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Variable Coordination Modes in Dialkyldithiophosphinato Complexes of Group 13 Metals: The X-ray Single Crystal Structures of Tris(diisobutyldithiophosphinato)gallium(III) and -indium(III)

Jin-Ho Park,[†] Paul O'Brien,*[,†]
Andrew J. P. White, and David J. Williams

Department of Chemistry, Imperial College of Science,
Technology and Medicine, South Kensington,
London, SW7 2AY, U.K.

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Introduction

Dithiophosphinato complexes have found application as solvent extraction reagents for metals, insectides and pesticides, flotation agents for mineral ores, and additives to lubricant oils and can be used as precursors for use in metal−organic chemical vapor deposition (MOCVD).[1−4] The structures of a number of zinc and cadmium complexes of substituted dithiophosphorus ligands of the type ($-S_2PR_2$), e.g., $[Zn(S_2PR_2)_2]_2$ (R = Et_2,[5] $^nPr_2$,[6] $^iBu_2$[4]) and $[Cd(S_2PR_2)_2]_2$ (R = Et_2,[7−9] $^iBu_2$,[4] Ph_2[10]), have been determined by X-ray crystallography. The related indium compounds $[In(S_2PR)_3]$ (R = Me,[11a] Et,,[11b] OEt,[11c] Ph[11a]) are monomeric in the solid state in contrast to the dinuclear formulations seen for the zinc and cadmium species. Barron et al.[12] have proposed that the structures of the related gallium compounds $[Ga(S_2PR_2)_3]$ (R = Me, Et) will be similar to the structures of their indium analogues, though these complexes have not been characterized crystallographically.

Here we report the X-ray crystal structures of the new compounds tris(diisobutyldithiophosphinato)indium(III) and -gallium(III), which, surprisingly, are not isostructural and are seen to exhibit distinctly different coordination modes. The gallium complex is, we believe, the first example of a tris(dialkyldithiophosphinato)gallium(III) compound to be structurally characterized

Table 1. Crystallographic Data for Compounds **1** and **2**

data	**1**	**2**
chemical formula	$C_{24}H_{54}P_3S_6In$	$C_{24}H_{54}P_3S_6Ga$
fw	742.8	697.7
space group	$R\bar{3}$ (No. 148)	*Cc* (No. 5)
T (°C)	20	20
a (Å)	14.551(1)	13.989(1)
b (Å)		24.800(2)
c (Å)	30.608(2)	11.061(1)
β (deg)		95.57(1)
V (Å^3)	5612.5(8)	3819.3(4)
Z	6	4
ρ_{calcd} (g cm^{-3})	1.319	1.213
λ (Å)	0.71073	1.54178
μ (mm^{-1})	1.11	5.33
$R_1{}^a$	0.032	0.061
$wR_2{}^b$	0.070	0.165

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Experimental Section

Sodium diisobutyldithiophosphinate (50% solution in water) was obtained from Fluka Ltd. $InCl_3$ and $GaCl_3$ were gifts from Epichem. Ltd., and solvents were obtained from BDH.

[In(S$_2$P^{i}Bu$_2$)$_3$] (1). The compound was prepared from sodium diisobutyldithiophosphinate and indium chloride ($InCl_3$) by the method of Kuchen and co-workers.[13] The white precipitate formed in aqueous solution was filtered under vacuum and recrystallized from toluene to give colorless crystals. Yield: ca. 85%. ^{1}H NMR (CDCl$_3$ 400 MHz) δ (ppm): 1.09 (d, 36H, $^3J_{H-H}$ = 6.7 Hz, CH$_3$), 1.93 (dd, 12H, $^3J_{H-H}$ = 6.0 Hz, CH$_2$), 2.54 (m, 6H, $^3J_{H-H}$ = 6.4 Hz, CH). ^{13}C NMR (CDCl$_3$, 400 MHz) δ (ppm): 24.86 (CH$_3$), 24.95 (CH), 47.36 (CH$_2$). ^{31}P NMR (C$_6$D$_6$, 500 MHz) δ (ppm): 67.68. IR major bands and tentative assignments: 603 cm^{-1}, ν(In−S); 722 cm^{-1}, ν(P═S). Anal. Calcd for $C_{24}H_{54}P_3S_6In$: C, 38.8; H, 7.3. Found: C, 38.1; H, 7.6.

[Ga(S$_2$P^{i}Bu$_2$)$_3$] (2). The reaction was carried out as above but using $GaCl_3$ in place of the indium source. Yield: ca. 82%. ^{1}H NMR (CDCl$_3$ 400 MHz) δ (ppm): 1.14 (d, 36H, $^3J_{H-H}$ = 6.7 Hz, CH$_3$), 2.15 (dd, 12H, $^3J_{H-H}$ = 6.1 Hz, CH$_2$), 2.38 (m, 6H, $^3J_{H-H}$ = 6.5 Hz, CH). ^{13}C NMR (CDCl$_3$, 400 MHz) δ (ppm): 24.71 (CH$_3$), 24.79 (CH), 48.15 (CH$_2$). ^{31}P NMR (C$_6$D$_6$, 500 MHz) δ (ppm): 68.24. IR major bands and tentative assignments: 615 cm^{-1}, ν(Ga−S); 720 cm^{-1}, ν(P═S). Anal. Calcd for $C_{24}H_{54}P_3S_6Ga$: C, 41.3; H, 7.8. Found: C, 41.2; H, 7.7.

