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A New Crystal Modification of Chromium Tetrafluoride: β-CrF_4**

Primož Benkič, Zoran Mazej,* and Boris Žemva

In memoriam Karel Lutar

Part of the investigations into reactions between chromium fluorides (CrF_2, CrF_3, CrF_5) and xenon fluorides (XeF_2, XeF_6) was a search for appropriate starting materials for the preparation of pure solid CrF_4.[1, 2] It was found that solid $XeF_2 \cdot CrF_4$ is quickly solvolyzed in anhydrous hydrogen fluoride (aHF) to give amethyst CrF_4.[1] Although the obtained CrF_4 was of very low crystallinity, its X-ray powder diffraction pattern indicated that it has a different crystal structure than CrF_4 prepared by direct fluorination of elemental chromium with an aHF/F_2 mixture at 573 K.[3] However, efforts to prepare single crystals of the new form of CrF_4 were plagued by the same preparative difficulties that prevent the growth of suitable single crystals of higher binary fluorides (high reactivity, moisture sensitivity, tendency to disproportionate, and thermal decomposition to lower valent compounds and elemental fluorine). Because of their reactivity they can be handled only in a few solvents, and their low solubility makes the preparation of single crystals from saturated solutions infeasible. For these reasons the preparation of single crystals of each 3d transition metal tetrafluoride represented a special challenge, and different preparation conditions were required in each case. We found that slow thermal decomposition of CrF_5 at 403 K yields large, beautiful, dark red-violet single crystals. Their color, vibrational data (see Supporting Information), and chemical analysis (see Experimental Section) confirmed that single crystals of CrF_4 were obtained. The presence of lower chromium fluorides (CrF_2, Cr_2F_5, or CrF_3) or oxyfluorides (CrF_2O, CrF_3O, CrF_4O, or CrF_2O_2) was excluded.

The crystal structures of the lower chromium fluorides (CrF_2,[4] Cr_2F_5,[5] CrF_3[6]) have long been known, and the crystal structure of CrF_4 was reported recently.[3] Here we report on a new crystal modification of CrF_4, which we named β-CrF_4 to distinguish it from the already known α-CrF_4.[3]

The tetrafluorides MF_4 can be divided into five groups. The first group contains MF_4 of larger M^{4+} ions (M = Hf, Ce, Pr, Tb, Th–Bk),[7] isostructural to β-ZrF_4;[7] the second the structurally related MF_4 (M = Rh, Os, Ir, Pt, Pd, Re);[8, 9] the third the structurally related NbF_4,[10, 11] SnF_4,[12] PbF_4,[12] VF_4,[10] and RuF_4;[11] and the fourth SeF_4 and TeF_4.[13] The fifth group includes TiF_4,[14] α-MnF_4,[15] β-MnF_4,[15] α-ZrF_4,[16] and α-CrF_4,[3] which represents unique examples. β-CrF_4 crystallizes in a new structural type. The basic unit of the crystal structure consists of four corner-sharing CrF_6 octahedra (Figure 1). Tetrameric rings are thus formed in which four Cr atoms are connected by *cis* bridging fluorine atoms. The coordination sphere around Cr atoms is completed by two *cis* terminal fluorine atoms and two *trans* bridging fluorine atoms

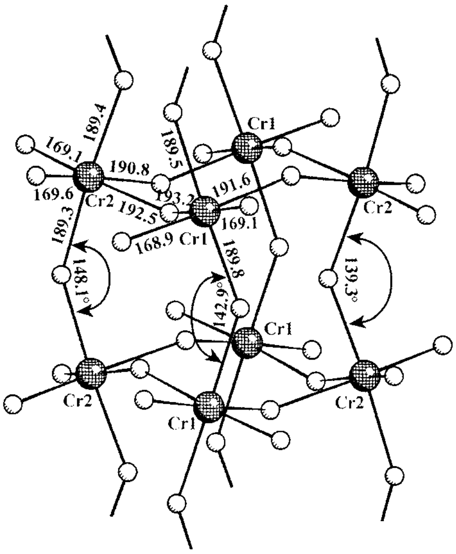

Figure 1. Section of the crystalline structure of β-CrF_4 showing tetrameric rings with bond lengths [pm] and angles [°].

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that connect tetrameric rings into columns running along the *c* axis. Neighboring columns are alternately shifted, as shown in Figure 2.

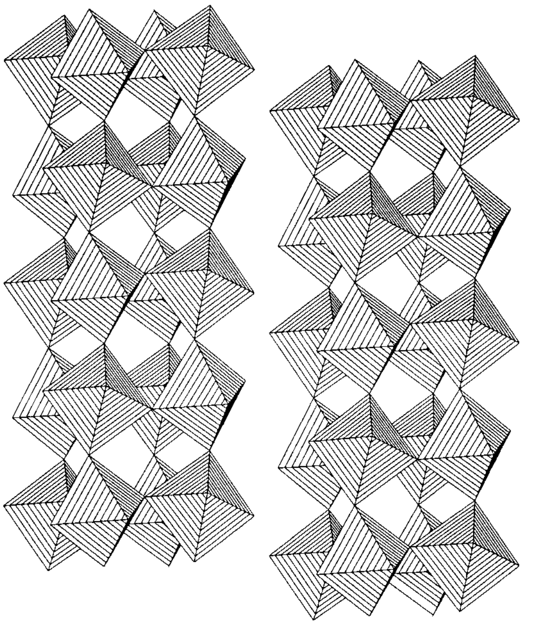

Figure 2. View perpendicularly on the shifted columns running along *c* axis in β-CrF_4.

