# SYNTHESIS AND CHARACTERIZATION OF DICARBORANYLMETHYLAMMONIUM POLYOXOMETALLATES

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*Dedicated to Dr. Bohumil Štíbr on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of polyhedral boron-containing compounds.*

The reaction of $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**) with $[NH_4]_6[Mo_7O_{24}][H_2O]_4$ in water instantly afforded a white precipitate: crystallization from acetone–hexane thence gave the hybrid dicarborane octamolybdate salt, $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH{=}CMe_2]_2[Mo_8O_{26}]$-$[Me_2CO]_{4.5}$ (**5**), whereas crystallization from acetonitrile–ether gave three further salts: $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH_2CHMe_2]_2[Mo_8O_{26}][MeCN]_2$ (**6**), $[C_2B_{10}H_{11}CH_2NH_3]_4$-$[Mo_8O_{26}][MeCN]_2[Et_2O]_2$ (**7**) and $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH_2Et]_2[Mo_8O_{26}][MeCN]_2$ (**8**). Similarly, treatment of an acidified solution of $Na_2WO_4$ with $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**) in water also yielded a white precipitate: crystallization from acetone–hexane afforded the salt $[C_2B_{10}H_{11}CH_2NH{=}CHMe_2]_4[W_{10}O_{32}][H_2O]_2[Me_2CO]_4$ (**10**), whereas crystallization from acetonitrile–ether gave the double salt $[C_2B_{10}H_{11}CH_2NH_3]_2[C_5H_5NH]_2[W_{10}O_{32}][MeCN]_2$-$[Et_2O]$ (**11**). All these 'globule–globule' salts **5**, **6**, **8**, **10** and **11** have been characterized by single-crystal X-ray diffraction analyses. Crystal structures reveal the presence of various small solvate molecules, together with an extensive network of hydrogen bonds between ammonium groups and oxygen atoms of the isopolyoxometallates. The isopropyl substituent in one of the carborane cations of the salts **6** and the ethyl substituent in one of the carborane cations of salts **8** may result from occluded isopropanol and ethanol in the starting salt **3** with alkylations of the primary ammonium group being assisted by isopolymolybdate anions. The presence of the pyridinium cation in **11** is believed to arise from contamination during work-up the reaction mixture.

**Keywords**: Carboranes; Polyoxometallates; Hybrid salts; Hydrogen bonds; Crystal structures.



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Polyoxoanions of early-transition elements on one hand, and polyhedral boron-containing compounds on the other, constitute two extensive classes of compounds with a wide range of structures and properties. Structurally, the globular aspects of their architectures are one of the most notable characteristics of each of these two classes. Each field has attracted the interest of many chemists for many years, and each field is the focus of much current research work[1–8].

Boron hydrides are generally based on three-dimensional polyhedra with triangular faces, which can incorporate into the cluster framework a large number of elements, from main-group elements through metal atoms to organometallic fragments. For example, the incorporation of carbon into the boron framework leads to the formation of carborane molecules, of which the icosahedral *ortho*-carborane, [*closo*-1,2-$C_2B_{10}H_{12}$], is perhaps the best known example. The exceptional stability of the *closo* {$C_2B_{10}$} cluster led to the fast development of its organic functional chemistry. Consequently, organic derivatives of this twelve-vertex *ortho*-carborane, as well as its *meta* and *para* isomers, [*closo*-1,7-$C_2B_{10}H_{12}$] and [*closo*-1,12-$C_2B_{10}H_{12}$] respectively, are numerous; this chemistry has been comprehensively reviewed[9–12] .

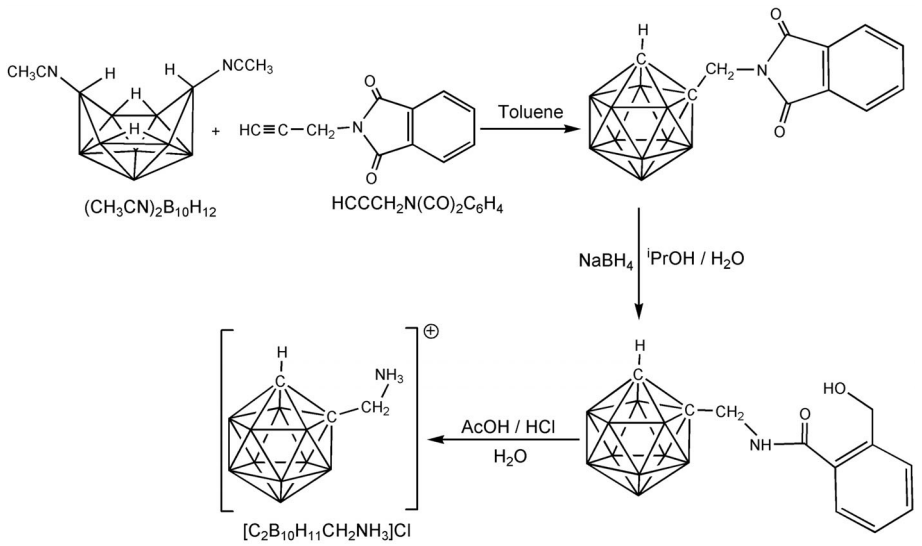
Polyoxometallates also exhibit three-dimensional structures that are generally based on regular polyhedra, though in a different sense to the boron-hydride polyhedral paradigms. Their structures are constructed using a network of metal–oxygen bonds, and, in most of the cases, can be rationalized as being derived from assemblies of {$MO_6$} octahedra sharing vertices and/or edges and/or faces: the metal occupying the octahedral space formed by the six oxygen atoms. Like the polyhedral boron-containing compounds, polyoxometallate anions also have the property to incorporate atoms from all parts of the Periodic Table into the cluster framework[3,5,7,13,14]. In contrast to the borane cluster compounds, however, the investigation and the exploitation of the functionalization of early-transition-element polyoxoanions developed somewhat later, and the known functional chemistry is not nearly as extensive or varied as that of the dicarboranes. However, there has been an acceleration in the development in this field over the last decade[15,16].

The extensive derivative chemistry of *ortho*-carborane and other polyhedral boranes has the potential to provide a large and tailorable library of precursors for the synthesis of contiguously covalent borane/polyoxometallate hybrid compounds, which could exhibit structural patterns and properties to complement those found in the reported organo- and organometallic-derivatives of polyoxometallates. In addition, the large

number of known aryl- and alkyl-ammonium salts of polyoxometallates[17–22] suggests that cationic ammonium derivatives of polyhedral boranes will also readily form salts with the polyoxometallate anions, for example by simple cation exchange. Thus, focusing on the synthesis and characterization of new inorganic compounds based on early-transition polyoxoanions and polyhedral boranes, we report a family of globule–globule salts that derive from isopolymolybdate and isopolytungstate anions and carboranylmethylammonium salts. The essential ideas were published in an earlier communication[23], and this paper builds upon the results described therein.

## RESULTS AND DISCUSION

The starting *ortho*-carboranylmethylammonium salt, $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**) can be obtained in a reasonable yield from the reaction between propargylphthalimide and the decaborane species 6,9-$(CH_3CN)_2$-*arachno*-$B_{10}H_{12}$, to give the 1-(phthalimidomethyl)-1,2-dicarba-*closo*-dodecaborane (**1**), followed by reduction of **1** with sodium borohydride and hydrolysis in acid conditions (Scheme 1)[24].




SCHEME 1
Synthesis of **3**

During the course of this synthetic work, we obtained the crystal structure of the intermediate (1,2-dicarba-*closo*-dodecaboranyl)methyl 2-(hydroxymethyl)benzene carboxamide, $C_2B_{10}H_{11}CH_2NHCOC_6H_4$-2-$(CH_2OH)$ (**2**) by a single-crystal X-ray diffraction analysis. This structure was deposited in the Cambridge database by other workers contemporaneously to the work described in this present paper[25], although, as far as we are aware, details of the crystal structure have not subsequently been described or discussed in the literature. The crystal and molecular structure of the first intermediate **1** has also been previously reported[26].

