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Crystal Structures of Members in Isostructural Series: Prediction of the Crystal Structure of Cs_2MnO_4 – a β-K_2SO_4 Type Isomorph

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Recent studies have shown that the crystal structure of members within a group of isostructural compounds may be successfully predicted. The β-K_2SO_4 group isomorphs of the general formula M_2XO_4 were chosen as a family of closely related compounds for which accurately refined crystal structures exist. It is shown that the unit cell parameters and the fractional atomic coordinates exhibit systematic variations with both cation and anion size, as well as with the Mulliken charge of the oxygen atom in the tetrahedral anion. It is thus possible to predict the crystal structure of a given member in the series only on the basis of its chemical composition. The structure of Cs_2MnO_4 predicted in this way is compared with the one refined earlier by X-ray diffraction. The agreement between the structural parameters in both structures is very good.

INTRODUCTION

A number of compounds are known to crystallize with the β-K_2SO_4 structure. Fairly accurate structures are available for β-K_2SO_4[1] and a number of its isomorphs: K_2SeO_4,[2,3] K_2CrO_4,[1,4] K_2MnO_4,[5] K_2FeO_4,[6] Rb_2SO_4,[7,8] Rb_2SeO_4,[9] Cs_2SO_4,[8,10] Cs_2SeO_4,[11] Cs_2CrO_4,[12] Cs_2FeO_4[13] and Rb_2CrO_4.[14,15] The structure of Cs_2MnO_4 is also known, but it is of questionable accuracy since only 71 reflections have been used in the X-ray powder structure refinement.[16] Incomplete powder diffraction data are available for Cs_2MoO_4 and Cs_2WO_4, which belong to the same group of isomorphs.[17]

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The structures of all the mentioned compounds are indeed very closely related in all respects. They all crystallize with the space group *Pnam*, Z = 4, and contain one type of fairly regular tetrahedral oxoanion XO_4 and two crystallographically different types of metal cations M^I and M^{II}, situated on mirror planes. The metal cations are coordinated by oxygen atoms forming irregular coordination polyhedra. The coordination numbers of M^I and M^{II}, according to various authors, vary between 9 and 11 (as always, it is difficult to set the limit beyond which chemical bonding may be disregarded).

Slightly different (still closely related) are the structures of $(NH_4)_2SO_4$,[18] $(NH_4)_2BeF_4$,[19,20] $(NH_4)_2MoS_4$,[21] $(NH_4)_2WS_4$,[22] Tl_2SO_4,[23] Tl_2SeO_4[24] and Tl_2CrO_4.[25] An important structural difference between β-K_2SO_4 and the four ammonium compounds is the existence of hydrogen bonds in the last, thus resulting in an appreciably lower coordination number (4 and 5, for the two types of ammonium anion), as compared to β-K_2SO_4 and its isomorphs. Spectroscopic evidence that $(NH_4)_2SO_4$ and K_2SO_4 are not strictly isostructural (isomorphous) may be given too.[26,27] The differences between the thallium compounds and the title compounds appear most probably as a result of stereoselectivity of the $6s^2$ lone pair in one (Tl^I) of the two different Tl^+ cations.[24]

More pronounced are the structural differences in $(NH_4)_2ZnCl_4$ – phase I [28] Rb_2ZnCl_4,[29] Cs_2BeCl_4,[30] Rb_2ZnBr_4,[31] Cs_2ZnBr_4, Cs_2CdBr_4 and Cs_2HgBr_4 [32], which also crystallize in space group *Pnam* with Z = 4. In all these compounds, the tetrahedral anions show a large bond-length and angular distortion. In the case of Rb_2ZnCl_4,[33] a structure with a disorder of the chlorine atoms was also considered. It seems that the considerably larger distortion of the tetrahedral anion in this group of compounds (compared to those containing oxoanions) is due to a synergetic effect: the much weaker bonding in these halogenoanions and the stronger repulsion between the bulky terminal atoms (Cl or Br) increase the 'plasticity' of the MX_4^{2-} anion.

