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A Cyclopentadienyl Bridge. The Crystal Structure of Tris(cyclopentadienyl)indium(III) at −100°

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The crystal structure of tris(cyclopentadienyl)indium(III), $In(C_5H_5)_3$, has been determined at −100° using X-ray counter data. The compound is orthorhombic with space group $P2_12_12_1$; the cell dimensions are a = 9.616 (1) Å, b = 9.702 (1) Å, c = 13.407 (2) Å, d_m = 1.6 (1) g/cm^3, and Z = 4. The structure was solved using the Patterson function and refined by full-matrix least-squares techniques to give a value of R = 0.036 and wR = 0.039 for the 1587 observed reflections. The structure consists of infinite polymeric chains with each chain unit comprised of an indium atom linked to two terminal and two bridging cyclopentadienyl groups. These cyclopentadienyl groups give rise to a slightly distorted In–C_4 tetrahedral environment around the indium atom. Each bridging group is shared between two indium atoms related by a twofold screw axis along b. The indium–carbon bond lengths are 2.24 (1) Å for the terminal groups and 2.37 (1) and 2.47 (1) Å for the two contacts with the bridging groups.

Introduction

Tris(cyclopentadienyl)indium(III) was first reported in 1957 by Fischer and Hofmann,[1] who found this substance as a side product in the preparation of cyclopentadienylindium(I) by the reaction of indium trichloride with some cyclopentadienide. Despite the fact that the starting point of this preparation is an indium(III) compound, the yield of tris(cyclopentadienylindium(III) (In(cp)$_3$) is low. It has been shown recently[2] that the use of lithium cyclopentadienide in place of the sodium salt gives rise to In(cp)$_3$ in good yield. While there are three possible bonding schemes involving the metal–cyclopentadienyl rings,[3] namely *polyhapto-*, *pentahapto-* or π type, and *monohapto-* or σ type, vibrational spectroscopic investigations suggested that on the basis of the criteria set out by Fritz the bonding of the cyclopentadienyl ligand in In(cp)$_3$ was of the σ-bonded diene type. Nuclear magnetic resonance studies showed only a single resonance in methylene dichloride solution at temperatures as low as −90°, implying fluxional behavior in the ligand.

Although there is now some understanding of the stereochemical behavior of the coordination compounds[4] of indium(III), the organometallic compounds of this element have not been thoroughly investigated. Indium triphenyl has recently been shown[5] to have a structure in which the approximately trigonal-planar molecules make short contacts with their neighbors by metal–carbon contacts. A similar situation exists in indium trimethyl, which is a tetramer in the solid state,[6] and in both of these systems the indium achieves trigonal-bipyramidal pentacoordination rather than a trigonal-planar arrangement. It therefore seemed appropriate to investigate the crystal structure of In(cp)$_3$ in order to establish with certainty the nature of the metal–ligand interaction, and to identify the coordination around the indium atom. The crystal was held at −100° in order to minimize the thermal motion of the carbon atoms.

The results show that two σ-bonded diene ligands are indeed involved, but that in addition a cyclopentadienyl group bridging two indium atoms results in a coordination number of four for the metal. It is believed that this structure is the first identification of bridging by a cyclopentadienyl ligand.

Experimental Section

Crystals of $In(C_5H_5)_3$ grow as light yellow parallelepipeds, with nearly equal dimensions along a and c and elongated along b. The compound is extremely unstable in air, and all the crystals used were sealed in Lindemann glass capillaries under dry nitrogen. Weissenberg photographs of the nets $h0l$–$h2l$ and precession photographs of the zones $0kl$, $hk0$, and hkh, taken with Cu Kα radiation, established the crystal system as orthorhombic and showed the following systematic absences: $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd. The space group is therefore $P2_12_12_1$.

A crystal of dimension 0.24 × 0.33 × 0.21 mm (parallel to a, b, and c, respectively) was mounted with the longest edge approximately parallel to Φ on a single crystal Cryo-Tip refrigerator (manufactured by Air Products and Chemicals, Inc). Cell dimensions were determined at both 25 and −100° from the least-squares analysis of 2θ values for 16 reflections (>30°), centered and measured on a Picker four-circle diffractometer using Mo Kα_1 radiation, with a take-off angle of 1.0°. These cell dimensions and other pertinent crystal data are given in Table I.

