Synthesis and Characterization of New Group 13 Complexes of 2-Acetylpyridine-S-methyldithiocarbazate. Single-Crystal Structure of $Me_2Ga[NC_5H_4C(CH_3)NNC(S)SMe]$ and $Me_2In[NC_5H_5C(CH_3)NNC(S)SMe]$

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The synthesis and characterization of the mononuclear group 13 heterocyclic carboxaldehyde methyldithiocarbazate complexes $Me_2M[NC_5H_4CRNNC(S)SCH_3]$ (M=Al, R=H(**1**); M=Ga, R=H(**2**); M=Al, R=CH_3(**3**); M=Ga, R=CH_3(**4**); M=In, R=CH_3(**5**)) are described. Compounds **1-5** were prepared by the reaction of MMe_3 (M= Al, Ga, In) with 2-formy or 2-acetylpyridine-*S*-methyldithiocarbazate in toluene. These compounds **1-5** have been characterized by microanalysis, NMR (^1H, ^{13}C) spectroscopy, mass spectra, and single-crystal X-ray diffraction. X-ray single-crystal diffraction analyses reveal that **4-5** are mononuclear metal compounds with coordination number of 5 and N,N,S coordination mode.

Introduction

α-*N*-Heterocyclic carboxaldehyde thiosemicarbazones comprise interesting classes of experimental cancer chemotherapeutic agents in that the ligands are strong metal chelating agents.[1] Extensive literatures on the antitumor properties of many α-*N*-heterocyclic carboxaldehyde thiosemicarbazones are now available. The terdentate heterocyclic carboxaldehyde thiosemicarbazones have been shown to form complexes with various transition-metal ions including Cu(II),[2] Ni(II),[3] Co(II),[4] Fe(II),[5] Hg(I),[6] and Tl(I).[6] Ga(III) and In(III) complexes of heterocyclic carboxaldehyde thiosemicarbazones have continued to attract attention due to the fact that radioactive congeners of gallium(^{67}Ga) and In (^{111}In, ^{113}In) are γ-ray emitters with energy which makes them useful for medical diagnostic agents.[7] Kepper and coworker[8] developed gallium(III) complexes employing ligands which themselves and antiviral and antitumor activity, such as α-N-heterocyclic carboxaldehyde thiosemicarbazones. Recently, we[9] have extensively studied the terdentate heterocyclic carboxaldehyde thiosemicarbazone complexes.

Motivated by an interest in the effects of α-N-heterocyclic carboxaldehyde thiosemicarbazones geometry on the coordination environments of aluminum, gallium, and indium, we began a systematic study of the use of terdentate ligands by replacing the R'NH groups at the terminal(N) position of the thiosemicarbazones with alkylthio groups for organometallic group 13 compounds. We now describe the interaction of the trimethylaluminum, gallium, and indium with N,N,S-terdentate ligand, pyridine-2-carbaldehyde-*S*-methyldithiocarbazate.

Experimental Section

All reactions and manipulations were conducted under a nitrogen atmosphere in an inert-atmosphere glovebox or by standard high-vacuum-line techniques. Toluene and hexane were distilled from sodium/benzophenone prior to use. Trimethylaluminum, gallium, and indium were purchased from Strem Chemicals, Inc., 2-Acetylpyridine and 2-formylpyridine were purchased from Aldrich. All ^1H and ^{13}C NMR spectra were recorded using a Bruker AM-360 spectrometer. ^1H NMR spectra were referenced against the residual ^1H impurity of the deuterated solvent, and ^{13}C NMR spectra were referenced against the ^{13}C resonance of the solvent. IR spectra were recorded on a Shimadzu FT IR-8501 spectrometer. Mass spectra were recorded on a high resolution VG70-VSEG instrument, and elemental analyses were performed by the Basic Science Center. The ligand $[NC_5H_4CRNNHC(S)SMe]$ (R=H, CH_3) were prepared by the literature method.[10]

