

The Structure of the Twelve Layer Barium Chromium Oxide, $\text{Ba}_2\text{Cr}_{7-x}\text{O}_{14}$ ($x \approx 0.5$)

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(Received 29 June 1971)

One of the products of reaction between BaO and CrO_2 at 1000°C and 60–65 kbar is the barium chromium oxide $\text{Ba}_2\text{Cr}_{7-x}\text{O}_{14}$ ($x \approx 0.5$). The compound crystallizes in space group $R\bar{3}m$ with hexagonal cell dimensions $a = 5.652 \pm 0.002$, $c = 27.77 \pm 0.03$ Å, three formula units per cell. The structure has been determined from 1068 independent reflections collected by counter methods and refined by least-squares methods to a conventional R value of 6.8%. The structure consists of a twelve layer close-stacked arrangement of close-packed layers, two O_4 layers alternating with two BaO_3 layers. Between O_4 layers there are chromium atoms in octahedral sites; between O_4 and BaO_3 layers there are chromium atoms in octahedral and tetrahedral sites, although the occupancy factor for the tetrahedral sites is only about 75%. The only available site between BaO_3 layers, an octahedral site, is not occupied. The tetrahedral Cr–O bond lengths, 1.638 ± 0.003 and 1.709 ± 0.010 Å, are consistent with Cr(VI), whereas the octahedral Cr–O bond lengths, 1.930 ± 0.003 , 1.947 ± 0.003 , 1.968 ± 0.005 , and 2.064 ± 0.004 , are consistent with Cr(III).

Introduction

The reaction between BaO and CrO_2 at high pressures and high temperatures produces a number of products (Chamberland, 1969). Several of these have been predicted to be polytypes of BaCrO_3 . One of these compounds had cell dimensions which indicated a twelve layer structure. Since the structure was based on a rhombohedral lattice, a close-packed structure similar to that observed for a number of rhenium containing compounds (Longo, Katz & Ward, 1965) was an obvious possibility. When Dr Chamberland offered us some good quality crystals of this '12R' barium chromium oxide, we decided it was an excellent opportunity to study the twelve layer structure in some detail. Not only was there an opportunity to accumulate more and better data, but there was also the simplification that in barium chromium oxide, unlike compounds such as $\text{Ba}_4\text{Re}_2\text{CoO}_{12}$, only one kind of cation, chromium, could occupy the octahedral sites.

Experimental

The barium chromium oxide used in our study was from the middle portion of a sample reacted at 1000°C and 60–65 kbar for two hours in a tetrahedral anvil press. The crystals were relatively thick black hexagonal plates or fragments of such plates. The crystal used for the structure determination was about $0.11 \times 0.20 \times 0.09$ mm.

Due to the small size of the available sample, ordinary chemical analysis was not possible and only a rough density of 5.4 g.cm^{-3} , measured on a Berman balance with toluene as the displacement liquid, could be obtained.

X-ray precession photographs showed hexagonal (trigonal) symmetry, Laue group $\bar{3}m$. The only system-

atic absences were those of a rhombohedral lattice, so the probable space group is one of $R32$, $R3m$, or $R\bar{3}m$.

Approximately 3200 reflections were measured on a computer-controlled Picker single-crystal diffractometer using graphite-monochromatized $\text{Mo K}\alpha$ radiation. The diffractometer was operated in the θ – 2θ scan mode, base scan width 3° , scan rate $2^\circ/\text{min}$, dispersion factor 0.692. Background was counted for 20 sec on each side of the peak. Hexagonal cell dimensions, $a = 5.652 \pm 0.002$, $c = 27.77 \pm 0.03$ Å, were determined by least-squares refinement of the diffractometer angles for twelve reflections.

Only reflections with k and l of the same sign were collected. For positive l , reflections out to $100^\circ 2\theta$ were measured; for negative l , reflections out to $50^\circ 2\theta$ were measured. Three standards were measured after every 40 reflections and showed no tendency to drift. Their standard deviations were 1.9%, 0.9%, and 2.9%.

