$A_{Br}=51$ ohm^{-1} cm^{-2} and $A_{PF_6}=92$ ohm^{-1} cm^{-2}. It is suggested, therefore, that the long apical Ni–Br bond length in complex (II) compared to the Ni–Br bond length of complex (I) is caused by the partial ionic character of this bond.

Conclusions

The determination of the structures of complexes (I) and (II) gives no indication of the possible structure of the green radical intermediate. However, the dimeric form of both complexes tends to indicate that the dimerization proceeds *via* a binuclear mechanism rather than by internal electron transfer at a mononuclear nickel species as has been suggested by other workers (Bogdanovic, Heinbach, Kroner, Wilke, Hoffmann & Brandt, 1969). Further the replacement of triisopropylphosphine by diphenylphosphinoethane without affecting the binuclear π-allyl suggests that the latter is a stable entity in solution.

References

Bogdanovic, B., Heinbach, P., Kroner, M., Wilke, G., Hoffmann, E. G. & Brandt, J. (1969). *Liebig's Ann.* **727**, 143.
Churchill, M. R. & O'Brien, T. A. (1970). *J. Chem. Soc.* (*A*), p. 206.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 105.
Davies, G. R., Mais, R. H. B. & Owston, P. G. (1967). *J. Chem. Soc.* (*A*), p. 1750.
Döbler, M. & Duerr, B. (1969). Personal communication.
Green, M. L. H., Munakato, H. & Smith, M. J. (1971). To be published.
Mais, R. H. B., Powell, H. M. & Henn, D. E. (1960). *Proc. Chem. Soc.* p. 415.
Munakato, H. (1971). D. Phil. thesis, Oxford.
North, A. C. T., Phillips, D. C. & Matthews, M. S. (1968). *Acta Cryst.* A**24**, 351.
Orioli, P. L. & Sacconi, L. (1968). *Chem. Commun.* p. 1310.
Spofford, W. A., Carfagna, P. D. & Amma, E. L. (1967). *Inorg. Chem.* **6**, 1553.
Watson, H. C., Shatton, D. M., Cobe, J. M. & Muirhead, H. (1970). *Nature, Lond.* **225**, 806.

The Crystal Structure of Trihydrazinium Hexafluorochromate, (N2H5)3CrF6

By Biserka Kojić-Prodić and S. Šćavničar

Institute 'Ruđer Bošković', Zagreb, Yugoslavia

R. Liminga

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

and M. Šljukić

Institute 'Ruđer Bošković', Zagreb, Yugoslavia

The crystal structure of trihydrazinium hexafluorochromate has been determined from 3-dimensional X-ray film data. The crystals are orthorhombic, space group $P2_12_12_1$, with 4 formula units in a cell of dimensions: $a=9\cdot223$, $b=9\cdot223$, $c=10\cdot536$ Å. The structure consists of $[CrF_6]^{3-}$ octahedra and $N_2H_5^+$ cations connected by NH$\cdots$F hydrogen bonds to form a three-dimensional network; the shortest N$\cdots$F contact is $2\cdot655$ Å. The mean Cr–F value is $1\cdot905$ Å. The N–N bond lengths range from $1\cdot390$ to $1\cdot466$ Å. The R value for 875 observed reflexions is $9\cdot9\%$.

Introduction

The present work represents part of the crystal structure investigation of a series of hydrazinium transition metal fluorocomplexes prepared by Slivnik, Pezdič & Sedej (1967) in the Institute 'Jožef Stefan', Ljubljana. The structures of $N_2H_6ZrF_6$ and $N_2H_6TiF_6$ have already been published (Kojić-Prodić, Šćavničar & Matković, 1971; Kojić-Prodić, Matković & Šćavničar, 1971). In this paper the crystal structure of the chromium compound $(N_2H_5)_3CrF_6$, is described.

