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### Synthesis of a New High-Pressure Scheelite-Type Polymorph of Cadmium Chromate<sup>1</sup>

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It is well known that the coordination of Cd in inorganic oxides can vary widely. Cd is tetrahedrally coordinated in the spinel CdCr<sub>2</sub>O<sub>4</sub> and octahedrally surrounded by six oxygens in CdO (NaCl structure). In the scheelite-type CdMoO<sub>4</sub>, Cd is eightfold coordinated, and in the perovskite-like CdTiO<sub>3</sub>, Cd is surrounded by 12 oxygens.

In our recent study of the system CdO-Cr<sub>2</sub>O<sub>3</sub>-O,<sup>2</sup> it was found that CdCrO<sub>4</sub> was dimorphic at pressures below 3.5 kbars. At low temperatures, CdCrO<sub>4</sub> has

TABLE I  
X-RAY DIFFRACTION POWDER DATA FOR CdCrO<sub>4</sub>-II<sup>a</sup>

$d, \text{\AA}$		$l/d^b$	$hkl$
Obsd	Calcd		
4.56	4.56	5	101
2.999	2.998	100	112
2.887	2.887	16	004
2.480	2.480	19	200
2.229	2.229	3	114
2.179	2.178	17	211
2.093	2.094	8	105
1.922	1.922	10	213
1.882	1.881	34	204
1.753	1.754	14	220
1.687	1.687	20	116
1.637	1.637	4	301
1.514	1.514	30	312
1.499	1.499	19	224
1.248	1.248	6	208
1.240	1.240	3	400
1.216	1.216	12	316

<sup>a</sup> Crystal data: Body-centered tetragonal;  $a_0 = 4.960 \text{ \AA}$ ,  $c_0 = 11.548 \text{ \AA}$ ; space group C<sub>4h</sub><sup>6</sup>-I<sub>41</sub>/a; scheelite structure.  
<sup>b</sup> Peak height intensities.

TABLE II  
CRYSTALLOGRAPHIC DATA FOR THE THREE KNOWN POLYMORPHS OF CdCrO<sub>4</sub><sup>a</sup>

Phase	Unit cell dimensions				Vol, $\text{\AA}^3$	Z	Calcd density, g/cm <sup>3</sup>	Bravais lattice type, space group, and structure
	$a_0, \text{\AA}$	$b_0, \text{\AA}$	$c_0, \text{\AA}$	$\beta(\text{mono}), \text{deg}$				
$\beta$ -CdCrO <sub>4</sub>	10.397	9.675	7.064	101.52	696.3	8	4.36	C-centered monoclinic, C <sub>2h</sub> <sup>3</sup> -C2/m, $\alpha$ -MnMoO <sub>4</sub> structure
$\alpha$ -CdCrO <sub>4</sub>	5.678	8.723	6.926	...	343.0	4	4.42	C-centered orthorhombic, D <sub>2h</sub> <sup>17</sup> -Cmcm, CrVO <sub>4</sub> structure
CdCrO <sub>4</sub> -II	4.960	...	11.548	...	284.1	4	5.34	Body-centered tetragonal, C <sub>4h</sub> <sup>6</sup> -I <sub>41</sub> /a, scheelite structure

<sup>a</sup> Data for  $\alpha$ - and  $\beta$ -CdCrO<sub>4</sub> are taken from ref 4.

the CrVO<sub>4</sub> structure,<sup>2-4</sup> while the high-temperature form ( $\beta$ -CdCrO<sub>4</sub>) has the  $\alpha$ -MnMoO<sub>4</sub> structure.<sup>2,4,5</sup> In both polymorphs, Cd is surrounded by a distorted octahedron of six oxygens. Owing to the known ability of Cd to assume a higher coordination, it is likely that a high-pressure polymorph of CdCrO<sub>4</sub> exists in which Cd has a coordination number higher than 6. To test this possibility, high-pressure experiments were carried out using an opposed-anvil apparatus. The apparatus used and the general experimental method have been described elsewhere.<sup>6</sup> The runs were generally air quenched with subsequent release of pressure. X-Ray patterns were taken with a Picker diffractometer, using Ni-filtered Cu K $\alpha$  radiation and glass slide mounts.

It was found that when  $\alpha$ - or  $\beta$ -CdCrO<sub>4</sub> was treated at about 40 kbars and 200-450 $^\circ$ , the major crystalline phase present in the quench product gave a scheelite-like X-ray pattern. The indexed powder data and

cell constants are given in Table I. The unit cell constants and intensities are in good agreement with the expected values for a scheelite-type CdCrO<sub>4</sub>. We have chosen to designate this new polymorph as CdCrO<sub>4</sub>-II, in accordance with recent practice of designating high-pressure phases.

We were unable to obtain CdCrO<sub>4</sub>-II in a pure state; crystalline impurities amounting to at least 5% were always present. At lower temperatures (below 200 $^\circ$ ) or at pressures well below 40 kbars (*e.g.*, 15 kbars) CdCrO<sub>4</sub>-II was always accompanied by some  $\alpha$ -CdCrO<sub>4</sub>. Quench products obtained from 250 to 450 $^\circ$  at 40 kbars gave (in addition to major amounts of CdCrO<sub>4</sub>-II) always traces or minor amounts of another crystalline phase (or phases). This other phase has never been obtained in major amounts and has not yet been identified. The more prominent  $d$  spacings of that phase are at  $d = 4.72, 3.787, 3.492, 3.275, 3.190, 2.783, 2.202, \text{ and } 1.637 \text{ \AA}$ . It is quite possible that these  $d$  spacings belong to more than one phase, especially since differences in intensity have been noted.