One may try to systematize these structures in order to extract some sort of structural information for compounds whose structures have either not been determined so far or their reliability is for some reason questionable. The purpose of the present paper is to confirm the success in elucidating structural information for members in a group of very closely related compounds.[15] The important preconditions are that (*i*) all compounds in question are strictly isostructural (the term isomorphous will be used as a synonym) and (*ii*) accurately refined crystal structures are available for a series of these compounds. By strictly isostructural[15] compounds were meant that crystallize with the same space group, the site symmetry and coordination numbers of the corresponding atoms being also the same. Thus, sulfates, selenates, chromates, manganates and ferrates of potassium, rubidium and cesium are all isomorphous. The structures of Rb_2MnO_4 and Rb_2FeO_4 have not been determined yet (to the best of our knowledge), the

structure of Rb_2CrO_4 was predicted and redetermined[15] and that of Cs_2MnO_4, as mentioned, is of questionable accuracy.[16] Since the accuracy of the predicted crystal structure of Rb_2CrO_4 was excellent (it was virtually identical to the redetermined structure),[15] it was decided to make an attempt to predict the structure of Cs_2MnO_4 (with the same sample used in the statistical analysis) and to compare the results of this prediction with the results of the existing structure determination.[16]

THE SAMPLE AND STATISTICAL MODEL

Previous results[34,35] proved that the knowledge of the effective ionic radii[36] of the constituent atoms enables successful prediction of the unit cell parameters, which were shown to vary in a predictable way. The correlations were highly significant, enabling predictions of unit cell parameters and yet unknown values for the effective ionic radii (*e.g.* the radius for hexacoordinated Ru^{2+}). It was already mentioned that an attempt was made to propose a simple method for prediction of the crystal structure of Rb_2CrO_4 and this appeared to be successful.[15] The same method is used in the present work.

The sample for the statistical analysis (multiple regression) were the data from accurately refined structures, by diffraction methods, of the β-K_2SO_4 isomorphs. The input data were the effective ionic radii of the constituent ions and the atomic charges* of the oxygen atoms in the tetrahedral anions (independent variables). Atomic charges were calculated at the *ab initio* Hartree-Fock (HF) SCF level of theory, with the GAUSSIAN 94 package[37] on a pentium PC-compatible computer, using 6–311+G (triple zeta) basis set. This basis set is characterized by a triple split (311) representation of the valence shell, (*i.e.* three sizes of contracted functions are used for the description of the valence shell), and with a six-Gaussian representation of the inner shell.[38–40] This set also includes diffuse functions for a better description of the anionic wavefunctions, following the recommendation of Raghavachari and Trucks.[40] The Mulliken scheme for the population analysis was applied.[41,42] Unit cell parameters and fractional atomic coordinates were the dependent variables. The STATGRAPHICS package[43] was used in the statistical calculations. Stepwise variable selection was performed. This is a multiple regression analysis, which includes or rejects an independent variable in the model, depending on the value of the *t*-statistics, in order to judge whether the inclusion of a given independent variable, in the presence of others, is statistically significant.

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* The importance of including the radii of the ions is out of the question. The atomic (Mulliken) charge was added to account for the different bonding ability of the oxygen atoms in various oxo-anions. In the calculation it was assumed (for consistency) that the X-O bondlength of an XO_4^{2-} anion is equal to the sum of Shannon's radii and no further optimization was performed.

