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Preparation and Single-Crystal X-Ray Structures of Four Related Mixed-Ligand 4-Methylpyridine Indium Halide Complexes

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Abstract

We describe the structures of four related indium complexes obtained during synthesis of solid-state materials precursors. Indium adducts of halides and 4-methylpyridine, $InX_3(pic)_3$ (X = Cl, Br; pic = 4-methylpyridine) consist of octahedral molecules with meridional *(mer)* geometry. Crystals of *mer*-$InCl_3(pic)_3$ (**1**) are triclinic, space group *P*1(bar) (No. 2), with a = 9.3240(3), b = 13.9580(6), c = 16.7268 (7) Å, α = 84.323(2), β = 80.938(2), γ = 78.274(3)°, Z = 4, R = 0.035 for 8820 unique reflections. Crystals of *mer*-$InBr_3(pic)_3$ (**2**) are monoclinic, space group *P*21/*n* (No. 14), with a = 15.010(2), b = 19.938(2), c = 16.593(3), β = 116.44(1)°, Z = 8, R = 0.053 for 4174 unique reflections. The synthesis and structures of related compounds with phenylsulfide (chloride) (**3**) and a dimeric complex with bridging hydroxide (bromide) (**4**) coordination is also described. Crystals of *trans*-$In(SC_6H_5)Cl_2(pic)_3$ (**3**) are monoclinic, space group *P*21/*n* (No. 14), with a = 9.5265(2), b = 17.8729(6), c = 13.8296(4), β = 99.7640(15)°, Z = 4, R = 0.048 for 5511 unique reflections. Crystals of $[In(\mu\text{-}OH)Br_2(pic)_2\cdot 2pic]_2$ (**4**) are tetragonal, space group = *I*4$_1$*cd* (No. 110) with a = 19.8560(4), b = 19.8560(4), c = 25.9528(6), Z = 8, R = 0.039 for 5982 unique reflections.

1.0 Introduction

In recent years, Group III (or 13) complexes have been the subject of numerous studies for use as potential precursors for electronic materials via chemical spray pyrolysis or chemical vapor deposition (Refs. 1 to 8). During our long-term thin-film solar cell research effort, we prepared derivatives of gallium (Ga) and indium (In) chlorides with chalcogenide ligands, determined their single-crystal structures and studied further reactions to produce new precursors for solid-state materials (Refs. 2, 4, 8, and 9). Our use of 4-methylpyridine or γ-picoline solvent and ligation has yielded complexes that readily provide single crystals suitable for X-ray diffraction structural studies (Refs. 10 to 14).

The literature is replete with examples of In and Ga complexes that are stabilized by pyridine-like ligands. In fact, pyridine adducts of the Group III (or 13) elements have been known since the early 1900s when Renz et al. reported the synthesis of a pyridine-indium trihalide compound (Ref. 15). However up until the early 1980s, the structures of these compounds were determined primarily by IR spectroscopy, Raman spectroscopy, and conductivity measurements (Refs. 16 to 20). These methods proved to be unreliable, and structures and packing arrangements remained unconfirmed. However, as implied above, the advent of X-ray crystallography has allowed for more detailed investigations of the structure of these compounds.

There have been reports of pyridine-M-X (M = Al, In, Tl; X = Cl, Br, I) compounds characterized by X-ray crystallography (Refs. 21 to 25). However, there have only been two reports where a substituted pyridine (4-methylpyridine (Ref. 26) and 4-ethylpyridine (Ref. 27)) has been used. The use of indium (I) halides as a starting material is unusual. Previously, *mer*-$InI_3(py)_3$ had been the only reported compound synthesized with indium (I) (Ref. 25).

In this report, we describe four new indium mixed halide/chalcogenide complexes obtained during attempts to prepare new mixed-ligand In(III) starting materials via oxidative addition. The disproportionation of indium (I) chloride in 4–methylpyridine (4-mepy) yields *mer*-$InCl_3$(4–mepy)$_3$, (**1**). The attempted reaction of indium (I) bromide with diphenydisulfide in 4–methylpyridine yields *mer*-$InBr_3$(4–mepy)$_3$, (**2**). A successful attempt to prepare an analogous benzenethiolate complex using the S-S bonded dimer with InCl resulted in oxidative addition and produced a disordered structure six-coordinate complex, *trans*-In(SC_6H_5)Cl_2(4-mepy)$_3$, (**3**). An unsuccessful reaction including adventitious water between diphenydiselenide and InBr produced a hydroxyl-bridged InBr complex, [In(μ-OH)Br_2(4-mepy)$_2$·2(4-mepy)]$_2$ (**4**).

2.0 Experimental

2.1 Materials and Methods

All operations of moisture and air sensitive materials were performed under an inert atmosphere employing standard Schlenk techniques using a double–manifold vacuum line and a Vacuum Atmospheres Corp. HE-43 DriLab glovebox. Solvents were purchased from Sigma-Aldrich Co. (St. Louis, MO) and whenever possible, distilled from sodium benzophenone ketyl or calcium hydride prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Indium (I) chloride and bromide (InCl and InBr) were purchased from Alfa Aesar (Ward Hill, MA), diphenyldisulphide and diphenyldiselenide (H_5C_6E-EC_6H_5; E= S, Se) were purchased from Sigma-Aldrich Co; all inorganic reactants were used as received.

2.2 Preparation of *mer*-$InCl_3$(4–methylpyridine)$_3$ (1)

A solution of InCl (0.5 g, 3.3 mmol) and H_5C_6Se-SeC_6H_5 (2.1 g, 6.7 mmol) in 30 mL (30 mmol) of freshly distilled 4–methylpyridine was stirred under a stream of argon for 9 days during which time the solution turned light yellow. The mixture was filtered through a column of celite. The resultant yellow filtrate was concentrated to one–half the original volume and mixed with 30 mL of freshly distilled hexane. The white ppt. was collected on a glass frit, washed with 2 aliquots each 20 mL of freshly distilled hexane and dried under vacuum for 18 hr. The crystallized product (0.8 g) was dissolved in 25 mL of 4–methylpyridine and stirred for 18 hr at room temperature producing a light yellow solution. The solution was concentrated to approximately 12 mL and layered with 30 mL of hexane. After several days, very pale yellow prismatic crystals, suitable for X–ray crystallography, were collected and analyzed, yield 0.569 g (1.2 mmol; 35%).

2.3 Preparation of *mer*-InBr$_3$(4–methylpyridine)$_3$ (2)

A solution of InBr (1.9 g, 9.8 mmol) in 20 mL (20 mmol) of freshly distilled 4–methylpyridine, (4–mepy), was stirred under a stream of argon. The solution turned milky grey color upon addition of 20 mL of a 4–methylpyridine solution of $H_5C_6S\text{-}SC_6H_5$ (4.5 g, 20 mmol) and subsequently became clear yellow after stirring for 6 days. The mixture was filtered through a column of celite. The resultant light yellow filtrate was concentrated to approximately 20 mL, mixed with 40 mL of freshly distilled hexane and placed in a freezer at –10 °C for 48 hr. Light yellow solid was collected onto a glass frit, washed with a 30 mL aliquot of freshly distilled hexane and dried under vacuum for 18 hr. The crystallized product (0.8 g) was dissolved in 23 mL of freshly distilled 4–methylpyridine and stirred for 18 hr at room temperature producing a light yellow solution. The solution was concentrated to approximately 12 mL and layered with 30 mL of hexane. After several days, clear prismatic crystals suitable for X–ray crystallography were collected and analyzed, yield 0.603 g (1.35 mmol; 14%).

2.4 Preparation of *trans*-In(SC$_6$H$_5$)Cl$_2$(4–methylpyridine)$_3$ (3)

A solution of InCl (0.5 g, 3.3 mmol) and $H_5C_6S\text{-}SC_6H_5$ (1.45 g, 6.7 mmol) was mixed under a stream of argon in in 30 mL (30 mmol) of freshly distilled 4–methylpyridine, (4–mepy), the milky yellow solution turned gray upon stirring for 6 days. The mixture was not filtered but simply layered with 15 mL of freshly distilled hexane. After one month, a significant mass of colorless prismatic crystals gathered at the bottom of the tube. Those deemed suitable for X–ray crystallography were collected and analyzed, yield 0.30 g (0.6 mmol; 18%).

2.5 Preparation of [In(μ-OH)Br$_2$(4–methylpyridine)$_2$·2(4-mepy)]$_2$ (4)

A solution of InBr (0.9 g, 4.8 mmol) in 20 mL (20 mmol) of freshly distilled 4–methylpyridine, (4–mepy), was stirred under a stream of argon. The solution turned milky grey color upon addition of 20 mL of a 4–methylpyridine solution of $H_5C_6Se\text{-}SeC_6H_5$ (2.2 g, 9.6 mmol) and subsequently became clear yellow after stirring for 9 days. The mixture was layered with 20 mL of freshly distilled hexane. After one month, a mass of colorless tabular crystals gathered at the bottom of the tube. Those deemed suitable for X–ray crystallography, were collected and analyzed, yield 0.70 g (0.5 mmol; 12%).