(2-Formylpyridine-S-methyldithiocarbazate)dimethylaluminum (1). To a stirred suspension of 2-formylpyridine-*S*-methyldithiocarbazate (1.02 g, 3.29 mmol) in toluene (35 mL) was added trimethylaluminum (0.35 g, 3.34 mmol) at room temperature. The stirred mixture was allowed to warm to 35 °C, during which the suspension dissolved. The resulting yellow solution was stirred at that temperature for 2h. The volume was reduced to *ca.* 10 mL. Cooling to 0 °C afforded the crystalline yellow product. Yield: 1.13 g (88%). mp 126-130 °C. ^1H NMR (300 MHz, C_6D_6): δ 7.83 (s, 1H, *CH*), 7.55 (m, 1H, *Ph*), 6.81 (m, 1H, *Ph*), 6.31 (m, 2H, *Ph*), 2.10 (s, 3H, S-CH_3), 0.05 (s, 6H, Al-CH_3); ^{13}C NMR (C_6D_6): δ 180.92, 145.29, 144.74, 140.98, 123.03, 122.60, 17.38, −0.04; IR (on KBr pellet; cm^{-1}) 2992 (w), 2985 (w), 1598 (m), 1572 (w), 1548 (w), 1525 (w), 1476 (m), 1438 (m), 1372 (m), 1342 (m), 1306 (m), 1194 (m), 1150 (m), 1101 (m), 1048 (s), 1002 (w), 955 (m), 848 (br), 778 (w), 750 (w), 692 (w), 658 (w), 632 (w); MS: m/z (relative intensity) 267 (M^+, 12), 237 (M^+-2Me, 25). Anal. Calcd. for $C_{10}H_{14}N_3S_2Al$: C, 44.95; H, 5.24. Found: C, 44.52; H, 5.08.

(2-Formylpyridine-S-methyldithiocarbazate)dimethylgallium) (2). **2** was prepared according to the similar method used for **1**, except that trimethylgallium was used instead of trimethylauminum. Yield: 92%. mp 156 °C (dec.). ^1H NMR (300 MHz, C_6D_6): δ 7.99 (s, 1H, *CH*), 7.72 (m, 1H, *Ph*), 6.64 (m, 1H, *Ph*), 6.31 (m, 1H, *Ph*), 6.16 (m,

1H, *Ph*), 2.46 (s, 3H, S-CH_3), 0.26 (s, 6H, Ga-CH_3); ^{13}C NMR (C_6D_6): δ 181.43 (*C*-S), 148.38 (*C*=N), 147.02, 146.75, 137.68, 125.15, 125.09 (*Ph*), 16.01 (S-CH_3), −0.93 (Ga-CH_3); IR (on KBr pellet; cm^{-1}): 2985 (w), 1602 (m), 1578 (w), 1550 (w), 1525 (w), 1482 (m), 1432 (m), 1395 (s), 1340 (s), 1302 (m), 1204 (w), 1198 (m), 1150 (m), 1122 (w), 1062 (s), 1006 (w), 978 (s), 938 (m), 898 (w), 776 (w), 750 (s), 698 (w), 660 (w), 638 (w); MS: m/z (relative intensity) 310 (M^+, 8), 280 (M^+-2Me, 18). Anal. Calcd. for $C_{10}H_{14}N_3S_2Ga$: C, 38.74; H, 4.52. Found: C, 38.48; H, 4.38.

(2-Acetylpyridine-*S*-methyldithiocarbazate)dimethylaluminum (3). **3** was prepared according to the similar method used for **1**, except that 2-acetylpyridine-*S*-methyldithiocarbazate was used instead of 2-formylpyridine-*S*-methyldithiocarbazate. Yield: 86%. mp 150 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ 7.87 (m, 1H, *Ph*), 6.68 (m, 1H, *Ph*), 6.42 (m, 2H, *Ph*), 2.32 (s, 3H, S-CH_3), 1.91 (s, 3H, CH_3), 0.01 (s, 6H, Al-CH_3); ^{13}C NMR (C_6D_6): δ 189. 78 (*C*-S), 158.43 (*C*=N), 147.31, 146.26, 139.48, 127.68, 123.05 (*Ph*), 16.06 (S-CH_3), 14.58 (CH_3), −0.04 (Al-CH_3); IR (on KBr pellet; cm^{-1}) 2910 (w), 1595 (w), 1574 (m), 1452 (m), 1420 (s), 1408 (s), 1362 (w), 1335 (w), 1313 (w), 1295 (m), 1272 (br), 1252 (m), 1165 (w), 1143 (w), 110 8(w), 1092 (w), 1058 (s), 1038 (m), 948 (m), 817 (m), 770 (s), 773 (w), 672 (m), 650 (m); MS: m/z (relative intensity) 281 (M^+, 14), 251 (M^+-2Me, 26). Anal. Calcd. for $C_{11}H_{16}N_3S_2Al$: C, 46.96; H, 5.69. Found: C, 46.61; H, 5.51.