The carborane-containing amide, **2**, crystallizes in the $P2_1/c$ space group with four independent molecules in the unit cell. They pack in chains along the *a* axis, linked through intermolecular O–H···O hydrogen bonds between the hydroxyl and carbonyl groups of adjacent molecules (O–O 2.6914(15) Å, Fig. 1). In addition, the molecules exhibit an intramolecular N–H···O hydrogen bond between the NH amide function and the oxygen atom of the hydroxymethyl substitutent (N–O 2.7651(16) Å, Fig. 1). The crystal structure of the previously reported phthalimidoamino-*ortho*-carborane **1** shows also chains along the *a* axis, which pack on the *bc* plane. The molecules in a chain exhibit short contact distances with molecules in adjacent chains through interactions between the hydrophilic $\{N(CO)_2C_6H_4\}$ fragments, and between the lipophilic $\{C_2B_9H_{11}\}$ groups[26].

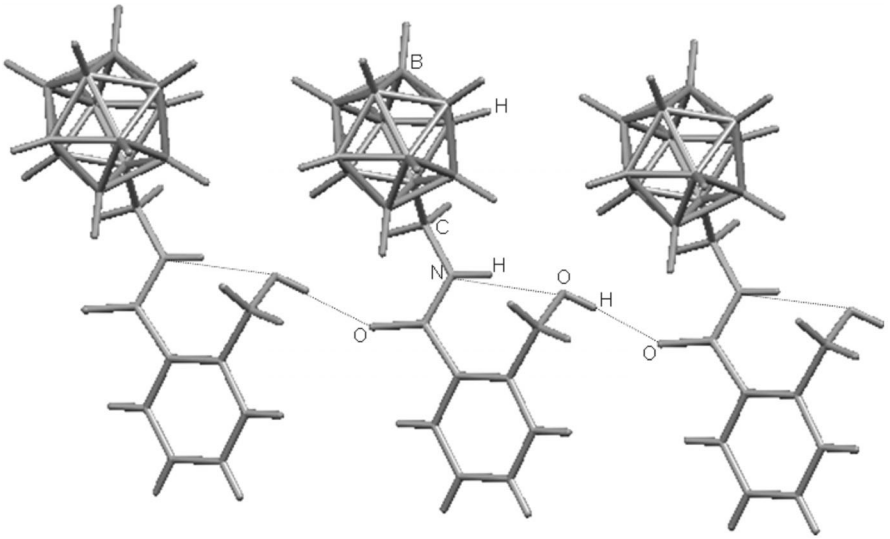



FIG. 1
View of hydrogen bonds in **2**

The reaction of ammonium heptamolybdate, $[NH_4]_6[Mo_7O_{24}][H_2O]_4$, with the carboranyl-containing salt **3** in water affords a white precipitate that, according to the results of the elemental analysis, is tentatively characterized as the heptamolybdate salt, $[C_2B_{10}H_{11}CH_2NH_3]_6[Mo_7O_{24}][H_2O]_x$ (**4**), where *x* is ca. 10 (see Experimental). Crystallization of this product by slow diffusion of hexane into a solution of the salt in acetone afforded crystals of the globule–globule salt, $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH{=}CMe_2]_2$-$[Mo_8O_{26}][Me_2CO]_{4.5}$ (**5**). In contrast, slow diffusion of ether into a solution of **4** in acetonitrile gave a new octamolybdate double salt, $[C_2B_{10}H_{11}CH_2NH_3]_2$-$[C_2B_{10}H_{11}CH_2NH_2CHMe_2]_2[Mo_8O_{26}][MeCN]_2$ (**6**). Interestingly, the crystallization of the product of the treatment of **3** with ammonium heptamolybdate (obtained from a preparation batch other than that above) from MeCN–$Et_2O$ afforded the octamolybdates $[C_2B_{10}H_{11}CH_2NH_3]_4[Mo_8O_{26}][MeCN]_2$-$[Et_2O]$ (**7**) and $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH_2Et]_2[Mo_8O_{26}][MeCN]_2$ (**8**).

Similarly, treatment of an acidified solution of $Na_2WO_4$ with $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**) in water yielded a white precipitate of formula $[C_2B_{10}H_{11}CH_2NH_3]_4[W_{10}O_{32}]$ (**9**). Crystallization of this salt from acetone–hexane afforded crystals of the globule–globule salt, $[C_2B_{10}H_{11}CH_2NH{=}CHMe_2]_4$-$[W_{10}O_{32}]$, as its $\{[H_2O]_2[Me_2CO]_4\}$ solvate **10** [23]. A crystallization of **9** from acetonitrile–ether yielded crystals of a new double salt, $[C_2B_{10}H_{11}CH_2NH_3]_2$-$[C_5H_5NH]_2[W_{10}O_{32}][MeCN]_2[Et_2O]$ (**11**), in which the incidence of pyridinium ions was surprising and obviously unexpected.

These results demonstrate that the composition of these types of hybrid salts can vary greatly, depending on the crystallization conditions. Thus, the use of acetone–hexane as the crystallization solvent system results in the formation of iminium functions in the polyhedral cations of the octamolybdate **5** and the decatungstate **10** (Fig. 2c). The N=C bond is most likely formed in a condensation reaction between acetone and the primary ammonium group of the starting carboranylmethylammonium (**3**). The origin of the isopropyl and ethyl groups in $[C_2B_{10}H_{11}CH_2NH_2CHMe_2]^+$ (Fig. 2b, salt **6**) and $[C_2B_{10}H_{11}CH_2NH_2Et]^+$ (Fig. 2d, salt **8**) is of interest since these alkyl substituents should not in principle be present in the reaction system. They may arise from the preparation of the $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**) starting material in which *iso*-propanol is used as reaction medium and ethanol as crystallization solvent. Presumably both alcohols remained occluded in the solid sample of **3** that was used for the preparation of the hybrid salts. Therefore, the reaction between isopropanol and ethanol with the carboranylmethylamine, $[C_2B_{10}H_{11}CH_2NH_2]$, could well be the origin of the formation of the secondary carboranylmethylammonium ions in **6** and **8**. In this regard, it is known that primary amines can be alkylated by

