[CONTRIBUTION NO. 604 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Electron Deficient Compounds. VIII. The Crystal and Molecular Structure of Trimethylindium[1]

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RECEIVED MARCH 13, 1958

Trimethylindium is a tetramer of symmetry $\bar{4}$ in the crystal, with methyl bridges of a new type. The tetramers appear to interact, though more weakly, through additional methyl bridges. Within each tetramer nearly trigonal $In(CH_3)_3$ "monomers" with short, "normal," $In-CH_3$ bonds are found. One $In-CH_3$ bond of each monomer points almost directly normal to the trigonal plane of another "monomer" within the tetramer, forming an unsymmetrical, linear $In-CH_3$.....In bridge. A second $In-CH_3$ bond of each monomer points approximately at the trigonal plane of a monomer in an adjacent tetramer to form another unsymmetrical CH_3-In.....CH_3 bridge. There are then five methyl groups about each indium, foeming a somewhat distorted trigonal bipyramid, with three short, 2.1 Å. bonds in the trigonal plane, and two much longer bonds, 3.1 Å. within the tetramer, 3.6 Å. to the next tetramer, on either side of the plane. Steric reasons for expecting the sharp-angled $M-CH_3-M$ bridges, found in trimethylaluminum and dimethylberyllium, to be unstable when M is a larger metal atom have been noted previously. A qualitative MO description of the new type of bonding is given.

Introduction

Trimethylaluminum dimerizes[2] and dimethylberyllium polymerizes[3] through methyl bridges with very sharp M–C–M bridge angles of 70 and 66°, respectively. Presumably the best overlap of one tetrahedral carbon orbital with orbitals from two different metal atoms to form one delocalized, three-atom, molecular orbital requires such sharp bond angles.[2,3] In higher members of the series, though excess metal orbitals still make such bond delocalization attractive, the larger metal atoms are expected to lead to metal–metal repulsion of a magnitude to render sharp bridge angles unstable.[3]

Trimethylindium has been reported to be a tetramer in solution at low temperatures,[4] but a monomer at higher temperatures and in the vapor.[5] Hence, there is reason to suppose that there is bond delocalization, but of a new type, in this compound.

Experimental Procedure

Preparation and Properties of Trimethylindium.—Trimethylindium was prepared by the method of Dennis, *et al.*,[4] by Dr. B. Zaslow and furnished to us in sealed tubes. The preparation consists of refluxing dimethylmercury with indium metal for several days and sublimation of the trimethylindium from the mercury and excess indium.

The pure compound is a colorless solid, melting at about 89°, and strongly birefringent. It is very reactive with water and air, so X-ray samples were prepared by sublimation into suitable capillaries on a vacuum line. Single crystals were grown by heating the capillaries in a water-bath and allowing the bath to cool slowly.

Many crystals were very unstable in the X-ray beam, perhaps due to small amounts of impurities, and decomposed after a few hours. However, a crystal was eventually obtained which was sufficiently stable in the beam to yield three-dimensional diffraction data. As had been noted before,[4] a tetragonal and a less common, less stable, pseudo-hexagonal (more likely triclinic) form was found to exist. The pseudo-hexagonal type was not investigated in this research.

X-Ray Data.—Timed-exposure precession photographs of the *hk*0, *hhl* and 0*kl* reciprocal levels were obtained with Zr-filtered Mo*K*α radiation. Equi-inclination Weissenberg photographs were obtained for the reciprocal levels, *hk*0, *hk*1, ... *hk*6, also with Zr-filtered Mo *K*α radiation using a combined multiple film and timed exposure method.

All intensities were estimated visually with a calibrated standard set of intensities. Precession data were corrected for Lorentz-polarization effects by means of a template.[6] The Weissenberg data were corrected for Lorentz-polarization effects from a table computed from the function given by Cochran.[7] Spot extension corrections for higher layer Weissenberg data were made from a Phillips chart.[8] Preliminary scale factors and crystal temperature factors were obtained from log F_c/F_0 *vs.* $\sin^2\theta/\lambda^2$ plots for each reciprocal level using parameters from the two-dimensional analysis.

