By-product lithium chloride is removed by filtration. All of the procedures to this point can be conducted on the bench top using Schlenk techniques. The products can be isolated by removal of benzene under vacuum and they can be purified further by vacuum distillation.

Alternatively, di-*n*-butylgallium chloride and *n*-butylgallium dichloride can be prepared from gallium chloride and tri-*n*-butylgallium by exchange reactions (eq 17 and 18, respectively).

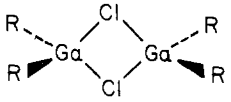
$$2GaR_3(l) + GaCl_3(s) = 3R_2GaCl(l) \qquad (17)$$

$$GaR_3(l) + 2GaCl_3(s) = 3RGaCl_2(l) \qquad (18)$$

Similar exchange reactions were used to prepare diethylgallium chloride,[2] diisobutylgallium chloride,[5] and diphenylgallium halides and phenylgallium dihalides.[6e] The exchange route to alkylgallium halides is the method of choice if a quantity of trialkylgallium is available because the reactions can be conducted free of solvent.

Molecular Association Studies. Previous reports have established the monomeric nature of trialkylgallium compounds (including tri-*n*-butylgallium) with the exception of trivinylgallium which is dimeric. Mixed alkylgallium halides (R_nGaCl_{3-n}, where R = methyl or ethyl and n = 0-2) are dimeric in hydrocarbon solvents.[19]

This study of the association of n-Bu_nGaCl_{3-n} compounds (where n = 1-3) in benzene solution is in agreement with previous reports of methyl and ethyl derivatives. Tri-*n*-butylgallium was shown to be monomeric over the concentration range studied while the butylgallium chlorides are dimeric over the same range of concentrations (see Figure 1). Chlorine-bridged structures are tentatively assigned to the dimeric *n*-butylgallium compounds (see structures I and II).[20]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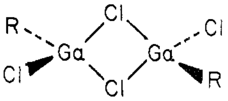
II

These tentative structures are in agreement with the structure assigned to $[RGaCl_2]_2$ compounds (where R = methyl or ethyl) which was based on infrared and Raman studies.[21]

Acknowledgments. R. A. K. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp. (Grant 6286), and the University of Northern Colorado Faculty Research and Publication Committee for providing financial support for this project. John Owen Callaway is indebted to the Boettcher Foundation for a personal education grant.

Registry No. $GaCl_3$, 13450-90-3; tri-*n*-butylgallium, 15677-44-8; di-*n*-butylgallium chloride, 17712-71-9; *n*-butylgallium dichloride, 43067-92-1; *n*-butyllithium, 109-72-8.

[19] For a general review of molecular association data see K. A. Yusada and R. Okawara, *Organometallic Chem. Rev.*, **2**, 255 (1967).

[20] For simplicity the trans form of dimeric-*n*-butylgallium dichloride is shown. The present study cannot rule out the cis form or a mixture of both cis and trans forms.

[21] C. Faraglis, F. Maggio, R. Cefalu, R. Basco and R. Barbieri, *Inorg. Nucl. Chem. Lett.*, **5**, 473 (1969).

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Indium-115 and Halogen Nuclear Quadrupole Resonance in Organoindium Halides and Related Compounds

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Received July 3, 1973 AIC30493F

^{115}In and halogen nqr have been observed in several dimethylindium compounds, two monoalkylindium dihalides, and indium tribromide. The nqr data indicate that Me_2InI and Me_2InBr have the Me_2TlBr type of structure with linear dimethylindium groups equatorially surrounded by a square-planar arrangement of halogens. The structure of Me_2InCl is indicated to be distorted from this and Me_2InF appears to have a nonlinear dimethylindium group like Me_2InOAc, whose nqr parameters are consistent with its known structure. $MeInI_2$ is confirmed by its nqr spectrum to be $[Me_2In][InI_4]$ whereas those of $MeInBr_2$ and $EtInI_2$ are consistent with halogen-bridged dimers, $[RInX_2]_2$. The ^{115}In nqr spectrum of $InBr_3$ indicates its structural similarity with InI_3 rather than with $InCl_3$.

Introduction

For suitable nuclei, nuclear quadrupole resonance[1,2] (nqr) represents a convenient way of gaining information on structure and bonding in the solid state. The structural information is often less ambivalent than that provided by other methods, save of course single-crystal diffraction methods, and is relatively easily obtained.