Crystal data

$(N_2H_5)_3CrF_6$ crystallizes in the hemihedral orthorhombic class. The dark-green crystals are sensitive to air and X-radiation.

$(N_2H_5)_3CrF_6$, orthorhombic

$a = 9 \cdot 223$ (7), $b = 9 \cdot 223$ (7), $c = 10 \cdot 536$ (5) Å*
$V = 896 \cdot 23$ Å^3
$D_m = 1 \cdot 950$, $D_c = 1 \cdot 965$ g.cm^{-3}
$Z = 4$
$\mu = 118 \cdot 8$ cm^{-1} for Cu $K\alpha$ radiation.
The systematic absences

$$h00: \quad h = 2n + 1$$
$$0k0: \quad k = 2n + 1$$
$$00l: \quad l = 2n + 1$$

indicate uniquely the space group $P2_12_12_1$ (D_2^4, No. 19).

Experimental

The unit-cell dimensions were determined from a powder photograph recorded with a Guinier–Hägg XDC-700 focusing camera using Cr $K\alpha_1$ radiation ($\lambda = 2 \cdot 28962$ Å) with silicon ($a = 5 \cdot 43054$ Å) as an internal standard. The cell parameters were fitted to the 17 measured θ values by the method of least squares. The density was measured at 25 °C using a pycnometer with decalin as the liquid.

Equi-inclination Weissenberg photographs were

* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

taken using filtered Cu $K\alpha$ radiation and the multiple-film technique (four films). 963 independent reflexions were recorded. Out of these, 875 had observable intensities, which were measured with a microdensitometer.

In order to minimize fluorescent radiation a thin aluminum foil was used in front of the films. Three crystals, shaped into spheres, were used with radii: $r_1 = 0 \cdot 0251$ cm, rotation about the [100] direction (six layer-lines); $r_2 = 0 \cdot 0170$ cm, rotation about [001] (zero layer-line); and $r_3 = 0 \cdot 0306$ cm, rotation about [001] (five layer-lines).

The crystals were covered with silicone oil and put into capillaries in order to prevent decomposition.

The corrections for absorption (spherical crystals), Lorentz and polarization factors were made in the usual way.

Structure determination

It follows from the space-group symmetry and the unit-cell content that all atoms are in general fourfold positions. The coordinates of the chromium atom were determined from a three-dimensional Patterson synthesis. An electron density calculation based on the chromium atom gave the locations of the fluorine and nitrogen atoms. The eleven scale factors, the coordinates, and isotropic temperature factors were refined

Table 1. *Observed and calculated structure factors*

The four columns are, in order, the indices k and l, $10F_o$ and $10F_c$.
Reflexions not included in the refinement are marked with an asterisk.

in several cycles of full-matrix least-squares calculations using the atomic scattering factors for the neutral atoms as given in *International Tables for X-ray Crystallography* (1962). This resulted in an R value of 12%. The weights w used were calculated according to the expression $w = 1 \cdot 0/[c_1^2 + (c_2 \cdot |F_o|)^2]$. The constant c_1 was put equal to $\sqrt{2 \cdot 0}$ for the strongest reflexions, equal to 2·0 for the weakest reflexions and otherwise equal to 1·0. The value used for the constant c_2 was 0·035. For all unobserved reflexions F_{min} values were calculated according to the Hamilton (1955) method. These were not included in the refinement.

