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An ^{27}Al NMR Study on the Complexes Present in the Solutions of Potassium Hexathiocyanatoaluminate(III)

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Synopsis. The species present in the solutions of potassium hexathiocyanatoaluminate(III) in various solvents were identified by ^{27}Al NMR spectra of the solutions. In dimethyl sulfoxide solution containing excess KSCN, the spectrum consists of 7 resonances due to $[\mathrm{Al(NCS)}_n(\mathrm{DMSO})_{6-n}]^{(3-n)+}$ (n=0—6), whereas a single resonance arising from $[\mathrm{Al(NCS)_6}]^{3-}$ was observed in propylene carbonate or acetone.

The ^{27}Al NMR spectrum of an aqueous solution containing aluminum chloride and potassium thiocyanate shows a resonance at about 6 ppm upfield from the line due to $[\mathrm{Al(H_2O)_6}]^{3+}$. The spectrum is similar to that of aqueous aluminum sulfate solution in which a separate resonance is located at 3 ppm upfield from the main one.[1] The upfield resonance of the former solution may be assigned to a species like $[\mathrm{Al(SCN)(H_2O)_5}]^{2+}$.

Wehrli and Wehrli[2] studied species present in $\mathrm{AlCl_3}$ solution of acetonitrile (AN) by ^{27}Al NMR. They showed that $\mathrm{AlCl_4}^-$ and various hexacoordinated solvation complexes exist in the solutions and the relative amount of the species depends on the concentration of the solute. ^{27}Al NMR spectra of AN solution containing $\mathrm{KAlCl}_x(\mathrm{SCN})_{4-x}$ have been reported.[3] It was shown that Cl^- and SCN^- mixed ligand tetracoordinated Al(III) species are in these solutions.

Since potassium hexathiocyanatoaluminate(III), is soluble in a variety of solvents, it seems interesting to identify the complexes present in aqueous and nonaqueous solutions. We have attempted to study the ^{27}Al NMR spectra of the solutions of the complex salt in various solvents.

Experimental

The preparation of potassium hexathiocyanatoaluminate(III) was almost similar to that described in the literature.[4] Anhydrous $\mathrm{AlCl_3}$ was added to a solution of six equivalent KSCN in AN and the precipitated KCl was filtered off. The solvent was then removed with distillation under reduced pressure. The residue was recrystallized from acetone. ^{27}Al NMR spectra were recorded on a JEOL FT-90Q at 23.3 MHz or on a Bruker AC-250 at 65.18 MHz. The temperature of the sample was 28 °C. The Al NMR shift was measured with an external standard of aqueous $\mathrm{NaAlO_2}$ solution. The shift data were then converted to the values with reference to the usual standard of $[\mathrm{Al(H_2O)_6}]^{3+}$ line. The error in the shift was estimated as ±1 ppm.

Results and Discussion

Figure 1 reproduces ^{27}Al NMR spectra of the solutions of potassium hexathiocyanatoaluminate(III) and of the solutions containing the salt and excess KSCN in dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), and AN. In these solutions, ^{27}Al NMR resonances were observed only in the region of hexacoordinated Al(III) species.[5] In DMSO with excess KSCN the spectrum consists of 7 resonances, which can be assigned to the hexacoordinated SCN^- and DMSO mixed ligand complexes. Since two upfield lines newly appear by adding excess KSCN, the most upfield narrow line at −34.0 ppm should be the resonance caused by hexathiocyanatoaluminate(III) ion. In DMA a broad resonance was located at downfield of the narrow resonance at −34.2 ppm, the relative intensity of which was increased by adding excess KSCN. A shoulder was observed at downfield side of the resonance of −33.0 ppm in AN solution. It disappeared in the solution containing excess KSCN. As is shown in Fig. 2, in propylene carbonate (PC), the spectrum consists of only one narrow resonance at −33.9 ppm which was unchanged by addition of excess KSCN. Addition of DMSO to the PC solution produces lines of SCN^--DMSO mixed ligand complex that are seen in the DMSO solution. The intensity of the lines increased with the increase of DMSO content in the solution. This will be the evidence for the fact that hexathiocyanatoaluminate(III) ion is the only Al spe-