TABLE I

CRYSTAL DATA[a]

Formula weight $In(C_5H_5)_3$ = 309.8

	25°	−100°
a, Å	9.668 (2)	9.616 (1)
b, Å	9.706 (2)	9.702 (1)
c, Å	13.451 (3)	13.407 (2)
V, Å^3	1262.2	1250.8

[a] d_{measd} = 1.6 (1) g/cm^3, d_{calcd} = 1.63 (1) g/cm^3, Z = 4, μ(Mo Kα) = 18.7 cm^{-1}, $F(000)$ = 616, λ(Cu Kα) = 1.5418 Å, λ(Mo Kα) = 0.71069 Å, and λ(Mo Kα) = 0.70926 Å.

Reflection intensities for the unique set of data were collected by the θ–2θ scan technique using niobium filtered Mo Kα radiation, with a take-off angle of 3.0°. The crystal was maintained at −100° throughout the data collection, and the temperature was not allowed to deviate more than ±3°. Each reflection was scanned for 1.0° in 2θ (extended for the splitting of α_1 and α_2) at a rate of 2°/min and the background counted for 10 sec at each end of the scan range. After every 50 reflections, two standard reflections were measured. The maximum variation in the intensity of any individual standard was less than ±1.0%.

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[1] E. O. Fischer and H. P. Hofmann, *Angew. Chem.*, **69**, 639 (1957).

[2] J. S. Poland and D. G. Tuck, submitted to *J. Organometal. Chem.*

[3] (a) J. L. Calderon, F. A. Cotton, and P. Legdins, *J. Amer. Chem. Soc.*, **91**, 2528 (1969); (b) E. Maslowsky and K. Nakamoto, *Inorg. Chem.*, **8**, 1108 (1969); (c) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 240 (1964).

[4] D. G. Tuck, Proceedings of the 191st CNRS Conference, "La Nature et les Proprietes des Liaisons de Co-ordination," Editions du CNRS, Paris, 1970, p 159.

[5] J. F. Malone and W. S. McDonald, *J. Chem. Soc. A*, 3362 (1970).

[6] E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 4141 (1958).

TABLE II

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

Atom	x	y	z	U
In	0.13432 (5)	0.17170 (5)	0.21570 (4)	**
C_1(a)	−0.0577 (8)	0.3252 (10)	0.2097 (8)	**
C_2(a)	0.0259 (9)	0.4372 (9)	0.2305 (8)	**
C_3(a)	0.0122 (10)	0.4732 (9)	0.3308 (7)	**
C_4(a)	−0.0815 (12)	0.3788 (10)	0.3745 (8)	**
C_5(a)	−0.1265 (11)	0.2915 (8)	0.3022 (10)	**
C_1(b)	0.2659 (9)	0.1958 (9)	0.0787 (7)	**
C_2(b)	0.1649 (11)	0.2258 (10)	0.0062 (7)	**
C_3(b)	0.1677 (10)	0.3620 (11)	−0.0119 (6)	**
C_4(b)	0.2741 (10)	0.4223 (10)	0.0461 (7)	**
C_5(b)	0.3356 (8)	0.3224 (12)	0.0992 (6)	**
C_1(c)	0.2398 (10)	0.1412 (11)	0.3628 (7)	**
C_2(c)	0.3441 (11)	0.0498 (8)	0.3265 (8)	**
C_3(c)	0.4646 (11)	0.1231 (11)	0.3144 (8)	**
C_4(c)	0.4419 (11)	0.2597 (11)	0.3467 (10)	**
C_5(c)	0.3093 (12)	0.2703 (11)	0.3757 (9)	**
H_1(a)	−0.1270	0.3493	0.1580	0.057
H_2(a)	0.0864	0.4849	0.1817	0.057
H_3(a)	0.1037	0.4674	0.3646	0.057
H_4(a)	−0.1096	0.3772	0.4457	0.057
H_5(a)	−0.1952	0.2166	0.3116	0.057
H_1(b)	0.3326	0.1267	0.0527	0.057
H_2(b)	0.1020	0.1581	−0.0260	0.057
H_3(b)	0.1054	0.4123	−0.0584	0.057
H_4(b)	0.2993	0.5212	0.0473	0.057
H_5(b)	0.4157	0.3348	0.1449	0.057
H_1(c)	0.2019	0.1077	0.4271	0.057
H_2(c)	0.3317	−0.0497	0.3125	0.057
H_3(c)	0.5533	0.0864	0.2876	0.057
H_4(c)	0.5115	0.3348	0.3473	0.057
H_5(c)	0.2655	0.3550	0.4027	0.057

