TABLE I
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES[a]

hkℓ	$\|F_o\|$	$F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$
000	--	68.0	$31\bar{3}$	8.9	9.4	$4\bar{1}\bar{3}$	8.1	7.6
100	24.6	20.9	$3\bar{1}\bar{1}$	13.7	12.9	420	7.4	7.2
$10\bar{1}$	36.9	36.3	$3\bar{1}\bar{2}$	12.8	12.9	421	4.8	6.6
110	28.3	22.7	320	8.0	9.9	422	8.2	5.4
$11\bar{1}$	25.9	24.2	321	9.8	9.9	$42\bar{1}$	5.3	6.1
200	21.6	21.1	$32\bar{1}$	10.5	12.0	$42\bar{3}$	8.6	6.1
$20\bar{1}$	18.6	19.4	$32\bar{2}$	11.1	11.3	$4\bar{2}\bar{2}$	9.0	7.1
$20\bar{2}$	16.6	17.0	$3\bar{2}\bar{2}$	13.0	12.1	$4\bar{2}\bar{3}$	8.0	5.9
210	24.7	20.6	330	6.3	7.7	431	4.9	4.6
211	15.9	14.6	331	5.3	6.8	500	3.7	5.8
$21\bar{1}$	14.4	14.7	332	9.2	5.9	$50\bar{1}$	5.7	6.3
$21\bar{2}$	20.0	20.1	$33\bar{1}$	5.8	6.2	$50\bar{2}$	6.0	5.8
$2\bar{1}\bar{1}$	18.9	20.2	400	10.1	10.9	$50\bar{3}$	3.7	4.6
220	14.7	14.4	$40\bar{1}$	7.5	8.8	510	5.2	5.1
221	14.9	13.3	$40\bar{2}$	8.7	8.7	$51\bar{1}$	6.5	5.7
222	10.3	10.5	$40\bar{3}$	5.8	5.9	$51\bar{2}$	5.2	4.8
$22\bar{1}$	12.6	16.9	$40\bar{4}$	6.6	6.4	$51\bar{4}$	4.8	3.2
$22\bar{2}$	16.6	16.7	410	7.0	8.4	$5\bar{1}\bar{3}$	5.9	4.5
300	13.1	13.2	411	9.3	7.7	520	7.8	4.8
$30\bar{1}$	13.4	15.5	$41\bar{1}$	8.2	9.3	521	5.8	4.1
$30\bar{2}$	12.0	12.2	$41\bar{2}$	7.3	8.9	$52\bar{1}$	6.0	4.8
$30\bar{3}$	12.2	11.7	$41\bar{3}$	10.0	6.5	$52\bar{2}$	7.0	4.5
310	13.8	13.9	$41\bar{4}$	4.4	4.5	$5\bar{2}\bar{3}$	4.0	3.8
311	12.2	11.8	$4\bar{1}\bar{1}$	9.9	10.0	531	5.6	4.9
$31\bar{1}$	12.2	13.7	$4\bar{1}\bar{2}$	9.2	8.0	$61\bar{2}$	4.3	3.2
$31\bar{2}$	9.5	9.8						

[a] Rhombohedral indexing.

TABLE II
ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS[a]

Rhombohedral cell

	x_r	y_r	z_r	β	
Ga	0	0	0	2.0 ± 0.4	∥ 3-fold axis
				6.1 ± 1.1	⊥ 3-fold axis
N	0.294 ± 0.015	0.294	0.294	10.9 ± 3.8	
C	0.462 ± 0.016	0.462	0.215 ± 0.013	10.1 ± 1.8	

Monoclinic cell: (0,0,0; $^1/_2$, $^1/_2$, 0) +

	x_m	y_m	z_m
Ga	0	0	0
N	0.294	0	0.294
C	.462	0	.215
2C′	.339	±0.124	.462

[a] Standard deviations are explicitly stated for the symmetrically independent parameters only.

molecules per unit cell and belonging to space group $Cm(C_s^3)$, with

$$a_m = 7.08\ \text{Å.} = a_r + b_r$$
$$b_m = 9.46\ \text{Å.} = -a_r + b_r$$
$$c_m = 5.91\ \text{Å.} = c_r$$
$$\beta_m = 118°35'$$

The standard deviations given in Table II were estimated by dividing the set of 75 independent $F_o(hkl)$'s into three parts of 25 each, refining each part separately, and analyzing the spread of the resulting values of the parameters. The high values of the standard deviations reflect the loss of accuracy generally experienced in light-atom parameters in the presence of heavy atoms, as well as the quantitative and qualitative shortcomings of the available experimental data.

