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DESCRIPTION OF MOLECULAR DISTORTIONS: V. ON THE JAHN-TELLER DISTORTION IN SOME HEXAAQUA COMPLEXES

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The distortions of the hexaaqua ions in many compounds are often ascribed to the Jahn-Teller effect. The investigation of two groups of compounds (alums and Tutton salts) containing $[M(H_2O)_6]^{n+}$ *"octahedra" in their structure reveals that the distortion indices of these octahedra are essentially the same throughout the series, i.e. the distortion is (except for the Cu-Tuton salts) independent of the nature of the metal ion. One is then led to the conclusion that, as a general rule, the Jahn-Teller effect is not the main cause for the distortion of the hexaaqua cations. It follows that the immediate environment of these ions and their site symmetry are responsible for the departure of the* $[M(H_2O)_6]^{n+}$ *groups from* O_h *(or, more rigorously,* T_h*) symmetry.*

INTRODUCTION

It is well known that the symmetry of many molecules is lowered in the solid state, compared to the symmetry of the "free" molecule [1-3]. This decrease of the molecular symmetry may be quantitatively described in a variety of ways [4-10]. The lowering of symmetry in crystals containing XY_6 groups is often ascribed to Jahn-Teller effect [11]. Thus, the tendency of removing the degeneracy of the electronic states is reflected on the shape of the molecule in the crystal, the larger effect producing larger distortion, too. Is it really so? The present study, as we shall see, does not seem to give support to this assumption.

DEFINITIONS AND CALCULATIONS

Two "families" of crystals: alums - $M^IM^{III}(SO_4)_2\cdot12H_2O$ and Tutton salts - $M^I_2M^{II}(RO_4)_2\cdot6H_2O$, were chosen for the present investigation because these compounds were extensively studied by methods of both X-ray and neutron diffraction [12-42]. Distortion indices were used as a measure for the distortion of the $[M(H_2O)_6]^{n+}$ (hereafter MW_6) complex cations and were defined analogously as for tetrahedral molecules [3] :

$$DI(MO) = \sum_{i=1}^{i=6} \frac{MO_i}{6MO_m} \tag{1}$$

$$DI(OMO) = \sum_{i=1}^{i=5}\sum_{j=i+1}^{j=6} \left[1-\delta_{i+3,j}\right] \frac{O_iMO_j}{12OMO_m} \tag{2}$$

$$DI(OO) = \sum_{i=1}^{i=5}\sum_{j=i+1}^{j=6} \left[1-\delta_{i+3,j}\right] \frac{O_iO_j}{12OO_m} \tag{3}$$

In the above equations, MO_i are the individual M-O distances, O_iMO_j are the O-M-O angles and O_iO_j are the O···O separations. The subscript $\underline{m}$ denotes the corresponding mean-values. The Cronecker δ function in the above equations ensures that summation is carried out only for those angles and distances, in which $|i - j| = 3$ (see Fig. 1 for atom numbering).

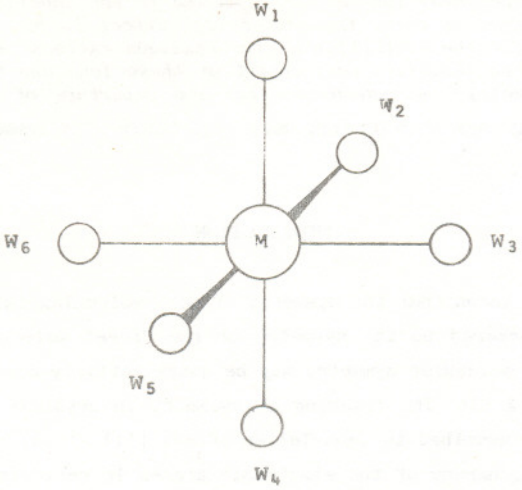

Fig. 1. Designation of atoms in the MW_6 group

The calculation was performed on CBM *Amiga 500* microcomputer with a program written in Microsoft Basic (the program is available upon request from the author). The input data were the unit cell parameters and the fractional coordinates of the seven (the central M and six O) atoms.