Anisotropic temperature factors were then introduced for all atoms and refined together with the atomic

Table 2. *Final coordinates and anisotropic thermal parameters* ($\times 10^4$)

The thermal parameters correspond to the expression
$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$

|	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	2382 (3)	2052 (2)	2036 (2)	47 (3)	42 (2)	39 (2)	1 (2)	3 (3)	3 (2)
F(1)	2166 (12)	2285 (11)	249 (8)	100 (15)	85 (11)	41 (7)	1 (11)	−17 (10)	32 (8)
F(2)	4222 (10)	1311 (11)	1736 (10)	32 (9)	105 (13)	74 (10)	16 (9)	4 (10)	−38 (10)
F(3)	1651 (11)	126 (9)	1915 (9)	88 (12)	55 (9)	55 (9)	−60 (9)	4 (11)	−3 (8)
F(4)	471 (8)	2810 (10)	2259 (9)	37 (8)	75 (11)	59 (9)	58 (9)	8 (8)	14 (9)
F(5)	2645 (11)	1730 (9)	3817 (9)	59 (11)	72 (9)	64 (8)	32 (10)	−4 (11)	1 (8)
F(6)	3228 (13)	3961 (10)	2235 (9)	111 (13)	61 (10)	57 (9)	−50 (11)	−4 (11)	−12 (8)
N(1)	336 (19)	−130 (20)	4471 (19)	70 (22)	106 (24)	108 (22)	−42 (17)	6 (19)	−6 (20)
N(2)	−905 (20)	643 (22)	4676 (17)	82 (20)	154 (27)	66 (15)	−15 (20)	19 (19)	−5 (17)
N(3)	4810 (19)	−43 (17)	4490 (13)	72 (19)	101 (22)	36 (12)	40 (16)	−50 (16)	−7 (14)
N(4)	5829 (22)	646 (19)	5370 (19)	131 (27)	96 (21)	81 (17)	−11 (20)	−3 (21)	−22 (16)
N(5)	7654 (15)	1747 (12)	2195 (12)	71 (15)	58 (13)	42 (11)	−37 (12)	1 (16)	6 (9)
N(6)	6698 (16)	2575 (15)	2984 (13)	86 (17)	85 (16)	38 (10)	17 (13)	24 (16)	51 (12)
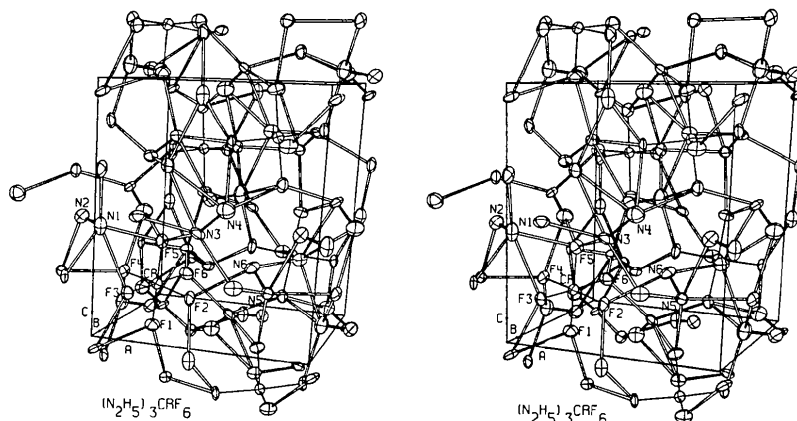
Fig. 1. Stereo pair, drawn with the program *ORTEP*, showing the structure of $(N_2H_5)_3CrF_6$. All contacts less than 3·10 Å are included.
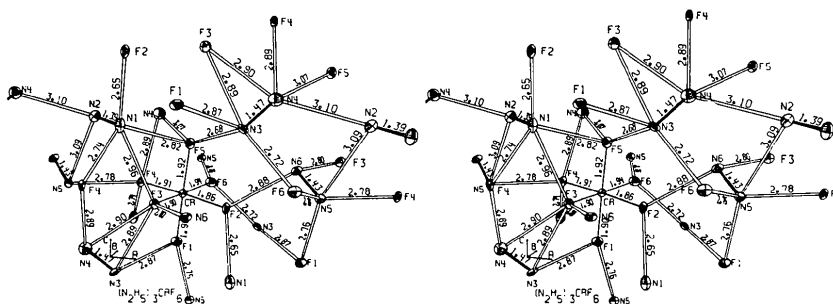

Fig. 2. Stereo pair showing the environments of the CrF_6^{3-} and $N_2H_5^+$ ions. The ellipsoids are scaled to enclose 50% probability. Covalent N–N bonds are filled, Cr–F bonds are drawn as single lines, and possible hydrogen bonds are open. All contacts less than 3·12 Å are included.

