CROATICA CHEMICA ACTA CCACAA **67** (2) 221–230 (1994)

ISSN 0011-1643 *Original Scientific Paper*
CCA–2179

Structural Correlations in Alums

Vladimir Petruševski and Slobotka Aleksovska

Institute of Chemistry, Faculty of Science,
Arhimedova 5, PO Box 162, 91001 Skopje, Macedonia

Received October 25, 1993

The crystal data for 57 SO_4, SeO_4 and BeF_4 alums of α and β type, with a general formula $M^IM^{III}(XY_4)_2 \cdot 12H_{12}O$, were extracted from literature. Multiple linear regression was employed in order to establish a correlation between the length of the unit cell axis (dependent variable) and (1–2) the effective ionic radii of both M^+ and M^{3+}; (3) the mean X–Y distance; (4) Pauling's electronegativity of atom Y; (5) the alum type; (6) the orbital quantum number of M^{3+} ion and (7) the number of d-electrons in the highest energy shell. The adjusted r^2 statistics had a high value (0.986), thus enabling the use of the regression equation for predictive purposes. The effective ionic radii for $CH_3NH_3^+$, NH_3OH^+, $N_2H_5^+$ and $C(NH_2)_3^+$ ions were calculated in this way. Some notes on the stability and existence of particular alums are also given.

INTRODUCTION

Alums are one of the largest classes of isomorphous compounds. The general formula of alums may be written as: $M^IM^{III}(XY_4)_2 \cdot 12H_2O$. The univalent cation may be Na^+, K^+, Rb^+, Cs^+, Tl^+ but also NH_4^+, $N_2H_5^+$, $CH_3NH_3^+$, NH_3OH^+ *etc.*. Ag-alums are assumed to exist[1,2] but have not been synthesized yet. The trivalent cation may be of Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} Ru^{3+}, Rh^{3+}, Ir^{3+} and Mo^{3+}. The tetrahedral group may be SO_4^{2-}, SeO_4^{2-} and BeF_4^{2-}. The water molecules are the only irreplaceable moieties in the structure.

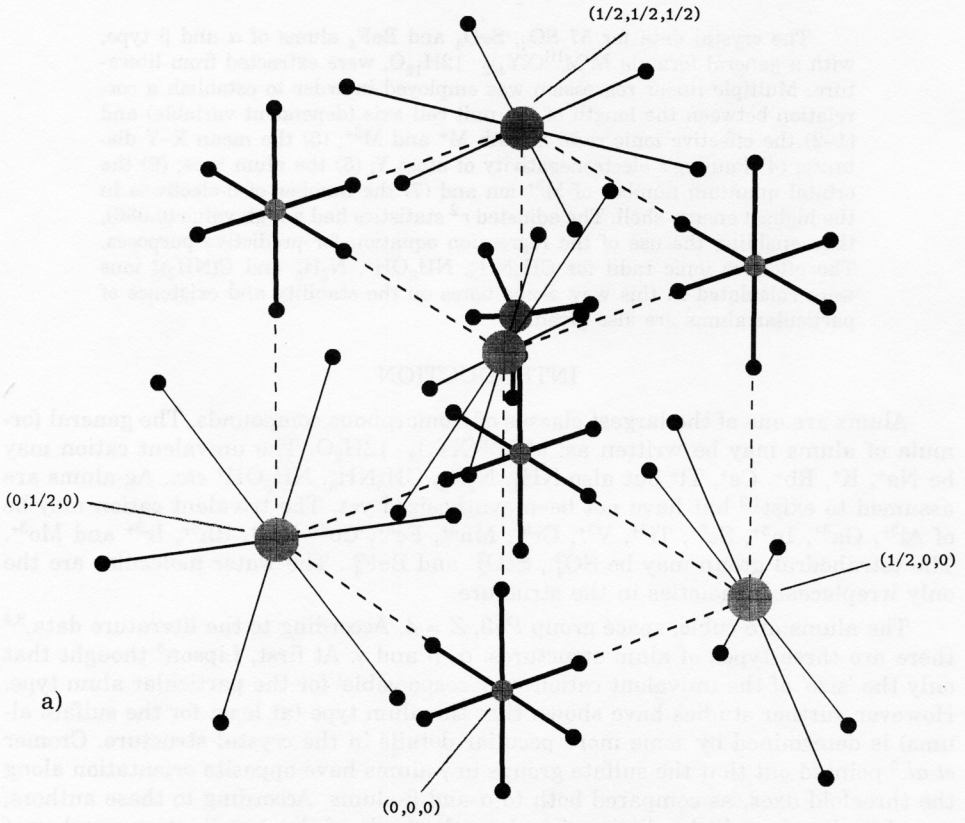
The alums are cubic, space group $Pa3$, $Z = 4$. According to the literature data,[3,4] there are three types of alum structures: α, β and γ. At first, Lipson[3] thought that only the 'size' of the univalent cation was 'responsible' for the particular alum type. However, further studies have shown that the alum type (at least for the sulfate alums) is determined by some more peculiar details in the crystal structure. Cromer *et al.*[5] pointed out that the sulfate groups in γ-alums have opposite orientation along the threefold axes, as compared both to α-and β-alums. According to these authors, α and β alums might be distinguished on the basis of the coordination number of the univalent cation, which is 6 in the case of α, but 12 in the case of β alums.