The gallium–gallium distance (5.91 Å.) and the fact that the structure contains only one Ga per lattice point preclude a hydrogen-bridge structure and thus confirm previous conclusions. The Ga–N distance 1.97 Å. with an estimated standard deviation of ±0.09 Å. is slightly larger than 1.94 Å. reported for this distance in gallium nitride.[11] Because of the large uncertainty in our Ga–N distance, firm conclusions cannot be drawn from this difference; however, it is noteworthy that the B–N distance in trimethylamine boron trifluoride (1.585 Å.)[12] is longer than in cubic boron nitride (1.565 Å.).[13] The compound $((CH_3)_3N)_2AlH_3$ has been investigated and found to have a linear N–Al–N skeleton with an Al–N bond distance of 2.18 Å.,[14] which is longer than that found for Ga–N in this study. This result is consistent with the similarity of gallium and aluminum covalent radii coupled with the unstable five-coordinated structure of bistrimethylamine alane.

Finally, the average N–C distance, 1.47 ± 0.06 Å., and C–N–C angle, 105 ± 10°, are, within their limits of accuracy, consistent with previous observations on the trimethylamine addition compound of boron trifluoride.

Acknowledgment.—Work performed at the University of Michigan was supported by the National Science Foundation, while that at Northwestern University was sponsored by the Advanced Research Projects Agency of the Department of Defense through the Northwestern Materials Research Center.

D. F. S. wishes to thank Dr. K. Nakatsu for frequent advice and S. Shriver for assistance with the calculations.

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Preparation of Nitryl Fluoride[1]

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Received May 10, 1963

Since Moissan and Lebeau[2] first claimed to have prepared nitryl fluoride in 1905, many improved methods for the preparation of this compound have been developed and the literature pertaining to the various methods has been excellently reviewed.[3,4]

Although Ruff, Menzel, and Neumann[5] prepared

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(1) This work was supported by the Advanced Research Projects Agency under Contract AF 33(616)-6149, ARPA Order 24-61, Project Code 9100.

(2) H. Moissan and P. Lebeau, *Compt. rend.*, **140**, 1621 (1905).

(3) G. Hetherington and P. L. Robinson, "Recent Aspects of the Chemistry of Nitrogen," Special Publication No. 10, The Chemical Society, London, 1957, p. 23.

(4) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).

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nitryl fluoride by the reaction of fluorine with nitrogen dioxide, Hetherington and Robinson[3] found this method to be unsuitable because the highly exothermic reaction, often accompanied by a flame, yields a mixture of oxyfluorides contaminated with silicon tetrafluoride. Aynsley, *et al.*,[6] developed a simpler method of preparation in which anhydrous sodium nitrite was allowed to react with elemental fluorine in glass equipment. Although a nearly quantitative yield of nitryl fluoride was obtained, it was again necessary to control the reaction temperature by adjusting the fluorine flow. This was required to prevent the nitrogen dioxide, formed as an intermediate, from burning with a hot, yellow flame in the fluorine and causing considerable glass attack.

We have found that nitryl fluoride may be prepared very readily in high yields by passing nitrogen dioxide over a stirred bed of cobaltic fluoride at 300°. The crude product obtained in an 89.5% yield based on N_2O_4 was essentially pure nitryl fluoride containing only trace amounts of nitrogen dioxide. The cobalt difluoride formed in the reactor was reconverted to the trifluoride by treatment with fluorine.