Table 3. *Interatomic distances and angles*

(a) Within the CrF_6^{3-} octahedron

Cr–F(1)	1·905 (9) Å
Cr–F(2)	1·856 (10)
Cr–F(3)	1·905 (9)
Cr–F(4)	1·911 (8)
Cr–F(5)	1·916 (10)
Cr–F(6)	1·937 (10)
F(1)–F(2)	2·618 (14)
F(1)–F(3)	2·697 (13)
F(1)–F(4)	2·676 (13)
F(1)–F(6)	2·780 (14)
F(2)–F(3)	2·618 (14)
F(2)–F(5)	2·659 (14)
F(2)–F(6)	2·663 (14)
F(3)–F(4)	2·728 (13)
F(3)–F(5)	2·654 (13)
F(4)–F(5)	2·776 (13)
F(4)–F(6)	2·755 (14)
F(5)–F(6)	2·702 (13)
F(1)–Cr–F(2)	88·2 (5)°
F(1)–Cr–F(3)	90·1 (4)
F(1)–Cr–F(4)	89·1 (4)
F(1)–Cr–F(5)	177·2 (4)
F(1)–Cr–F(6)	92·7 (4)
F(2)–Cr–F(3)	88·2 (4)
F(2)–Cr–F(4)	177·3 (5)
F(2)–Cr–F(5)	89·7 (5)
F(2)–Cr–F(6)	89·1 (5)
F(3)–Cr–F(4)	91·3 (4)
F(3)–Cr–F(5)	88·0 (4)
F(3)–Cr–F(6)	176·1 (5)
F(4)–Cr–F(5)	93·0 (4)
F(4)–Cr–F(6)	91·5 (4)
F(5)–Cr–F(6)	89·1 (4)

(b) Within the $N_2H_5^+$ ions

N(1)–N(2)	1·390 (26) Å
N(3)–N(4)	1·466 (25)
N(5)–N(6)	1·433 (19)

(c) Possible hydrogen bond contacts (all contacts < 3·25 Å are listed)

N(1)–F(2)	2·655 (23) Å
N(1)–F(4)	2·736 (21)
N(1)–F(5)	2·820 (21)
N(1)–F(3)	2·963 (22)
N(1)–F(1)	3·151 (21)
N(2)–N(5)	3·090 (22)
N(2)–N(4)	3·100 (27)
N(2)–F(5)	3·155 (22)
N(2)–F(2)	3·246 (22)
N(3)–F(5)	2·676 (19)
N(3)–F(6)	2·724 (19)
N(3)–F(1)	2·870 (19)
N(3)–F(3)	2·889 (17)
N(3)–F(2)	3·205 (17)
N(4)–F(4)	2·894 (21)
N(4)–F(3)	2·896 (22)
N(4)–F(5)	3·065 (21)
N(4)–N(2)	3·100 (27)
N(4)–N(6)	3·183 (24)
N(4)–N(5)	3·244 (23)
N(5)–F(6)	2·761 (15)
N(5)–F(1)	2·763 (15)
N(5)–F(4)	2·778 (16)
N(5)–N(2)	3·090 (22)
N(5)–F(2)	3·227 (16)
N(5)–N(4)	3·244 (23)
N(6)–F(3)	2·805 (17)
N(6)–F(2)	2·881 (17)
N(6)–N(4)	3·183 (24)

parameters and one scale factor. The interlayer scale factors were fixed at the values obtained above in the isotropic refinement. An isotropic extinction parameter was also applied, assuming the same extinction for the three crystals used for the data collection (Coppens & Hamilton, 1970). The refined value of the isotropic extinction parameter is $g = 4285(540)$. The extinction correction factors applied on F_o were in the range 1·00 to 1·43. The total number of parameters varied was 119. The final R value for all non-hydrogen atoms was 9·9%. Attempts to locate the hydrogen atoms from a difference Fourier synthesis were unsuccessful. The observed and calculated structure factors are listed in Table 1. Table 2 lists the final atomic parameters.