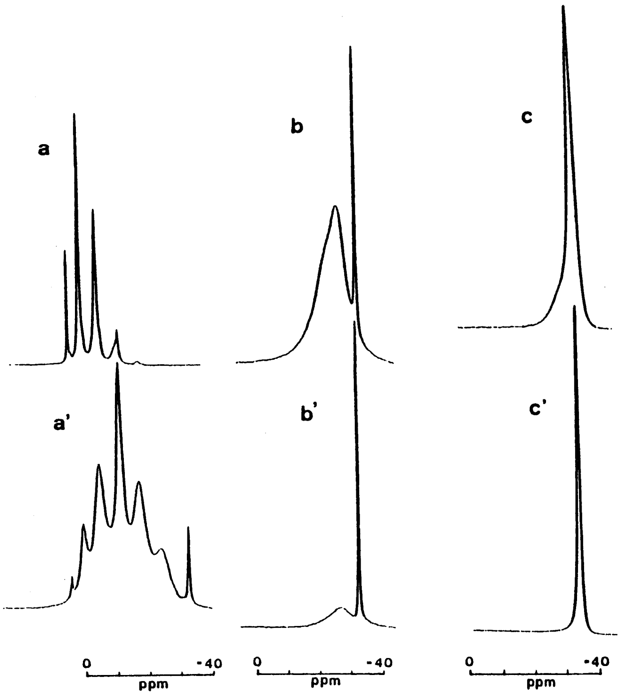

Fig. 1. ^{27}Al NMR spectra at 65.18 MHz of potassium hexathiocyanatoaluminate(III) in a) DMSO, a′) DMSO containing KSCN, b) DMA, b′) DMA containing KSCN, c) AN, c′) AN containing KSCN. The concentration of the solutions are indicated in Tables 1 and 2.

cies present in the solvent of low coordinating ability. In acetone (AC) the situation was similar to that in PC. The solution and that containing excess KSCN gave a single resonance at −33.9 ppm. In this way the shift of Al species containing six SCN^- in its coordination sphere was determined as −34 ppm.

The shift of $[Al(AN)_6]^{3+}$, in which AN coordinates to Al through N atom is reported as −32.7 ppm.[2] Since the shifts of hexaethylisocyanatoaluminum ion, $[Al(SCNEt)_6]^{3+}$, and tris(dimethyldithiocarbamato)-aluminum, $[Al(S_2CNMe_2)_3]$, are reported as 20[8] and 22 ppm,[9] respectively, the shift of $[Al(SCN)_6]^{3-}$ would be around 20 ppm, if SCN^- coordinates to Al through S atom. Thus it can be concluded that SCN^- coordinates to Al^{3+} through N atom in these solutions and we will write the formula of the complex as $[Al(NCS)_6]^{3-}$.

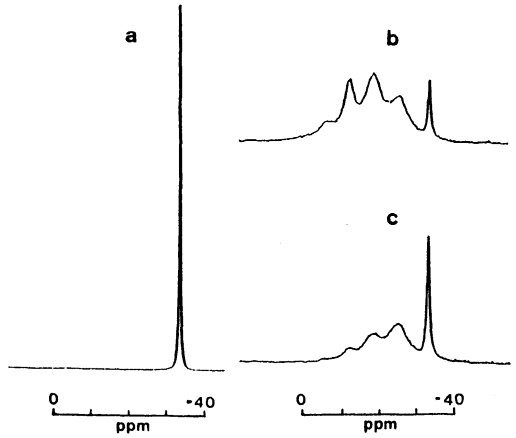

Fig. 2. ^{27}Al NMR spectra at 23.3 MHz of potassium hexathiocyanatoaluminate(III) in a) PC, b) PC-DMSO, Al:PC:DMSO mole ratio=1:122:10, and c) PC-DMSO, Al:PC:DMSO mole ratio=1:126:4.4.