RESULTS AND DISCUSSION

The results of the calculation are summarized in Table I and II, for Tutton salts and alums respectively. The distortion indices are largest for the Cu-Tutton salts. This is a strong indication that in all these cases

Table I. *Distortion indices in some Tutton salts*

Compound	*DI(MO)*	*DI(OMO)*	*DI(OO)*	Ref.
$(NH_4)_2Cu(SO_4)_2\cdot6H_2O$	0.0525	0.0093	0.0269	12
$(NH_4)_2Cu(SO_4)_2\cdot6H_2O$	0.0612	0.0093	0.0316	12
$(NH_4)_2Zn(SO_4)_2\cdot6H_2O$	0.0104	0.0086	0.0068	13
$(NH_4)_2Ni(SO_4)_2\cdot6H_2O$	0.0099	0.0100	0.0079	14
$(NH_4)_2Mg(SO_4)_2\cdot6H_2O$	0.0128	0.0042	0.0077	15
$(NH_4)_2Cd(SO_4)_2\cdot6H_2O$	0.0108	0.0178	0.0140	16
$(NH_4)_2Mn(SO_4)_2\cdot6H_2O$	0.0092	0.0105	0.0097	17
$(NH_4)_2V(SO_4)_2\cdot6H_2O$	0.0092	0.0116	0.0099	18
$(NH_4)_2Fe(SO_4)_2\cdot6H_2O$	0.0121	0.0103	0.0091	18
$(NH_4)_2Co(SO_4)_2\cdot6H_2O$	0.0078	0.0119	0.0094	18
$(NH_4)_2Cu(SO_4)_2\cdot6H_2O$	0.0419	0.0105	0.0215	19
$(NH_4)_2Cu(SO_4)_2\cdot6H_2O$	0.0448	0.0102	0.0230	20
$(NH_4)_2Co(BeF_4)_2\cdot6H_2O$	0.0116	0.0121	0.0095	21
$(NH_4)_2Ni(CrO_4)_2\cdot6H_2O$	0.0089	0.0166	0.0131	22
$(NH_4)_2Ni(SeO_4)_2\cdot6H_2O$	0.0042	0.0114	0.0089	23
$(NH_4)_2Ni(BeF_4)_2\cdot6H_2O$	0.0086	0.0108	0.0091	24
$(NH_4)_2Cu(SeO_4)_2\cdot6H_2O$	0.0483	0.0119	0.0248	25
$(enH_2)Ni(SO_4)_2\cdot6H_2O$	0.0012	0.0127	0.0103	26
$(ND_4)_2Ni(SO_4)_2\cdot6H_2O$	0.0058	0.0083	0.0065	27
$K_2Zn(SO_4)_2\cdot6H_2O$	0.0205	0.0057	0.0101	28
$K_2Ni(SO_4)_2\cdot6H_2O$	0.0134	0.0062	0.0338	29
$K_2Cu(SeO_4)_2\cdot6H_2O$	0.0652	0.0156	0.0338	30

Table II. *Distortion indices for some alums*

Compound	*DI(MO)*	*DI(OMO)*	*DI(OO)*	Ref.
$CsMo(SO_4)_2\cdot 12H_2O$	0.0000	0.0110	0.0086	31
$CsAl(SO_4)_2\cdot 12H_2O$	0.0000	0.0083	0.0065	32
$CsTi(SO_4)_2\cdot 12H_2O$	0.0000	0.0028	0.0022	33
$CsRh(SO_4)_2\cdot 12H_2O$	0.0000	0.0233	0.0183	34
$CsIr(SO_4)_2\cdot 12H_2O$	0.0000	0.0379	0.0298	34
$CsV(SO_4)_2\cdot 12H_2O$	0.0000	0.0107	0.0084	35
$CsCr(SO_4)_2\cdot 12H_2O$	0.0000	0.0084	0.0066	35
$CsMn(SO_4)_2\cdot 12H_2O$	0.0000	0.0107	0.0084	35
$CsCo(SO_4)_2\cdot 12H_2O$	0.0000	0.0214	0.0168	35
$CsFe(SO_4)_2\cdot 12H_2O$	0.0000	0.0131	0.0102	35
$CsAl(SO_4)_2\cdot 12H_2O$	0.0000	0.0101	0.0079	35
$CsGa(SO_4)_2\cdot 12H_2O$	0.0000	0.0069	0.0054	35
$CsIn(SO_4)_2\cdot 12H_2O$	0.0000	0.0150	0.0118	35
$(CH_3NH_3)Al(SO_4)_2\cdot 12H_2O$	0.0000	0.0020	0.0016	36
$(CH_3NH_3)Al(SO_4)_2\cdot 12H_2O$	0.0000	0.0106	0.0083	37
$(CH_3NH_3)Cr(SO_4)_2\cdot 12H_2O$	0.0000	0.0025	0.0020	38
$(NH_3OH)Al(SO_4)_2\cdot 12H_2O$	0.0000	0.0031	0.0024	39
$NH_4Al(SO_4)_2\cdot 12H_2O$	0.0000	0.0038	0.0030	37
$NH_4Al(SO_4)_2\cdot 12H_2O$	0.0000	0.0021	0.0016	40
$RbAl(SO_4)_2\cdot 12H_2O$	0.0000	0.0034	0.0027	40
$RbCr(SO_4)_2\cdot 12H_2O$	0.0000	0.0344	0.0270	41
$KAl(SO_4)_2\cdot 12H_2O$	0.0000	0.0037	0.0029	40
$NaAl(SO_4)_2\cdot 12H_2O$	0.0000	0.0001	0.0000	42

