

the aromatic system by such substitution can be attributed either to poor overlap of the aromatic  $\pi$  system and the  $\pi$  system on the metal or to a more facile change of the carbonyl system in relation to the pentafluorophenyl group.

The values of  $\phi_p$  seem to increase with increased substitution. This is consistent with a reduction in  $\pi$ -acceptor character of the two-electron donors on manganese, causing increased donation to the pentafluorophenyl system.

Of particular interest is the low shielding of the ortho fluorine atoms in these manganese compounds, which in fact exhibit the lowest  $\phi_o$  values of any reported pentafluorophenyl derivatives. A large paramagnetic contribution to the screening is to be expected by analogy with the  $^{19}\text{F}$  nmr results for  $\alpha$ -fluorine atoms present in perfluoroalkylmetal complexes.<sup>15,16</sup> However in contrast to these perfluoroalkyl complexes, pentafluorophenyl derivatives show a higher sensitivity to the electronegativity of the atom to which the perfluoroorganic group is attached.<sup>1</sup>

In a few compounds it was possible to measure the coupling of phosphorus to para fluorine. Thus the para fluorine nmr spectra were observed as triplets of doublets for monosubstituted compounds or as triplets of triplets for disubstituted derivatives. A triplet of triplets would also be expected if  $J_{24}$  were significant and the phosphorus coupling were negligible. We believe, however, that the assignment of the smaller coupling to phosphorus is correct, since  $J_{24}$  was insignificant<sup>17</sup> in all other compounds and the phosphorus coupling was significant in all phosphine and phosphite derivatives which allowed measurement. Taking this assignment as correct, it follows that both phosphorus atoms in the bis(triethyl phosphite) and bis(diphenylphosphino)ethane derivatives are in magnetically equivalent and most probably symmetrically equivalent environments.

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(17) In view of the  $\phi_p$  values and the quite firmly established  $J_{24} - \phi_p$  relationship, a value of  $J_{24}$  close to zero is expected.

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## The Crystal Structure of Lithium Thiochromite, $\text{LiCrS}_2$

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The crystal structures of the alkali thiochromites,

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$\text{MCrS}_2$ , where  $\text{M} = \text{Na}, \text{K},$  and  $\text{Rb}$ , have been studied in some detail and all these compounds are rhombohedral.<sup>3-5</sup> On the other hand, the lithium analog,  $\text{LiCrS}_2$ , was reported to be cubic.<sup>6</sup> Examination of the powder diffraction pattern, especially at the smaller  $d$  spacings, showed deviations from those calculated from a cubic cell, and a structure of lower symmetry was indicated for the lithium compound as well. We have recently grown single crystals of  $\text{LiCrS}_2$ , and a definitive crystal structure determination became possible.

### Experimental Section

**Sample Preparations.**—Both polycrystalline powders and single crystals of  $\text{LiCrS}_2$  were prepared. The powder samples were made by heating dried stoichiometric mixtures of  $\text{Li}_2\text{CO}_3$  and  $\text{Cr}_2\text{O}_3$ , contained in a graphite boat, at  $800^\circ$  in an argon gas flow saturated with  $\text{CS}_2$ . The single crystals were grown under similar conditions but with a  $\text{Li}_2\text{CO}_3:\text{Cr}_2\text{O}_3$  molar ratio of 10:1. This mixture was converted to the sulfides at  $800^\circ$ , the temperature was then rapidly raised to  $1100^\circ$ , the  $\text{CS}_2$ -saturated argon flow was reduced to less than  $1 \text{ cm}^3/\text{min}$ , and the temperature was decreased at the rate of  $10^\circ/\text{hr}$ . Thin hexagonal platelets of  $\text{LiCrS}_2$  remained after the excess  $\text{Li}_2\text{S}$  was washed away with water. The carbon boats used during growth were attacked by the molten  $\text{Li}_2\text{S}$ . A total chemical analysis was not possible because both the powders and the crystals were contaminated with carbon. However, the ratios of chromium to lithium as determined by flame atomic absorption of both polycrystalline and single crystal samples agreed to within 0.6%, averaging 5.9 by weight. This value is in reasonable agreement with the calculated value of 7.5 considering that the mutual interference of these atoms was not investigated. The density of a polycrystalline sample which was least contaminated with carbon, as determined by displacement in  $\text{CCl}_4$  at  $25^\circ$ , was  $3.01 \text{ g/cm}^3$  with a reproducibility of  $\pm 0.04 \text{ g/cm}^3$ . The small amount of sample available and its contamination with carbon precluded high accuracy in the density measurement.

The crystals of  $\text{LiCrS}_2$  are hexagonal platelets with the crystal  $c$  axis normal to the plate. In appearance they are black and reflecting and the surface was unchanged after long exposure to air. Accurate unit cell dimensions were determined by least-squares fit of the back-reflection lines of the X-ray powder photograph obtained at  $25^\circ$  with Ni-filtered  $\text{Cu K}\alpha$  radiation using a 114.6-cm diameter camera. Film shrinkage corrections were made.