The abundant (96%) indium isotope, ^{115}In, is an eminently suitable subject for nqr studies. Its nuclear spin of $^9/_2$ allows both the asymmetry parameter, η, and the nuclear quadrupole coupling constant, e^2Qq/h, to be obtained from simple frequency measurements on polycrystalline samples.[1,2] These frequencies are often in ranges convenient for current instrumentation[3] and the large magnetic moment of ^{115}In produces relatively large transition probabilities.

Organoindium compounds are the least studied of all group IIIb organometallics and thus we turned to ^{115}In and ligand nqr as a means of gaining information on these compounds and allowing them to be placed in better perspective with those of thallium, gallium, and aluminum. In the case of aluminum there is a substantial body of nqr information[4,5] with which to compare the indium data.

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[1] T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, 1, (1958).

[2] E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969.

[3] G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instrum.*, **35**, 698 (1964); **36**, 702 (1965).

Table I. ^{115}In Room-Temperature Nqr Frequencies and Derived Parameters

No.	Compd	ν_1,[a] MHz	ν_2, MHz	ν_3, MHz	ν_4, MHz	η	e^2Qq/h, MHz
1	Me_2InOAc	64.44	81.56	127.96	171.96	0.26_5	1037.64
2	Me_2InF		83.97	129.84	173.72	0.18_5	1045.04
3	Me_2InCl	54.03	98.85	149.70		0.09_6	1200.16
4	Me_2InBr	50.88	101.81	152.87	203.50	0.00_0	1221.69
5	Me_2InI	49.40	98.79	148.17		0.00_0	1185.47
6	$Me_2In[InI_4]$	54.33	105.87	159.16	212.16	0.04_8	1277.59
7	$MeInBr_2$	59.82	46.71	68.99	95.73	0.56_4	590.15
8	$EtInI_2$	53.24	45.26	69.56	95.51	0.48_4	584.52
9	$InBr_3$	14.18	23.69	36.20	48.43	0.14_2	291.11
10	InI_3[b]	37.51	26.99	36.27	51.24	0.68_7	321.01

[a] $\nu_1 = \pm^1/_2$-$\pm^3/_2$, $\nu_2 = \pm^3/_2$-$\pm^5/_2$, etc. [b] R. G. Barnes, S. L. Segal, P. J. Bray, and P. A. Casasella, *J. Chem. Phys.*, 26, 1345 (1957). η and e^2Qq/h are as computed by us but differ insignificantly from those of the original authors.

Experimental Section

The dimethylindium compounds are all known compounds and were prepared and purified according to the procedures of Clark and Pickard.[6] The monoalkylindium dihalides were also prepared in accordance with the literature.[7,8] The indium tribromide was Alfa Ultrapure and was used without further purification. All indium compounds and other air-sensitive materials were manipulated in an atmosphere of dry, oxygen-free argon or under vacuum. The nqr frequencies were found and measured using a self-quenched super-regenerative spectrometer with automatic coherency control as described by Peterson and Bridenbaugh.[3] The quench frequency was maintained near 10^{-3} of the main frequency and Zeeman modulation was employed. The frequencies were measured by spectrum-analyzing techniques[3] with a Hewlett-Packard 5245L electronic counter as the ultimate frequency check.

Results

The ^{115}In nqr frequencies are compiled in Table I and the halogen frequencies in Table II. ^{113}In satellite resonances were observed in most cases. The ^{81}Br resonances were observed for all the ^{79}Br ones listed. The ^{37}Cl resonance of **3** was not, but in view of the low s/n (~2) of the ^{35}Cl resonance this was not unexpected. For those compounds having large ^{115}In asymmetry parameters, **7** and **8**, the two "forbidden" transitions $\nu(\pm^1/_2$-$\pm^5/_2)$ and $\nu(\pm^3/_2$-$\pm^7/_2)$ were also observed as the sum of $\nu_1 + \nu_2$ and of $\nu_2 + \nu_3$, respectively;[9] for two compounds with moderate asymmetry parameters, **3** and **9**, the first forbidden transition $(\nu_1 + \nu_2)$ was observed, all in accordance with the calculations of Cohen.[9] The ^{115}In asymmetry parameters and coupling constants were calculated from precomputed tables.[10]

The assignment of frequencies to bridging or terminal halogen (see Discussion) for **8** is based on the assumption that, as in the dimeric trihalides of group IIIb, bridging halogens occur at lower frequencies. In the case of **7**, for which no other ^{79}Br resonances could be found, the halogen frequencies are too close together to assign but it is still assumed that one of the two resonances corresponds to each type of halogen.