Atom	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In	0.0313 (2)	0.0233 (2)	0.0330 (2)	0.0000	−0.0003 (3)	0.0015 (2)
C_1(a)	0.049 (4)	0.037 (4)	0.064 (5)	0.020 (4)	−0.008 (5)	−0.001 (6)
C_2(a)	0.042 (5)	0.043 (4)	0.060 (7)	0.013 (4)	0.009 (5)	0.012 (5)
C_3(a)	0.045 (5)	0.037 (4)	0.058 (5)	0.011 (4)	−0.009 (4)	−0.003 (4)
C_4(a)	0.088 (8)	0.045 (5)	0.056 (6)	0.033 (5)	0.031 (6)	0.021 (5)
C_5(a)	0.044 (4)	0.026 (3)	0.124 (10)	0.002 (4)	0.019 (7)	0.003 (5)
C_1(b)	0.037 (4)	0.040 (5)	0.053 (5)	−0.003 (4)	0.012 (4)	−0.005 (4)
C_2(b)	0.072 (7)	0.055 (5)	0.039 (4)	−0.023 (5)	0.007 (5)	−0.005 (4)
C_3(b)	0.056 (6)	0.082 (7)	0.031 (4)	−0.006 (5)	−0.001 (4)	0.015 (4)
C_4(b)	0.054 (5)	0.051 (5)	0.039 (5)	−0.012 (4)	0.007 (4)	0.008 (4)
C_5(b)	0.041 (4)	0.056 (5)	0.046 (4)	−0.012 (5)	0.006 (3)	0.007 (5)
C_1(c)	0.046 (5)	0.067 (7)	0.042 (5)	−0.007 (5)	−0.012 (4)	0.011 (5)
C_2(c)	0.067 (7)	0.033 (4)	0.067 (6)	0.002 (4)	−0.030 (5)	0.008 (4)
C_3(c)	0.053 (5)	0.056 (5)	0.058 (6)	0.008 (5)	−0.017 (5)	0.006 (5)
C_4(c)	0.056 (6)	0.048 (6)	0.088 (8)	−0.011 (5)	−0.031 (6)	0.010 (b)
C_5(c)	0.070 (7)	0.047 (5)	0.061 (7)	0.009 (5)	−0.030 (6)	−0.005 (5)

[a] Estimated standard deviations in the least significant figures are given in parentheses. [b] Anisotropic vibration tensor components U_{ij} (Å^2) for the expression: $T = \exp[-2\pi(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]$.

In this manner, intensities for 2088 reflections with $2\theta < 60°$ were measured; of these, 1587 were considered observed reflections, having a net count greater than 2.5σ, where σ was taken as (total count + background)$^{1/2}$. Lorentz and polarization factors were applied to give structure factors in the usual manner; no correction for absorption was made. (This could lead to a maximum error of ±2.6% in the intensity.)

Structure Determination

Examination of the three-dimensional Patterson function[7] revealed the indium atom position. One cycle of full-matrix least-squares refinement of the scale factor and the indium atom positional parameters (assuming an isotropic temperature factor of 3.5 Å^2) was carried out yielding an unweighted conventional R value of 20.7%.[8] A three-dimensional Fourier map was computed from which the remaining 15 nonhydrogen atoms were located. Least-squares refinement on the indium and 15 carbon atoms, varying the scale, positional parameters, and isotropic temperature factors, reduced R to 6.7%. An electron-density difference map (based on all data with $(\sin\theta)/\lambda < 0.4$ Å^{-1}) revealed that the indium atom was moving anisotropically and also indicated the positions of 14 of the 15 hydrogen atoms. (H_5(a) appeared at only half the height of the other hydrogen atoms.) Up to this point unit weights were used in the least-squares refinement.

