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CATIONIC INFLUENCE IN ANIONIC ORGANOALUMINUM CHEMISTRY. SYNTHESIS AND STRUCTURE OF DIMETHYLTHALLIUM ISOTHIOCYANATOTRIMETHYLALUMINATE

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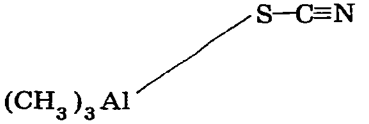
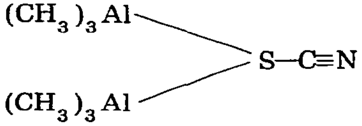
Summary

The reaction of TlSCN with $Al(CH_3)_3$ has been found to yield $[(CH_3)_2Tl][Al(CH_3)_3NCS]$. The crystal structure of dimethylthallium isothiocyanatotrimethylaluminate has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the monoclinic space group $C2/m$ with cell dimensions $a = 16.031(8)$, $b = 12.447(6)$, $c = 6.410(3)$ Å, $\beta = 106.17(5)°$, and $\rho_{calc} = 1.99$ g/cm^3 for $Z = 4$. Least-squares refinement has given a conventional weighted R factor of 0.073 for 587 independent observed reflections. The anion lies in a crystallographic mirror plane, and the thallium atom resides on a two-fold axis. The coordination requirements of the thallium atom are believed to be responsible for the stabilization of the N-bonding mode of the isothiocyanate group in the anion.

Introduction

Although trimethylaluminum is generally regarded as a hard Lewis acid, spectroscopic studies [1,2] have indicated that in $[N(CH_3)_4][Al_2(CH_3)_6SCN]$ and $[N(CH_3)_4][Al(CH_3)_3SCN]$ the bonding of the thiocyanate ion is through the sulfur atom:





Similar results [2] were also obtained for the 2/1 selenium analogue, $[N(CH_3)_4][Al_2(CH_3)_6SeCN]$. Since the structure of the anion is of para-

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mount importance in the assessment of the unusual thermal behavior of these substances [3,4], we have sought to study the influence of the counter ion on the anionic geometry.

Experimental

Dimethylthallium isothiocyanatotrimethylaluminate was prepared by the sealed tube reaction of thallium(I) thiocyanate with trimethylaluminum in toluene:

$$3\ \mathrm{TlSCN} + 3\ \mathrm{Al(CH_3)_3} \xrightarrow{100^\circ} [\mathrm{(CH_3)_2Tl}][\mathrm{Al(CH_3)_3NCS}] + 2\ \mathrm{Tl} + 2\mathrm{(CH_3)_2AlSCN}$$

The presence of thallium metal was verified by elemental analysis, but $(CH_3)_2AlSCN$ [5] was not identified and is shown only for material balance. Dimethylaluminum thiocyanate is, however, quite a reasonable candidate, and studies of anionic organoaluminum azides have allowed the identification of $(CH_3)_2AlN_3$ in related reactions [6].

Single crystals of $[(CH_3)_2Tl][Al(CH_3)_3NCS]$ were grown from toluene solution and sealed in thin-walled glass capillaries. The crystal system is monoclinic. Systematic absences allow the space group to be *C*2, *Cm*, or *C*2/*m*. The lattice parameters as determined from a least-squares refinement of $(\sin\theta/\lambda)^2$ values of 12 reflections are: $a = 16.031(8)$, $b = 12.447(6)$, $c = 6.410(3)$ Å, $\beta = 106.17(5)^\circ$, and $\rho_{calc} = 1.99$ g/cm^3 for $Z = 4$. Data were measured on an Enraf—Nonius CAD-4 diffractometer with graphite crystal monochromated copper radiation. The crystal, an irregular block of approximate dimensions 0.10 mm × 0.20 mm × 0.20 mm, was aligned on the diffractometer such that no symmetry axis was coincident with the ϕ axis of the diffractometer.

