

ON THE STRUCTURAL AND MAGNETIC PROPERTIES
OF $K_3CrTe_3O_{12}$, $Na_3CrTe_3O_{12}$ AND $NaCrTe_2O_8$

Pavel DANIHELKA

Department of Chemistry,

Institute of Mining and Metallurgy, 708 33 Ostrava

Received April 20th, 1982

$K_3CrTe_3O_{12}$, $Na_3CrTe_3O_{12}$, and $NaCrTe_2O_8$ were obtained by reacting telluric acid or amorphous potassium tellurate with molten alkali dichromates, and their structural and magnetic properties were studied. The three substances are paramagnetic, with magnetic moments corresponding to the chromium oxidation state III. The sodium compounds obey the Curie-Weiss law up to the temperature of decomposition, the potassium compound follows this law up to a temperature of 800 K, above which the magnetic moment of chromium decreases probably on account of a partial reversible oxidation of chromium by the tellurium(VI) present. The three substances investigated were indexed in the tetragonal system and their lattice parameters were calculated. The two sodium salts involve the same basic structure motif, *viz.* $Te_{12}O_{48}^{24-}$.

The building structure unit of telluric acid and tellurates is a TeO_6 octahedron; in this respect these substances differ from their apparent analogues — sulphuric acid and sulphates. In addition to substances with isolated TeO_6^{6-} octahedra, a number of compounds with condensed structures exist in which the tellurate octahedra combined into more complex formations. By connection of two octahedra *via* their edges a $Te_2O_{10}^{8-}$ anion is formed, as found, *e.g.*, in $K_4H_4Te_2O_{10} \cdot 7.3 H_2O$ (ref.¹). The condensation can be extended by applying higher temperatures and pressures; in this manner structures can be obtained involving infinite chains joined by their corners such as in KH_3TeO_5 (ref.²) or by their edges such as in $KHTeO_4$ (ref.³), or involving a network of octahedra joined mutually by their corners such as in H_2TeO_4 (ref.⁴).

A suitable medium in which high temperature and crystallization pressures can be applied is molten inorganic salts, from which a number of alkali tellurates and tellurate-tellurites with condensed structure have been obtained^{5,6}. By using dichromate as the reaction medium a new element can be introduced: if the salt is decomposed, some of the products remain in the melt, and ultimately chromium is introduced into the reaction product. When telluric acid or amorphous potassium tellurate is introduced into the molten dichromate a reaction takes place manifesting itself by evolution of gas; amorphous potassium tellurate in $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ melts gives $K_3CrTe_3O_{12}$ or $Na_3CrTe_3O_{12}$, respectively, telluric acid affords $K_3CrTe_3O_{12}$

and $\text{NaCrTe}_2\text{O}_8$, respectively⁷. Since these substances cannot be transferred into solution undisturbed, the attention was focussed on their properties in the solid phase. The aim of the present work was to establish the temperature dependence of the magnetic susceptibility of $\text{K}_3\text{CrTe}_3\text{O}_{12}$, $\text{Na}_3\text{CrTe}_3\text{O}_{12}$, and $\text{NaCrTe}_2\text{O}_8$, to determine the oxidation state of chromium in these substances, and to calculate the lattice parameters of their elementary cells.

EXPERIMENTAL

Hexahydrogentelluric acid was prepared by oxidation of elementary tellurium with hydrogen peroxide⁸, amorphous potassium tellurate ($\text{K}_2\text{H}_6\text{Te}_2\text{O}_{10}$) was obtained by precipitation from telluric acid solution with excess potassium salt at pH 8.5. Tellurium was a product of Pramet, Šumperk, the remaining chemicals were furnished by Lachema, Brno, in a reagent grade purity.

$\text{K}_3\text{CrTe}_3\text{O}_{12}$ was synthesized by reacting telluric acid with a tenfold excess of potassium dichromate at 700 K, $\text{Na}_3\text{CrTe}_3\text{O}_{12}$ and $\text{NaCrTe}_2\text{O}_8$ were prepared by reacting amorphous potassium tellurate and telluric acid, respectively, with anhydrous sodium dichromate at 620 K. After a reaction period of 20 h the reaction mixture was cooled down, multiply decanted with water, collected, and dried at 380 K.

