Roth, and Martin[3] included the In and Mn systems but was not extended to Cr.

Experimental

Mixtures of 30 g. of H_3BO_3 (A.R. grade), 0.3 g. of Cr_2O_3 ("Purified" grade), and 0.3 g. of $CaCO_3$ (A.R. grade) were heated cautiously in a platinum dish to dehydrate the H_3BO_3. The dish containing the anhydrous melt was then heated in a Globar furnace to the selected temperature inside a deep cylindrical mullite container which was covered by a mullite lid. After cooling, the melt was extracted by prolonged boiling in water.

Reaction for 12 hr. at 1100° gave almost complete conversion to a green crystalline material (I), having a consistent X-ray pattern different from that for Cr_2O_3. Crystals up to about 0.1 mm. on a side were obtained. The faces were well developed and not etched by the boiling water treatment. In some samples a few faint X-ray reflections were noted for Cr_2O_3 and $CaCO_3$ (calcite). The latter could be eliminated by treatment with dilute HCl.

Reaction for 12 hr. at 1175° gave a similar result, but at 900° only slight conversion to I occurred; at 1250° only Cr_2O_3 was obtained.

Subsequent experiments showed that the addition of $CaCO_3$ to the reaction mixture was not essential for the formation of I, although the reaction and crystallization rates were increased by this addition. $CaSO_4$ appeared to be of comparable effectiveness as a "mineralizer." Decrease of the H_3BO_3 content by a factor of 10 did not modify the results.

X-Ray diffraction powder data (Table I) were obtained for I using a Norelco diffractometer with Cu Kα radiation (λ = 1.5405 Å.). The reflections have been indexed in terms of a hexagonal unit cell (calcite or $NaNO_3$-type structure) with a_0 = 4.5775 Å., c_0 = 14.258 Å. The space group is $R\bar{3}c$ (D_{3d}^6). Emission spectrographic analysis showed only chromium and boron as major constituents. *Anal.* Calcd.: Cr, 46.94. Found: Cr, 45.8. Using the stoichiometry $CrBO_3$ and six formula weights per hexagonal unit cell (from the $NaNO_3$ structure), the calculated density is 4.270 g./cc. This compares favorably with the experimental density 4.2 g./cc. determined with a Beckman air pycnometer.

Index of refraction measurements on I using the Na D line were unsuccessful because of the intense green color of the crystals. Using a mercury source with a green filter a value greater than 2.0 was indicated. This rather high value is consistent with calculations based on refraction data for Cr_2O_3 and B_2O_3.

Differential thermal analysis experiments on I showed an endothermic peak at 1220° (heating). This was irreversible. X-Ray examination of the material after cooling showed that Cr_2O_3 was the only crystalline phase.

TABLE I
CALCULATED AND OBSERVED *d*-SPACINGS AND OBSERVED INTENSITIES FOR $CrBO_3$

hkl	*I* obsd.	*d* obsd., Å.	*d* calcd., Å.
012	92	3.46	3.464
104	100	2.651	2.651
110	19	2.288	2.288
113	42	2.062	2.062
202	27	1.909	1.909
024	17	1.732	1.732
116	33	1.648	1.649
018	16	1.625	1.626
122	18	1.466	1.466
214	14	1.381	1.381
1·0·10	3	1.342	1.342
208	7	1.325	1.325
300	20	1.3212	1.3214
119	4	1.3026	1.3026
00·12	3	1.1882	1.1881
0·2·10	4	1.1574	1.1574
128	6	1.1469	1.1468
220	6	1.1443	1.1443
312	4	1.0866	1.0866
1·1·12	3	1.0546	1.0545
134	8	1.0506	1.0506
2·1·10	4	1.0329	1.0328
226	6	1.0310	1.0310
404	5	0.9548	0.9548
318	6	.9356	.9357
2·0·14	2	.9058	.9059
232	5	.9019	.9021
3·0·12	8	.8833	.8835
324	6	.8811	.8812
1·0·16	2	.8692	.8694

Discussion

The present results show that, below 1220°, Cr_2O_3 and B_2O_3 react in a melt containing excess B_2O_3 to form a stable compound (I) identified as chromium borate, $CrBO_3$. Previous failure to obtain this simple compound can be attributed in part to ready volatilization of B_2O_3 near 1000°. This will rapidly deplete the B_2O_3 content of any near-equimolar mixture of Cr_2O_3 and B_2O_3. The decomposition of $CrBO_3$ at 1220° also limits the temperature range over which it might have been obtained. Even below 1220° the vapor pressure of B_2O_3 over $CrBO_3$ at high temperatures may be appreciable. At room temperature $CrBO_3$ is stable in air and unaffected by boiling water or by most acids. Decomposition occurs in fused alkali, as might be expected.