After correcting for background, symmetry-related reflections were averaged, which reduced the data set to 1068 independent reflections; 89 had intensities less than twice the square root of the background and were labelled unobserved. Lorentz and polarization corrections, as well as other data treatment and computations, were carried out using X-RAY 67 (Stewart, 1967).

Structure determination and refinement

The cell dimensions are consistent with a twelve layer stacking of close packed O_4 and/or BaO_3 layers. Of the 43 twelve-layer stacking sequences, only one is rhombohedral, space group $R\bar{3}m$ (*International Tables for X-ray Crystallography*, 1959). For the composition BaCrO_3 , all the layers would be BaO_3 and all of the O_6 octahedral sites would be occupied by Cr. Such close-packed structures have been found for a number of complex oxides containing barium and smaller cations

(Katz & Ward, 1964). The compound $\text{Ba}_4\text{Re}_2\text{CoO}_{12}$, for example, is rhombohedral and has a unit cell composed of twelve BaO_3 layers, although only nine of the twelve octahedral sites are occupied by rhenium and cobalt (Longo, Katz & Ward, 1965). The cell dimensions for $\text{Ba}_4\text{Re}_2\text{CoO}_{12}$ are $a=5.71$, $c=27.7$ Å as compared to $a=5.65$, $c=27.77$ Å for the barium chromium oxide, so it was reasonable to postulate a related structure. However, after least-squares refinement of z parameters and isotropic temperature factors for all atoms, the conventional R value, $\sum ||F_o| - |F_c|| / \sum |F_o|$, was still 0.35. In addition, the temperature factor for chromium in one of the threefold positions became improbably large.

A Patterson map showed concentrations of peaks indicating that most, if not all of the cations were in special positions. The number of very large peaks, however, did not correspond to the expected number of Ba–Ba interactions, and there were too many medium sized peaks to sort out into Ba–Cr and Cr–Cr interactions.

An examination of the $hk0$ data was sufficient to reveal the source of the difficulty. The x and y coordinates for Ba and Cr in the initial model are all 0,0; $\frac{1}{3}$, $\frac{2}{3}$; and $\frac{2}{3}$, $\frac{1}{3}$. The R value for the $hk0$ data with these coordinates was 0.17, so another special position was indicated. When Cr was placed in a ninefold position (x, y equal to $\frac{1}{2}, 0$) a model was developed for which $R(hk0)$ was 0.023, a dramatic improvement. The proposed new model is given in Table 1. The ideal composition is $\text{Ba}_2\text{Cr}_7\text{O}_{14}$, quite different from the original assumption of BaCrO_3 .

Confirmation that the Cr:Ba ratio was indeed greater than 1:1 was obtained by an examination of compounds with Cr:Ba ratios of 1:2, 2:3 and 1:1 with a Kevex energy dispersive spectrometer attached to a Cambridge Stereoscan scanning electron microscope. Lacking suitable standards, it was not possible to make meaningful quantitative estimates; however, it was clear that the Cr:Ba ratio for our crystal was higher than that for any of the comparison samples.

Refinement of z parameters and isotropic thermal

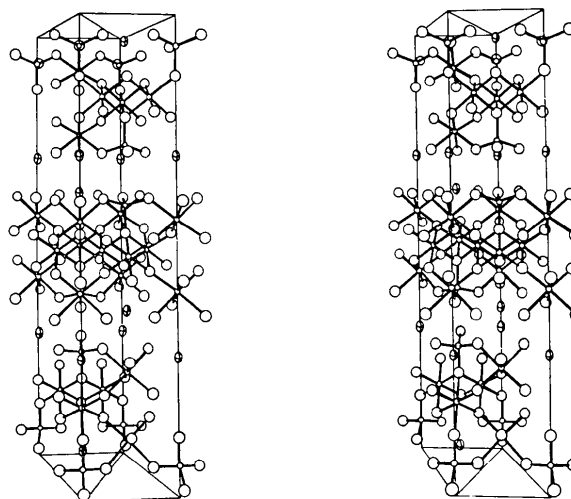


Fig. 1. Stereoscopic illustration of unit cell and contents plus oxygens needed to complete coordination polyhedra for Cr. The Cr atoms are shown as small spheres, O atoms as large spheres, and Ba atoms as ellipsoids.

parameters reduced R to 0.122. Allowing atom multipliers for the three crystallographic kinds of Cr to vary resulted in no change for Cr(1) and Cr(2), but that for Cr(3) decreased and reduced R to 0.101. Allowing anisotropic thermal motion for Ba and Cr and refining the x parameters for O(1) and O(2) reduced R to 0.068.