Table II. Halogen Nqr Frequencies in Indium Compounds at Room Temperature

No.	Compd	Halogen ν_1 (^{35}Cl, ^{79}Br, or ^{127}I), MHz
3	Me_2InCl	8.80
4	Me_2InBr	68.67
7	$MeInBr_2$	101.59,[a] 102.92[a]
9	$InBr_3$[b]	103.15,[c] 123.20[d]
5	Me_2InI	71.46[e]
8	$EtInI_2$	137.88,[c] 160.48[d]
6	$Me_2In[InI_4]$	144.77, 148.16
10	InI_3[f]	123.73,[c,g] 173.41[d,h]

[a] Bridging and terminal halogen but too close to assign. [b] G. W. Ludwig, *J. Chem. Phys.*, 25, 159 (1956). [c] Bridging halogen. [d] Terminal halogen. [e] $\nu_2 = 143.01$ MHz, $\eta = 0.00$, $e^2Qq/h = 476.41$ MHz. [f] S. L. Segel and R. G. Barnes, *J. Chem. Phys.*, 25, 578 (1956), and reference *b* above. [g] $\nu_2 = 229.19$ MHz, $\eta = 0.237$, $e^2Qq/h = 772.34$ MHz. [h] Average of close doublet; ν_2(average of close doublet) = 346.76 MHz, $\eta = 0.00$, $e^2Qq/h = 1156.08$ MHz.

Discussion

1. **Theory.** The data will be discussed in terms of the classical Townes-Dailey approximation in which the components of the electric field gradient tensor at a given nucleus are determined solely by the population imbalances of the nonspherical valence shell orbitals of that atom.[1,2] In the present case, for both indium and halogen, these orbitals will be construed as the valence-shell p orbitals. In this approach, the main component of the field gradient tensor, eq_{zz} ($=eq$ in e^2Qq/h), is given by

$$\frac{eq_{zz}}{eq_0} = \frac{eq}{eq_0} = N_z - {}^1/_2(N_x + N_y) \tag{1}$$

Cyclic permutation of the indices gives the corresponding expressions for the other components, eq_{yy} and eq_{xx}. The asymmetry parameter, η, may then be expressed as

$$\eta = \frac{3(N_x - N_y)}{2N_z - (N_x + N_y)} \tag{2}$$

from the definition[1,2] of η in terms of eq_{ii}. Here the N_i are the populations of the three valence-shell p orbitals in that set which coincides with the principal axes of the field gradient tensor. The constant of proportionality, eq_0, is formally the field gradient due to a single valence-shell p electron and the corresponding coupling constant, e^2Qq_0/h, may be obtained in various ways.[1,2]

We turn now to the specific cases of interest in the present context. For a R_2In^+ cation in which the C-In-C segment is linear and the indium is sp hybridized, $N_x = N_y = 0$ and $N_z = {}^1/_2(a + a) = a$, a being the population of either indium sp orbital. From (2) then, $\eta = 0$, as expected, and from (1)

$$eq/eq_0 = a \tag{3}$$

If this cation is now bent at indium in the xz plane (Figure 1), the p_x and p_y indium orbitals will, with the s orbital, form a second set of two s and p hybridized orbitals in the xy plane. If two ligands, X, now bond equally to these hybrids, the general equation for the field gradient at indium

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(4) M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Amer. Chem. Soc.*, 93, 1030 (1971).

(5) M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Chem. Soc., Dalton Trans.*, 2381 (1973).

(6) H. C. Clark and A. L. Pickard, *J. Organometal Chem.*, 8, 427 (1967).

(7) J. S. Poland and D. G. Tuck, *J. Organometal. Chem.*, 42, 315 (1972).

(8) M. J. S. Gynane, L. G. Waterworth, and J. I. Worrall, *J. Organometal. Chem.*, 43, 257 (1972).

