JOURNAL OF SOLID STATE CHEMISTRY 3, 364–368 (1971)

The Crystal Structure of Silver Chromate

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Received November 13, 1970

Single crystals of silver chromate were prepared by slow diffusion of potassium chromate and silver nitrate solutions in a gel-filled U-tube. The thin tabular crystals belong to the orthorhombic space group *Pnma* with $a = 10.063(11)$, $b = 7.029(4)$, $c = 5.540(2)$ Å, and $Z = 4$. Intensity data were measured with a $\theta - 2\theta$ step-scan technique using an automated diffractometer and MoK_α radiation. The structure was solved by heavy atom methods and refined by full matrix least-squares techniques with anisotropic thermal parameters used only for the heavy atoms to a final residual of $R = 0.064$ for the 325 observed reflections used in the analysis. The silver atoms are coordinated to the oxygen atoms of the chromate to generate an interlocking network that propagates throughout the crystal. The two crystallographically independent silver atoms have coordinations best described as tetragonal bipyramidal and distorted tetrahedral, respectively. The shortest Ag–O distance is 2.34 Å. The silver–oxygen interactions perturb the tetrahedron of the chromate group with Cr–O distances of 1.69, 1.67, and 1.63(1) Å and angles varying from 106.1 to 111.6(8)°. The metal atom coordination in silver chromate is compared to that of potassium chromate.

Introduction

During recent studies on alternate methods of growing single crystals, we were successful in growing single crystals of silver chromate. Examination of these crystals by X-ray film techniques revealed the possible orthorhombic space group *Pnma*. Potassium chromate is also known to crystallize in space group *Pnma* (*1*) in a cell of similar dimensions (matching similar unit cell dimensions the equivalent potassium chromate space group would be *Pmcn*). Although the ionic radii of potassium and silver are similar (1.33 vs 1.26) (*2*), these compounds exhibit marked differences in properties, such as solubility. Therefore, we felt it would be of interest to proceed with the crystal structure analysis of silver chromate in order to compare the structures of the two compounds.

Experimental

Crystal Data:

Ag_2CrO_4, $M = 331.73$. Orthorhombic *Pnma*, $F(000) = 600\ e$,

$a = 10.063(11)$, $b = 7.029(4)$, and $c = 5.540(2)$ Å at $T \approx 24$°C,

$Z = 4$, $V = 391.9$ Å^3, $D_c = 5.62$ g/cm^3, $D_m = 5.62$ g/cm^3

MoK_α ($\lambda = 0.7107$ Å), $\mu = 123$ cm^{-1}.

Thin tabular single crystals of silver chromate were prepared by slow diffusion of potassium chromate and silver nitrate solutions (0.5 *M*) in a U-tube filled with gel. Precession and Weissenberg photographs exhibited *mmm* Laue symmetry with the following systematic absences: $0kl$ when $k + l = 2n + 1$ and $hk0$ when $h = 2n + 1$. These extinctions are consistent with either space group $Pn2_1a$ or *Pnma*. The unit cell parameters and their standard deviations were obtained by a least-squares fit to 13 independent high-order reflection angles whose centers were determined by left-right, top-bottom beam-splitting techniques on a previously aligned Hilger–Watts four-circle automated diffractometer (MoK_α, $\lambda = 0.71069$ Å). The observed density was taken from the literature (*3*).

A crystal of approximate dimensions $0.006 \times 0.100 \times 0.118$ mm was mounted on a glass fiber with the *b* axis (0.118 mm) nearly parallel to the ϕ axis and was used for data collection. Data were

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* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2774.

taken at room temperature utilizing a fully automated Hilger–Watts four-circle diffractometer equipped with scintillation counter. MoK_α ($\lambda = 0.7107$ Å) radiation was used with balanced (Zr–Y) filters to obtain intensity and individual background readings. The θ–2θ step-scan technique with a 4.5° take-off angle was used to record 1056 independent reflections within a 2θ sphere of 70° ($\sin\theta/\lambda = 0.807$ Å^{-1}). A counting rate of 0.2048 sec/step of 0.01° in θ was employed with a variable scan range of 50 steps plus 2/degθ. The rest of the experimental arrangement has already been discussed in some detail (*4*). As a general check on electronic and crystal stability, the intensities of three standard reflections were measured periodically during the data collection. Comparison of these values indicated that no decomposition had occurred.