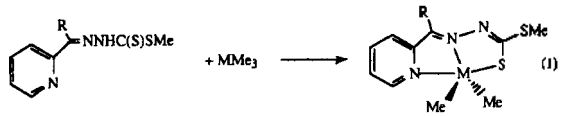
(2-Acetylpyridine-*S*-methyldithiocarbazate)dimethylgallium (4). **4** was prepared according to the similar method used for **1**, except that 2-acetylpyridine-*S*-methyldithiocarbazate and trimethylgallium were used instead of 2-formylpyridine-*S*-methyldithiocarbazate and trimethylaluminum, respectively. Yield: 94%. mp 145-150 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ 7.83 (m, 1H, *Ph*), 6.81 (m, 1H, *Ph*), 6.63 (m, 1H, *Ph*), 6.46 (m, 1H, *Ph*), 2.44 (s, 3H, S-CH_3), 2.06 (s, 3H, CH_3), 0.26 (s, 6H, Ga-CH_3); ^{13}C NMR (C_6D_6): δ 193.11 (*C*-S), 155.50 (*C*=N), 148.39, 145.82, 138.22, 124.92, 122.31 (*Ph*), 15.96 (S-CH_3), 15.03 (CH_3), −0.57 (Ga-CH_3); IR (on KBr pellet; cm^{-1}) 2938 (w), 1587 (w), 1574 (m), 1472 (m), 1420 (s), 1362 (w), 1313 (w), 1295 (m), 1282 (w), 1252 (w), 1210 (w), 1188 (w), 1178 (m), 1138 (m), 1092 (m), 1050 (m), 1032 (m), 1014 (s), 1004 (m), 932 (s), 812 (m), 762 (m), 733 (m), 668 (w), 620 (m); MS: m/z (relative intensity) 324 (M^+, 16), 294 (M^+-2Me, 28). Anal. Calcd. for $C_{11}H_{16}N_3S_2Ga$: C, 40.76; H, 4.94. Found: C, 40.28; H, 4.62.

(2-Acetylpyridine-*S*-methyldithiocarbazate)dimethylindium (5). **5** was prepared according to the similar method used for **1**, except that 2-acetylpyridine-*S*-methyldithiocarbazate and trimethylindium were used instead of 2-formylpyridine-*S*-methyldithiocarbazate and trimethyl-aluminum, respectively. Yield: 82%. mp 152 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.94 (m, 1H, *Ph*), 7.21 (m, 1H, *Ph*), 6.94 (m, 1H, *Ph*), 6.52 (m, 1H, *Ph*), 2.38 (s, 3H, S-CH_3), 2.14 (s, 3H, CH_3), 0.17 (s, 6H, In-CH_3); ^{13}C NMR (C_6D_6): δ 184.74 (*C*S), 164.28 (*C*N), 154.22, 148.82, 138.64, 132.29 (*Ph*), 17.22 (S-CH_3), 15.37 (CH_3), −0.17 (In-CH_3); IR (on KBr pellet; cm^{-1}) 2922 (w), 1582 (w), 1570 (w), 1481 (m), 1422 (s), 1406 (s), 1368 (w), 1310 (w), 1298 (m), 1280 (m), 1275 (sh), 1258 (w), 1214 (w), 1182 (w), 1178 (sh), 1142 (m), 1128 (w), 1098 (m), 1054 (m), 1037 (m), 1021 (s), 1012 (m), 938 (s), 817 (m), 792 (w), 764 (m), 738 (m), 662 (w), 624 (w). Anal. Calcd. for $C_{11}H_{16}N_3S_2In$: C, 35.82; H, 4.33, Found: C, 35.23; H, 4.11.

Crystal Structure Determination of 4 and 5. A yellow crystal of compound **4** crystallized from toluene (0 °C) was mounted in a glass capillary in a random orientation. A summary of the crystal and X-ray structural analysis data for compound **4** is presented in Table 3. All measurements for **4** were made on a Rigaku AFC65 diffractometer with graphite monochromated Mo K_α radiation (λ=0.71069 Å) and a 12KW rotating anode generator. From the systematic absences of *0kl* ($k+l\neq 2n$) and *hk0* ($h\neq 2n$), the space group could be determined to be orthorhombic *Pnma*. The data were collected at a temperature of −120±1 °C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. A total of 1488 reflections which were measured after every 150 reflections remain constant throughout data collection. Crystal of **5** was grown from toluene at −15 °C. Crystal of **5** was mounted on a thin glass fiber and sealed under argon. Data sets of **5** were collected on a Rigaku/RAXISIIa area detector employing graphite-monochromated Mo Kα radiation (λ=0.71069 Å) at a temperature of 253 K. The structures were solved by direct methods. Refinements were by full-matrix least-squares techniques based on F to minimize the quantity $\Sigma W(|F_o|-|F_c|)^2$ with $w=1/\sigma^2(F)$. Non-hydrogen atoms of **4** and **5** were refined anisotropically. Hydrogen atoms at difference map positions were included in the structure factor calculation.