(9) M. H. Cohen, *Phys. Rev.*, 96, 1278 (1954).

(10) M. J. S. Dewar, D. B. Patterson, and J. S. Wasson, unpublished work.

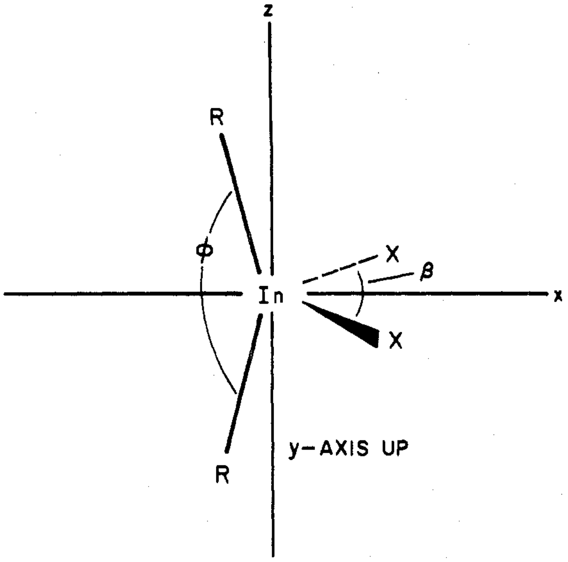

Figure 1. Orientation of the axes of the field gradient tensor at indium in an approximately tetrahedral R_2InX_2 group. The *interorbital* angles ϕ and β are shown as equivalent to those formed by the internuclear axes although this is not necessarily always the case.

in the resulting R_2InX_2 moiety may be derived,[2,11] *i.e.*

$$eq/eq_0 = (a - b)/(1 + \eta/3) \qquad (4)$$

Here b is the population of an indium hybrid orbital participating in the bond to X. The term in η is simply a correction for the bending of the R_2In^+ cation since[2,11]

$$\eta = -3 \cos \beta \qquad (5)$$

and[2,11]

$$\cot^2 \phi/2 + \cot^2 \beta/2 = 1 \qquad (6)$$

The angles ϕ and β are as shown in Figure 1.

In the case of monovalent halogen, if an unhybridized p_z orbital of population c is used for bonding, $N_z = c$ and $N_x = N_y = 2$ so that from (2) $\eta = 0$ and from (1)

$$eq/eq_0 = c - 2 \qquad (7)$$

The case of divalent halogen is formally similar to that of R_2InX_2 discussed above.[2,11] Here the R groups are replaced by lone pairs so that $N_z = 2 = a$, giving (8) from (4).

$$eq/eq_0 = (2 - c)/(1 + \eta/3) \qquad (8)$$

Equation 9 which is analogous to (6) and in which γ is the interorbital angle between the two halogen bonding orbitals also holds.

$$\eta = -3 \cos \gamma \qquad (9)$$

2. **Dimethylindium Compounds.** The discussion is facilitated by an X-ray structure determination for dimethylindium acetate which has recently appeared.[12] The dimethylindium group is nonlinear, with a CInC angle of 152°. Each indium is coordinated to two pairs of oxygens. The first pair consists of the two oxygens of the fully bidentate acetate group. A four-membered chelate ring is thus formed with the small OInO angle of 53.6°. The second pair consists of one oxygen from each of two neighboring acetates. All four oxygens are in the xy plane of Figure 1. The longer pair of indium-oxygen bonds form an angle of 171.5° at indium; *i.e.*, each such bond deviates less than 5° from the y axis of Figure 1.

The interaction with this more distant pair of oxygens is of course not considered in the derivation of eq 4 and 5. Furthermore, the XInX angle (Figure 1) of 53.6° cannot be equated with β since the latter angle cannot be less than 90°. (At least formally, highly bent indium-oxygen bends would have to be postulated.) These particular features of dimethylindium acetate are expected to complicate further the application of the already approximate theoretical treatment given above.

