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THE CRYSTAL AND MOLECULAR STRUCTURE OF $K[Al_2(CH_3)_6SCN]$, A COMPOUND WHICH CONTAINS AN *S,N*-BRIDGING THIOCYANATE LIGAND

RIZ SHAKIR, MICHAEL J. ZAWOROTKO and JERRY L. ATWOOD*
Department of Chemistry, University of Alabama, University, Alabama 35486 (U.S.A.)
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Summary

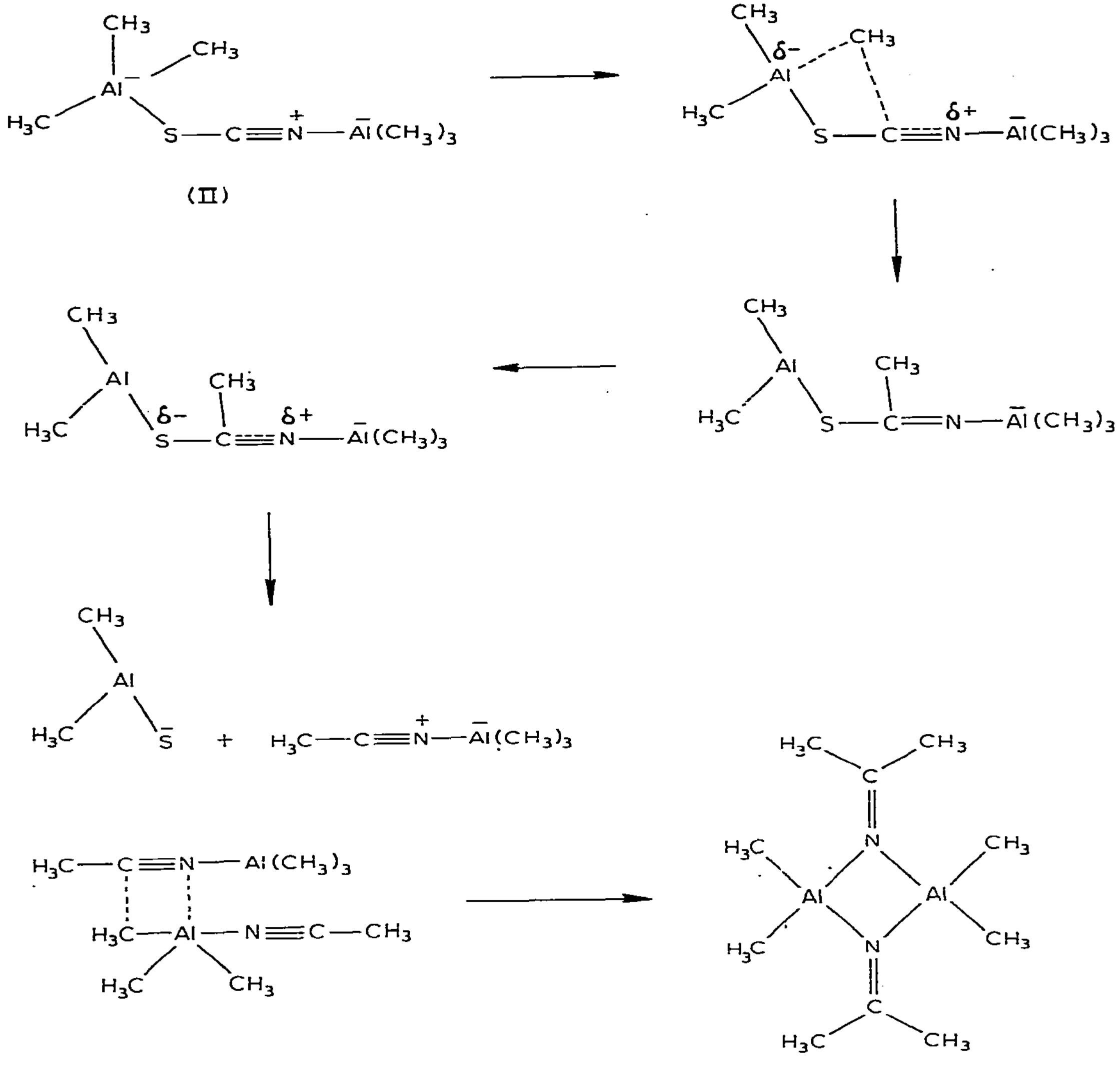
The crystal structure of $K[Al_2(CH_3)_6SCN]$ has been determined from single-crystal X-ray diffraction data collected by counter methods. The compound crystallizes in the monoclinic space group $C2/m$ with unit cell parameters a 18.579(8), b 8.168(5), c 11.753(6) Å, β 126.80(4)°, and ρ_{calc} 1.12 g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.028 for 722 independent observed reflections. The anion exhibits an *S,N*-bridging thiocyanate. The SCN is linear, and the C≡N—Al angle is 173.4(4)°. The Al—N bond is normal, 1.951(5) Å, but the Al—S bond length, 2.489(2) Å, implies a rather weak interaction. A distance of ca. 2.35 Å would have been expected. The sulfur atom appears to be using *p*-orbitals in its bonding scheme, since the Al—S—C bond angle is 97.3(2)°.