The terminal Cr–F bond lengths are considerably shorter (168.9 to 169.6 pm) than those between Cr and bridging fluorine atoms (189.3 – 193.2 pm) and are comparable to corresponding bond lengths in α-CrF_4 ($Cr-F_{term}$ 167.7, $Cr-F_{br} = 187-193$ pm).[5] Angles in CrF_6 units are in the range of quite regular octahedra. The angles of the fluorine bridges Cr1-F-Cr2 that form the tetrameric rings (Figure 1) are 140.59(8) and 151.08(8)°, while Cr1-F-Cr1 and Cr2-F-Cr2 angles in columns (Figure 1) are 139.34(11), 142.86(8), and 148.12(11)°. The shortest nonbonding distances between terminal fluorine atoms and chromium atoms in neighboring columns are in the range of 355.8 – 392.6 pm. The shortest distances between *cis* bridging fluorine atoms (249.8 – 250.7 pm) are, as expected, longer than corresponding distances in the structure of α-CrF_4 (228.3 pm), which is dominated by isolated columns of edge-sharing octahedra.[3]

Finally, there are some common structural features of all known 3d transition metal tetrafluorides. α-CrF_4 is dominated by isolated columns of edge-sharing CrF_6 octahedra.[3] TiF_4 consists of rings formed by three corner-sharing TiF_6 octahedra,[14] and β-CrF_4 of rings formed by four corner-sharing CrF_6 octahedra, additionally connected through *trans*-fluorine atoms into isolated infinite columns. On the other hand, tetrameric rings in VF_4 and α-MnF_4, both composed of MF_6 octahedra linked through *cis*-fluorine atoms, form layers (VF_4)[10] or a three-dimensional network (α-MnF_4).[15] However, the question why each of these simple 3d tetrafluorides crystalizes in a different structural type is still open.

Experimental Section

CrF_5 was prepared according to ref. [17] Single crystals of CrF_4 were prepared by slow thermal decomposition of CrF_5. At 77 K 2.3 g of CrF_5 was sublimed into a nickel reaction vessel in an all-Teflon vacuum line equipped with Teflon valves. The autoclave was placed in an oven preheated to 403 K and kept for 5 months at this temperature. Then the reaction vessel was cooled to room temperature, and volatile components were pumped off. Some CrF_5 was still present in reaction vessel. The autoclave was opened in a dry-box under an inert atmosphere, and dark red-violet single crystals of CrF_4 were found inside. Some of them were ground for chemical analysis (calcd (%) for CrF_4: Cr 40.66, F 59.34; found: Cr 40.3, F 58.7, corresponding to molar ratio Cr:F of 1:3.99). The X-ray powder diffraction pattern of the powder obtained by grinding single crystals of CrF_4 was the same as that calculated from the crystal structure of β-CrF_4.

Crystal data:[20] CrF_4, $M_r = 127.99$, space group *C*2/*c* (No. 15), crystal system monoclinic, $a = 1457.0(9)$, $b = 972.0(6)$, $c = 719.0(4)$ pm, $\beta = 102.68(2)°$, $V = 0.993(1)$ nm^3, $Z = 16$, $\rho_{calcd} = 3.42$ g cm^{-3}. Data collection: Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation, ω-scan technique, $T = 200$ K, θ range 2.54 – 30.10° in $-19 \le h \le 15$, $-12 \le k \le 13$, $-7 \le l \le 9$, reflections collected: 3452, independent reflections: 1211 ($R_{int} = 0.024$), observed reflections [$I > 2\sigma(I)$]: 988, $\mu = 4.487$ mm^{-1}, multiscan absorption correction, transmission factors: 0.280 to 0.410. The structure was solved by heavy-atom Patterson methods and expanded by using Fourier techniques. Refinement by full-matrix least-squares methods on F^2. Data-to-parameter ratio: 13.2:1. Final *R* indices: $R1 = 0.022$ [$I > 2\sigma(I)$], $wR2 = 0.067$ [$I > 2\sigma(I)$], $R1 = 0.037$ (all data), $wR2 = 0.072$ (all data), GOF on F^2 1.17, largest difference peak/hole: 468/ – 635 e nm^{-3}. Data were collected and processed with the CrystalClear (Rigaku) software suite[18] and refined with SHELX97.[19]

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[20] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412032. Vibrational spectra of β-CrF_4 are available in the Supporting Information.