

The synthesis and properties of the hexachloroniobates and hexachlorotantalates of Na, K, Rb, and Cs

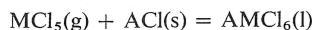
DONALD R. SADOWAY¹ AND S. N. FLENGAS

Department of Metallurgy and Materials Science, University of Toronto, Toronto, Ont., Canada M5S 1A4

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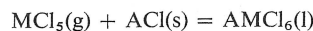
The compounds NaNbCl₆, NaTaCl₆, KNbCl₆, KTaCl₆, RbNbCl₆, RbTaCl₆, CsNbCl₆, and CsTaCl₆ were synthesized in a closed system by the reaction of NbCl₅ or TaCl₅ vapour with solid alkali-metal chloride as follows



where M is Nb or Ta, and A is Na, K, Rb, or Cs. The X-ray powder diffraction patterns of these compounds were obtained. Temperatures of various phase transformations were determined cryoscopically.

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On a synthétisé les composés NaNbCl₆, NaTaCl₆, KNbCl₆, KTaCl₆, RbNbCl₆, RbTaCl₆, CsNbCl₆ et CsTaCl₆ dans un système fermé en faisant réagir du NbCl₅ ou du TaCl₅ à l'état vapeur avec un chlorure de métal alcalin solide d'après la réaction



où M est soit Nb ou Ta et A est Na, K, Rb ou Cs. On a pu obtenir les spectres de diffraction de rayon-X des poudres de ces composés. On a déterminé les températures de diverses transformations de phase par une méthode cryoscopique.

[Traduit par le journal]

Introduction

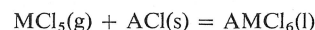
The pentachlorides of niobium and tantalum are known to react with alkali-metal chlorides to produce hexachloroniobate(V) and hexachlorotantalate(V) compounds of the general formula, AMCl₆, where A is an alkali metal and M is either Nb or Ta. These compounds contain thermodynamically stable forms of the volatile covalently bonded pentachlorides and, as such, are of interest in the extractive metallurgy of niobium and tantalum. Although these compounds have been the subjects of earlier investigations, the results of different studies vary considerably and, in some cases, are contradictory.

In the present investigation the compounds NaNbCl₆, NaTaCl₆, KNbCl₆, KTaCl₆, RbNbCl₆, RbTaCl₆, CsNbCl₆, and CsTaCl₆ have been synthesized by a method different from those previously employed, as well as, by a conventional technique. The X-ray powder diffraction patterns of these compounds have been obtained. The temperatures of various phase transformations have been determined by cryoscopy.

Experimental

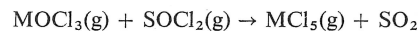
The principal method of compound preparation in this study was the reaction of MCl₅ vapour with ACl powder at a

temperature above the melting point of the AMCl₆ compound under synthesis. The reaction may be represented as follows:

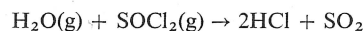


This was a batch operation conducted in a closed non-isothermal system and was actually a modification of a method used previously in this laboratory to prepare chlorotitanates, chlorozirconates, and chlorohafnates of alkali-metal chlorides and alkaline-earth chlorides (1-3). A variation of this method in which molten KNbCl₆ and KTaCl₆ are produced in a continuous operation has been reported (4).

The compounds NbCl₅ or TaCl₅ were obtained from Research Organic/Inorganic Chemical Corporation, Belleville, NJ, U.S.A., and were certified to be of purity 99.99 and 99.9% respectively. Although they were supplied sealed in bottles under a dry nitrogen atmosphere hydrolysis occurred and oxychlorides were present. To purify the salts either of two methods was used. The first method was to sublime the salt in a stream of helium saturated with thionyl chloride as described by Keneshea *et al.* (5). Oxychloride and water reacted according to



and



where M represents Nb or Ta. The purified compounds were sublimed into glass ampoules and sealed under vacuum for storage. The second method, described by Brown (6), was to dissolve the pentachloride compound in freshly distilled thionyl chloride, allow the mixture to digest for 24 h, and filter the solution through a fritted disc having a nominal pore size of 5 μm. The SOCl₂ was evaporated from the filtrate and the remaining salt was sublimed in a sealed tube. Reagent grade alkali-metal chlorides were ground to a particle size of -200 mesh. They were dehydrated by exposure to a mixture of chlorine and HCl gases for several hours at 500°C.