Results and Discussion

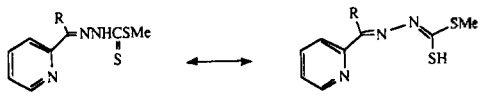
Synthesis and Characterization of $(Me_2M)[NC_5HCRNNC(S)SCH_3]$ (M=Al, Ga, In; R=H, CH_3). The reaction of 2-formyl or 2-acetylpyridine-*S*-methyldithiocarbazate with trimethylaluminum, gallium, and indium in toluene at 30 °C affords the corresponding organo-aluminum, gallium, and indium complexes, in which one hydrogen atom has been lost from the aza hydrogen atom (eq. 1). The resulting yellow compounds **1-5** were isolated as air-sensitive, crystalline solids in high yields. These complexes



R = H , M = Al (1) ; R = H , M = Ga (2)
R = Me , M = Al (3) ; R = Me , M = Ga (4)
R = Me , M = In (5)

are readily soluble in benzene and toluene and they are insoluble in hexane. The complexes **1-5** have been characterized by ^{1}H, ^{13}C NMR, IR, mass spectra, and elemental analyses. The structures of compounds **4** and **5** were determined by X-ray diffraction. The initial indication of the mononuclear formulation for **4** stemmed from the observation of a parent ion in the mass spectrum at m/z 324, followed by a series of fragmentations attributable to the loss of Me groups. The ^{1}H NMR spectrum of **1** shows resonances at 2.44 and 2.06 ppm due to the hydrogen atoms of S-CH_3 and C-CH_3, respectively. The methyl groups of the gallium center give rise to one signal at δ 0.26 in the region

expected for a σ-bonded species due to the hydrogen atoms of the Ga-Me group. The chemical shift is consistent with prior observations of five-coordinate Ga atoms.[11] The ^{13}C NMR spectrum of **4** shows one resonance at −0.57 ppm due to the carbon atom of the Ga-CH_3 in five-coordinate environment. The carbons attached to the imine groups appear at 193.11 and 155.50 ppm in the ^{13}C NMR spectrum. The resonance at 193.11 ppm is assigned to the carbon atom bonded to S atom. The value is within the range observed for other metal complexes.[9] The infrared spectrum of **4** indicates the mode of the ligand coordination. The peak at 1587 cm^{-1} is assigned to the ring deformation mode. Positive shift of the mode compared to that of the ligand indicates that the pyridyl nitrogen coordinates to the gallium moiety. The streching mode of ν(CS) at 762 cm^{-1} is significantly decreased. This could involve an azine ⟷ imine-hydrazone tautomerism, *i.e.* a 1,3-proton shift. The compounds **1, 2, 3, 5** have been characterized by spectroscopic data assigned similarly to that of **4**.



Although all the spectral data of **4** are consistent with the schematic structure shown in eq. 1, it was not possible to deduce the exact structure of **4**. Hence we undertook a crystallographic investigation to determine the solide state structure.

Description of the Molecular Structure of $(Me_2Ga)[NC_5H_4CMeNNC(S)SMe]$. Crystals **4** suitable for X-ray diffraction study were grown from toluene at 0 °C. A summary of data collection and crystallographic parameters are given in Table 1. Atomic positional parameters are given in Table 2, while selected bond lengths and angles are given in Table 3. An ORTEP diagram of the solid state structure giving the atom-numbering scheme used in the table is shown in Figure 1. The molecule contains GaNCCN and GaNNS five-membered rings. The gallium atom is coplanar with N(1), C(8), and C(8)*. The bond angle of N(1)-Ga(1)-C(8) is 152.3(1)°. The overall structure of Ga may be described as a distorted trigonal bipyramid. The distortion is mainly caused by the rigid geometry of the 2-acetylpyridine-*S*-methyldithiocarbazate ligand (bite angle, *i.e.*, N(1)-Ga(1)-N(3) 72.9(2)°; N(1)-Ga(1)-S(1) 79.4(1)°). The coordination sphere of Ga is completed by the remaining nitrogen and sulfur atoms. The Ga(1)-S(1) distance (2.488(2) Å) is comparable to those observed for $Ga(SC_5H_4N)_3$ (2.420(3) Å)[12] and $[Ga_2(OC_2H_5)_2(SC_5H_4N)_4]$ (2.431(2) Å).[12]