The determination of the occupancy factor for Cr(3) was complicated by the correlation between the occupancy factor and the thermal parameters. When the Cr(3) β 's were fixed at the values found for full occupancy, the occupancy factor was about 80%; when the parameters were all allowed to vary simultaneously, the occupancy factor was about 60%. If we assume that the octahedral Cr are Cr(III) and the tetrahedral Cr are Cr(VI), charge balance requires 75% occupancy of the tetrahedral sites. The formula thus becomes $\text{Ba}_2\text{Cr}_{6.5}\text{O}_{14}$. A refinement with this composition and all atoms anisotropic again yielded $R=0.068$. Clearly, the occupancy of the Cr(3) sites is still open to some

Table 1. Atomic parameters for $\text{Ba}_2\text{Cr}_{7-x}\text{O}_{14}$

Space group $R\bar{3}m$ (No. 166). Errors in the last place are given in parentheses. Anisotropic temperature factor: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Values of β are $\times 10^5$.

	Ba	Cr(1)	Cr(2)	Cr(3)*	O(1)	O(2)	O(3)
Position	6(c)	9(d)	6(c)	6(c)	18(h)	18(h)	6(c)
Initial x, y, z	0, 0, $\frac{7}{24}$	$\frac{1}{2}, 0, \frac{1}{2}$	0, 0, $\frac{5}{12}$	0, 0, $\frac{1}{15}$	$\frac{1}{6}, \frac{5}{6}, \frac{5}{8}$	$\frac{1}{6}, \frac{5}{6}, \frac{1}{24}$	0, 0, $\frac{1}{8}$
x	0	$\frac{1}{2}$	0	0	0.1719 (6)	0.1724 (5)	0
y	0	0	0	0	0.8281	0.8276	0
z	0.29331 (3)	$\frac{1}{2}$	0.42638 (7)	0.06546 (14)	0.6167 (2)	0.4614 (2)	0.1269 (3)
β_{11} or B	474	396 (27)	321	554	0.80 (6)	0.51 (5)	0.53 (9)
β_{22}	474	368	321	554			
β_{33}	32 (1)	17 (1)	19 (1)	26 (3)			
β_{12}	237 (6)	184 (18)	161 (14)	277 (34)			
β_{13}	0	1 (3)	0	0			
β_{23}	0	3	0	0			

Occupancy factor converged to 60%, $R=6.8\%$. With occupancy fixed at 75%, R somewhat higher (7.2%). With all atoms anisotropic, occupancy varying or fixed at 75%, $R=6.8\%$. In all cases position parameters agreed within σ .

question and at this stage depends somewhat on chemical assumptions.

In the early part of the refinement, neutral-atom form-factors were used, but when it became apparent that Cr was present in more than one oxidation state, form factors for Ba^{2+} , Cr^{3+} , Cr^{6+} , and O^{2-} were used. These were taken directly or extrapolated from the tables of Cromer & Waber (1965). There was, however, essentially no change resulting from the use of ionized-atom form factors.

Final parameters are listed in Table 1, and a stereo drawing of the unit cell, using Johnson's Program ORTEP (1965) is shown in Fig. 1.