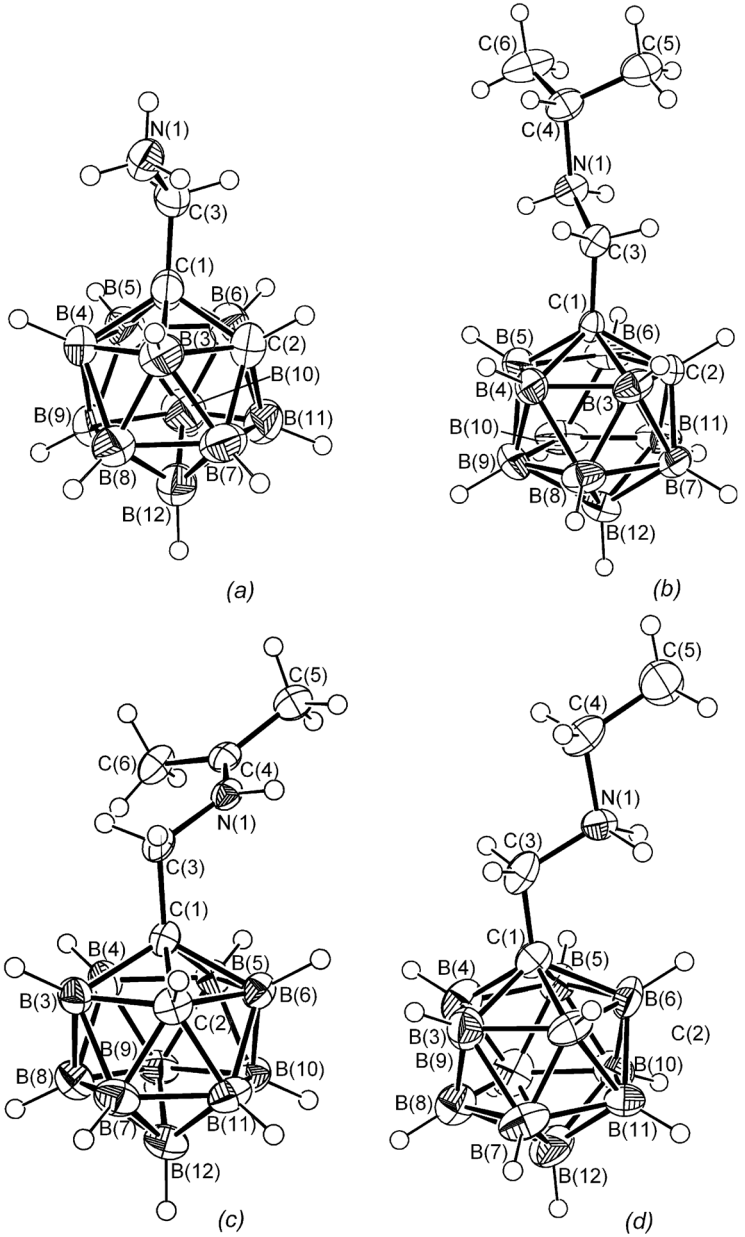



FIG. 2
Molecular structures of carborane-containing cations found in salts **5**, **6**, **7**, **8** and **11** (a); **6** (b); **5** and **10** (c); **8** (d)

alcohols to obtain secondary amines: a reaction that is catalyzed, e.g., by $[Cp^*IrCl_2]_2$ in the presence of base[27,28]. Under the crystallization conditions of the carborane-containing salts reported here, the molybdate anions could promote N-alkylation of the ammonium group in $[C_2B_{10}H_{11}CH_2NH_3]^+$, leading to the formation of the N-alkylated polyhedral cations observed in the salts **6** and **8** (Fig. 2b and 2d).

On the other hand, the origin of the pyridinium cation in the decatungstate **11** is more obscure, since the preparation of either the starting materials or the hybrid salts does not involve the use of pyridine, and, although the catalytic formation of substituted pyridines from nitriles and alkynes is well documented[29], the simple crystallization of **4** in $CH_3CN$–$Et_2O$ is not likely to promote the formation of the pyridinium cation found in **11**. Thus, the most probable source is contamination of the reaction vessel with pyridine.

Each of the solid-state structures of compounds **5**, **6**, **7** and **8** is based on a matrix of carborane-containing cations and β-octamolybdate $[Mo_8O_{26}]^{4-}$ anions. These anions are composed of eight $\{MoO_6\}$ octahedra joined by shared edges. The result is two octagonal $\{Mo_4O_4\}$ rings of which each has a central oxygen atom, O(13), bound to the four molybdenum atoms. This oxygen atom is bound to an molybdenum atom from the other $\{Mo_4O_4\}$ ring, with the reciprocal O → Mo linkage occurring to Mo(1) (Fig. 3): the

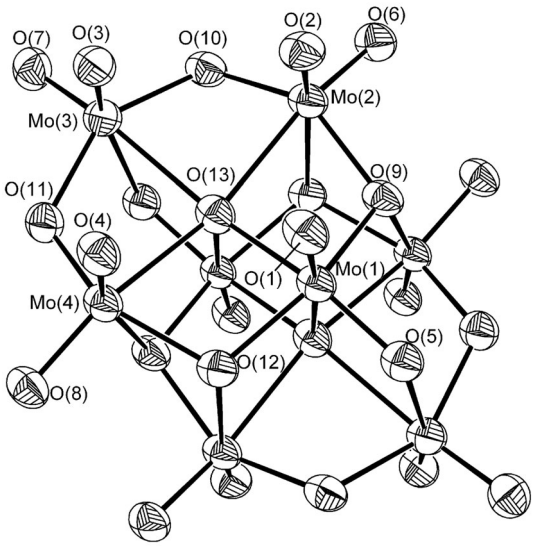



FIG. 3
Molecular structure of the $[Mo_8O_{26}]^{4-}$ anions found in the salts **5**, **6**, **7** and **8**

centre of symmetry of the β-octamolybdate relates both rings. The interatomic distances and angles of the $[Mo_8O_{26}]^{4-}$ cage found in these hybrid salts, **5**, **6**, **7** and **8**, conform to values previously reported[30,31]. Likewise, the deltahedral clusters and the organic pendant groups in the carboranyl cations of these salts, are also within the ranges found for other substituted *closo*-carboranes[26,32,33].

One of the most interesting features of the structures of **5**, **6**, **7** and **8** is the extensive network of N–H···O hydrogen bonds between the hydrophilic arms of the carboranyl cations and the terminal oxygen atoms, O(1), O(2), O(3) and O(4), of the octamolybdate anions. Each salt exhibits its particular hydrogen-bond network, with subtle differences as well as common features. Thus, in salt **5** (Fig. 4), although the carboranylmethylammonium cation shows a positional disorder that resembles two interwoven clusters (see Fig. 1 in supplementary material), it is clear that the cation interacts with the four terminal oxygen atoms, O(1), O(2), O(3) and O(4), of the two octagonal $\{MoO_4\}$ rings of the β-octamolybdate anion, forming bifurcated N–H···O hydrogen bonds with two of the N–H groups (N···O 2.954(5) Å (average)), whereas the third N–H vector of the ammonium group is engaged in another single N–H···O hydrogen bond with an acetone molecule (N···O 2.816(6) Å, Fig. 4).

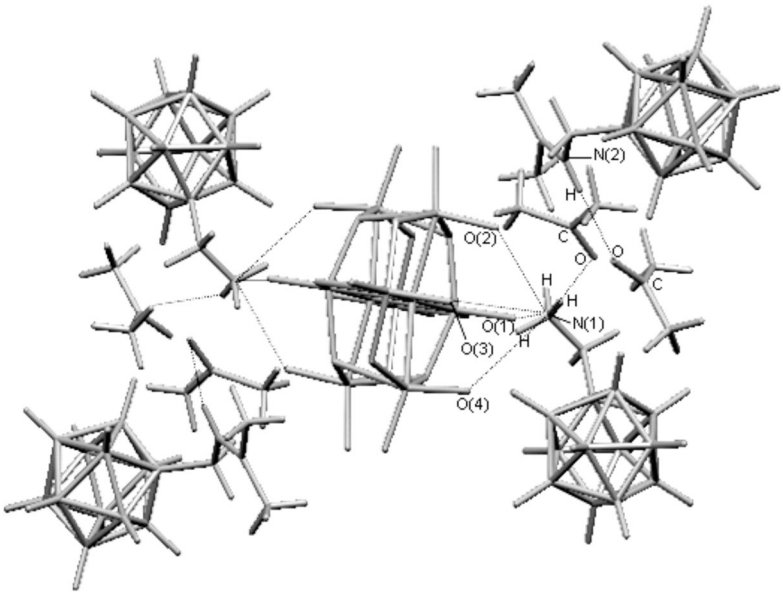



FIG. 4
N–H···O hydrogen bonds in compound **5**

In the extended crystal structure of compound **5** (Fig. 5) the octamolybdate anions pack along the crystallographic *a* direction forming columns that are associated with flanking ribbons of carboranylmethylammonium cations. The repetition of these columns on the *bc* plane results in layers of octamolybdates flanked by layers of carborane-containing cations. The carboranylmethyliminim cations form a single N–H···O hydrogen bond with acetone molecules (Fig. 4), leading to the formation of acetone queues that follow the columns of the hydrogen-bonded $[C_2B_{10}H_{11}CH_2NH_3]^+/[Mo_8O_{26}]^{4-}$ partners (Fig. 5).