The occurrence of $CrBO_3$ as a hexagonal calcite-type structure is consistent with the structure-type boundaries, in relation to ionic radius, reported for borates by Levin, Roth, and Martin.[3]

Acknowledgment.—The assistance of J. R. Carter and J. F. Fitzgerald is gratefully acknowledged.

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[3] E. M. Levin, R. S. Roth, and J. B. Martin, *Am. Mineralogist*, **46**, 1030 (1961).

CONTRIBUTION FROM THE CRYSTALLOGRAPHY LABORATORY,
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Single Crystal Studies on Some Clathrates of Tetra-(4-methylpyridine)-nickel(II) and Cobalt Dithiocyanates[1]

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This note reports and discusses the crystal data from single crystals of some clathrate compounds of tetra-(4-methyl pyridine)-nickel(II) and cobalt(II) dithiocyanates previously described by Hart and Smith.[3] The compounds were prepared as described in their

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[1] This research was aided by a grant from the Office of Saline Water, U. S. Dept. of the Interior.

[2] On leave from the University of New South Wales, Australia.

TABLE I
CRYSTAL DATA

	Compound	Obsd. density, g. cm.$^{-3}$	Cell dimensions a, Å.	Cell dimensions c, Å.	Cell dimensions V, Å.^{3}	Host molecules per unit cell	Guest molecules per unit cell	Mole ratio guest/complex	Magnetic moment, B.M.
Host	$Ni(4\text{-mepy})_4(SCN)_2$								
Guest	CH_3OH	1.17	16.72	22.73	6354	8	4.2	0.53	
	$C_2H_5NO_2$	1.24	16.69	22.67	6315	8	5.4	.67	
	C_6H_6	1.27	16.76	22.74	6388	8	6.6	.83	
	$C_6H_5NO_2$	1.30	16.73	22.97	6429	8	5.4	.67	
	$p\text{-}C_6H_4(CH_3)_2$	1.26	16.79	22.40	6314	8	4.2	.53	3.04[3]
	$p\text{-}C_6H_4Cl_2$	1.34	16.74	22.76	6377	8	5.5	.69	3.05[3]
Host	$Co(4\text{-mepy})_4(SCN)_2$								
Guest	C_6H_6	1.26	16.68	23.14	6438	8	4.5	.57	
	$C_2H_5NO_2$	1.24	16.53	22.73	6211	8	5.4	.67	

paper. Beautiful blue octahedral crystals of the tetra-(4-methylpyridine)-nickel(II) dithiocyanate clathrate were obtained from nitroethane, methanol, benzene, and nitrobenzene by allowing the solutions saturated at room temperature to stand in a refrigerator at 5° for a few days. Pink octahedral crystals of the corresponding cobalt(II) compound were crystallized from benzene and nitroethane in a similar manner.

It is interesting to note that for those clathrates that contain guest components which are solids at room temperature or which do not dissolve the host complex, the guest molecules can be introduced into the lattice by an exchange reaction between the benzene clathrate and the desired guest dissolved in *n*-hexane and the replacement occurs without a morphological change in the clathrate crystals.

X-Ray diffraction photographs of the single crystals were obtained on a precession instrument with Mo Kα radiation and on a Weissenberg instrument with Cu Kα radiation. To avoid the noticeable decrepitation of the crystals, those used for X-ray examination were coated with a thin layer of silicone grease. The crystal densities were measured by the flotation method using a mixture of *n*-hexane and carbon tetrachloride. The magnetic moments in Table I are those reported by Hart and Smith.[3] We remeasured the value for the nickel host complex on a Gouy type balance, at room temperature, and obtained a value of 3.01 B.M., in agreement with their value of 3.07 B.M.

All the nickel and cobalt clathrated compounds were isomorphous. The diffraction data showed the Laue symmetry 4/m and spectra present only for (hkl) with $h + k + l = 2n$, $(hk0)$ with $h = 2n$ and $k = 2n$, $(h00)$ with $h = 2n$, $(00l)$ with $l = 4n$. The space group is therefore $I4_1/a$. The unit cell dimensions, observed densities, and calculated number of molecules in the unit cell are given in Table I. The number of guest molecules and the mole ratio of guest to complex are calculated from the observed data with the assumption that there are always eight host molecules per unit cell.