Structure Determination

Unit Cell and Space Group.—Trimethylindium was found to be tetragonal with lattice constants: $a = b = 13.24 \pm 0.01$ Å., $c = 6.44 \pm 0.01$ Å.

The lattice parameter *a* was determined by back reflection methods[9] and the lattice parameter, *c*, was determined from precession photographs on which *a* was used as an internal calibration. With 8 molecules per unit cell, $\rho_{\text{calcd}} = 1.88$ g./cc., while $\rho_{\text{obs}} = 1.57$ g./cc.[4] The Laue class was observed to be $C_{4h}-4/m$ with the systematic extinctions

(*hk*0) reflections absent for $h + k = 2n + 1$
(00*l*) reflections absent for $l = 2n + 1$

This uniquely fixed the space group as $P4_2/n$.

Determination of Atomic Positions

The diffraction data indicated that the metal atoms were in the general 8-fold set of positions $\pm[x, y, z;\ {}^1/_2 - x, {}^1/_2 - y, z;\ {}^1/_2 - y, x, {}^1/_2 - z;\ y, {}^1/_2 - x, {}^1/_2 + z]$.[10] Metal atom parameters were determined from conventional two-dimensional Patterson projections and trial and error methods. Carbon atom positions were obtained by a combination of conventional heavy atom Fourier techniques[11] (an indication of the resolution obtained from this very heavy metal-carbon system can be seen in Fig. 1), difference Fourier syntheses and

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[1] Presented before the American Chemical Society Convention, New York, N. Y., September, 1957. This paper is based in part on the Ph.D. thesis presented by E. L. Amma to Iowa State College in partial fulfillment of the requirements for the Ph.D. degree, December, 1957.

[2] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

[3] A. I. Snow and R. E. Rundle, *Acta Cryst.*, **4**, 348 (1951).

[4] L. M. Dennis, R. W. Work, E. G. Rochow and E. M. Chamot, THIS JOURNAL, **56**, 1047 (1934).

[5] (a) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941); (b) L. Pauling and A. W. Laubengayer, *ibid.*, **480** (1941).

[6] J. Waser, *Rev. Sci. Instr.*, **22**, 567 (1951).

[7] W. Cochran, *J. Sci. Instr.*, **25**, 253 (1948).

[8] D. C. Phillips, *Acta Cryst.*, **9**, 819 (1956).

[9] M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 20.

[10] "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952, p. 176. Note: the origin used here is not at the center of symmetry given in the tables at 3/4, 1/4, $\overline{1/4}$ from $\bar{4}$ on p. 176.

[11] H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, England, 1953, Chapter 7.

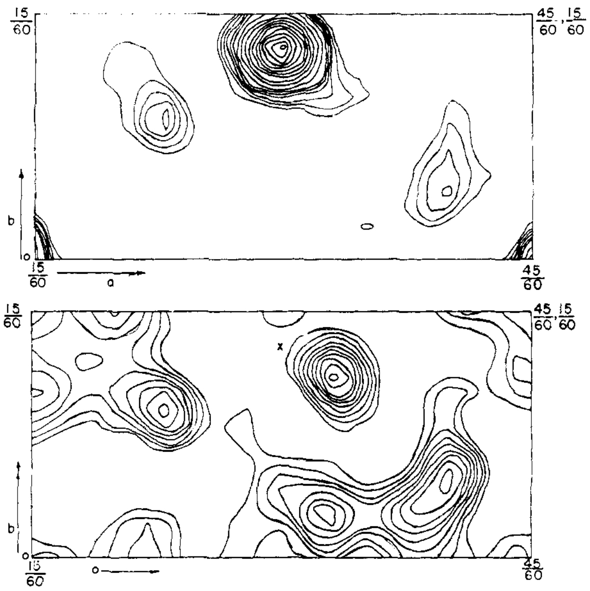

Fig. 1.—Fourier projections onto (001): (A, top) Direct Fourier. Heavy peak is indium, lighter peaks are two of the three unique carbon atoms. (B, bottom) Partial difference Fourier. Metal atom only has been subtracted out. X is indium position. Third carbon appears near X.

three-dimensional Fourier blocks.[12] The structure was refined on an I. B. M. 650 by a least squares method with individual but isotropic atomic temperature factors.[13] The least squares program (kindly furnished to us by Dr. D. H. Templeton of the University of California) was originally designed for only orthorhombic symmetry, but it was modified for monoclinic symmetry. Trimethylindium was reduced to monoclinic symmetry by doubling the parameters and including those reflections in the refinement dependent by tetragonal symmetry but independent by monoclinic symmetry. Interatomic distances were computed on the I. B M. 650 with a program from Dr. Templeton, and bond angles were computed manually. Standard deviations of bond distances were computed with conventional formulas.[14] Final results after four least square cycles are shown in Table I. Bond distances and bond angles are given in Table II.