The diffracted intensities were collected by the ω–2θ scan technique with a take-off angle of 3°. The scan rate was variable and was determined by a fast (20°/min) prescan; if more than 20 net counts were obtained, a slow scan was performed. Based on the desired attainment of 3000 total counts in the slow scan, the calculated speeds ranged from 7 to 0.2°/min. Stationary background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation: scan range = $A + B\tan\theta$, where $A = 1.0^\circ$ and $B = 0.5^\circ$. Aperture settings were determined in a like manner with A = 4 mm and B = 4 mm. Other diffractometer parameters have been reported elsewhere [5]. As a check on the stability of the diffractometer and the crystal, two standard peaks were measured periodically during data collection. The crystal appeared to decompose linearly with respect to X-ray exposure time; the data were scaled appropriately.

The standard deviations of the intensities, σ_I, were estimated from the formula:

$$\sigma_I = \{[C_N + (T_c/2T_B)^2 \cdot (B_1 + B_2)] + (0.02)^2 \cdot [C_N + (T_c/2T_B)^2 \cdot (B_1 + B_2)]^2\}^{0.5}$$

where C_N is the counts collected during scan time T_c and B_1 and B_2 are background intensities, each collected during the background time T_B. A total of 587 reflections for which $I > \sigma(I)$ were obtained from one unique quadrant of data measured out to $2\theta = 100°$.

The intensities were corrected for Lorentz and polarization effects but not for absorption because of the irregular shape of the crystal.

Fourier calculations were made with the ALFF [7] program. The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS [8]. The function $\Sigma W \cdot (|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Tl, S, Al, N, C, and H were taken from the compilations of Cromer and Waber [9], and the scattering by thallium was corrected for the real and imaginary components of anomalous dispersion using Cromer's table [10]. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE [11] program. Crystal structure illustrations were obtained with the program ORTEP [12].

Solution and refinement of the structure

The thallium atom was located with the initial three-dimensional Patterson map, and several electron density maps preceded by partial least-squares refinement cycles revealed all the non-hydrogen atoms in the asymmetric unit based on the centric space group *C2/m*. Subsequent isotropic refinement led to a reliability index, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.11. Anisotropic refinement gave final values of $R_1 = 0.082$ and $R_2 = [\Sigma W \cdot (|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{0.5} = 0.073$. A weighting scheme based on essentially unit weights was used and unobserved reflections and two reflections (110, 200) believed to be suffering from secondary extinction were not included. Refinement was attempted in the acentric space groups *C2* and *Cm*, but large parameter correlations and no improvement in the *R* factors led to the assumption that the correct choice is *C2/m*. Statistical tests based on normalized structure factors failed to differentiate the centric from the acentric choices. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference Fourier map showed as its major feature one peak of 2.2 $e^-/Å^3$ near the thallium atom. The final value for the standard deviation of an observation of unit weight was 1.17. The final values of the positional and thermal parameters are given in Table 1*.

Discussion

In the reaction of thallium(I) thiocyanate with trimethylaluminum, the autoxidation - reduction of Tl^{1+} to Tl^{3+} and Tl^0 was not expected, although the very high stability of compounds of the type R_2TlX is well-known [13]. It

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* The Table of structure factors has been deposited as NAPS Document No. 02214, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Made checks or money

TABLE 1

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS [a,b] FOR $[(CH_3)_2Tl][(CH_3)_3AlNCS]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	0.5000	0.3192(2)	0.0000	0.0060(1)	0.0072(1)	0.0282(6)	0.0000	−0.0028(2)	0.0000
S	0.0764(7)	0.0000	−0.2337(18)	0.0043(6)	0.0074(9)	0.0299(35)	0.0000	−0.0004(11)	0.0000
Al	0.3535(7)	0.0000	0.2732(18)	0.0043(6)	0.0084(10)	0.0260(38)	0.0000	−0.0025(12)	0.0000
N	0.2354(20)	0.0000	0.0336(64)	0.0019(16)	0.0116(35)	0.0600(146)	0.0000	−0.0012(40)	0.0000
C(1)	0.3841(13)	0.3239(34)	−0.2685(39)	0.0015(9)	0.0173(33)	0.0318(84)	−0.0011(22)	0.0033(22)	−0.063(60)
C(2)	0.1674(20)	0.0000	−0.0722(74)	0.0014(14)	0.0079(32)	0.0850(207)	0.0000	−0.013(44)	0.0000
C(3)	0.3216(25)	0.0000	0.5457(51)	0.0054(20)	0.0132(42)	0.0131(105)	0.0000	−0.059(39)	0.0000
C(4)	0.4089(22)	0.1306(33)	0.1821(54)	0.0052(17)	0.0231(61)	0.0382(110)	−0.0013(21)	−0.0103(37)	−0.0086(54)