Likewise, the $[C_2B_{10}H_{11}CH_2NH_3]^+$ cation in **6** (Fig. 6) interacts with the terminal oxygen atoms, O(1), O(2), O(3) and O(4), of the octamolybdate anion via two of its N–H groups, forming bifurcated N–H···O hydrogen bonds (2.839(3) Å (average)). In contrast to the interaction in **5**, the third available NH of the carboranymethylammonium forms a hydrogen bond with the terminal oxygen atom, O(8), of a second adjacent molybdate anion (2.822(3) Å, Fig. 6). The isopropyl-substituted carboranyl cation is hydrogen-bonded to one molecule of acetonitrile (N–H···N 3.086(5) Å),

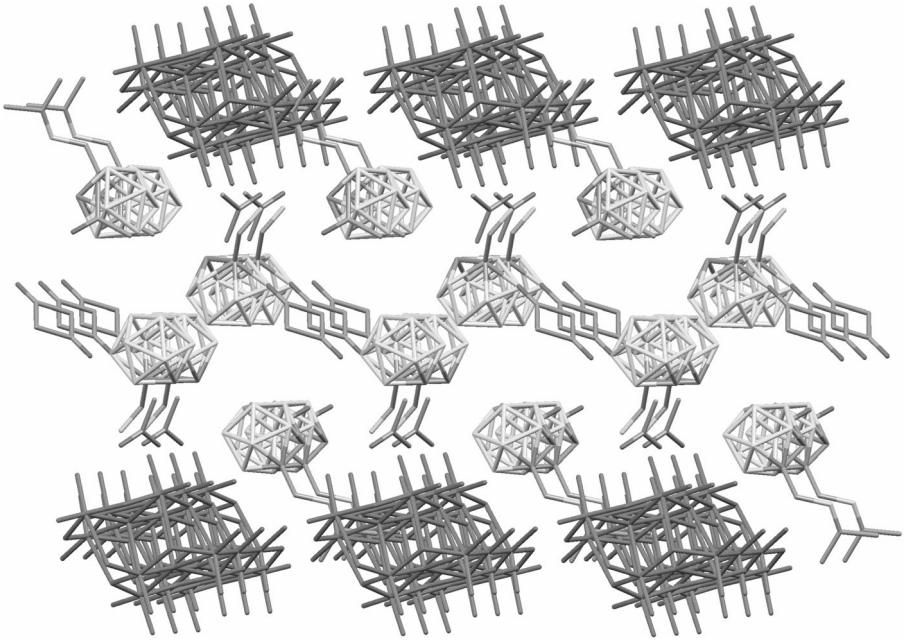


FIG. 5
Crystal packing of **5** along the *a* axis

resembling somewhat the situation in **5**, where the iminium cation is hydrogen-bonded to a molecule of acetone, thus avoiding the interaction with the anions.

The packing of **6** can also be described as columns of molybdate anions running along the crystallographic *c* axis, carrying on their flanks the carborane cations, with the pendant methylammonium arms of these cations hydrogen-bonded to them (Fig. 7). The imminum cation follows the same direction, this time partnered with the acetonitrile solvate. Overall, the structure can also be described as layers of isopolymolybdate anions with the carborane-containing cations and solvate molecules packed between them.