TABLE I[a]

FINAL PARAMETERS, STANDARD DEVIATIONS AND ATOM TEMPERATURE FACTORS

Atom	x	y	z	σx	σy	σz	B/λ^2
In	0.2140	0.0038	0.4124	0.0002	0.0002	0.0005	10.3
C_1	.1420	.1282	.2684	.0027	.0027	.0070	9.29
C_2	.1710	.9620	.7086	.0028	.0027	.0067	8.94
C_3	.3422	.9282	.2785	.0028	.0028	.0071	9.37

$$R_1 = \frac{\sum_i \left| |F_0|_i - |F_c|_i \right|}{\sum_i |F_0|_i} = 11.8\%$$

[a] Calculated and observed structure factors may be obtained by ordering Document 5554 from the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C., remitting $1.25 for 35mm microfilm or $1.25 for photocopies by check or money order payable to Chief of Photoduplication Service, Library of Congress.

TABLE II

BOND DISTANCES (Å.) AND ANGLES

In_1–C_3	2.15	± 0.04	Short bridge bond within tetramer
In_2–C_3	3.11	± .04	Long bridge bond within tetramer
In_1–C_1	2.12	± .04	Short bridge bond to another tetramer
In–C_2	2.06	± .04	Unbridged In–C distance
In_3–C_1	3.59	± .04	Long bridge bond to another tetramer
In_1–In_2	5.235	± .004	Closest In–In distance within tetramer
In_1–In_3	5.665	± .004	Closest In–In distance between tetramers
In_1–In_4	6.79	± .004	Distance across tetramer
C_3–C_3	3.78	± .05	Bridge methyl contact distances within tetramer
In–C–In			Bridge angle within tetramer is linear within exptl. error
C_1–In–C_3	Angle = 122°		
C_2–In–C_3	Angle = 117°		"Monomer"
C_1–In–C_2	Angle = 119°		

Discussion

Description of Structure.—Trimethylindium is a tetramer or, more exactly, a pseudo-tetramer in the shape of a tetrahedron flattened along one fourfold screw axis. The nearest metal atoms within the tetramer (5.24 Å., In_1–In_2), Table II and Fig. 2, are held together by linear, asymmetric, electron

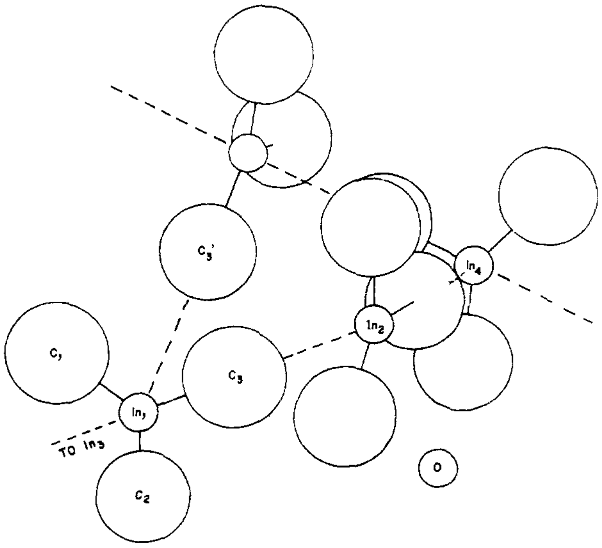

Fig. 2.—The trimethylindium tetramer. Weak bridge bonds to neighboring tetramers are indicated by dashed lines.