A host framework structure of eight molecules of $\{Co,Ni\}(4\text{-}CH_3C_5NH_4)_4(SCN)_2$ per unit cell is compatible with the dimensions and symmetry of the crystal lattice. If the metal atoms occupy the space group fourfold positions (a) and (b) or the eightfold positions (e), they will be tetrahedrally coördinated. In the eightfold positions (c) and (d) they would have a square-planar, or a regular or distorted octahedral coördination. The magnetic data eliminate the square-planar complex. They favor the regular or distorted octahedral coördination, since the observed values for the Ni(II) compounds are closer to the octahedral d_8 spin-only value of 2.83 B.M. than to that expected for a tetrahedral complex, which should be much greater than 2.83 B.M.

On the basis of eight molecules of the complex forming the unit cell of the host lattice, the number of guest molecules can be calculated from the observed density to an accuracy of about 2%. The mole ratio of guest to complex is found to be significantly less than 1:1, and it approaches this stoichiometry only in the case of the benzene compound. This is contrary to the

TABLE II
INTERPLANAR DISTANCES (Å.) FOR THE MORE PROMINENT REFLECTIONS FROM THE *p*-XYLENE AND *p*-DICHLOROBENZENE CLATHRATES, AND THE LATTICE PARAMETERS FROM THESE DATA, DERIVED BY ITERATIVE LEAST SQUARES ANALYSES[a]

p-Dichlorobenzene clathrate			*p*-Xylene clathrate		
hkl	d_{calcd}	d_{obsd}[3]	*hkl*	d_{calcd}	d_{obsd}[3]
200	8.37	8.63 s	101	13.43	13.34 m
301	5.42	5.41 m	200	8.39	8.36 vs
114	5.13	5.14 m	211	7.12	7.14 s
312	4.80	4.93 w	301	5.43	5.41 s
204	4.71	4.70 m	222	5.24	5.23 s
224	4.10	4.05 w	312	4.80	4.86 w
411	4.00		204	4.66	4.60 s
402	3.93	3.94 s	321	4.56	
314	3.87	3.87 m	411	4.01	4.02 w
332	3.72	3.67 s	323	3.95	3.95 m
116	3.61		215	3.85	3.80 m
107	3.19	3.19 w	420	3.75	
512	3.15	3.15 w	413	3.57	3.65 s
521	3.08	3.08 w	116	3.56	3.62 m
			422	3.56	3.61 m
			501	3.32	3.32 w
			325	3.22	3.19 w
			226	3.16	

p-Dichlorobenzene clathrate:
$a = 16.737 \pm 0.028$ Å.
$c = 22.762 \pm 0.086$ Å.

p-Xylene clathrate:
$a = 16.791 \pm 0.026$ Å.
$c = 22.395 \pm 0.199$ Å.

[a] We are grateful to Dr. H. Evans, U. S. Geological Survey, Washington, D. C., for the least squares computation of the lattice parameters from the powder data given in this table.

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(3) M. I. Hart and N. O. Smith, *J. Am. Chem. Soc.*, **84**, 1816 (1962).

deductions of a 1:1 molar composition from the thermodynamic study of the *p*-xylene and *p*-dichlorobenzene $Ni(4\text{-mepy})_4(SCN)_2$ by Hart and Smith.[3] Using our single crystal data, we were able to satisfactorily interpret the powder data given in their paper, as shown in Table II. There is no doubt that the clathrate lattice was the same in both investigations.

It was not possible to identify the powder data for the unclathrated complex on the basis of the tetragonal cell of the clathrates and this supports Hart and Smith's conclusion that the clathrated and unclathrated complexes have different crystal structures.

CONTRIBUTION FROM THE GENERAL CHEMICAL DIVISION,
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Dichlorofluoramine[1]

BY BERNARD SUKORNICK, RICHARD F. STAHL,
AND JOSEPH GORDON

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The recent preparation of chlorodifluoramine[2] raised the question of the existence of its more highly chlorinated analog, dichlorofluoramine. We now wish to report the synthesis and characterization of this compound.