¹Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

To prepare the compound, $AMCl_6$, equimolar amounts of ACl and MCl_5 were placed in a borosilicate glass reaction tube, which is shown in Fig. 1. To minimize hydrolysis of the reagents this operation was performed in a glove box filled with anhydrous helium. With its ends stoppered the reaction tube was removed from the glove box and the end nearer the ACl was flame sealed. Next, the reaction tube was evacuated and the ACl was heated to $400^\circ C$. During this time the reaction tube was being evacuated to exhaust the gas which was desorbing off the surface of the ACl powder. After 12 h the reaction tube was flame sealed under vacuum. It was placed in a furnace with two independently controlled elements. The MCl_5 was heated to the temperature at which its pressure was approximately 1.5 atm, i.e. $266^\circ C$ for $NbCl_5$ and $257^\circ C$ for $TaCl_5$ (7). Except in the case of the $NaCl$ the other alkali chlorides were heated to approximately $10^\circ C$ above the melting point of the corresponding $AMCl_6$ compound. Reaction times were of the order of several hours. Power to both furnace elements was then disconnected simultaneously and the reaction tube was furnace-cooled. The high pressures over the molten compounds, $NaNbCl_6$ and $NaTaCl_6$, necessitated their preparation in the solid state. Time of reaction was 3 days.

Despite all precautions, a small amount of fibrous white substance remained behind in the MCl_5 part of the reaction tube. This was probably hydrolysed MCl_5 . The reaction tube was opened in the glove box and the glass boat was weighed to determine the amount of MCl_5 which had reacted with the ACl and, therefore, the composition of the material in the boat.

For the sake of comparison, some of the compounds were synthesized by precipitation from solutions of $SOCl_2$ - ICl (6, 8). Attempts were made to prepare all $AMCl_6$ compounds by this method; however, only $CsNbCl_6$, $CsTaCl_6$, and $RbTaCl_6$ could be produced in quantity.

Other investigators (9-13) have made these compounds by mixing the appropriate quantities of $NbCl_5$ or $TaCl_5$ with ACl and slowly heating the mixture to its melting temperature. The melt is then cooled and the solid product is ground in a dry atmosphere. This method was not used in the present study because it was felt that gas-solid reaction reduces the contamination of the product.

$KNbCl_6$ and $KTaCl_6$ have also been prepared by two other methods. In one, the reaction of a mixture of K_2O and Nb_2O_5 or Ta_2O_5 with CCl_4 is conducted in a sealed ampoule at $400^\circ C$ (14). In the other, specified amounts of KCl and $NbCl_5$ or $TaCl_5$ dissolved in $SOCl_2$ are heated, excess KCl is removed by filtration, and $SOCl_2$ is evaporated from the filtrate (15). These methods, however, have low yields and are used mainly for the preparation of spectral samples of small mass.

At room temperature the hexachloroniobates are green. Upon heating they turn yellow-orange, and their melts are red. On exposure to moisture for several minutes the solids turn blue, they are white when completely hydrolysed.

The solid hexachlorotantalates and all their hydrolysis products are white. The molten hexachlorotantalates are transparent and have a faint lemon-yellow colour.

Results

X-ray Powder Patterns

The X-ray powder patterns were obtained with a Debye-Scherrer 114.8 mm camera, exposed for 1 h to CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) filtered through nickel. In a glove box filled with helium the specimens were ground and screened to -200 mesh and hermetically sealed in 0.3 mm quartz glass capillaries.