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[12] This technique was developed by D. R. Fitzwater of our laboratory. The blocks consist of a 4 × 4 × 4 grid, where the grid spacing is 1/80 of the unit cell. The program is such that the function is calculated for each of the 64 points in the block in one computation. The block can be arbitrarily located anywhere in the unit cell.

[13] This routine was programmed for the I. B. M. 650 by Drs. M. Senko and D. H. Templeton. It can be used with a constant or variable weighting factor; we used the variable weighting factor, which is more consistent with error theory.

[14] F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, **6**, 385 (1935).

deficient bridges with a short In–C distance of 2.15 Å. (In$_1$–C$_3$), and a long In–C distance of 3.11 Å., (In$_2$–C$_3$). The metal atoms of one tetramer are bonded to metal atoms of adjoining tetramers by other nearly linear, electron deficient methyl bridges with short In–C distances of 2.12 Å. (In$_1$–C$_1$), slightly shorter than reported for the gaseous monomer (2.16 Å.)[6b] and long In–C distances of 3.59 Å. (In$_3$–C$_1$). These long In–C distances are 0.48 Å. longer than similar distances within the tetramer; hence the molecules appear to be weakly linked and are not true tetramers. This arrangement makes the crystal a three-dimensional network of methyl bridges, but this three-dimensional network is in reality composed of two mutually exclusive three-dimensional networks which are interlaced by means of the fourfold screw axis.

The three methyl groups bonded to a particular metal atom by more or less "normal" covalent distances (In$_1$–C$_1$, 2.12 Å.; In$_1$–C$_2$, 2.06 Å.; In$_1$–C$_3$, 2.15 Å.) are chemically as well as crystallographically distinct. C$_1$ and C$_3$ participate in inter- and intratetrameric bridge bonding, respectively, but C$_2$ is non-bridged, a free methyl group. The three closest methyl groups about an indium atom form a slightly distorted trigonal monomer, weakly linked into tetramers and still more weakly linked to other tetramers.

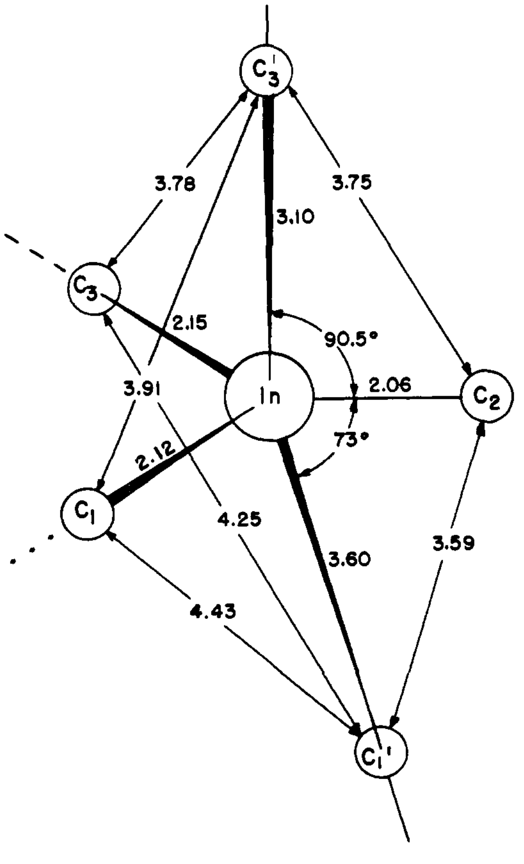

Fig. 3.—Configuration about indium. C$_1$, C$_2$ and C$_3$ are in a plane, with <C–In–C nearly 120°. C$_3$ is a carbon within the tetramer, while C$_1$ is a carbon in a neighboring tetramer.