The intensity data were also corrected for Lorentz-polarization effects and for effects due to absorption ($\mu = 123$ cm^{-1}). The absorption correction was made using the program of Wehe, Busing, and Levy (*5*); the maximum and minimum transmission factors were 0.927 and 0.494, respectively. The estimated error in each intensity measurement was calculated by

$$[\sigma(I)]^2 = [C_T + C_B + (0.05C_T)^2 + (0.10C_B)^2 + (0.05C_R)^2]/A^2,$$

where C_T, C_B, C_R, and A are the total count, background count, net count, and transmission factor, respectively. The estimated standard deviation of each structure factor was calculated from the estimated errors in the intensity by the method of finite differences (*6*). Based on the measurement of symmetry extinct reflections, it was decided that only those reflections for which $I \geqslant 3\sigma(I)$ would be considered observed. The results reported below are based on the 325 remaining observed reflections. A very low percentage of observed reflections were obtained at the high 2θ limit.

Solution and Refinement

The positions of all heavy atoms were readily determined from a three-dimensional Patterson function. These positional parameters along with the assigned variable isotropic thermal parameters, were refined two cycles in the centric space group *Pnma* by a full matrix least-squares procedure minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$. Examination of the resulting electron density map revealed the oxygen positions with the chromate group lying on a mirror plane as required by the centric space group *Pnma*. Isotropic refinement of 18 scale, positional, and thermal parameters converged to a conventional R factor ($R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.082 and to a weighted R-factor

$$R_\omega = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2)^{1/2}$$

of 0.090. A difference electron-density map revealed anisotropic motion of the heavy atoms. Additional refinement using anisotropic thermal parameters for the heavy atoms converged to a discrepancy factor of $R = 0.064$ and a weighted discrepancy factor $R_\omega = 0.073$. The largest shift during the last cycle was less than 0.002 times its own standard deviation. A final electron-density difference map showed no peak heights greater than 0.6 e/Å^3.

The relativistic Hartree-Fock X-ray scattering factors for neutral atoms of Doyle and Turner (*7*) were used, with those of silver and chromium including the real and imaginary parts of anomalous dispersion (*8*). Based on the agreement of the large structure factors no extinction correction was necessary. Anisotropic refinement of the oxygen positions lowered the value of R less than 0.002 with no appreciable shifts in the other parameters. Refinement in the acentric space group produced no significant improvement in either the R factor or standard deviations.

The final positional and thermal parameters and their estimated standard deviations as derived from the inverse matrix of the final least-squares cycle are given in Table I. The final values of the observed

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR SILVER CHROMATE[a]

Atom	x	y	z	β_{11}[b] or B
Ag(1)	0.5[c]	0.5[c]	0.5[c]	50(2)
Ag(2)	0.1340(2)	0.25[c]	0.5033(7)	81(2)
Cr	0.3161(3)	0.25[c]	−0.0161(12)	22(2)
O(1)	0.1506(19)	0.25[c]	−0.0677(34)	1.9(4)
O(2)	0.3502(19)	0.25[c]	0.2789(37)	1.8(4)
O(3)	0.3845(14)	0.9353(23)	−0.1417(26)	2.1(2)

Atom	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	111(4)	154(5)	0[c]	1(7)	0[c]
Ag(2)	128(5)	167(7)	0[c]	30(7)	0[c]
Cr	81(7)	77(12)	0[c]	19(7)	0[c]

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the last significant digits.

[b] β's × 10^4, the β_{ij} are defined by: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

[c] Atomic parameter fixed by symmetry.

TABLE II

Observed and Calculated Structure Factors (×10) for Silver Chromate

H = 0

K	L	FO	FC
0	2	3238	3460
0	4	2092	2081
0	6	1234	1225
0	8	595	668
1	3	552	-571
1	7	220	-219
2	0	965	-948
2	2	641	-630
2	4	580	-553
3	1	289	-281
3	3	349	312
3	5	342	326
4	0	2919	2972
4	2	2274	2280
4	4	1638	1626
4	6	912	901
4	8	537	506
5	1	163	-139
5	3	224	-332
6	0	568	-591
6	2	205	-237
6	4	195	-163
8	0	1046	1032
8	2	975	936
8	4	824	784
8	6	411	427

H = 1

K	L	FO	FC
0	1	142	132
0	2	596	561
0	3	386	340
0	5	204	142
1	1	254	-194
1	2	178	150
1	3	307	-275
1	5	237	-260
2	1	2414	2416
2	3	2073	2044
2	5	1149	1152
2	7	622	651
3	1	374	362
3	2	210	172
4	1	235	247
4	2	173	151
5	2	179	134
6	1	1248	1222
6	2	197	-161
6	3	923	930
6	5	656	652
6	7	418	449
10	1	397	425
10	3	333	351