The results for $NbCl_5$ and $TaCl_5$ which had been purified by precipitation from $SOCl_2$, as described above, agree well with earlier work by Douglass and Staritzky (16) for $NbCl_5$ and Rolsten (17) for $TaCl_5$.

The X-ray patterns of the eight compounds $AMCl_6$, where A is Na, K, Rb, or Cs, and M is Nb or Ta have been obtained. Despite the fact that in some cases the specimens did not consist of exactly equimolar amounts of ACl and MCl_5 extraneous lines which could be attributed to these small variations in composition were not found. Furthermore, in the case of $RbTaCl_6$, $CsNbCl_6$, and $CsTaCl_6$, which were successfully synthesized both by the reaction of MCl_5 vapour with ACl powder and by precipitation from $SOCl_2$ - ICl solutions, the two patterns obtained were identical.

Only three X-ray studies of $AMCl_6$ compounds have been reported. Kozhina *et al.* (13) studied $KNbCl_6$ and $KTaCl_6$, Smirnova and Tsintsius (18), $RbNbCl_6$ and $CsNbCl_6$, and Bagnall and Brown (8), $CsNbCl_6$ and $CsTaCl_6$.

There is excellent agreement between the results of this work and that reported by Kozhina *et al.* (13) for $KNbCl_6$ and $KTaCl_6$ respectively.

The results of this work are also in agreement with the main lines obtained by Smirnova and Tsintsius (18) for $RbNbCl_6$.

The results of this study for $CsTaCl_6$ agree with those of Bagnall and Brown (8). The latter prepared their samples by precipitation from $SOCl_2$ - ICl solutions; in this study samples were prepared both by that method and by the reaction of $CsCl$ with $TaCl_5$ vapour. Although the pattern by Bagnall and Brown has more lines, both patterns agree on lines of greater intensity. Samples prepared herein by precipitation and by solid-vapour reaction were irradiated; all gave the same results. Furthermore, this powder pattern was successfully indexed. No explanation is given for the extra lines reported by Bagnall and Brown.

The X-ray diffraction patterns for the alkali hexachloroniobate and alkali hexachlorotantalate compounds which have been obtained in this laboratory may be found in the Depository of Unpublished Data, CISTI, at the National Research Council of Canada.²

The X-ray diffraction pattern for the compound $CsNbCl_6$ was also obtained. Previous data by Smirnova and Tsintsius (18) and by Bagnall and Brown (8) are contradictory. As seen in Table 1, the present work is in better agreement with the results by Bagnall and Brown (8) who prepared the compound by

²Copies of these data are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

$$T = T_f, AMCl_6 + 10 \text{ K}$$

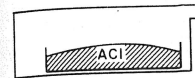


FIG. 1. Reaction apparatus for chloroniobate(V) and

the $SOCl_2$ - ICl method of co-melting eq $CsCl$ used by Smirnova and Tsintsius (18).

In this study samples were prepared both by precipitation and by the reaction of $CsCl$ with $TaCl_5$ irradiated. In all cases, a sample balance $CsCl$ was used. The pattern, a sample balance $CsCl$, was identical with that of the sample prepared by the reaction of $CsCl$ with $TaCl_5$ irradiated. In all cases, the intensity of the lines was the same. The presence of $CsCl$ in the sample does not affect the pattern. The two allotropic modifications of $CsNbCl_6$ were investigated in different investigations. Nevertheless, the patterns for $CsNbCl_6$ were identical. The powder pattern for $CsNbCl_6$ was indexed. X-ray diffraction patterns for $NaNbCl_6$, $NaTaCl_6$, and $CsTaCl_6$ were obtained in this laboratory and are available in the Depository of Unpublished Data.