Refinement using a weighting function $w = 1/\sigma_F^2$, where for observed reflections

$$\sigma_F = \frac{1}{\sqrt{n}} \cdot \frac{1}{2\sqrt{Lp}} \cdot \left\{ [N_T + \text{BG} + (0.02N_T)^2] / (N_T - \text{BG}) \right\}^{1/2}$$

and for unobserved reflections $\sigma_F = \frac{1}{\sqrt{n}} \cdot \frac{1}{\sqrt{Lp}} [\text{BG}]^{1/2}$

with n the number of symmetry related reflections averaged, N_T the total counts, and BG the background

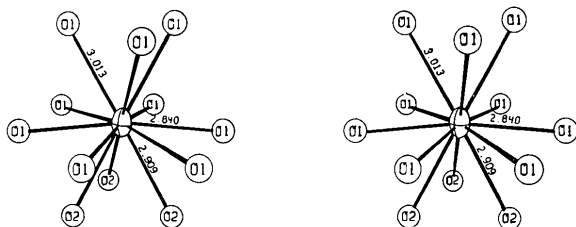


Fig. 2. Stereoscopic illustration of barium coordination. O(1)'s are in BaO_3 layers; O(2)'s are in O_4 layers.

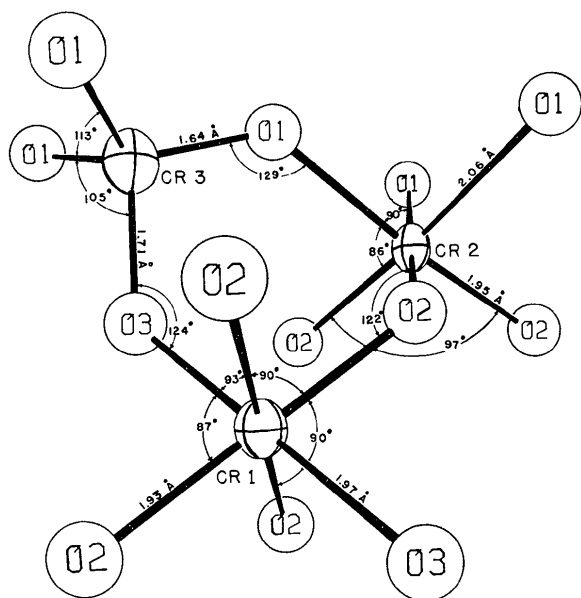


Fig. 3. The coordination of the three types of chromium.

counts, gave the same R value and essentially the same parameters as the unit-weight refinement. Examination of the intense reflections suggested that a secondary extinction correction was not necessary. Anomalous dispersion corrections had very little effect. The linear absorption coefficient based on the calculated density is 147.6 cm^{-1} . No absorption corrections were made, although the averaging of related reflections should partially compensate for this omission.

Oxygen atoms had been placed originally from peaks on a difference map phased by the cations alone. The highest peaks on a final difference map were less than one half as high as these oxygen peaks.

Discussion

The compound may be described as a twelve-layer close-stacked arrangement of close-packed layers, two O_4 layers alternating with two BaO_3 layers. Three of the four octahedral sites between O_4 layers are occupied by Cr. Between O_4 and BaO_3 layers, one tetrahedral site and the one octahedral site are used. Both are occupied by Cr, although the occupancy factor for the tetrahedral site is about 75%. Between BaO_3 layers there is one octahedral site available, but it is not occupied.

The compound may be compared with other complex metal oxides in certain structural features, even though the compositions are quite different overall. The three chromium atoms between O_4 layers in octahedral sites with the octahedra sharing edges to form 3-rings is similar to the molybdenum arrangement in,

Table 2. *Electrostatic bond strengths*

To O(1): 3 Ba at $\frac{1}{2} + 1$ Cr(2) at $\frac{1}{2} + 0.75$ Cr(3) at $1\frac{1}{2} = 2\frac{1}{2}$	
To O(2): 1 Ba at $\frac{1}{2} + 2$ Cr(1) at $\frac{1}{2} + 1$ Cr(2) at $\frac{1}{2}$	$= 1\frac{3}{8}$
To O(3): 3 Cr(1) at $\frac{1}{2} + 0.75$ Cr(3) at $1\frac{1}{2}$	$= 2\frac{5}{8}$