The thorough structure investigations of Beattie *et al.*[8] of a number of Cs-alums revealed that this criterion is not universal. A new criterion has been proposed,[8]

based on the geometry of the $M^{I}Ow_6$ groups. These 'polyhedra' are almost planar in the case of β-alums, the Ow–M^{I}–Ow angles being in the range of 60.0 – 60.2° (*cf.* Figure 1a). On the other hand, the Ow–M^{I}–Ow angle in α-alums is about 65° on the average, thus corresponding to highly distorted octahedra (*cf.* Figure 1b). It should also be noted that, in most cases, the orientation of the $M^{III}Ow_6$ octahedra with respect to the cell axes, differs in α-and β-alums (Figure 1).

In our previous paper,[9] knowing only the composition of a particular salt, we were able to predict accurately the unit cell volume of the Tutton salts* by using statistical methods. The same appears to be possible for alums too, the precision of the prediction being even higher. Furthermore, as the alums are cubic, the prediction of the lattice constant is straightforward.

Another problem is the existence and stability of particular isomorphs. It is, namely, expected that even for a large class of isomorphous compounds there are some limits within which the structural entities may be varied. This has already



* Tutton salts make another large family of isomorphous crystals, having the general formula $M^{I}_2M^{II}(XY_4)_2 \cdot 6H_2O$ (M^{I} = K^+, Rb^+, Tl^+, NH_4^+, Cs^+; M^{II} = Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} *etc.*; the tetrahedral group may be SO_4^{2-}, SeO_4^{2-}, BeF_4^{2-} and CrO_4^{2-} – an important difference with respect to the alum family