As this study was completed, no compounds were prepared. Attempts were made to determine the structures of the tantalate compounds of polycrystalline form, whether the structure is hexagonal by method of the present study and the complete structure of the compound. The calculated structure factors for $NaNbCl_6$ and $CsTaCl_6$ may be found in the Depository of Unpublished Data.²

Good agreement was obtained for $NaNbCl_6$ and $CsTaCl_6$ with the results of Bagnall and Brown (8) who prepared the compound by

The measurements were compared with those of the structure of $NaNbCl_6$ with $a = 9.80 \text{ \AA}$. The calculated d -spacings are

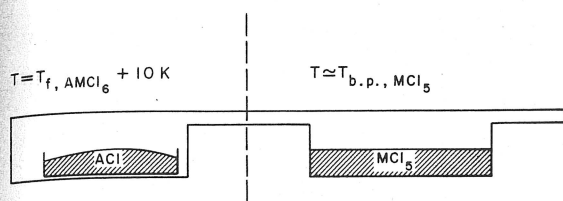


FIG. 1. Reaction apparatus for the synthesis of alkali hexachloroniobate(V) and hexachlorotantalate(V) compounds.

the SOCl_2 - ICl method as compared to the method of co-melting equimolar amounts of NbCl_5 and CsCl used by Smirnova and Tsintsius.

In this study samples which had been prepared both by precipitation from SOCl_2 - ICl solutions and by the reaction of CsCl with NbCl_5 vapour were irradiated. In all cases, the pattern given in Table 1 was obtained. To determine the effect of CsCl on the pattern, a sample of composition $X_{\text{CsNbCl}_6} = 0.535$, balance CsCl , was irradiated. The powder pattern was identical with the exception of the reflection at 2.91 Å, the intensity of which had increased with the presence of CsCl . In other experiments with CsNbCl_6 two allotropic modifications were detected. Perhaps different investigators have seen different allotropic forms. Nevertheless, five different samples of CsNbCl_6 were irradiated in this study, and all five gave the powder pattern in Table 1.

X-ray diffraction patterns for the compounds NaNbCl_6 , NaTaCl_6 , and RbTaCl_6 also obtained in this laboratory are given in Table 2.

As this study was the first to identify these compounds no comparison can be made with existing data.

Attempts were made to determine the crystal structures of the hexachloroniobate and hexachlorotantalate compounds. Although the data were those of polycrystalline samples, it was possible to test whether the structures were cubic, tetragonal, or hexagonal by means of nomographs. A summary of the results of these calculations is given in Table 3 and the complete indexed X-ray powder patterns and the calculated and experimentally obtained d -spacings for NaNbCl_6 , KNbCl_6 , KTaCl_6 , RbTaCl_6 , and CsTaCl_6 may be found at the Depository of Unpublished Data.²

Good agreement with the measured pattern of NaNbCl_6 was obtained by assuming this compound to have a tetragonal structure.

The measured powder pattern of KNbCl_6 is compared with that generated on the assumption that its crystal structure is cubic with a cell dimension $a = 9.80$ Å. The agreement between observed and calculated d -spacings is excellent. This confirms a

TABLE 1. Comparison of powder X-ray diffraction patterns of CsNbCl_6

This study		Bagnall and Brown (8)		Smirnova and Tsintsius (18)	
d (Å)	Intensity†	d (Å)	Intensity	d (Å)	Intensity
				6.45	vs
5.55	vw	5.98	m ⁻		
		5.63	m		
		5.32	s ⁻	5.37	w
4.86	sm	4.92	s	4.91	vvs
4.73	m	4.79	s		
		4.33	m	4.32	vw
		3.94	w	3.91	w
3.82	w	3.88	s ⁻		
		3.43	s	3.45	s
		3.41	s		
3.39	w	3.38	w ⁻		
		3.18	w		
		3.13	m		
		3.02	m ⁺		
		2.99	m ⁺		
2.91	vw*	2.79	vvs	2.80	vvs
2.76	sm	2.77	s ⁻		
2.72	m	2.75	s ⁻		
		2.68	w	2.67	s
		2.64	m		
		2.49	w ⁻		
		2.47	w ⁻		
		2.41	w ⁻	2.40	w
2.37	w	2.39	m ⁺		
2.14	m	2.15	m ⁺	2.15	vs
2.12	w	2.12	m		
		2.07	w ⁻		
		2.05	m ⁻		
		2.04	w ⁻		
		2.02	m ⁻		
		1.99	w		
		1.97	w		
		1.93	w		
		1.92	w		
		1.90	w		
1.81	w	1.82	m ⁺	1.82	vs
1.80	vw	1.80	w		
		1.79	w		
				1.76	vw
		1.70	w		
		1.69	w		
		1.68	w		
1.66	w	1.66	m ⁻		
		1.65	m ⁻		
		1.59	w ⁻		
1.52	vw			1.53	s
1.51	vw				
1.46	vw				