All of the Al NMR shift of species coordinated octahedrally to ligands through O atom such as $[Al(DMF)_6]^{3+}$ (−2.6 ppm)[5] and $[Al(H_2O)_6]^{3+}$ (0 ppm) are around 0 ppm. Thus the most downfield resonance at 3.1 ppm in the DMSO solution can be assigned to $[Al(DMSO)_6]^{3+}$. Other 5 lines located between 3.1 and −34 ppm due to $[Al(NCS)_6]^{3-}$ may be assigned to $[Al(NCS)_n(DMSO)_{6-n}]^{(3-n)+}$, where n=1 to 5. Table 1 compares the observed shifts with those calculated by applying the pairwise additivity model.[6] In the present octahedral complex with two kinds of ligand, NCS^- and DMSO, the pairwise additivity parameters to be evaluated are $\eta_{O\text{-}O}$, $\eta_{N\text{-}N}$, and $\eta_{O\text{-}N}$, and the chemical shift of Al was calculated by summing the appropriate combination of twelve parameters corresponding to twelve edges of the octahedral complex in question. Although our spectra could not resolve lines from cis and trans isomers with n of 2, 3, and 4, the observed shifts are consistent with those calculated for cis isomers which were predicted[7] as giving narrower lines than those of trans isomers.

Table 1. Comparison between Observed and Calculated ^{27}Al Chemical Shifts of Al^{3+}- SCN^-- DMSO Mixed Ligand Complexes

Species	Obsd. shift/ppm (half width/Hz)		Calcd. shifts/ppm applying pair additive approximation[a)]
	$K_3[Al(NCS)_6]$[b)]	$K_3[Al(NCS)_6]$ +KSCN[c)]	
$[Al(DMSO)_6]^{3+}$	3.1(25)	3.1(65)	3.10
$[Al(DMSO)_5(NCS)]^{2+}$	−0.7(52)	−0.7(80)	−0.70
$[Al(DMSO)_4(NCS)_2]$	−5.8(70)	−5.3(108)	cis −5.7
			trans −4.5
$[Al(DMSO)_3(NCS)_3]$	−12.2(100)	−12.3(75)	cis −11.9
			trans −10.7
$[Al(DMSO)_2(NCS)_4]^-$	−18.4(100)	−18.3(—)	cis −18.1
			trans −16.9
$[Al(DMSO)(NCS)_5]^{2-}$	—	−25.3(—)	−25.4
$[Al(NCS)_6]^{3-}$	—	−34.0(52)	−34.00

a) Additivity parameter values(ppm): $\eta_{O\text{-}O}$=0.258; $\eta_{N\text{-}N}$=−2.833; $\eta_{O\text{-}N}$=−0.691. These values are estimated from the observed shifts of $[Al(DMSO)_6]^{3+}$, $[Al(NCS)_6]^{3-}$, and $[Al(DMSO)_5(NCS)]^{2+}$. b) 0.1 M. c) 0.3 M $K_3[Al(NCS)_6]$ and 3 M KSCN (1 M= 1 mol dm^{-3}).

Table 2. Chemical Shifts and Linewidths of Resonances in the Solutions of $K_3[Al(NCS)_6]$ and Those Containing Excess KSCN

Solvent	Solute	Shift/ppm (linewidth/Hz)	
AN	0.3 M $K_3[Al(NCS)_6]$		−33.0(140)
	0.4 M $K_3[Al(NCS)_6]$, 3 M KSCN		−33.3(65)
DMA	0.07 M $K_3[Al(NCS)_6]$	−28.5(610)	−34.2(35)
	0.05 M $K_3[Al(NCS)_6]$, 2 M KSCN	−28.5(580)	−34.2(20)
PC	0.2 M $K_3[Al(NCS)_6]$		−33.9(15)
	0.2 M $K_3[Al(NCS)_6]$, 2 M KSCN		−33.9(15)
AC	0.2 M $K_3[Al(NCS)_6]$		−33.9(65)
	0.2 M $K_3[Al(NCS)_6]$, 2 M KSCN		−33.9(41)

In DMA, the main species present in the solution of $K_3[Al(NCS)_6]$ appear to be $[Al(NCS)_n(DMA)_{6-n}]^{(3-n)+}$ of n of 5 or 4. Since the shift of $[Al(AN)_6]^{3+}$ is very close to that of $[Al(NCS)_6]^{3+}$, no definite conclusion could be drawn for the species present in the AN solution. It seems interesting that while a solvent of high coordinating ability like DMSO competes with SCN^- in coordinating Al^{3+}, a solvent of relatively low coordinating ability like AN competes with Cl^- in occupying the octahedral sites of Al^{3+}.[2] Table 2 gives the shifts of the complexes.

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