Experimental

In a 0.25-in. diameter copper U-tube surrounded by an ice bath was placed 15.0 g. (0.23 mole) of powdered sodium azide. Chlorine monofluoride, diluted with nitrogen, was passed over the solid for 8 hr. at the rate of 2.4 g. (0.044 mole) per hour. During the first 30 min. of reaction, chlorine azide formed almost exclusively. Thereafter, $FNCl_2$ appeared as the major product accompanied by small quantities of F_2NCl. The latter two gases were collected in a −80° trap. Subsequent distillation through an all-metal still equipped with a vapor-phase take-off provided 3.6 g. (20%) of $FNCl_2$, b.p. −2 to −3°. *Anal.* Calcd.: F, 18.28; Cl, 68.24; N, 13.48. Found: F, 18.13; Cl, 68.10; N, 13.47.[3]

The mass spectrum of dichlorofluoramine, obtained on a Consolidated Electrodynamics Model 21–103 mass spectrometer, is given in Table I. The cracking pattern provides strong corroborative evidence for the postulated structure. In particular, observation of the proper chlorine isotope effect for the parent peak confirms its identity.

The absence of any significant parent peak for NF_2Cl would indicate that the sample was relatively free of this compound.

One band was observed in the F^{19} n.m.r. spectrum of dichlorofluoramine. From the data given in Table II, it can be seen that this signal lies very close to the F^{19} chemical shifts for NF_3 and NF_2Cl. Therefore, it is quite likely that the N–F bonds in all three compounds are closely related electronically.

The infrared spectrum of dichlorofluoramine contains two strong bands at 12.0 and 12.2 μ. Both bands lie well within the N–F stretching region, although the one at 12.0 μ is probably best identified with the N–F stretch in $FNCl_2$.

The compound absorbed at 2700 Å. in the ultraviolet. On exposure to a 360-watt high pressure mercury ultraviolet lamp, $FNCl_2$ partially decomposed to *cis*-difluorodiazine and, presumably, chlorine.

TABLE I

FRAGMENTATION PATTERN OF $NFCl_2$

m/e	Ion	Relative intensity
14	N^+	16.8
19	F^+	5.2
24.5	NCl^{+2}	0.80
25.5		0.28
33	NF^+	17.5
49	NCl^+	100
51		32.2
68	$NClF^+$	77.9
70		
84	NCl_2^+	1.6
86		1.1
88		0.19
103	NCl_2F^+	1.68
105		1.05
107		0.20

TABLE II

F^{19} N.M.R. AND INFRARED SPECTRA OF SOME N–F COMPOUNDS

Compound	F^{19} chem. shift, p.p.m.[a]	Principal N–F str. bands, μ
NF_3	-145 ± 1	9.7, 11.0
NF_2Cl[1]	-140.6	10.8, 11.7
$NFCl_2$	-128.7	12.0

[a] Measured relative to $CFCl_3$.

Small quantities of dichlorofluoramine also are formed by the reaction of chlorine azide and chlorine monofluoride. This fact, together with the initial formation of chlorine azide from sodium azide and chlorine monofluoride, suggests that ClN_3 is an intermediate in the formation of $FNCl_2$ *via* the NaN_3–ClF reaction

$$NaN_3 + ClF \longrightarrow ClN_3 + NaF$$
$$ClN_3 \longrightarrow [ClN\!<] + N_2$$
$$[ClN\!<] + ClF \longrightarrow FNCl_2$$

At present, however, there is no clear-cut evidence for the existence of the postulated chlorazene intermediate, ClN<.

Milligan[4] photolyzed samples of chlorine azide trapped in an argon matrix at 4.2°K. He attributed the appearance of infrared absorptions at 818 and 824 cm.$^{-1}$ on irradiation and the disappearance of these bands on warming to the formation and decomposition of chlorazene. Dimerization of ClN< also was suggested, but no dichlorodiazene, ClN=NCl, could be isolated.

Although no explosions have been encountered in handling gaseous $FNCl_2$, the liquid is extremely sensitive to friction and shock.

Acknowledgment.—We wish to thank Miss Rita Juurik for the elemental analyses.

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[1] This work was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Alabama, under Contract No. DA-30-069-ORD-2638.

[2] R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

[3] Chlorine and fluorine analyses were obtained by reaction with sodium in liquid ammonia at 25° for 148 hr. Nitrogen was determined by a modified Dumas method.

(4) D. E. Milligan, *J. Chem. Phys.*, **35**, 372 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A Silicon Metal Trap for the Safe Disposal of Chlorine Trifluoride

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The standard disposal method for chlorine trifluoride involves the use of a soda lime tower.[1,2] The chlorine