When the contributions from the hydrogen atoms (at their calculated positions) were included in the structure factors, and two cycles of least-squares refinement were completed, an electron-density difference map indicated that the carbon atoms had significant anisotropic thermal motion. Further refinement with these variables included gave a final R value of 3.6% and a weighted R of 3.9%.[9] The last stages of refinement were carried out with a weighting scheme of $\sigma = \sqrt{A}$ for $B \leqslant F_o \leqslant C$,

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(7) All calculations were performed on IBM 360/50 and 370/155 computers. Programs used were FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin); BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury); ORFFE, Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy); ORTEP, Fortran thermal-ellipsoid plot program for crystal structure illustrations (C. K. Johnson); and MEANPLANE, calculation of weighted mean planes through atom groups with esd's (M. E. Pippy and F. R. Ahmed).

(8) $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $wR = \{\Sigma w(||F_o| - |F_c||)^2/\Sigma wF_o^2\}^{1/2}$.

(9) A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2832. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)[a]

(a) Intramolecular Bonded Contacts

In–C$_1$(a)	2.374 (7)	C$_1$(b)–C$_2$(b)	1.405 (14)
In–C$_3$(a)^b	2.466 (8)	C$_2$(b)–C$_3$(b)	1.344 (14)
In–C$_1$(b)	2.243 (9)	C$_3$(b)–C$_4$(b)	1.412 (13)
In–C$_1$(c)	2.237 (9)	C$_4$(b)–C$_5$(b)	1.340 (13)
		C$_5$(b)–C$_1$(b)	1.426 (13)
C$_1$(a)–C$_2$(a)	1.381 (13)	C$_1$(c)–C$_2$(c)	1.425 (14)
C$_2$(a)–C$_3$(a)	1.395 (13)	C$_2$(c)–C$_3$(c)	1.370 (14)
C$_3$(a)–C$_4$(a)	1.412 (14)	C$_3$(c)–C$_4$(c)	1.411 (15)
C$_4$(a)–C$_5$(a)	1.358 (15)	C$_4$(c)–C$_5$(c)	1.337 (16)
C$_5$(a)–C$_1$(a)	1.443 (15)	C$_5$(c)–C$_1$(c)	1.430 (14)

(b) Interatomic Angles Selected from Bonded Contacts

C$_1$(a)–In–C$_3$(a)^b	92.1 (3)	C$_5$(a)–C$_1$(a)–C$_2$(a)	105.8 (9)
C$_1$(a)–In–C$_1$(b)	110.2 (4)	C$_1$(a)–C$_2$(a)–C$_3$(a)	109.6 (8)
C$_1$(a)–In–C$_1$(c)	117.7 (4)	C$_2$(a)–C$_3$(a)–C$_4$(a)	107.4 (9)
C$_3$(a)^b–In–C$_1$(b)	101.4 (3)	C$_3$(a)–C$_4$(a)–C$_5$(a)	108.1 (9)
C$_3$(a)^b–In–C$_1$(c)	112.2 (3)	C$_4$(a)–C$_5$(a)–C$_1$(a)	109.0 (8)
C$_1$(b)–In–C$_1$(c)	118.7 (3)	C$_5$(b)–C$_1$(b)–C$_2$(b)	106.2 (8)
In–C$_1$(a)–C$_2$(a)	92.0 (5)	C$_1$(b)–C$_2$(b)–C$_3$(b)	108.4 (9)
In–C$_1$(a)–C$_5$(a)	100.7 (6)	C$_2$(b)–C$_3$(b)–C$_4$(b)	108.8 (9)
In–C$_1$(a)–H$_1$(a)	134.1	C$_3$(b)–C$_4$(b)–C$_5$(b)	108.2 (8)
In–C$_3$(a)^b–C$_4$(a)^b	101.4 (6)	C$_4$(b)–C$_5$(b)–C$_1$(b)	108.3 (8)
In–C$_3$(a)^b–C$_2$(a)^b	101.4 (6)	C$_5$(c)–C$_1$(c)–C$_2$(c)	104.9 (8)
In–C$_3$(a)^b–H$_3$(a)^b	125.7	C$_1$(c)–C$_2$(c)–C$_3$(c)	108.2 (8)
In–C$_1$(b)–C$_2$(b)	95.8 (6)	C$_2$(c)–C$_3$(c)–C$_4$(c)	108.7 (10)
In–C$_1$(b)–C$_5$(b)	101.7 (6)	C$_3$(c)–C$_4$(c)–C$_5$(c)	108.0 (10)
In–C$_1$(b)–H$_1$(b)	130.1	C$_4$(c)–C$_5$(c)–C$_1$(c)	110.1 (10)
In–C$_1$(c)–C$_2$(c)	90.3 (6)		
In–C$_1$(c)–C$_5$(c)	101.3 (6)		
In–C$_1$(c)–H$_1$(c)	131.8		