Introduction

In our initial report [1] of the synthesis of $K[Al_2(CH_3)_6SCN]$, the structure was postulated to exhibit an *S,N*-bridging thiocyanate group on the basis of steric considerations. Shortly thereafter Weller, Wilson, and Dehnicke communicated [2] the preparation of a wide range of related compounds, and deduced that the thiocyanate bridges the trimethylaluminum units through only the sulfur atom [2,3]. Their arguments were based on the existence of compounds such as $Cs[Al_2(C_2H_5)_6Cl]$ [4] and the assignment of $\nu_{as}(AlSAl)$ and $\nu_s(AlSAl)$ at 315 and 179 cm^{-1}. The steric considerations were further weakened by the results of the crystal structures of $K[Al_2(CH_3)_6N_3]$ [5] and $Cs[Al_2(CH_3)_6N_3]$ [6], in which the azide ion bridges through a single nitrogen atom. Chemical evidence for the *S,N*-bridging mode was, however, set forth in the report of the thermal decomposition of $K[Al_2(CH_3)_6SCN]$ according to eq. 1 [7].

$$2\,K[Al_2(CH_3)_6SCN] \xrightarrow{120^\circ C} \underset{(I)}{[(CH_3)_2AlNC(CH_3)_2]_2} + \underset{\text{(not isolated)}}{2\,K[(CH_3)_2AlS]} \qquad (1)$$

The mechanism of eq. 1 could easily be understood if the existence of II were accepted as the starting point for the following sequence:



(II)

(I)

The last step of the mechanism involves the well-known thermal nitrile rearrangement [8]. We now offer proof that II is in fact a proper description of the $[Al_2(CH_3)_6SCN]^-$ ion.

Experimental

$K[Al_2(CH_3)_6SCN]$ was prepared by the sealed tube reaction of a 1/2 mole ratio of KSCN and $Al(CH_3)_3$ in toluene. The liquid layering effect [9] was noted immediately but the reaction was driven to completion by the elevation of the temperature to 60°C for 1 h.

TABLE 1

CRYSTAL DATA

Mol. formula	$KAl_2C_7SNH_{18}$
Mol. weight	241.3
Linear abs. coeff. (cm^{-1})	12.4
Calc. density ($g\ cm^{-3}$)	1.12
Max. crystal dimensions (mm)	0.30 × 0.30 × 0.55
Space group	$C2/m$
Molecules/unit cell	4
Cell constants [a] a (Å)	18.579(8)
b (Å)	8.168(5)
c (Å)	11.753(6)
β (°)	126.80(4)
Cell volume (Å^3)	1428.2

[a] Mo-K_α radiation, λ 0.71069 Å. Ambient temperature of 23 ± 1°C.

Single crystals of the colorless, air-sensitive compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections accurately centered on an Enraf—Nonius CAD-4 diffractometer are given in Table 1. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in the usual manner [10].

One independent quadrant of data was measured out to $2\theta = 50°$. A total of 722 observed reflections $[I > 3\sigma(I)]$ were obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption (μ 12.4 cm^{-1}).

The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS [11]. The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [12] for K, S, Al, N and C. The scattering for potassium was corrected for the real and imaginary components of anomalous dispersion with the table of Cromer and Liberman [13]. The hydrogen atom scattering factors were from ref. 14.