As shown, this reaction, unlike the method of Aynsley and co-workers,[6] utilizes the fluorine quantitatively.

$$N_2O_4 + 2CoF_3 \longrightarrow 2FNO_2 + 2CoF_2$$

$$2CoF_2 + F_2 \longrightarrow 2CoF_3$$

An attempt to prepare nitrosyl fluoride by passing nitric oxide over heated cobaltic fluoride was unsuccessful. Either the nitric oxide or the expected product reacted completely with the cobalt fluoride, perhaps to form an addition compound, and no gaseous products were obtained.

Experimental

Nitrogen dioxide (40 g., 0.85 mole) was passed over a stirred bed of cobaltic fluoride (9 moles) at 300° during 30 min. The stirred monel reactor was identical with that described by Barbour, Barlow, and Tatlow.[7] Crude FNO_2 (50 g., 0.77 mole) was collected in liquid nitrogen-cooled traps.

The crude product was distilled from a copper flask held at −60 to −65° through copper tubing into a copper receiver maintained at −78°. The product (43 g.) distilled into the receiver. About 5 g. of product remained in the distillation flask, mainly in the vapor phase.

Anal. Calcd. for FNO_2: N, 21.6; F, 29.2. Found: N, 21.6; F, 28.6.

Attempts to determine the molecular weight of the FNO_2 were hindered by the very fast reaction of the product with the glass equipment.

The cobalt difluoride formed in the reactor was reconverted to the trifluoride by treatment with fluorine. The temperature of the reactor was maintained at 300° during this operation. The regeneration cycle was considered completed when the exit gases from the reactor would ignite cotton linters.

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[6] E. E. Aynsley, G. Hetherington, and P. L. Robinson, *J. Chem. Soc.*, 1119 (1954).

[7] A. K. Barbour, G. B. Barlow, and J. C. Tatlow, *J. Appl. Chem.*, **2**, 127 (1952).

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Metal–Olefin Compounds. III. Some Compounds of Copper(I) Containing Cyclic Olefins[1]

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Received May 11, 1963

The reactions of copper(I) chloride and copper(I) bromide with olefinic and acetylenic hydrocarbons have received considerable attention[3,4] because of the similarity to the silver(I)–olefin complexes and possible commercial applications involving the separation of olefins *via* the formation of copper(I) compounds. Recent interest[5,6] in the copper–olefin compounds has been focused on the preparation of compounds containing cyclic olefins; however, very little information exists on the structures[7-9] of these compounds.

Our continuing interest in the properties and structures[10] of metal–olefin compounds prompted us to prepare a series of copper(I)–olefin compounds. An examination of the previously reported methods for the preparation of these compounds indicated that the products formed were polycrystalline materials unsuitable for single crystal X-ray diffraction studies or finely divided powders of poorly defined stoichiometry. We have found that suitable crystalline products can be isolated by treating an ethanol solution containing the appropriate copper(II) halide and an olefinic compound[11] with sulfur dioxide.

This procedure is particularly adaptable to the isolation of complexes containing cyclic polyolefins; however, cyclic monoolefins such as cyclohexene, cycloheptene, and cyclooctene also yield complexes. The complexes containing monoolefins were relatively unstable and reliable analytical results could not be obtained on this series.

Several factors have been noted that influence the composition, purity, yield, and crystallinity of the product isolated from this procedure. The quantity of ethanol used as a solvent appears to directly influence

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[1] For the previous paper in this series, see *J. Am. Chem. Soc.*, **83**, 2768 (1961).

[2] To whom communications concerning this paper should be addressed.

[3] R. N. Keller, *Chem. Rev.*, **28**, 229 (1941).

[4] M. A. Bennett, *ibid.*, **62**, 611 (1962), and references cited therein.

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[8] J. H. van den Hende, Abstracts, Annual Meeting, Am. Cryst. Assoc., 1962, p. 36.

[9] J. H. van den Hende and W. C. Baird, *J. Am. Chem. Soc.*, **85**, 1009 (1963).

[10] The structures of several of the copper(I)–olefin compounds have been or are currently under investigation and the results of these studies will be reported in the near future.

[11] After completion of this phase of the problem, another preparative method was reported by Schrauzer and Eichler.[6] This technique has not been investigated by us as to suitability for preparing crystalline complexes of copper(I)–olefins for X-ray diffraction procedures.