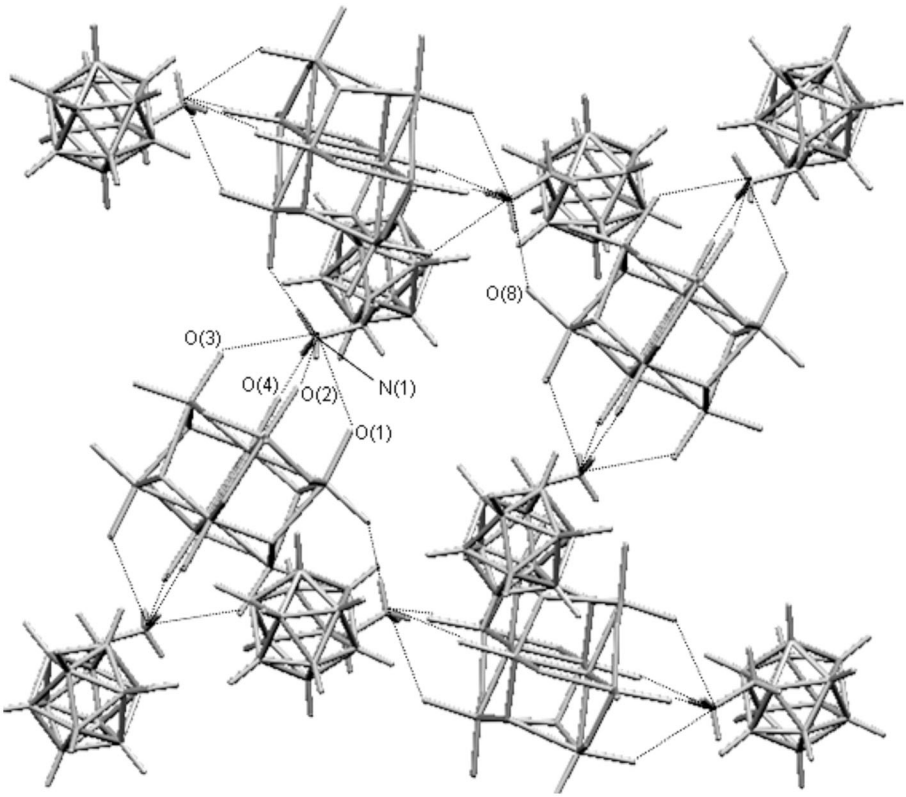



FIG. 6
N–H···O hydrogen bonds in compound **6**

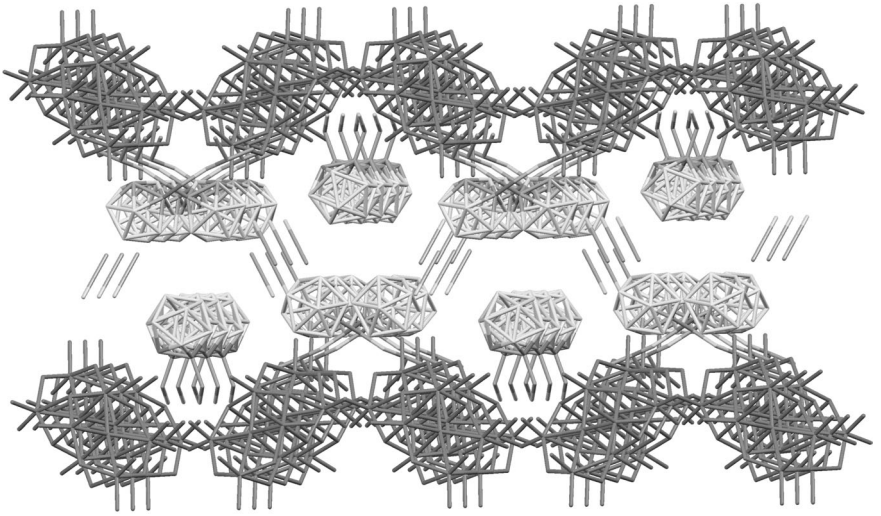


FIG. 7
Crystal packing of **6** along the *c* axis

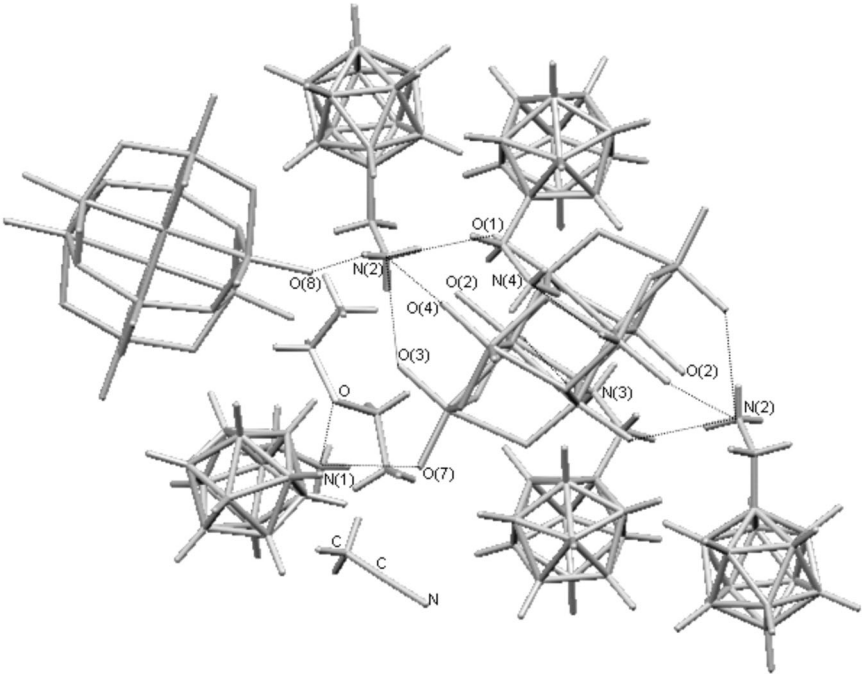



FIG. 8
Hydrogen bonds in compound **7**

The crystal structure of the hybrid molybdate salt **7** (Fig. 8) which contains only $[C_2B_{10}H_{11}CH_2NH_3]^+$ cations, also exhibits bifurcated hydrogen-bond interactions of two NH hydrogen atoms of the $NH_3$ ammonium function with the terminal oxygen atoms of the octagonal $\{Mo_4O_4\}$ unit. However, the contact distance N(2)···O(2) at 3.223(7) Å is significantly longer than the distances between the nitrogen atom of the ammonium group and the terminal oxygen atoms, O(1), O(3) and O(4) (N(2)···O 2.893(3) Å (average)) of the β-octamolybdate. The third hydrogen atom of the $NH_3$ unit binds to the terminal oxygen atom, O(8), of an adjacent anion [N···O 2.916(7) Å, Fig. 8]. This third hydrogen bond is *trans* to the somewhat long N(2)···O(2) vector, suggesting that the interaction with an adjacent anion is disturbing, to a degree, the interaction of the two $NH_3$ hydrogen atoms with the four terminal oxygen atoms. In addition, a second, crystallographically independent, $[C_2B_{10}H_{11}CH_3NH_3]^+$ cation is hydrogen-bonded to a molecule of ether (N···O 2.766(18) Å) and to the terminal oxygen atom, O(7), of a molybdate (N(1)···O 2.902(17) Å).

A similar $\{NH_3\}/\{Mo_4O_4\}$ bifurcated hydrogen-bond interaction is also present in the crystal structure of **8** (Fig. 9) with an average N···O contact

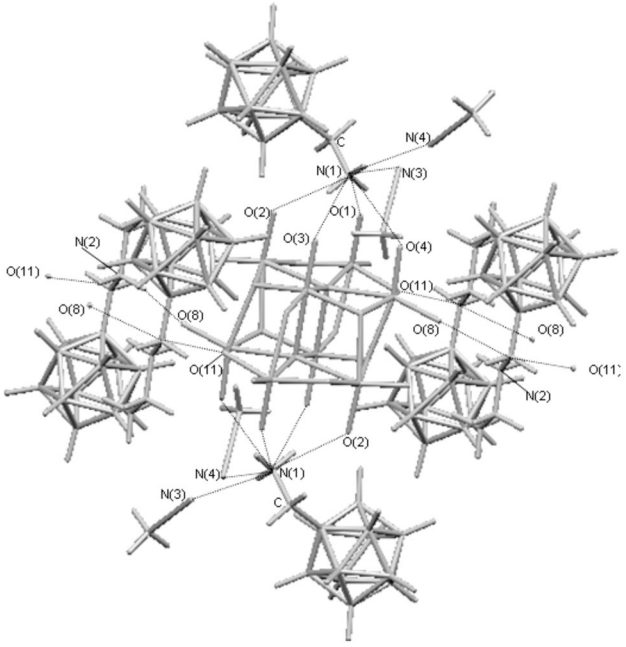



FIG. 9
View of the hydrogen bonding found in compound **8**

distance between the terminal oxygen atoms, O(1), O(3) and O(4), and the ammonium nitrogen atom of 2.893(3) Å. A third N–H vector of the ammonium group interacts with two acetonitrile molecules (N(1)···N(3) 3.027(17) Å, N(1)···N(4) 2.959(15) Å), forming bifurcated N(1)–H···O hydrogen bonds (Fig. 9). The N(1)···O(2) contact distance at 3.025(14) Å is *trans* to the vector that results from the sum of the N(1)···N(3) and N(1)···N(4) vectors, resulting in an elongation of the hydrogen bond between the terminal oxygen atom, O(2), and the ammonium group compared with the other three terminal oxygen/ammonium bonds. Additionally, the ethyl-ligated carboranyl cations in **8** are found to be linked to two adjacent anions through NH···O hydrogen bonds between the two NH groups of the cations and the oxygen atoms of two adjacent anions. In one of these hydrogen bonds, the terminal oxygen atom, O(8), acts as H-aceptor, whereas in the adjacent isopolymolybdate the acceptor is the Mo–O–Mo bridging oxygen atom, O(11) (Fig. 9).

The packing of **7** and **8** (Figs 10 and 11, respectively) resembles that described for **5** and **6**, and thus it can be seen that the anions form columns along the crystallographic *a* axis with the hydrogen-bonded cations flanking them and forming, in turn, ribbons of polyhedral cations. The overall

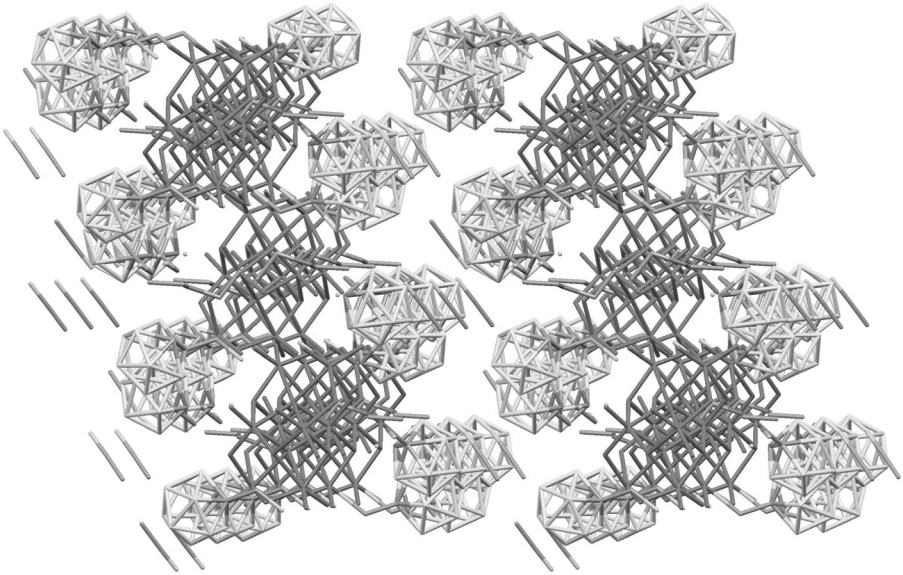


FIG. 10
Crystal packing of **7** along the *b* axis

structures might be viewed as layers of anions sandwiching layers of polyhedral cations. $[C_2B_{10}H_{11}CH_2NH{=}CHMe_2]_4[W_{10}O_{32}][H_2O]_2[Me_2CO]_4$ and $[C_2B_{10}H_{11}CH_2NH_3]_2[C_5H_5NH]_2[W_{10}O_{32}][MeCN]_2[Et_2O]$, compounds **10** and **11**, respectively, are two double salts that contain polyhedral cations partnered with the decatungstate anions, $[W_{10}O_{32}]^{4-}$. The molecular structure of this isopolytungstate (Fig. 12) can be regarded as consisting of two square-planar pyramids of tungsten atoms bridged by oxygen atoms on the direction of the edges: these two pyramids are linked by four bridging oxygen atoms. Each tungsten atom bears a terminal oxygen atom, and there are two internal oxygen atoms, one on the square-base of each pyramid, co-