Crystallographic Structural Determination. Crystallographic data for **1** and **2** are summarized in Table 1. Data were collected on Siemens P4/PC diffractometers using graphite-monochromated Mo Kα and Cu Kα radiation for **1** and **2**, respectively. The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2. The polarity of **2** was determined by a combination of R-factor tests [$R_1^+ = 0.0614$, $R_1^- = 0.0624$] and by use of the Flack parameter [$x^+ = -0.16(14)$, $x^- = +1.15(14)$]. CCDC: 163820 (**1**) and 163821 (**2**).

Results and Discussion

Compounds **1** and **2** are soluble in most organic solvents and can be recrystallized from toluene at room temperature to give transparent white crystals. Both compounds gave satisfactory elemental analysis and were further characterized by NMR (^{1}H, ^{13}C, ^{31}P), IR, TGA, and X-ray methods. The compounds are stable at room temperature for several months.

The X-ray analysis shows the indium complex (**1**) to have the anticipated approximately D_3 symmetric structure shown

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* Author to whom correspondence should be addressed. E-mail: paul.obrien@man.ac.uk.

[†] Current address: The Manchester Materials Science Centre and Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

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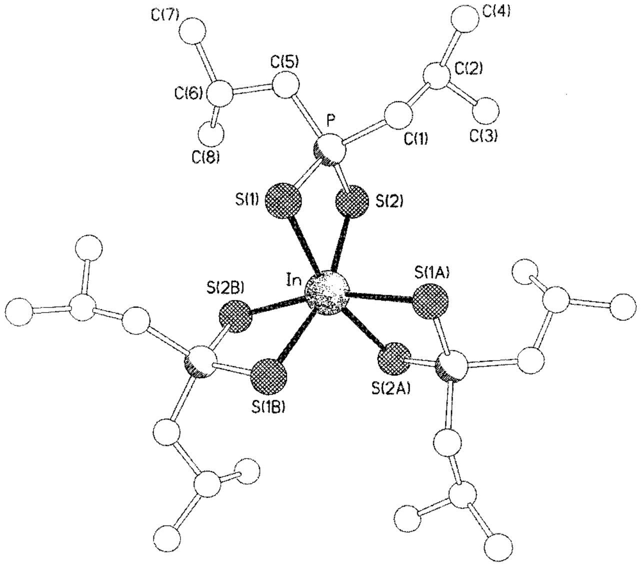

Figure 1. The molecular structure of $[\mathrm{In}(\mathrm{S_2P^iBu_2})_3]$ (**1**). Selected bond lengths (Å) and angles (deg); In−S(1) 2.6493(9), In−S(2) 2.6100(8), P−S(1) 2.0225(12), P−S(2) 2.0212(11), S(1)−In−S(2) 77.53(2), S(1)−In−S(1A) 90.82(3), S(1)−In−S(2A) 100.55(3), S(2)−In−S(2A) 93.30(3), S(1)−In−S(2B) 163.73(3).

in Figure 1; the crystallographic symmetry is C_3. The geometry at indium is trigonally distorted octahedral as a consequence of the restricted bite of the chelating diisobutyldithiophosphinate ligand [S(1)−In−S(2) 77.53(2)°], the trans angles each being 163.73(3)°. The In−S bond lengths [2.610(1) and 2.649(1) Å] are noticeably different but lie within the range observed for other indium dithiophosphinate species.[11] Distortions from tetrahedral geometry at the phosphorus centers are small, the largest deviation being in the C−P−C angle [103.7(2)°]; the P−S distances are essentially the same at 2.021(1) and 2.023(1) Å.

Although examples of pairs of simple compounds that show four-coordination for gallium but five- or six-coordination for indium have been reported,[14] to date, all previously structurally characterized pairs of analogous indium/gallium tris(chelates) with (O,O′) or (S,S′) ligands have been shown to be isostructural[15,16] (interestingly, no examples of corresponding pairs of complexes with (O,S) chelates have been identified). However, whereas in the structure of $[(^i\mathrm{Bu_2PS_2})_3\mathrm{In}]$ (**1**) the metal center was found to be six-coordinate (vide supra), here in striking contrast the metal center in $[(^i\mathrm{Bu_2PS_2})_3\mathrm{Ga}]$ (**2**) is four-coordinate, being bound to only one chelating and two pendant diisobutyldithiophosphinate ligands in a distorted tetrahedral geometry (Figure 2). The bite angle of the chelating ligand is noticeably increased [at 87.03(9)°], cf. that in **1**, and the "tetrahedral" angle between the sulfur atoms of the two pendant ligands is 116.7(2)°. The chelating Ga−S distances [2.316(3) and 2.337(3) Å] are significantly longer than those to the two pendant ligands [2.253(3) and 2.260(3) Å], possibly reflecting the localization of the negative charge onto a single donor atom in the latter cases. This localization is also reflected by a small asymmetry in the P−S bond lengths to the coordinated and noncoordinated sulfur atoms (Figure 2). The distances to the other sulfur atoms, which are 3.215(4) Å to S(6) and 3.457(4) Å to S(4), are far too long to be considered as bonds. The bonding Ga−S distances seen here are shorter than those seen in the only other previously reported GaSPS chelate[17] where they are in the range 2.449−2.472 Å.