The crystal structures of the compounds have been refined by various groups of authors. Therefore, inconsistencies in the cell choice, orientation of axes and atom designation are not unexpected. In order to avoid possible confusion, all data were transformed to match the choices made in β-K_2SO_4.[1]

Each dependent variable d (numerical value of a unit cell parameter or fractional atomic coordinate) was presented as a function of the type:

$$d = m \cdot R(M^+)/Å + n \cdot R(X\text{-}O)/Å + p \cdot O_{charge} + q \quad (1)$$

where $R(M^+)$ is the effective ionic radius[36] for the hexacoordinated univalent cation, R(X-O) is the sum of the effective ionic radii for the tetracoordinated central atom X (*i.e.* for the X^{6+} ion) and the oxygen atom (O^{2-} ion with CN = 2) in the XO_4^{2-} group, O_{charge} is the calculated Mulliken charge for the oxygen atom and q is a constant. The univalent cations in this family of crystals are known to be 9, 10 or 11 coordinated, but (for consistency) values for the effective ionic radii for M^+ ions were taken for coordination number (CN) 6, since these values are usually considered to be most reliable.* Parameters m, n, p and q for each dependent variable are to be determined by multiple regression. The input data are given in Tables I, IIa and IIb. Regression results are presented in Table III.

TABLE I

Independent variables used as input data in regression analyses[a]

Compound	$R(M^+)$/Å	$R(XO_4^{2-})$/Å	O_{charge}
K_2SO_4	1.38	1.47	–0.864
K_2SeO_4	1.38	1.63	–1.019
K_2CrO_4	1.38	1.61	–0.736
K_2MnO_4	1.38	1.605	–0.689
K_2FeO_4	1.38	1.60	–0.628
Rb_2SO_4	1.52	1.47	–0.864
Rb_2SeO_4	1.52	1.63	–1.019
Cs_2SO_4	1.67	1.47	–0.864
Cs_2SeO_4	1.67	1.63	–1.019
Cs_2CrO_4	1.67	1.61	–0.736
Cs_2FeO_4	1.67	1.60	–0.628

[a] Values for effective ionic radii taken from Shannon.[36] O_{charge} is the calculated Mulliken charge of the O atom at the tetrahedron vertex.

* It is self-evident that the values for 9, 10 and 11 coordinated metal cations are correspondingly larger than those for 6 coordinated.

TABLE IIa

Input data for the dependent variables in multiple regression analyses[a]

Param.	K_2SO_4	K_2SeO_4	K_2CrO_4	K_2MnO_4	K_2FeO_4	Rb_2SO_4	Rb_2SeO_4	Cs_2SO_4	Cs_2SeO_4	Cs_2CrO_4	Cs_2FeO_4
a/Å	7.476	7.661	7.663	7.667	7.690	7.820	7.961	8.239	8.3777	8.427	8.4286
b/Å	10.071	10.466	10.388	10.359	10.328	10.441	10.794	10.937	11.2760	11.200	11.0533
c/Å	5.763	6.003	5.922	5.895	5.855	5.979	6.161	6.256	6.4340	6.300	6.2812
x(M1)	0.67377	0.6705	0.66544	0.66338	0.66297	0.67564	0.6729	0.67704	0.67676	0.6689	0.6667
y(M1)	0.41062	0.4157	0.41449	0.41302	0.41054	0.40923	0.4111	0.40941	0.40999	0.4099	0.4088
x(M2)	–0.01104	–0.0057	–0.01105	–0.01217	–0.01456	–0.01208	–0.0096	–0.01123	–0.01048	–0.0153	–0.0146
y(M2)	0.70406	0.7095	0.69980	0.69855	0.69667	0.70280	0.7072	0.70145	0.70606	0.6963	0.6949
x(X)	0.23298	0.2242	0.22900	0.22946	0.23110	0.23734	0.2296	0.24060	0.23482	0.2359	0.2324
y(X)	0.41971	0.4200	0.42059	0.42058	0.42132	0.41875	0.4204	0.41726	0.41877	0.4196	0.4188
x(O1)	0.03790	0.0126	0.01550	0.01659	0.01730	0.05000	0.0258	0.06260	0.03920	0.0410	0.0417
y(O1)	0.41660	0.4251	0.42000	0.41677	0.41480	0.41430	0.4179	0.41330	0.41780	0.4124	0.4116
x(O2)	0.29630	0.3024	0.30240	0.30122	0.29970	0.29740	0.2995	0.29770	0.30220	0.2934	0.2963
y(O2)	0.55820	0.5644	0.57000	0.57172	0.57330	0.55300	0.5634	0.54540	0.55460	0.5611	0.5604
x(O3)	0.30090	0.2931	0.30220	0.30584	0.30840	0.30370	0.2999	0.30390	0.30320	0.3054	0.3065
y(O3)	0.35220	0.3471	0.34710	0.34773	0.34880	0.35370	0.3511	0.35540	0.35250	0.3532	0.3523
z(O3)	0.04120	0.0271	0.02330	0.02270	0.01970	0.04830	0.0331	0.05760	0.04180	0.0356	0.0342

