

Crystal Structure of Tl_2CrO_4

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Single crystals of Tl_2CrO_4 have been prepared by diffusion controlled slow growth in silica-gel medium. The crystal structure has been determined by a three-dimensional X-ray diffraction study. The crystals are orthorhombic, space group $Pm\bar{c}n$, with $a = 5.910$, $b = 10.727$, and $c = 7.910$ Å. The structure is isomorphous with K_2CrO_4 , Rb_2CrO_4 , and Cs_2CrO_4 .

Introduction

Structural data for thallos chromate has been sought in relation to interpreting its vibrational spectra. The isomorphous chromates, K_2CrO_4 , Rb_2CrO_4 , and Cs_2CrO_4 , show a regular progression of Raman frequencies which may be correlated with cation-chromium separations in the crystals (1). If thallos chromate is assumed to be isomorphous, it might be expected that the Raman frequencies of this compound would fit the trends established in the isomorphous alkali-metal chromates. However, thallos chromate displays much lower frequencies than might be predicted on the basis of reasonable estimates of thallium-chromium distances in an isomorphous structure (2, 3). The present study has been undertaken to determine if structural peculiarities are present which might account for the unique vibrational spectra of thallos chromate.

Although early crystallographic studies of thallos chromate (4) suggested a lack of isomorphism with potassium chromate, powder pattern X-ray data (5) show strong similarities with data obtained for thallos sulfate, which is isomorphous with potassium chromate. Single-crystal X-ray study of thallos chromate has been hampered previously by the powdered form in which the salt is customarily obtained and by the apparent lack of a naturally occurring mineral of the same chemical composition. We have succeeded in growing single crystals of thallos chromate, thereby enabling the present X-ray study of its structure.

Experimental Methods

Single crystals of thallos chromate were obtained by a technique of diffusion-controlled slow growth in silica-gel medium (6, 7). A solution was prepared by mixing 3.24 g of anhydrous sodium chromate, 100 ml of 0.5 *M* acetic acid, and 100 ml of a sodium silicate solution having a specific gravity of 1.06 g/ml. Thirty-milliliter aliquots of this solution were transferred rapidly to a series of 25×200 -mm test tubes, where gelling took place. A 30-ml aliquot of 0.2 *M* thallos nitrate solution was added to each test tube. The test tubes were stoppered and stored in an upright position at room temperature. Yellow needle crystals of thallos chromate developed in the gel within 1 month. Crystals were obtained by breaking the tube, removing the gel plug containing the crystals, and hand picking the desired specimens. Crystals produced in this manner displayed a similar morphology to that of potassium chromate. They were orthorhombic prisms of the form $\{011\}$, with elongation parallel to the crystallographic *a* axis. The crystals were soft and easily fractured, but pronounced cleavages were not observed.

A single crystal with dimensions $0.2 \times 0.06 \times 0.005$ mm was mounted along its long dimension (*a* axis) and used for all X-ray work. Cell dimensions and three-dimensional intensities were measured with a Picker full-circle diffractometer, using Zr-filtered $\text{MoK}\alpha$ radiation ($\lambda = 0.710688$ Å) and a pulse-height analyzer adjusted to cut off 10% of the diffracted intensity. Cell dimensions were calculated from measurements of 2θ for

selected reflections. Intensities were measured by θ - 2θ scans over a range of $\pm 1^\circ$ at a scan rate of $2^\circ/\text{min}$. A total of 186 nonzero independent reflections were converted to structure factors after correction for absorption by the method of Templeton and coworkers (8). This method involves plotting the intensity of a reflection at $\chi = 90^\circ$ as a function of ϕ and is applicable to thin crystals. All calculations were performed with a CDC-3600 computer from a remote time-sharing console. A local version of the least-squares program of Gantzel, Sparks, and Trueblood was used.

Cell Dimensions

The orthorhombic unit cell has the following dimensions:

$$\begin{aligned} a &= 5.910 \pm 0.004 \text{ \AA} \\ b &= 10.727 \pm 0.006 \text{ \AA} \\ c &= 7.910 \pm 0.004 \text{ \AA} \end{aligned}$$

These values are only in fair agreement with the powder work of Abbad and Rivoir (5), who found $a = 5.91$, $b = 10.68$, and $c = 7.80 \text{ \AA}$. The calculated density is 6.96 g/cm^3 . The probable space group from systematic absences is $D_{2h}^{16} - Pmcn$. This choice is confirmed by the successful refinement of the structure. The general positions are $\pm(x, y, z; \frac{1}{2} - x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z)$.

