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  - (a) J. S. Cha, S. E. Lee, and H. S. Lee, *Bull. Korean Chem. Soc.*, **12**, 644 (1991); (b) The reducing properties of other derivatives will follow shortly in series.
  - The standard procedure for preparation of the dialkyl-amino-substituted derivatives of  $\text{LiAlH}_4$  is described in ref. 3 a. The  $^{27}\text{Al}$ -NMR spectra of LTDEA, LTDBA, and LTDHA showed a broad singlet at  $\delta$  120, 128 and 129.5 ppm, respectively, relative to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ .

### Synthesis of Homoleptic Ionic Indium(III) Thiocyanates and Molecular Structure of $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3-2,6-\text{Me}_2)_4]$

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Indium and its compounds have been widely used in various fields ranging from nuclear medicine to microelectronics.<sup>1-6</sup> Particularly, sulfur-containing indium complexes found their use in both extremes. Indium(III) complexes of thiocarbamate, alkylxanthate and dialkyldithiophosphate ligands have been exploited as blood cell labelling agents with reduced cell toxicity.<sup>7</sup> On the other hand, organoindium precursors involving sulfur have been employed in the improved preparation of thin transparent conducting indium oxide film.<sup>8</sup> Prompted by the foregoing significance of sulfur-containing indium complexes and the lack of X-ray crystallographically characterized homoleptic indium thiolate, the tetramethylammonium salts of  $[\text{In}(\text{SR})_4]^-$  (1:  $\text{SR} = \text{SC}_6\text{H}_5$ ; 2:  $\text{SR} = \text{SC}_6\text{H}_3-2,6-\text{Me}_2$ ) were prepared and structurally characterized, accounts of which are described in this report.

The methanolic solution of NaSR, generated *in situ* by the reaction of sodium metal (2 mmol) in *ca.* 20 ml of  $\text{CH}_3\text{OH}$

**Table 1.** Summary of Crystal Data, Intensity Collection, and Final Structure Refinement for  $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3-2,6-\text{Me}_2)_4]$

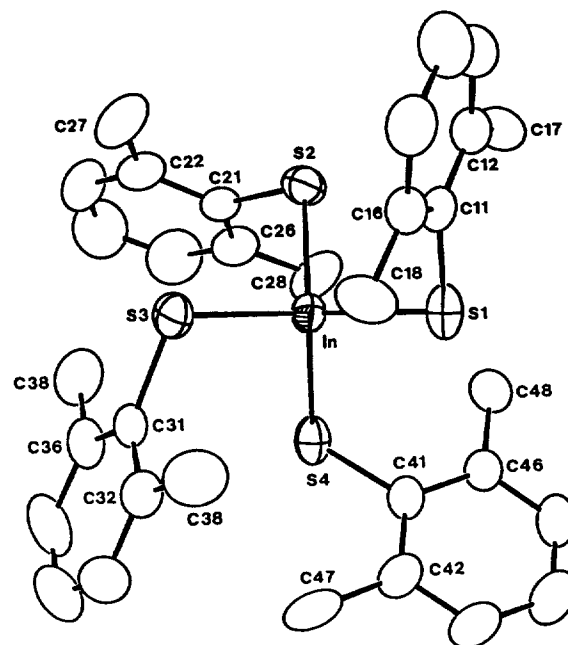
formular	$\text{C}_{36}\text{H}_{48}\text{InNS}_4$
f.w.	737.8
crystal system	monoclinic
space group	$P2_1/n$
<i>a</i> , Å	10.894(3)
<i>b</i> , Å	19.313(3)
<i>c</i> , Å	17.393(3)
$\beta$ , deg	91.74(2)
<i>V</i> , Å <sup>3</sup>	3657.7(12)
<i>Z</i>	4
temp, °C	23
<i>F</i> (000)	1524.0
radiation source	$\text{MoK}\alpha$ ( $\lambda = 0.71073$ Å)
scan mode	$\omega/2\theta$
$2\theta$ limit, deg	2-50
no. of collected data	4970
no. of unique data	4785
no. of obsd data ( $F > 6\sigma(F)$ )	4363
no. of variables	436
<i>R</i>	0.0376
<i>R</i> <sub>w</sub>	0.0410