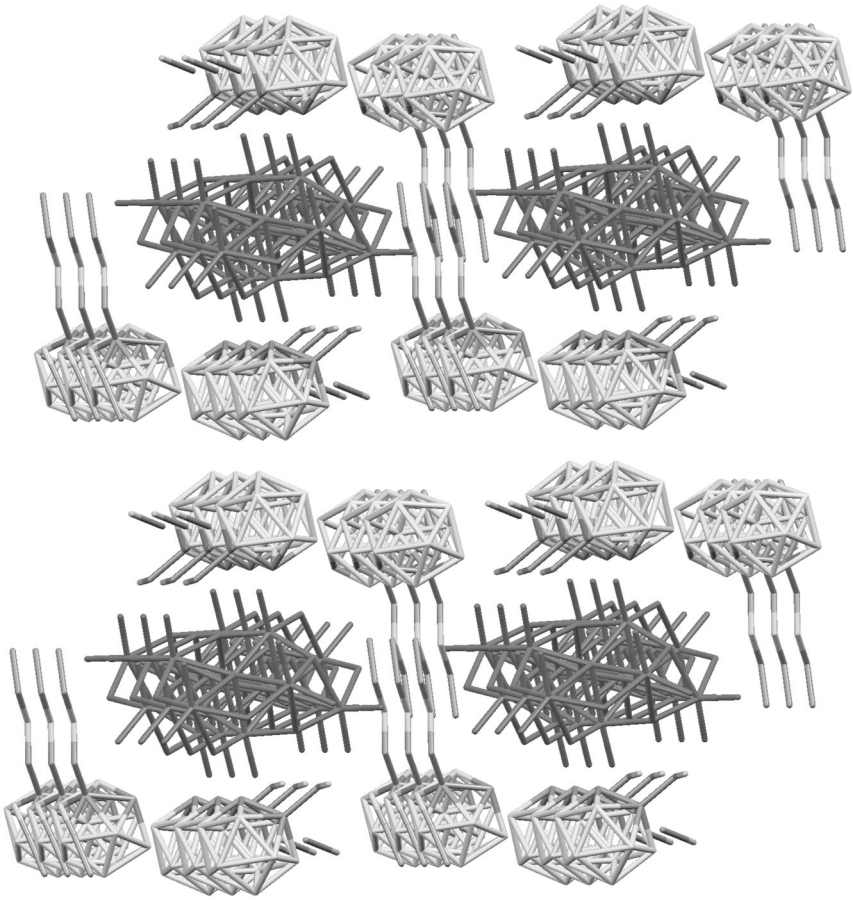


FIG. 11
Crystal packing of **8** along the *a* axis

ordinated to the five tungsten atoms that constitute the pyramid. Alternatively, the anions may be described as two identical $\{W_5O_{16}\}$ units composed of edge-shared $\{WO_6\}$ octahedra (Fig. 12). The intermolecular distances and angles of the $[W_{10}O_{32}]^{4-}$ fall within the ranges previously found for this isopolyanion[34–36].

We have previously reported that compound **10** exhibits a structure based on layers of isopolytungstate anions formed by the packing of chains of anions that grow parallel to the *b* direction[23]. Resembling the pattern found for the isomolybdate salts **5–8**, in **10** the iminium cations form an extensive network of NH···O hydrogen bonds with the W–O teminal and W–O–W bridging oxygen atoms of the $[W_{10}O_{32}]^{4-}$ anions and with the entrained water molecules. In turn, the $H_2O$ molecules use one hydrogen atom to bond to the carbonyl group of an acetone molecule (O–H···O bond), and the other to form a bifurcated hydrogen bond with the terminal oxygen atom, O(1), and the bridging oxygen atom, O(10), of two adjacent anions[23].

The salt **11** has a polyhedral carboranyl cation and an aromatic pyridinium cation. As mentioned above, the source of the $[C_5H_5NH]^+$ cation is not clear, and probably arises from contamination of the reaction media. In any event, the X-ray analysis of **11** gives opportunity to compare its crystal structure with that of **10**, and to evaluate if the substitution of a

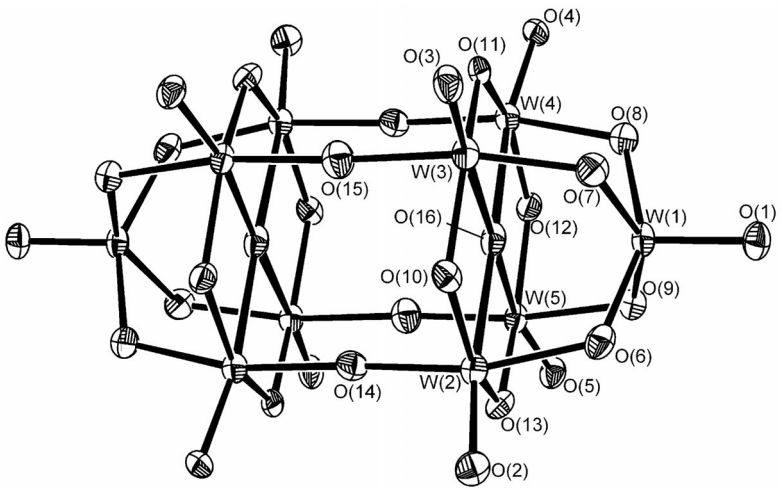



FIG. 12
Molecular structure of the $[W_{10}O_{32}]^{4-}$ anions found in the salts **10–11**

carboranylmethylammonium cation by an aromatic N-heterocyclic cation has any significant effect on the overall structure of the hybrid salts. In **11**, the ammonium groups of the carboranyl cations use one hydrogen atom to bond to the terminal oxygen atoms, O(1) and O(2), of two adjacent decatungstate anions (N(1)···O(1) 2.813(12) Å, N(1)···O(2) 2.839(12) Å, Fig. 13), forming a bifurcated N–H···O interaction. A second N–H vector is engaged in a N–H···O hydrogen bond with the terminal oxygen atom, O(2), of a third decatungstate (N(1)···O(2) 2.914(12) Å), whereas the third N–H vector forms a hydrogen bond with an acetonitrile molecule (N(1)···N(2) 2.875(17) Å, Fig. 13). Each pyridinium cation bonds to an ether molecule (N–H···O 2.729(14) Å).

The resulting $\{[C_2B_{10}H_{11}CH_2NH_3]_2[W_{10}O_{32}]_2[C_5H_5NH][Et_2O]\}$ unit is the basic building block of the crystal structure of **11**: its repetition on the plane *bc* gives rise to layers of anions that in turn are formed by columns that can be regarded as growing along the *a* axis, or alternatively along the *b* direction. In a similar fashion to the structures described above, the overall packing in **11** may be viewed in terms of *bc* layers of oxometalate anions

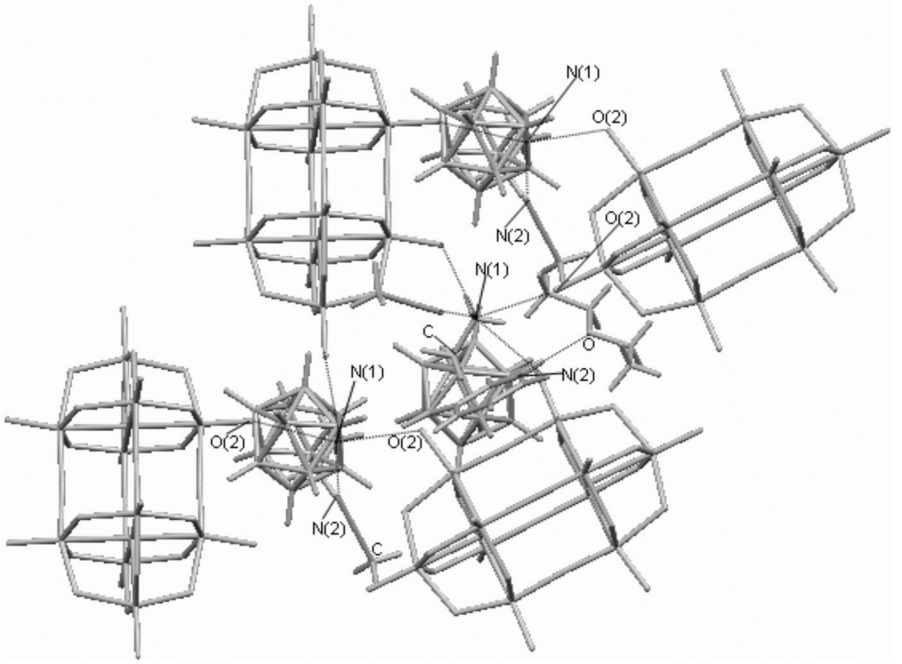



FIG. 13
Hydrogen bonds in compound **11**

flanked above and below by layers of the dicarboranylmethylammonium cations (Fig. 14).