Structure Determination

The Tl^+ ions and Cr atoms were assigned coordinates based on the K_2CrO_4 structure (9). Refinement of the heavy atoms by full-matrix least-squares calculation with anisotropic thermal parameters resulted in an R factor of 0.10. A difference Fourier map was calculated with phases from the Tl and Cr parameters. The three highest peaks on this map were then included as oxygen in the least squares calculation to complete the trial structure. Atomic scattering factors

TABLE I
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL	H	K	L	OBS	CAL
0	0	4	224	223	1	1	0	74	84	2	1	6	104	101	3	4	4	50	67
0	0	6	284	285	1	1	2	329	338	2	2	1	183	169	3	5	0	111	101
0	1	2	156	141	1	1	3	56	57	2	2	2	259	293	3	5	2	98	94
0	1	3	305	292	1	1	4	219	206	2	2	4	144	150	3	5	5	131	140
0	1	4	51	45	1	1	5	148	143	2	2	5	146	155	3	6	1	147	151
0	1	6	89	85	1	1	6	71	77	2	2	7	72	83	3	6	2	138	136
0	1	8	76	79	1	1	7	137	131	2	3	1	182	176	3	6	3	129	143
0	2	1	128	108	1	1	8	123	131	2	3	2	176	195	3	6	4	124	128
0	2	2	289	319	1	2	1	228	217	2	3	3	130	131	3	6	5	97	93
0	2	4	175	178	1	2	2	184	141	2	3	4	208	233	3	7	0	160	142
0	2	5	186	179	1	2	3	48	58	2	3	5	114	118	3	7	1	56	54
0	2	8	122	112	1	2	4	73	60	2	4	1	103	106	3	8	1	141	139
0	3	1	181	184	1	2	5	143	145	2	4	2	147	143	3	9	2	161	179
0	3	2	175	211	1	2	6	94	78	2	4	3	52	63	4	0	0	461	440
0	3	3	187	196	1	2	7	109	120	2	4	4	89	82	4	0	4	132	133
0	3	4	246	246	1	3	0	496	505	2	4	5	93	89	4	0	6	204	190
0	3	5	101	95	1	3	4	102	104	2	4	7	139	140	4	1	2	102	90
0	4	0	94	96	1	3	6	186	214	2	5	1	224	253	4	1	3	190	170
0	4	1	166	168	1	4	1	153	149	2	5	2	92	85	4	2	1	68	73
0	4	2	220	210	1	4	2	117	105	2	5	4	75	68	4	2	2	164	195
0	4	4	67	75	1	4	3	287	329	2	5	5	182	191	4	2	5	135	124
0	4	5	97	92	1	4	4	78	72	2	5	7	126	133	4	3	1	109	109
0	4	7	176	157	1	4	5	101	109	2	6	0	251	250	4	3	2	108	136
0	4	8	70	82	1	5	0	110	109	2	6	2	153	176	4	3	4	160	169
0	5	1	275	288	1	5	2	108	102	2	6	6	79	76	4	4	1	80	92
0	5	2	143	125	1	5	5	167	168	2	7	2	56	56	4	4	2	115	128
0	5	4	125	110	1	6	1	195	189	2	7	3	255	251	4	5	1	170	182
0	5	5	213	212	1	6	2	187	169	2	8	0	209	213	4	5	2	99	79
0	5	7	137	145	1	6	3	180	182	2	8	1	61	65	4	5	4	58	74
0	6	0	234	236	1	6	4	129	155	2	9	1	78	69	4	5	5	140	141
0	6	2	156	161	1	6	5	132	111	2	9	2	112	122	4	6	0	170	165
0	6	6	76	82	1	6	6	79	60	2	10	0	169	183	4	6	2	98	118
0	7	2	66	68	1	6	7	123	122	3	0	4	219	220	4	7	1	78	71
0	7	3	269	256	1	7	0	184	172	3	1	0	70	69	4	7	3	186	172
0	7	4	92	97	1	7	6	71	93	3	1	2	262	248	4	8	0	162	157
0	7	5	88	97	1	8	2	61	59	3	1	4	175	164	5	0	2	91	106
0	8	0	242	225	1	8	5	137	130	3	1	5	115	118	5	0	4	135	147
0	8	1	136	104	1	9	2	195	207	3	1	6	67	68	5	1	2	166	174
0	8	5	126	114	1	9	4	89	106	3	1	7	118	113	5	1	5	94	88
0	8	6	105	98	1	10	3	101	106	3	2	1	172	162	5	2	1	95	111
0	9	2	142	144	1	11	0	231	191	3	2	5	113	111	5	3	0	268	262
0	9	3	94	77	2	0	0	624	585	3	3	0	374	381	5	6	1	91	98
0	9	4	101	110	2	0	2	72	67	3	3	4	70	82	5	6	2	103	102
0	10	0	202	178	2	0	4	186	170	3	3	6	147	175	5	7	0	117	97
0	10	1	58	51	2	0	6	263	253	3	4	1	109	107	6	0	0	261	255
1	0	2	222	201	2	1	2	168	154	3	4	2	84	89					
1	0	4	262	259	2	1	3	242	222	3	4	3	226	264					