* CsCl gives a reflection at 2.92 Å, $I/I_1 = 100$. s = strong, sm = medium strong, m = medium, w = weak, vw = very weak, vvw = very very weak.

similar conclusion made previously by Kozhina *et al.* (13).

The measured powder patterns of RbNbCl_6 , CsNbCl_6 , and NaTaCl_6 could not be correlated

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TABLE 2. X-ray diffraction powder patterns for the compounds NaNbCl₆, NaTaCl₆, and RbTaCl₆

NaNbCl ₆		NaTaCl ₆		RbTaCl ₆	
$X_{\text{NbCl}_5} = 0.485$		$X_{\text{TaCl}_5} = 0.474$		$X_{\text{TaCl}_5} = 0.501$	
$X_{\text{NaCl}} = 0.515$		$X_{\text{NaCl}} = 0.526$		$X_{\text{RbCl}} = 0.499$	
d (Å)	Intensity	d (Å)	Intensity	d (Å)	Intensity
6.38	m	5.52	s	5.94	sm
5.55	s	5.24	s	5.18	sm
5.29	s	4.68	s	4.82	s
4.70	s	3.40	vw	4.67	sm
2.89	sm	3.32	w	3.79	m
2.82	sm	2.86	s	3.35	sm
2.34	m	2.80	s	3.03	vw
2.15	w	2.35	s	2.94	vw
2.10	w	2.19	vw	2.72	s
2.00	w	2.15	w	2.59	w
1.96	w	2.10	m	2.34	w
1.60	w	1.95	wm	2.10	s
1.26	w	1.89	wm	1.92	vw
		1.83	wm	1.79	sm
		1.78	wm	1.77	vw
		1.66	wm	1.57	vw
		1.60	wm	1.52	vw
		1.40	wm	1.51	vw
				1.48	vw
				1.44	vw

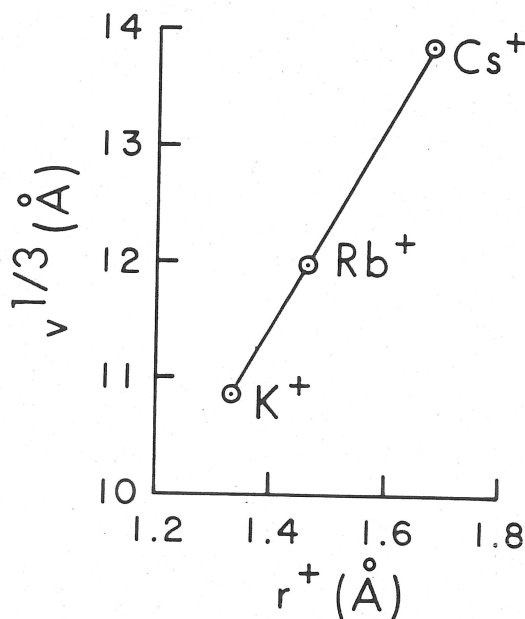
TABLE 3. Cell dimensions and crystal structures of alkali hexachloroniobate and hexachlorotantalate compounds

Compound	Structure	a (Å)	c (Å)
NaNbCl ₆	Tetragonal	11.20	10.57
KNbCl ₆	Cubic	9.80	—
KTaCl ₆	Hexagonal	11.62	10.97
RbTaCl ₆	Hexagonal	11.92	14.00
CsTaCl ₆	Hexagonal	12.60	19.52

without ambiguity to any of the structures considered. This is in contrast with claims by previous investigators that RbNbCl₆ and CsNbCl₆ are both tetragonal (18). However, these compounds are known to have more than one allotropic modification, and it is possible that the samples prepared herein had different crystal structures.