H = 2

K	L	FO	FC
0	0	767	800
0	2	831	752
0	3	163	-172
0	4	415	442
0	6	307	317
1	0	750	759
1	2	1178	1115
1	3	254	240
1	4	480	477
1	6	255	233
2	0	1931	2304
2	1	530	-481
2	2	1833	1735
2	4	1169	1132
2	6	659	640
2	8	301	351
3	0	1016	-1065
3	2	844	-777
3	3	189	-209
3	4	223	-213
3	6	287	-260
4	0	449	475
4	1	174	167
4	2	540	500
4	4	356	338
4	6	258	236
5	2	510	569
5	4	329	325
6	0	861	1004
6	2	943	862
6	4	646	653
6	6	377	394
7	0	292	-300
7	2	323	-319
8	2	255	205
10	2	314	327

H = 3

K	L	FO	FC
0	1	3045	3260
0	2	344	303
0	3	2297	2240
0	5	1386	1367
0	7	865	881
1	1	903	-889
1	2	157	-192
1	3	788	-760
1	5	489	-462
1	6	208	-217
2	2	199	162
2	3	394	-349
3	1	898	916
3	3	410	436
3	5	314	369
3	6	282	237
3	7	239	245
4	1	2006	1997
4	3	1699	1653
4	5	1052	1046
4	7	655	670
5	1	495	-440
5	3	557	-488
5	5	360	-309
7	1	257	341
7	3	244	248
8	1	770	790
8	3	760	757
8	5	504	515
9	1	259	-207

H = 4

K	L	FO	FC
0	0	748	-706
0	1	181	-195
1	0	323	369
1	3	269	236
1	4	290	282
2	0	2283	2459
2	2	2077	2051
2	4	1539	1507
2	6	758	758
2	8	325	429
3	0	448	-392
3	1	230	241
3	2	209	-167
3	4	218	-206
5	3	179	152
6	0	1303	1348
6	2	1026	1003
6	6	497	499
10	0	401	458
10	2	349	362

H = 5

K	L	FO	FC
0	1	1297	1324
0	2	252	-240
0	3	725	706
0	5	522	529
0	7	342	371
1	1	425	477
1	3	401	408
1	4	194	205
1	5	335	357
1	6	203	197
2	1	1129	1170
2	3	764	707
2	5	522	495
2	7	369	327
3	1	492	-479
3	2	185	-268
3	3	301	-253
3	5	333	-290
4	1	762	766
4	3	627	620
4	5	420	416
4	7	273	247
5	1	250	251
6	1	506	523
6	3	523	521
6	5	352	337
7	1	246	-180
8	1	296	274
8	3	306	302

H = 6

K	L	FO	FC
0	0	1931	1955
0	2	1564	1566
0	4	1174	1163
0	6	678	618
0	8	372	357
1	0	1110	-1101
1	2	1136	-1152
1	3	273	-282
1	4	703	-716
1	6	431	-403
2	1	247	253
2	2	248	264
2	4	203	162
3	0	1077	1160
3	2	867	914
3	3	275	265
3	4	462	492
3	6	361	399
4	0	1411	1409
4	2	1105	1110
4	4	848	850
4	6	475	501
5	0	643	-594
5	2	730	-703
5	4	549	-500
5	6	316	-266
7	0	397	479
7	2	382	449
8	0	610	641
8	2	504	507
8	4	379	407
9	0	346	-301

H = 7

K	L	FO	FC
0	1	316	356
0	3	279	253
1	1	619	719
1	3	601	646
1	4	167	-94
1	5	360	382
2	1	1142	1216
2	3	1141	1108
2	5	698	713
2	7	434	472
3	1	763	-732
3	3	477	-427
3	5	294	-316
3	7	298	-255
4	1	247	299
4	3	220	165
5	1	311	419
5	3	392	463
6	1	626	689
6	3	605	597
6	5	398	423
7	1	425	-338
7	3	321	-265
8	1	266	168

H = 8

K	L	FO	FC
0	0	1107	1133
0	2	750	787
0	4	556	529
0	5	202	123
0	6	395	399
1	0	186	227
1	2	261	276
1	5	216	156
2	0	597	640
2	2	509	519
2	4	298	323
2	5	206	-160
2	6	274	279
3	2	281	-246
4	0	723	695
4	2	567	594
4	4	425	462
4	6	271	281
6	0	327	284
6	2	301	348
6	4	342	286
8	0	283	253
8	2	309	262

H = 9

K	L	FO	FC
0	1	637	596
0	3	620	690
0	5	416	426
1	1	805	-733
1	3	553	-599
1	5	473	-466
2	1	575	523
2	3	446	483
2	5	274	305
3	1	601	654
3	3	418	497
3	5	314	409
4	1	509	518
4	3	461	463
4	5	329	330
5	1	520	-475
5	3	435	-414
5	5	380	-331
6	1	388	358
7	1	281	340