followed by the addition of 2 mmol HSR ( $\text{SR} = \text{SC}_6\text{H}_5$ ;  $\text{SC}_6\text{H}_3-2,6-\text{Me}_2$ ), was anaerobically treated with a solution of  $\text{InCl}_3$  (0.5 mmol) in  $\text{CH}_3\text{OH}$ . The reaction mixture was stirred for 3 hrs at ambient temperature and then was treated with a solution of  $\text{NMe}_4\text{Br}$  (0.5 mmol) in  $\text{CH}_3\text{OH}$ , resulting in the precipitation of white microcrystalline solids which were collected and washed firstly with  $\text{CH}_3\text{OH}$  and with  $\text{Et}_2\text{O}$  several times. Recrystallization of the dried solid product from  $\text{DMF}/\text{Et}_2\text{O}$  afforded analytically pure white crystalline  $(\text{NMe}_4)\cdot\mathbf{1}$  and  $(\text{NMe}_4)\cdot\mathbf{2}$  in the yield of 51 and 60%, respectively.<sup>9</sup> Analytical and spectroscopic data suggest 1:1:4 ratio of  $(\text{NMe}_4)^+ : \text{In}(\text{III}) : (\text{SR})^-$  and single crystal X-ray diffraction study reveals the composition of  $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3-2,6-\text{Me}_2)_4]$ .<sup>10,11</sup> In Table 1 and 2, crystallographic data and the atomic coordinates of non-hydrogen atoms for  $(\text{NMe}_4)\cdot\mathbf{2}$  are listed, respectively.

The crystal structure of  $(\text{NMe}_4)\cdot\mathbf{2}$  consists of well-separated cations and anions. The structure of  $\text{NMe}_4^+$  is not unusual and will not be discussed any further. As the ORTEP view in Figure 1 and the molecular model indicate, the geometry of the entire anion **2** lacks in symmetry, leading to  $C_1$  point group symmetry. The  $C_1$  nature of **2** is rather unusual since  $S_4$  symmetry is common for many  $R_4M$  type compounds.<sup>13</sup> In fact, the  $[\text{M}(\text{SR})_4]$  units in  $(\text{PPh}_4)_2[\text{Fe}(\text{SPh})_4]$ ,<sup>14</sup>  $(\text{NEt}_4)[\text{Fe}(\text{SPh})_4]$ ,<sup>15</sup> and  $(\text{NEt}_4)[\text{Fe}(\text{SC}_6\text{H}-2,3,5,6-\text{Me}_4)_4]$ <sup>16</sup> are known to have  $S_4$  point group symmetry although the same unit in  $(\text{NEt}_4)[\text{Ga}(\text{SPh})_4]$ <sup>17</sup> has a pseudo  $C_2$  axis. Four  $\text{SC}_6\text{H}_3-2,6-\text{Me}_2$  groups in **2** are arranged such that only two groups are related by two-fold axis while the others are not. For example, for a given pseudo  $C_2$  axis defined by  $\text{S1InS2}$  and  $\text{S3InS4}$  planes, the S1-aryl and the S2-aryl groups are only symmetrically related. Similarly, only the S1-aryl and the S3-aryl groups are symmetric with respect to a  $C_2$  axis that bisects the S1-In-S2 and the S1-In-S3 angles. Taken alone,

**Table 2.** Atomic Coordinates for  $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3\text{-2,6-Me}_2)_4]$ 

Atom	x	y	z	$U_{eq}$ ( $\text{\AA}^2$ )
In	0.2082(<1)	0.1932(<1)	0.0269(<1)	0.0339
S1	0.0659(1)	0.1858(1)	-0.0857(1)	0.0496
S2	0.2483(1)	0.0756(1)	0.0771(1)	0.0511
S3	0.4072(1)	0.2439(1)	-0.0083(1)	0.0469
S4	0.1107(1)	0.2664(1)	0.1226(1)	0.0448
C11	0.1448(4)	0.1315(3)	-0.1521(3)	0.0375
C12	0.1278(5)	0.0597(3)	-0.1496(3)	0.0453
C13	0.1801(6)	0.0193(3)	-0.2054(4)	0.0594
C14	0.2459(6)	0.0478(4)	-0.2643(4)	0.0684
C15	0.2621(5)	0.1183(4)	-0.2669(3)	0.0599
C16	0.2130(5)	0.1619(3)	-0.2103(3)	0.0449
C17	0.0579(6)	0.0249(4)	-0.0865(4)	0.0654
C18	0.2346(7)	0.2392(3)	-0.2141(4)	0.0714
C21	0.3318(5)	0.0886(3)	0.1654(3)	0.0424
C22	0.4620(6)	0.0855(3)	0.1681(4)	0.0600
C23	0.5231(7)	0.0945(4)	0.2365(5)	0.0796
C24	0.4604(9)	0.1057(4)	0.3040(5)	0.0954
C25	0.3328(8)	0.1057(4)	0.3031(4)	0.0809
C26	0.2667(6)	0.0975(3)	0.2344(3)	0.0529
C27	0.5320(6)	0.0743(4)	0.0953(5)	0.0817
C28	0.1295(6)	0.0963(4)	0.2357(4)	0.0714
C31	0.4062(4)	0.3276(3)	0.0357(3)	0.0419
C32	0.3782(5)	0.3858(3)	-0.0106(4)	0.0548
C33	0.3840(6)	0.4058(3)	0.0239(5)	0.0702
C34	0.4184(6)	0.4590(4)	0.0987(5)	0.0805
C35	0.4463(6)	0.4016(4)	0.1435(4)	0.0723
C36	0.4385(5)	0.3354(3)	0.1126(3)	0.0539
C37	0.3429(8)	0.3795(5)	-0.0957(4)	0.0865
C38	0.4624(7)	0.2737(4)	0.1640(4)	0.0717
C41	-0.0292(4)	0.2961(3)	0.0781(3)	0.0376
C42	-0.0385(5)	0.3646(3)	0.0523(3)	0.0512
C43	-0.1513(5)	0.3884(3)	0.0234(3)	0.0590
C44	-0.2530(5)	0.3468(4)	0.0202(3)	0.0591
C45	-0.2436(5)	0.2795(3)	0.0444(3)	0.0540
C46	-0.1322(4)	0.2527(3)	0.0737(3)	0.0408
C47	0.0706(7)	0.4130(4)	0.0582(6)	0.0902
C48	-0.1269(6)	0.1785(3)	0.1013(3)	0.0584
N01	0.1708(4)	0.3555(2)	0.3417(2)	0.0382
C01	0.1923(10)	0.2801(4)	0.3416(5)	0.1035
C02	0.1944(8)	0.3801(4)	0.4206(4)	0.0903
C03	0.0454(7)	0.3696(5)	0.3169(6)	0.1097
C04	0.2575(7)	0.3887(4)	0.2895(4)	0.0935