2.6 Methodology of Single Crystal X–ray Structural Analysis

Pertinent crystallographic data for all structures (1-4) are summarized in Table I. Selected crystals were sealed in glass capillaries and mounted on an automated diffractometer. Intensity measurements were performed using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined from least-squares refinement of 25 reflections obtained from an automatic centering program. Intensity data were collected with the ω-2θ method. There was no observable decay during the data collections. The data sets were corrected for Lorentz and polarization effects. Except for compound **2**, an empirical absorption correction using SCALEPACK was applied (Ref. 28). Scattering factors were taken from the *International Tables for Crystallography* (Ref. 29). Crystallographic drawings were done using programs ORTEP (Ref. 30) and PLUTON (Ref. 31).

2.6.1 Details for *mer*-InCl$_3$(4–methylpyridine)$_3$ (1)

A prismatic crystal of approximate dimensions 0.31- by 0.28- by 0.19-mm was mounted in a glass capillary on a Nonius KappaCCD diffractometer. Refinement was performed on an AlphaServer 2100 computer using SHELX-97 (Ref. 32). The space group was determined by ABSEN (Ref. 33). There were no systematic absences; the space group was determined to be *P*1-bar. The structure was solved using the program PATTY in DIRDIF-99 (Ref. 34). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

TABLE I.—SUMMARY OF CRYSTAL DATA AND X-RAY STRUCTURE REFINEMENT FOR COMPOUNDS **1 - 4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{18}H_{21}N_3Cl_3In$	$C_{18}H_{21}N_3Br_3In$	$C_{24}H_{26}N_3SCl_2In$	$C_{48}H_{58}N_8O_2Br_4In_2$
Molecular weight	500.57	633.91	573.26	1328.33
Crystal system	Triclinic	Monoclinic	Monoclinic	Tetragonal
Space group	*P*-1bar (No. 2)	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	$I4_1cd$ (No. 110)
a, Å	9.3240(3)	15.010(2)	9.5265(2)	19.8560(4)
b, Å	13.9580(6)	19.938(2)	17.8729(6)	19.8560(4)
c, Å	16.7268(7)	16.593(3)	16.7268(7)	26.9528(6)
α, °.	84.323(2)	90	90	90
β, °	80.938(2)	116.44(1)	99.7640(15)	90
γ, °	78.274(3)	90	90	90
V, $Å^3$	2099.8(2)	4447(1)	2320.6(2)	10626.4(7)
Z	4	8	4	8
D_{calc}, g cm^{-3}	1.58	1.894	1.54	1.66
μ, mm^{-1}	1.499	63.95	1.347	3.877
F(000)	1000	2432	1080	5248
Crystal size, mm	0.31- by 0.28- by 0.19	0.22- by 0.28- by 0.34	0.45- by 0.30- by 0.27	0.20- by 0.20- by 0.10
Temperature, K	203	298	150	193
θ range collection, °	4.0 to 27.5	1.0 to 20.0	5.0 to 27.88	4.0 to 27.0
Data collected	16223	4360	19543	30972
Unique data (R_{int})	8820 (0.045)	4174 (0.050)	5511 (0.035)	5982 (0.091)
T_{max}, T_{min}	0.76, 0.67	1.37, 0.76	0.70, 0.54	0.68, 0.39
Data with $I > 2\sigma(I)$	7117	1991 ($I > 6\sigma$)	4977	4453
$R(F_o)^a$	0.035	0.053	0.048	0.039
$wR(F_o^2)^b$	0.071[c]	0.0609[d]	0.107[e]	0.078[f]
Largest diff. peak and hole, e $Å^{-3}$	0.33, –0.77	1.17, –0.47	0.89, –1.02	0.52, –1.09
Goodness of fit (GOF) on F^2	1.030	0.97	1.127	1.002
CCDC deposit no.	176766	176768	185220	176767

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$

[b] $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2)/\Sigma w(|F_o^2|^2]^{1/2}$

[c] $w = 1/[\sigma^2(F_o^2) + (0.0103P)^2 + 1.2690P]$

[d] $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 6P]$

[e] $w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 5.9629P]$

[f] $w = 1/[\sigma^2(F_o^2) + (0.0369P)^2]$; where $P = (F_o^2 + 2F_c^2)/3$ for all

2.6.2 Details for *mer*-$InBr_3$(4–methylpyridine)$_3$ (2)

A clear prismatic crystal of approximate dimensions of 0.22- by 0.28- by 0.34-mm was mounted in a glass capillary. The diffraction data were collected on an Enraf-Nonius CAD-4F computer controlled kappa axis diffractometer. The space group was determined to be $P2_1/a$. Calculations were performed on a VAX using Enraf-Nonius MolEN (Ref. 35). An empirical absorption correction based on the method of Walker and Stuart was also applied (Ref. 36). Crystal structures were solved using the structure solution program SHELX-86 (Ref. 32). Interpretation of a Patterson map led to the location of the indium atom in **2**. The remaining non-hydrogen atoms were located and refined through a series of difference Fourier maps and full-matrix least-squares refinements. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and added to the structure factor calculations, but their positions and isotropic thermal parameters were not refined.

2.6.3 Details for *mer*-In(SC_6H_5)Cl_2(4–methylpyridine)$_3$ (3)

A prismatic crystal of approximate dimensions 0.45- by 0.30- by 0.27-mm was mounted in a glass capillary on a Nonius KappaCCD diffractometer. Refinement was performed on an AlphaServer 2100 computer using SHELX-97 (Ref. 32). The space group was determined by ABSEN (Ref. 33). From the systematic presences of h0l (h+1=2n) and 0k0 (k=2n) and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$. The structure was solved using the program PATTY in DIRDIF-99 (Ref. 34). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

2.6.4 Details for $[In(\mu\text{-}OH)Br_2(4\text{–methylpyridine})_2\cdot 2(4\text{-mepy})]_2$ (4)

A tabular crystal of approximate dimensions 0.20- by 0.20- by 0.10-mm was mounted in a glass capillary on a Nonius KappaCCD diffractometer. Refinement was performed on an AlphaServer 2100 computer using SHELX-97 (Ref. 33). The space group was determined by ABSEN (Ref. 33). From the systematic presences of 0kl (l=2n), h0l (2h + l = 4n), and 00l (l = 4n) and from subsequent least-squares refinement, the space group was determined to be $I4_1cd$. The structure was solved using the program PATTY in DIRDIF-99 (Ref. 34), remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded.

3.0 Results and Discussion

3.1 Single-Crystal X-ray Structures of *mer*-$InX_3(4\text{-mepy})_3$ (X = Cl, Br) (1 and 2)

The crystal-structure determination reveals that $InCl_3(pic)_3$ (**1**) and $InBr_3(pic)_3$ (**2**) exist as two structurally independent neutral monomers (designated **a** and **b**) whose central metal atom has six coordinate geometry; both compounds adopt a slightly distorted *mer*-octahedral geometry. Molecular structures of **1** and **2** are shown in Figure 1 and Figure 2, respectively; a list of selected bond distances and angles are given in Table II and Table III, respectively.

