

β -K₂SO₄-Type Isomorphs: Prediction of Structures and Refinement of Rb₂CrO₄S. ALEKSOVSKA,^a S. C. NYBURG,^{b*} LJ. PEJOV^a AND V. M. PETRUŠEVSKI^a^a*Institut za hemija, PMF, Univerzitet 'Sv. Kiril i Metodij', Skopje, Macedonia, and* ^b*Department of Chemistry, King's College, London WC2R 2LS, England. E-mail: s.nyburg@kcl.ac.uk*

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Abstract

The crystal structures of members within a group of isostructural compounds may be successfully predicted. This is demonstrated for the β -K₂SO₄ group isomorphs with the general formula M_2XO_4 , which were chosen as a family of very closely related compounds nearly all with accurately refined crystal structures. The unit-cell parameters and the fractional atomic coordinates are shown to exhibit systematic variations with both cation and anion size, as well as the Mulliken charge on the O atom in the tetrahedral anion. This allows the prediction of the crystal structures of members in the series, with only the chemical composition of the compound being known. The agreement is good, except for an early structure determination of Rb₂CrO₄. The now refined structure gives excellent agreement with that predicted.

1. Introduction

A large number of compounds of the general formula M_2XO_4 have structures very closely related to that of β -K₂SO₄ (Table 1). They are all orthorhombic, space group $Pnam$, $Z = 4$. The two cations, atom X and two independent O atoms of XO_4 lie on mirror planes in the four special equivalent positions $x, y, \frac{1}{4}$ etc. (Fig. 1). The remaining independent O atom lies in eight general equivalent positions.

Slightly different (although still related to the above) are the structures related to (NH₄)₂SO₄ and Tl₂SO₄ (Table 1b). The principal difference between the structure of β -K₂SO₄ and those of the four ammonium compounds is the existence of hydrogen bonds, thus resulting in appreciably lower coordination numbers (4 and 5 for the two types of ammonium anion) compared with β -K₂SO₄ and its isomorphs.† On the other hand, the differences between the thallium compounds and the title compounds arise most probably as a consequence of stereoselectivity of the 6s² lone pair in one (Tl^I) of the two different Tl⁺ cations (Fábry & Brec-

† Further evidence that (NH₄)₂SO₄ and K₂SO₄ are not strictly isostructural (isomorphous) may be given by the non-statistical substitution of K⁺ with NH₄⁺, found in the solid solutions of these two salts (Petruševski & Sherman, 1993; Srinivasan *et al.*, 1983).

Table 1. Structures isomorphous with (a) β -K₂SO₄, (b) (NH₄)₂SO₄ and Tl₂SO₄, and (c) (NH₄)₂ZnCl₄

| | |
|---|--|
| (a) | |
| β -K ₂ SO ₄ | McGinney (1972) |
| K ₂ SeO ₄ | Kálmán <i>et al.</i> (1970, 1971) |
| K ₂ CrO ₄ | McGinney (1972) and Toriumi & Saito (1978) |
| K ₂ MnO ₄ | Palenik (1967) |
| K ₂ FeO ₄ | Hoppe <i>et al.</i> (1982) |
| Rb ₂ SO ₄ | Nord (1974) and Weber <i>et al.</i> (1989) |
| Rb ₂ SeO ₄ | Takahashi <i>et al.</i> (1987) |
| Rb ₂ CrO ₄ | Smith & Colby (1941) |
| Cs ₂ SO ₄ | Nord (1976) and Weber <i>et al.</i> (1989) |
| Cs ₂ SeO ₄ | Zúñiga <i>et al.</i> (1991) |
| Cs ₂ CrO ₄ | Morris <i>et al.</i> (1981) |
| Cs ₂ FeO ₄ | Mader & Hoppe (1991) |
| Cs ₂ MnO ₄ | Kopelev <i>et al.</i> (1991)† |
| (b) | |
| (NH ₄) ₂ SO ₄ | Schlemper & Hamilton (1966) |
| (NH ₄) ₂ BeF ₄ | Garg & Srivastava (1979) and Onodera & Shiozaki (1981) |
| (NH ₄) ₂ MoS ₄ | Lapasset <i>et al.</i> (1976) |
| (NH ₄) ₂ WS ₄ | Sasvári (1963) |
| Tl ₂ SO ₄ | Pannetier & Gaultier (1966) |
| Tl ₂ SeO ₄ | Fábry & Breczewski (1993) |
| Tl ₂ CrO ₄ | Carter & Margulis (1972) |
| (c) | |
| (NH ₄) ₂ ZnCl ₄ (phase 1) | Matsunaga (1982) |
| Rb ₂ ZnCl ₄ | Secco & Trotter (1983) |
| Cs ₂ BeCl ₄ | Gaebell & Meyer (1984) |
| Rb ₂ ZnBr ₄ | Hogervorst & Helmholdt (1988) |
| Cs ₂ ZnBr ₄ | Plesko <i>et al.</i> (1980) |
| Cs ₂ CdBr ₄ | Plesko <i>et al.</i> (1980) |
| Cs ₂ HgBr ₄ | Plesko <i>et al.</i> (1980) |