The magnetic susceptibilities were determined in the temperature region of 77–950 K by the Faraday method on a Newport Instrument C 4B Type A magnet applying $H \partial H / \partial x$ values of $3 \cdot 1 \cdot 10^{11} - 8 \cdot 8 \cdot 10^{12} \text{ A}^2 \text{ m}^{-3}$. The measurements were accomplished in evacuated quartz flasks on a quartz spring balance; $\text{CoHg}(\text{CSN})_4$ was used for calibration.

The mass susceptibilities χ were obtained, their values were converted to the molar magnetic susceptibilities χ_M , which in turn were corrected for diamagnetism to afford the χ_M^{cor} values. According to the Curie-Weiss law,

$$\chi_M^{\text{cor}} = N\mu^2 / [3k(T - \Delta)]$$

(μ is the magnetic moment and Δ is the Weiss constant; the remaining symbols have their conventional meaning), the reciprocal corrected magnetic susceptibility should be linearly dependent on temperature.

The powder X-ray diffraction patterns were obtained by Guinier's method, in the diffraction angle range of $5^\circ - 45^\circ$, on a Philips PW 1009/30 instrument; monochromatized $\text{CuK}_{\alpha 1}$ radiation with a wavelength of 154.05 pm was used. Silicon served as internal standard, the line positions were read from the film by means of a Delft-Holland Y 886 vernier.

The density of the substances was measured in a 2 cm^3 Gay-Lussac pycnometer at 298 K using freshly distilled *p*-xylene as the suspension liquid.

RESULTS AND DISCUSSION

Magnetic Properties

The temperature dependences of the magnetic parameters for the tellurates under study are given in Table I; the reciprocal corrected molar susceptibilities are plotted against temperature in Figs 1 and 2.

For $\text{K}_3\text{CrTe}_3\text{O}_{12}$ the dependence of the reciprocal susceptibility on temperature is linear, in agreement with the Curie-Weiss law, over the region of 77–800 K; the

TABLE I
Magnetic properties of $K_3CrTe_3O_{12}$, $Na_3CrTe_3O_{12}$, and $NaCrTe_2O_8$

Temperature K	$10^{-8} \chi$ $m^3 kg^{-1}$	$10^{-8} \chi_M^{cor}$ $m^3 mol^{-1}$	$10^6 1/\chi_M^{cor}$ $mol m^{-3}$
$K_3CrTe_3O_{12}^a$			
77	25.2	19.0	5.25
193	12.7	9.72	10.3
298	9.86	7.61	13.1
373	7.02	5.49	18.2
458	6.01	4.74	21.1
557	5.03	4.01	24.9
665	4.08	3.31	30.2
741	3.68	3.01	33.2
793	3.36	2.77	36.0
850	2.89	2.43	41.2
908	2.55	2.17	46.0
953	1.99	1.75	57.0
$Na_3CrTe_3O_{12}^b$			
77	19.04	13.50	7.4
196	12.04	8.62	11.6
298	8.46	6.13	16.3
382	6.77	4.95	20.2
476	5.76	4.26	23.5
554	5.04	3.75	26.6
661	4.31	3.24	30.8
715	3.91	2.97	33.7
762	3.67	2.79	35.8
852	3.39	2.60	38.4
$NaCrTe_2O_8^c$			
77	36.10	16.70	6.0
195	21.22	9.88	10.1
298	16.11	7.54	13.3
415	12.30	5.80	17.2
481	11.02	5.21	19.2
553	9.97	4.73	21.1
633	8.75	4.17	24.0
702	7.85	3.76	26.6
753	7.41	3.56	28.1

The correction for diamagnetism was made using a χ_D value of $a - 2.74 \cdot 10^{-9}$, $b - 2.44 \cdot 10^{-9}$, $c - 1.608 \cdot 10^{-9} m^3 mol^{-1}$.

