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Abstract

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CHROMIUM CHALCOGENOSULFIDES

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1. Chromium salts with mixed anions became known comparatively recently, thanks to the work of Hendi and Gregory ([1], [2]), who synthesized and studied $CrCl_2Br$, $CrCl_2I$, and $CrBr_2I$. These compounds were obtained by the direct action of halogens on divalent chromium salts according to the reaction:

$$2CrX_2 + Y_2 = 2CrX_2Y.$$

The occurrence of such a process, in our opinion (see ([3], [4])), is due to the absence, on the chromium atom in these compounds, of an ionic charge of +2, and on the halogens of negative charges of −1. In fact, the ionicity of the bond in the molecules $CrCl_2$ and $CrBr_2$ is respectively 39 and 33% ([5]), and in the crystalline state (for coordination number 6) 67 and 64%. Hence the total coordination charge on the chromium atom ((5), p. 106) is equal for $CrCl_2$ to:

$$L_k = -(1 - 0.67) \times 6 + 2 = +0.02\,e,$$

for $CrBr_2$

$$L_k = -(1 - 0.64) \times 6 + 2 = -0.16\,e.$$

Since the bond in Cr–S is still more covalent—for molecules the ionicity is 24%, for the crystal 59%—the negative charge on the chromium atom in CrS will be still greater:

$$L_k = -(1 - 0.59) \times 6 + 2 = -0.46\,e.$$

Fig. 1. Thermograms of chromium sulfide and chalcogenosulfides

The latter circumstance leads to the result that, under the action of oxidizing agents, it is first of all, or exclusively, the valence of the metal that must increase.

Fig. 2. Thermogram of the polymorphic transformation of CrS

Fig. 3. IR spectrum of chromium oxysulfide Cr_2S_2O

Figure 1: Fig. 3. IR spectrum of chromium oxysulfide Cr_2S_2O

2. Divalent chromium sulfide was obtained by elemental synthesis. Specifically, accurate weighed portions of chromium and sulfur were placed in a quartz ampoule, which was evacuated, sealed, and placed in an electric furnace. The temperature in the furnace was raised in the usual way to 360°, and then (at a rate of 40° per hour) to a temperature of 480–500°, at which the ampoule was held for 4 hours; then the temperature was likewise slowly raised to 900° and maintained there for 24 hours, after which slow cooling was carried out.

The analysis of chromium sulfide was carried out as follows. A weighed portion of CrS (about 0.1–0.2 g) was fused with Na_2O_2 at 600–700°, then the melt was decomposed with water and the filtrate—a Na_2CrO_4 solution—after addition of hydrochloric acid and potassium iodide, was titrated with thiosulfate. The average value of Cr was 61.08%, as against 61.86% calculated.

The density of the CrS samples obtained in this way was 4.24 ± 0.02 g/cm^3; the X-ray pattern, taken with copper radiation, is given in Table 1.

Fig. 3. IR spectrum of chromium oxysulfide Cr_2S_2O

The incorporation of selenium and tellurium into CrS was carried out by fusing exact quantities of CrS and Se or Te in sealed ampoules at temperatures of 240 and 500°, respectively, for 30 (Se) or 35 (Te) hours. The criterion for completion of the reaction was the unchanging density value, which for the product of combination with selenium is 4.95, and with tellurium 5.58 g/cm^3.

The contents of the ampoules were analyzed for chromium by the method described above; selenium and tellurium were determined in elemental form by the usual procedures ([6]). As a result of the analyses performed:

Found, %: Cr 42.90; Se 32.01
Cr_2S_2Se. Calculated, %: Cr 42.09; Se 31.95

Found, %: Cr 33.90; Te 43.14
Cr_2S_2Te. Calculated, %: Cr 35.17; Te 42.14

Seleno- and tellurosulfides of chromium are black powders, insoluble in water, alkalis, and organic media. In acids these substances dissolve only upon heating; moreover, in the series HCl–H_2SO_4–HNO_3 the solubility increases (is facilitated).

Table 1

X-ray constants of chromium sulfide and chromium chalcogenosulfides

CrS intensity	CrS d/n	Cr_2S_2Se intensity	Cr_2S_2Se d/n	Cr_2S_2Te intensity	Cr_2S_2Te d/n
medium	3.003	medium	3.795	very strong	4.97
strong	2.655	very strong	3.023	strong	4.03
very strong	2.368	medium	2.670	strong	2.926
very strong	2.071	strong	2.380	strong	2.590
very strong	1.935	very strong	2.075	very strong	2.447
strong	1.618	medium	2.001	medium	2.227
weak	1.596	weak	1.763	strong	2.036
very strong	1.445	medium	1.744	strong	1.720
weak	1.328	medium	1.648	very strong	1.643
medium	1.113	medium	1.328	»	1.497
strong	1.056	very strong	1.250	»	1.428
strong	0.9984	very strong	1.190	weak	1.395
medium	0.9760	weak	1.102	very strong	1.363
weak	0.9160	medium	1.078	»	1.320
		weak	0.9962	»	1.291
		weak	0.9754	»	1.259
				»	1.245
				»	1.179
				»	1.087
				»	1.047
				»	0.9814

The X-ray patterns of these substances, taken with copper radiation, are given in Table 1.