Table 3. *Interatomic distances and angles*

Distances		
Ba—O(1)	(same layers)	$2.840 \pm 0.002 \text{ \AA}$
Ba—O(1)	(different layers)	3.013 ± 0.005
Ba—O(2)		2.909 ± 0.005
Cr(1)—O(2)		1.930 ± 0.003
Cr(1)—O(3)		1.968 ± 0.005
Cr(2)—O(1)		2.064 ± 0.004
Cr(2)—O(2)		1.947 ± 0.003
Cr(3)—O(1)		1.638 ± 0.003
Cr(3)—O(3)		1.709 ± 0.010
Angles		
O(2)—Cr(1)—O(2)	(O's in same layer)	$90.0 \pm 0.2^\circ$
O(2)—Cr(1)—O(3)	(O's in same layer)	93.0 ± 0.2
O(2)—Cr(1)—O(2)	(O's in different layers)	90.0 ± 0.2
O(2)—Cr(1)—O(3)	(O's in different layers)	87.1 ± 0.2
O(1)—Cr(2)—O(1)		89.8 ± 0.2
O(2)—Cr(2)—O(2)		97.3 ± 0.2
O(1)—Cr(2)—O(2)		86.4 ± 0.2
O(1)—Cr(3)—O(1)		113.4 ± 0.2
O(1)—Cr(3)—O(3)		105.2 ± 0.2

for example, Zn₂Mo₃O₈ (McCarroll, Katz & Ward, 1957; Ansell & Katz, 1966). However, there is no 'clustering' in the present case. The adjacent BaO₃ layers with unoccupied octahedral sites are found in compounds like Ba₅Ta₄O₁₅ (Galasso & Katz, 1961; Shannon & Katz, 1970). The analogy with the A₂Mo₃O₈ compounds goes further than the Cr₃O₈ arrangement, since on both sides of the two O₄ layers, the octahedral site and a tetrahedral site are occupied. The four layer sequence in the A₂Mo₃O₈ compounds is: O₄; A(tet), A(oct); O₄; 3 Mo(oct); O₄; A(tet), A(oct); O₄. In the structurally idealized Ba₂Cr_{7-x}O₁₄, a four layer sequence is: BaO₃; Cr(tet), Cr(oct); O₄; 3 Cr(oct); O₄; Cr(tet), Cr(oct); BaO₃. The sequence is repeated three times in the c repeat distance of the hexagonal cell. The layer sequence for the A₂Mo₃O₈

compounds in the Zhdanov notation is 22, i.e., ABCB..., whereas, thinking of barium and oxygens simply as equal spheres, the Zhdanov notation for Ba₂Cr_{6.5}O₁₄ is 31, i.e., ABCACABCBCAB.... A set of four layers for A₂Mo₃O₈ could be described as ABAC and a set of four layers in Ba₂Cr_{6.5}O₁₄ could be described as ABAB to emphasize the similarities. In the first case the tetrahedral and octahedral sites of alternate layers are staggered in the c direction; in the second case, octahedral sites are in line; tetrahedral sites, because of the barium atoms, are staggered. These features may be seen more clearly by comparing Fig. 1 of this paper with Fig. 2 of Ansell & Katz (1966).

The question of the oxidation states of chromium was not answered in a direct way. However, the

Table 4. Observed and calculated structure factors

Columns are l, 10|F_o|, 10|F_c|. Unobserved reflections are marked by an asterisk.