TABLE II
ATOMIC COORDINATES^a

Atom	x	y	z
Tl(1)	0.25	0.0840(5)	0.3277(8)
Tl(2)	0.25	0.7050(4)	0.5098(7)
Cr	0.25	0.075(2)	0.776(2)
O(1)	0.25	0.082(6)	0.986(11)
O(2)	0.25	0.577(7)	0.215(10)
O(3)	0.019(9)	0.150(5)	0.706(6)

^a Standard deviations are given in parentheses as deviations in the last significant figures.

for Tl^+ and neutral Cr and O were taken from the International Tables for X-ray Crystallography (10). A correction for anomalous dispersion of thallium was included in the calculations. Isotropic thermal parameters were held fixed at 2.5 \AA^2 for oxygen. In the final refinement the function minimized was $\sum w(F_o - F_c)$, with the weight $w = 1/\sigma^2$, where σ is the estimated standard deviation of F_o . The refinement rapidly converged to a conventional R factor of 0.07 for the 186 observed reflections. Table I lists the final values of observed and calculated structure amplitudes, Tables II and III list the final parameters, and Table IV lists interatomic distances and angles. The standard deviations listed are calculated from the least-squares results and assume random errors in the observed intensities. Since systematic errors due to the approximate nature of the absorption correction and the lack of correction for extinction are likely, these deviations should be considered lower limits to the possible error.

Discussion

Thallos chromate is isomorphous with the alkali-metal chromates, K_2CrO_4 , Rb_2CrO_4 , and

TABLE III

ANISOTROPIC THERMAL PARAMETERS^a IN THE FORM
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(1)	0.012(2)	0.0043(6)	0.0077(10)	0	0	-0.003(2)
Tl(2)	0.016(2)	0.0035(5)	0.0058(10)	0	0	0.000(1)
Cr	0.001(6)	0.001(2)	0.003(4)	0	0	0.000(5)

^a Standard deviations are given in parentheses as deviations in the last significant figures.

TABLE IV
INTERATOMIC DISTANCES AND ANGLES^a

Atoms	Distance (\AA)	Atoms	Angle ($^\circ$)
Cr-O(1)	1.66	O(1)-Cr-O(2)	108.7
Cr-O(2)	1.71	O(1)-Cr-O(3)	108.0
Cr-O(3)	1.67	O(2)-Cr-O(3)	111.5
		O(3)-Cr-O(3)	108.9
Cr-Tl(1)	3.54		
Cr-Tl(1)'	3.67		
Cr-Tl(1)''	3.51		
Cr-Tl(2)	3.53		
Cr-Tl(2)'	3.68		

^a Standard deviations are approximately 0.08 \AA for distances involving oxygen and 0.02 \AA for all other distances.

Cs_2CrO_4 . It is not isomorphous with Ag_2CrO_4 (13), although the cell dimensions are similar and the space group is the same. Figure 1 shows the (100) projection of the structure, and Table V gives a comparison of distances in the isomorphous alkali-metal chromates with comparable distances in Tl_2CrO_4 . The average Cr-O distance of 1.68 \AA found for Tl_2CrO_4 (cf. Table IV) agrees within experimental error with the value of 1.66 \AA found in recent studies of $(\text{NH}_4)_2\text{CrO}_4$ (14, 15). The average O-Cr-O angle is 109.3° , approximately the tetrahedral angle.