Solution and refinement of structure

The structure was solved by the application of the direct methods program MULTAN [15]. Refinement showed that the correct choice of space group is the centric $C2/m$. Initial placement of the entire model afforded a reliability index $R_1 = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.086$. Conversion to anisotropic temperature parameters and further refinement led to final values of $R_1 = 0.028$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2} = 0.031$. Hydrogen atoms were located on a difference Fourier map but were not refined. Unit weights were used at all stages and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The final value of the esd of an observation of unit weight

TABLE 2

FINAL FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a] FOR $K[Al_2(CH_3)_6SCN]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.48484(9)	0.0000	0.2603(1)	0.00516(7)	0.0137(2)	0.0176(2)	0.0000	0.0057(1)	0.0000
S	0.72275(9)	0.0000	0.5563(1)	0.00358(7)	0.0278(4)	0.0081(2)	0.0000	0.0031(1)	0.0000
Al(1)	0.8110(1)	0.0000	0.2530(2)	0.00377(7)	0.0147(3)	0.0091(2)	0.0000	0.0037(1)	0.0000
Al(2)	0.8724(1)	0.0000	0.7924(2)	0.00342(8)	0.0134(3)	0.0085(2)	0.0000	0.0031(1)	0.0000
N	0.7837(3)	0.0000	0.3893(4)	0.0051(2)	0.020(1)	0.0105(6)	0.0000	0.0048(3)	0.0000
C(1)	0.6906(4)	0.0000	0.0673(6)	0.0051(3)	0.018(1)	0.0114(8)	0.0000	0.0042(4)	0.0000
C(2)	0.8818(2)	0.2014(5)	0.2924(4)	0.0053(2)	0.0202(9)	0.0155(6)	−0.0007(4)	0.0055(3)	0.0004(6)
C(3)	0.8344(4)	0.0000	0.9151(5)	0.0052(3)	0.020(1)	0.0103(7)	0.0000	0.0045(4)	0.0000
C(4)	0.9265(2)	0.2020(5)	0.7831(4)	0.0045(2)	0.0168(8)	0.0134(5)	−0.0003(3)	0.0044(3)	0.0017(5)
C(5)	0.7590(3)	0.0000	0.4590(5)	0.0035(3)	0.015(1)	0.0085(7)	0.0000	0.0023(4)	0.0000
H(1) [C(1)]	0.6600	0.0980	0.0560	5.0					
H(2) [C(1)]	0.6990	0.0000	−0.0080	5.0					
H(3) [C(2)]	0.8750	0.2300	0.2100	5.0					
H(4) [C(2)]	0.9470	0.1800	0.3700	5.0					
H(5) [C(2)]	0.8600	0.2900	0.3200	5.0					
H(6) [C(3)]	0.8800	0.0000	1.0100	5.0					
H(7) [C(3)]	0.7960	0.0980	0.8930	5.0					
H(8) [C(4)]	0.8910	0.3000	0.7700	5.0					
H(9) [C(4)]	0.9900	0.2100	0.8800	5.0					
H(10) [C(4)]	0.9320	0.1980	0.7100	5.0					

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

was 1.25. The final values of the positional and thermal parameters are given in Table 2 *.

Discussion

The structure of the anion and the atom numbering scheme are presented in Fig. 1. The thiocyanate group, both aluminum atoms, and two of the methyl carbon atoms lie in a crystallographic mirror plane.

The versatility of coordination of the thiocyanate ligand is well documented for transition metal complexes [16] but the structure of $K[Al_2(CH_3)_6SCN]$ reveals the first instance of *S,N*-bonding for a Main Group metal compound. The SCN group is strictly linear (the S—C—N angle is 179.4(5)°), and the S—C and N≡C bond lengths, 1.640(6) and 1.156(6) Å, respectively, agree well with those found in related transition metal structures [17,18].

The structural parameters of the known $X—C≡N—Al(CH_3)_3$ compounds are given in Table 4. Those associated with $K[Al_2(CH_3)_6SCN]$ agree well with the ones from the 1/1 complex $Cs[Al(CH_3)_3NCS]$ [19]. It thus appears that the addition of the second trimethylaluminum molecule to the sulfur atom has little effect on the $—SCN—Al(CH_3)_3$ bond lengths and angles. (The only significant change is a lengthening of the S—C bond by 0.03 Å.) The Al—N bond distance is near the mean for organoaluminum compounds, but shorter than the 2.02(1) Å in $CH_3CN \cdot Al(CH_3)_3$ [20] and 2.08(4) Å in $[(CH_3)_2Tl][Al(CH_3)_3NCS]$ [21].