† Not accurately refined. Incomplete powder data are also available for Rb₂MoO₄ and Cs₂MoO₄ (Kools *et al.*, 1970).

zewski, 1993). This stereoselectivity seems to induce additional distortion of the already distorted coordination polyhedron around Tl^I.

Even more pronounced are the differences in structures related to (NH₄)₂ZnCl₄ (Table 1c), which also crystallize in space group $Pnam$ with $Z = 4$. In all these compounds the tetrahedral anions show large bond and angular distortion. Rb₂ZnCl₄, a structure with disorder in the Cl atoms, was also considered (Itoh *et al.*, 1983).

Having all these structural data available, one may try to systematize them in order to extract some sort of structural information for compounds whose structures have either not been determined so far or whose reliability is for some reason questionable. The purpose of this paper is to present a possible way of elucidating structural information for members in a group of very closely related compounds. The important precondition is that (i) all compounds in question have to be strictly isostructural (isomorphous) and (ii) accurately refined crystal structures are available for a number of these compounds. By *strictly isostructural* (or isomorphous) is meant compounds that crystallize with the same *space group* and at least the *site symmetry* and the *coordination numbers* of the corresponding atoms are also the same. For instance, the sulfates, selenates, chromates, manganates and ferrates of potassium, rubidium and caesium are beyond doubt all strictly isostructural (15 compounds in all). The structures of Rb₂MnO₄ and Rb₂FeO₄ have not yet been determined, but those of K₂MnO₄ and K₂FeO₄ are known (Table 1a). We have predicted the structures of all four compounds. The agreement for the K compounds is very good. The structure of Cs₂MnO₄ is not accurately known. As to

Table 2. Values of the independent variables used as input data in regression analyses

Values for effective ionic radii taken from Shannon (1976). O_{charge} is the calculated Mulliken charge of the O atom at the tetrahedron vertex.

| Compound | $R(M^+)$ | $R(XO_4^{2-})$ | O_{charge} |
|----------------------------------|----------|----------------|---------------------|
| K ₂ SO ₄ | 1.38 | 1.47 | -0.864 |
| K ₂ SeO ₄ | 1.38 | 1.63 | -1.019 |
| K ₂ CrO ₄ | 1.38 | 1.61 | -0.736 |
| K ₂ MnO ₄ | 1.38 | 1.605 | -0.689 |
| K ₂ FeO ₄ | 1.38 | 1.60 | -0.628 |
| Rb ₂ SO ₄ | 1.52 | 1.47 | -0.864 |
| Rb ₂ SeO ₄ | 1.52 | 1.63 | -1.019 |
| Cs ₂ SO ₄ | 1.67 | 1.47 | -0.864 |
| Cs ₂ SeO ₄ | 1.67 | 1.63 | -1.019 |
| Cs ₂ CrO ₄ | 1.67 | 1.61 | -0.736 |
| Cs ₂ FeO ₄ | 1.67 | 1.60 | -0.628 |

Rb₂CrO₄, when this project was commenced, the agreement between prediction and observation was poor. This we attributed to the fact that the structure was determined some 50 years ago. We have therefore carried out a new structure determination which we report here. The refined structure agrees well with the predictions.

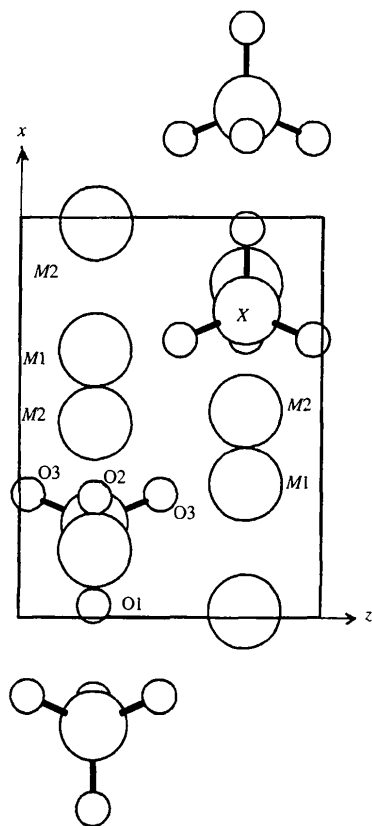


Fig. 1. Crystal structure in y -projection of compounds M_2XO_4 isomorphous with β -K₂SO₄.