Nonetheless some minor variations between the Tl_2CrO_4 structure and those of the alkali-metal chromates are seen. For example, the accepted order of ionic radii is $\text{K}^+ < \text{Rb}^+ < \text{Tl}^+ < \text{Cs}^+$, and it might be expected that the chromium-cation distances in isomorphous chromates would follow this trend. This is observed, for the most

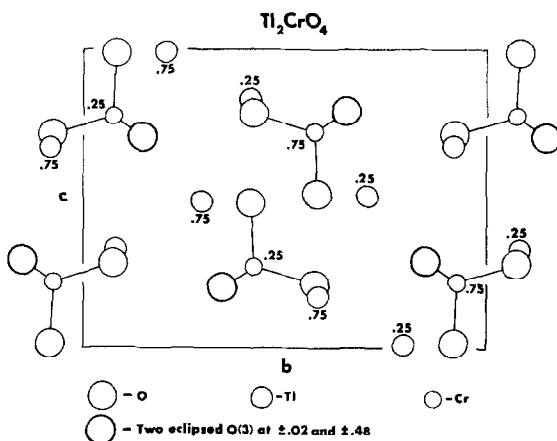


FIG. 1. Projection of the Tl_2CrO_4 structure on (100).

TABLE V

EQUIVALENT CHROMIUM-CATION DISTANCES IN THE ISOMORPHOUS CHROMATES

	K ₂ CrO ₄ ^a (Å)	Rb ₂ CrO ₄ ^b (Å)	Cs ₂ CrO ₄ ^c (Å)	Tl ₂ CrO ₄ ^d (Å)
Cr-M(1)	3.15	3.33	3.51	3.54
	3.53	3.60	3.78	3.68
	3.56	3.69	3.66	3.51
Av	3.41	3.54	3.65	3.58
Cr-M(2)	3.38	3.72	3.91	3.53
	3.63	3.88	3.92	3.68
	3.50	3.80	3.92	3.61

^a Calculated from the data of Zachariassen and Ziegler (9).

^b Calculated from the data of Smith and Colby (11).

^c Calculated from the data of Miller (12).

^d This work.

part, in the alkali-metal chromates. However, the Tl-Cr distances do not agree with this trend. The Cr-Tl(1) distances are both shorter and longer than expected, while the Cr-Tl(2) distances are significantly shorter than expected. While these differences may contribute to the unique vibrational spectra of Tl₂CrO₄ compared to those of the isomorphous alkali-metal chromates, a simple quantitative correlation is not evident. It appears that other factors, such as electronegativity of the cation, significantly contribute to the unique physical and spectral properties of this compound.

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References

1. R. L. CARTER AND C. E. BRICKER, *Spectrochim. Acta* **27A**, 569 (1971).
2. R. L. CARTER, dissertation, Univ. of Kansas, 1970. *Diss. Abst. Int.* **31B**, 6474 (1971). University Microfilms Order No. 13,284, 207 pages.
3. R. L. CARTER AND C. E. BRICKER, unpublished data.
4. J. W. RETGERS, *Z. Phys. Chem.* **8**, 6 (1891) (cf. p. 39 ff.).
5. M. ABBAD AND L. RIVOIR, *An. Soc. Espan. Fis. Quim.* **43**, 831 (1943).
6. H. N. HOLMES, *J. Phys. Chem.* **21**, 709 (1917).
7. C. L. STRONG, *Sci. Amer.* **206**, 155 (1962).
8. L. K. TEMPLETON, D. H. TEMPLETON, AND A. ZALKIN, *Acta Crystallogr.* **17**, 933 (1964).
9. W. H. ZACHARIASEN AND G. E. ZIEGLER, *Z. Kristallogr.* **80**, 164 (1931).
10. "International Tables for X-ray Crystallography," Vol. 3, p. 202. Kynoch Press, Birmingham, England, 1962.
11. H. W. SMITH, JR., AND M. Y. COLBY, *Z. Kristallogr.* **103A**, 90 (1940).
12. J. J. MILLER, *Z. Kristallogr.* **99A**, 32 (1938).
13. M. L. HACKERT AND R. A. JACOBSON, *J. Solid State Chem.* **3**, 364 (1971).
14. J. S. STEPHENS AND D. W. J. CRUICKSHANK, *Acta Crystallogr.* **B20**, 437 (1970).
15. B. M. GATEHOUSE AND P. LEVERETT, *J. Chem. Soc., A* **1969**, 1857.