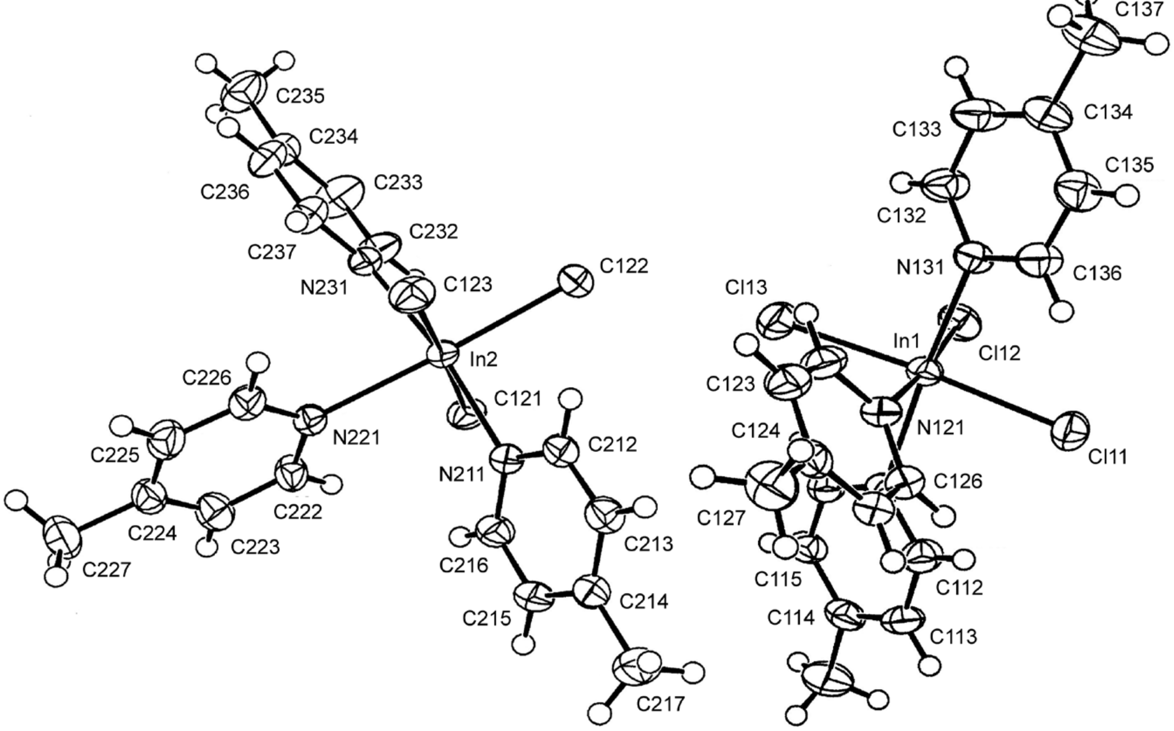

Figure 1.—ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of both structural isomers of *mer*-$InCl_3(4\text{-mepy})_3$:**1b** – In2**,** left side of figure and **1a** – In1**,** right side of figure as sited in the unit cell.

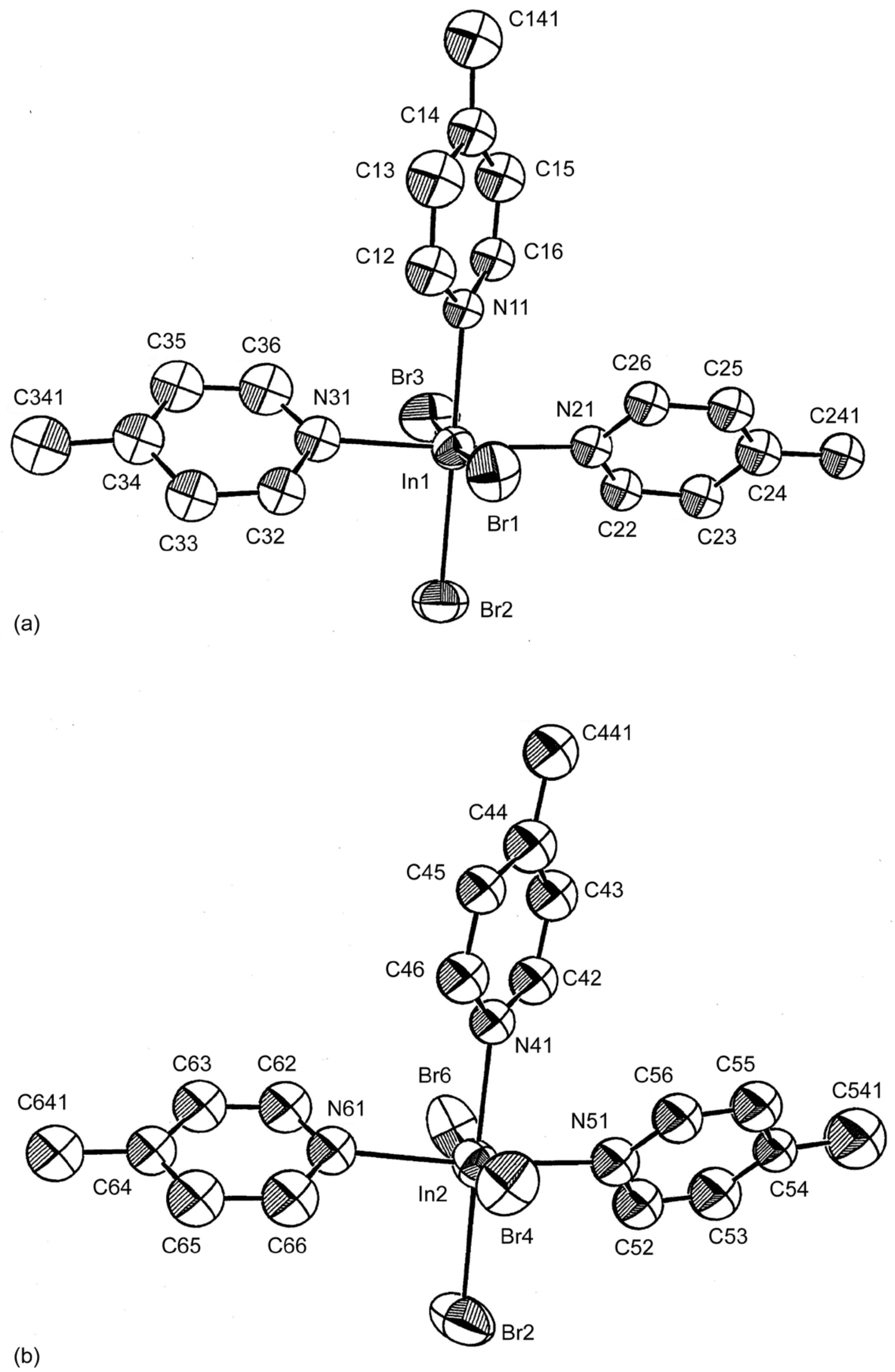

Figure 2.—(a) ORTEP diagram with 50% thermal ellipsoids and atomic labeling scheme of In(1) structural isomer of *mer*-InBr_3(4-mepy)$_3$ (**2a**) (hydrogen atoms not shown for clarity). (b) ORTEP diagram with 50% thermal ellipsoids and atomic labeling scheme of In(2) structural isomer of *mer*-InBr_3(4-mepy)$_3$ (**2b**) (hydrogen atoms not shown for clarity).

TABLE II.—SELECT BOND DISTANCES (Å) AND ANGLES (°)
FOR COMPOUND **1** (*mer*-$\mathrm{InCl_3(pic)_3}$)

In(1)-N(111)	2.312(2)	Cl(12)-In(1)-Cl(11)	94.37(3)
In(1)-N(121)	2.324(2)	Cl(13)-In(1)-Cl(11)	175.45(3)
In(1)-N(131)	2.311(2)	Cl(12)-In(1)-Cl(13)	89.71(3)
In(1)-Cl(11)	2.4821(8)	N(211)-In(2)-N(231)	172.69(8)
In(1)-Cl(12)	2.4610(9)	N(211)-In(2)-N(221)	88.90(8)
In(1)-Cl(13)	2.4753(8)	N(231)-In(2)-N(221)	83.80(8)
In(2)-N(211)	2.287(2)	N(211)-In(2)-Cl(22)	94.15(6)
In(2)-N(221)	2.359(2)	N(231)-In(2)-Cl(22)	93.15(6)
In(2)-N(231)	2.301(2)	N(221)-In(2)-Cl(22)	176.86(6)
In(2)-Cl(21)	2.4744(8)	N(211)-In(2)-Cl(21)	89.03(7)
In(2)-Cl(22)	2.4701(8)	N(231)-In(2)-Cl(21)	90.53(6)
In(2)-Cl(23)	2.4780(8)	N(221)-In(2)-Cl(21)	88.71(6)
N(111)-C(112)	1.345(4)	N(211)-In(2)-Cl(23)	88.93(7)
N(111)-C(116)	1.344(4)	N(231)-In(2)-Cl(23)	91.18(6)
N(121)-C(122)	1.352(4)	N(221)-In(2)-Cl(23)	88.80(6)
N(121)-C(126)	1.337(4)	Cl(22)-In(2)-Cl(21)	90.57(3)
N(131)-C(132)	1.328(4)	Cl(22)-In(2)-Cl(23)	92.02(3)
N(131)-C(136)	1.333(4)	Cl(21)-In(2)-Cl(23)	176.81(3)
N(211)-C(212)	1.346(4)	C(116)-N(111)-C(112)	116.7(3)
N(211)-C(216)	1.347(4)	C(116)-N(111)-In(1)	118.3(2)
N(221)-C(222)	1.336(4)	C(112)-N(111)-In(1)	124.6(2)
N(221)-C(226)	1.344(4)	C(126)-N(121)-C(122)	116.4(3)
N(231)-C(232)	1.326(4)	C(126)-N(121)-In(1)	125.0(2)
N(231)-C(237)	1.333(4)	C(122)-N(121)-In(1)	118.5(2)
N(131)-In(1)-N(111)	173.28(9)	C(116)-N(111)-C(112)	116.7(3)
N(131)-In(1)-N(121)	83.62(9)	C(116)-N(111)-In(1)	118.3(2)
N(111)-In(1)-N(121)	91.32(9)	C(112)-N(111)-In(1)	124.6(2)
N(131)-In(1)-Cl(11)	88.87(7)	C(212)-N(111)-C(216)	116.6(3)
N(111)-In(1)-Cl(11)	86.69(7)	C(212)-N(211)-In(2)	120.8(2)
N(121)-In(1)-Cl(11)	89.80(7)	C(216)-N(211)-In(2)	122.6(2)
N(131)-In(1)-Cl(12)	93.65(7)	C(222)-N(221)-C(226)	116.3(3)
N(111)-In(1)-Cl(12)	91.71(7)	C(222)-N(221)-In(2)	122.3(2)
N(121)-In(1)-Cl(12)	174.98(6)	C(226)-N(221)-In(2)	121.4(2)
N(131)-In(1)-Cl(13)	92.91(7)	C(232)-N(231)-C(237)	116.7(3)
N(111)-In(1)-Cl(13)	91.17(7)	C(232)-N(231)-In(2)	119.7(2)
N(121)-In(1)-Cl(13)	86.23(7)	C(237)-N(231)-In(2)	123.5(2)