H = 10

K	L	FO	FC
0	0	425	469
0	2	453	476
0	4	236	292
0	6	291	270
1	0	555	588
1	2	571	578
1	4	433	465
1	6	263	302
2	0	712	724
2	2	547	491
2	4	373	395
3	0	652	-623
3	2	493	-486
3	4	434	-352
3	6	322	-295
4	0	288	314
4	2	414	385
4	4	274	266
5	0	325	369
5	2	371	400
5	4	254	346
6	0	307	368
7	0	392	-309
7	4	309	-220

H = 11

K	L	FO	FC
0	1	489	470
0	3	399	406
1	3	231	-69
2	1	445	453
2	3	308	343
2	4	219	-102
2	5	254	264
4	1	368	347
4	3	311	312
6	1	303	296
6	3	285	243

H = 12

K	L	FO	FC
0	0	294	246
0	2	328	264
1	0	496	-431
1	2	450	-430
2	0	434	439
2	2	544	463
2	4	331	361
3	0	282	327
3	2	342	395
5	0	379	-323
5	2	375	-307
6	0	311	311
6	2	301	272

H = 13

K	L	FO	FC
0	1	615	594
0	3	472	392
1	1	323	334
1	3	323	293
3	1	381	-298
3	3	347	-261
4	1	438	446

H = 14

K	L	FO	FC
0	0	259	209
2	0	328	280
2	2	344	335
4	0	253	189

H = 15

K	L	FO	FC
2	1	332	334

H = 16

K	L	FO	FC
0	0	429	391

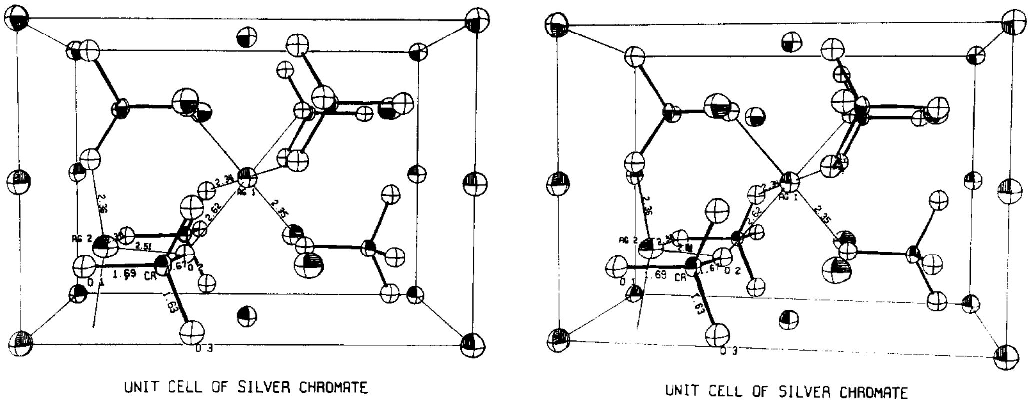

FIG. 1. Stereogram of the unit cell showing heavy atom coordination polyhedra.

and calculated structure factors (×10) are listed in Table II. Bond lengths and angles with their standard deviations were calculated by OR FFE. A stereogram of the unit cell is given in Fig. 1.

Description of the Structure

The structure of silver chromate consists of chromate groups linked together by silver atoms to form a three-dimensional network through the crystal. The two crystallographically independent silver atoms have different coordination polyhedra. Positioned on a center of symmetry, the coordination of Ag(1) can be best described as a tetragonal bipyramid with approximate D_{4h} symmetry. The coordination of Ag(2), which lies on the mirror plane, forms a badly distorted tetrahedron with average O–Ag–O angle being 107° but ranging from 84 to 139°. Also on the mirror plane is the chromate group which describes a slightly distorted tetrahedron with average Cr–O distance of 1.66 Å and angles ranging from 106.1 to 111.6(8)°. The coordination of oxygens O(1) and O(2) is roughly tetrahedral with each coordinated to three silver atoms with bond angles of 104 to 125°. The other independent oxygen atom O(3) is coordinated to just two silvers, and the Cr–O(3) distance is 0.04 Å shorter than the remaining Cr–O distances. Bond distances and angles for all the heavy atom coordination polyhedra are listed in Table III (see also Fig. 1). The covalent nature of the silver–oxygen bonds is evidenced by their directional character and comparatively short metal–oxygen distances. Literature values for average Ag–O distances for six coordinate silver (*9*) and for four coordinate Cr (VI)–O (*10*) are 2.42 and 1.65 Å, respectively.