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotopic Displacement Parameters (Å^2×10^3) for Compound **4**

Atom	x	y	z	B(eq)[a]
Ga(1)	0.74241(5)	1/4	0.08683(4)	1.95(3)
S(1)	0.6017(1)	1/4	0.1971(1)	2.93(7)
S(2)	0.3528(1)	1/4	0.18733(9)	2.93(8)
N(1)	0.5872(4)	1/4	0.0239(3)	1.8(2)
N(2)	0.4792(4)	1/4	0.0601(3)	2.0(2)
N(3)	0.7879(4)	1/4	−0.0430(3)	2.2(2)
C(1)	0.4833(5)	1/4	0.1370(3)	2.1(2)
C(2)	0.5839(5)	1/4	−0.0523(3)	1.9(2)
C(3)	0.6975(5)	1/4	−0.0920(3)	2.1(2)
C(4)	0.7092(5)	1/4	−0.1732(4)	2.9(3)
C(5)	0.8204(6)	1/4	−0.2044(4)	3.8(4)
C(6)	0.9118(5)	1/4	−0.1552(4)	3.5(3)
C(7)	0.8937(5)	1/4	−0.0738(4)	2.8(3)
C(8)	0.8181(4)	0.0113(6)	0.1038(2)	2.9(2)
C(9)	0.4780(5)	1/4	−0.1004(3)	2.5(3)
C(10)	0.2492(5)	1/4	0.1083(4)	3.2(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic dispalcement parameter defined as (4/3) $[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

Ga(1)-S(1)	2.488(2)	N(1)-N(2)	1.499(6)
Ga(1)-N(1)	2.101(4)	N(1)-C(2)	1.293(7)
Ga(1)-N(3)	2.267(5)	N(2)-C(1)	1.306(7)
Ga(1)-C(8)	1.965(4)	N(3)-C(3)	1.341(7)
S(1)-C(1)	1.716(6)	N(3)-C(7)	1.339(7)
S(2)-C(1)	1.744(6)	C(2)-C(3)	1.484(8)
S(2)-C(10)	1.805(6)	C(2)-C(9)	1.480(7)
S(1)-Ga(1)-N(1)	79.4(1)	Ga-N(1)-C(2)	122.3(4)
S(1)-Ga(1)-N(3)	152.3(1)	N(2)-N(1)-C(2)	114.4(4)
S(1)-Ga(1)-C(8)	100.7(1)	N(1)-N(2)-C(1)	114.0(4)
N(1)-Ga(1)-N(3)	72.9(2)	Ga(1)-N(3)-C(3)	114.8(4)
N(1)-Ga(1)-C(8)	117.4(1)	Ga(1)-N(3)-C(7)	126.5(4)
N(3)-Ga(1)-C(8)	92.2(1)	C(3)-N(3)-C(7)	118.8(5)
C(8)-Ga(1)-C(8)	123.7(3)	S(1)-C(1)-S(2)	114.2(3)
Ga(1)-S(1)-C(1)	94.7(2)	S(1)-C(1)-N(2)	128.6(4)
C(1)-S(2)-C(10)	102.6(3)	N(1)-C(2)-C(3)	115.3(5)
Ga(1)-N(1)-N(2)	123.3(3)	N(1)-C(2)-C(9)	125.2(5)

Table 3. Crystal and X-ray Structural Analysis Data for Compound **4** and **5**

	4	**5**
empirical formula	$C_{11}H_{16}N_3S_2Ga$	$C_{11}H_{16}N_3S_2In$
molecular weight	324.11	369.21
crystal color/habit	yellow/prismatic	yellow
crystal system; space group	orthorhombic; *Pnma*	orthorhombic; $P2_12_12_1$
a/Å	11.650(2)	11.003
b/Å	7.256(2)	13.891
c/Å	16.979(4)	9.583
V/Å^3	1435(1)	1464.768
D_c/gcm $^{-3}$	0.750	1.67
μ(Mo Kα)/cm^{-1}	10.86	18.80
Z	2	4
reflection measured	1488	1569
observed reflections [I>3.00σ(I)]	1051	1334
number of parameters refined	100	154
goodness of fit	1.57	1.72
R_1	0.035	0.040
R_w	0.041	0.044

$R_1=\Sigma||F_o|-|F_c||/[\Sigma|F_o|]$ $R_w=\Sigma w(F_o^2-F_c^2)^2]/[\Sigma wF_o^2]\}^{1/2}$