Dihedral Angles around Indium

C$_1$(a)–In–C$_3$(a)^b/C$_1$(b)–In–C$_1$(c)	92.6 (3)
C$_1$(a)–In–C$_1$(b)/C$_1$(c)–In–C$_3$(a)^b	94.8 (3)

[a] Esd's in the least significant figures are given in parentheses. [b] Atoms from molecule related by symmetry transformation $\bar{x}$, $^1/_2 + y$, $^1/_2 - z$ to that given by the coordinates in Table II.

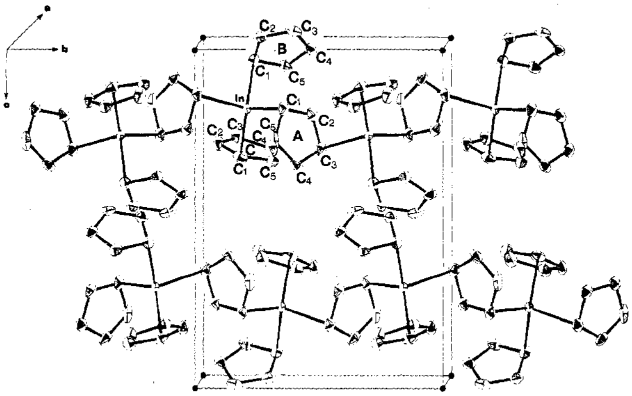

Figure 1.—The molecular structure of In(C$_5$H$_5$)$_3$ viewed down the *a* axis.

TABLE IV[a]

Mean planes as $Ax + By + Cz + D = 0$

Plane	Atoms in plane	A	B	C	D	χ^2 [b]	Max dev, Å	Dev of C$_1$
1	C$_1$(a), C$_2$(a), C$_3$(a), C$_4$(a), C$_5$(a)	−0.7533	0.6171	−0.2273	−1.7299	3.4	0.017	
2	C$_2$(b), C$_3$(b), C$_4$(b), C$_5$(b)	0.6508	−0.1500	−0.7443	−0.6411	0.0	0.000	0.047
3	C$_2$(c), C$_3$(c), C$_4$(c), C$_5$(c)	−0.2737	0.2473	−0.9295	4.8518	1.0	0.008	0.039

[a] Equations, expressed in Å, refer to axes *x*, *y*, and *z*, parallel to *a*, *b*, and *c*, respectively. [b] $\chi^2 = \Sigma_{i=1}{}^n(P_i{}^2/\sigma^2(P_i))$ where *lc* is the number of atoms in the plane and $\sigma^2(P_i) = A\sigma^2(x_i) + B\sigma^2(y_i) + C\sigma^2(z_i)$. $\sigma(x_i)$ is the estimated standard deviation in the *x* direction of atom *i* and P_i is the distance of the atom from the plane.

$\sigma = (AB/F_o)^{1/2}$ for $F_o < B$, and $\sigma = (AF_o/C)^{1/2}$ for $F_o < C$ (where $A = 1.2$, $B = 25.0$, and $C = 35.0$). A was chosen such that the error of fit was equal to unity, B and C were chosen to give constant values of $\Sigma w\Delta^2/n$ over ranges of F_o and sin θ.

Values for the scattering factors for the nonhydrogen atoms were taken from Cromer and Waber,[10] while those for hydrogen were from Stewart, *et al.*[11] Anomalous dispersion corrections, f' and f'', for the indium atom were those given by Cromer.[12]

The positional and thermal parameters for all the atoms obtained in the final cycle of refinement are listed in Table II; interatomic distances and angles are given in Table III. Errors in these distances and angles include both correlation between atomic parameters and errors in the cell dimensions. The equations of planes through selected atoms of the cyclopentadiene rings are given in Table IV.