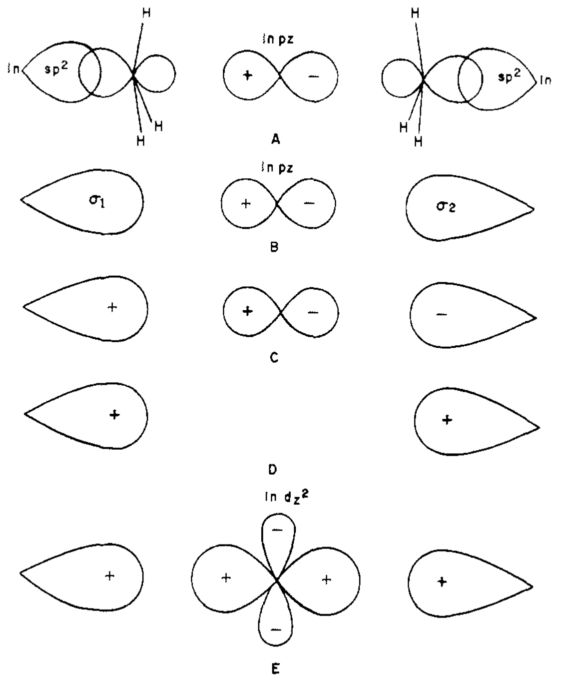

Fig. 4.—Schematic and idealized representation of long bonds in trimethylindium: (A) presumed flattened metal groups with small back-side lobe for long bond; (B) small back lobe is represented by σ-orbitals; (C) bonding MO; (D) non-bonding MO; (E) possibly significant MO using indium d$_{z^2}$-orbital.

The local configuration of methyl groups about a metal atom is that of a distorted trigonal bipyramid, Fig. 3. The "normal" bonds extend from the metal atom in the center to the carbon atoms at the vertices of an approximate equilateral triangle. The In–C intratetrameric long bridge bond (In$_2$–C$_3$, 3.11 Å.) extends from the center to a carbon atom at one apex and the intertetrameric long bridge bond (In$_3$–C$_1$, 3.59 Å.) extends to the other apex. The two long bridge bonds are inclined at an angle of 163° to one another; hence the trigonal bipyramid is distorted. However, the plane of the "monomer" is, within experimental accuracy, perpendicular to the intratetrameric long bridge bond.

Although the intertetrameric bridge (3.59 Å.) bond is rather long in comparison with normal covalent bonds, it is sufficiently shorter than the sum of the van der Waals radii of In and methyl (2.2 and 2.0 Å., respectively)[15] to be indicative of an interaction over and above van der Waals forces. It may be argued that the van der Waals radius of the metal atom (2.2 Å.) is not reliably known, but it is noteworthy that the nearest unbridged methyl-indium distance is 4.60 Å. Also, the methyl group of the intertetrameric long bridge bond is abnormally close, 3.59 Å., to the free methyl group on the metal participating in the long bridge bond. This shortening by 0.4 Å. of the usual methyl–methyl distance of 4.0 Å. supports the contention that both methyl groups are bonded to the same atom. Other abnormally short methyl–methyl distances are between the intratetrameric bridge methyl and the free methyl group on the metal atom partici-

(15) L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1949, p. 189.

pating in the intertetrameric bridge bond (C_3–C_2, 3.75 Å.) and the distance between adjacent bridge methyl groups (C_3–C_3, 3.78 Å.).

An upper limit to the bond energy of these long bridge bonds can be obtained from the heat of sublimation of trimethylindium at the melting point (14 kcal./mole of monomer).[16] Therefore, assuming the vapor is monomeric at the melting point, the sum of the dissociation energies of the two long bridge bonds per monomer is less than 14 kcal./mole by the amount of the van der Waals energy of the crystal.

The metal–metal distance across the tetrahedron (In_1–In_4), perpendicular to the four-fold inversion axis is 6.79 Å. This is much too long for metal–metal bonding.

Though the tetrameric nature of trimethylindium has been confirmed, the reason that the cryoscopic molecular weight indicated a tetramer[4] is still somewhat obscure. It is possible that the intertetrameric bridge bond is just weak enough to be disrupted by solution forces, and the intratetrameric bridge bond is just strong enough not to be broken in solution, but this seems at least somewhat fortuitous.