**Figure 1.** ORTEP diagram of the anion (2) of  $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3\text{-2,6-Me}_2)_4]$ .**Table 3.** Selected Bond Distances ( $\text{\AA}$ ) and Bond Angles (deg) for  $(\text{NMe}_4)[\text{In}(\text{SC}_6\text{H}_3\text{-2,6-Me}_2)_4]$ 

In-S1	2.452(1)	In-S2	2.474(1)
In-S3	2.467(1)	In-S4	2.461(1)
S1-C11	1.798(5)	S2-C21	1.779(5)
S3-C31	1.790(5)	S4-C41	1.785(5)
C11-C12	1.398(7)	C12-C13	1.384(8)
C13-C14	1.382(9)	C14-C15	1.373(10)
C15-C16	1.412(8)	C11-C16	1.407(7)
C12-C17	1.512(8)	C16-C18	1.514(8)
C21-C22	1.415(8)	C22-C23	1.365(10)
C23-C24	1.387(12)	C24-C25	1.391(12)
C25-C26	1.379(9)	C21-C26	1.417(8)
C22-C27	1.517(10)	C26-C28	1.504(9)
C31-C32	1.405(8)	C32-C33	1.396(9)
C33-C34	1.343(12)	C34-C35	1.386(11)
C35-C36	1.385(9)	C31-C36	1.382(8)
C32-C37	1.527(10)	C36-C38	1.510(10)
C41-C42	1.398(7)	C42-C43	1.392(8)
C43-C44	1.373(9)	C44-C45	1.371(9)
C45-C46	1.402(7)	C41-C46	1.403(7)
C42-C47	1.510(9)	C46-C48	1.505(7)
N01-C01	1.475(9)	N01-C02	1.467(8)
N01-C03	1.446(9)	N01-C04	1.475(9)
S1-In-S2	109.4(<1)	S1-In-S3	111.8(<1)
S1-In-S4	107.4(<1)	S2-In-S3	107.7(<1)
S2-In-S4	110.9(<1)	S3-In-S4	109.8(<1)
In-S1-C11	103.8(2)	In-S2-C21	105.1(2)
In-S3-C31	103.8(2)	In-S4-C41	105.6(2)

the  $\text{InS}_4$  unit is distorted from  $T_d$  symmetry by a slight compression along the noncrystallographic  $S_4$  axis as indicated by the presence of the  $\text{S1-In-S3}$  ( $111.8(1)^\circ$ ) and  $\text{S2-In-S4}$  ( $110.9(1)^\circ$ ) angles greater than  $109.5^\circ$  and other  $\text{S-In-S}$  angles similar ( $\text{S1-In-S2}$ ,  $109.4(1)^\circ$ ;  $\text{S3-In-S4}$ ,  $109.8(1)^\circ$ ) to or smaller ( $\text{S1-In-S4}$ ,  $107.3(1)^\circ$ ;  $\text{S2-In-S3}$ ,  $107.7(1)^\circ$ ) than  $109.5^\circ$ . The average value ( $88.2^\circ$ ) of three dihedral angles between two  $\text{SInS}$  planes that define  $C_2$  axis also reflects the extent of distortion of the  $\text{InS}_4$  unit.