TABLE III.—SELECT BOND DISTANCES (Å) AND ANGLES (°) FOR COMPOUND **2** (*mer*-InBr$_3$(pic)$_3$)

In(1)-N(11)	2.31(2)	Br(1)-In(1)-Br(2)	94.2(1)
In(1)-N(21)	2.30(2)	Br(1)-In(1)-Br(3)	175.2(1)
In(1)-N(31)	2.24(2)	Br(2)-In(1)-Br(3)	90.1(1)
In(1)-Br(1)	2.640(4)	N(41)-In(2)-N(51)	84.7(7)
In(1)-Br (2)	2.593(4)	N(41)-In(2)-N(61)	89.4(7)
In(1)-Br (3)	2.614(4)	N(51)-In(2)-N(61)	173.9(7)
In(2)-N(41)	2.31(2)	N(41)-In(2)-Br(4)	86.5(5)
In(2)-N(51)	2.27(2)	N(51)-In(2)-Br(4)	89.7(5)
In(2)-N(61)	2.31(2)	N(61)-In(2)-Br(4)	91.5(5)
In(2)-Br(4)	2.617(4)	N(41)-In(2)-Br(5)	178.2(4)
In(2)-Br(5)	2.571(4)	N(51)-In(2)-Br(5)	93.7(6)
In(2)-Br(6)	2.650(4)	N(61)-In(2)-Br(5)	92.2(5)
N(11)-C(12)	1.35(3)	N(41)-In(2)-Br(6)	86.4(5)
N(11)-C(16)	1.37(3)	N(51)-In(2)-Br(6)	88.4(5)
N(21)-C(22)	1.31(3)	N(61)-In(2)-Br(6)	89.6(5)
N(21)-C(26)	1.34(3)	Br(4)-In(2)-Br(5)	94.3(1)
N(31)-C(32)	1.33(3)	Br(4)-In(2)-Br(6)	172.7(1)
N(31)-C(36)	1.28(4)	Br(5)-In(2)-Br(6)	92.8(1)
N(41)-C(42)	1.33(2)	C(16)-N(11)-C(12)	116.(2)
N(41)-C(46)	1.32(3)	C(16)-N(11)-In(1)	124.(2)
N(51)-C(52)	1.40(4)	C(12)-N(11)-In(1)	120.(2)
N(51)-C(56)	1.34(4)	C(26)-N(21)-C(22)	115.(2)
N(61)-C(62)	1.29(4)	C(26)-N(21)-In(1)	122.(2)
N(61)-C(66)	1.36(3)	C(22)-N(21)-In(1)	123.(1)
N(11)-In(1)-N(21)	87.5(6)	C(36)-N(31)-C(32)	114.(2)
N(11)-In(1)-N(31)	87.6(7)	C(36)-N(31)-In(1)	127.(2)
N(21)-In(1)-N(31)	174.0(8)	C(32)-N(31)-In(1)	119.(2)
N(11)-In(1)-Br(1)	87.8(5)	C(42)-N(41)-C(46)	117.(3)
N(21)-In(1)-Br(1)	86.7(5)	C(42)-N(41)-In(2)	120.(2)
N(31)-In(1)-Br(1)	89.7(5)	C(46)-N(41)-In(2)	123.(2)
N(11)-In(1)-Br(2)	178.0(5)	C(52)-N(51)-C(56)	115.(2)
N(21)-In(1)-Br(2)	92.9(5)	C(52)-N(51)-In(2)	117.(2)
N(31)-In(1)-Br(2)	92.1(6)	C(56)-N(51)-In(2)	128.(2)
N(11)-In(1)-Br(3)	87.9(5)	C(62)-N(61)-C(66)	117.(2)
N(21)-In(1)-Br(3)	89.3(5)	C(62)-N(61)-In(2)	124.(1)
N(31)-In(1)-Br(3)	94.0(5)	C(66)-N(61)-In(2)	119.(2)

Compound **1** has four total complexes per unit cell, existing as pairs of structural isomers. These two isomers (**1a** and **1b**) differ only slightly in their bond distances and angles around the central atom. In both **1a** and **1b** the arrangement of ligands is *mer*–type with the two equatorial 4–picoline rings, N(111) and N(131) for **1a** and N(211) and N(231) for **1b**, bent away from the axial chlorine atoms, Cl(12) and Cl(22) for both complexes, respectively.

The In-N(*trans*) bond lengths for **1** (2.31 Å average) are comparable to $InCl_3(py)_3$ (2.30 Å average) (Ref. 23) and $InCl_3$(4-ethylpyridine)$_3$ (2.31 Å average) (Ref. 27). This indicates that the electron donating strength of pyridine, 4-methylpyridine, and 4-ethylpyridine are similar (Ref. 23). The In-N(*cis*) bond length is longer (2.32 Å), which is also seen in $InCl_3(py)_3$ (2.38 Å). The In-Cl(*trans*) bond lengths are also comparable for **1** (2.48 Å average), $InCl_3(py)_3$ (2.48 Å average), and $InCl_3$(4-ethylpyridine)$_3$ (2.46 Å average). The distinct shortening of the In-Cl(*cis*) bond length is present (2.46 Å) as is seen in $InCl_3$(4-ethylpyridine)$_3$ (2.41 Å), but not $InCl_3(py)_3$.

Due to the repulsive interactions between the pyridine ligands, the compound assumes a distorted octahedron with meridional geometry (Ref. 21). The Cl-In-Cl(*trans*) bond angle in **1** is 175.45°. A similar distortion is present in $InCl_3(py)_3$ (176°) (Ref. 23) and $InCl_3$(4-ethylpyridine)$_3$ (172.04°) (Ref. 27). The N-In-N(trans) bond angles are 173.28° for 1, 175.1 for $InCl_3(py)_3$, and 172.49° for $InCl_3$(4-ethylpyridine)$_3$. The pyridine rings and chlorine atoms are both bent away from the *cis* chlorine atom presumably due to repulsive forces.

Compound **2** has eight total complexes per unit cell, existing as pairs of structural isomers. The complex exists as a trivalent monomer whose central metal atom is six- coordinate. The coordination sphere around the central indium atom is a distorted octahedron. The equatorial sites are occupied by a set of bromine atoms and two picoline rings. The remaining bromine atom and picoline ring occupy the axial sites. The three Br atoms are positioned in a *mer*–fashion around the central indium atom.

The two structural isomers (**2a** and **2b**) like the compound **1** isomers, also differ only slightly in their bond distances and angles around the central atom. In both **2a** and **2b** the arrangement of ligands is *mer*–type with the two equatorial 4–picoline rings, N(21) and N(31) for **2a** and N(51), and N(61) for **2b**, slightly bent away from the axial bromine atoms, Br(2) and Br(5) for both complexes, respectively.

The In-N(*trans*) bond length for **2** (2.27 Å average) is comparable but shorter than for $InBr_3(py)_3$ (2.30 Å average) (Ref. 21). The In-N(*cis*) bond length is longer at 2.31 Å for **2** and 2.32 Å for $InBr_3(py)_3$. The In-Br(*trans*) bond lengths are also similar to the previously reported structure, 2.63 Å average for **2** and 2.61 Å average for $InBr_3(py)_3$. The shortening of the In-Br(*cis*) bond (2.59 Å) occurs for both **2** and $InBr_3(py)_3$ (Ref. 21).

The Br-In-Br(*trans*) bond angle in **2** is 174.2 °. As in **1**, a similar distortion is present in the pyridine analog, $InBr_3(py)_3$ (176.4°) (Ref. 21). The N-In-N(*trans*) bond angle is 174.0° for **2** and 175° for $InBr_3(py)_3$. Both of these bond angles show that the pyrdine rings and the bromine atoms are bent away from the *cis*-bromine atom.

