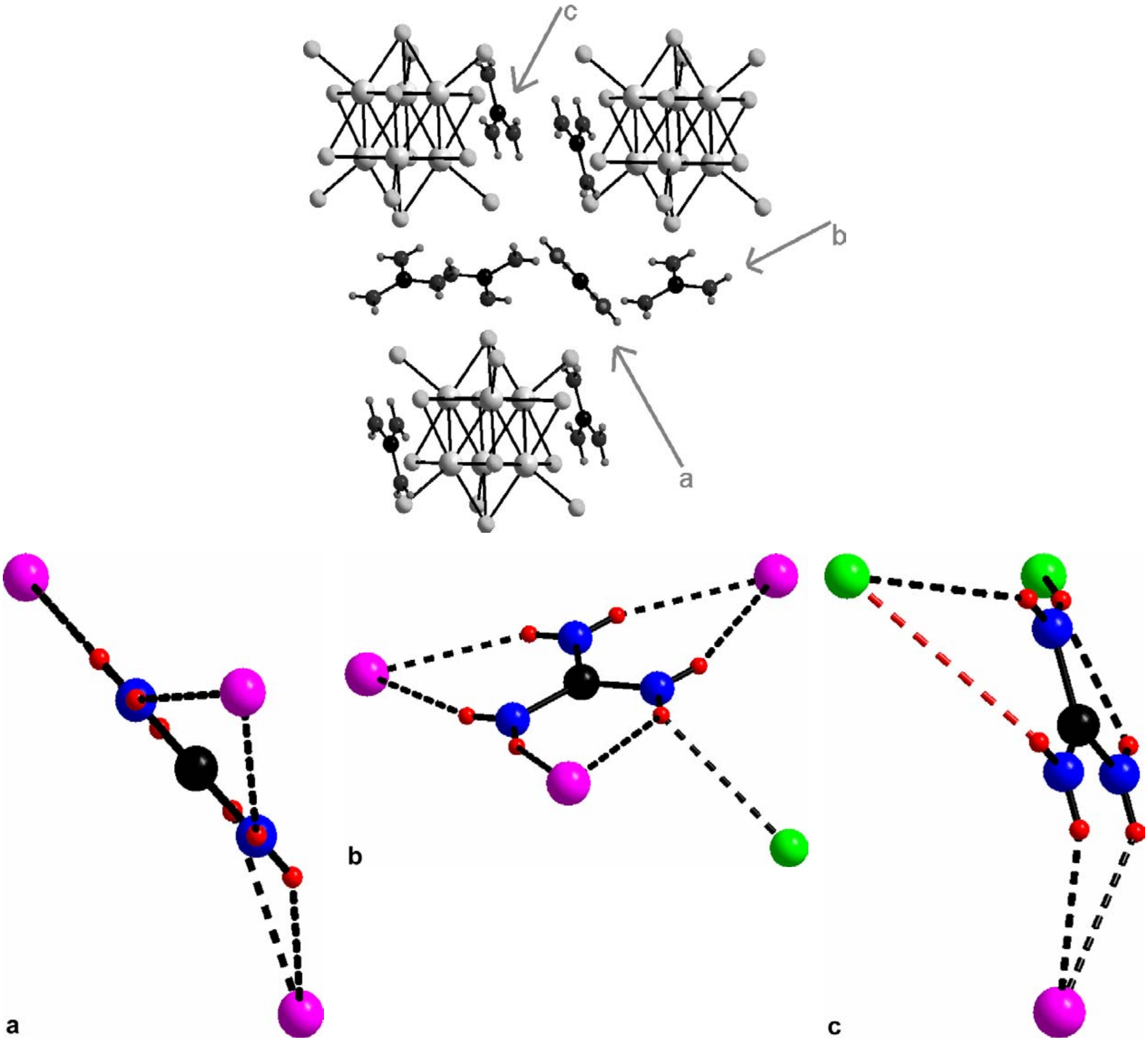

Fig. 3. An overview of the guanidinium molecules in compound II. **(a)** The hydrogen bonded chloride surrounding guanidinium molecule. **(b)** The hydrogen bonded chloride surrounding guanidinium molecule. **(c)** The hydrogen bonded chloride surrounding guanidinium molecule; red bond slightly longer (3.34 Å).
For al: green, cluster chloride; purple, free chloride; black, carbon; blue, nitrogen; red, hydrogen.