Weiss constant is $\Delta = -40$ K. The magnetic moment of chromium is $\mu = 3.48 \cdot 10^{-23}$ A m², which corresponds to 3.86 B.M., per chromium atom. Since the spin-only magnetic moment of the Cr³⁺ cation, with three unpaired electrons, is 3.87 B.M. and the spin-orbital interaction is low for this ion, it can be inferred that in K₃CrTe₃O₁₂ at temperatures up to 800 K chromium is present in oxidation state III, all tellurium occurring in oxidation state VI. Above 800 K the magnetic moment decreases, probably owing to an oxidation-reduction reaction between chromium and tellurium transforming part of the chromium ions into oxidation state VI. In this oxidation state chromium is devoid of unpaired electrons and is diamagnetic or very weakly paramagnetic by temperature independent paramagnetism, so that it is possible, from the drop of the magnetic moment, to estimate the loss of chromium in oxidation state III; at 950 K this loss is approximately 25%. The reaction is reversible; after cooling, the magnetic susceptibility follows the initial course and the X-ray diffraction patterns are identical too.

Na₃CrTe₃O₁₂ obeys the Curie-Weiss law up to a temperature of 850 K; the Weiss constant is $\Delta = -100$ K. The magnetic moment of chromium, $3.67 \cdot 10^{-23}$ A m², or 3.96 B.M., indicates that in this compound, too, the element is present in oxidation state III. At temperatures above 850 K the magnetic susceptibility values are irreproducible and at approximately 900 K the sample decomposes to a mixture of chromium sesquioxide, tellurium dioxide, and amorphous tellurites. The flasks crack easily owing to the evolution of oxygen.

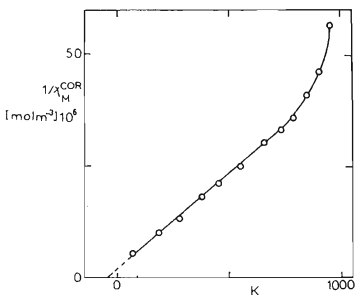


FIG. 1

Dependence of the reciprocal magnetic susceptibility of K₃CrTe₃O₁₂ on temperature. The intercept, for the straight line segment, gives the Weiss constant

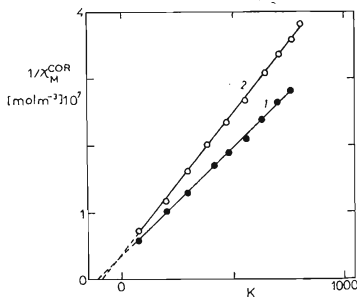


FIG. 2

Dependence of the reciprocal magnetic susceptibilities of NaCrTe₂O₈ 1 and Na₃CrTe₃O₁₂ 2 on temperature

$NaCrTe_2O_8$ also follows the Curie-Weiss law, with a Weiss constant value of $\Delta = -111$ K, up to 750 K. Above this temperature, again, the substance decomposes and consequently, irreproducible results are obtained. The magnetic moment per chromium atom is $4 \cdot 10 \cdot 10^{-23} \text{ A m}^2$, hence, 4.42 B.M. This value might lead to the conclusion that the element is in part present in oxidation state II, for which the spin-only magnetic moment is 4.90 B.M.; however, occurrence of a Cr^{2+} ion in the substance in question is highly improbable with regard to the oxidative nature of the melt, and is ruled out on stoichiometric grounds, no oxidation state higher than VI being known for tellurium. Most probably, chromium again occurs in oxidation state III, and some effect other than that of unpaired electrons of chromium is responsible for the increased magnetic moment. Paramagnetism has been reported for alkali tellurates and tellurate-tellurites prepared by reactions in salt melts^{5,7} as well as for substances obtained from a decomposition of telluric acid⁹. In such cases the crystal lattice is not perfectly developed and the X-ray diffraction lines are less sharp. This is consistent with our results: while for $K_3CrTe_3O_{12}$, for which the experimental magnetic moment is nearly identical with the theoretical value, the diffraction lines are sharpest, for $Na_3CrTe_3O_{12}$ with a slightly enhanced magnetic moment the lines are less sharp, and for $NaCrTe_2O_8$, with a relatively high magnetic moment, the diffraction lines are markedly diffuse.