The measured X-ray powder patterns of KTaCl₆, RbTaCl₆, and CsTaCl₆ corresponded well with those generated by assuming each to possess a hexagonal crystal structure. Previously, Kozhina *et al.* (13) on the basis of their measurements suggested that KTaCl₆ was hexagonal. The cell dimensions were given as $a = 11.87$ Å and $c = 10.79$ Å and agree well with estimates of this work, which are, $a = 11.62$ Å and $c = 10.97$ Å. There are no structural data reported in the literature for either RbTaCl₆ or CsTaCl₆.

Figure 2 shows that the cube root of the volume of

FIG. 2. Variation of cell size with alkali-metal cation radius for the compounds KTaCl₆, RbTaCl₆, and CsTaCl₆.

the unit cell varies linearly with the radius of the alkali-metal cation, indicating that these three compounds are isostructural.

Cryoscopy

The approximate melting points and temperatures of the solid transformations were found by cryoscopy. Each sample weighed approximately 20 g and was contained in an evacuated fused quartz ampoule. The ampoule contained a glass well which allowed a thermocouple to be placed at the heart of the salt sample. For immersion into a vertical tube furnace the ampoule was contained in a grounded metal sheath which served to prevent induction of spurious voltages in the thermocouple by the ac field of the furnace windings. Furnace temperature was controlled by a variable autotransformer. To maintain a fixed cooling rate an electric motor drove down the variable autotransformer through a variable-ratio gear reductor. Each sample was cooled several times at different rates ranging from 0.5 K/min to 2.5 K/min to obtain data which were free from the effects of undercooling. The thermocouple, 22 gauge, Chromel-P vs. Alumel, ASTM type K, was certified by the Hoskins Manufacturing Co., Detroit, MI, U.S.A., and was checked in this laboratory against a platinum-13% rhodium vs. platinum standard, manufactured by Egelhard Industries, Carteret, NJ, U.S.A.

The output from the thermocouple was recorded on a multirange chart recorder, Honeywell ElectroniK 193, after compensation by a Sargent zero

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TABLE 4. Phase transformations of the alkali-metal hexachloroniobates and hexachlorotantalates

Compound	Melting point (°C)	Eutectic* (°C)	Solid-solid transformations (°C)	Reference
NaNbCl ₆	444(i)		299, 245	This work
	430(i)		247	19
	450(i)		256	9
	468(i)		259	12
				11
NaTaCl ₆	484(i)		225	This work
	470(i)		223	20
	470(i)		232	10
				11
KNbCl ₆	400	370	299	This work
	400	378		11
	396	376	334	12
	396	366	321, 160	19
	394	368		23
	365		156	21
KTaCl ₆	401	373	311, 138	This work
	410	370	312, 160	20
	420			11
			305	This work
RbNbCl ₆	380(i)			11
RbTaCl ₆	417		313, 261	This work
	416	382		11
CsNbCl ₆	535		290	This work
	528	434		11
	528	444	300	21
CsTaCl ₆	540		296	This work
	548	442	294	22
	555	446		11

NOTE: (i) denotes that the compound melts incongruently.
*The eutectic temperature is that of the ACI-AMCl₆ subsystem.

displacement recorder accessory. The results are summarized in Table 4. The most striking feature is that all the AMCl₆ compounds proved to be polymorphic in the solid state.