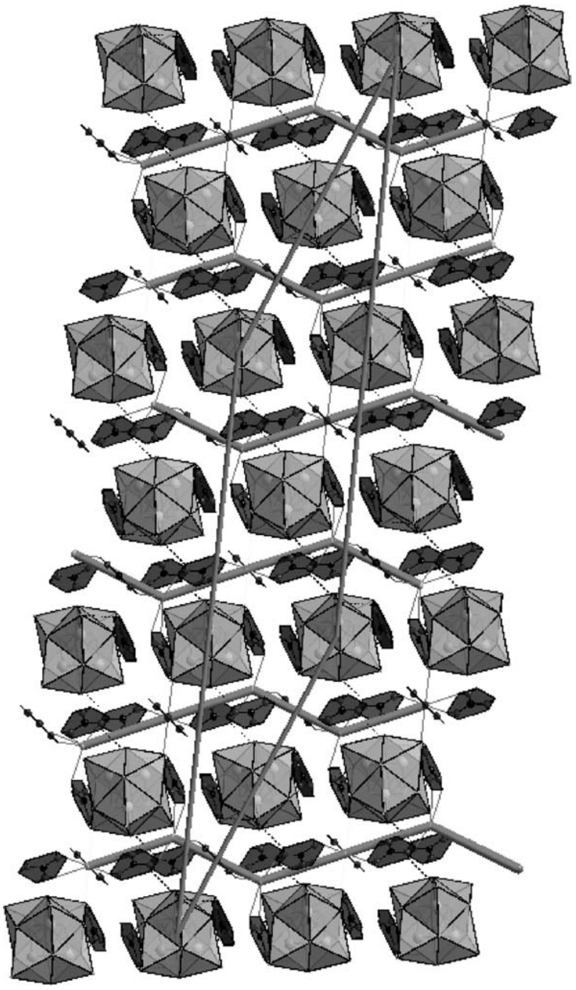

Fig. 4. The slightly puckered layer of guanidinium and free chlorides in compound II.

ing a slightly puckered layer (a 3^6 net) together with non-cluster Cl (Fig. 4). The second kind of guanidinium ions connects the layers and couples directly to the octahedral $[Mo_6Cl_{14}]^{2-}$ clusters that are situated between the layers. The triangular units are generally much less regular in this compound, and the Cl-H distances range from 2.5 to 3.1 Å for both non-cluster Cl and terminal cluster Cl. A complication that arises is that the generally inert μ^3-bonded cluster chlorines exhibit distances around 3.0 Å as well, although these are hardly bonding.

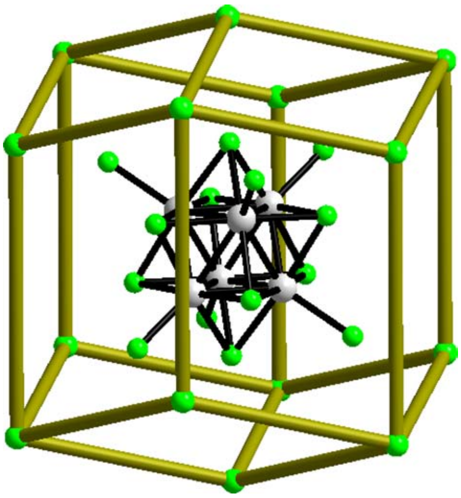

Fig. 5. The rhombic dodecahedron built up by non cluster Cl^- surrounding the Mo(II)- cluster in compound II.

