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A NEW COÖRDINATION TYPE AROUND FLUORINE ATOM

Sir:

In connection with the studies carried on from a long time in our Institute on metalloörganic complexes containing bridge bonds,[1,2,3] we have undertaken the X-ray structural study of the compound $KF \cdot 2Al(C_2H_5)_3$ (I), for the first time synthesized and studied by Ziegler *et al.*[4].

A $KF \cdot 2Al(C_2H_5)_3$ solution is obtained by reaction of finely ground KF with a stoichiometric quantity of $Al(C_2H_5)_3$ dissolved in toluene, at about 60°. We then have obtained good crystals of (I) by slow evaporation of toluene from the solution at room temperature.

Our X-ray analysis has confirmed that the complex (I) has the ionic structure $K^+[(C_2H_5)_3Al\text{-}F\text{-}Al(C_2H_5)_3]^-$ [5]; moreover we have surprisingly obtained definite evidence of colinearity among Al–F–Al atoms. In fact, the ordinary Patterson analysis led us to the conclusion that the rhombohedral unit cell of (I), containing only one molecule, is centrosymmetrical, so that K^+ ion and F atom are bound to lay on two crystallographic centers of symmetry, while the Al–F distance, successively determined by Fourier methods (1.80 ± 0.06 A.), clearly indicates that the atoms are bonded together.

The unit cell of (I) has the constants: $a = b = c = 8.95 \pm 0.05$ Å.; $\alpha = \beta = \gamma = 55° 20' \pm 1°$, space group $R\bar{3}$; $N = 1$.

At this point of the refinement, we can assign fractional coördinates of first approximation to all the atoms (excepting hydrogen atoms). The present satisfying accordance between observed and calculated structure factors on the $(1\bar{1}1)$ and $(1\bar{1}0)$ projections ($R = 0.17$) allows us to conclude that: (1) the Al–F–Al axis is a threefold axis, with inversion center, for the $[(C_2H_5)_3Al\text{-}F\text{-}Al(C_2H_5)_3]^-$ ion; (2) the coördination type around the aluminum atom is tetrahedral, with normal Al–C[6] and C–C distances, while the Al–F distance appears to be close to that observed for instance in Na_3AlF_6.[7] It is to be noted that this datum is in contrast with the fact that usual bridge bond distances are somewhat longer (0.20 ÷ 0.30 A.) than the corresponding single bond distances.[1,6,8]

If we suppose a sp hybridization for the fluorine atom, a partial π-bond character on the Al–F bond may arise from a certain overlap between the $2p_y$ and $2p_z$ filled fluorine orbitals and the 3d empty aluminum orbitals. This hypothesis seems to us particularly supported by recent studies, which demonstrate the ability of F[9] and C[10] coördinated atoms to reduce the size of the 3d orbitals of second row elements.

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INSTITUTO DI CHIMICA
INDUSTRIALE DEL POLITECNICO
PIAZZA LEONARDO DA VINCI 32
MILANO, ITALY

G. NATTA
G. ALLEGRA
G. PEREGO
A. ZAMBELLI

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