Overall, for both molecules, the shortening of the In-X(cis) (X = Cl, Br) bond would indicate that while the electron donating strength of the pyrdine groups is similar, the more electron-donating methyl and ethyl groups are able to slightly strengthen the In-X(*cis*) bond.

Unlike the $InX_3(py)_3$ (X = Cl,Br) compounds reported by Small and Worrall (Refs. 21 and 23), there is no molecule of solvation in the crystal structure. This is significant because until now only compounds with iodine as the halogen have been characterized without a molecule of solvation. This was thought to be due to the extra bulk of the iodine ligand (Ref. 25). The characterization of $InCl_3$(4-ethylpyridine)$_3$ also has no molecule of solvation, however the authors did not comment on this occurrence (Ref. 27). It appears that the bulk of the pyridine ligand also has an effect on the crystallization of the compound.

When compared to other compounds of the type InX_3L_3 (X = Cl, Br, I; L = py, pic), a trend is observed. As is shown in Figure 3 and Figure 4, as the size of the halogen increases (decreasing electronegativity) and the electron donating effect of the pyridine ring increases, the In-X(*cis*) and In-X(*trans*) bond lengths both increase.

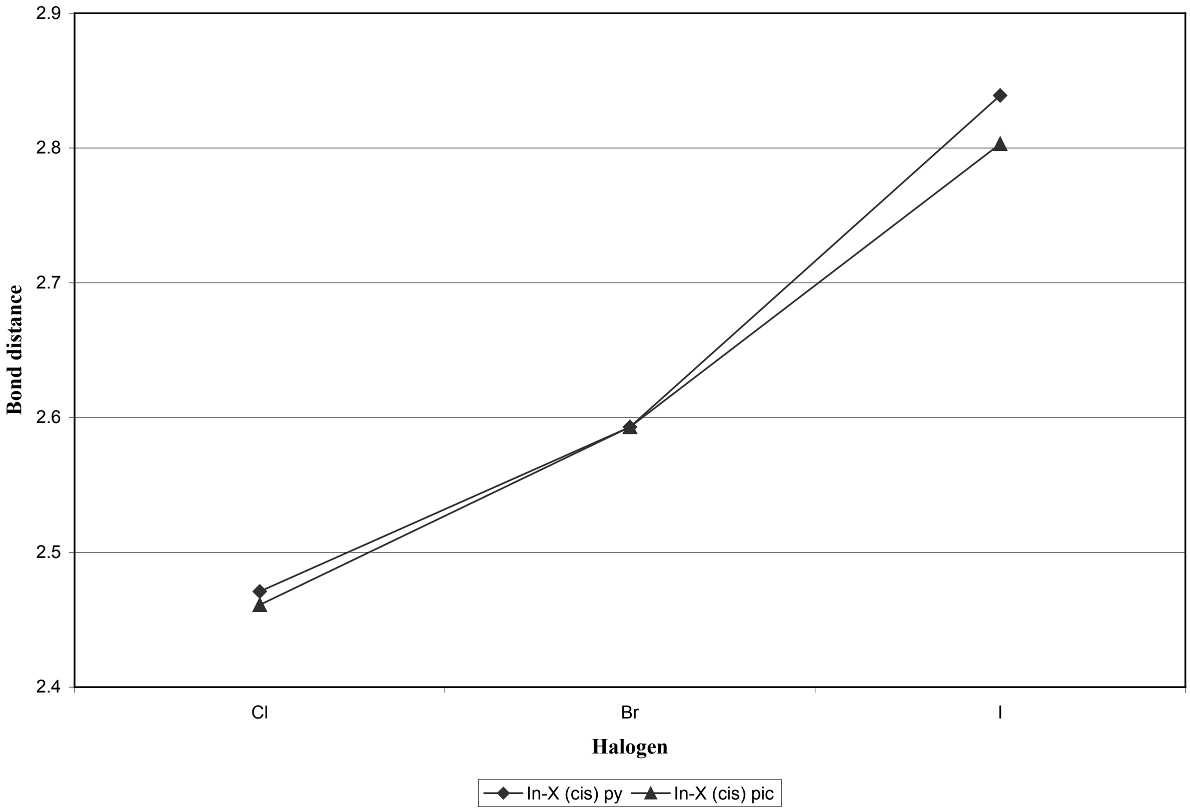

Figure 3.—In-X(*cis*) bond lengths of pyridine (py) versus 4-methylpyridine (pic) from the literature and this study.

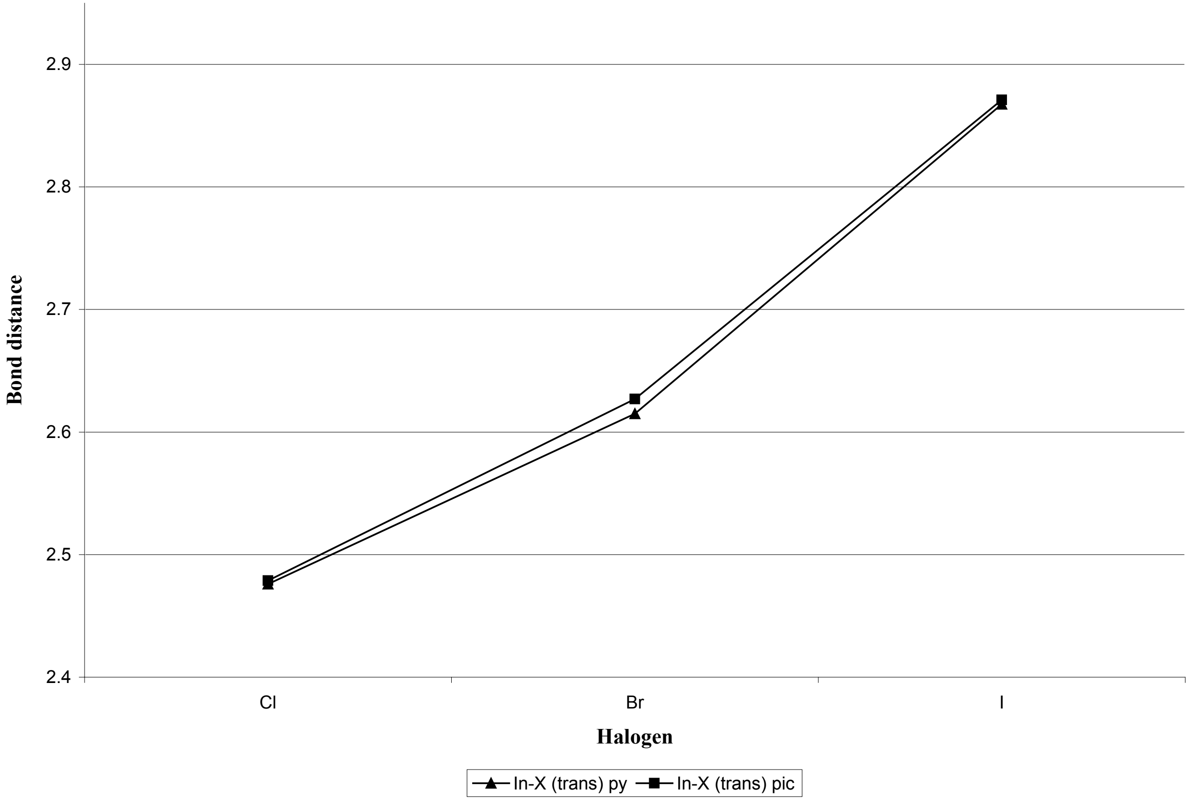

Figure 4.—In-X(*trans*) bond lengths of pyridine (py) versus 4-methylpyridine (pic) from the literature and this study.

3.2 Single-Crystal Structures of Chalcogenide-Containing Indium Compounds (3 and 4)

As we complete our discussion of the structures of the two more coordinatively-complex molecules, it is instructive to do so in the context of the seven Ga (Refs. 10 to 12,14, and 37) and nine In ((**1-4**) and (Refs. 6, 13, 14, 38, and 39)) complexes prepared and structurally characterized over the past 20 years with halide and/or chalcogenide (S or O) ligands, many with coordinated 4-mepy (see Table VI).

Compound **3** (Figure 5 and Table IV) has several structural features in common with compounds previously structurally characterized. The In-S bond length of the phenylthiolate ligand is significantly shorter (~ 0.14Å) than the In-S of the two homoleptic *tris*-dithiocarbamate complexes (Refs. 6 and 38) but slightly longer (~ 0.06Å) than the In-S bond of the five-coordinate thioglycolate dianion (Ref. 39). This can be explained by the de-localized nature of the dithiocarbamate ligand and the π-back bonding from the negatively charged thiolate and thioglycolate ligands that shorten the In-S bonds. As expected, this results in a slight weakening and lengthening of the In-Cl bond (by 0.02Å) when compared to the *mer*-trichloride complex (**1**). The average In-N bond length of three picoline ligands is unremarkable at 2.309(3) Å.