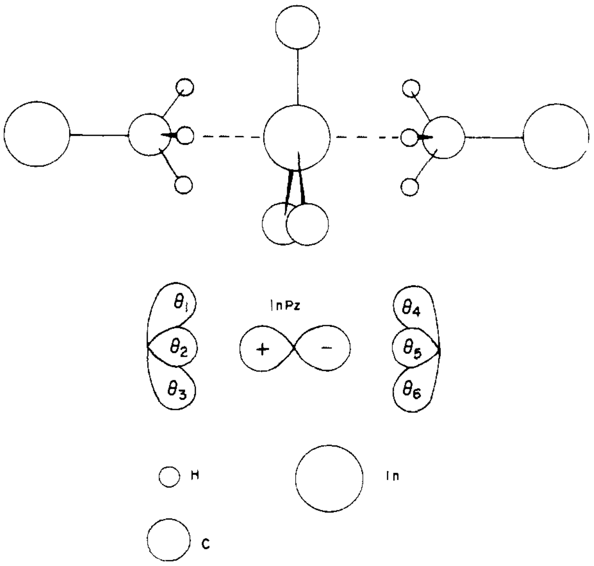

Fig. 5.—Schematic representation of possible hyperconjugative bonding. θ's represent C–H bond orbitals. In the bonding MO, $a[(\theta_1 + \theta_2 + \theta_3) - (\theta_4 + \theta_6 + \theta_6)]$ combines with In p_z.

Discussion of Bonding.—An approximate interpretation of the bonding in pseudo-tetrameric trimethylindium can be simplified if the structure is somewhat idealized as follows: (1) the metal atom is taken to be trigonally hybridized, as indicated by the geometry of the "normal" bonds; (2) the two long bridge bonds are considered to be equal; (3) both long bridge bonds about a particular metal atom are assumed to be normal to the trigonal plane; (4) the carbon atoms of the bridge methyl groups are taken to be at least partially trigonally hybridized, leading to an In–C bond with a small lobe on the back side of the carbon.

Figure 4A is intended to represent this idealization where, in the figure, the central indium forms three "normal" sp^2 bonds to methyl groups, not shown, and is left with an unoccupied p-orbital, as shown. The bridge bonding is then reduced to a three-center, 4-electron problem, where the four electrons come from the In–C bonds on either side of the central indium, through the lobes on the back side of the methyl groups in Fig. 4A.

In Fig. 4B, σ_1 and σ_2 represent the lobes on the back side of the In–C bonds in 4A, and these are to be treated as σ-orbitals, lower in energy than normal because they are not carbon orbitals but In–C MO's.

In Fig. 4C and D are depicted the two occupied MO's, $\phi_C = ap_z \times b(\sigma_1 - \sigma_2)$ and $\phi_D = c(\sigma_1 + \sigma_2)$, where ϕ_C is a bonding MO and ϕ_D is a non-bonding MO for the C–In–C system. (It is to be remembered that ϕ_D is non-bonding only with respect to the central indium, since σ_1 and σ_2 are bonding MO's of the carbons atoms with the terminal indium atoms shown in 4A.) The antibonding MO, $\phi_{AB} = a'p_z - b'(\sigma_1 - \sigma_2)$ will not be occupied in this 4-electron system, and is not shown.

Of possible significance is the use of the outer $6d_z{}^2$-orbital of indium which belongs to the same representation as ϕ_C, and may combine with it to form an MO as illustrated in 4E. We presume that because it is of higher energy the $6d_z{}^2$ orbital is not as important as $5p_z$, and that most of the bridge bonding comes from ϕ_C.

It is also possible that the bridge bonding involves a hyperconjugative effect, where electrons in the bridge are drawn from C–H rather than C–In bonds. If the C–H bond orbitals are designated θ_1, θ_2, θ_3, θ_4, θ_5 and θ_6 as in Fig. 5, $\psi_1 = a(\theta_1 + \theta_2 + \theta_3) - a(\theta_4 + \theta_5 + \theta_6)$ can combine with the In p_z-orbital; $\psi_2 = a'[(\theta_1 + \theta_2 + \theta_3) + (\theta_4 + \theta_5 + \theta_6)]$ can combine with the In $d_z{}^2$-orbital. Other combinations could combine, through a π-type of bonding with the In d_{xz}, d_{yz}-orbitals but presumably this should be unimportant for this long bridge-bond distance.

