The Preparation and Crystal Structure of a Ruthenium Carbonyl Fluoride $[Ru(CO)_3F_2]_4$

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Summary A product of the reaction of ruthenium pentafluoride with carbon monoxide has been isolated and its structure shown to be based on a tetrameric unit $[Ru(CO)_3F_2]_4$, with bridging fluorine atoms.

DURING the investigation of the reactions of carbon monoxide with ruthenium pentafluoride, a non-volatile carbonyl fluoride of ruthenium, formulated as $Ru(CO)F_{3\cdot5}$, was reported.[1] This product reacts further with carbon monoxide at high pressure (100 atm) and temperature (200°) to give a pale yellow crystalline solid with i.r. absorption bands in the carbonyl stretching region at 2141 (m), 2058 (s), and 2000 cm^{-1} (w, sh), a pattern similar to that given by the dihalogenotricarbonylruthenium compounds $[Ru_2(CO)_6X_4$; X = Cl, Br, I].[2] The mass spectrum shows peaks corresponding to $Ru_2(CO)_6F_3^+$ and $Ru_2(CO)_5F_4^+$ species, both of which show stepwise loss of all carbon monoxide. The solid is moisture-sensitive and reacts with hydrochloric acid to give dichlorotricarbonylruthenium, $Ru_2(CO)_6Cl_4$.

To characterise this product, a crystal structure determination was undertaken. A crystal was picked out by hand and mounted in a sealed glass capillary. *Crystal data*: $C_{12}Ru_4O_{12}F_8$, M 940·28, tetragonal, $a = 11{\cdot}053$, $c = 9{\cdot}376$ Å, $U = 1146$ Å^3, $D_c = 2{\cdot}73$, $Z = 8$, space group $I\bar{4}2m$ (D_{2d}^{11} ; No. 121) or $I\bar{4}$ (S_4^2; No. 82). Reflections to $\sin \theta/\lambda = 0{\cdot}80$ (Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å) were collected with a Stoe Automatic Weissenberg Diffractometer.

Ruthenium atom positions were obtained from a Patterson synthesis, and the electron density synthesis phased by ruthenium showed the molecule to be a fluorine-bridged tetramer $[Ru(CO)_3F_2]_4$. The appearance of the light atom peaks on the Fourier synthesis suggests that the true molecular symmetry is only $\bar{4}$ (S_4). However, least-squares refinement of atomic parameters is most successful assuming a disordered structure, in which approximately equal numbers of the two possible orientations of this molecule with respect to the symmetry elements of $I\bar{4}2m$ occur randomly in the crystal. The molecular structure is derived from an idealised $\bar{4}2m$ (D_{4d}) model by making slight displacements of the light atoms away from the vertical mirror planes and dihedral two-fold axes of point group $\bar{4}2m$. In support of this proposal, the R-value for this model is 0·064 for 601 independent reflections, compared with 0·077 for a nondisordered $\bar{4}2m$ structure, and 0·077 for the 838 reflections† of a non-disordered $\bar{4}$ model. Temperature factors for the light atoms in the non-disordered models are also impossibly large.

The presence of disorder necessarily gives rise to large uncertainties in bond lengths and angles, but the overall stereochemistry is clear (Figure). The carbonyl fluoride is based on the ruthenium pentafluoride tetrameric unit,[3] three of the terminal fluorine atoms on each ruthenium atom have been replaced by carbonyl groups. The Ru–F–Ru bridge angle has an average value of 145°, compared with 132° in RuF_5. The average Ru–C bond length (1·83 ± 0·06 Å) is similar to the average Ru–C bond length in $Ru_3(CO)_{12}$ (1·91 ± 0·04 Å).[4]

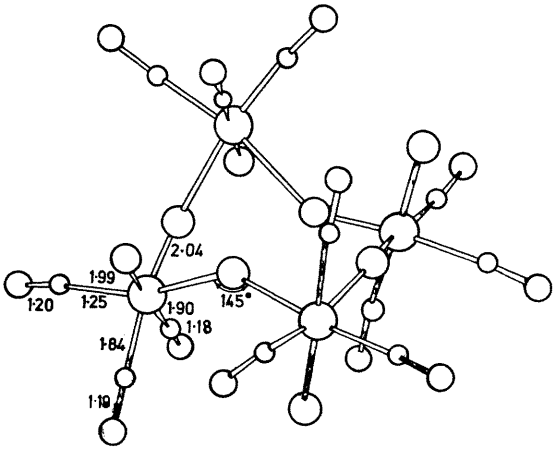

FIGURE. *Molecular Structure of* $[Ru(CO)_3F_2]_4$. *Bond lengths in angstroms, estimated standard deviations of* Ru–C, F *bonds* ±0·07 Å, C–O *bonds* 0·09 Å.

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† Some of these reflections are equivalent in $\bar{4}2m$ symmetry.

The tetrameric form of the difluorotricarbonylruthenium described here contrasts with the suggested structures of the chloro-, and iodo-analogues,[3] and the reported structure of the bromo-analogue,[5] which are all dimeric.

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