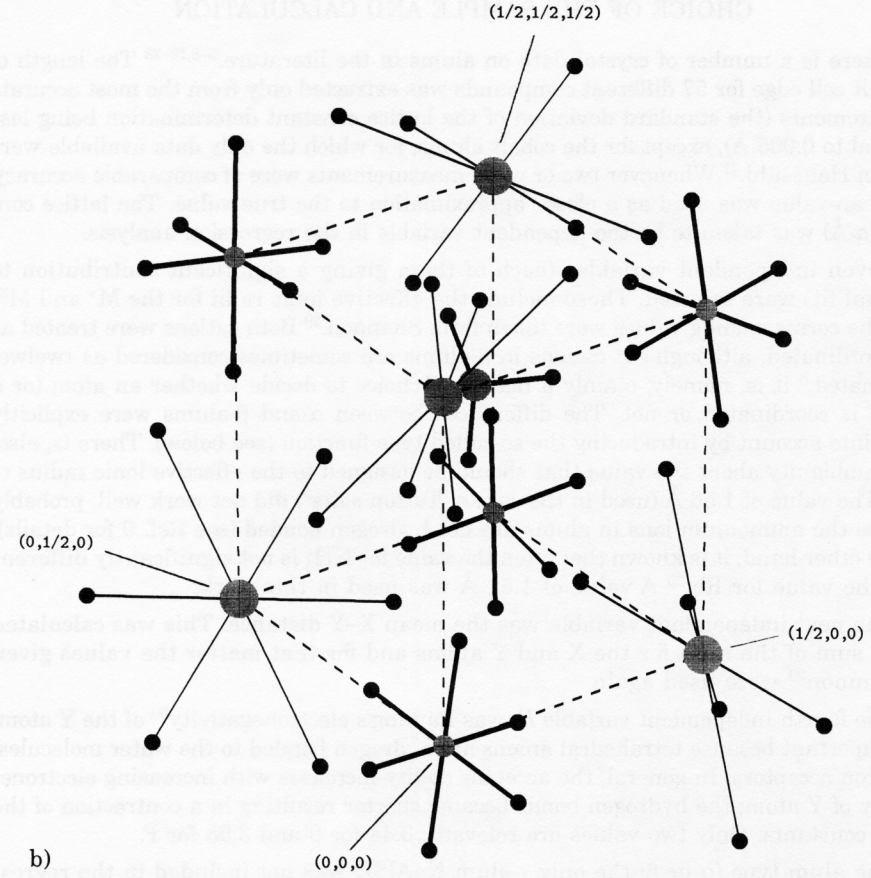


Figure 1. Schematical presentation of a part (1/8) of the unit cell of β-alum, $CsAl(SO_4)_2 \cdot 12H_2O$ (a) and α-alum, $RbAl(SO_4)_2 \cdot 12H_2O$ (b). The octahedra at (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) are $Al(H_2O)_6^{3+}$ cations; $Cs(H_2O)_6^{+}$ (a) i.e. $Rb(H_2O)_6^{+}$ (b) are at (1/2,0,0), (0,1/2,0), (0,0,1/2) and (1/2, 1/2,1/2). Sulfate ions lie on *C*3 (not drawn) axes inside the dashed region. For clarity, hydrogen atoms are not shown.

been discussed earlier[1] and, on the basis of the ionic radii for M^+ and M^{3+}, the existence of particular isomorphous (*e.g.* Li alums) was simply ruled out. Few more details on this subject will be discussed in the present paper.

Briefly, a word on the abbreviations used throughout the text. Every alum will be denoted by four symbols. The first three reveal the nature of M^{I}, M^{III} and Y; the fourth is always D, which stands for dodecahydrate. Therefore, RbVSD is an abbreviation for $RbV(SO_4)_2 \cdot 12H_2O$; CsCrBeD – for $CsCr(BeF_4)_2 \cdot 12H_2O$ *etc.* In the case of NH_4^+, $CH_3NH_3^+$, NH_3OH^+, $N_2H_5^+$ and $C(NH_2)_3^+$, the abbreviations used are A, M, Ha, Hy and Gu.

CHOICE OF THE SAMPLE AND CALCULATION

There is a number of crystal data on alums in the literature.[5–8,10–28] The length of the unit cell edge for 57 different compounds was extracted only from the most accurate measurements (the standard deviation of the lattice constant determination being less or equal to 0.005 Å), except for the cobalt alums, for which the only data available were those of Haussühl.[11] Whenever two or more measurements were of comparable accuracy, the mean-value was used as a closer approximation to the true value. The lattice constant (a/Å) was taken to be the dependent variable in the regression analysis.

Seven independent variables (each of them giving a significant contribution to the final fit) were selected. These include the effective ionic radii for the M^+ and M^{3+} ions; the corresponding values were taken from Shannon.[29] Both cations were treated as six- coordinated, although M^+ cations in β-alums are sometimes considered as twelwe-coordinated;[5] it is, namely, mainly a matter of choice to decide whether an atom (or a group) is coordinated or not. The differences between α-and β-alums were explicitly taken into account by introducing the so-called type-function (see below). There is, also, some ambiguity about the value that should be assigned to the effective ionic radius of NH_4^+. The value of 1.56 Å (used in the case of Tutton salts[9]) did not work well, probably because the ammonium ions in alums are not hydrogen bonded (see Ref. 9 for details). On the other hand, it is known that often the value for NH_4^+ is not significantly different from the value for Rb.[29] A value of 1.51 Å was used in this work.

The next independent variable was the mean X–Y distance. This was calculated as the sum of the radii for the X and Y atoms and for that matter the values given by Shannon[29] were used again.