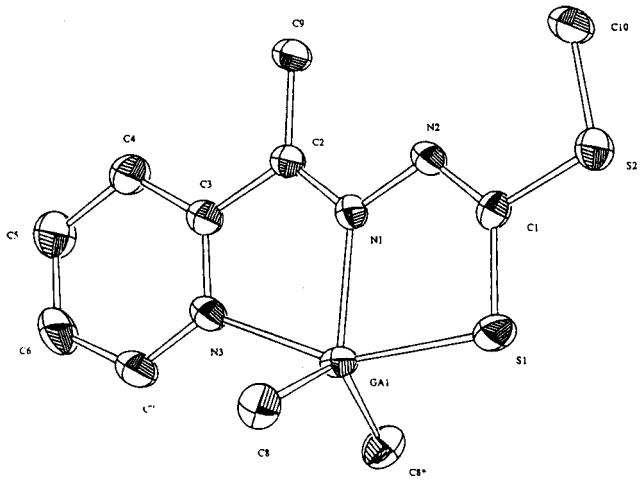


Figure 1. ORTEP diagram for 4 and atom labelling scheme.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotopic Displacement Parameters ($Å^2 \times 10^3$) for Compound **5**

Atom	x	y	z	B(eq)[a]
In1	0.48973(5)	0.46789(4)	0.37805(6)	3.25(1)
S11	0.7086(2)	0.4362(2)	0.4694(3)	4.46(6)
S12	0.7921(2)	0.3573(2)	0.7304(2)	3.79(5)
N1	0.2807(6)	0.4171(6)	0.4139(7)	3.5(2)
N8	0.4665(6)	0.3722(5)	0.5774(7)	2.9(2)
N9	0.5616(6)	0.3526(5)	0.6659(7)	3.3(2)
C2	0.1894(9)	0.4454(7)	0.334(1)	4.4(2)
C3	0.0687(8)	0.4258(8)	0.360(1)	4.3(2)
C4	0.0445(8)	0.3703(7)	0.478(1)	4.3(2)
C5	0.1378(7)	0.3388(7)	0.5598(10)	3.7(2)
C6	0.2548(7)	0.3652(6)	0.5284(9)	3.2(2)
C7	0.3616(7)	0.3387(7)	0.617(1)	3.3(2)
C10	0.6673(8)	0.3806(6)	0.623(1)	3.4(2)
C13	0.7250(9)	0.3008(8)	0.881(1)	5.2(2)
C14	0.3421(9)	0.2821(8)	0.7469(10)	4.4(2)
C15	0.4492(9)	0.6105(7)	0.455(1)	4.0(2)
C16	0.496(1)	0.3977(7)	0.1789(9)	4.9(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as (4/3) $[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)b_{13}+bc(\cos\alpha)\beta_{23}]$.

The pyridyl Ga(1)-N(3) distance (2.267(5) Å) is slightly longer than the amido Ga(1)-N(1) distance (2.101(4) Å), a feature consistent with the literature.[13] The imine C(1)-N(2) bond distance (1.306(7) Å) is shorter than that of single bond distance of C-N. The short bond distance demonstrates the involvement of 1,3-proton shift. The Ga(1)-C (8) bond distance (1.965(4) Å) falls well within the range commonly observed for five-coordinate gallium complexes.[14]

Description of the Molecular Structure of (Me$_2$In)[NC$_5$H$_4$CMeNNC(S)SMe]. Crystals **5** suitable for X-ray diffraction study were grown from toluene at −15 °C. A summary of data collection and crystallographic parameters are given in Table 1. Atomic positional parameters are given in Table 4, while selected bond lengths and angles are given in Table 5. An ORTEP diagram of the solid state