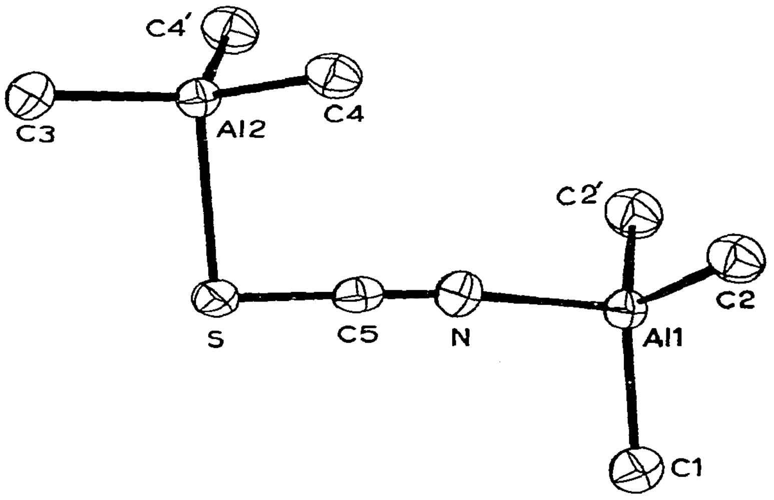


Fig. 1. Structure and atom numbering scheme for $[Al_2(CH_3)_6SCN]^-$.

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* The table of structure factors has been deposited as NAPS Document No. 03423. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR $K[Al_2(CH_3)_6SCN]$

Bond lengths			
Al(1)—N	1.951(5)	Al(2)—C(3)	1.952(6)
Al(1)—C(1)	1.981(5)	Al(2)—C(4)	1.971(4)
Al(1)—C(2)	1.982(4)	S—C(5)	1.640(6)
Al(2)—S	2.489(2)	N—C(5)	1.156(6)
Bond angles			
N—Al(1)—C(1)	103.1(2)	C(3)—Al(2)—C(4)	117.6(1)
N—Al(1)—C(2)	105.7(1)	C(4)—Al(2)—C(4′)	113.9(2)
C(1)—Al(1)—C(2)	114.3(1)	Al(2)—S—C(5)	97.3(2)
C(2)—Al(1)—C(2′)	112.5(2)	Al(1)—N—C(5)	173.5(4)
S—Al(2)—C(3)	99.6(2)	S—C(5)—N	179.4(5)
S—Al(2)—C(4)	101.8(1)		

TABLE 4

COMPARISON OF RELATED PARAMETERS FOR MOLECULES WITH THE X—C≡N—$Al(CH_3)_3$ GROUP

Compound	Al—N (Å)	N≡C (Å)	X—C (Å)	Al—N—C (°)	N—C—X (°)	Ref.
$Cs[Al(CH_3)_3NCS]$	1.944(10)	1.166(13)	1.606(11)	176(1)	179(1)	19
$K[Al_2(CH_3)_6SCN]$	1.951(5)	1.156(6)	1.640(6)	173.5(4)	179.4(5)	This study
$CH_3CN \cdot Al(CH_3)_3$	2.02(1)	1.18(2)	1.45(2)	179(1)	178(1)	20
$[(CH_3)_2Tl][Al(CH_3)_3NCS]$	2.08(4)	1.11(4)	1.54(4)	171(2)	175(2)	21

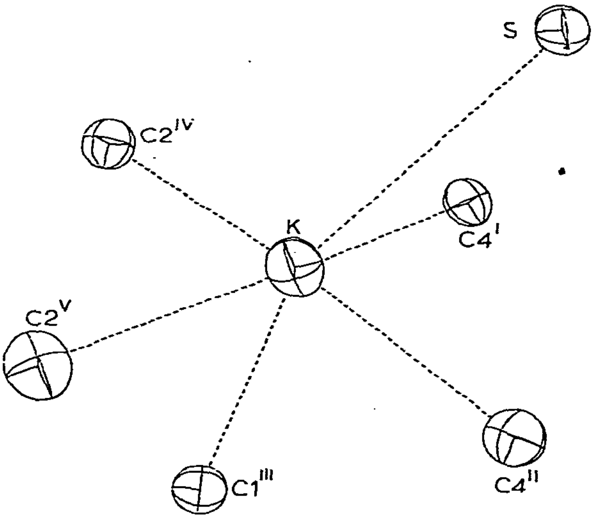

Fig. 2. Potassium ion environment in $K[Al_2(CH_3)_6SCN]$.

It was surprising to find the sulfur atom coordinated to only one trimethylaluminum molecule, and even more so to note the apparent weakness of the Al—S linkage implied by the separation of 2.489(2) Å. Two methods of evaluation of this bond may be used. Firstly, the only other reported Al—S distance in an organometallic compound ($[\mathrm{CH_3SAl(CH_3)_2}]_\infty$), 2.348(4) Å [22], is much shorter. Secondly, Al—Cl bond lengths have been commonly found to occur in the range of 2.17(1) Å [23] for terminal bonds to 2.260(4) Å [24] for a bridging situation. Since the covalent radius [25] of sulfur is 0.05 Å greater than that of chlorine, one might expect an Al—S bond length of ca. 2.30 Å. It is also of interest to note that the sulfur atom appears to be using *p*-orbitals in its bonding scheme, as the Al—S—C bond angle is 97.3(2)°.