The fourth independent variable E, was Pauling's electronegativity[30] of the Y atom. It is important because tetrahedral anions are hydrogen bonded to the water molecules, as proton acceptors. In general, the acceptor ability increases with increasing electronegativity of Y atom; the hydrogen bonds became shorter resulting in a contraction of the lattice constants. Only two values are relevant: 3.44 for 0 and 3.98 for F.

The alum type (α or β; the only γ-alum NaAlSD was not included in the regression analysis) was taken into account in the following way: it is an empirical fact that the unit cell edges of β-alums are larger than those of α-alums, This is, obviously, a singular behavior (no continuous transition from α to β type is possible). Therefore, the alum type-function was taken as a Cronecker delta function – $\delta_{i\beta}$, its value being 1 for β alums (i = β) and 0 for α alums (i = α).

It was noted, at this stage, that the agreement between the calculated and found values of the lattice parameter a was rather good; yet, some discrepancies were obvious. The fit was apparently 'bad' for the alums of the high spin ions: Co, Rh, Ir. Also, the values obtained from the regression equation were somewhat high for Ga and In alums, but not for the Al alums (Al has an empty d-shell). Therefore, two more independent variables were included, both giving significant improvement to the regression equation: the angular momentum (*i.e.* the orbital quantum number – L) and the d-electronic configuration (*i.e.* n – number of d-electrons) of the highest energy shell of M^{3+} ion. The former (the orbital quantum number) was calculated using the rules given by Hund*; the latter (the ion configuration) may be found in

* Treating the M^{3+} ions as being 'free'. This is, of course, an oversimplification.

most textbooks on general and inorganic chemistry. The addition of further explanatory variables (such as S – the spin quantum number of M^{3+} ion) appeared to be statistically insignificant. Also, it was not necessary to consider either cross or higher order terms in the regression equation.

All relevant data for the independent variables are summarized in Table I.

The calculations were performed on a Commodore *Amiga-500* microcomputer. A BASIC-coded program for multiple linear regression analysis was used.[31] The calculations were later repeated on a PC-compatible machine, using the 'STATGRAPH' statistical package. The results were, for all practical purposes, the same.

RESULTS AND DISCUSSION

As a result of the least-squares best-fit procedure, the length of the unit cell edge may be presented in the form:

$$a = b + c \cdot R(M^{+}) + d \cdot R(M^{3+}) + e \cdot R(X\text{–}Y) + f \cdot E(Y) + g \cdot \delta_{i\beta} + h \cdot L(M^{3+}) + i \cdot n(M^{3+})$$

and the values of the coefficient obtained by linear regression, are given in Table II.

TABLE I.

Values od the independent variables used as input data in the regression analysis (radii of the univalent and trivalent cation; the orbital quantum number and the number of d-electrons in the trivalent cation; the X–Y distance and Paulings electronegativity)

	$R(M^{+})$/Å	$R(M^{3+})$/Å	$L(M^{3+})$	$n(M^{3+})$	$R(X\text{–}Y)$/Å	$E(Y)$
K^{+}	1.38					
Tl^{+}	1.50					
NH_4^{+}	1.51					
Rb^{+}	1.52					
Cs^{+}	1.67					
Al^{3+}		0.535	0	0		
Ga^{3+}		0.620	0	10		
In^{3+}		0.800	0	10		
Sc^{3+}		0.745	0	0		
Ti^{3+}		0.670	2	1		
V^{3+}		0.640	3	2		
Cr^{3+}		0.615	3	3		
Mn^{3+}		0.645	2	4		
Fe^{3+}		0.645	0	5		
Co^{3+}		0.545	6	6		
Mo^{3+}		0.690	3	3		
Ru^{3+}		0.680	0	5		
Rh^{3+}		0.665	6	6		
Ir^{3+}		0.680	6	6		
SO_4^{2-}					1.47	3.44
SeO_4^{2-}					1.63	3.44
BeF_4^{2-}					1.555	3.98

TABLE II

Numerical values of the coefficients, calculated by regression analysis (t-statistic is a quotient of the numerical value and its standard deviation)