2. Statistical model – survey of the diffraction data

For some time, we have been interested in both the spectroscopic properties and structural relationships between the compounds of the β -K₂SO₄ family (Petruševski & Sherman, 1990, 1994). Encouraged by the results obtained previously (Petruševski & Aleksovska, 1991, 1994), where the knowledge of the effective crystal radii (Shannon & Prewitt, 1969; Shannon, 1976) of the constituent atoms led to a successful prediction of the unit-cell parameters, an attempt was made to implement a simple method to predict the crystal structures of these isomorphs. This appeared to be possible by means of statistical analyses. In fact, previous results proved that the unit-cell parameters in Tutton salts and alums vary in a regular and predictable way with composition (Petruševski & Aleksovska, 1991, 1994). In the case of both classes of compounds, the factors of principal significance were the effective ionic radii of the constituent atoms. The correlations were highly significant and led to predictions of unit-cell parameters and of unknown values for the effective ionic radii (e.g. the radius for hexa-coordinated Ru²⁺). A possible isomorphism between Tutton salts and dimethylammonium metal(III) sulfate hexahydrates (Galešić & Jordanovska, 1992) has also been discussed (Petruševski, 1994).

In the present study the source data in the statistical analysis (multiple regression) were the effective crystal

Table 3. Regression parameters used in the prediction of dependent variables [cf. (1)]

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

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

radii of the constituent ions and the atomic charges† of the O atoms in the tetrahedral anions. Atomic charges were calculated at the *ab initio* Hartree–Fock (HF) SCF level of theory [with the GAUSSIAN94 (Frisch *et al.*, 1995) package, on a pentium IBM compatible PC and a dual pentium-pro Digital workstation], using a 6-311 + G (triple zeta) basis set. This set includes diffuse functions for a better description of the anionic wavefunctions. The Mulliken scheme for the population analysis was applied (Mulliken, 1955*a,b*). Atomic charges obtained by fitting to the electrostatic potential, with point selections according to the CHelp (Chirlian & Francl, 1987) and CHelpG (Breneman & Wiberg, 1990) scheme, were also calculated, but these electrostatic-potential-derived values gave somewhat worse results compared with those obtained using the Mulliken scheme. Although the potential-derived charges may seem more realistic, one has to be aware that, in general, atomic charges are not quantum-mechanical observables, so they cannot be computed exactly ‘from first principles’. Thus, having in mind the arbitrariness of all charge assignment schemes, the use of Mulliken charges for this correlation seems to be fully justified. It should be mentioned, in addition, that characterizations of even rather involved molecular systems are often performed employing Mulliken population analysis (Dimitrova, 1995, and references therein).

The parameters to be determined are the cell dimensions and atomic coordinates. Assuming the cell

† The importance of including the radii of the ions is unquestionable. The atomic (Mulliken) charge was added to account for the different bonding ability of the O atoms in various oxo anions. In the calculation it was assumed (for consistency) that the X–O bond length of an XO₄[−] anion is equal to the sum of Shannon’s radii and no further optimization was performed. The package GAUSSIAN94 (Frisch *et al.*, 1995) was employed for the quantum mechanical calculations.

to be orthorhombic requires the determination of three parameters. Within this isostructural group the observed variation in each cell parameter is ~12%. As seen above, five atoms are in special positions whose variable parameters are *x* and *y* (ten parameters) and one O atom is in a general equivalent position (three parameters). Within the group there is a wide range of observed parameter variation, some such as *x* (O1) varying by 0.05, whereas the smallest variation is in *y* (O1), only 0.0026. Thus, in all, 16 parameters need to be determined.

The STATGRAPHICS (Statistical Graphics Corporation, 1989) package on an IBM PC-486 was used in the statistical calculations. Stepwise variable selection was performed. This is a multiple regression analysis that includes or rejects an independent variable in the model, depending on the value of the *t*-statistics. The point is to judge whether the inclusion of a given independent variable, in the presence of other variables, is statistically significant.