[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parametersdefined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

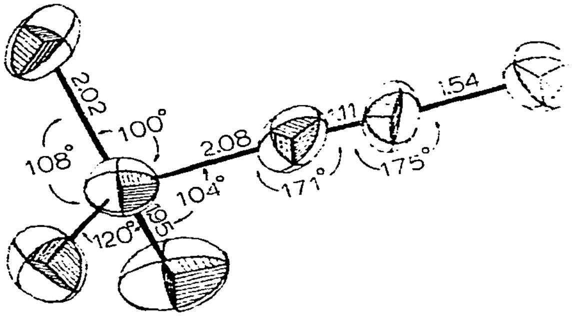

Fig. 1. Structure of the anion of $[(CH_3)_2Tl][Al(CH_3)_3NCS]$ with the atoms displayed as their 50% probability ellipsoids for thermal motion. The standard deviations of the bond distances are less than 0.04 Å, and the bond angles, 2°.

should also be noted that a common preparation [14] of R_3Tl involves the disproportionation of RTl to thallium metal and the thallium(III) organometallic.

The structure of the isothiocyanatotrimethylaluminate anion, as illustrated by Fig. 1, shows the essentially linear coordination of the nitrogen-bonded thiocyanate ion. The anion lies in a crystallographic mirror plane, and the thallium atom resides on a two-fold axis in the space group *C*2/*m*. The dimethylthallium ion is essentially linear [carbon—thallium—carbon bond angle = 177(2)°]. The aluminum—nitrogen bond length [2.08(4) Å], although quite long, is not significantly different at the 95% confidence level from those found in related compounds [4,15].

The bonding modes of ambidentate ligands such as SCN^- have been studied in detail for several transition metal complexes [16,17]. The nature of the metal atom, the electronic and steric character of other ligands in the coordination sphere, and the nature of the physical state of the complex have all been shown to exert a strong influence on the type of metal—thiocyanate linkage. By the same token, there are two possible explanations for the existence of the N-bonded thiocyanate ion in $[(CH_3)_2Tl][Al(CH_3)_3NCS]$ as opposed to the S-bonded thiocyanate ion in $[N(CH_3)_4][Al(CH_3)_3SCN]$. Lattice effects due to the different packing abilities of the cations may be important, but the coordination requirements of the thallium atom probably play the

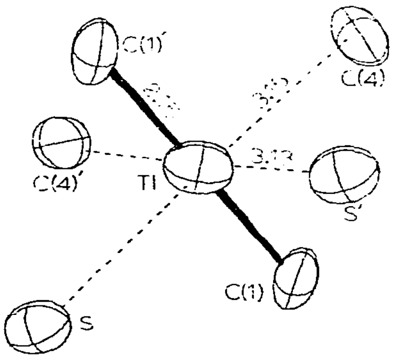

Fig. 2. Coordination sphere of the thallium atom in $[(CH_3)_2Tl][Al(CH_3)_3NCS]$.

major role. The environment of the thallium atom (Fig. 2) is essentially octahedral: two bonded methyl carbon atoms at 2.15(2) Å, two sulfur atoms at 3.13(1) Å, and two nonbonded aluminum methyl carbon atoms at 3.15 Å, with corresponding angles at the central metal atom close to 90°. Although the Tl—S bond must be largely electrostatic in character, it likely provides the driving force for the stabilization of the N-bonded thiocyanate group in the anion. Other structural studies of anionic organoaluminum pseudohalides now in progress should further clarify the nature of the influence of the counter ion on the geometry of the anion.

Acknowledgements

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