The arylthiolate ligands in the  $[\text{M}(\text{SR})_4]$  unit are known to adopt a unique  $\text{M-S-Aryl}$  conformation in which the planes

of the aryl rings are parallel<sup>14,15,17</sup> or perpendicular<sup>16,17</sup> to the  $\text{M-S}$  bonds. The latter thiolate conformation observed in  $[\text{Fe}$

(SC<sub>6</sub>H-2,3,5,6-Me<sub>4</sub>)<sub>4</sub>]<sup>-</sup>(3)<sup>16</sup> indicates the role of *o*-methyl groups in preventing the aryl rings from lying parallel to the Fe-S bonds. In the anion **2**, such a steric influence is operative resulting in rather random perpendicular conformations. For each In-S-Aryl group, the dihedral angle between the InSC plane and aryl ring is 93.6(2)° (S1 case), 86.5(2)° (S2 case), 98.9(2)° (S3 case) or 77.2° (S4 case). The presence of *o*-substituents in the aryl ring also affects the In-S-C angles listed in the Table 3 and the average value of 104.6° can be compared to the Fe-S-C angles (average 102.4°)<sup>16</sup> of **3**.

The average In-S distance of 2.464 Å in **2** is in good agreement with the sum of Shannon's ionic radii<sup>18</sup> of tetrahedral In(III) (0.76 Å) and S<sup>2-</sup> (1.70 Å) as well as with that (average 2.450 Å) of (PPh<sub>4</sub>)[BrIn(SPh)<sub>3</sub>].<sup>12</sup> For the sake of comparison, it is also interesting to note that gallium(III), the lighter congener of indium(III), and high-spin iron(III), a similar transition element analogue of gallium(III),<sup>19</sup> form M-S distances of 2.260 Å (M=Ga) and 2.297 Å (M=Fe) in [M(SPh)<sub>4</sub>]<sup>-</sup> anions.

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- (NMe<sub>4</sub>)·**1**: Anal. Found (Calc.) for C<sub>28</sub>H<sub>32</sub>InNS<sub>4</sub>: C, 52.2 (53.8); H, 5.4 (5.2); N, 2.1 (2.2); S, 18.8 (20.5) %; <sup>1</sup>H-NMR (*d*<sub>6</sub>-DMSO), 3.1 (s, 12H, Me<sub>4</sub>N), 6.9-7.3 (m, 20H, C<sub>6</sub>H<sub>5</sub>) ppm. (NMe<sub>4</sub>)·**2**: Anal. Found (Calc.) for C<sub>36</sub>H<sub>48</sub>InNS<sub>4</sub>: C, 58.5 (58.6); H, 6.8 (6.6); N, 2.3(1.9); S, 17.6 (17.4) %; <sup>1</sup>H-NMR(*d*<sub>6</sub>-DMSO), 2.1 (s, 24H, S-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>), 3.1 (s, 12H, Me<sub>4</sub>N), 6.8 (m, 12H, S-C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>) ppm.
- Crystallographic data for (NMe<sub>4</sub>)·**2** is given in Table 1. Diffraction data were collected on an Enraf-Nonius CAD4 single crystal X-ray diffractometer at room temperature. The data did not show any significant decay during data collection. The unit cell was determined on the basis of accurately centered reflections that were widely separated in reciprocal space with 17° < 2θ < 23°. The data was corrected for Lorentz, polarization and absorption effects. The indium atom was located by the Patterson map (SHELXS 86) and the remaining nonhydrogen atoms were located by use of block-matrices least-square procedures and ΔF syntheses (SHELX 76). All calculations were performed on the CRAY2S/4-128 Supercomputer. All phenyl groups were refined as non-rigid groups and all hydrogens included in calculated positions, *d*<sub>C-H</sub> = 1.08 Å. A final difference electron density was essentially featureless with maximum peak of 0.54 eÅ<sup>-3</sup>. The anisotropic thermal parameters and the final values of observed and calculated structural factors are available from the corresponding author upon request.
- To our knowledge, no X-ray crystallographically characterized homoleptic In(III) tetrathiolate has been reported to date although Na<sup>+</sup> and NEt<sub>4</sub><sup>+</sup> salts of [In(SPh)<sub>4</sub>]<sup>-</sup> anion were previously prepared by reacting In(SPh)<sub>3</sub> with NaSPh and further with NEt<sub>4</sub>Cl.<sup>12</sup>
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- Gallium(III) and high-spin iron(III) are known to have similar coordination chemistry owing to their similar charges and ionic radii (Ga(III) = 0.61 Å; Fe(III) = 0.63 Å).<sup>18</sup>