TABLE IV.—SELECT BOND DISTANCES (Å) AND ANGLES (°) FOR COMPOUND **3** (*trans*-In$(SC_6H_5)Cl_2(pic)_3$)

In-N(11)	2.280(3)	Cl(1)-In-Cl(2)	170.65(4)
In-N(21)	2.344(3)	Cl(1)-In-S(3)	91.89(4)
In-N(31)	2.303(3)	Cl(2)-In-S(3)	97.04(4)
In-Cl(1)	2.4931(11)	N(11)-In-Cl(1)	89.70(9)
In-Cl(2)	2.4939(10)	N(31)-In-Cl(1)	88.30(9)
In-S(3)	2.4582(12)	N(21)-In-Cl(1)	84.74(9)
N(11)-C(12)	1.338(5)	N(11)-In-Cl(2)	92.06(9)
N(11)-C(16)	1.344(5)	N(31)-In-Cl(2)	88.34(8)
N(21)-C(22)	1.337(5)	N(21)-In-Cl(2)	86.28(9)
N(21)-C(26)	1.342(5)	C(1)-S(3)-In	118.0(3)
N(21)-C(22)	1.335(5)	C(12)-N(11)-C(16)	117.8(4)
N(21)-C(26)	1.337(5)	C(12)-N(11)-In	121.2(3)
S(3)-C(1)	1.765(9)	C(16)-N(11)-In	121.0(3)
C(1)-C(2)	1.402(14)	C(22)-N(21)-C(26)	117.9(4)
C(1)-C(6)	1.393(13)	C(22)-N(21)-In	121.6(3)
		C(26)-N(21)-In	119.8(3)
N(11)-In-N(31)	169.63(12)	C(32)-N(31)-C(36)	117.5(4)
N(11)-In-N(21)	84.61(12)	C(32)-N(31)-In	121.9(3)
N(21)-In-N(31)	85.08(11)	C(36)-N(31)-In	120.5(3)
N(11)-In-S(3)	96.43(9)	C(2)-C(1)-C(6)	117.8(10)
N(31)-In-S(3)	93.80(9)	C(6)-C(1)-S(3)	121.3(9)
N(21)-In-S(3)	176.47(9)	C(2)-C(1)-S(3)	120.8(7)

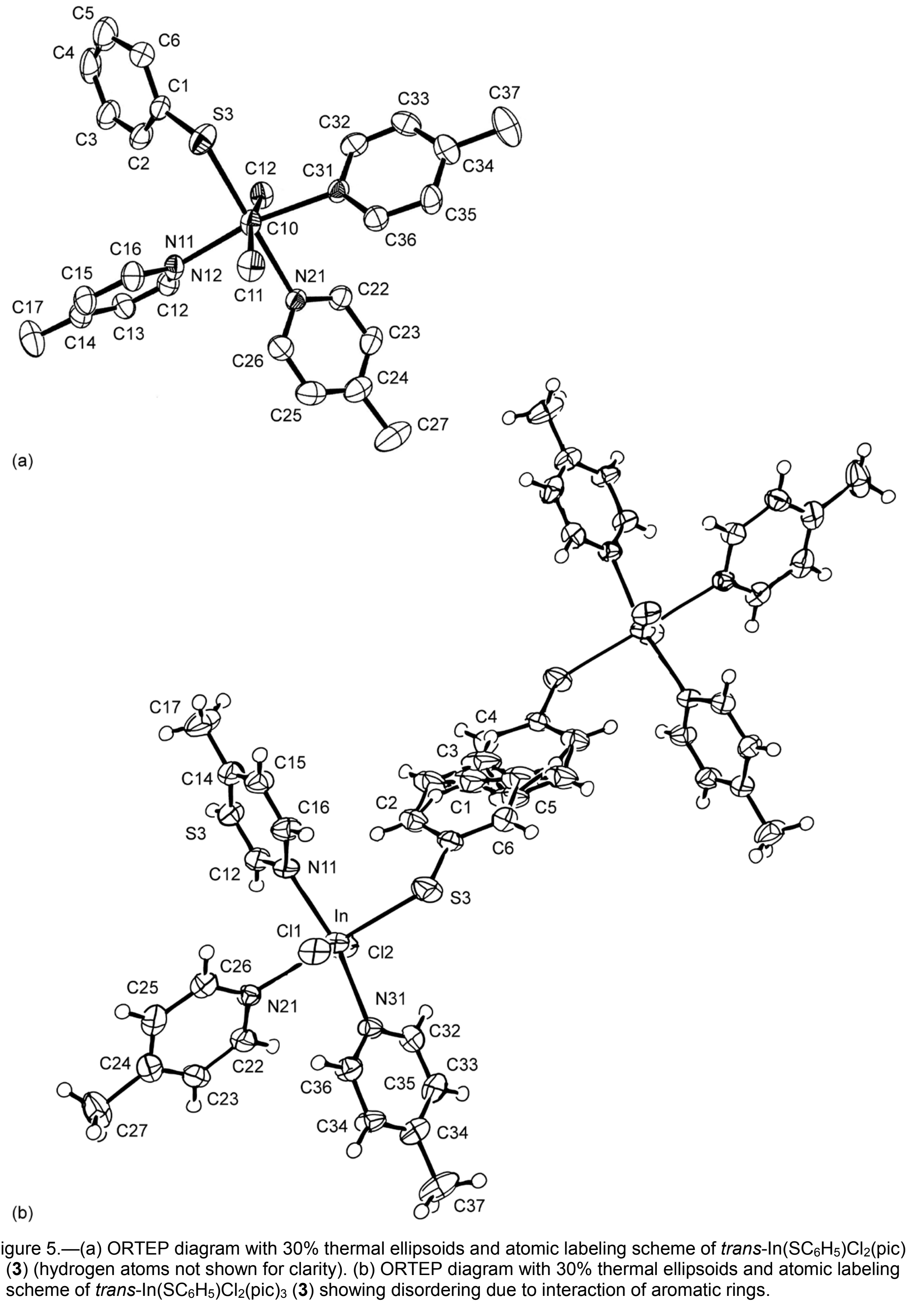

Figure 5.—(a) ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of *trans*-In(SC_6H_5)Cl_2(pic)$_3$ (**3**) (hydrogen atoms not shown for clarity). (b) ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of *trans*-In(SC_6H_5)Cl_2(pic)$_3$ (**3**) showing disordering due to interaction of aromatic rings.

Compound **4** (Figure 6 and Table V) is unusual in our experience in that it is the only dimeric In complex that we prepared. A trimeric Ga basic carboxylate was the other multi-nuclear product of our Ga and In oxidative addition chemistry program (Ref. 12); adventitious water was also found in that final structure attached to the M(III) centers. The equatorial In-Br bond length (2.6232(9) Å) is within experimental error the same as the *mer*-tribromide complex (**2**). Not surprisingly, the bridging hydroxide In-O bond length (2.127(5) Å) is significantly shorter than the chelating benzoate In-O bond of the eight-coordinate tris-benzoate (Ref. 13) (by 0.18Å) or the seven-coordinate mixed chloro-benzoato compound (Ref. 14) (by 0.17Å); it is also shorter than the average In-O bond of the five-coordinate thioglycolate dianion (Ref. 39) (by ~ 0.1Å). The In-N bond length (2.319(5)) of the axial picoline ligands is very slightly longer (by 0.03Å) than the *mer*-tribromide (**2**) and practically within experimental error. The very similar In-Br and In-N bond lengths to compound **2** confirms that **4** is an In(III) compound with bridging hydroxides as opposed to an In(II) species with bridging waters.

The bridging di-chalcogenide (E-In-E) (E = S, O) feature of compound **4** is what would be expected from an unconstrained (H)O-In-O(H) moiety (74.6(3)°). In contrast, the two chelating benzoate complexes have a much narrower O-In-O “bite” or bond angle of ~ 56° (Refs. 13 and 14). The constrained dithiocarbamate complexes have a S-In-S bond angle of ~ 70° (Refs. 6 and 38); the mixed-chalcogenide chelating thioglycolate (Ref. 39) has a S-In-O bond angle of 82.5(1)°.

While doubly-bridged $\text{In}_2(\text{OH})_2$ halide moieties are unusual, a search of the literature provides several interesting examples of such a structural feature. A dimeric In β-diketiminate chloro-hydroxide complex results as a minor product from the reaction of the lithium salt and InCl (Ref. 40). The complex $[\{\text{HC}(\text{CMeNAr})_2\}\text{InCl}(\mu\text{-OH})]_2$ is a five-coordinate In(III) dimer with a central $\text{In}_2(\text{OH})_2$ core. The O-In-O bond angle is 71.47(5)°; this smaller angle (by 3°) is likely a result of the bulky β-diketiminate chelate around each In ion. The average In-O bond length of 2.13(2) Å is similar to 2.127(5) Å of compound (**4**). Moisture contamination is also likely the source of the bridging hydroxides (Ref. 40), in an analogous manner to the unintended production of compound **4**, see discussion below.