Coefficient	Numerical value	Standard deviation	*t*-statistic
b/Å	10.1328	0.0726	139.52
c	0.5903	0.0256	23.04
d	0.7729	0.0366	21.10
e	1.2925	0.0365	35.42
f/Å	−0.3185	0.0153	−20.87
g/Å	0.0350	0.0060	5.78
h/Å	−0.0091	0.0011	−8.20
i/Å	−0.0031	0.0007	−4.22

adjusted r^2 statistics = 0.986

It is to be noted that the value (0.986) of the adjusted r^2 statistic is very high. In order to provide an even better picture of the predictive strength of the regression equation and the fit between the actual and predicted values for a (the unit cell edge), additional results are given in Figure 2 and Table III.

Using equation (1), the values for the effective ionic radii for some substituted ammonium ions were calculated. The results are given in Table IV. It should be men-

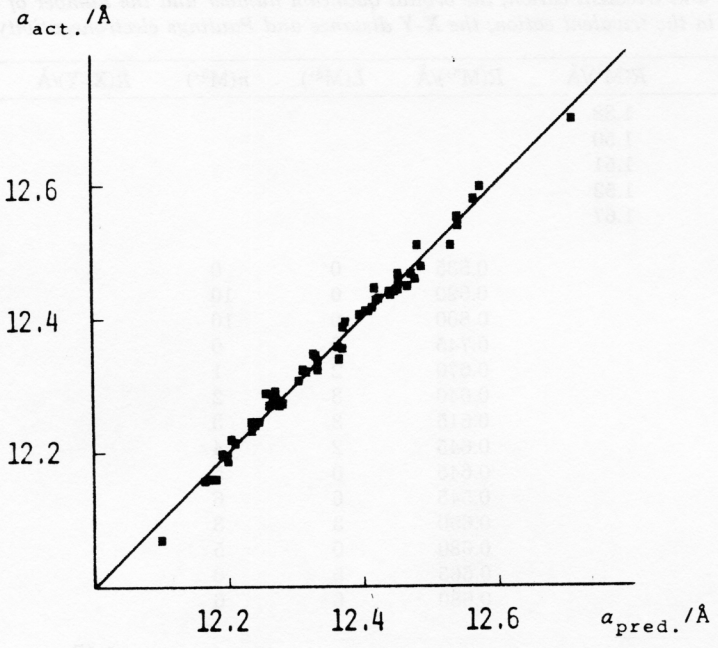


Figure 2. Agreement between the actual and predicted values of the lattice constants in the studied alums.

TABLE III

Actual and predicted values for the lattice constant in the studied alums, together with various measures for the error of the estimate