h	k	l	10 F _o	10 F _c	h	k	l	10 F _o	10 F _c	h	k	l	10 F _o	10 F _c
0 0 0 L	53	993	-826	22 2621 -2859	17 1684 1595	16 1659 -150	29 1210 -1238	5 3 3 L	25 1315 -1317	4 631 612	25 373 -430	6 4 4 L	7 5 4 L	
6 524 161	0 5 5 L	25 1029 -1069	20 19 133	25 1029 -1069	20 19 133	25 1029 -1069	20 19 133	0 2182 2028	31 884 910	10 1118 1083	31 704 754	2 3 4 L	2 5 4 L	-100
9 2811 -3567	37 517 51	0 3777 3512	28 2381 265	31 1585 1503	25 175 147	22 2431 -2510	35 370 -313	3 1448 1318	34 788 780	34 233 261	3 458 809	34 233 261	3 458 809	34 233 261
12 1855 -2175	1 5 17 -485	3 2402 2299	31 2081 193	26 588 -527	25 1029 -1069	25 1029 -1069	25 1029 -1069	6 959 -878	37 323 -322	16 542 487	37 410 337	8 297 -243	8 297 -243	8 297 -243
15 2155 -2324	4 9 33 155	4 9 33 155	37 730 679	32 857 -838	31 1472 1470	31 1472 1470	31 1472 1470	9 607 -547	40 856 831	19 1053 -1067	40 228 54	11 588 -531	11 588 -531	11 588 -531
18 775 927	7 2081 193	40 0 0 -16	40 0 0 -16	35 178 259	34 517 424	34 517 424	34 517 424	15 941 -947	46 0 0 67	25 737 -751	5 5 5 L	17 563 574	17 563 574	17 563 574
21 1815 2124	10 373 363	43 995 -494	43 995 -494	41 504 440	40 167 -55	1 353 -329	10 587 -602	45 570 449	47 917 1000	28 700 726	47 917 1000	47 917 1000	47 917 1000	47 917 1000
24 2753 3013	13 695 632	46 1072 -917	46 1072 -917	44 512 426	43 995 -494	43 995 -494	43 995 -494	24 648 681	55 0 0 220	31 873 855	0 1117 1145	0 1117 1145	0 1117 1145	0 1117 1145
27 734 -825	16 124 -130	49 191 -24	49 191 -24	44 512 426	43 995 -494	43 995 -494	43 995 -494	32 839 311	30 399 311	30 399 311	3 762 730	3 762 730	3 762 730	3 762 730
30 1442 1438	19 561 -515	52 205 -125	52 205 -125	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	6 505 -527	6 505 -527	6 505 -527	6 505 -527
33 676 -716	22 1015 -1865	55 261 127	55 261 127	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	0 166 -293	0 166 -293	0 166 -293	0 166 -293
36 964 -931	25 862 -828	58 286 308	58 286 308	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	3 881 615	3 881 615	3 881 615	3 881 615
39 1401 1404	28 413 467	61 311 364	61 311 364	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	6 349 -333	6 349 -333	6 349 -333	6 349 -333
42 459 407	31 1172 1190	64 336 389	64 336 389	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	6 1025 -884	6 1025 -884	6 1025 -884	6 1025 -884
45 0 0 62	34 393 375	67 351 333	67 351 333	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	9 697 -818	9 697 -818	9 697 -818	9 697 -818
48 905 778	37 517 51	70 373 363	70 373 363	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	12 1315 -1248	12 1315 -1248	12 1315 -1248	12 1315 -1248
51 804 -101	40 186 75	73 439 421	73 439 421	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	15 1090 -1059	15 1090 -1059	15 1090 -1059	15 1090 -1059
54 936 792	43 460 426	76 491 457	76 491 457	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	18 754 -730	18 754 -730	18 754 -730	18 754 -730
57 568 -439	46 869 -726	79 714 -704	79 714 -704	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	21 1100 1130	21 1100 1130	21 1100 1130	21 1100 1130
60 904 -87	49 964 -87	82 819 -82	82 819 -82	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	24 605 354	24 605 354	24 605 354	24 605 354
63 1172 1190	52 219 -473	85 926 -473	85 926 -473	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	27 777 807	27 777 807	27 777 807	27 777 807
66 1464 -1455	55 1044 -1455	88 988 -1455	88 988 -1455	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311