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

In(1)-S(1)	2.600(3)	N(8)-N(9)	1.374(9)
In(1)-N(1)	2.430(7)	N(8)-C(7)	1.30(1)
In(1)-N(8)	2.342(6)	N(9)-C(10)	1.29(1)
In(1)-C(15)	2.159	C(2)-C(3)	1.38(1)
In(1)-C(16)	2.144(9)	C(3)-C(4)	1.39(1)
S(11)-C(10)	1.72(1)	C(4)-C(5)	1.37(1)
S(12)-C(10)	1.749(9)	C(5)-C(6)	1.37(1)
S(12)-C(13)	1.32(1)	C(6)-C(7)	1.49(1)
N(1)-C(2)	1.32(1)	C(7)-C(14)	1.49(1)
N(1)-C(6)	1.34(1)		
S(11)-In(1)-N(1)	141.3(2)	In(1)-N(8)-C(7)	122.4(6)
S(11)-In(1)-N(8)	74.4(2)	N(9)-N(8)-C(7)	115.3(7)
S(11)-In(1)-C(15)	103.4(3)	N(8)-N(9)-C(10)	115.3(7)
S(11)-In(1)-C(16)	101.1(3)	N(1)-C(2)-C(3)	124.4(9)
N(1)-In(1)-N(8)	67.4(2)	C(2)-C(3)-C(4)	116.2(9)
N(1)-In(1)-C(15)	91.3(3)	N(1)-In(1)-C(16)	91.4(4)
N(8)-In(1)-C(15)	102.8(3)	N(8)-In(1)-C(16)	118.2(3)
C(15)-In(1)-C(16)	136.6(4)	In(1)-S(11)-C(10)	96.8(3)
C(10)-S(12)-C(13)	103.4(5)	In(1)-N(1)-C(6)	118.2(8)
In(1)-N(1)-C(6)	118.2(6)	C(2)-N(1)-C(6)	118.2(8)
In(1)-N(8)-N(9)	122.2(5)	S(12)-C(10)-N(9)	117.4(7)

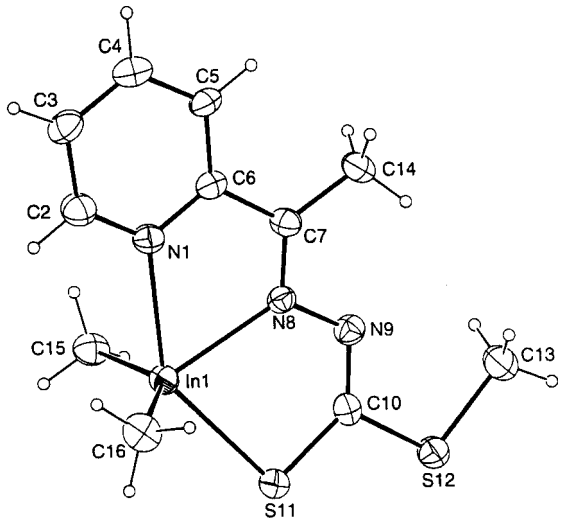


Figure 2. ORTEP diagram for **5** and atom labeling scheme.

structure giving the atom-numbering scheme used in the tables is shown in Figure 2.

Of paramount significance is the coordination of the indium atom in **5**. An examination of In(1) reveals it to be five-coordinate being bonded to an axially positioned methyl carbon, C(15), in addition to two nitrogen atoms, one carbon, and one thiolato atom. As the N(1)-In(1)-S(11) and N(8)-In(1)-C(16) bond angle are 141.3(2)° and 118.2(3)°, respectively, the coordination environment about In(1) may be described as square pyramidal. Such is completely unprecedented. The literature reveals many other structural reports of neutral five-coordinate organoindium complexes.[15] Of these complexes only a few have square pyramidal coordination,[16] while the others have trigonal bipyramidal coordination. The In(1)-N(1) distance in the square pyramid is

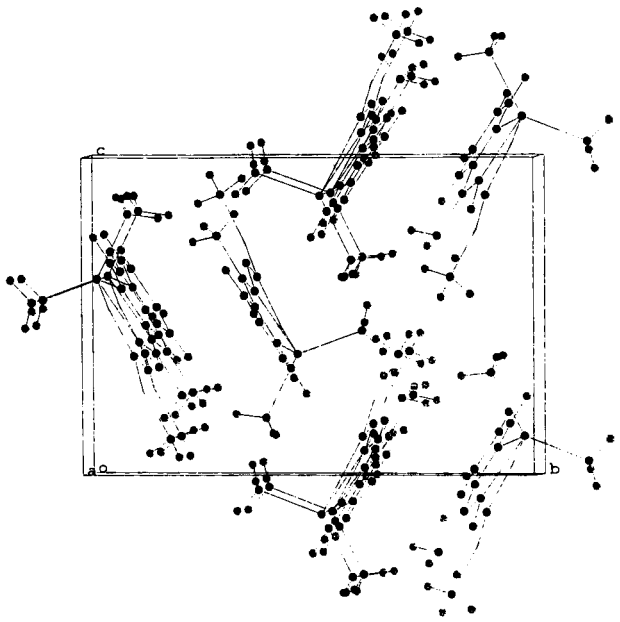


Figure 3. Packing diagram for **5**.