**Crystal Data for  $\text{LiCrS}_2$ .**—The crystal data for  $\text{LiCrS}_2$  are as follows: mol wt 123.06; trigonal; space group  $P\bar{3}m1$  or  $P3m1$ ;  $a = 3.456 \pm 0.001 \text{ \AA}$ ,  $c = 6.020 \pm 0.002 \text{ \AA}$ ,  $Z = 1$ ,  $V = 62.60 \text{ \AA}^3$ ;  $d_{\text{calcd}} = 3.26 \text{ g/cm}^3$ ;  $d_{\text{obsd}} = 3.01 \text{ g/cm}^3$ .

Intensity data for the  $h0l$ ,  $h1l$ , and  $h2l$  levels were recorded by the equiinclination Weissenberg method using Ni-filtered  $\text{Cu K}\alpha$  radiation, all possible reflections for this wavelength being included in these levels. A multiple-film technique was used and the reflection intensities were estimated visually by comparison with a standard intensity scale. The crystal used was cut from a platelet parallel to one of the hexagon sides and perpendicular to the plate thickness. It was 0.12 mm long ( $b$  axis) and had an almost square cross section 0.053 mm on edge. Absorption corrections were made using a cylindrical approximation. Since the absorption is large,  $\mu = 516/\text{cm}$ , maximum errors in the approximation used are estimated to be as high as 9% for the reflections most sensitive to the difference between real and assumed crystal shapes, but the average error will be much less than this. A set of  $F$  values was obtained for each level after application of Lorentz and polarization factors and the three sets

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TABLE I  
 STRUCTURAL PARAMETERS FOR LiCrS<sub>2</sub><sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$
Cr	0	0	0		0.082 (11)	0.082	0.0038 (12)	0.041
Li	0	0	1/2	2.3 (1.2)				
S	1/3	2/3	0.2247 (7)		0.069 (10)	0.069	0.0051 (12)	0.034

<sup>a</sup> The temperature factor expressions are  $\exp(-B(\sin^2\theta)/\lambda^2)$  for Li and  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk)]$  for Cr and S.

were brought to a single scale *via* common reflections. This single scale factor was the only one refined.

### Structure Determination and Refinement

The cell dimensions strongly suggest that the structure is based on a close-packed assembly of sulfur atoms, with the metal atoms in octahedral or tetrahedral sites. Such an arrangement allows only four physically reasonable possibilities for the atomic positions and all of these have been investigated. These are as follows. (1) Space group  $P\bar{3}m1$  with Cr in (a) 0, 0, 0; Li in (b) 0, 0, 1/2; 2S in (d)  $\pm 1/3, 2/3, z, z = 1/4$ . (2) Space group  $P3m1$  with Cr in (a) 0, 0,  $z, z = 0$ ; Li in (a) 0, 0,  $z, z \simeq 1/2$ ; S in (b)  $1/3, 2/3, z, z \simeq 1/4$ ; S in (c)  $2/3, 1/3, z, z \simeq 3/4$ . (3) Space group  $P3m1$  with Li in (b)  $1/3, 2/3, z, z \simeq 5/8$ ; Cr and S atoms as in (2). (4) As in (3) with Li and Cr interchanged.

The intensities of the reflections for which  $I_{hkl}$  and  $I_{h\bar{k}\bar{l}}$  were equal (those for which  $h - k = 3n$ ) gave good agreement with the intensities expected for a structure in which chromium and sulfur atoms were located in the same positions as the atoms in the Cd(OH)<sub>2</sub> structure type, that is, the heavier atom positions in structure (1) above or small deviations from these positions in the noncentrosymmetric structures (2) and (3). Structure (4) which involves a radical rearrangement of the heavy scatterers could be ruled out. The structure was first refined using these reflections alone and excellent agreement was obtained with the sulfur parameter  $z = 0.225$  in structure (1). However, for the reflections for which the intensities of  $hkl$  and  $h\bar{k}\bar{l}$  were unequal, the intensity difference observed was always less than that calculated. It was clear that the crystal was twinned at 60° in the (00.1) plane. From a detailed comparison of the observed and calculated intensities for all such reflection pairs a twin factor  $x$  (the ratio of the minor to the major twin) was derived as 0.272 from the equations

$$I_{\text{obsd}}(hkl) = I_{\text{calcd}}(hkl) + xI_{\text{calcd}}(h\bar{k}\bar{l}) - xI_{\text{calcd}}(hkl) \quad (1)$$

$$I_{\text{obsd}}(h\bar{k}\bar{l}) = I_{\text{calcd}}(h\bar{k}\bar{l}) + xI_{\text{calcd}}(hkl) - xI_{\text{calcd}}(h\bar{k}\bar{l}) \quad (2)$$

$$x = \frac{\sum \{I_{\text{obsd}}(hkl) - I_{\text{calcd}}(hkl)\}}{\sum \{I_{\text{calcd}}(h\bar{k}\bar{l}) - I_{\text{calcd}}(hkl)\}}$$