Compound	Type	Actual a/Å	Predicted a/Å	Δa/Å	R/%
CsAlSD	β	12.356	12.371	−0.015	0.12
CsGaSD	β	12.410	12.406	0.004	0.03
CsInSD	β	12.538	12.545	−0.007	0.06
CsScSD	β	12.510	12.534	−0.024	0.19
CsTiSD	β	12.466	12.454	0.011	0.09
CsVSD	β	12.445	12.419	0.026	0.21
CsCrSD	β	12.404	12.397	0.007	0.06
CsMnSD	β	12.428	12.426	0.002	0.02
CsFeSD	β	12.440	12.441	−0.001	0.01
CsRuSD	β	12.447	12.468	−0.021	0.17
CsMoSD	β	12.442	12.455	−0.013	0.10
CsCoSD	α	12.292	12.271	0.021	0.17
CsRhSD	α	12.357	12.364	−0.007	0.06
CsIrSD	α	12.395	12.375	0.020	0.16
RbAlSD	α	12.244	12.248	−0.004	0.03
RbGaSD	α	12.272	12.283	−0.011	0.09
RbInSD	α	12.426	12.422	0.004	0.03
RbTiSD	β	12.339	12.366	−0.027	0.22
RbVSD	β	12.345	12.331	0.014	0.12
RbCrSD	α	12.277	12.273	0.004	0.03
RbFeSD	α	12.321	12.317	0.004	0.03
RbCoSD	α	12.160	12.183	−0.023	0.19
KAlSD	α	12.158	12.165	−0.007	0.06
KVSD	β	12.288	12.257	0.031	0.25
KCrSD	α	12.197	12.191	0.006	0.05
KFeSD	α	12.244	12.235	0.009	0.08
KCoSD	α	12.070	12.100	−0.030	0.25
KGaSD	α	12.186	12.200	−0.14	0.11
TlAlSD	α	12.232	12.236	−0.004	0.03
TlVSD	β	12.348	12.328	0.020	0.16
TlCrSD	α	12.270	12.261	0.009	0.07
TlFeSD	α	12.307	12.306	0.001	0.01
TlGaSD	α	12.288	12.271	0.017	0.14
TlInSD	α	12.410	12.410	0.000	0.00
AAlSD	α	12.241	12.242	−0.001	0.01
AVSD	β	12.337	12.334	0.003	0.03
ACrSD	α	12.274	12.267	0.007	0.05
AFeSD	α	12.322	12.311	0.011	0.09
ACoSD	α	12.160	12.177	−0.017	0.14
AGaSD	α	12.269	12.277	−0.008	0.06
AInSD	α	12.416	12.416	0.000	0.00
KAlSeD	α	12.386	12.372	0.014	0.11
RbAlSeD	α	12.453	12.455	−0.002	0.01
CsAlSeD	α	12.552	12.543	0.009	0.07
TlAlSeD	α	12.434	12.443	−0.009	0.07
AAlSeD	α	12.439	12.449	−0.010	0.08
RbCrSeD	α	12.460	12.480	−0.020	0.16
CsCrSeD	α	12.580	12.569	0.011	0.09
ACrSeD	α	12.466	12.474	−0.008	0.06
RbGaSeD	α	12.477	12.489	−0.012	0.10
CsGaSeD	α	12.597	12.578	0.019	0.15
AGaSeD	α	12.508	12.483	0.025	0.20
CsInSeD	α	12.700	12.717	−0.017	0.13
ACrBeD	α	12.218	12.205	0.013	0.11
RbCrBeD	α	12.214	12.211	0.003	0.02
CsCrBeD	β	12.323	12.335	−0.012	0.09
TlCrBeD	α	12.195	12.199	−0.004	0.03

TABLE IV

Calculated values for the effective ionic radii of some substituted ammonium ions, in α- and β-alums

Compound	a/Å	$R(M^+)$/Å
HaAlSD	12.314	1.656
HaFeSD	12.394	1.632
HaGaSD	12.348	1.631
	mean-value	*1.640*
MaAlSD	12.501	1.889
MaGaSD	12.543	1.902
MaInSD	12.669	1.880
MaCrSD	12.538	1.909
MaVSD	12.584	1.947
MaFeSD	12.571	1.890
MaAlSeD	12.684	1.849
MaCrSeD	12.496	1.944
	mean-value	*1.901*
GuVSD	12.776	2.240
GuCrBeD	12.671	2.275
	mean-value	*2.257*
HyAlSD	12.392	1.705

tioned that the calculated mean value for $R(CH_3NH_3^+)$ is in fair agreement with the previously reported[9] values (1.89 and 1.99 Å).

The stability of the alums as a function of M^I and M^{III} has already been discussed in the literature.[1] If the tetrahedral anion is included too, then the (empirical) general rule is that the stability of a particular alum increases by increasing $R(M^+)$ and by decreasing $R(M^{3+})$ and $R(X–Y)$. Sulfate alums are, therefore, more stable than the selenate ones.

If only *metal* cations are considered, a very rough stability criterion may be given in terms of the quotient of $R(M^+)$ and $R(M^{3+})$: *the larger the quotient of M^+ and M^{3+} effective ionic radii – the greater the stability of the alums.* The variation of this quotient by composition is presented in Table V.

Obviously, Li^+ is too small and cannot be accommodated in an alum-like structure (however, the existence of *double salts* of lithium sulfate with $M_2^{III}(SO_4)_3$ could not be excluded in this way). On the other hand, Tl^{3+} is 'too large' and the alum structure is unstable. Even with Cs^+, dihydrate is formed rather than dodecahydrate.[32] For the same reason (large M^{3+} cations *i.e.* low $R(M^+)/R(M^{3+})$ values), the double sulfates of the rare earths and alkali metals do not form alum-like structures.

