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## Correlations Between Effective Crystal Radii and Unit Cell Volume in Tutton Salts

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The unit cell volumes of 29 Tutton salts (the general formula of which is  $M_2^I M^{II} (XY_4)_2 \cdot 6H_2O$ ) were retrieved from the literature. Assuming that the unit cell volume may be represented by a function of the type:  $V = a + b R(M^+) + c R(M^{2+}) + d R(X-Y) + e E_Y (R(M^+))$  where  $R(M^{2+})$  are the effective crystal radii of the uni- and divalent cations, respectively;  $R(X-Y)$  is the X-Y distance in the tetrahedral anion and  $E_Y$  is the Pauling electronegativity of the Y atoms, the multiple linear regression analysis was applied. The agreement between the observed and the predicted values of  $V$  is rather good (adjusted  $r^2 = 0.966$ ), thus allowing to predict the values for effective crystal radii of ions that have not been published so far. In line with this, the Ru-Tutton salts are predicted to be low-spin  $Ru^{2+}$  hexaaquacomplexes. Some points concerning the possibility of the existence of particular isomorphs are also discussed.

### INTRODUCTION

Tutton salts are double salts with the general formula  $M_2^I M^{II} (XY_4)_2 \cdot 6H_2O$ , where  $M^I = K, NH_4, Rb, Cs, Tl$ ;  $M^{II} = Mg, Mn, Fe, Co, Ni, Cu$  etc.; and  $Y = O, X = S, Se$  or  $Cr$ . The crystal structures of a number of Tutton salts with these oxo-anions have been determined by both X-ray and neutron diffraction.<sup>1-25</sup> Some  $BeF_4^-$  compounds are also known.<sup>3,26,27</sup> It seems interesting to mention that Ru also forms Tutton salts.<sup>28</sup> The structure of ethylenediammonium-Ni Tutton salt has recently been determined.<sup>29</sup> All compounds crystallize in the space group  $P2_1/a$  ( $P2_1/c$ ) with  $Z = 2$ . The water molecules are coordinated to  $M^{2+}$ , thus forming an octahedron (which is, except for the Cu-Tutton salts, fairly regular), and are hydrogen bonded to the O (or F) atoms of the  $XY_4$  groups.

Many physico-chemical properties of the compounds are expected to depend on the radii (ionic, covalent or the so-called 'crystal radii', introduced by Shannon<sup>30,31</sup>) of the constituents. It seemed desirable to investigate the relationship between these parameters and the unit cell volume of different Tutton salt compounds. The expected relationship, however, may not be a simple one, depending on the magnitude of the

cooperative crystal effects which may be highly specific and, hence, unpredictable. In an attempt to establish this relationship, the multiple linear regression analysis was employed.

The stability of the crystals is also expected to depend (possibly, in a complicated way) on the crystal radii of the entities. Hapburn and Phillips<sup>32</sup> have studied, for that matter, the stability of alums ( $M^I M^{III} (RO_4)_2 \cdot 12H_2O$ ), and concluded that the stability of alums increases with the increasing size of the  $M^{I+}$  cation and with the decreasing size of  $M^{3+}$ . It seemed interesting to check whether a similar conclusion could be drawn in the case of Tutton salts.

### CALCULATION AND RESULTS

The calculations (*i.e.* regression analyses were performed on Commodore-Amiga microcomputer using a BASIC program,<sup>33</sup> which was slightly modified. Double precision variables were used in order to suppress accumulation of rounding errors. Satisfactory results were obtained without inclusion of either cross or higher-order terms in the regression analyses.

A preliminary survey of the data indicated that the 'dimension' of the mono- and divalent cations, as well as of the anion, influences the volume of the unit cell. The values for the effective crystal radii of  $M^+$ ,  $M^{2+}$ , X and Y were taken from Shannon<sup>31</sup> and are given in Table I, together with other relevant data (the X-Y distance was calculated as:  $R(X-Y) = R(X) + R(Y)$ ; the values for  $R(M^{2+})$  refer to the high spin state of the  $d$  ions). The corresponding value for the  $NH_4^+$  ion in this class of compounds was estimated at 1.56 Å, assuming that  $R(NH_4^+) + (O^{2-}) = R(N \cdots O)$ , the latter quantity being the hydrogen bond distance between the nitrogen atom of the ammonium ion and the sulfate (selenate, chromate) oxygens to which it is H-bonded. The mean value of this distance, calculated on the basis of the X-ray data for ANiSH, ANiSeH and ANiCrH,<sup>7,23,25</sup> was found to be 2.91 Å.