X-Ray Diffraction Patterns

The three tellurates under study were obtained as microcrystalline powders; the quality of the diffraction, as mentioned above, decreases in the order $K_3CrTe_3O_{12}$, $Na_3CrTe_3O_{12}$, $NaCrTe_2O_8$. When the time for which the preparations are allowed to rest in the dichromate melt is shortened appreciably, ill-developed crystals result and weak and diffuse lines are observed. Striving to prepare high-quality crystals we carried out a series of long-run preparations (the longest lasted 60 days), but

TABLE II

Lattice parameters of the tellurates under study (tetragonal crystal system)

Compound	a^a pm	c pm	V^a nm^3
$K_3CrTe_3O_{12}$	710.18 (4)	1 159.42 (6)	0.58476 (7)
$Na_3CrTe_3O_{12}$	1 029.2 (1)	988.3 (2)	1.0467 (3)
$NaCrTe_2O_8$	1 029.0 (4)	988.0 (5)	1.0461 (6)

^a The numbers in parentheses give the standard deviations for the last valid digits.

TABLE III

Diffraction angles θ , interplanar spacings d , and relative intensities of the diffraction lines for the tellurates under study

h	k	l	θ_{obs} deg	θ_{calc} deg	Δ^a deg	d_{obs} pm	d_{calc} pm	I/I_0
$\text{K}_3\text{CrTe}_3\text{O}_{12}$								
0	0	2	7.626	7.635	0.009	580.4	579.7	8
2	0	2	14.735	14.737	0.002	302.8	302.8	10
0	0	4	15.411	15.411	0.000	289.8	289.9	7
2	2	0	17.859	17.865	0.006	251.2	251.1	3
2	2	2	19.531	19.530	-0.001	230.4	230.4	1
0	0	6	23.493	23.491	-0.002	193.2	193.2	4
4	0	0	25.709	25.711	0.002	177.6	177.5	6
2	0	6	26.990	26.988	-0.002	169.7	169.7	2
4	2	0	29.009	29.015	0.006	158.8	158.8	1
2	2	6	30.202	30.198	-0.004	153.1	153.1	2
4	0	4	30.590	30.580	-0.010	151.4	151.4	5
3	3	4	32.091	32.098	0.007	145.9	146.0	1
4	0	6	36.099	36.099	0.000	130.7	130.7	3
2	2	8	37.863	37.854	-0.008	125.5	125.5	1
0	0	10	41.632	41.632	0.000	115.9	115.9	1
4	4	4	41.963	41.960	-0.003	115.2	115.2	2
4	0	8	43.314	43.219	0.005	112.3	112.3	2
2	0	10	44.330	44.336	0.006	110.2	110.2	1
$\text{Na}_3\text{CrTe}_3\text{O}_{12}$								
1	1	1	7.554	7.553	-0.001	586.0	586.0	1
2	0	0	8.592	8.609	0.017	515.6	514.6	10
1	0	2	9.949	9.957	0.008	445.8	445.4	5
2	1	2	13.216	13.221	0.005	336.9	336.8	6
2	2	2	15.230	15.242	0.012	293.2	293.0	1
4	0	0	17.426	17.420	-0.006	257.2	257.3	4
4	2	0	19.548	19.555	0.007	230.2	230.1	4
2	2	4	22.160	22.138	-0.022	204.2	204.4	1
4	4	0	25.053	25.048	-0.005	181.9	181.9	4
6	1	2	28.752	28.764	0.012	160.1	160.1	2
6	3	0	30.119	30.136	0.017	153.5	153.4	1
3	3	5	30.198	30.178	-0.020	153.1	153.2	1
3	0	6	31.248	31.249	0.001	148.5	148.5	1
6	4	0	32.672	32.663	-0.009	142.7	142.7	2
6	1	5	36.819	36.818	-0.001	128.5	128.5	1
2	0	8	39.873	39.884	0.011	120.1	120.1	1
7	2	5	42.061	42.058	-0.003	115.0	115.0	1