There is some evidence that CdCrO<sub>4</sub>-II is always accompanied by appreciable amounts of an amorphous phase. Quench products obtained from runs near 520 $^\circ$  at 40 kbars give a nearly amorphous product

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with barely detectable traces of  $\text{CdCrO}_4\text{-II}$  and the other unidentified phase. There is evidence that such an amorphous phase is also present in quench products obtained from lower temperature runs (250–450°) where  $\text{CdCrO}_4\text{-II}$  is the major crystalline phase. All the X-ray patterns of  $\text{CdCrO}_4\text{-II}$  were of lower intensity than would be expected for the amount of powder used. Moreover, a prominent broad high-intensity region at low  $2\theta$  values was always present, again suggesting the presence of an amorphous phase. Further evidence for an amorphous phase is given by infrared data.

Infrared spectra were taken for (a) a sample rich in  $\text{CdCrO}_4\text{-II}$  and (b) a nearly amorphous  $\text{CdCrO}_4$  specimen. The spectra are very similar to each other and also resemble the spectrum of  $\alpha\text{-CdCrO}_4$ .<sup>7</sup> The frequencies (in  $\text{cm}^{-1}$ ) are compared below. The data

$\text{CdCrO}_4\text{-II}$ -containing sample	Amorphous	$\alpha\text{-CdCrO}_4$
915 + 898	912	915
855	855	865
802	790	805

suggest that the  $\text{CdCrO}_4\text{-II}$ -rich samples probably contain much amorphous material and that the  $\text{CrO}_4$  groups in the amorphous phase are similar to those in  $\alpha\text{-CdCrO}_4$ .

In summary, it is instructive to compare the crystallographic data for the three polymorphs of  $\text{CdCrO}_4$ . This is done in Table II. Especially noteworthy is the large increase in density in going from  $\alpha$ - or  $\beta$ - $\text{CdCrO}_4$  to  $\text{CdCrO}_4\text{-II}$ . Such a density increase is to be expected in view of the coordination change in Cd, *i.e.*, going from a coordination of six in  $\alpha$ - and  $\beta$ - $\text{CdCrO}_4$  to an eightfold coordination in scheelite-type  $\text{CdCrO}_4\text{-II}$ .

The complete elucidation of the phase equilibria of  $\text{CdCrO}_4$  at high pressures may require high-pressure X-ray techniques. The fact that a nearly amorphous phase is obtained as quench product from the higher temperature region indicates perhaps that there exists still another high-pressure phase, which is, however, nonquenchable.

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## A Cation Derived from $\text{BH}_2^+$ and Acetonitrile

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In a number of recent publications it has been demonstrated that displacement of iodide ions from an iodoborane adduct is a facile route for the synthesis of

boronium compounds containing the  $\text{BH}_2^+$  unit.<sup>1–5</sup> Although displacement by nitrogen bases can apparently be inhibited by steric factors<sup>4</sup> and can be directed to alternate accessible basic sites, such as the oxygen atom in dimethylformamide,<sup>5</sup> the practical limits imposed on the stability of the boron cation by the weakness of the base have not been established. Even such a weak base as 2-fluoropyridine ( $\text{p}K_a = -0.44$ ) forms a stable cation.<sup>4</sup> It is therefore of interest to report the synthesis of a reasonably stable cation of  $\text{BH}_2^+$  in which trimethylamine and the very weak base acetonitrile is coordinated to boron.

### Results and Discussion

The synthesis of the cation  $(\text{CH}_3)_3\text{NBH}_2\text{NCCH}_3^+$  was accomplished in a straightforward manner by iodide displacement from trimethylamine-iodoborane in benzene solution. The identity of the iodide salt was established by conversion to the hexafluorophosphate derivative and by its ir and nmr spectra. The infrared spectrum shows a strong doublet between 2400 and 2500  $\text{cm}^{-1}$  assigned to the B–H stretches and a very intense absorption at 1150  $\text{cm}^{-1}$  which corresponds to the  $\text{BH}_2$  deformation.<sup>1</sup> There also is a relatively broad and intense absorption at 2375  $\text{cm}^{-1}$  which is indicative of a coordinated  $\text{RC}\equiv\text{N}$  group.<sup>6</sup> The proton nmr spectrum shows two singlets of appropriate relative intensity, shifted downfield relative to the free ligands.<sup>4</sup> Boron-attached hydrogens could not be detected. The <sup>11</sup>B spectrum also showed large line broadening, so that the expected triplet appeared as a very broad band with a width consistent with the magnitude of the coupling constants observed in related compounds.

The iodide salt was decomposed into trimethylamine-iodoborane and acetonitrile at 130°, a substantially lower temperature than the 200° which was apparently necessary for the similar decomposition of bis(trimethylamine)boronium chloride or bromide<sup>7</sup> in which the stronger base trimethylamine was displaced from boron.

Facile displacement of acetonitrile was also evidenced by the behavior of the iodide salt in pyridine solution. The band characteristic of free acetonitrile appeared in the proton spectrum within minutes after dissolution, while trimethylamine remained coordinated to boron. The latter base was only relatively slowly displaced by pyridine at room temperature.

The cation hydrolyzed relatively rapidly in water, so that derivatives could be prepared only in cold solution and with rapid work-up. The pH of hydrolyzing solutions initially was strongly acidic but on

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