Structure Description and Discussion

Tris(cyclopentadienyl)indium(III), In(cp)$_3$, exists as a polymeric solid, made up of parallel chains of –(In(cp)$_2$)–cp–(In(cp)$_2$)–· · ·, where the atoms within one chain are related by successive operations of a twofold screw axis parallel to *b*. Figure 1 is a diagram showing this arrangement. The closest adjacent metal atoms (In$_1$–In$_2$, 5.57 Å) are held together in the chain by cp bridges with one In–C distance of 2.37 Å (In$_1$–C$_1$(a)) and a longer In–C distance of 2.47 Å (In$_2$–C$_3$(a)). Each indium atom has a slightly distorted tetrahedral environment.

Examination of the anisotropic thermal parameters reveals that the carbon atoms comprising the cyclopentadienyl rings show pronounced motion in the ring plane normal to radial vectors. This situation is consistent with the fluxional behavior shown by the compound in solution. Furthermore, the motion of the indium atom is very much less along the chain axis (*b*) than in the plane normal to the axis, where it is approximately isotropic. This view is also supported by the fact that only *a* and *c* contract significantly on cooling.

The Cyclopentadienyl Rings in In(cp)$_3$.—There are two different types of cyclopentadienyl rings in the crystal structure of In(cp)$_3$, namely one bridging (ring A) and two formally monodentate (rings B and C). The derived bond lengths and angles in these two latter ligands show that these rings in B and C are identical within experimental error, and we shall treat them as such in the subsequent discussion. The bond lengths in these rings are in good agreement with the earlier postulate[2] of a σ-bonded diene ring, since the C$_2$–C$_3$ and C$_4$–C$_5$ bonds are substantially shorter than the remaining C–C bonds.

In both rings, the C$_5$–C$_1$–C$_2$ angle is significantly smaller (105–106°) than the other C–C–C angles

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(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(108–110°). The structure of rings B and C is very similar to the σ-bonded C_5H_5 rings in $(C_5H_5)_3$MoNO[3a] and $(C_5H_5)_4$Ti.[13] The double bonds in the 2 and 4 positions agree very well and the single bonds in the 1, 3, and 5 positions are slightly shorter in In(cp)$_3$. The features of these rings are also close to those found for the parent cyclopentadiene molecule.[14,15]

The rings show some nonplanarity, with C_1 lying 0.05 and 0.04 Å out of the C_2–C_3–C_4–C_5 plane for the B and C rings, respectively. This result is in agreement with Cotton's observation that "there is no significant dihedral bend across the C_2–C_5 line." The dihedral angles between the C_2–C_3–C_4–C_5 and C_5–C_1–C_2 planes for rings B and C are 3.2 and 2.5°, only slightly greater than the 2.2° and <1° values reported by Cotton for similar rings.

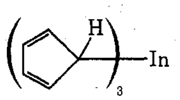
Equally, the angle which the In–C_1 axis makes with the ring is 102°, close to the value expected if C_1 is essentially an sp^3-hybridized carbon, with a hydrogen atom occupying the fourth bonding position at this carbon atom. We may note in this context that for all the carbon atoms in the three rings, the presence of one hydrogen atom on each carbon atom was demonstrated both by the values of the relevant interatomic angles, and by the presence of electron density peaks on a difference map.

Ring A, which serves to bridge two indium atoms, is less easily described. The shortest bond, C_4–C_5, has approximately the same length as the "double bonds" of the diene rings B and C. The differences in the lengths of the carbon–carbon bonds C_1–C_2, C_2–C_3, and C_3–C_4 are not experimentally significant, although C_5–C_1 is long, again being similar to the longer bonds in rings B and C. The planarity of ring A indicates a greater degree of electron delocalization than is found in rings B and C.