TABLE V.—SELECT BOND DISTANCES (Å) AND ANGLES (°)
FOR COMPOUND **4** $[\text{In}(\mu\text{-OH})\text{Br}_2(4\text{–mepy})_2\cdot 2(4\text{-mepy})]_2$

In(1)-O(1)	2.126(5)	Br(1)-In(1)-N(11)	90.1(1)
In(1)-N(11)	2.331(5)	Br(1)-In(1)-Br(1)	98.92(4)
In(1)-Br(1)	2.6232(9)	O(1)-In(2)-O(1)	74.5(2)
In(2)-O(1)	2.127(5)	O(1)-In(2)-N(21)	84.4(1)
In(2)-N(21)	2.307(5)	N(21)-In(2)-O(1)	94.8(1)
In(2)-Br(2)	2.6146(9)	N(21)-In(2)-N(21)	179.0(2)
N(11)-C(12)	1.340(8)	O(1)-In(2)-Br(2)	167.2(1)
N(11)-C(16)	1.348(8)	Br(2)-In(2)-O(1)	95.6(1)
N(21)-C(22)	1.338(8)	Br(2)-In(2)-N(21)	88.5(1)
N(21)-C(26)	1.341(8)	Br(2)-In(2)-N(21)	92.1(1)
		Br(2)-In(2)-Br(2)	95.30(4)
O(1)-In(1)-O(1)	74.6(3)	In(1)-O(1)-In(2)	105.5(1)
O(1)-In(1)-N(11)	95.2(1)	C(12)-N(11)-C(16)	117.5(6)
N(11)-In(1)-O(1)	88.2(1)	C(12)-N(11)-In(1)	120.2(4)
N(11)-In(1)-N(11)	175.8(2)	C(16)-N(11)-In(1)	122.2(4)
O(1)-In(1)-Br(1)	166.8(1)	C(22)-N(21)-C(26)	117.7(6)
Br(1)-In(1)-O(1)	93.5(1)	C(22)-N(21)-In(2)	121.7(4)
Br(1)-In(1)-N(11)	87.2(1)	C(26)-N(21)-In(2)	120.3(4)

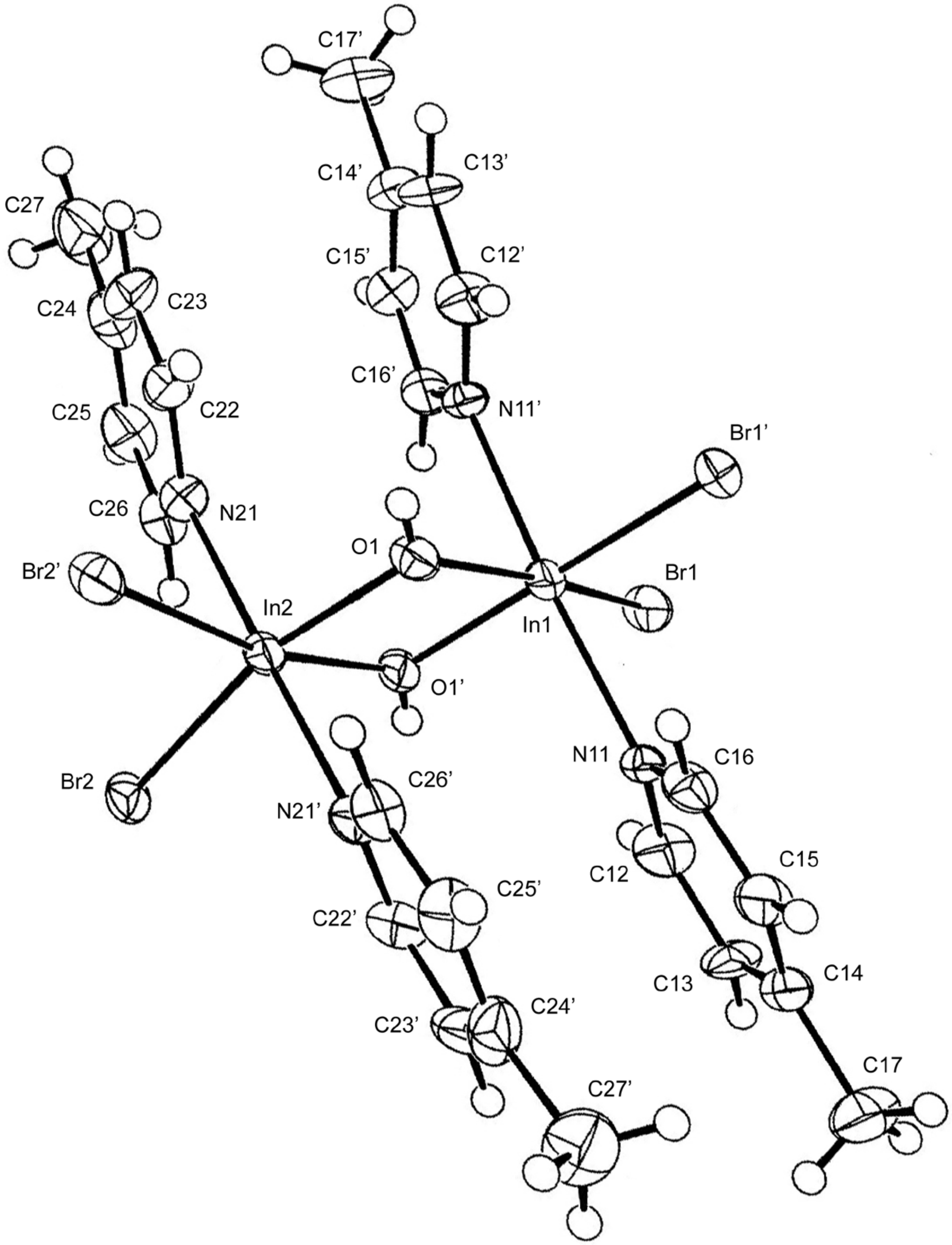

Figure 6.—ORTEP diagram with 30% thermal ellipsoids and atomic labeling scheme of [In(μ-OH)Br_2(4–mepy)$_2$·2(4-mepy)]$_2$ (**4**).

Synthesis of chiral In(III) tridentate-chelating diaminophenol complexes resulted in synthesis of a di-hydroxy-bridged iodo-In(III) dimer with a $(N_2O)InI(\mu\text{-}OH)_2$ coordination environment (Ref. 41). The O-In-O bond angle of 74.03(6)° is within 0.5° of the angle in compound **4**; however, the average In-O bond length is 0.02Å longer at 2.147(7) Å. Reaction of $InCl_3$ with an unsymmetrical triaromatic-N_2O_2 tetradentate-chelating ligand produces a water-bridged chloro-In-chelated dimer with two six-coordinate In(III) units with an $InClO_3N_2$ ligand set (Ref. 42). The average In-O bond length is 2.162(5) Å; the longer bond is expected for a neutral aquo-bridged moiety. An In(II)-O(aquo) bond would be expected to be even longer; this is further support for a doubly-bridging hydroxy-In(III) for compound **4**.

3.3 Oxidative Addition Chemistry: Preparation of New Indium and Gallium Compounds

A summary of In and Ga compounds prepared in our laboratories is shown in Table VI. The attempted oxidative addition reactions of diaryldichalcogenide with In(I) halides resulted in disproportionation and subsequent formation of *mer*-$InX_3(4mepy)_3$ (X = Cl, Br) complexes. A simplified reaction (1) is given below. As expected, the yield obtained was ~ 33% or less. There is no straightforward explanation for the participation (if any) of the un-reacted dichalcogenides. A successful reaction is described below. It should be noted that the chloride complex(**1**) has been isolated several times during attempted oxidative addition reactions with InCl or simple attempted reactions of $InCl_3$ with phosphines.

$$3\ InX + \text{excess 4-mepy} \rightarrow 2\ In^0 + mer\text{-}InX_3(4mepy)_3 \qquad (1)$$

The synthesis of compound **3** and *attempted synthesis* of the bromide analog that resulted in compound **4** can be described as oxidative addition and disproportionation (2) and disproportionation and hydrolysis (3), respectively, with the cleavage of the disulfide bond and subsequent electron transfer producing benzenethiolate or hydroxide ligands; yielding trivalent metal complexes. Another potential source of water in reaction three could be the solvent not being thoroughly dried. It is interesting to note that Stender and Power also produced a bridging hydroxide dimer from an oxidative addition reaction with InX (Ref. 40).