[a] Unit cell parameters and fractional atomic coordinates taken from references mentioned in the introduction; z-fractional coordinates for atoms from M1 to O2 are fixed to 1/4 by symmetry.

TABLE IIb

Fitted values of the structural parameters for the eleven compounds included in regression analyses

Param.	K_2SO_4	K_2SeO_4	K_2CrO_4	K_2MnO_4	K_2FeO_4	Rb_2SO_4	Rb_2SeO_4	Cs_2SO_4	Cs_2SeO_4	Cs_2CrO_4	Cs_2FeO_4
a/Å	7.4755	7.6301	7.6703	7.6750	7.6828	7.8366	7.9912	8.2234	8.3781	8.4182	8.4308
b/Å	10.0874	10.4568	10.3620	10.3427	10.3208	10.4735	10.8430	10.8873	11.2568	11.1620	11.1208
c/Å	5.7874	5.9881	5.8969	5.8801	5.8598	5.9944	6.1951	6.2162	6.4169	6.3257	6.2885
x(M1)	0.6734	0.6713	0.6649	0.6639	0.6626	0.6754	0.6733	0.6777	0.6756	0.6692	0.6669
y(M1)	0.4112	0.4134	0.4131	0.4131	0.4130	0.4096	0.4118	0.4079	0.4101	0.4098	0.4097
x(M2)	–0.0100	–0.0076	–0.0119	–0.0126	–0.0135	–0.0111	–0.0088	–0.0124	–0.0100	–0.0143	–0.0159
y(M2)	0.7041	0.7089	0.7001	0.6986	0.6967	0.7027	0.7075	0.7013	0.7061	0.6973	0.6939
x(X)	0.2331	0.2256	0.2288	0.2294	0.2301	0.2369	0.2294	0.2409	0.2335	0.2367	0.2380
y(X)	0.4195	0.4209	0.4207	0.4207	0.4206	0.4187	0.4200	0.4177	0.4191	0.4189	0.4189
x(O1)	0.0377	0.0134	0.0157	0.0163	0.0169	0.0499	0.0256	0.0629	0.0386	0.0409	0.0422
y(O1)	0.4173	0.4229	0.4181	0.4172	0.4161	0.4148	0.4204	0.4121	0.4177	0.4128	0.4109
x(O2)	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990	0.2990
y(O2)	0.5577	0.5663	0.5710	0.5716	0.5726	0.5523	0.5610	0.5466	0.5552	0.5598	0.5614
x(O3)	0.3007	0.2973	0.3035	0.3045	0.3058	0.3022	0.2989	0.3039	0.3006	0.3067	0.3091
y(O3)	0.3514	0.3476	0.3481	0.3482	0.3483	0.3537	0.3498	0.3561	0.3523	0.3527	0.3530
z(O3)	0.0420	0.0270	0.0220	0.0214	0.0204	0.0489	0.0339	0.0562	0.0413	0.0363	0.0347

TABLE III

Regression parameters used in prediction of the dependent variables[a]