It is possible to reject alternative descriptions of the In–ring A–In interaction, namely those involving a bridging π-bonded cyclopentadienyl ring similar to that in indium(I) cyclopentadienide[16] or a *polyhapto*-cyclopentadienyl of the type found in $(C_5H_5)_3$MoNO, implying additional weaker In–C bonds. The In–C distances shown are shorter than the In–ring center distances (unlike the In(I) compound), and in addition the plane of the ring with respect to the two indium atoms does not correspond to a π-bonded ligand (see Figure 1). Also the In–C_2 and In–C_5 distances of 2.79 and 3.00 Å are so much longer than the In–C_1 distance of 2.37 Å that their involvement in bonding to the indium atom is clearly unimportant.

Comparison with Spectroscopic Results.—In an earlier paper,[2] infrared spectral evidence led to the conclusion that In(cp)$_3$ involves σ-bonded diene type ligands, following the earlier analysis of the spectra of cyclopentadienyl complexes published by Fritz.[3] It was noted however that the spectra were more complex than those given by this author. The present work confirms that the σ-bonded diene ligands were correctly identified; some, at least, of the additional bands in the spectrum must arise from the bridging ring A.

Nmr studies of In(cp)$_3$ in solution showed only a single resonance even at low temperatures, implying a very rapid "ring-whizzing" process. This result is in keeping with a structure



in solution, undergoing rapid electronic rearrangement by a series of 1,2-shifts. Fluxional behavior leading to loss of chemical identity among the ring protons could also arise by an intramolecular process, involving a transition state in which a cyclopentadiene ring bridges two molecules, as in ring A, although the absence of any significant temperature dependence in the nmr spectrum makes this mechanism unlikely. Evidence for ring rotation even in the solid state is also provided by the anisotropic ellipsoids of the carbon atoms, indicating motion in the ring plane around the ring axis.

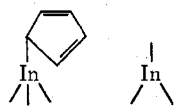
The Nature of the Indium–Carbon Bonding.—The bonds formed by indium to C_1 of rings B and C appear to be best described as predominantly σ character, on the basis of the bond lengths and interatomic angles at C_1. The bond lengths are compared with those for a series of related compounds in Table V.

TABLE V

Compound	M–C distance, Å	
$Cd(CH_3)_2$	2.112	a
$In(CH_3)_3$	2.06–2.15	Ref 6
$Sn(CH_3)_4$	2.14	b
$In(C_6H_5)_3$	2.11–2.16	Ref 5
$Sn(C_6H_5)_4$	2.12–2.14	c

[a] K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.*, **38**, 1516 (1960). [b] E. O. Schlemper, *Inorg. Chem.*, **6**, 2017 (1967). [c] P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 911 (1970).

The bonding to ring A raises two problems, the first of which is the large difference in the lengths of the indium–carbon bonds. Ring A, which serves to bridge indium atoms, may be regarded as a μ-1,3-cyclopentadienyl group. The bonding in this ring may be crudely described in terms of resonance involving cannonical forms of the type shown (others are also possible but would appear to be less important).



This description is consistent with the long In–C distances (bond order ~0.4 on the Pauling scale), and also the short value found for C_4–C_5. While C_5–C_1 appears possibly significantly longer than both C_1–C_2 and C_2–C_3 the value found for C_3–C_4 is not. This may be related to the fact that the In–C_1 bond is significantly shorter than that to C_3.

The second problem is that the bonding system is electron deficient. The bond angles, and the electron-density difference map, show that carbon atoms C_1 and C_3 each carry a hydrogen atom, and all the additional chemical evidence shows that there is no gain or loss of hydrogen between solid and solution phases. In this respect then, the structure has features in common with $(InMe_3)_4$ and InPh$_3$. In the former,[6]

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indium is pentacoordinate, with three short In–C bonds and two larger intermolecular contacts. In In(Ph)$_3$, bonds from the metal to the α carbon of phenyl groups on two neighboring molecules together with three planar In–C bonds again result in a coordination number of five.[5] These conclusions, and the present structure, are in agreement with results for InX$_3$ (X = halide or pseudohalide) species, where the three-coordinate monomer readily undergoes dimerization or adduct formation to give coordination numbers of four, five, or six.[4] The electron deficiency is however apparently unique to the three organoindium compounds in this context. It may be that this can be regarded as a type of electron donation in which the donor is not in its ground state, as is usually assumed for (say) a pyridine adduct, but in some electronically excited state. Thus in In(cp)$_3$, the diene structure (rings B and C) represents the first excited state of the cyclopentadienyl group, while the structure of ring A corresponds to the second excited level. Indium(I) cyclopentadienyl, in contrast apparently involves the ground-state (symmetrical) structure of the ligand. Further work on this problem is planned.