First, regression analysis was carried out for the nine ammonium sulfate and for the five copper sulfate Tutton salts, separately. The independent variable was  $R(M^{2+})$ , or  $R(M^+)$ . The results showed (as expected) that a correlation exists (the RBSQ, or adjusted  $r^2$ , values were 0.840 and 0.960, respectively). However, extension to a larger number of Tutton salts, with both  $M^{2+}$  and  $M^+$  cation different, is not possible unless a multiple regression analysis is performed. When both cations were varied, a much closer agreement between the calculated and observed unit cell volumes (RBSQ = 0.964, for 19 data triplets) was found. Inclusion of the data for selenates and chromates was made possible by introducing another independent variable – the X-Y distance, *i.e.*  $R(X-Y)$ , followed by an increase in RBSQ to 0.967. Finally, tetrafluoroberyllates were included together with a fourth explanatory variable – electronegativity  $E$  of the Y atom<sup>34</sup> – to account for the 'softness' of the anion. The  $XY_4^{2-}$  are hydrogen bonded and due to the increased proton-acceptor ability of the F atom and its smaller van der Waals radius, the water molecules and  $BeF_4$  groups are packed more tightly. This results in a decrease of the unit cell volume of  $BeF_4$  compounds with respect to  $SO_4$ . The best-fit regression equation may be presented in the form:

$$V = a + b \cdot R(M^+) + c \cdot R(M^{2+}) + d \cdot R(X-Y) + e \cdot E_y \quad (1)$$

The values of the coefficients together with their standard errors and  $t$ -statistics are given in Table II.

TABLE I

Input data in the regression analysis, for the studied Tutton salts (acronyms are used to identify the nature of  $M^I$ ,  $M^{II}$  and  $XY_4$  ions; A — ammonium and (enH<sub>2</sub>) — ethyldiammonium; S, Se, Cr and Be stand for SO<sub>4</sub>, SeO<sub>4</sub>, CrO<sub>4</sub> and BeF<sub>4</sub>, respectively. Electronegativities E<sub>b</sub> and E<sub>f</sub> were taken to be 3.44 and 3.98. The rightmost H stands for hexahydrate). Whenever two or more structure determinations were available, less accurate data for the unit cell volumes (marked with —) were not included in the statistical treatment. The data included are marked with + (if more than one accurate value exists for a given compound, the mean value is used in the statistical analysis).

Values for effective crystal radii are taken from Ref. 31

Compound	$R(M^{2+})/\text{\AA}$	$R(M^+)/\text{\AA}$	$R(X-Y)/\text{\AA}$	$V/\text{\AA}^3$	Reference
ACuSH	0.73	1.56	1.47	687.3	[1] —
ACuSH	0.73	1.56	1.47	697.7	[2] —
ACuSG	0.73	1.56	1.47	692.0	[3] +
ACuSH	0.73	1.56	1.47	690.3	[4] +
ACuSH	0.73	1.56	1.47	691.6	[5] +
ANiSH	0.69	1.56	1.47	682.7	[6] +
ANiSH	0.69	1.56	1.47	692.3	[7] —
AZnSH	0.74	1.56	1.47	697.7	[8] —
AZnSH	0.74	1.56	1.47	691.0	[9] +
AMgSH	0.72	1.56	1.47	706.9	[7] —
AMgSH	0.72	1.56	1.47	697.1	[10] +
ACdSH	0.95	1.56	1.47	727.6	[11] +
AMnSH	0.83	1.56	1.47	716.5	[12] +
AVSH	0.79	1.56	1.47	714.2	[13] +
AFeSH	0.78	1.56	1.47	704.3	[13] +
ACoSH	0.745	1.56	1.47	691.7	[14] +
ACoSH	0.745	1.56	1.47	690.6	[13] +
KMgSH	0.72	1.38	1.47	654.7	[15] +
KNiSH	0.69	1.38	1.47	646.8	[16] +
KZnSH	0.74	1.38	1.47	654.3	[17] +
KCuSH	0.73	1.38	1.47	655.0	[18] +
KCoSH	0.745	1.38	1.47	657.8	[14] +
RbCuSH	0.73	1.52	1.47	686.1	[19] +
RbCoSH	0.745	1.52	1.47	683.4	[14] +
CsCuSH	0.73	1.67	1.47	727.4	[20] +
CsCoSH	0.745	1.67	1.47	726.7	[14] +
TlCuSH	0.73	1.50	1.47	688.1	[21] +
KCuSeH	0.73	1.38	1.63	690.6	[22] +
ANiSeH	0.69	1.56	1.63	720.6	[23] +
ACuSeH	0.73	1.56	1.63	725.9	[24] +
ANiCrH	0.69	1.56	1.61	714.5	[25] +
ACuBeH	0.73	1.56	1.555	684.9	[3] +
ACoBeH	0.745	1.56	1.555	682.8	[26] +
ANiBeH	0.69	1.56	1.555	676.1	[27] +
KRuSH	----	1.38	1.47	649.8	[28] —
RbRuSH	----	1.52	1.47	686.3	[28] —
(enH <sub>2</sub> )NiSH	0.69	----	1.47	757.6	[29] —