On the other hand, the results in Table V do suggest that Ag^+ alums could possibly exist. Our attempts to synthesize AgAlSD have failed so far, probably because the solubility of Ag_2SO_4 is very low[33] and it precipitates almost completely due to the effect of the common SO_4^{2-} ion. Perhaps it could be synthesized from a saturated $Al_2(SO_4)_3$ solution, containing Ag^+ ions. AgAlSeD (and, possibly, AgAlBeD) could, in

TABLE V

$R(M^{+})/R(M^{3+})$ ratio for various uni- and trivalent metals as a criterion for the existence of particular alums; bold – alum exists; underlined – alum existence possible; italic existence improbable

	Li	Na	Ag	K	Tl	Rb	Cs
Al	*1.421*	1.907	2.150	**2.579**	**2.804**	**2.841**	**3.121**
Co	*1.394*	1.872	2.110	**2.532**	2.752	**2.789**	**3.064**
Cr	*1.236*	1.659	1.870	**2.244**	**2.439**	**2.472**	**2.715**
Ga	*1.226*	1.645	1.885	**2.226**	**2.419**	**2.452**	**2.694**
V	*1.188*	*1.594*	1.797	**2.156**	**2.344**	**2.375**	**2.609**
Fe	*1.178*	*1.581*	1.783	**2.140**	**2.326**	**2.357**	**2.589**
Mn	*1.178*	*1.581*	1.783	2.140	2.326	2.357	**2.589**
Rh	*1.143*	*1.534*	1.729	**2.075**	**2.256**	**2.286**	**2.511**
Ti	*1.134*	*1.522*	1.716	2.060	2.239	**2.269**	**2.493**
In	*1.118*	*1.500*	1.691	2.029	2.206	2.235	**2.456**
Ru	*1.118*	*1.500*	1.691	2.029	2.206	2.235	**2.456**
Mo	*1.101*	*1.478*	1.667	2.000	2.174	2.203	**2.420**
Nb	*1.056*	*1.417*	*1.597*	1.917	2.083	2.111	2.319
Ta	*1.056*	*1.417*	*1.597*	1.917	2.083	2.111	2.319
Sc	*1.020*	*1.369*	*1.544*	1.852	2.013	2.040	**2.242**
In	*0.950*	*1.275*	*1.438*	1.725	**1.875**	**1.900**	**2.087**
Tl	*0.859*	*1.153*	*1.299*	*1.559*	1.695	1.718	1.887
Dy	*0.833*	*1.118*	*1.261*	*1.513*	1.645	1.667	1.831
Gd	*0.810*	*1.087*	*1.226*	*1.471*	*1.599*	*1.620*	1.780
Eu	*0.803*	*1.077*	*1.214*	*1.457*	*1.584*	*1.605*	1.763
Ce	*0.752*	*1.010*	*1.139*	*1.366*	*1.485*	*1.505*	1.653
La	*0.736*	*0.988*	*1.114*	*1.337*	*1.453*	*1.473*	*1.618*

principle, also exist. Nb^{3+} and Ta^{3+} alums are also expected to exist, although they have not been synthesized yet.

It is important to make attempts to prepare all compounds the existence of which has been predicted. If these attempts appear to be successful, then the criteria mentioned above might be useful in the case of other isomorphous series, as well. If, on the other hand, these attempts fail, then it could be concluded that the existence of the alum structure is governed by some more peculiar and subtle mechanism of interactions and energy minimizing. If so, efforts should be made to discover the true nature of this mechanism.

Acknowledgement. – The authors are indebted to Dr Ivan Grozdanov for the suggestions made. The financial support of the Ministry of Science of the Republic of Macedonia is sincerely appreciated.

REFERENCES

1. J. R. I. Hepburn and R. F. Phillips, *J. Chem. Soc.* (1952) 2569.
2. I. Filipović and S. Lipanović, *General and Inorganic Chemistry*, Školska knjiga, Zagreb, 1978.
3. H. Lipson and H. A. Beevers, *Proc. Roy. Soc.* **A148** (1935) 664.
4. H. Lipson, *ibid.* **A151** (1935) 347.
5. D. T. Cromer, M. I. Kay, and I. A. C. Larson, *Acta Crystalogr.* **21** (1966) 383.
6. A. H. C. Ledsham and H. Steeple, *ibid.* **B24** (1968) 320.