The calculations were done on the computers CAE 90–40 in Zagreb and CDC 3600 in Uppsala. The programs used for the CDC 3600 computer have been briefly described by Jönsson & Liminga (1971).

Description and discussion of the structure

The structure of $(N_2H_5)_3CrF_6$ consists of $[CrF_6]^{3-}$ anions and $N_2H_5^+$ cations. The chromium atom is surrounded by six fluorine atoms arranged at the corners of a slightly distorted octahedron with an average Cr–F bond distance of 1·905 Å $[(Cr^{3+}) = 0·68, r(F^-) = 1·36$ Å; Pauling, 1960]. The structure is illustrated in Fig. 1. The interatomic distances and angles are listed in Table 3; most of the distances are also given in Fig. 2.

The six independent nitrogen atoms are grouped into three $N_2H_5^+$ pairs with different environments. The bond lengths are as follows: N(1)–N(2) = 1·390, N(3)–N(4) = 1·466, and N(5)–N(6) = 1·433 Å. Similar values have been reported earlier, e.g. 1·42 Å in $LiN_2H_5SO_4$ (Padmanabhan & Balasubramanian, 1967); 1·432 Å in $N_2H_5BF_4$ (Conant & Roof, 1970); 1·461 Å in $N_2H_5ClO_4$ (Conant & Roof, 1970); and 1·474 Å in $N_2H_5ClO_4$. $\frac{1}{2}H_2O$ (Liminga, 1967).

As can be seen in Fig. 2 the $N_2H_5^+$ ions have different environments. In Fig. 2 all contacts < 3·12 Å are given, but in the discussion below the N···F contacts are considered only if they are < 3·00 Å. These latter may correspond to N–H···F hydrogen bonds according to Hamilton & Ibers (1968). The atom N(1) is surrounded by four fluorine atoms at 2·655, 2·736, 2·820 and 2·963 Å, whereas the nearest fluorine around N(2) is at 3·15 Å. Four fluorine atoms are also found around N(3) at 2·676, 2·724, 2·870 and 2·889 Å. The atom N(4) has only two fluorine neighbours at 2·894 and 2·896 Å. The fluorine F(3) is nearly equidistant from N(3) and N(4). Around the atom N(5) three fluorine atoms are at 2·761, 2·763 and 2·778 Å, whereas N(6) has two fluorine neighbours at 2·805 and 2·881 Å.

Although the hydrogen atoms were not located, the NH_3^+ parts of the $N_2H_5^+$ ions can easily be recognized as the atoms N(1), N(3) and N(5) because of the greater number of fluorine neighbours. All N···F contacts around the NH_2 parts are larger than 2·80 Å. Comparing the N···F distances one can see that both N(1) and

N(3) have two shorter and two longer N$\cdots$F contacts, whereas at N(5) all three N$\cdots$F distances are almost equal. Around the NH$_3^+$ parts of the pairs N(1)–N(2) and N(3)–N(4) the number of fluorine atoms at possible hydrogen bond distances is greater than three; this might allow the existence of bifurcated hydrogen bonds among some of them.

The two shortest nitrogen contacts between two different N$_2$H$_5^+$ cations are: N(2)$\cdots$N(5)=3·09, N(2)$\cdots$N(4)=3·10 Å. These may correspond to weak NH$\cdots$N interactions.