We had previously postulated that the Al—NCS linkage in $[\mathrm{(CH_3)_2Tl}][\mathrm{Al(CH_3)_3NCS}]$ was stabilized by a Tl···S interaction. It now appears that the reaction follows the expected hard acid—hard base formulation, and that the mode of coordination in 1/1 complexes of this type may be independent of the nature of the cation. In the present case, the shortest K···S contact is 3.637(2) Å, while there are five K···C distances less than 3.5 Å: $\mathrm{K\cdots C(4)^{I}}$[*] = 3.151(4) Å, $\mathrm{K\cdots C(4)^{II}}$ = 3.151(4) Å, $\mathrm{K\cdots C(1)^{III}}$ = 3.229(5) Å, $\mathrm{K\cdots C(2)^{IV}}$ = 3.263(4) Å, and $\mathrm{K\cdots C(2)^{V}}$ = 3.263(4) Å. An illustration of the potassium ion environment is shown in Figure 2.

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References

1 J.L. Atwood, P.A. Milton, and S.K. Seale, J. Organometal. Chem., 28 (1971) C29.
2 F. Weller, I.L. Wilson and K. Dehnicke, J. Organometal. Chem., 30 (1971) C1.
3 F. Weller and K. Dehnicke, J. Organometal. Chem., 36 (1972) 23.
4 K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, Ann. Chem., 629 (1960) 33.
5 J.L. Atwood and W.R. Newberry, III, J Organometal. Chem., 65 (1974) 145.
6 R.D. Rogers and J.L. Atwood, unpublished results.
7 S.K. Seale and J.L. Atwood, J. Organometal. Chem., 73 (1974) 27.
8 J.R. Jennings, J.E. Lloyd and K. Wade, J. Chem. Soc., (1965) 5083.
9 J.L. Atwood, in N.N. Li (Ed.), Recent Developments in Separation Science, Vol. III, CRC Press, Cleveland, Ohio, 1977, p. 195—209.
10 J.L. Atwood, W.E. Hunter and K.D. Crissinger, J. Organometal. Chem., 127 (1977) 403.
11 Crystallographic programs used on a UNIVAC 1110 include ORFLS (structure factor calculation and least-squares refinement, by W.R. Busing, K.O. Martin and H.A. Levy), ORFFE (distances and angles with esd's, by W.R. Busing, K.O. Martin and H.A. Levy), ORTEP (thermal ellipsoid drawings, by C.K. Johnson), FOURIER (D.J. Hodgson's version of Dellaca and Robinson's program), and BPL (least-squares planes, by W.E. Hunter).
12 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
13 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
14 International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962, p. 202.
15 G. Germain, P. Main and M. Woolfson, Acta Crystallogr. A, 27 (1971) 368.

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[*] Atoms with Roman numeral superscripts are related to those given in Table 2 by: $\mathrm{C(4)^{I}}$, $(\frac{3}{2}-x, \frac{1}{2}-y, 1-z)$; $\mathrm{C(4)^{II}}$, $(\frac{3}{2}-x, -\frac{1}{2}+y, 1-z)$; $\mathrm{C(1)^{III}}$, $(1-x, -y, -z)$; $\mathrm{C(2)^{IV}}$, $(-\frac{1}{2}+x, -\frac{1}{2}+y, z)$; $\mathrm{C(2)^{V}}$, $(-\frac{1}{2}+x, \frac{1}{2}-y, z)$.

16 A.H. Norbury and A.I.P. Sinha, Quart. Rev., 24 (1970) 69.
17 A. Mangia, M. Nardelli and G. Pelizzi, Acta Crystallogr., B30 (1974) 487.
18 M. Cannas, G. Carta, A. Cristini and G. Marongiu, J. Chem. Soc. Dalton, (1976) 300.
19 R. Shakir, M.J. Zaworotko and J.L. Atwood, unpublished results.
20 J.L. Atwood, S.K. Seale and D.H. Roberts, J. Organometal. Chem., 51 (1973) 105.
21 S.K. Seale and J.L. Atwood, J. Organometal. Chem., 64 (1974) 57.
22 D.J. Brauer and G.D. Stucky, J. Amer. Chem. Soc., 91 (1969) 5462.
23 J.L. Atwood, D.C. Hrncir and W.R. Newberry, III, Cryst. Struct. Comm., 3 (1974) 615.
24 R.D. Rogers, W.J. Cook and J.L. Atwood, Inorg. Chem., in press.
25 L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, N.Y., 3rd ed., 1960, p. 249.