The results of this work for NaNbCl₆ and NaTaCl₆ agree well with the findings of Palkin and Chikanov (19). Attempts were made to measure the melting points of the incongruently melting compounds. However, the dissociation vapour pressures are so high at this temperature that the fused quartz cells explode. Aside from the well defined solid-solid transformation at 245°C, which occurs with an estimated large enthalpy of transition, NaNbCl₆ showed signs of a solid-solid transformation at 299°C, which has not been reported in the literature. It occurs with an estimated very small enthalpy of transition.

KNbCl₆ is the most thoroughly studied of all the AMCl₆ compounds. Investigators seem to agree that it melts at approximately 395–400°C and that the KNbCl₆-KCl eutectic temperature is in the vicinity of 370°C. The solid-solid transformation temperatures vary greatly. Palkin and Chikanov (19) claim two transformations, one at 321°C and another at

160°C, the latter occurring with a large enthalpy of transition. In this investigation, none of the samples of KNbCl₆ or KNbCl₆-KCl showed any evidence of the latter. Indeed, the transformation reported herein to occur at 299°C is elusive and was observed only in samples whose composition was almost pure KNbCl₆.

The results for KTaCl₆ agree well with those of Palkin and Chikanov (20) for the KTaCl₆-KCl eutectic temperature and the temperature of the $\alpha \rightarrow \beta$ transformation. The latter occurs with an estimated small enthalpy change. Although this study quotes the temperature of the $\beta \rightarrow \gamma$ transformation to be 138°C in contrast to 160°C reported by Palkin and Chikanov (20), both studies estimate the enthalpy change which accompanies this transition to be extremely large. The melting point of KTaCl₆, determined herein as 401°C, was a rather elusive quantity to measure because the liquidus from pure KTaCl₆ to the KTaCl₆-KCl eutectic at 48 m/o TaCl₅ is very steep, varying 40–50 K in a composition range of 2 m/o.

Only Huber *et al.* (11) have studied the phase

changes of RbNbCl_6 and RbTaCl_6 . RbNbCl_6 reportedly melts incongruently at 360°C . In this study the liquidus was identified at 380°C ; however, there was no thermal arrest at 360°C . The $\alpha \rightarrow \beta$ transformation, which occurs at 305°C with an estimated large enthalpy change, has been discovered in this investigation. Huber *et al.* and this study report effectively identical values for the melting point of RbTaCl_6 . It appears that this study is the first to discover the $\alpha \rightarrow \beta$ transformation of RbTaCl_6 . This occurs at 313°C with an estimated large enthalpy change. The cooling curves suggested that there may be still another phase change occurring at 261°C with an estimated small enthalpy change.

The melting point of CsNbCl_6 was measured herein to be 535°C , in good agreement with previous estimates (11, 21). The $\alpha \rightarrow \beta$ transition at 290°C with a large enthalpy change has been identified. Morozov in his book (21) reports the existence of a solid-solid transformation at 300°C . Unfortunately, there is no reference to the original study. The measured melting point and temperature of the solid-solid transformation of CsTaCl_6 agree well with those determined by Morozov and Simonich (22).

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1. S. N. FLENGAS. *Ann. N.Y. Acad. Sci.* **79**, 853 (1960).
2. R. L. LISTER and S. N. FLENGAS. *Can. J. Chem.* **41**, 1548 (1963).
3. R. L. LISTER and S. N. FLENGAS. *Can. J. Chem.* **42**, 1102 (1964).