Potassium chromate also crystallizes in space group *Pnma* with $Z = 4$. Although the unit cell dimensions are similar, the two structures are not isomorphous; the equivalent potassium chromate space group is *Pmcn*. The metal-atom coordination polyhedra are very different in the two structures. In the ionic potassium salts (K_2CrO_4 and K_2MnO_4) (*1*) all groups lie on the mirror planes. The potassium–oxygen coordination is complex with little or no directional character and exhibits nine and tenfold coordination. Metal–oxygen distances range from 2.7 to about 3.2 Å compared to the 2.34 to 2.62 Ag–O distances found in silver chromate.

The structural results on these two compounds are in good agreement with their solubilities. Potassium chromate is water soluble and the complex metal coordination found in its structure is typical of ionic

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN SILVER CHROMATE[a]

	Distance (Å)		Angle (deg)
Ag(1)–O(1)	2.35(1)	O(1)–Ag(1)–O(2)	86.8(4)
Ag(1)–O(2)	2.62(1)	O(1)–Ag(1)–O(3)	87.7(4)
Ag(1)–O(3)	2.34(1)	O(2)–Ag(1)–O(3)	88.9(4)
Ag(2)–O(1)	2.38(2)	O(1)–Ag(2)–O(2)	115.7(6)
Ag(2)–O(2)	2.51(2)	O(1)–Ag(2)–O(3)	110.2(3)
Ag(2)–O(3)	2.36(2)	O(2)–Ag(2)–O(3)	84.3(4)
		O(3)–Ag(2)–O(3)	139.1(7)
Cr–O(1)	1.69(1)	O(1)–Cr–O(2)	111.6(9)
Cr–O(2)	1.67(1)	O(1)–Cr–O(3)	110.1(6)
Cr–O(3)	1.63(1)	O(2)–Cr–O(3)	109.3(6)
		O(3)–Cr–O(3)	106.1(10)

[a] Symbols used refer to atom type only (Fig. 1). Symmetry operations are not given. Ag(1) lies on a center of symmetry so all other O–Ag(1)–O angles are related to those given.

compounds. Silver chromate is quite insoluble in polar solvents such as water and the more directional metal coordination of its structure is more representative of covalent compounds. Also, the electronegativity of silver (1.42) (*11*) is close to that of chromium (1.56) which is dissimilar to that of potassium (0.91). Thus the ionic compound potassium chromate crystallizes with complex potassium–oxygen coordinations providing many near neighbors to minimize the electrostatic repulsions of the ions, while in the more covalent silver chromate there is substantial directional silver–oxygen coordination to provide maximum overlap for some formation of covalent bonds. The differences in the two structures is, therefore, in accord with the different nature of the binding forces for the two solids.

References

1. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 12, p. 285, Longmans, Green and Co., London, 1932. Refer also to the recent structure determination of potassium manganate (V = 468.2 Å^3), G. J. Palenik, *Inorg. Chem.* **6**, 507 (1967) which is isomorphous with potassium chromate (V = 468.6 Å^3).

2. L. Pauling, "The Nature of the Chemical Bond," p. 514, Cornell University Press, Ithaca, N.Y., 1960.

3. "Handbook of Chemistry and Physics," p. 648, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

4. W. Ozbirn and R. A. Jacobson, *Inorg. Chim. Acta.* **4**, 377 (1970).

5. In addition to various local programs written at this Laboratory, other programs used in this study were Wehe, Busing, and Levy's ABCOR to correct for absorption, a modification of Busing, Martin, and Levy's OR FLS which allows for correction for the real and imaginary parts of anomalous dispersion, Busing, Martin, and Levy's OR FFE function and error program, and Johnson's OR TEP to prepare the figures.

6. D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.* **86**, 1660 (1964).

7. P. A. Doyle and P. S. Turner, *Acta Crystallogr. Sect. A* **24**, 390 (1968).

8. D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, pp. 215, 216, Table 3.3.2C, The Kynoch Press, Birmingham, England, 1962.

9. "International Tables for X-ray Crystallography," Vol. III, p. 260, Table 4.1.1, The Kynoch Press, Birmingham, England, 1962.

10. G. Colloti, L. Conti, and M. Zocchi, *Acta Crystallogr.* **12**, 416 (1959); J. S. Stephens and D. W. J. Cruickshank, *Acta Crystallogr. Sect. B* **26**, 437 (1970).

11. Allred-Rochow values from *J. Inorg. Nucl. Chem.* **5**, 264 (1958).