TABLE III
(Continued)

h	k	l	θ_{obs} deg	θ_{calc} deg	Δ^a deg	d_{obs} pm	d_{calc} pm	I/I_0
$NaCrTe_2O_8$								
2	0	0	8.600	8.610	0.010	515.1	514.5	10
1	0	2	9.988	9.960	-0.028	441.1	445.3	5
2	1	2	13.230	13.224	-0.006	336.6	336.7	8
3	0	1	13.800	13.752	-0.048	322.9	324.0	7
4	0	0	17.438	17.423	-0.015	257.0	257.3	6
4	2	0	19.578	19.558	-0.020	229.9	230.1	6
2	2	4	22.121	22.143	0.022	204.5	204.4	1
4	4	0	25.037	25.052	0.015	182.0	181.9	1
2	1	5	25.074	25.101	0.027	181.8	181.6	5
6	1	2	28.802	28.770	-0.032	159.9	160.0	3
3	0	6	31.287	31.257	-0.030	148.3	148.4	2
6	1	5	36.830	36.826	-0.004	128.5	128.5	2
5	4	3	32.209	32.230	0.021	144.5	144.4	1
6	1	5	36.830	36.826	-0.004	128.5	128.5	2
7	2	5	42.056	42.068	0.012	115.0	115.0	1

^a $\theta_{calc} - \theta_{obs}$; the values largely lie within the limits of experimental error.

after approximately 10 h no additional improvement was achieved; long-term heating in air or in evacuated quartz flasks did not add to the quality either.

We were able to index all the three tellurates in the tetragonal system; the a and c parameters were calculated from the interplanar distance values d and the h , k , l indices. The calculation was optimized, by using a computer, by minimizing the standard deviations of the lattice parameters. The results are given in Table II. In a reverse manner the diffraction data then were back calculated from the obtained lattice parameters; these theoretical values, along with the experimental data, are given in Table III.

Based on the elementary cell volumes, relative molecular masses, and experimental densities, the numbers of formula units in an elementary cell were calculated. For $K_3CrTe_3O_{12}$, with a density of $\rho = 4.39 \cdot 10^3 \text{ kg m}^{-3}$, the value obtained is 2.08; hence, there are two formula units in an elementary cell whose proper content thus is $K_6Cr_2Te_6O_{24}$ in agreement with the symmetry requirements of the tetragonal system.

For $\text{NaCrTe}_2\text{O}_8$ ($\rho = 4.37 \cdot 10^3 \text{ kg m}^{-3}$) and $\text{Na}_3\text{CrTe}_3\text{O}_{12}$ ($\rho = 4.49 \cdot 10^3 \text{ kg} \cdot \text{m}^{-3}$) there are $6.009 \approx 6$ and $4.07 \approx 4$ formula units in an elementary cell, respectively; hence, in both cases the anion part of an elementary cell is $\text{Te}_{12}\text{O}_{48}^{24-}$. In view of the nearly identical lattice parameters and X-ray powder diffractograms for the two substances (for 11 reflections the differences are less than 0.05°) it can be assumed that the $\text{Te}_{12}\text{O}_{48}^{24-}$ tellurate motif is practically the same in the two sodium-chromium tellurates, the charge being compensated by different numbers of sodium and chromium cations.

For the three substances in question the stoichiometry is $(\text{TeO}_4^{2-})_n$. Eliminating the rather unlikely and so far unobserved connection of the tellurate octahedra *via* their faces, this motif can be considered to consist either in a chain structure of edge-joined octahedra, or in a planar structure of octahedra joined in four corners, the condensed structure involving the whole lattice in both cases. Other theoretical possibilities involving a formation of isolated polyanions similar to those of molybdenum, are not very likely with regard to the fact that all of the three alkali-chromium tellurates are extremely insoluble and resistant to long-term action of acids. The powder X-ray diffraction patterns fail to provide sufficient data for gaining a deeper insight into the arrangement of the tellurate octahedra, and single crystals of these substances could not be as yet prepared; therefore it cannot be decided which of the arrangements suggested is the most probable.

The author wishes to thank Associate Professor L. Jenšovský, Department of Inorganic Chemistry, Charles University, Prague, for valuable advice, and the staff of the Department of Inorganic Chemistry, Oslo University, Norway, for assistance in the final stage of this work.

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Translated by P. Adámek.