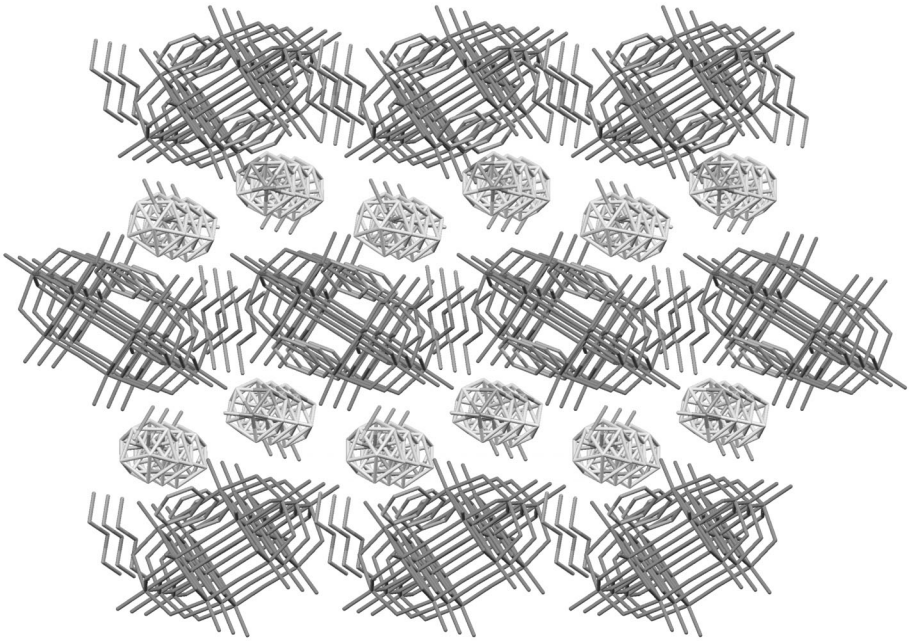


FIG. 14
Crystal packing of **11** along the *a* axis

## CONCLUSIONS

The use of the carboranylmethyammonium chloride **3** as starting material in metathetical reactions with oxometalate anions of molybdenum and tungsten has afforded a new series of "globule–globule" hybrid salts. The final composition of the crystals depends critically on the crystallization conditions. The double salts **6** and **8** exhibit carborane cations substituted at the N atom with isopropyl and ethyl groups, respectively, whereas **5** and **10** contain polyhedral iminium cations. Thus, this study has resulted in the crystallographic characterization of four *ortho*-carborane-containing cations (Fig. 2). The iminium function found in **5** and **10** may reasonably be ascribed to the condensation of acetone with the primary ammonium group of the starting carboranylmethylammonium salt **3**. In contrast, the source of the isopropyl and ethyl substituents is not clear, but the hypothesis that the alkylation may have occurred due to reaction between the polyhedral

amines and free isopropanol and ethanol is appealing, since this suggests that, under the right conditions, polyoxometallate anions could catalyze the alkylation of amines by alcohols.

The crystal structures of all these globule–globule salts can be regarded as results of the packing of layers of anions between which the cations are intercalated. The hydrophilic pendant primary alkylammonium, secondary alkylammonium and iminium groups are bound to, and thence face, the anionic oxometalated layers, forming, together with the solvent molecules, an extensive network of hydrogen bonds, which are the main pillars of the structure. By contrast, the lipophilic dicarboranyl heads are oriented toward the internal side of the anionic layer gap. There is a clear interactive complementarity between the $NH_3$ group of the unsubstituted $[C_2B_{10}H_{11}CH_2NH_3]^+$ cation and the terminal oxygen atoms, O(1), O(2), O(3) and O(4), of the $[Mo_8O_{26}]^{4-}$ anions.

These new salts have the capability of assimilating a variety of small molecules in the interglobular cavities. It is interesting to observe how the combination of the globular nature of the ions, coupled with the hydrophilicity of the ammonium and iminium groups and the marked hydrophobicity of the dicarborane residue, contribute to the observed intercalation and, thereby, the scavenging of small polar solvent molecules.

## EXPERIMENTAL

### General Procedures

All the reactions were performed in the presence of air. The crystallization solvents, acetone and hexane, were used directly from the commercial containers without previous drying. $Na_2[WO_4]$ and $MoO_3$ were purchased commercially and used as received. The aminomethyl-*ortho*-carborane hydrochloride, $[C_2B_{10}H_{11}CH_2NH_3]Cl$, was prepared according to literature procedures[24]. Elemental analyses were performed on a Perkin–Elmer 24000 microanalytical analyzer. IR spectra ($\nu$ in $cm^{-1}$) were recorded on a NICOLET 740 FT-IR spectrometer.

### Synthesis of $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**)

According to the reported procedure[24], the aminomethyl-*ortho*-carborane hydrochloride was synthesized from the 1-(phthalimidomethyl)-1,2-dicarba-*closo*-dodecaborane (**1**), which was prepared from the reaction of propargylphthalimide and the decaborane–acetonitrile adduct in toluene. Following this procedure, 5.00 g of **1** were isolated, and subsequently crystallized in toluene to give single crystals suitable for X-ray diffraction analysis. The reaction of **1** with sodium borohydride afforded $C_2B_{10}H_{11}CH_2NHCOC_6H_4$-2-$(CH_2OH)$ (**2**). Crystallization of **2** from ethanol yielded crystals that were studied by X-ray diffraction analysis. Final treatment of **2** with HCl afforded the salt $[C_2B_{10}H_{11}CH_2NH_3]Cl$ (**3**).

Synthesis of Molybdates

An amount of 0.1322 g (0.107 mmol) of ammonium heptamolybdate, $[NH_4]_6[Mo_7O_{24}]\cdot[H_2O]_4$, was dissolved in 25 ml of water, and the resulting solution was subsequently treated with 0.1357 g (0.64 mmol) of $[C_2B_{10}H_{11}CH_2NH_3]Cl$, previously dissolved in 15 ml of hot water. A white precipitate was instantly formed, and the resulting suspension was stirred for 10 min. The white precipitate was collected by filtration and dried in air. For $C_{18}H_{116}B_{60}Mo_7N_6O_{34}$ (2281.39) calculated: 9.48% C, 5.13% H, 3.68% N; found 9.40% C, 4.87% H, 3.58% N. Based on these data, the proposed formulation of the white precipitate is $[C_2B_{10}H_{11}CH_2NH_3]_6[Mo_7O_{24}][H_2O]_x$ (**4**), in which, given the deviation in the elemental analysis, the number of water molecules is uncertain (for the calculated element percentage, $x = 10$). IR (KBr, disk): 3448 vs ($H_2O$), 3048 w (NH), 2957 w (NH), 2586 s (BH), 1022 m (MoO), 946 s (MoO), 912 s (MoO), 843 m (MoO).