The variations in  $x$  calculated separately for different groups of reflections indicate an accuracy of  $\pm 0.01$ . Substituting  $I_{\text{cor}}$  for  $I_{\text{calcd}}$  in eq 1 and 2 and subtracting eq 2 from eq 1

$$I_{\text{obsd}}(hkl) - I_{\text{obsd}}(h\bar{k}\bar{l}) = (1 - 2x)\{I_{\text{cor}}(hkl) - I_{\text{cor}}(h\bar{k}\bar{l})\}$$

The corrected intensities were obtained by adding to  $I_{\text{obsd}}$ , as shown in eq 1,  $x\{I_{\text{cor}}(hkl) - I_{\text{cor}}(h\bar{k}\bar{l})\} = x/(1 - 2x)\{I_{\text{obsd}}(hkl) - I_{\text{obsd}}(h\bar{k}\bar{l})\}$ . Several crystals were later examined but none showed a smaller degree of twinning than the original crystal although more extensive twinning was observed.

To locate the lithium atom a difference electron density was computed for the space group  $P\bar{3}m1$ . The only outstanding peak ( $4.2 \text{ e}^- \text{ \AA}^{-3}$ ) occurred at the octahedral site 0, 0, 1/2. The highest electron density at a tetrahedral site was only  $0.8 \text{ e}^- \text{ \AA}^{-3}$ . Including the lithium atom at (b) 0, 0, 1/2, the structure was refined using a modified Busing-Levy full-matrix least-squares program. An empirical weighting scheme was used setting  $w = 1/\sigma^2$  with  $\sigma = 0.67 + 0.022F_o$ . The 00.1 reflection which was severely extinguished was omitted from the refinement. Three cycles of isotropic refinement gave  $R = 0.082$  and  $R_w = 0.103$ . This was followed by three cycles of anisotropic refinement for the chromium and sulfur atoms while the lithium atom was kept isotropic. Convergence was achieved with  $R = 0.068$  and  $R_w = 0.080$ . According to Hamilton's test<sup>7</sup> the anisotropic temperature factors give results significantly better at the 0.005 level. The refined structural parameters with their standard deviations are given in Table I and the final calculated and observed structure factors in Table II. The scattering

 TABLE II  
 OBSERVED AND CALCULATED STRUCTURE FACTORS  
 FOR LiCrS<sub>2</sub><sup>a</sup>

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
00.0	-	59.66	22.1	7.53	6.15	10·-1	34.04	33.83
*00.1	18.32	24.78	10.0	8.90	8.37	10·-2	32.18	32.34
00.2	3.72	-2.27	10.1	3.91	-4.94	10·-5	13.11	12.44
00.3	5.48	5.83	10.2	20.83	21.63	10·-6	20.64	20.21
00.4	26.41	27.73	10.3	28.36	29.64	10·-7	7.73	7.32
00.5	20.34	20.26	10.4	14.87	14.33	20·-1	4.99	-3.38
00.6	3.03	2.54	10.5	3.52	-3.50	20·-2	13.40	14.31
00.7	2.74	-2.19	10.6	5.18	4.07	20·-3	19.56	21.51
11.0	33.65	31.10	10.7	15.26	14.92	20·-4	9.19	10.34
11.1	13.99	14.19	20.0	5.97	5.25	20·-5	3.52	-3.30
11.3	3.91	3.31	20.1	22.89	21.49	21.0	4.01	3.11
11.4	18.88	20.28	20.2	22.69	21.77	21.2	10.27	10.53
11.5	15.36	15.49	20.5	9.49	9.54	21.3	14.48	16.85
11.6	2.35	1.58	20.6	17.51	16.03	21.4	6.55	7.92
30.0	18.49	17.53	21·-5	7.92	7.59	21.5	3.91	-2.92
30.1	6.61	7.71	21·-2	17.12	16.49	31.1	11.54	10.72
30.4	11.25	12.72	31·-2	5.87	6.71	31.2	4.78	10.81
22.0	13.79	14.08	21·-1	18.29	16.22			

<sup>a</sup> Cu K $\alpha$  radiation.  $F_o$  for one formula unit;  $F_c$  scaled to  $F_o$ .

factors used are those given in ref 8 corrected for anomalous dispersion.<sup>9</sup> The thermal ellipsoids for both the chromium and sulfur atoms are compressed along

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the  $c$  axis with axial ratios of 2.3 and 1.8, respectively. In a refinement in which the weights of the reflections which had been modified by the twin factor were reduced by a factor of 2, these axial ratios both changed to 1.9. Thus the thermal parameters are at least not drastically sensitive to the twin factor correction, but this and the approximate absorption corrections are possible sources of systematic errors and the standard deviations should be regarded as minimal.

