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## SHORT COMMUNICATIONS

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**The structures of dimethylammonium metal(III) sulfate hexahydrates (metal = Al, Cr).** By VLADIMIR M. PETRUŠEVSKI, *Institute of Chemistry, Faculty of Natural Sciences and Mathematics, POB 162, 91001 Skopje, Macedonia*

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### Abstract

In a recent article [Galešić & Jordanovska (1992). *Acta Cryst.* **C48**, 256–258], the structures of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} \cdot \text{C}_2\text{H}_8\text{N}^+ \cdot 2\text{SO}_4^{2-}$  and the corresponding chromium analogue were refined in the  $P2_1n$  space group. Despite the formal difference between the formula unit of these compounds,  $RM^{III}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and the general formula of the Tutton salts,  $M_2^I M^{III}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , both studied compounds may be considered as variations in the Tutton salt structure.

Alums and Tutton salts are two very large classes of double salts. The general formula of the alums is  $M^I M^{III}(XY_4)_2 \cdot 12\text{H}_2\text{O}$  and that of Tutton salts is  $M_2^I M^{III}(XY_4)_2 \cdot 6\text{H}_2\text{O}$ . In both classes of compounds,  $M^I = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Ti}^+, \text{NH}_4^+$  and  $XY_4 = \text{SO}_4^{2-}, \text{SeO}_4^{2-}, \text{BeF}_4^{2-}$ . However, for the alum family,  $M^I$  might also be  $\text{CH}_3\text{NH}_3^+, \text{NH}_3\text{OH}^+, \text{N}_2\text{H}_5^+, \text{C}(\text{NH}_2)_3^+$  etc. On the other hand,  $\text{CrO}_4^{2-}$  Tutton salts have been proven to exist. The nature of  $M^{II}$  is specific for Tutton salts only ( $M^{II} = \text{Mg}^{2+}, \text{V}^{2+}, \text{Cr}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Ru}^{2+}$ ) and  $M^{III}$  is specific for alums ( $M^{III} = \text{Al}^{3+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Sc}^{3+}, \text{Ti}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}, \text{Mo}^{3+}, \text{Ru}^{3+}, \text{Rh}^{3+}, \text{Ir}^{3+}$ ).

As long as the formula is considered, the title compounds resemble the alum family, with the exception that they are hexahydrates rather than dodecahydrates. Probably for this reason the authors (Galešić & Jordanovska, 1992) discussed the crystal structures of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} \cdot \text{C}_2\text{H}_8\text{N}^+ \cdot 2\text{SO}_4^{2-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} \cdot \text{C}_2\text{H}_8\text{N}^+ \cdot 2\text{SO}_4^{2-}$  in relation to the alum structures: the mean Al—O<sub>w</sub> distance was basically the same as in a number of alum structures and the  $(\text{CH}_3)_2\text{NH}^+$  group was disordered around the inversion center – as are  $\text{NH}_4^+, \text{NH}_3\text{OH}^+$  and  $\text{CH}_3\text{NH}_3^+$  – in the corresponding Al alums etc. (Lipson, 1935; Fletcher & Steeple, 1964; Abdeen, Will & Weiss, 1981; Abdeen *et al.*, 1981). However, both compounds crystallize in the space group  $P2_1/c$ , thus making impossible any further comparison with the cubic ( $Pa\bar{3}$ ) alums.

It is interesting to note that the similarities between the diethylammonium aluminium sulfate hexahydrate (DAISH) and diethylammonium chromium sulfate hexa-

hydrate (DCrSH), on one hand, and the Tutton salts, on the other, are so close that not only are all these compounds isostructural, but the title compounds may even be encountered as a peculiar type of variation in this family of compounds. The following arguments may be given to support this assertion:

(a) The space group symmetry of the Tutton salts ( $P2_1/a$ ) and of the title compounds ( $P2_1/n$ ) is the same, as is the number of formula units (two) in the unit cell.