In both compounds the $[Mo_6Cl_{14}]^{2-}$ cluster is encaged in a network formed by guanidinium and non-cluster chloride. In compound I this is very clear-cut, and the direct bonding between the cluster chlorides and the $C(NH_2)_3$–Cl network is weak while in compound II direct bonding between the clusters and the latter network is evident. The cages in compound II are all identical. They may be defined by the free chloride ions that form an elongated rhombic dodecahedron (Fig. 5). All these are centered by the $[Mo_6Cl_{14}]^{2-}$ clusters. In compound I, in contrast, the $C(NH_2)_3$-Cl network forms two different kinds of cages; octahedral and cube-octahedral, in an arrangement reminiscent of the perovskite structure. Here, all the octahedral, and half the cube-octahedral voids are empty, creating a highly porous structure.

3.2. Unit cell views of compounds I and II are shown in Figs. 6a and 6b

To verify the high porosity of compound I, the density calculated from X-ray data was compared to density measurements with a 0.1 cm^3 sample holder in a AccuPyc 1330 pycnometer from Micromeritics. The results from x-ray analysis is 1.8879 g/cm^3 and from the pycnometer, 1.9396(9) g/cm^3, the difference of 0.0517 g/cm^3 in reasonable agreement with the X-ray calculations.

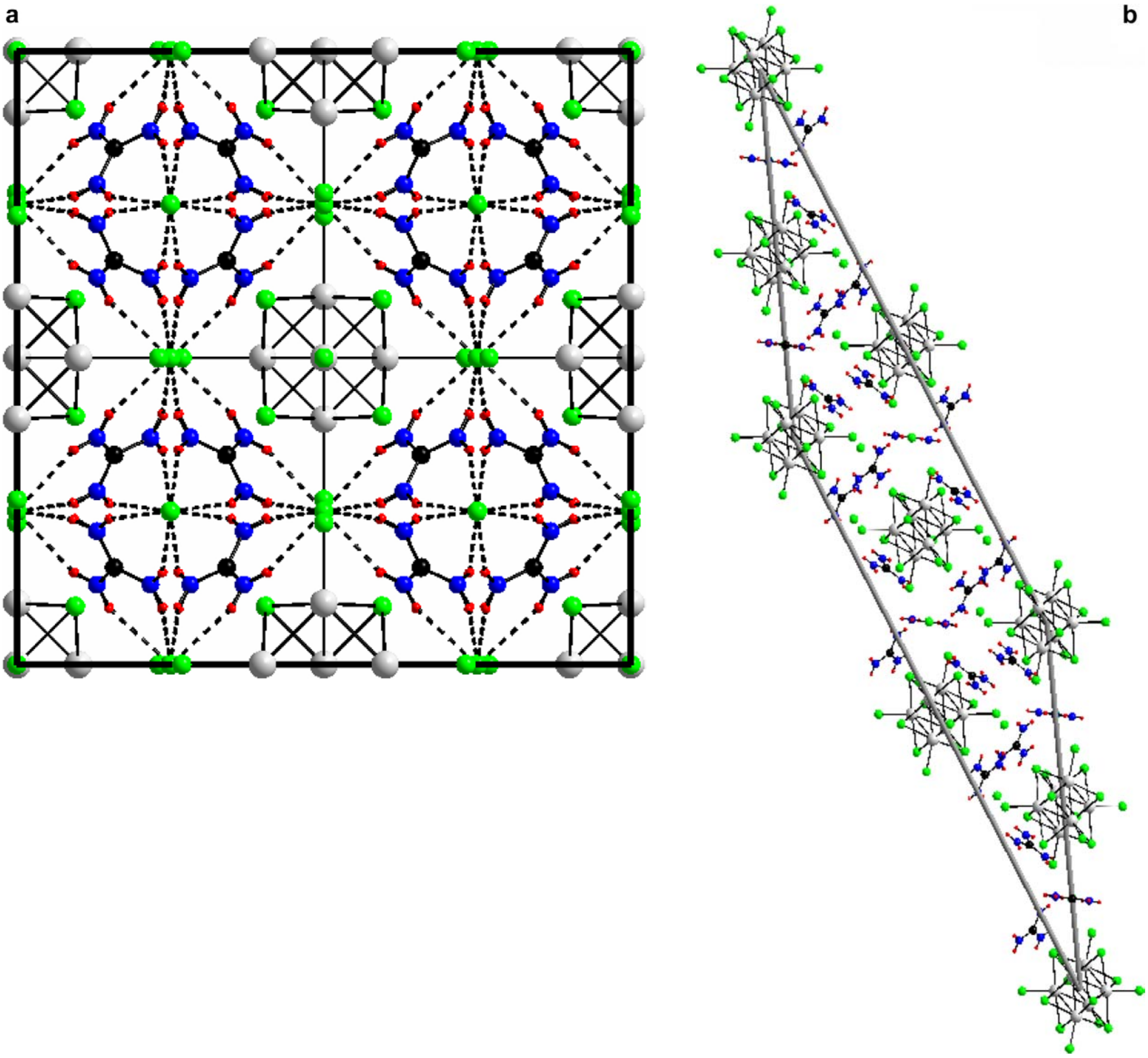

Fig. 6. **(a)** The unit cell of compound (I) $[(Mo_6Cl_8)Cl_6]Cl_6(C(NH_2)_3)_8$ along (1 0 0). **(b)** The unit cell of compound (II) $[(Mo_6Cl_8)Cl_6]Cl_3(C(NH_2)_3)_5$ along (1 0 0).