$$2\ InCl + H_5C_6SSC_6H_5 \rightarrow InCl_2(SC_6H_5)(4\text{-}Mepy)_3 + In^0 \qquad (2)$$

$$2\ InBr + H_5C_6Se\text{-}SeC_6H_5\ (wet) \rightarrow [InBr_2(\mu\text{-}OH)(4\text{-}Mepy)_2]_2 + In^0 \qquad (3)$$

During the structural discussion above, another example of oxidative addition chemistry resulted Ga_2Cl_4 when reacted with a more powerful oxidant (tetraethylthiuram disulfide (TETD)) to produce a mixture of gallium-containing products demonstrating simple solvolysis, disproportionation, and oxidative addition (4) (Ref. 10).

$$Ga_2Cl_4 + \{(H_5C_2)_2NC(S)S\text{-}\}_2 \rightarrow Ga_2Cl_4pic_2 + [GaCl_2pic_4]GaCl_4 + GaCl_2pic_2(dtc) \qquad (4)$$

Finally, a yet more powerful oxidant (benzoyl peroxide ($H_5C_6C(O)O\text{-}OC(O)C_6H_5$)) reacted with both Ga_2Cl_4 (5) and InCl (6) to undergo clean oxidative addition with cleavage of the peroxide bond and single and double addition, respectively for one- and two-electron oxidation to form trivalent six- and seven-coordinate metal complexes, respectively (Ref. 14).

$$Ga_2Cl_4 + H_5C_6C(O)O\text{-}OC(O)C_6H_5 \rightarrow 2\ GaCl_2(4\text{-}Mepy)_2(O_2CC_6H_5) \qquad (5)$$

$$InCl + H_5C_6C(O)O\text{-}OC(O)C_6H_5 \rightarrow InCl(4\text{-}Mepy)_2(O_2CC_6H_5)_2 \qquad (6)$$

TABLE VI.—SUMMARY OF STRUCTURAL PARAMETERS OF INDIUM AND GALLIUM COORDINATION COMPOUNDS PREPRARED IN OUR LABORATORIES

Compound[a,b]	Brief description of structure with notable features[a-e]	M-X (ave.; Å)	M-N (ave.; Å)	M-S (ave.; Å)	M-O (ave.; Å)	E-M-E' (ave.;°)	Text Ref./ **Cpd.**
$GaCl_2(S_2CN(CH_3)_2)pic_2$	Pseudo-O_h; *cis*-Cl's; *trans*-pic's; chelated dtc	2.2806(20)	2.149(5)	2.4705(20)	----	72.40(7) E = E' = S	11
$GaCl_2(S_2CN(C_2H_5)_2)pic_2$	Pseudo-O_h; *cis*-Cl's; *trans*-pic's; chelated dtc	2.287(1)	2.146(6)	2.479(1)	----	72.01(6) E = E' = S	10
$Ga_2Cl_4pic_2$	Ga-Ga bonded; pseudo-T_d Ga; *cis*-Cl's; *trans*-pic's	2.195(2)	2.005(6)	----	----	----	10
$[Ga_3(\mu_3\text{-}O)pic_3(\phi CO_2)_6]GaCl_4$	Ga_3O core-basic carboxylate; pseudo-O_h GaO_5N; all six benzoates bridging	2.203(1)[f]	2.08(1)	----	1.985(6)[h] 1.874(8)[i]	----	12
$[GaCl_2pic_4]GaCl_4{\cdot}pic_{0.5}$	Pseudo-O_h cation; axial Cl's; equitorial pic's; $GaCl_4^-$ anion	2.320(3)[g] 2.157(3)[f]	2.106(5)	----	----	----	10
$[Hpic][Ga(CH_2SC(O)O)_2pic]$	Pseudo-square pyramidal; five-coord. anion; axial pic	----	2.017(4)	2.243(1)	2.004(3)	87.9(1) E = O; E' = S	37
$GaCl_2(\phi CO_2)pic_2{\cdot}(pic)$	Pseudo-O_h; *cis*-Cl's; *trans*-pic's; chelated benzoate	2.2410(11)	2.105(3)	----	2.101(3)	62.83(10) E = E' = O	14
mer-$InCl_3(pic)_3$	Pseudo-O_h; *mer*-Cl's	2.4735(9)	2.316(2)	----	----	----	**1**
mer-$InBr_3(pic)_3$	Pseudo-O_h; *mer*-Br's	2.614(4)	2.29(2)	----	----	----	**2**
trans-$InCl_2(S\phi)pic_3$	Pseudo-O_h; *trans*-Cl's; *trans*-pic's; $S\phi$ *trans* to pic	2.4935(11)	2.309(3)	2.4582(11)	----	----	**3**
$[In(\mu\text{-}OH)Br_2pic_2{\cdot}2(pic)]_2$	(OH)-bridged In_2O_2 core; co-equitorial with Br; axial pic's	2.6189(9)	2.319(5)	----	2.127(5)	74.6(3) E = E' = O	**4**
$In(\phi CO_2)_3pic_2$	Pseudo-square pyramidal; eight-coord.; axial benzoate	----	2.335(6)	----	2.308(6)	56.2(3) E = E' = O	13
$In(S_2CN(CH_3)_2)_3$	Pseudo-O_h; three chelating dithiocarbamates	----	----	2.594(2)	----	69.50(6) E = E' = S	38
$In(S_2CN(CH_2\phi)_2)_3$	Pseudo-O_h; three chelating dithiocarbamates	----	----	2.5934(6)	----	69.84(2) E = E' = S	6
$[Hpic]_2[InCl(CH_2SC(O)O)_2]$	Pseudo square pyramidal; 5-coord di-anion, axial Cl	2.425(2)	----	2.408(2)	2.222(2)	82.5(1) E = O; E' = S	39
$InCl(\phi CO_2)_2pic_2{\cdot}(pic)$	Pentagonal bipyramidal; 7-coord; Cl & pic axial ligands	2.4132(15)	2.299(4)	----	2.299(4)	56.28(13) E = E' = O	14

[a] Pic = 4-methylpyridine

[b] $\phi = C_6H_5$

[c] O_h = octahedral

[d] T_d = tetrahedral

[e] dtc = dithiocarbamate

[f] anion ($[GaCl_4]^-$) Ga-Cl bond

[g] cation; ($[GaCl_2pic_4]^+$) Ga-Cl bond

[h] benzoate Ga-O bond

[i] triply bridging central O (μ_3-O) Ga-O bond

4.0 Conclusions

Four new indium mixed halide/chalcogenide complexes obtained during attempts to prepare new mixed-ligand In(III) starting materials via oxidative addition. Disproportionation of In(I) halide starting materials resulted in un-anticipated reactions in three of four cases. Stronger oxidizing reagents had produced more easily predicted chemistry during other chemical reaction studies involving reduced In and Ga halides. An unusual doubly bridged hydroxide In(III) bromide picoline complex (**4**) resulted from inclusion of adventitious water in the resulting product, analogous to a previously obtained basic Ga carboxylate (Ref. 12). A combination of oxidative addition and disproportionation resulted in a mixed-ligand chloride phenyl thiolate complex (**3**). Our results point once again to the rich chemistry still to be explored involving lower oxidation state Group 13 metal halide starting materials and potential new routes to solid state precursor materials.

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14. ABSTRACT
We describe the structures of four related indium complexes obtained during synthesis of solid-state materials precursors. Indium adducts of halides and 4-methylpyridine, $InX_3(pic)_3$ (X = Cl, Br; pic = 4-methylpyridine) consist of octahedral molecules with meridional *(mer)* geometry. Crystals of *mer*-$InCl_3(pic)_3$ (**1**) are triclinic, space group *P*1(bar) (No. 2), with a = 9.3240(3), b = 13.9580(6), c = 16.7268 (7) Å, á = 84.323(2), β = 80.938(2), γ = 78.274(3)Z = 4, R = 0.035 for 8820 unique reflections. Crystals of *mer*-$InBr_3(pic)_3$ (**2**) are monoclinic, space group *P*21/*n* (No. 14), with a = 15.010(2), b = 19.938(2), c = 16.593(3), β = 116.44(1)Z = 8, R = 0.053 for 4174 unique reflections. The synthesis and structures of related compounds with phenylsulfide (chloride) (**3**) and a dimeric complex with bridging hydroxide (bromide) (**4**) coordination is also described. Crystals of *trans*-$In(SC_6H_5)Cl_2(pic)_3$ (**3**) are monoclinic, space group *P*21/*n* (No. 14), with a = 9.5265(2), b = 17.8729(6), c = 13.8296(4), β = 99.7640(15)Z = 4, R = 0.048 for 5511 unique reflections. Crystals of $[In(\mu\text{-}OH)Br_2(pic)_2]_2$ (**4**) are tetragonal, space group = $I4_1cd$ (No. 110) with a = 19.8560(4), b = 19.8560(4), c = 25.9528(6), Z = 8, R = 0.039 for 5982 unique reflections.

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