Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Solid state structure and solution behavior of compounds of the type $M[Al_2(CH_3)_6X]$

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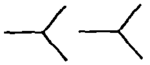
(Received May 2nd, 1972)

The preparation and properties of compounds of general formula $M[Al_2(CH_3)_6X]$, where M = alkali metal or tetramethylammonium ion and X = pseudohalide ion, have been the subject of several recent discussions[1–3]. Dehnicke has formulated the structures of $[N(CH_3)_4][Al_2(CH_3)_6N_3]$ and $[N(CH_3)_4][Al_2(CH_3)_6SCN]$ on the basis of infrared and Raman spectroscopic data[4,5], and our group has investigated the thermolysis of $K[Al_2(CH_3)_6SCN]$[2]. We wish now to report the first crystal structure analysis of a compound of this type, $K[Al_2(CH_3)_6N_3]$, and to report the novel interaction of these substances with aromatic molecules.

Crystal data: Crystal system, triclinic; space group, $P\bar{1}$; $a = 11.960(5)$, $b = 11.327(5)$, $c = 10.705(5)$ Å; $\alpha = 93.68(4)$, $\beta = 97.33(4)$, $\gamma = 99.20(4)°$; $\rho_{\text{calcd.}} = 1.06$ g.cm^{-3} for $Z = 4$. A total of 1631 independent observed reflections were measured on an Enraf–Nonius CAD-4 automated diffractometer using Cu-K_α radiation ($2\theta \leqslant 140°$). Absorption corrections were not made because of the moderate size of the linear absorption coefficient ($\mu = 39.5$ cm^{-1}) and the highly irregular shape of the crystal. The structure solution was accomplished by direct methods[6], and has been refined by full-matrix anisotropic least-squares methods to a reliability index of $R = 10.7\%$. The relatively high R value is due in part to the fact that the hydrogen atoms which make up 15% of the electron density have not been located.

There are two chemically nonequivalent molecules in the asymmetric unit. The difference lies in the conformation of the carbon atoms of the methyl groups on the aluminum atoms as viewed down the nitrogen chain:

C_{2v}



C_s

However, the bond distances do not differ to within the estimated standard deviations (0.02 Å), and only the C_{2v} configuration is shown in Fig. 1. The average nitrogen–

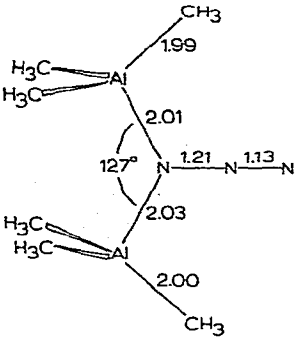


Fig. 1. Structure of the C_{2v} form of the $[Al_2(CH_3)_6N_3]^-$ anion.

nitrogen–nitrogen bond angle is 178(1)°. In the asymmetric azide group the average terminal bond length of 1.13(2) Å and bridge-nitrogen–nitrogen distance of 1.21(2) Å are in good agreement with those found in singly bonded azide ions[7]. On the other hand, the planar nature of the aluminum–nitrogen skeleton (no deviation greater than 0.01Å from the least-squares best-fit plane of the skeleton) lends credence to a resonance form involving sp^2 hybridization of the terminal nitrogen atoms.

Just as the two anionic units differ chemically, so also do the two potassium ions differ environmentally. One is closely coordinated to the terminal nitrogen atoms on two anionic units (2.92, 2.95Å) while the other is packed in the vicinity of three methyl groups (3.11, 3.18, 3.22 Å).

One of the most remarkable forms of behavior exhibited by $M[Al_2(CH_3)_6X]$ ($M = K, Cs, N(CH_3)_4$; $X = N_3$, SCN, Cl, I) is the interaction with aromatic molecules (benzene, toluene, *p*-xylene). If, for example, $K[Al_2(CH_3)_6N_3]$ is heated in benzene for a short time at 70 °C, two immiscible liquid layers are obtained. The lower, more viscous fraction contains benzene "complexed" to $K[Al_2(CH_3)_6N_3]$ and the top fraction, pure benzene. The liquid complex exists at room temperature and has been characterized by nuclear magnetic resonance techniques. It is possible to reclaim $K[Al_2(CH_3)_6N_3]$ by cooling the substance in liquid nitrogen to initiate crystallization★.

The approximate number of benzene molecules associated with a $K[Al_2(CH_3)_6N_3]$ unit (as established by NMR integrations) varies from two up to as many as five, and is a function of the temperature and of the heating time in the initial preparation.

The non-stoichiometric nature of the "complex" of $K[Al_2(CH_3)_6N_3]$ with small aromatic molecules is reminiscent of a clathrate type of behavior. The anion (Fig. 1) is rather bulky and the negative charge is localized to a considerable extent on one side of the ion. A possible explanation of the bonding in the "complex" involves the orientation of the anionic units such as to form a cage about a variable number of potassium ions and aromatic molecules. Further studies on these and related systems are in progress.

★ Satisfactory analyses have been obtained for all 2/1 compounds dealt with except for the tetramethylammonium salts. NMR integrations were used to verify the composition of these substances.

ACKNOWLEDGEMENTS

We are grateful to the National Science Foundation for support of this work under Grant GP-24852, and for departmental assistance in the purchase of the X-ray diffractometer.

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