Since the crystal structures of the compounds were refined by various groups of authors, there are differences in the choice of cell, orientation of axes and atom designation. In order to avoid possible confusion, all data were transformed to match the choices made in β-K₂SO₄ (McGinnety, 1972). It should be mentioned, in passing, that there is a misprint in one of the fractional coordinates of Rb₂SeO₄ (Takahashi *et al.*, 1987) The paper gives 0.4911 as the *x* coordinate of Rb(1), whereas it should be 0.4111.

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

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

where $R(M^+)$, in Å, is the effective crystal radius

(Shannon, 1976) for the hexa-coordinated† univalent cation, $R(X-O)$, in Å, is the sum of the effective crystal radii for the tetra-coordinated central atom X (i.e. for the X^{6+} ion) and the O atom (O^{2-} ion with CN = 2) in the XO_4^{2-} group, O_{charge} is the calculated Mulliken charge for the O atom and q is a constant. The parameters m , n , p and q for each dependent variable are to be determined by multiple regression. Dependent variables are listed in Table 2 and the regression results in Table 3.

It will be seen that the predictive strength of the regression equations is, in most cases, very high. This is shown by the value of the coefficient of determination (R_{adjusted}^2), which is higher than 0.9 for 10 out of the 16 dependent variables. For one parameter, $x(\text{O}2)$, there is no correlation between the chosen set of independent variables and the 11 values of the dependent variable. However, the total variation in the numerical values of the dependent variable $x(\text{O}2)$ is 0.006 and, therefore, may be considered as a parameter that is rather insensitive to the variations of atomic radii/atomic charges. In such cases the experimental errors in the determination of the fractional atomic coordinates also become an important factor in the scatter of the points. Consequently, for $x(\text{O}1)$, where the range of the sample is 0.05 (an order of magnitude higher), the coefficient of determination reaches the highest value (0.999) in the class.

3. Crystal structure of Rb₂CrO₄

3.1. X-ray data

The structure of Rb₂CrO₄ was determined by photographic methods over 50 years ago (Smith & Colby, 1941). The calculated distances and angles in the CrO₄²⁻ anion differed appreciably from the values in K₂CrO₄ and Cs₂CrO₄ (McGinnety, 1972; Morris *et al.*, 1981), suggesting rather low accuracy. This notion was confirmed by the prediction of the structure (see below). In fact, all calculations showed sufficiently large differences from the early X-ray crystal structure analysis to warrant a refinement.

X-ray intensity data were collected on an automated four-circle Picker diffractometer using Zr-filtered Mo $K\alpha$ radiation with pulse-height analysis. The correction θ_0 was checked against 12 reflections at $\theta = 32^\circ$ from a crystal of sodium chloride. Data reduction and all other computations were carried out using the NRCVAX package (Gabe *et al.*, 1989). Crystal data are

Table 4. *Experimental details*

| | |
|--|---|
| Crystal data | |
| Chemical formula | Rb ₂ CrO ₄ |
| Chemical formula weight | 286.93 |
| Cell setting | Orthorhombic |
| Space group | <i>Pnam</i> |
| <i>a</i> (Å) | 7.976 (4) |
| <i>b</i> (Å) | 10.692 (1) |
| <i>c</i> (Å) | 6.057 (2) |
| <i>V</i> (Å ³) | 516.5 (3) |
| <i>Z</i> | 4 |
| <i>D_x</i> (Mg m ⁻³) | 3.690 |
| Radiation type | Mo $K\alpha$ |
| Wavelength (Å) | 0.70930 |
| No. of reflections for cell parameters | 8 |
| θ range (°) | 20.99–21.01 |
| μ (mm ⁻¹) | 20.29 |
| Temperature (K) | 297 |
| Crystal form | Needle |
| Crystal size (mm) | 0.60 × 0.13 × 0.10 |
| Crystal colour | Yellow |
| Data collection | |
| Diffractometer | Picker NRC |
| Data collection method | $\theta/2\theta$ scans |
| Absorption correction | Integration |
| <i>T_{min}</i> | 0.1047 |
| <i>T_{max}</i> | 0.1908 |
| No. of measured reflections | 1662 |
| No. of independent reflections | 501 |
| No. of observed reflections | 468 |
| Criterion for observed reflections | $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$ |
| <i>R_{int}</i> | 0.113 |
| θ_{max} (°) | 24.95 |
| Range of <i>h, k, l</i> | –9 → <i>h</i> → 9 –12 → <i>k</i> → 12 0 → <i>l</i> → 7 |
| No. of standard reflections | 1 |
| Frequency of standard reflections | Every 100 reflections |
| Intensity decay (%) | 1.0 |
| Refinement | |
| Refinement on | <i>F</i> |
| <i>R</i> | 0.051 |
| <i>wR</i> | 0.062 |
| <i>S</i> | 8.46 |
| No. of reflections used in refinement | 468 |
| No. of parameters used | 41 |
| Weighting scheme | Unit |
| (Δ/σ) _{max} | 0.002 |
| $\Delta\rho_{\text{max}}$ (e Å ⁻³) | 2.28 |
| $\Delta\rho_{\text{min}}$ (e Å ⁻³) | –1.98 |
| Extinction method | Larson (1970) |
| Extinction coefficient | 1.98 (16) |
| Source of atomic scattering factors | <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV) |
| Computer programs | |
| Data reduction | NRCVAX DATRD2 (Gabe <i>et al.</i> , 1989) |
| Structure solution | NRCVAX SOLVER (Gabe <i>et al.</i> , 1989) |
| Structure refinement | NRCVAX LSTSQ (Gabe <i>et al.</i> , 1989) |
| Preparation of material for publication | NRCVAX TABLES (January 1994 Version) |