(b) The following structural characteristics are typical for the Tutton salts: six water molecules (three different types) at general positions, coordinated to a divalent metal which is on an inversion center; one type of tetrahedral anion and one type of univalent cation, all of which are at general positions. In the title compounds, six water molecules of three different types are found at positions of symmetry 1 and are coordinated to a trivalent (Al or Cr) metal cation, which is on an inversion center. Also, there is one type of tetrahedral anion at general positions and one type of univalent (dimethylammonium) cation disordered across an inversion center, with an occupancy factor of 0.5.\* This disorder resembles that found in the alum family of crystals.

(c) The distortion indices (Baur, 1974) of the  $\text{AlO}_6$  ( $\text{CrO}_6$ ) octahedra are closer to the values found (Petruševski, 1990) in the Tutton salts than to those found in alums (*cf.* Table 1). Also, the  $\text{SO}_4$  tetrahedra seem to have 'normal' bond lengths, as in the majority of the Tutton salts; in the alum family, as a result of extensive thermal motion, the S—O bond lengths are often slightly contracted (by as much as 0.02 Å) when compared (*cf.* Table 2) with the 'ideal'  $\text{SO}_4$  bond length (Murray-Rust, Bürgi & Dunitz, 1978).† No disorder was found in the sulfate group (the sulfate groups in the  $\alpha$  alums are, as a

\* The authors (Galešić & Jordanovska, 1992) mention that the occupancy factors for Al, Cr and N are all 0.5, which is incorrect because Al (Cr) ions *fully occupy* the  $\bar{1}$  positions. It is the *multiplicity* of these positions (2) that is one half of the multiplicity of the positions of general symmetry (4).

† The values for the S—O bond lengths in alums increase at low temperatures, as the thermal motion becomes less pronounced (Brorson & Gajhede, 1987; Best & Forsyth, 1991).

Table 1. Distortion indices (Baur, 1974) of the  $M(\text{H}_2\text{O})_6$  groups in (a) some aluminium and chromium alums, (b) various Tutton salts and (c) the title compounds

Data for alums and Tutton salts are taken from the literature (Petruševski, 1990). Due to the highly pronounced Jahn–Teller distortion, Tutton salts of copper were not listed.

Compound	Type	DI(MO)	DI(OMO)	DI(OO)
<b>(a)</b>				
$(\text{CH}_3\text{NH}_3)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\alpha$	0	0.0106	0.0083
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\alpha$	0	0.0038	0.0030
$(\text{NH}_3\text{OH})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\alpha$	0	0.0031	0.0024
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\alpha$	0	0.0037	0.0029
$\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\alpha$	0	0.0034	0.0027
$\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\beta$	0	0.0083	0.0065
$\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\beta$	0	0.0084	0.0066
$(\text{CH}_3\text{NH}_3)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\beta$	0	0.0020	0.0016
$(\text{CH}_3\text{NH}_3)\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\beta$	0	0.0025	0.0020
$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$\gamma$	0	0.0001	0.0000
<b>(b)</b>				
$(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0104	0.0086	0.0068
$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0099	0.0100	0.0079
$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0128	0.0042	0.0077
$(\text{NH}_4)_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0108	0.0178	0.0140
$(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0092	0.0105	0.0097
$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0121	0.0103	0.0091
$(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0078	0.0119	0.0094
$(\text{NH}_4)_2\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0092	0.0116	0.0099
$(\text{NH}_4)_2\text{Ni}(\text{BeF}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0086	0.0108	0.0091
$(\text{NH}_4)_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0042	0.0114	0.0089
$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0089	0.0166	0.0131
$(\text{C}_2\text{H}_{10}\text{N}_2)\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0012	0.0127	0.0103
<b>(c)</b>				
$[\text{C}_2\text{H}_8\text{N}]\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0039	0.0239	0.0188
$[\text{C}_2\text{H}_8\text{N}]\text{Cr}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$		0.0026	0.0274	0.0215

rule, orientationally disordered along the threefold symmetry axis).