69 1815 2124	58 1242 -1865	91 1117 -1865	91 1117 -1865	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	33 1637 1461	33 1637 1461	33 1637 1461	33 1637 1461
72 2155 2324	61 1411 -2324	94 1311 -2324	94 1311 -2324	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	6 1025 -884	6 1025 -884	6 1025 -884	6 1025 -884
75 2505 2675	64 1600 -2675	97 1500 -2675	97 1500 -2675	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	9 697 -818	9 697 -818	9 697 -818	9 697 -818
78 2855 3045	67 1789 -3045	100 1689 -3045	100 1689 -3045	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	12 1315 -1248	12 1315 -1248	12 1315 -1248	12 1315 -1248
81 3205 3395	70 1978 -3395	103 1878 -3395	103 1878 -3395	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	15 1090 -1059	15 1090 -1059	15 1090 -1059	15 1090 -1059
84 3555 3745	73 2167 -3745	106 2067 -3745	106 2067 -3745	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	18 754 -730	18 754 -730	18 754 -730	18 754 -730
87 3905 4095	76 2356 -4095	109 2256 -4095	109 2256 -4095	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	21 1100 1130	21 1100 1130	21 1100 1130	21 1100 1130
90 4255 4445	79 2545 -4445	112 2445 -4445	112 2445 -4445	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	24 605 354	24 605 354	24 605 354	24 605 354
93 4605 4795	82 2734 -4795	115 2634 -4795	115 2634 -4795	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	27 777 807	27 777 807	27 777 807	27 777 807
96 4955 5145	85 2923 -5145	118 2823 -5145	118 2823 -5145	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311
99 5305 5295	88 3112 -5295	121 3012 -5295	121 3012 -5295	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	33 1637 1461	33 1637 1461	33 1637 1461	33 1637 1461
102 5655 5445	91 3301 -5445	124 3201 -5445	124 3201 -5445	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	6 1025 -884	6 1025 -884	6 1025 -884	6 1025 -884
105 6005 5595	94 3490 -5595	127 3390 -5595	127 3390 -5595	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	9 697 -818	9 697 -818	9 697 -818	9 697 -818
108 6355 5745	97 3679 -5745	130 3579 -5745	130 3579 -5745	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	12 1315 -1248	12 1315 -1248	12 1315 -1248	12 1315 -1248
111 6705 5895	100 3868 -5895	133 3768 -5895	133 3768 -5895	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	15 1090 -1059	15 1090 -1059	15 1090 -1059	15 1090 -1059
114 7055 6045	103 4057 -6045	136 3957 -6045	136 3957 -6045	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	18 754 -730	18 754 -730	18 754 -730	18 754 -730
117 7405 6195	106 4246 -6195	139 4146 -6195	139 4146 -6195	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	21 1100 1130	21 1100 1130	21 1100 1130	21 1100 1130
120 7755 6345	109 4435 -6345	142 4335 -6345	142 4335 -6345	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	24 605 354	24 605 354	24 605 354	24 605 354
123 8105 6495	112 4624 -6495	145 4524 -6495	145 4524 -6495	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	27 777 807	27 777 807	27 777 807	27 777 807
126 8455 6645	115 4813 -6645	148 4713 -6645	148 4713 -6645	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311	30 399 311
129 8805 6795	118 5002 -6795	151 4902 -6795	151 4902 -6795	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -917	32 839 311	30 399 311	30 399 311	33 1637 1461	33 1637 1461	33 1637 1461	33 1637 1461
132 9155 6945	121 5191 -6945	154 5091 -6945	154 5091 -6945	50 472 -395	49 1072 -917	49 1072 -917	49 1072 -							