Addition of further explanatory variables (e.g. the number of  $d$  electrons and/or the orbital quantum number of the  $M^{2+}$  ion) slightly improved the predictive strength of the regression equation, but appeared to be statistically insignificant (the values of the  $t$ -statistics were low).

TABLE II

Results of the statistical analyses ( $\sigma$  — standard deviation of the corresponding numerical value;  $t$ -statistic is a quotient of the numerical value and its  $\sigma$ ; RBSQ — adjusted  $r^2$  statistic)

Coeff.	Numer. value	$\sigma$	$t$ -statistic
$a/\text{\AA}^3$	111.552	35.054	3.18
$b/\text{\AA}^2$	167.617	18.471	9.07
$c/\text{\AA}^2$	228.903	10.923	20.96
$d/\text{\AA}^2$	200.731	16.927	11.86
$e/\text{\AA}^3$	-55.396	5.580	-9.93
RBSQ = 0.966			

## DISCUSSION

The final results are presented in Tables II and III. The agreement between the calculated and the observed values for the unit cell volumes is very good. However, the  $R$ -values should be accepted with caution: one has the (wrong) impression that the prediction is more accurate than it really is. If the unit-cell volume in *any* compound was 'predicted' to be, say,  $700 \text{ \AA}^3$  (this prediction is obviously of not value),  $R/\%$  would not exceed 8. In order to have a more reliable estimate for the predictive strength of the regression equation, a quantity called  $R_{\text{scal}}$  was introduced. It was set equal to  $\Delta V$  scaled with the range of the  $V$  sample. In this case, the range is  $80.8 \text{ \AA}^3$ , i.e.  $V(\text{ACdSH}) - V(\text{KNiSH})$ . The maximum  $R_{\text{scal}}/\%$  is about 11 (AVSH), which seems acceptable. The agreement between the predicted and observed unit cell volumes, could also be judged from Figure 1.

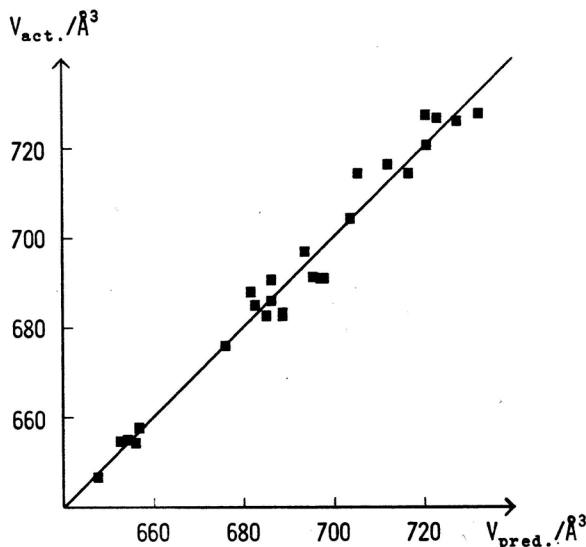


Figure 1. Correlation between actual and predicted unit cell volumes in Tutton salts.

TABLE III

Actual and predicted values for the unit-cell volumes, together with various measures for the error of the estimate