As can be seen in Fig. 2 the fluorine atoms F(1), F(2) and F(5) are each linked to two different N$_2$H$_5^+$ cations, with one longer (>2·80 Å) and one shorter contact (<2·80 Å). Fluorine F(6) has two N$_2$H$_5^+$ ions at nearly equal distances. In the vicinity of F(3) there are three N$_2$H$_5^+$ cations at rather long distances. The F(4) atom is surrounded by three cations with two short N$\cdots$F distances and one longer.

By inspection of the powder diffraction patterns the analogous vanadium compound (N$_2$H$_5$)$_3$VF$_6$, has been found to be isomorphous with (N$_2$H$_5$)$_3$CrF$_6$.

References

CONANT, J. W. & ROOF, R. B. (1970). *Acta Cryst.* B26, 1928.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71.

HAMILTON, W. C. (1955). *Acta Cryst.* 8, 185.

JÖNSSON, P. G. & LIMINGA, R. (1971). *Acta Chem. Scand.* 25, 1729.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids.* New York: Benjamin.

KOJIĆ-PRODIĆ, B., MATKOVIĆ, B. & ŠĆAVNIČAR, S. (1971). *Acta Cryst.* B27, 635.

KOJIĆ-PRODIĆ, B., ŠĆAVNIČAR, S. & MATKOVIĆ, B. (1971). *Acta Cryst.* B27, 638.

LIMINGA, R. (1967). *Acta Chem. Scand.* 21, 1217.

PADMANABHAN, V. M. & BALASUBRAMANIAN, R. (1967). *Acta Cryst.* 22, 532.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SLIVNIK, J., PEZDIČ, J. & SEDEJ, B. (1967). *Mh. Chem.* 98, 204.

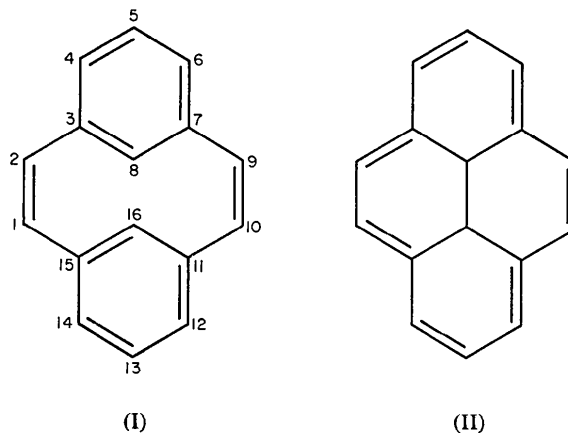# The Crystal Structure of [2.2]Metacyclophane-1,9-diene

BY A. W. HANSON AND M. RÖHRL*

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6

Crystals of the title compound, C$_{16}$H$_{12}$, are monoclinic, $P2_1/a$, with $a=13·25$ (1), $b=5·640$ (5), $c=7·350$ (5) Å, $\beta=95·39$ (5)°, $Z=2$. 833 of a possible 931 independent reflexions in the range sin $\theta/\lambda \leq 0·59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures and refined by block-diagonal least-squares methods to a final R index of 0·054. The molecule has crystallographic inversion symmetry and non-crystallographic, but fairly precise, mirror symmetry. The phenyl rings are parallel, but displaced stepwise to avoid too close mutual contact, and they suffer severe boat-distortion. The distance between the carbon positions 8 and 16 of opposing phenyl rings is 2·57 Å. The length of the double bonds in the inter-phenyl bridges is 1·341 (3) Å.

Introduction

The title compound (I) is one of a number of cyclophanes prepared by Professor Boekelheide and his associates. Many of these compounds are highly strained, and it is of interest to compare the chemical and geometrical consequences of such strain. (I) is somewhat unstable, undergoing (in solution) a light-mediated transformation to the corresponding dihydro-pyrene (II) and ultimately to pyrene (Mitchell & Boekelheide, 1970). The structure analysis was under-

(I)　　　　　　　　(II)