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Notes

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Adducts between Tetrasulfur Tetranitride and Aluminum Halides

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Molecular 1:1 adducts are formed between tetrasulfur tetranitride and a variety of Lewis acids.[1] Crystallographic data on two of these, S$_4$N$_4$·SbCl$_5$[2] and S$_4$N$_4$·BF$_3$,[3] have shown them to retain the eight-membered S$_4$N$_4$ ring, but with a conformation in which the sulfur and nitrogen positions are approximately interchanged. The four sulfur atoms lie in the plane and the four nitrogen atoms form the bisphenoid with the Lewis acid bonded to nitrogen. Aluminum chloride, on the other hand, reacts[4] with tetrasulfur tetranitride in thionyl chloride to give a salt, S$_5$N$_5$$^+$AlCl$_4$$^-$, rather than a molecular adduct. We describe here the preparation of simple 1:1 adducts between tetrasulfur tetranitride and aluminum halides.

Results and Discussion

Tetrasulfur tetranitride and aluminum chloride reacted slowly at room temperature in 1,2-dichloroethane to give a deep red crystalline product whose elemental analysis corresponded to that of a 1:1 adduct. This material was very sensitive to moisture and underwent hydrolysis in air to give tetrasulfur tetranitride which could be recovered in 95% yield from the adduct. The material decomposed on attempted vacuum sublimation to give a gummy intractable product. The infrared spectrum showed strong absorption at 1045, 960, and 860 cm^{-1} assignable[5,6] to sulfur–nitrogen absorption, as well as a strong band at 500 cm^{-1} assignable[7] to an aluminum–nitrogen stretch. The similarity between the ir spectrum of S$_4$N$_4$·AlCl$_3$ and those[1] of S$_4$N$_4$·SbCl$_5$ and S$_4$N$_4$·BF$_3$ strongly suggests an analogous structure for the three compounds. The aluminum chloride adduct also resembles S$_4$N$_4$·BCl$_3$ in adding a further mole of antimony pentachloride.[1,8] This material of composition S$_4$N$_4$·AlCl$_3$·SbCl$_5$ could be prepared from either antimony pentachloride and S$_4$N$_4$·AlCl$_3$ or aluminum chloride and S$_4$N$_4$·SbCl$_5$. An attempt to displace aluminum chloride from the mixed diadduct by vacuum sublimation led mainly to decomposition. Only very small traces of S$_4$N$_4$·SbCl$_5$ could be recovered in this manner. This is in contrast to S$_4$N$_4$·BCl$_3$·SbCl$_5$ where[1] boron trichloride is lost on heating to 85–90° under vacuum.

A similar 1:1 adduct between aluminum bromide and tetrasulfur tetranitride was observed to form upon mixing the two materials in 1,2-di*bromo*ethane. In 1,2-di*chloro*ethane, however, aluminum bromide and tetrasulfur tetranitride gave only S$_4$N$_4$·AlCl$_3$. Since a sample of S$_4$N$_4$·AlBr$_3$ was recovered unchanged after refluxing for 36 hr in 1,2-dichloroethane, exchange of halide with solvent must have occurred in the free aluminum bromide prior to complex formation. The exchange of halide between aluminum bromide and chloroalkanes is expected[9] to occur in the absence of S$_4$N$_4$. There can be no significant amount of reversible dissociation of the adduct once it is formed. This result is consistent with the failure to recover either starting materials or the adduct on attempted sublimation. It is in contrast to the behavior of S$_4$N$_4$·BF$_3$ where[1] boron trifluoride and tetrasulfur tetranitride can be recovered on thermal decomposition *in vacuo* (although the S$_4$N$_4$ ring does not survive when the adduct is heated in a sealed tube). S$_4$N$_4$·BCl$_3$, on the other hand, undergoes sublimation at 115°.

The minimal success in displacing aluminum chloride from S$_4$N$_4$·AlCl$_3$·SbCl$_5$, the failure of bromide to ex-

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