† Although, as mentioned, the univalent cations in this family of crystals are known to be 9-, 10- or 11-coordinated, values for the effective crystal radii for M^+ ions were taken for coordination number (CN) 6, since they are usually considered to be most reliable.

Table 5. Unit-cell parameters and fractional atomic coordinates in Rb_2CrO_4

The predicted and redetermined structures (present work; standard deviations given in parentheses refer to the least significant digit) are given together for the purposes of comparison. $|\delta|$ is the absolute difference between values in the columns indicated. The coordinates $z(Rb1)$, $z(Rb2)$, $z(Cr)$, $z(O1)$ and $z(O2)$ are all necessarily 0.25, and are not listed.

| Parameter | Predicted (i) | Redetermined (ii) | $ \delta_{ii} - i $ |
|-----------|---------------|-------------------|---------------------|
| a (Å) | 8.0314 | 7.976 (4) | 0.0554 |
| b (Å) | 10.7482 | 10.692 (1) | 0.0562 |
| c (Å) | 6.1039 | 6.057 (2) | 0.0469 |
| $x(Rb1)$ | 0.6670 | 0.66788 (23) | 0.0009 |
| $y(Rb1)$ | 0.4115 | 0.41051 (17) | 0.0010 |
| $x(Rb2)$ | -0.0131 | -0.01460 (22) | 0.0015 |
| $y(Rb2)$ | 0.6987 | 0.69781 (16) | 0.0009 |
| $x(Cr)$ | 0.2326 | 0.2331 (4) | 0.0005 |
| $y(Cr)$ | 0.4199 | 0.42117 (25) | 0.0013 |
| $x(O1)$ | 0.0279 | 0.0285 (19) | 0.0006 |
| $y(O1)$ | 0.4155 | 0.4145 (14) | 0.0010 |
| $x(O2)$ | 0.2990 | 0.2980 (18) | 0.0010 |
| $y(O2)$ | 0.5656 | 0.5658 (13) | 0.0002 |
| $x(O3)$ | 0.3050 | 0.3057 (13) | 0.0007 |
| $y(O3)$ | 0.3503 | 0.3510 (9) | 0.0007 |
| $z(O3)$ | 0.0289 | 0.0306 (16) | 0.0017 |

given in Table 4. The redetermined cell dimensions and atomic coordinates are listed in Table 5.†

3.2. Predicted structures

The results of the multiple regression are summarized in Tables 5 and 6. It may be seen that virtually all parameters of the predicted structure (except for the a and b axes) are equal within one standard deviation to the corresponding values of the redetermined structure. Selected interatomic distances and interbond angles are set out in Table 6. The average deviation of Rb—O distances between predicted and redetermined structures is ~ 1.8 pm, that of Cr—O distances is also 1.8 pm and the deviation of the O—Cr—O angles is 0.5° .