7. A. H. C. Ledsham and H. Steeple, *ibid.* **B25** (1969) 398.
8. J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton* (1981) 2105.
9. V. Petruševski and S. Aleksovska, *Croat. Chem. Acta* **64** (1991) 577.
10. G. E. Bacon and W. E. Gardner, *Proc. Roy. Soc.* **A246** (1958) 78.
11. S. Haussühll, *Z. Kristalogr.* **116** (1961) 371.
12. R. O. Flecher and H. Steeple, *Acta Crystalogr.* **15** (1962) 960.
13. R. O. W. Flecher and H. Steeple, *ibid.* **17** (1964) 290.
14. D. T. Cromer, M. I. Kay, and A. C. Larson, *ibid.* **22** (1967) 182.
15. A. C. Larson and D. T. Cromer, *ibid.* **22** (1967) 793.
16. D. T. Cromer and M. I. Kay, *ibid.* **22** (1967) 800.
17. A. H. C. Ledsham and H. Steeple, *ibid.* **B24** (1968) 1287.
18. A. Lari-Lavassani, C. Avinens, and L. Cot, *C. R. Acad. Sci. C.* **268** (1969) 1781.
19. A. Lari-Lavassani, L. Cot, and C. Avinens, *C. R. Acad. Sci. C.* **270** (1970) 1973.
20. A. H. Ledsham, H. Steeple, and W. Hughes, *Acta Crystalogr.* **26** (1970) 1240.
21. M. I. Kay and D. T. Cromer, *ibid.* **26** (1966) 1349.
22. N. Strupler, *Bull Soc. Chim. Fr.* **7** (1970) 2451.
23. B. I. Bashkov, L. N. Komissarova, F. M. Spiridonov, and V. M. Shackii, *Kristallografiya* **16** (1971) 598.
24. J. Sygusch, *Acta Crystalogr.* **B30** (1974) 662.
25. A. M. Abdeen, G. Will, and A. Weiss, *Z. Kristallogr.* **154** (1981) 45.
26. A. M. Abdeen, G. Will, W. Schäfer, A. Kirfel, M. O. Bargouth, K. Recker, and A. Weiss, *ibid.* **157** (1981) 147.
27. R. S. Armstrong, J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton* (1981) 2105.
28. J. K. Beattie, S. P. Best, B. W. Skelton, and A. H. White, *ibid.* (1983) 1973.
29. R. D. Shannon, *Acta Crystalogr.* **A32** (1976) 751.
30. J. E. Huheey, *Inorganic Chemistry*, 3rd edition, New-York, Harper & Row, 1983, pp. 146–148,
31. J. Hudson, *Practical Computing*, February, (1983) 113.
32. J. M. Manoli, P. Herpin, and A. Dereigne, *Acta Crystallogr.* **B28** (1972) 806.
33. R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 64th edition, CRC Press, Boca Raton, 1984.

SAŽETAK

Strukturne korelacije u stipsama (alaunima)

Vladimir Petruševski i Slobotka Aleksovska

U literaturi citirani kristalografski podaci za 50 stipsa (alauna) formule $M^{I}M^{III}(XY_4)_2 \cdot 12H_2O$ (M^{I} = Na^+, K^+, Rb^+, Cs^+, Tl^+, NH_4^+ $N_2H_5^+$, $CH_3NH_3^+$, NH_3OH^+; M^{III} = Al^{3+}, Ga^{3+}, In^{3+}, SC^{3+}, Tl^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ru^{3+}, Ir^{3+}, Mo^{3+}; XY_4^{2-} = SO_4^{2-}, $BeFO_4^{2-}$) upotrijebljeni su za izračunavanje korelacija između (1) dimenzija jedinične ćelije, (2) ionskih radiusa kationa M^{I} i M^{III}, (3) srednje udaljenosti između atoma u anionu (X–Y), (4) Paulingove elektronegativnosti atoma Y, (5) tipa stipse (alauna), (6) orbitalnog kvatnog broja atoma M^{3+}, i (7) broja d-elektrona u najvišoj energetskoj ljuski.