2.430(7) Å. The amido In(1)-N(8) distance (2.342(6) Å) is slightly shorter than that of pyridyl In-N bound, indicating that the negatively charged amido atom is a stronger donor to the indium center than the neutral imine atom. The In(1) C(15) (2.159(9) Å) and In(1)-C(16) (2.144(9) Å) bond distances are typical for five-coordinate indium complexes. The imine N(9)-C(10) bond distance (1.29(1) Å) is shorter than that of single bond distance of C-N. The short bond distance demonstrates the involvement of the 1,3-proton shift.

The use of the 2-acetylpyridine-*S*-methyldithiocarbazate as ligand in the organometallic chemistry of aluminum, gallium, and indium leads to mononuclear organometallic complexes of these metals having uncommon coordination geometry. X-ray crystallographic studies and spectroscopic data confirm that these complexes represent five-coordinate geometry. Our continuing investigations are oriented concerning factors which determine coordination geometry in five-coordinate organoaluminum, gallium, and indium complexes.

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Supporting Information Available. Table of bond distances and angles, atomic coordination, fractional coordinates, thermal parameters, and least-squares results for **4** and **5** (16 pages). Suppementary meterisls are available from one of the authors (J. Ko) upon request.

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Pulsed Amperometric Detection of Metal Ions Complexing with EDTA in a Flow Injection System**

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A general and universal detection method, which can be used in high performance liquid chromatography (HPLC) and flow injection analysis (FIA) system for the determination of any metal ions complexing with ethylenediaminetetraacetic acid (EDTA), is demonstrated. Pulsed amperometric detection scheme is applied in a flow-through thin layer electrochemical cell at an Au working electrode. Fluctuation of peak current level at the same flow rate of carrier solution is minimized at this solid working electrode, whereas not at a dropping mercury electrode. Removal of dissolved oxygen can be omitted with this detection method, which is a required step for cathodic detection methods. Also, a group of metal ions can be determined selectively and indirectly with this detection scheme.

Introduction

Since the detection and quantitative measurement of metal ions require various analytical techniques, numerous research efforts have been focused to find a universal detection scheme which can be applied to metal ions as widely as possible. EDTA is one of the well known complexing agents and widely used in many fields such as commercial detergents, cleaning reagents, environment, and agriculture etc. Metal EDTA systems have been studied extensively using mercury electrodes. However, such systems can usually give us little information because oxidation potential of mercury itself is very close to those of metal EDTA complexes.[1]

Detections of rare earth metal ions with electrochemical techniques after separation by high performance liquid chromatography were reported by Boissonneau *et al.*,[2] where EDTA was mixed in the flow stream of rare earths at the exit of HPLC column. Concentration of the elements was then indirectly determined by measuring anodic diffusion current of EDTA at a dropping mercury electrode in a flow cell. A similar setup with different complexing agent, diethylenetriaminepentaacetic acid (DTPA), has been used for the determination of Tm, Ho, Yb rare earths because DTPA has a larger formation constant than EDTA and oxidation potential of DTPA is less interfered by oxidation of mercury electrode.[3] We have demonstrated here a general and universal method for the determination of any metal ions complexing with EDTA in flow injection analysis composed of a thin layer cell with a gold working electrode.

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**This article is dedicated to Prof. Woon-kie Paik (Sogang Univ.) in commemoration of his 60th birthday.

Experimental

Reagents. All chemicals including EDTA (Aldrich Chemical Co.) and ammonium acetate buffer prepared from acetic acid and ammonium acetate (Duksan Chemical Co.) were used as received without further purification. Water obtained through a Milli-Q purification system was used to prepare solutions and electrolytes.

Instrumentation. All electrochemical measurements were made by Amel potentiostat (Model No. 553) and function generator (Model No. 568). All data were recorded by IBM XT compatible computer with a data acquisiton card and home-made softwares. A thin layer type EG & G electrochemical cell (Model No.1303, *ca.* 13 μL), which composed of a dual Au electrode, was employed in these experiments. One of the two was used as a working electrode, the other was used as a counter electrode. A reference electrode (Ag/AgCl (3.0 M), EG&G Cat. No. 219054E) was inserted into the cell through holes in its top cover. All electrode potentials are reported with respect to the Ag/AgCl reference electrode.

A flow injection analysis system was assembled in our laboratory. The system consisted of a peristaltic pump (Gilson, Model No. Miniplus 2) for propelling the electrolytes, an injection unit attached to the pneumatic actuator (Rheodyne, Model No. 5701) for sample injection, and flow-through thin layer electrochemical cell (EG & G, Model No. 1303) connected to the potentiostat. The details of experimental setup were described in our previous paper.[4]

Results and Discussion

The use of a pulsed-potential waveform for detection of