Slow diffusion of hexane into a solution of compound **4** in acetone led to the formation of crystals from which a monocrystal was chosen for X-ray diffraction analysis. The crystallographic study revealed the structure of a octamolybdate with the formula $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH{=}CMe_2]_2[Mo_8O_{26}][Me_2CO]_{4.5}$ (**5**). IR (KBr, disk): 3216 vs (OH, NH), 2591 s (BH), 1448 vs, 1195 s (MoO), 1128 s (MoO), 1070 s (MoO), 807 m (MoO), 625 s. Elemental analysis of the remaining batch of crystals afforded the following percentages: 15.00% C, 4.10% H, 2.40% N, which conformed reasonably well to the formula $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH{=}CMe_2]_2[Mo_8O_{26}][Me_2CO]_3$ (Calculated: 15.19% C, 4.25% H, 2.62% N). IR (KBr, disk): 3448 vs (OH), 3042 w (NH, CH), 2590 s (BH), 1602 s (broad), 1508 m (broad), 900 s (MoO), 874 s (MoO), 722 m (MoO), 654 s.

In contrast, crystallization of the white precipitate (formed as compound **4**) in an acetonitrile solution by slow diffusion of ether, afforded a batch of crystals from which a single specimen was studied by X-ray diffraction analysis. The structure of this crystal showed a new octamolybdate salt of formula $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH_2CHMe_2]_2[Mo_8O_{26}]\cdot[MeCN]_2$ (**6**). For the batch of crystals $C_{22}H_{82}B_{40}Mo_8N_6O_{26}$ (2046.88) calculated: 12.91% C, 4.04% H, 4.11% N; found: 12.28% C, 3.70% H, 4.11% N. IR (KBr, disk): 3216 vs (OH, CH), 2591 s (BH), 2370 m (CN), 2248 m (CN), 1654 m (broad), 1448 vs (broad), 1195 s (MoO), 1128 s (MoO), 1098 s (MoO), 1070 s (MoO), 977 s, 807 s, 625 vs, 548 m, 512 m.

The procedure above was followed several times with different amounts of the ammonium heptamolybdate and the aminomethyl-*ortho*-carborane hydrochloride, although the 1 to 6 molar ratio of molybdate/carborane was maintained. However, subsequent crystallization of the resulting initial precipitate, which wass formed immediately in the aqueous phase from $CH_3CN$–$Et_2O$, afforded octamolybdate salts that contain carborane cations with different substituents on the nitrogen atom and with no substituents. Different co-crystallization molecules were also present. Thus, the salts $[C_2B_{10}H_{11}CH_2NH_3]_4[Mo_8O_{26}][MeCN]_2[Et_2O]_2$ (**7**) and $[C_2B_{10}H_{11}CH_2NH_3]_2[C_2B_{10}H_{11}CH_2NH_2Et]_2[Mo_8O_{26}][MeCN]_2$ (**8**) were obtained and thence characterized by single-crystal X-ray diffraction analyses.

Synthesis of Tungstates

An amount of 0.41897 g (1.27 mmol) of sodium tunsgtate, $Na_2WO_4$, was dissolved in 20 ml of boiling water, and the resulting colorless solution was subsequently acidified with 5 ml of boiling 0.5 M HCl. A yellow solution was formed, into which 0.1074 g (0.508 mmol) of $[C_2B_{10}H_{11}CH_2NH_3]Cl$, dissolved in 15 ml of hot water, was added. A white precipitate was instantly formed, and the reaction mixture was then cooled with an ice bath. The product

TABLE I
Experimental X-ray diffraction parameters and crystal data

| Parameter | **5** | **6** | **7** | **8** | **11** |
|---|---|---|---|---|---|
| Empirical formula | $C_{15.75}H_{49.50}B_{20}Mo_4N_2O_{15.25}$ | $C_{22}H_{82}B_{40}Mo_8N_6O_{26}$ | $C_{12}H_{45}B_{20}Mo_4N_3O_{14}$ | $C_{12}H_{42}B_{20}Mo_4N_4O_{13}$ | $C_{28}H_{70}B_{20}N_6O_{34}W_{10}$ |
| Molecular weight, g mol$^{-1}$ | 1111.03 | 2046.86 | 1055.47 | 1050.46 | 3089.6 |
| Crystal size, mm | 0.07 × 0.18 × 0.23 | 0.4 × 0.29 × 0.11 | 0.2 × 0.15 × 0.03 | 0.11 × 0.08 × 0.06 | 0.09 × 0.01 × 0.01 |
| Crystal system | triclinic | monoclinic | monoclinic | triclinic | monoclinic |
| Space group | *P*-1 | $P2_1/c$ | $P2_1/c$ | *P*-1 | $P2_1/c$ |
| *a*, Å | 11.1957(2) | 16.6464(1) | 16.7391(8) | 10.807(2) | 12.7138(2) |
| *b*, Å | 11.2293(2) | 16.1735(1) | 17.0879(9) | 11.671(2) | 11.7585(2) |
| *c*, Å | 18.7811(3) | 14.333(2) | 13.9919(6) | 16.093(3) | 23.5664(3) |
| α, ° | 92.3850(6) | | | 92.82(3) | |
| β, ° | 101.0880(7) | 104.8480(10) | 105.734(2) | 106.22(3) | 94.1770(10) |
| γ, ° | 108.2340(8) | | | 101.99(3) | |
| *V*, Å$^3$ | 2187.57(7) | 3730.1(5) | 3852.2(3) | 1894.0(7) | 3513.71(9) |
| *Z* | 2 | 4 | 4 | 2 | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.687 | 1.822 | 1.82 | 1.842 | 2.92 |
| μ(MoKα), mm$^{-1}$ | 1.177 | 1.369 | 1.33 | 1.351 | 16.377 |
| Temperature, K | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $2\theta_{max}$, ° | 54.94 | 55.00 | 54.98 | 54.94 | 52.00 |
| No. of reflections collected | 39215 | 87197 | 38173 | 18749 | 54820 |
| No. of independent reflections | 9976 | 8553 | 8757 | 7402 | 6872 |
| No. of reflections observed ($I > 2\sigma(I)$) | 7112 | 7862 | 6461 | 4774 | 5541 |
| No. of parameters refined | 652 | 473 | 493 | 482 | 447 |
| *R* (*Rw*) | 0.0438 (0.1327) | 0.0248 (0.0693) | 0.0558 (0.1504) | 0.0867 (0.2732) | 0.0396 (0.0987) |
| GOF | 1.02 | 1.05 | 1.10 | 1.05 | 1.11 |

was collected by filtration and dried in air. For $C_{12}H_{64}B_{40}N_4O_{32}W_{10}$ (3047.59) calculated: 4.73% C, 2.12% H, 1.84% N; found: 4.90% C, 2.40% H, 1.90% N. Based on the elemental analysis and the IR spectrum, the proposed formula of the white precipitate is $[C_2B_{10}H_{11}CH_2NH_3]_4[W_{10}O_{32}]$ (**9**) (1.2498 g, 0.41 mmol, 80%). Crystallization of this compound in acetone–hexane led to the isolation of the decatungstate salt, $[C_2B_{10}H_{11}CH_2NH{=}CMe_2]_4[W_{10}O_{32}][Me_2CO]_4[H_2O]_2$ (**10**)[23]. For $C_{36}H_{108}B_{40}N_4O_{38}W_{10}$ (3476.21) calculated: 12.44% C, 3.13% H, 1.61% N; found: 12.10% C, 3.35% H, 1.65% N. In contrast, crystallization of compound **9** from acetonitrile–ether afforded a batch of crystals from which a monocrystal was chosen for an X-ray diffraction analysis. The crystallographic study revealed the structure of a decatungstate with the formula $[C_2B_{10}H_{11}CH_2NH_3]_2$-$[C_5H_5NH]_2[W_{10}O_{32}][MeCN]_2[Et_2O]_2$ (**11**).

X-ray Crystallography

Intensity data were collected on a Nonius Kappa CCD area detector diffractometer with graphite-monocromated MoKα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects, and for absorption. Key details of the data collection are reported in Table I. The structures were solved and refined using the programs SHELXS86 and SHELXL97 [37,38], respectively. Programs Ortep-3 [39] and PLATON [40] were used to prepare figures and crystallographic data gathered in the supplementary material.

CCDC 777594 (for **5**), 777595 (for **6**), 777596 (for **7**), 777597 (for **8**), 201208 (for **10**) and 777598 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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