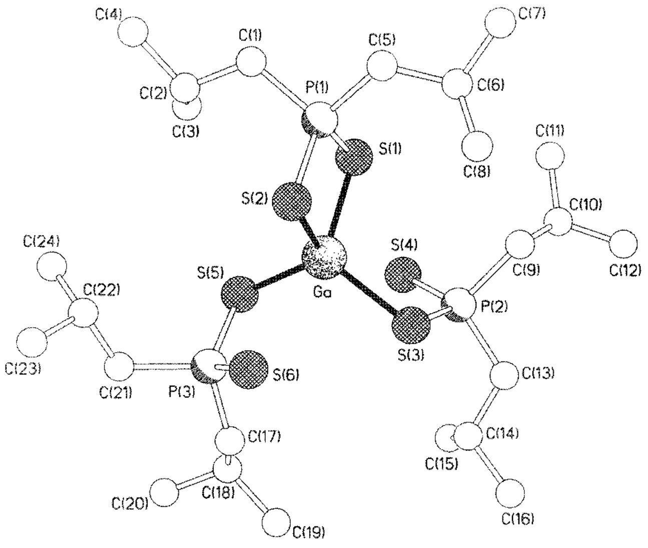

Figure 2. The molecular structure of $[\mathrm{Ga}(\mathrm{S_2P^iBu_2})_3]$ (**2**). Selected bond lengths (Å) and angles (deg); Ga−S(1) 2.337(3), Ga−S(2) 2.316(3), Ga−S(3) 2.253(3), Ga−S(5) 2.260(3), P(1)−S(1) 2.030(3), P(1)−S(2) 2.025(3), P(2)−S(3) 2.085(4), P(2)−S(4) 1.961(5), P(3)−S(5) 1.995(7), P(3)−S(6) 1.948(8), S(1)−Ga−S(2) 87.03(9), S(1)−Ga−S(3) 113.18(12), S(1)−Ga−S(5) 108.26(14), S(2)−Ga−S(3) 114.19(11), S(2)−Ga−S(5) 113.6(2), S(3)−Ga−S(5) 116.7(2).

There are examples of tris(chelates) of dialkyldithiophosphinates to antimony[18] where there is a substantial asymmetry in the chelating distances (ca. 0.5 Å), though in each of these cases there are three long and three short bonds. In the complex formed between diphenyldithiophosphinate and cobalt(III),[19a] we see a pattern of coordination that is intermediate between that exhibited by indium in **1** and that present in **2**. In this cobalt complex there are two chelating ligands and one pendant ligand.

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The closest analogues to the gallium structure **2** are that formed between thallium and dicyclohexyldithiophosphinate[20] and those formed between diphenyl- and di-*p*-tolyldithiophosphinate and zinc[19] where in each case there are one chelating and two pendant ligands.

The reason for this unprecedented difference in coordination behavior between **1** and **2** is not immediately apparent. Initially we thought that it was a consequence of the very much shorter Ga−S coordination distances [due to the smaller ionic radii of six-coordinate Ga(III), 0.62 Å, cf. 0.80 Å for six-coordinate In(III)] which would result in steric overcrowding around the metal center if all three ligands were chelating. However, inspection of transition metal complexes of dithiophosphinates where the metal has a similar ionic radius [six-coordinate Fe(III) 0.55,[21] Co(III) 0.55,[22] Cr(III) 0.62,[23] V(III) 0.64,[24] Ir(III) 0.68,[25] and Mo(III) 0.69 Å[26]] shows them all to be capable of forming tris(chelates). It is well-known, however, that substituted dithiophosphinate ligands have a tendency to stabilize different, and sometimes unusual, coordination polyhedra.[27] The two compounds can be used as precursors to grow thin films of indium sulfide and gallium sulfide.[28] However, due to their low volatility compared to the corresponding dithiocarbamates, the compounds may have more use as precursors for the growth of nanocrystalline materials of indium or gallium sulfide by thermolysis in trioctylphoshphine oxide (TOPO), where volatility of the precursors is not essential.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of [Ga($S_2P^iBu_2$)$_3$] and [In($S_2P^iBu_2$)$_3$] including the coordinates, full lists of bond lengths and angles, and the thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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