Since ψ_1 belongs to the same representation as ϕ_C (above), it can combine with it to give an MO in which the bridge bonding involves electrons from both In–C and C–H bonds, and it may be that both effects are appreciable. Intuitively it appears, however, that if the type of bonding illustrated in Fig. 4 is most important, then the methyl groups of the bridge should be deformed toward planarity, to provide the lobe illustrated in 4A, whereas if the bonding depicted in Fig. 5 is important the C–H bonds would, if anything, bend more toward the central indium. Because the In–C bonds are no doubt much weaker than C–H bonds, we suppose the bonding illustrated in Fig. 4 is more important than that in Fig. 5.

In principle the more important of the above effects could be determined by determining hydrogen positions, but this would be no trivial matter even for neutron diffraction, as there are nine crystallographically independent hydrogen atoms (27 positional parameters) in the structure, even if

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[16] F. D. Rossini, D. D. Wagan, W. H. Evans, S. Levine and I. Jaffe, U. S. Dept. of Commerce Circular 500 of the National Bureau of Standards, 1952, p. 661.

it is assumed that there is no rotational disordering of the methyl groups in the structure. The same consideration, and others, makes it seem difficult to interpret n.m.r. or spectral information.

The higher homologs of trimethylindium do not appear to be associated. Triethylindium melts at −32,[17] 120° below trimethylindium. This is not unexpected, since the type of bridges found in trimethylindium are sterically incompatible with higher homologs.

It is somewhat surprising that freezing point depression measurements of trimethylthallium in benzene indicate that it is monomeric.[18] Since the covalent radii of In and Tl are very similar, one might expect it, too, to be associated, especially since its melting point (38°) is relatively high compared to truly monomeric solids such as tetramethyllead. It is, of course, possible that trimethylthallium is tetrameric in the crystal, but that entropy effects lead to dissociation in solution.

Acknowledgments.—The authors are much indebted to Drs. Templeton and Senko of the University of California for I. B. M. 650 programs noted in the text and to Mr. D. R. Fitzwater for a three-dimensional block program as well as help with all our computations on the I. B. M. 650.

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(17) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 139.

(18) H. Gilman and R. G. Jones, THIS JOURNAL, **68**, 517 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Electron-exchange Reactions between Large Complex Cations[1]

BY EUGENE EICHLER AND ARTHUR C. WAHL

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The rates of the electron-exchange reactions (1) between $\mathrm{Fe(phen)_3^{++}}$ and $\mathrm{Fe(phen)_3^{+++}}$[2] and (2) between $\mathrm{Os(dipy)_3^{++}}$ and $\mathrm{Os(dipy)_3^{+++}}$[3] have been investigated both by optical-active and by isotopic-tracer methods, and the rates have been found to be immeasurably large. Limits on the specific reaction rates, calculated with the assumption of second-order kinetics, for reaction 1 are $>10^2$ *M* sec.$^{-1}$ (at 25°) and $>10^5$ *M* sec.$^{-1}$ (at 0°) and for reaction 2 are $>10^3$ *M* sec.$^{-1}$ (at 4°) and $>10^5$ *M* sec.$^{-1}$ (at 0°), the smaller numbers coming from the optical-active measurements, which are free from separation-induced exchange uncertainties. Colorimetric observations led to specific rate limits at 0° of $>3 \times 10^6$ *M* sec.$^{-1}$ for the net reactions between $\mathrm{Os(dipy)_3^{++}}$ and $\mathrm{Fe(phen)_3^{+++}}$, between $\mathrm{Os(dipy)_3^{++}}$ and $\mathrm{Fe(dipy)_3^{+++}}$, and between $\mathrm{Fe(phen)_3^{++}}$ and $\mathrm{Ru(dipy)_3^{+++}}$ and of $>5 \times 10^4$ *M* sec.$^{-1}$ for the net reaction between $\mathrm{Os(dipy)_3^{++}}$ and $\mathrm{Ru(dipy)_3^{+++}}$. No reduction in the rate of the $\mathrm{Os(dipy)_3^{++}}$–$\mathrm{Fe(phen)_3^{+++}}$ reaction was observed when resolved rather than racemic reactants were used.

Introduction

The rate of electron exchange between $\mathrm{Os(dipy)_3^{++}}$ and $\mathrm{Os(dipy)_3^{+++}}$[2] was investigated by Dwyer and Gyarfas[3] by observing the decrease in optical activity with time after mixing *d*-$\mathrm{Os(dipy)_3^{++}}$ with *l*-$\mathrm{Os(dipy)_3^{+++}}$. They reported that the rate was large but indicated that it was measurable, 95 sec. being required for complete racemization at 5° and 5×10^{-5} *M* reactant concentrations.