It seems therefore that the proposed method gives very good results, at least for a series of strictly isostructural compounds. The real advantage of the method is that it may give accurately predicted structures for compounds that can only be obtained in powder or microcrystalline form or are chemically unstable. For instance, the structures of Rb_2MnO_4 and Rb_2FeO_4 may be predicted in this way, since no single-crystal study is available for either compound. An accurate structure is known for K_2MnO_4 (Palenik, 1967) and our predictions fit the structure very well, the largest discrepancy in any atomic parameter being

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: LI0250). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. Selected interatomic distances (Å) and angles ($^\circ$) in Rb_2CrO_4 ($|\delta|$ as for Table 5)

| Distance (Å) | Predicted (i) | Refined (ii) | $ \delta_{ii} - i $ |
|--------------|---------------|--------------|---------------------|
| Rb1—O1 | 2.899 | 2.876 (16) | 0.022 |
| Rb1—O2 | 3.388 | 3.385 (15) | 0.003 |
| Rb1—O2 | 3.074 | 3.051 (2) | 0.023 |
| Rb1—O3 | 3.272 | 3.243 (10) | 0.029 |
| Rb1—O3 | 3.312 | 3.285 (10) | 0.027 |
| Rb1—O3 | 3.083 | 3.071 (10) | 0.012 |
| Rb2—O1 | 3.062 | 3.048 (15) | 0.014 |
| Rb2—O1 | 3.292 | 3.260 (6) | 0.032 |
| Rb2—O2 | 2.886 | 2.865 (15) | 0.021 |
| Rb2—O2 | 2.949 | 2.936 (14) | 0.013 |
| Rb2—O3 | 2.889 | 2.890 (10) | 0.001 |
| Rb2—O3 | 2.945 | 2.924 (10) | 0.021 |
| Cr—O1 | 1.645 | 1.634 (16) | 0.017 |
| Cr—O2 | 1.654 | 1.631 (14) | 0.023 |
| Cr—O3 | 1.649 | 1.632 (10) | 0.017 |
| O1—Cr—O2 | 110.4 | 111.0 (8) | 0.6 |
| O1—Cr—O3 | 109.8 | 109.5 (5) | 0.3 |
| O2—Cr—O3 | 108.4 | 108.8 (5) | 0.4 |
| O3—Cr—O3' | 109.9 | 109.0 (5) | 0.9 |

Table 7. Predicted structures of Rb_2MnO_4 and Rb_2FeO_4

| | Rb_2MnO_4 | Rb_2FeO_4 |
|----------|-------------|-------------|
| a (Å) | 8.036† | 8.044 |
| b (Å) | 10.729 | 10.707 |
| c (Å) | 6.087 | 6.067 |
| $xRb1$ | 0.6660 | 0.6646 |
| $yRb1$ | 0.4115 | 0.4114 |
| $xRb2$ | -0.0138 | -0.0147 |
| $yRb2$ | 0.6973 | 0.6954 |
| xMn/Fe | 0.2332 | 0.2339 |
| yMn/Fe | 0.4198 | 0.4198 |
| $xO1$ | 0.0285 | 0.0291 |
| $yO1$ | 0.4147 | 0.4136 |
| $xO2$ | 0.2990 | 0.2990 |
| $yO2$ | 0.5662 | 0.5672 |
| $xO3$ | 0.3061 | 0.3074 |
| $yO3$ | 0.3504 | 0.3506 |
| $zO3$ | 0.0283 | 0.0273 |

Predicted dimensions of the MnO_4^{2-} and FeO_4^{2-} anions (Å and $^\circ$)

| | MnO_4^{2-} | FeO_4^{2-} |
|-------------|--------------|--------------|
| Mn/Fe—O1 | 1.646 | 1.649 |
| Mn/Fe—O2 | 1.657 | 1.663 |
| Mn/Fe—O3 | 1.649 | 1.650 |
| O1—Mn/Fe—O2 | 110.5 | 110.7 |
| O1—Mn/Fe—O3 | 109.9 | 109.9 |
| O2—Mn/Fe—O3 | 108.3 | 108.3 |
| O3—Mn/Fe—O3 | 109.9 | 109.9 |

† Cell dimensions from powder diagram (Herbstein *et al.*, 1971): 8.00 (2), 10.65 (2), 6.08 (2) Å.

0.0022. Only powder data are available for Rb_2MnO_4 (Herbstein *et al.*, 1971). In view of the good agreement obtained for K_2MnO_4 and the good agreement between the predicted and observed unit-cell parameters for Rb_2MnO_4 , we give the predicted atomic coordinates in

Table 7. Our calculations for K₂FeO₄ yield equally good results (maximum discrepancy in atomic parameters, 0.0026) and we accordingly predict the, as yet unknown, structure of Rb₂FeO₄ (Table 7). Our goal will be to fully determine these two structures by crystallographic methods.

Further work on the kieserite group isomorphs (Aleksavska *et al.*, 1998) is also in progress.

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