4. W. SCHELLER and J. RENARD. German patent no. 1136681, September 20, 1962; *Chem. Abstr.* **58**, 3127 (1963).
5. F. J. KENESHEA, D. CUBICCIOTTI, G. WITHERS, and H. EDING. *J. Phys. Chem.* **72**, 1272 (1968).
6. D. BROWN. *Inorg. Synth.* **9**, 88 (1967).
7. D. R. SADOWAY and S. N. FLENGAS. *Can. J. Chem.* **54**, 1692 (1976).
8. K. W. BAGNALL and D. BROWN. *J. Chem. Soc.* 581 (1964).
9. I. S. MOROZOV and B. G. KORSHUNOV. *Zh. Neorg. Khim.* **1**, 145 (1956); *Engl. trans.: Russ. J. Inorg. Chem.* **1**(1), 150 (1956).
10. I. S. MOROZOV, B. G. KORSHUNOV, and A. T. SIMONICH. *Zh. Neorg. Khim.* **1**, 1646 (1956); *Engl. trans.: Russ. J. Inorg. Chem.* **1**(7), 203 (1956).
11. K. HUBER, E. JOST, E. NEUENSCHWANDER, M. STUDER, and B. ROTH. *Helv. Chim. Acta*, **41**, 2411 (1958).
12. A. P. PALKIN and N. D. CHIKANOV. *Zh. Neorg. Khim.* **4**, 898 (1959); *Engl. trans.: Russ. J. Inorg. Chem.* **4**, 407 (1959).
13. I. I. KOZHINA, V. P. KUSTOVSKAYA, I. V. VASIL'KOVA, and M. P. SUSAREV. *Vestn. Leningr. Univ. Fiz., Khim.* **23**(16), 113 (1968).
14. S. M. HORNER, R. J. H. CLARK, B. CROCIANI, D. B. COPLEY, W. W. HORNER, F. N. COLLIER, and S. Y. TYREE, JR. *Inorg. Chem.* **7**, 1859 (1968).
15. CIBA, Ltd. British patent no. 876802, September 6, 1961; *Chem. Abstr.* **56**, 11224 (1961).
16. R. M. DOUGLASS and E. STARITZKY. *Anal. Chem.* **29**, 315 (1957).
17. R. F. ROLSTEN. ADI 5487, Library of Congress, Washington, DC, U.S.A.
18. E. K. SMIRNOVA and V. M. TSINTSIUS. *Zh. Neorg. Khim.* **16**, 566 (1971); *Engl. trans.: Russ. J. Inorg. Chem.* **16**, 303 (1971).
19. A. P. PALKIN and N. D. CHIKANOV. *Zh. Neorg. Khim.* **7**, 1370 (1962); *Engl. trans.: Russ. J. Inorg. Chem.* **7**, 705 (1962).
20. A. P. PALKIN and N. D. CHIKANOV. *Zh. Neorg. Khim.* **7**, 2388 (1962); *Engl. trans.: Russ. J. Inorg. Chem.* **7**, 1239 (1962).
21. I. S. MOROZOV. *Primenenie Khloro V Metallurgii Redkikh i Tsvetnykh Metallov*, Nauka, Moscow, 1966, p. 222.
22. I. S. MOROZOV and A. T. SIMONICH. *Zh. Neorg. Khim.* **2**, 1907 (1957); *Engl. trans.: Russ. J. Inorg. Chem.* **2**(8), 311 (1957).
23. O. R. GAVRILOV and L. A. NISEL'SON. *Zh. Neorg. Khim.* **11**, 209 (1966); *Engl. trans.: Russ. J. Inorg. Chem.* **11**, 114 (1966).

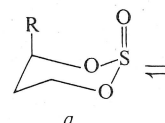
Trimethylene sulfite on ring

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For over 15 years trimethylene sulfite has been an interesting problem. The literature includes studies (1-3), ultrasonic spectroscopy (1, 6-11), electron diffraction (1-3), and X-ray diffraction (6-11). The predominant question has been: trimethylene sulfite is a substituted cyclohexane being ca. 2.1 kcal/mole more stable than the exocyclic oxygen atom. The question is: as to whether the ring does it ring invert is a twist conform



On the basis of (6-11, 19), and ¹H NMR that twist forms are possible. The possibility of *syn*- and *anti*- forms and a single CH_3 substituent these interpretations of Pihlaja and co-workers. These considerations are based on from twist forms of CH_3 and an axial