Eimer and Medalia[4] used conventional isotopic-tracer methods to investigate the exchange reaction between the tris-(5,6-dimethyl-1,10-phenanthroline) complexes of iron(II) and iron(III). They found complete exchange in 15 sec., indicating either that the rate in 0.5 *f* $\mathrm{H_2SO_4}$ was immeasurably large (specific rate $> 10^3$ *M* sec.$^{-1}$ at 0°) or that complete exchange was induced by the separation methods.

We undertook the measurement of the $\mathrm{Os(dipy)_3^{++}}$–$\mathrm{Os(dipy)_3^{+++}}$ and $\mathrm{Fe(phen)_3^{++}}$–$\mathrm{Fe(phen)_3^{+++}}$ exchange rates by the isotopic-tracer method modified to include rapid mixing and quenching techniques, which had made possible measurements of the large rates of exchange between $\mathrm{MnO_4^{--}}$ and $\mathrm{MnO_4^{-}}$[5] and between $\mathrm{Fe(CN)_6^{----}}$ and $\mathrm{Fe(CN)_6^{---}}$.[6] However, since immeasurably large rates were found, we repeated the experiments of Dwyer and Gyarfas[3] and applied a similar optical-active method to the $\mathrm{Fe(phen)_3^{++}}$–$\mathrm{Fe(phen)_3^{+++}}$ system.

Experimental

Chemicals.—Mallinckrodt "analytical reagent" grade chemicals were used without purification, with these exceptions: G. F. Smith Co. sodium perchlorate, Eastman Kodak Co. camphorsulfonic acid, and Eimer and Amend *p*-toluenesulfonic acid, while Eastman Kodak Co. Practical dimethyl sulfate was redistilled at atmospheric pressure. Eimer and Amend C.P. nitromethane was purified by the method of Thompson, *et al.*[7] Mallinckrodt U.S.P. potassium tartrate was recrystallized from $\mathrm{H_2O}$.

Stock solutions of $\mathrm{Fe(phen)_3^{++}}$ were prepared by dissolving equivalent amounts of $\mathrm{FeSO_4 \cdot 7H_2O}$ or $\mathrm{Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ and 1,10-phenanthroline (G. F. Smith). The $\mathrm{Fe(phen)_3^{+++}}$ solutions were prepared immediately before each run by dilution of appropriate amounts of $\mathrm{Fe(phen)_3^{++}}$ with dilute sulfuric acid and oxidation with $\mathrm{PbO_2}$. Excess $\mathrm{PbO_2}$ and the product $\mathrm{PbSO_4}$ were removed by centrifugation.

Tris-(2,2′-dipyridyl)-osmium(II) chloride was prepared by the method of Burstall, Dwyer and Gyarfas.[8] The compound was purified by recrystallization. Stock solutions of $\mathrm{Os(dipy)_3^{++}}$ were prepared from weighed amounts of the compound. The $\mathrm{Os(dipy)_3^{+++}}$ solutions were prepared by $\mathrm{PbO_2}$ oxidation of $\mathrm{Os(dipy)_3^{++}}$ in dilute $\mathrm{H_2SO_4}$.

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(1) This work was supported by the National Science Foundation. The paper was abstracted from the Ph.D. thesis of Eugene Eichler, Washington University, 1955.

(2) dipy = 2,2′-dipyridyl; phen = 1,10-phenanthroline; en = ethylenediamine.

(3) F. P. Dwyer and E. C. Gyarfas, *Nature*, **166**, 481 (1950).

(4) L. Eimer and A. I. Medalia, THIS JOURNAL, **74**, 1592 (1952).

(5) J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957); **75**, 5133 (1953).

(6) A. C. Wahl and C. P. Deck, *ibid.*, **76**, 4054 (1954).

(7) C. J. Thompson, H. J. Coleman and R. V. Holm, *ibid.*, **76**, 3445 (1954).

(8) F. H. Burstall, F. P. Dwyer and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).