In view of the low scattering power of the lithium atom efforts were made to establish its position more conclusively. Structure (3), with lithium in a tetrahedral site of space group  $P\bar{3}m1$  gave  $R = 0.104$  and  $R_w = 0.136$ . Refinement of this structure increased the lithium (isotropic)  $B$  to  $43.8 \text{ \AA}^2$  in three cycles showing conclusively that this site was incorrect. Refinement with no lithium in the structure converged with  $R = 0.083$  and  $R_w = 0.103$ . The structure with lithium in the octahedral site is thus preferable at better than the 0.005 significance level. Structure (2) in which the atoms are essentially in the same positions as structure (1) but with small deviations resulting in a noncentrosymmetric arrangement was tested by refinement in the space group  $P\bar{3}m1$ . Changes in positional parameters were all less than  $1.5\sigma$  indicating that the space group is  $P\bar{3}m1$  within experimental error, although, as in any structure, small deviations to lower symmetry may exist below this level.

### Discussion

Our samples were prepared at higher temperatures and under different conditions from those used by Sergent and Prigent. There is a possibility that we may have obtained a different high-temperature form of  $\text{LiCrS}_2$ , but we feel that our material and theirs are of the same phase. First, the X-ray patterns of slowly cooled powders and single crystals were identical and there was no sign of a crystallographic change. The possibility of cubic indexing of the powder pattern arises from the fact that the  $c/a$  ratio is almost exactly  $\sqrt{3}$ . Second, the molar susceptibility of a powder sample at  $4.5^\circ\text{K}$  was  $8 \times 10^{-3}$ , which agrees well with a value extrapolated from high temperatures as measured by Sergent and Colin.<sup>10</sup>

The structure found for  $\text{LiCrS}_2$  is derived from that of the NiAs type by an ordering of the lithium and chromium atoms in the octahedral sites. The strong tendency of chromium to occupy octahedral sites is well known, while in different structures lithium occupies either octahedral or tetrahedral sites. The interatomic distances found are as follows: Cr-S, 2.415 (3)  $\text{\AA}$ ; Li-S, 2.597 (4)  $\text{\AA}$ ; Li-Cr, 3.010  $\text{\AA}$ . The ionic radii for  $\text{Li}^+$  and  $\text{Cr}^{3+}$  are 0.60 and 0.64  $\text{\AA}$ , respectively, while the corresponding metallic radii are 1.58 and 1.29  $\text{\AA}$ .<sup>11</sup> Since the Li-S distance is 0.18  $\text{\AA}$  greater than the Cr-S distance, some degree of metallic character is indicated. However, from the fact that the Li-Cr distance is 0.14  $\text{\AA}$  greater than the sum of the metallic radii, it appears

that there is no direct interaction between these two atoms. This is in agreement with the high resistivity measured for  $\text{LiCrS}_2$ .<sup>10</sup>

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## Circular Dichroism of Alkaline Copper(II) $d$ -Tartrate Complexes

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Circular dichroism and anomalous rotatory dispersion, phenomena jointly known as the "Cotton effect," were first discovered in alkaline solutions of copper  $d$ -tartrate.<sup>1</sup> However, no systematic circular dichroism investigation of these solutions has previously been made. A wide variety of alkaline copper  $d$ -tartrate complexes have been proposed as the result of investigations by potentiometry,<sup>2-6</sup> optical rotation,<sup>2-4</sup> visible spectroscopy,<sup>7</sup> and esr.<sup>8</sup>

Because of its high stereochemical specificity circular dichroism has been previously found to have utility in elucidating the structure of copper complexes of amino acids<sup>9</sup> and dipeptides.<sup>10</sup> In this note three alkaline copper  $d$ -tartrate complexes have been verified and characterized by circular dichroism. From their diverse Cotton effect behavior deductions are made concerning the modes of chelation involved.

### Experimental Section

All chemicals were reagent grade and were used as received. Solutions for optical measurements were prepared from standardized  $\text{Cu}(\text{ClO}_4)_2$  and  $d$ -tartaric acid solutions with final pH levels adjusted by NaOH addition.

CD measurements in the 200-650-nm range were made on a Durrum JASCO ORD/UV/5 dichrograph and in the 650-1000-nm range on a Shimadzu QV-50 instrument. A Cary Model 15 spectrophotometer was employed for the absorption spectra. Values of  $\epsilon$  and  $\Delta\epsilon$  were calculated by the standard definitions and are based on the concentration of  $\text{Cu}(\text{II})$ .

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