(d) Another indication that the title compounds may be considered as variations in the Tutton salt structures is the structure of the related diprotonated ethylenediammonium compound  $[\text{C}_2\text{H}_{10}\text{N}_2]\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Healy, Patrick & White, 1984). The compound is monoclinic, space group  $P2_1/c$ , and crystallizes with  $Z = 2$ . It shows all structural peculiarities characteristic of Tutton salts (three types of water molecules at general positions, a divalent cation on an inversion center, one type of tetrahedral anions *etc.*). In fact, the authors have already pointed to the great similarity between  $[\text{C}_2\text{H}_{10}\text{N}_2]\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the '... Tutton salts, to which complexes of the present type may present an attractive alternative'.

(e) Concerning the arguments given above, the formula units of  $[\text{C}_2\text{H}_{10}\text{N}_2]\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} \cdot \text{C}_2\text{H}_8\text{N}^+ \cdot 2\text{SO}_4^{2-}$  may perhaps be more consistently written as  $[\frac{1}{2}(\text{C}_2\text{H}_{10}\text{N}_2)]_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $[\frac{1}{2}(\text{C}_2\text{H}_8\text{N})]_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . In the first compound the complex cation lies exactly on an inversion center; in the second this symmetry is achieved only statistically, as a result of both occupational and orientational disorder. Previous work (Petruševski & Aleksovska, 1991) has shown that the unit cell volumes in Tutton salts are very well correlated with the effective ionic radii of the constituent ions (Shannon, 1976). This enabled us to estimate the effective ionic radii of  $\frac{1}{2}(\text{C}_2\text{H}_{10}\text{N}_2^{2+})$  and  $\frac{1}{2}(\text{C}_2\text{H}_8\text{N}^+)$ , given the values for the volumes of the corresponding unit cells and the data for the effective crystal radii. The estimated values are

Table 2. Mean values of the S—O bond lengths in (a) alums, (b) Tutton salts and (c) the title compounds; the value for an isolated 'ideal'  $\text{SO}_4$  ion (Murray-Rust, Bürgi & Dunitz, 1978) is also given

Compound	$R(\text{S—O})$ (Å)	Literature
<b>(a)</b>		
$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.456	Cromer, Kay & Larson (1967)
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.483	Larson & Cromer (1967)
$\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.462	Larson & Cromer (1967)
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.451	Larson & Cromer (1967)
$\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.474	Cromer, Kay & Larson (1966)
$(\text{NH}_3\text{OH})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.460	Abdeen, Will & Weiss (1981)
$(\text{CH}_3\text{NH}_3)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.450	Abdeen <i>et al.</i> (1981)
$\text{CsCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.467	Beattie, Best, Skelton & White (1981)
<b>(b)</b>		
$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.476	Montgomery & Lingafelter (1964)
$(\text{NH}_4)_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.467	Montgomery & Lingafelter (1966)
$(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.466	Montgomery, Chastain & Lingafelter (1966)
$(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.466	Montgomery, Chastain, Natt, Witkowska & Lingafelter (1967)
$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.476	Montgomery, Chastain, Natt, Witkowska & Lingafelter (1967)
$(\text{NH}_4)_2\text{V}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.480	Montgomery, Chastain, Natt, Witkowski & Lingafelter (1967)
$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.472	Maslen, Watson & Moore (1988)
$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.475	Maslen, Ridout, Watson & Moore (1988)
$(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.474	Maslen, Watson, Ridout & Moore (1988)
$[\text{C}_2\text{H}_{10}\text{N}_2]\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.475	Healy, Patrick & White (1984)
<b>(c)</b>		
$[\text{C}_2\text{H}_8\text{N}]\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.470	Galešić & Jordanovska (1992)
$[\text{C}_2\text{H}_8\text{N}]\text{Cr}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.471	Galešić & Jordanovska (1992)
'Ideal' $\text{SO}_4$ ion	1.472	Murray-Rust <i>et al.</i> (1978)

$$R[\frac{1}{2}(\text{C}_2\text{H}_{10}\text{N}_2^{2+})] = 2.29 \quad \text{and} \quad R[\frac{1}{2}(\text{C}_2\text{H}_8\text{N}^+)] = 2.46 \text{ \AA}.$$

These values are reasonable and may be compared with the values for the effective ionic radii for  $\text{NH}_3\text{OH}^+$  (1.65 Å),  $\text{CH}_3\text{NH}_3^+$  (1.90 Å) and  $\text{C}(\text{NH}_2)_3^+$  (2.26 Å), which were calculated previously (Petruševski & Aleksovska, 1991, 1994).