Nevertheless, the ^{115}In nqr parameters are in general agreement with the X-ray structure. In particular, the nonlinear dimethylindium group is revealed both by the nonzero ^{115}In η (0.27) and by the apparently reduced (see below) ^{115}In coupling constant. Equations 5 and 6 predict $\eta > 0$ for $\phi < 180°$ and the $(1 + \eta/3)^{-1}$ term of eq 4 then provides for some reduction in the coupling constant. There is not an exact quantitative correspondence between ϕ and η, the η corresponding to the X-ray value of ϕ being only 0.094, but, in view of the factors discussed above, one is not expected. The asymmetry parameter can be quite sensitive to small deviations from an ideal structure.[13]

Dimethylindium fluoride has ^{115}In nqr parameters similar to those of the acetate so that some structural similarity is evident. It seems safe to assert that the dimethylindium group is nonlinear here and that the rest of the coordination pattern about indium may be similar to that of the acetate as well. That is, each bent dimethylindium group may have a pair of neighbor fluorines nearest the indium with a relatively small FInF angle (although likely larger than the corresponding OInO angle in the acetate since there is no chelate ring) as well as a more distant pair of fluorines with a relatively large FInF angle. Possibly, all four fluorines are in, or nearly in, the xy plane of Figure 1.

A family of structures which would fulfill these criteria are those built up from $[Me_2InF]_n$ groups with $n \geqslant 2$ and having additional indium-fluorine coordination between the groups. These groups correspond to cyclic dimers, trimers, etc. of Me_2InF or even a linear polymer (*cf.* $[Me_2AlSMe]_n$[14]) if $n = \infty$.

Dimethylindium bromide and iodide exhibit ^{115}In nqr parameters which are distinctly different from those of the fluoride and acetate. Both of the former compounds have zero values for η as well as substantially higher ^{115}In coupling constants. Also, the ^{127}I asymmetry parameter for dimethylindium iodide (that of bromine, $I = {}^3/_2$, is not derivable from the pure nqr data) is also zero. These zero asymmetry parameters place severe constraints on the structural possibilities for these compounds. The dimethylindium group must be linear and the metal-halogen coordination must be such that the axial symmetry of the linear dimethylindium group is preserved and an axially symmetric environment for the halogen provided. These requirements appear to be uniquely met by the dimethylthallium bromide type of structure.[15-17]

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(11) P. A. Casabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, 30, 1393 (1959).

(12) F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 248 (1973).

(13) M. G. Clark, *Chem. Phys. Lett.*, 13, 316 (1972).

(14) D. G. Brauer and G. D. Stucky, *J. Amer. Chem. Soc.*, 91, 5462 (1969).

(15) (a) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 1, 3rd ed., Methuen, London, 1967, Chapter 3; (b) Houben-Weyl, "Methoden der Organischen Chemie," Vol. XIII/4, G. Thieme, Stuttgart, 1970.

(16) H. M. Powell and D. M. Crowfoot, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 87, 370 (1934).

(17) A. G. Lee, *Quart. Rev., Chem. Soc.*, 24, 310 (1970).

Here the crystal consists of layers, each of which is an infinite two-dimensional square lattice comprised of alternating halogen and metal atoms with the carbon-metal bonds of the linear dimethylthallium groups normal to the plane of the lattice. Linear dimethylmetal groups are thus equatorially surrounded by a square-planar arrangement of halogens, each of which is in turn likewise surrounded by four metal atoms. The layers are staggered so that the carbon atoms in one layer are opposite the halogen atoms in the two adjacent layers. Both halogen and metal atoms are in the axially symmetric environments required by the nqr data.

The conclusion that the dimethylindium groups are linear in the iodide and bromide is the opposite of that reached by Clark and Pickard on the basis of ir data.[6] They observed bands corresponding to both the antisymmetric and the symmetric C-In-C stretch. Supposedly, the latter should be ir inactive for a linear C-In-C group but, assuming that their assignments are correct, a breakdown of this selection rule in the solid state, which is not uncommon, would have led them to the erroneous conclusion that the C-In-C groups are nonlinear.

Dimethylthallium iodide and chloride have the same structure as the bromide but the fluoride, as was predicted,[16] apparently does not.[18] As noted above, dimethylindium fluoride certainly does not. Dimethylindium chloride[6,19] has a nonzero ^{115}In η and an ^{115}In coupling constant which is between that of the iodide and bromide rather than lying above that of the latter. Thus dimethylindium chloride cannot have the dimethylthallium bromide type of structure although its distortions therefrom appear small.