composition clearly calls for more than one oxidation state. The existence of three different oxidation states is highly unlikely. However, KCr_3O_8 contains both Cr(III) and Cr(VI) (Wilhelmi, 1958), and the bond lengths in $\text{Ba}_2\text{Cr}_{6.5}\text{O}_{14}$ are consistent with Cr(III) in the octahedral sites and Cr(VI) in the tetrahedral sites. With this assumption, charge balance requires that some cation sites be unoccupied, which is consistent with the reduced occupancy factor found for chromium in the tetrahedral sites.

The sum of electrostatic bond strengths assuming the above oxidation states and occupancy is given in Table 2. The value of $2\frac{3}{8}$ to O(3) is, of course, quite high. It should be noted, however, that where a chromium atom has bonds to O(3), these bonds are appreciably longer than its bonds to O(2) or O(1): Cr(1)–O(2) = 1.93 *vs.* Cr(1)–O(3) = 1.97; Cr(3)–O(1) = 1.64 *vs.* Cr(3)–O(3) = 1.71. The bond lengthening would, in effect, decrease the high sum of electrostatic bond strengths.

Atomic parameters are listed for initial and final positions in Table 1. The maximum shift to error ratio in the final cycle was 0.035. Table 3 lists some interatomic distances and bond angles, and Table 4 lists observed and calculated structure factors.

A stereoscopic view of the barium coordination is shown in Fig. 2. The coordination of the three types of chromium, [Cr(1) is $^{VI}\text{Cr(III)}$, Cr(2) is $^{VI}\text{Cr(III)}$, and Cr(3) is $^{IV}\text{Cr(VI)}$], is shown in Fig. 3.

The authors are grateful to Dr B. L. Chamberland for the crystals used in this study and for helpful discussions. Financial assistance was provided by the National Science Foundation through grant GP 8481. Computations were carried out in the Computer Center of the University of Connecticut, which is supported in part by grant GJ-9 of the National Science Foundation. Photographs of the Figures and the table of structure factors were prepared by the University of Connecticut Photographic Laboratory.

References

- ANSELL, G. B. & KATZ, L. (1966). *Acta Cryst.* **21**, 482.
 CHAMBERLAND, B. L. (1969). *Inorg. Chem.* **8**, 286.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 GALASSO, F. & KATZ, L. (1961). *Acta Cryst.* **14**, 647.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KATZ, L. & WARD, R. (1964). *Inorg. Chem.* **3**, 205.
 LONGO, J. M., KATZ, L. & WARD, R. (1965). *Inorg. Chem.* **4**, 235.
 MCCARROLL, W. H., KATZ, L. & WARD, R. (1957). *J. Amer. Chem. Soc.* **79**, 5410.
 SHANNON, J. & KATZ, L. (1970). *Acta Cryst.* **B26**, 102.
 STEWART, J. M. (1967). *X-RAY 67 Program System*, University of Maryland, College Park, Maryland.
 WILHELMI, K. -A. (1958). *Acta Chem. Scand.* **12**, 1965.

Acta Cryst. (1972). **B28**, 1223

The Crystal Structure of 3-Phenyl-2,4-(1*H*,3*H*)-quinazolinedione

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(Received 17 August 1971)

The crystal structure of 3-phenyl-2,4-(1*H*,3*H*)-quinazolinedione, $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$, has been determined from three-dimensional photographic data. The crystals are monoclinic and the space group is $P2_1/c$ with four molecules in the unit cell. The axial parameters are $a = 5.799 \pm 0.002$, $b = 8.339 \pm 0.009$, $c = 22.962 \pm 0.007$ Å, and $\beta = 94.16 \pm 0.04^\circ$. The structure was deduced from a sharpened Patterson synthesis and refined by means of the block-diagonal least-squares method to the final *R* index of 0.104 for 2255 independent non-zero reflexions. The molecules are placed in pairs around a centre of symmetry, connected by two C=O...H–N hydrogen bonds of length 2.821 Å. The quinazoline rings are superimposed at the intervals of 3.5 Å along the *b* axis, with their long axes approximately parallel to the [001] direction. The benzene ring is rotated by 65.0° from the quinazoline ring because of the steric effect of the two carbonyl groups.

Introduction

3-Phenyl-2,4-(1*H*,3*H*)-quinazolinedione is a model compound of polyquinazolinedione, one of the poly-

mers having the properties of thermal stability and solubility in polyphosphoric acid and organic polar solvents, which were prepared by the cyclopolycondensation reaction of the open-chain precursor (Tohyama, Kurihara, Ikeda & Yoda, 1967; Yoda, 1968, 1969). It was prepared by the reaction of anthranilic acid and phenyl isocyanate in the presence of polyphosphoric acid (PPA) (Kurihara & Yoda, 1965, 1966).

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