Dependent var.	m	n	p	q	$(R_{adjusted})^2$
a/Å	2.57908	1.18523	0.22567	2.36889	0.997
b/Å	2.75848	2.13064	–0.18438	2.98931	0.986
c/Å	1.47847	1.01167	–0.25069	2.04336	0.983
x(M1)	0.01487	–0.03747	–0.02513	0.68620	0.981
y(M1)	–0.01136	0.01353	rejected	0.40702	0.580
x(M2)	–0.00827	rejected	–0.01500	–0.01152	0.783
y(M2)	–0.00968	rejected	–0.03111	0.69056	0.986
x(X)	0.02705	–0.03845	0.00862	0.25974	0.962
y(X)	–0.00613	0.00868	rejected	0.41521	0.787
x(O1)	0.08702	–0.15457	–0.00279	0.14242	0.999
y(O1)	–0.01797	0.01996	–0.01587	0.39904	0.811
x(O2)	rejected	rejected	rejected	0.29896	0.000
y(O2)	–0.03845	0.07496	0.02168	0.51931	0.968
x(O3)	0.01117	rejected	0.02175	0.30406	0.658
y(O3)	0.01605	–0.02379	rejected	0.36423	0.924
z(O3)	0.04920	–0.11862	–0.02612	0.12588	0.992

[a] Variables with t-statistics lower than 3 were rejected in the stepwise selection model.

RESULTS

The predictive strength of the regression equations (*cf.* Table III) is, in most cases, very high. A measure for the 'goodness of fit' is the coefficient of determination $(R_{adjusted})^2$. This quantity is higher than 0.9 for 10 out of 16 dependent variables. In one case (the x(O2) parameter), no correlation was found between the chosen set of independent variables and the 11 values of the dependent variable, but it should be noted that the total variation in the numerical values of the dependent variable x(O2) is 0.009. It is, therefore, rather insensitive to the variations of atomic radii/atomic charges. In such cases, the experimental errors in the determination of the fractional atomic coordinates are believed to be an important factor in the scatter of the points. On the other hand, for x(O1) the range of the sample is 0.05 (about an order of magnitude higher) and the coefficient of determination reaches the highest value (0.999) in the class.

Predicted Cs_2MnO_4 Structure

The results of the crystal structure prediction are summarized in Tables IV and V. It may be seen that all parameters of the predicted structure agree well with the corresponding values of the determined structure.[16]

However, the results of this prediction are not so strong as in the case of Rb_2CrO_4.[15] For instance, the differences in the fractional coordinates of Cs1, Cs2 as well as the Cs-O distances are rather pronounced. Somewhat surprisingly, the positions of heavy atoms (Cs1 and Cs2) appear to be the most inaccurate. It is suspected that this might be due to inaccuracy of the structure refinement (which was after all done on the basis of a total of 71 reflections; only for a comparison, the structures of K_2SO_4/K_2CrO_4 [1] were determined from 864/964 reflections and the structure of Rb_2CrO_4 [15] was redetermined using a set of 468 significant independent reflections). In other words, one should be cautious when dealing with the standard deviations of the fractional atomic coordinates in all cases where the number of reflections is small as these do not reflect the accuracy of determination properly.

The average absolute deviation of Cs-O distances between predicted and redetermined structures is about 0.06 Å, that of Mn-O distances is 0.008 Å and the deviation of the O-Mn-O angles is 0.7°. Since these deviations are

TABLE IV

Unit-cell parameters and fractional atomic coordinates in Cs_2MnO_4[a]