It is evident from the data of Table 1 that the substances obtained are individual compounds, although, as can be concluded from comparison of the lines, the selenosulfide has a lattice similar to that of CrS. This circumstance has been noted in analogous cases before, for example in the case of mixed copper compounds ([7]).

The thermograms of chromium seleno- and tellurosulfide are shown in Fig. 1 together with the data for CrS. Comparison of the thermograms again indicates

the individuality of the products synthesized by us.

From the thermogram of the initial chromium sulfide it is evident that this substance has one endothermic effect (330°) and two exothermic effects

(578 and 725°). In accordance with the usual ideas, one may expect that the first effect is due to a phase transformation, and the second to oxidation of the substance. Therefore we heated CrS in air at temperatures of 330, 580, and 730° and investigated the samples treated in this way.

When chromium sulfide is heated for 16 h at the lower temperature, no change in the weight or appearance of the sample occurs. However, its density increased to 4.50 g/cm^3 and the X-ray pattern changed greatly; it is given in Table 1. Thus, here we are dealing with a polymorphic transformation, which is clearly reproduced on thermograms during successive heating and cooling (Fig. 2).

Table 2

X-ray constants of chromium sulfide, oxysulfide, and oxide

β · CrS intensity	β · CrS d/n	Cr_2S_2O intensity	Cr_2S_2O d/n	Cr_2O_3 intensity	Cr_2O_3 d/n
med.	8.36	med.	2.974	med.	3.62
med.	6.92	s.	2.653	s.	2.67
sl.	4.40	v. sl.	2.462	med.	2.17
s./med.	4.076	v. sl.	2.151	v. sl.	2.03
sl.	3.801	v. s.	2.076	med.	1.81
med./s.	3.537	sl.	2.031	v. s.	1.67
v. sl.	3.305	v. s.	1.789	v. sl.	1.58
sl.	2.948	s.	1.716	med.	1.465
v. sl.	2.770	sl.	1.665	med.	1.432
med.	2.640	v. sl.	1.619	sl.	1.294
v. sl.	2.462	» »	1.598	v. sl.	1.236
v. sl.	2.358	» »	1.424	» »	1.209
v. s.	2.066	sl.	1.325	» »	1.172
sl.	2.010	»	1.287	» »	1.148
s.	1.726	»	1.101	» »	1.123
sl.	1.651	»	1.053	sl.	1.087
sl.	1.612			sl.	1.041
v. sl.	1.479			v. sl.	1.025
v. sl.	1.440			v. sl.	0.946
sl.	1.328				
v. sl.	1.296				
sl.	1.103				
sl.	1.049				

Heating at 580° leads to a change in weight, namely to its increase. The increase

in weight proceeds until the composition of the sample reaches the formula Cr_2S_2O, as is also indicated by direct analysis of the product obtained:

Cr_2S_2O. Found, %: Cr 56.48
Calculated, %: Cr 56.52

The density of chromium oxysulfide is 4.57 g/cm^3; its X-ray pattern is given in Table 2 together with the X-ray patterns of chromium sulfide heated at 330° and chromium oxide according to (8).

Comparison of the X-ray patterns shows that the oxysulfide is an individual compound. Recording the infrared spectrum on a UR-10 instrument in the region 400–1000 cm^{-1} made it possible to answer one more question about the chemical structure of the oxysulfide, namely, to determine the presence of a Cr^III–O bond, since the absorption band in the oxysulfide proved to be at the very same position as in pure chromium(III) oxide. There is no reason to speak of an admixture of chromium oxide in the sulfide, since the X-ray pattern of the oxysulfide is completely individual. The spectrum of the oxysulfide is shown in Fig. 3.

Thus, as a result of direct oxidation of CrS we obtained the oxide, seleno-, and tellurosulfides of chromium. These compounds have been characterized by physicochemical methods, and their individuality is beyond doubt. In addition, a phase transformation of chromium sulfide has been found, which it undergoes at a temperature of 330°.

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Note: Figure translations are in progress. See original paper for figures.

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