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Thermal behavior of anionic organoaluminum thiocyanates

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Alkali metal halides react with aluminum alkyls to form anionic complexes in which the two trialkylaluminum units are bridged together by the halide ion[1,2]. We report here the preparation of the analogous thiocyanate complexes:

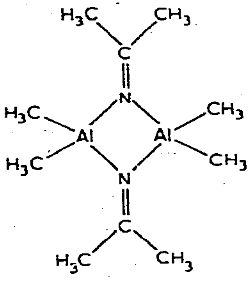
$$\mathrm{MSCN} + 2\mathrm{AlR_3} \rightarrow \mathrm{M[R_3AlSCNAlR_3]}$$

(M = alkali metal; R = methyl group)

The white crystalline compound $K[Al_2(CH_3)_6SCN]$ (m.p. 99–101°) was prepared by the vacuum line distillation of 0.01 mole $(CH_3)_3Al$ onto 0.005 mole KSCN. The sample tube was then sealed and the temperature raised to 85° for one hour. Reaction was deemed to have reached completion when no liquid trimethylaluminum was observed in the vessel. The sample was opened under a nitrogen atmosphere and placed under a vacuum of 10^{-5} mm Hg for a period of several hours. No trimethylaluminum was recovered from the cold trap. (Anal.: Found: C, 35.09; H, 7.88. Calcd. for $K[Al_2(CH_3)_6SCN]$: C, 34.83; H, 7.52%.) Addition of higher mole ratios of $(CH_3)_3Al$ to KSCN than 2/1 resulted in all cases in the recovery of the trimethylaluminum in excess of the 2/1 ratio.

Infrared absorptions occur at 2920s, 2870sh, 2810m, 2100m, 2070s, 1190m, 1155s, 800m, 715s,br, 630s, 600s, 520m, 490w, 480w, 450w cm^{-1}. The strong characteristic N–C stretching frequency at 2070 cm^{-1} agrees well with the values reported for both the sulfur-bridged trimer $[(C_2H_5)_2AlSCN]_3$ (2075 cm^{-1})[3], and the thiocyanate-bridged polymer $(CH_3)_3SnNCS$ (2079 cm^{-1})[4,5]. For $K[(CH_3)_3AlSCNAl(CH_3)_3]$ steric considerations strongly favor a bridging arrangement involving both sulfur and nitrogen atoms in the thiocyanate group.

If $K[(CH_3)_3AlSCNAl(CH_3)_3]$ is heated for several hours at temperatures in excess of 120°, the initially colorless melt gradually changes to yellow and finally to deep red. From the melt a quantity of a clear, colorless, crystalline product sublimes which elemental analysis shows to have the empirical formula $C_5H_{12}NAl$. Infrared and NMR spectra are consistent with the formulation of the substance as isopropylidenaminodimethylaluminum[6]. Wade and coworkers first isolated the compound from the thermal rearrangement of the neutral addition complex of trimethylaluminum and acetonitrile and proposed a dimeric structure:



Preliminary single crystal X-ray diffraction studies have now proved the two substances to be identical. The crystal system is triclinic and the unit cell parameters are:

$$a = 7.04 \pm 0.01\ \text{Å};\ b = 7.77 \pm 0.01\ \text{Å};\ c = 8.60 \pm 0.01\ \text{Å};\ \alpha = 115.6 \pm 0.2^\circ;$$
$$\beta = 105.8 \pm 0.2^\circ;\ \gamma = 92.4 \pm 0.2^\circ.$$

The formation of $[(CH_3)_2CNAl(CH_3)_2]_2$ from the thermal decomposition of $K[(CH_3)_3AlSCNAl(CH_3)_3]$ demonstrates that the thiocyanate group can be broken down in a bridging environment under relatively mild conditions. Studies aimed at the elucidation of the mechanism of decomposition are currently in progress.

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