Parameter	Kopelev *et al.*[14]	Predicted (this paper)
a/Å	8.432 (8)	8.4229
b/Å	11.083 (13)	11.1427
c/Å	6.290 (6)	6.3089
x(Cs1)	0.650 (1)	0.6682
y(Cs1)	0.384 (1)	0.4098
z(Cs1)	1/4	0.2500
x(Cs2)	–0.022 (1)	–0.0150
y(Cs2)	0.708 (1)	0.6958
z(Cs2)	1/4	0.2500
x(Mn)	0.237 (2)	0.2373
y(Mn)	0.416 (2)	0.4189
z(Mn)	1/4	0.2500
x(O1)	0.041 (2)	0.0416
y(O1)	0.410 (4)	0.4120
z(O1)	1/4	0.2500
x(O2)	0.296 (5)	0.2990
y(O2)	0.559 (2)	0.5605
z(O2)	1/4	0.2500
x(O3)	0.307 (3)	0.3077
y(O3)	0.347 (2)	0.3529
z(O3)	0.0346 (10)	0.0357

[a] Data from Kopelev *et al.*[16] were transformed to match the choice in β-K_2SO_4[1] and are compared with the predicted structure. Standard deviations given in parentheses refer to the last significant digits.

TABLE V

Selected distances and angles in the structure of Cs_2MnO_4[a]

Distance/Å	Kopelev *et al.*[14]	Predicted (this paper)
Cs1 – O1	3.298 (24)	3.145
Cs1 – O1	3.728 (48)	3.741
Cs1 – O2	3.380 (43)	3.534
Cs1 – O2 2×	3.190 (07)	3.184
Cs1 – O3 2×	3.284 (28)	3.384
Cs1 – O3 2×	3.476 (29)	3.432
Cs1 – O3 2×	3.199 (26)	3.206
Cs2 – O1	3.345 (45)	3.198
Cs2 – O1 2×	3.410 (18)	3.383
Cs2 – O2	3.149 (39)	3.044
Cs2 – O2	3.004 (31)	3.135
Cs2 – O3 2×	2.977 (21)	3.060
Cs2 – O3 2×	3.058 (22)	3.102
Mn – O1	1.654 (24)	1.650
Mn – O2	1.661 (33)	1.661
Mn – O3 2×	1.664 (19)	1.649
Angle/°		
O1 – Mn – O2	109.7 (16)	110.9
O1 – Mn – O3 2×	109.6 (15)	109.8
O2 – Mn – O3 2×	109.4 (15)	108.1
O3 – Mn – O3'	109.0 (13)	110.1

[a] Values from X-ray diffraction (Kopelev *et al.*[16]) and the predicted ones are presented simultaneously. Standard deviations of distances/angles (given in parentheses) refer to the least significant digit.

larger than those between the predicted and redetermined structure of Rb_2CrO_4 (0.018 Å for Rb-O distances; 0.018 Å and 0.5°, for Cr-O distances and O-Cr-O angles),[15] we encourage our crystallographic colleagues to redetermine the structure of Cs_2MnO_4 in order to check whether previous structure determination (and, more specifically, the positions of the cesium atoms) based on X-ray powder diffraction data was really not accurate enough.

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SAŽETAK

Kristalne strukture članova izostrukturnog niza. Pretkazivanje kristalne strukture Cs_2MnO_4 izomorfnog s β-K_2SO_4

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Kako su pokazale nedavne studije, kristalna struktura članova iz skupine izostrukturnih spojeva može se uspješno pretkazati. Skupina spojeva s općom formulom M_2XO_4, izomorfnih s β-K_2SO_4, izabrana je kao skup veoma povezanih spojeva za koji postoje točno utočnjene kristalne strukture. Pokazano je da parametri i jedinične ćelije i frakcijske atomske koordinate, pokazuju sustavne promjene u vezi s veličinom kationa i aniona, te Mullikenova naboja kisikova atoma u tetredarskom anionu. Prema tome moguće je, samo na temelju kemijskog sastava, pretkazati kristalnu strukturu danog člana u nizu. Tako pretkazana struktura Cs_2MnO_4 uspoređena je sa strukturom utočnjenom ranije iz podataka dobivenih difrakcijom. Slaganje strukturnih parametara obje strukture vrlo je dobro.