A sufficient source of the differences in structure among these dimethylmetal monohalides is simply the sizes of the halide anions involved. In the dimethylthallium bromide structure, nonbonded methyl-methyl interactions can occur diagonally across the square-planar $[MX]_2$ rings. With too small an MX distance, these interactions become prohibitively great. It was pointed out some time ago that the radius of the fluoride anion is too small to maintain such a structure with the dimethylthallium cation[16] and this would of course be even more the case for the dimethylindium cation. It is interesting to note that dimethyltin difluoride has a structure analogous to that of dimethylthallium bromide but with every other dimethylmetal group missing, which suffices to eliminate the nonbonded interactions between them.[20]

The chloride anion appears to represent a borderline case in terms of anion radius, the MX distance being large enough to maintain the undistorted structure in the dimethylthallium compound but not in the dimethylindium compound. For the bromide anion, the reported ^{115}In nqr parameters for the diethylindium compound ($\eta = 0.12$ and $e^2Qq/h = 1158$ MHz, at 77°K)[21] indicate some distortion from the ideal structure having linear C-In-C groups and square-planar halogen coordination in the case of the bulkier diethylindium cation. Even in the ideal structure a small asymmetry parameter might arise from the lack of threefold symmetry in the ethyl group itself but the reduced coupling constant is indicative of a distorted structure.

For the substantially smaller dialkylaluminum and dialkylgallium cations, the dimethylthallium bromide structure appears sterically infeasible even for the iodide. Thus the size of the metal atom, and correspondingly the equatorial radius of the dialkylmetal cation, appears to be a significant factor in the dramatic change in structure and properties between the dialkylaluminum and dialkylgallium halides on the one hand and the dialkylindium and dialkylthallium halides on the other.

It was noted above that bending a linear dimethylindium cation will in itself cause a reduction in the ^{115}In coupling constant according to eq 4-6. However, the observed ^{115}In coupling constant of dimethylindium acetate is about 15% below that of the bromide or iodide whereas the observed value of ϕ for the acetate corresponds to only a 3% reduction in the coupling constant. Similar considerations apply to dimethylindium fluoride unless ϕ is substantially smaller for this compound. It thus seems that most of the reduction is to be attributed to more effective transfer of electron density from the anions to the indium p_x and p_y orbitals of the dimethylindium cation in those compounds in which this cation is nonlinear. Intrinsic differences in the anions notwithstanding, this appears to be a straightforward consequence of the admixture of s character into the relevant indium orbitals when the cation is bent.

Methylindium diiodide (**6**, Tables I and II) is confirmed by its ^{115}In nqr parameters to be in fact a dimethylindium compound, the tetraiodoindate, in agreement with the conclusion of two other groups based on other evidence.[7,8] The dimethylindium cation here appears to be linear[7,8] consistent with its ^{115}In coupling constant, the highest in Table I. If this is the case, the small ^{115}In η observed must arise from a small difference in the coordination of the tetraiodoindate anions to the indium p_x and p_y orbitals of the cation. This is also indicated by the ^{127}I nqr spectrum of the compound which is a symmetrical doublet (Table II) requiring the iodine atoms of the anion to occur in two groups of two in the crystal, assuming that all of the anions are equivalent. Consistent with this, the Raman spectrum of the anion, as has been pointed out,[7] shows that its symmetry is lower than T_d.

3. Monoalkylindium Dihalides and Indium Trihalides. In contrast to the marked structural differences between the dialkyl halides of indium on the one hand and those of aluminum and gallium on the other, there appears to be substantial structural similarity between the monoalkyl dihalides, as well as the trihalides, of all three metals. Both the trihalides[22] (except the trichlorides of indium and aluminum) and the monoalkyl dihalides[7,8,23] appear to have halogen-bridged dimers of the formula unit as a basic structural unit in the solid state.

Both metal and halogen nqr spectra have been extensively investigated for the trihalides of these elements.[11,24-26] We have, however, obtained the previously unreported ^{115}In nqr spectrum of indium tribromide. The indium coupling constant is 91% of that of indium triiodide. The indium asymmetry parameter (0.14) is substantially lower than is usually observed for the metal atoms in similar compounds (InI_3, 0.69;[24] $GaCl_3$, 0.87;[27] $AlBr_3$, 0.73[11]). The low asymmetry parameter might be attributable to interdimer

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(18) W. Beck and E. Schuierer, *J. Organometal. Chem.*, 3, 55, (1965).