The hydrogen bonds of the water molecules in DAISH and DCrSH are rather strong, resembling the strong hydrogen bonding found in the alums. This is, however, a consequence of the highly charged and polarizable  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$  cations. It is well known from the literature that the water molecules in a number of different compounds containing  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  or  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ , such as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (Buchanan & Harris, 1968),  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (Spundflasche, Fink & Seifert, 1989),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Hermansson, 1983) *etc.*, are strongly hydrogen bonded.

Concerning all the arguments presented above, the title compounds have much more in common with the Tutton salt family than with the alum family of crystals. It seems worthwhile to undertake vibrational spectroscopic investigations of both DAISH and DCrSH, in order to learn whether further similarities exist between any of the above-mentioned classes of compounds.

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**Estimate of two general relationships between the number of atoms and the volumes of the unit cells of compounds containing only non-metallic *p*-block elements.** BY PASCUAL ROMÁN,\* CARMEN GUZMÁN-MIRALLES and ANTONIO LUQUE, *Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain*

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**Abstract**

Compounds with the general formula  $C_aH_bN_cO_dX_x$  (where  $X$  = boron and/or a non-metallic element of the third to fifth period;  $b \geq 1$ ;  $a, c, d, e \dots x \geq 0$ ) have been studied using the Cambridge Structural Database as a source of data and a search tool. Two relationships between the volume ( $V$ ) and the number of formula units ( $Z$ ) in the unit cell have been established that account for the individual contributions of elements to the cell volume in terms of their element period number. The two improved relationships have 84.3 and 82.7% of entries, respectively, within the 10% error boundary, and they are more accurate than other expressions described in the literature.

**Introduction**

Empirical relationships are often of considerable value in many areas of science. An interesting crystallographic example is the estimation of  $Z$ , the number of formula units in the crystallographic unit cell, using the Kempster & Lipson (1972) relationship, hereafter referred to as KL, which has often been used in the crystal structure determination of organic and organometallic compounds:

$$Z_{\text{est}} = (V/18)/N, \quad (1)$$

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where  $N$  is the number of non-H atoms per formula unit and  $V(\text{Å}^3)$  is the volume of the unit cell. However, (1) leads to some important differences between  $Z$  and  $Z_{\text{est}}$  for many compounds and there have been attempts to improve this expression by taking into account the contribution of H atoms (Srinivasan & Rajan, 1975).

Previously (Román, Guzmán-Miralles & Luque, 1993), we analysed organic compounds containing elements of the second period, except boron, and two expressions ( $F_{1/2}$  and  $F_{1/3}$ ) were obtained which take into account the different contributions of H and non-H atoms. Thus,

$$Z_{\text{est}} = (V/A)/(BN_H + CN), \quad (2)$$

where  $A = 12$ ,  $B = 1/2$  for  $F_{1/2}$ , and  $A = 14$ ,  $B = 1/3$  for  $F_{1/3}$ .  $N_H$  is the number of H atoms per formula unit, and  $B$  is their 'contribution factor' to the unit-cell volume. The contribution factor from non-H atoms of the second period,  $C$ , was taken as 1. Elements belonging to high periods were excluded from this study since their volumes are larger than those of the second period.

The aim of the present study is to develop a general expression that can also be applied to compounds containing larger non-metallic *p*-block elements. A total of 2303 crystal structures, of general formula  $C_aH_bN_cO_dX_x$  (where  $X = B$  or any non-metallic element of the third to fifth period), were taken as the starting point for this study.