For both: green, chloride; grey, molybdenum; black, carbon; blue, nitrogen; red, hydrogen

References

[1] Stein, Melde, Schroden, Adv. Mater. 12 (2000) 1403.

[2] Yaghi, O'Keeffe, Ockwig, Chae, Eddaoudi, Kim, Nature 423 (2003) 705.

[3] Murata, Murata, Komatsu, J. Am. Chem. Soc. 125 (24) (2003) 7152.

[4] Beauvais, Shores, Long, JACS 122 (2000) 2763.

[5] Naumov, Virovets, Sokolov, Artemkina, Fedorov, Angew. Chem., Int. Ed. Engl. 37 (1998) 1943.

[6] Gray, Rudzinsky, Nocera, Holm, Inorg. Chem. 38 (1999) 5932.

[7] Brammer, Burgard, Rodger, Swearingen, Rath, Chem. Commun. (2001) 2468.

[8] Selby, Orto, Carducci, Zheng, Inorg. Chem. 41 (2002) 6175.

[9] S. Bain, Ellis, Inorg. Chem. Acta 325 (2001) 171.

[10] D. Hagrman, P. Hagrman, Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 3165.

[11] D. Yan, Lachgar, Chem. Commun. 21 (2004) 2390.

[12] R. Selby, Zheng, Acc. Chem. Res. 36 (2003) 933.

[13] Yoshimura, Iasaki, Kim, Kitmaura, Naumov, Sokolov, Fedorov, Chem. Lett. (1999) 1121.

[14] Guilbaud, Deluzet, Domercq, Molinié, Coulon, Boubekeur, Batail, Chem. Commun. 18 (1999) 1867.

[15] Brosset, Arkiv Kemi Mineral. o. Geol. (1945) (Band 20 A. No 7).

[16] Blomstrand, J. Prakt. Chem. (1859) 88–119 [Ch 77].

[17] Flemström, Hirsch, Sehlstedt, Lidin, Ojamäe, Solid-State Sci. 4 (2002) 1017–1022.

[18] G.M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.

[19] Petricek, Dusek, JANA2000, Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, 2000.

[20] S. Lee, A.B. Mallik, Z Xu, E.B, Lobokovsky, L. Tran, Acc. Chem. Res., submitted.