Compound	Actual V/Å <sup>3</sup>	Predicted V/Å <sup>3</sup>	ΔV/Å <sup>3</sup>	R/%	R <sub>scal</sub> /%
ACuSH	691.30	695.52	-4.22	0.61	5.21
ANiSH	682.70	688.81	-6.11	0.90	7.56
AZnSH	691.00	697.19	-6.19	0.90	7.67
AMgSH	697.11	693.84	3.27	0.47	4.05
ACdSH	727.60	732.39	-4.79	0.66	5.92
AMnSH	716.50	712.28	4.22	0.59	5.22
AVSH	714.20	705.57	8.63	1.21	10.68
AFeSH	704.30	703.90	0.40	0.06	0.49
ACoSH	691.10	698.03	-6.93	1.00	8.57
KMgSH	654.70	652.64	2.06	0.32	2.55
KNiSH	646.80	647.61	-0.81	0.12	1.00
KZnSH	654.30	655.99	-1.69	0.26	2.08
KCuSH	655.00	654.31	0.69	0.10	0.85
KCoSH	657.80	656.83	0.97	0.15	1.21
RbCuSH	686.10	686.36	-0.26	0.04	0.32
RbCoSH	683.40	688.87	-5.47	0.80	6.77
CsCuSH	727.40	720.69	6.71	0.92	8.30
CsCoSH	726.70	723.21	3.49	0.48	4.32
TlCuSH	688.10	681.78	6.32	0.92	8.30
KCuSeH	690.60	686.43	4.17	0.60	5.16
ANiSeH	720.60	720.93	-0.33	0.05	0.41
ACuSeH	725.90	727.63	-1.73	0.24	2.14
ANiCrH	714.50	716.91	-2.41	0.34	3.00
ACuBeH	684.90	682.66	2.24	0.33	2.77
ACoBeH	682.80	685.18	-2.38	0.35	2.95
ANiBeH	676.10	675.96	0.14	0.02	0.18

The high value of RBSQ (the adjusted  $r^2$ , cf. Table II) suggests that the correlation is strong enough to predict the values of the (unknown) effective crystal radii. The effective radii for hexaquaRu<sup>2+</sup> were estimated in this way. The values for  $R(\text{Ru}^{2+})$  in KRuSH and RbRuSH Tutton salts were calculated as 0.703 and 0.730 Å, respectively. Although close to each other, both values seem to be very low for the effective crystal radii of Ru<sup>2+</sup>, especially when compared with the corresponding value for Fe<sup>2+</sup> (0.78 Å). It should be concluded that, if the estimate is correct, it must correspond to the effective crystal radius value of Ru<sup>2+</sup> in its *low-spin* state (the 0.78 Å value for Fe<sup>2+</sup> is referred to its *high-spin* state, the corresponding value for low spin Fe<sup>2+</sup> being 0.61 Å<sup>31</sup>). It would be interesting to check this prediction experimentally.

Double salts of methylammonium with copper, nickel, cobalt and zinc sulfate have been recently synthesized<sup>35</sup> and appear to have the same general formula as Tutton salts. However, these salts are triclinic,<sup>35</sup> and their crystal structure is completely different (e.g. four water molecules and two sulfate oxygens are coordinated to M<sup>2+</sup>). If this change in the structure type is to be explained in terms of effective ionic radii, it must be assumed that methylammonium is 'too large' to be accommodated in the Tutton salt structure. In other words, there may be a critical size of the univalent cation, above which the monoclinic structure is unstable. The preliminary investigations of alums,<sup>36</sup> suggested that  $R(\text{NH}_3\text{CH}_3^+) \approx 1.90$  Å and  $R(\text{NH}_3\text{OH}^+) \approx 1.65$  Å. Another es-

timate, based on the data for the triclinic double sulfates,<sup>35</sup> gives values of 1.89 and 1.99 Å for the effective crystal radius of  $\text{CH}_3\text{NH}_3^+$ . Although the latter value seems to be somewhat high, this estimate is in agreement with the assumption that the size of the methylammonium cation is above the 'critical' one. On the other hand, the value of the effective crystal radius of  $\text{NH}_3\text{OH}^+$  is close to the one for  $\text{Cs}^+$ ; if our assumption is correct, hydroxylammonium Tutton salts are expected to exist. Further work will show whether this assumption is correct.

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## SAŽETAK

**Korelacija između stvarnih kristalnih radiusa i volumena jediničnih ćelija u Tuttonovim solima***V. Petruševski i S. Aleksovska*

Volumeni 29 soli s općom formulom  $M^I_2M^{II}(XY_4)_2 \cdot 6H_2O$  [ $M^I = K, NH_4, Rb, Cs, Tl$ ;  $M^{II} = Mg, Mn, Fe, Co, Ni, Cu$ ;  $X = S, Se, Cr$ ;  $Y = O$ ] izračunani su primjenom linearne regresijske analize, pretpostavljeno je da se volumen jedinične ćelije može izraziti funkcijom  $V = a + b \cdot R(M^+) + c \cdot R(M^{2+}) + d \cdot R(X-Y) + e \cdot E_y R(M^+)$  gdje su  $R(M^+)$  i  $R(M^{2+})$  stvarni kristalni radiusi jedno- i dvovalentih kationa,  $R(X-Y)$  je međuatomski razmak u tetraedarskom anionu;  $E_y$  je elektronegativnost atoma Y. Dobiveno je dobro slaganje između izračunanih i stvarnih vrijednosti V. Tom se metodom može pretkazati kristalni radius iona za koji nema podataka u literaturi.