the Jahn-Teller effect is pronounced and could be invoked as an explanation for the departure of the hexaaqua cations from O_h symmetry. However, in all other cases no clear relationship between the distortion and the nature of the divalent metal could be identified. For instance, the distortion of MgW_6, ZnW_6 and CdW_6 is larger than in NiW_6, CoW_6 and MnW_6, although Mg is an *s*-element and Zn and Cd have filled *d*-subshells. Admittedly, this conclusion could not be considered as definite because a number of Tutton salt-structures have been refined more than 20 years ago and hence they are understandably less accurate. Moreover, it may be difficult to decide which MW_6 is more distorted because both **bond-lenght** and **angular distortion** may be present in this class of compounds and may be considered as mutually independent.

The last problem has been overcome when the distortions of MW_6 groups in alums were considered (cf. Table II). As a consequence of the high site-symmetry of the M^{3+} cation (S_6), it follows that the *DI(MO)* values are equal to zero for any alum. In that case, the ratio *DI(OMO)/DI(OO)* is constant throughout the series of alums, its value being 1.273. Thus, a single parameter, say *DI(OMO)*, could be taken as a measure for the distortion of the MW_6 octahedra in alums. It should also be noted that the structures of many alums have been precisely refined, hence the results in Table II are more reliable than the corresponding results for Tutton salts.

It is expected that the Jahn-Teller distortion is very pronounced in Cu^{2+} and Mn^{3+} complexes. Contrary to that, the distortion of MnW_6 is far from being the largest (cf. Table II). The distortion of InW_6 is considerably large, compared to the distortions of the aqua complexes of V, Cr, Mn, Fe, Mo - which are all *d*-elements. The situation resembles the one mentioned earlier, in the case of Tutton salts.

CONCLUSION

The present results clearly show that, although important, the Jahn-Teller effect could not be considered as a main cause for the distortions found in hexaaqua complexes. The site-symmetry and the details of the crystal structure (the immediate environment of the MW_6 groups) seem to have a dominant role. It would be interesting to study in an analogous way other complexes of the same metals, *e.g.* $[M(NH_3)_4]^{n+}$ and $[M(NH_3)_6]^{n+}$ and to compare the results thus obtained with the present ones.

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ОПИС НА ДЕФОРМАЦИИТЕ КАЈ МОЛЕКУЛИТЕ: V. JAHN-TELLER-ОВСКИ ДЕФОРМАЦИИ КАЈ НЕКОИ ХЕКСААКВА КОМПЛЕКСИ

Владимир Петрушевски

Деформациите на хексааквакомплексните јони кај различни соединенија честопати се припишуваат на Jahn-Teller-овскиот ефект. Испитувањето на две групи соединенија (стипси и Тутонови соли), кои содржат $M(H_2O)_6$ "октаедри" во својата структура, покажува дека деформационите индекси на овие октаедри се, главно, константни за целата серија. Деформацијата е, според тоа (со исклучок на Тутоновите соли на Cu), независна од природата на металниот јон. Врз основа на тоа, заклучено е дека Jahn-Teller-овскиот ефект не е главна причина поради која доаѓа до деформација на хексааква катјоните. Битна улога би имале, од друга страна, кристалната околина на комплексните јони и нивната *site*-симетрија.

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