(19) C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, 9, 1998 (1970).

(20) E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 5, 995 (1966).

(21) L. M. Golubinskaya, V. I. Bregadze, E. V. Bryuchova, V. I. Svergun, G. K. Semin, and O. Yu. Okhlobystin, *J. Organometal. Chem.*, 40, 274 (1972).

(22) N. N. Greenwood, D. J. Prince, and B. P. Straughan, *J. Chem. Soc. A*, 1694 (1968), and references therein.

(23) J. Weidlein, *J. Organometal. Chem.*, 17, 213 (1969).

(24) R. G. Barnes, S. L. Segel, P. J. Bray, and P. A. Casasella, *J. Chem. Phys.*, 26, 1345 (1957), and preceding papers.

(25) G. W. Ludwig, *J. Chem. Phys.*, 25, 159 (1956).

(26) H. R. Booker and T. A. Scott, *J. Chem. Phys.*, 41, 475 (1964).

coordination in the tribromide which would likely increase the axial symmetry about indium. The halogen resonances also appear relatively somewhat low in the tribromide which might be ascribed to the same cause. The Raman and ir data for indium tribromide are consistent with some such interaction but the conclusion[22] that these data show that the structure of the tribromide is similar to that of the trichloride with fully six-coordinate indium can be rejected on the basis of the nqr data which unequivocally show the basic structural similarity of indium tribromide and triiodide.

There is considerable convergence in the ^{115}In nqr parameters for ethylindium diiodide and methylindium dibromide with respect to those of the parent trihalides (Table I). Nevertheless, the bromine resonances of the dibromide still appear relatively low with respect to the halogen resonances of the diiodide (Table II). The vibrational spectra of these compounds have been interpreted as consistent with the halogen-bridged dimer structure (trans) for the diiodide[7,8] but as indicating a more complex structure for the dibromide.[8] The halogen nqr data tend to bear this out to some degree but the observation of only one type of indium site of substantial coupling constant in the dibromide precludes the structures considered.[8] The structure of the dibromide likely differs from that of the diiodide only in having some interdimer indium-halogen coordination.

In any case, the close similarity of the relative (to e^2Qq_0/h) metal atom coupling constants of the dimeric trihalides of aluminum, gallium, and indium, which was noted some time ago,[11] appears to be maintained at the stage of the monoalkyl dihalides for aluminum and indium. The ratio of the average indium coupling constant of the two monoalkylindium dihalides of Table I to the average of the two indium trihalides is 1.92. This may be compared to 1.88, the ratio of the average ^{27}Al coupling constant of two monoalkylaluminum dichlorides[4,5] to that of aluminum tribromide. In contrast, the ratio of the average of the ^{115}In coupling constants of dimethylindium iodide and bromide to the average of those of the two indium trihalides is 3.93 which is substantially greater than 2.69, the ratio of the average ^{27}Al coupling constant of seven dialkylaluminum halides[4,5] to that of aluminum tribromide.

4. Halogen Resonances. The trends in the halogen resonances of these compounds are in general in accord with what would be expected from the structural differences between the compounds but there are some intriguing features. Thus upon replacing one of the terminal halogens of each indium in the bridged dimer structure of the trihalide by an alkyl group to give that of the monoalkyl dihalide there is a drop in the frequency of the remaining terminal halogen. This is a straightforward consequence of the increased inductive electron donation to indium and thus also to the remaining terminal halogen in the monoalkylindium compound, which results in an increase in *c*, eq 7, and a lowering of the nqr frequency.

The same mechanism would be expected to apply to the bridging halogens but this is apparently not the case. There is very little difference in the nqr frequency of the bridging bromines in indium tribromide and in methylindium dibromide while the bridging iodines of ethylindium diiodide actually have a higher $\nu(\pm^1/_2\text{-}\pm^3/_2)$ frequency than do those of indium triiodide. The likelihood of interdimer coordination in the bromide series complicates the situation here, and, in the case of the iodine compounds, the relatively high sensitivity[9] of ν_1 to η makes it uncertain how accurately the relative iodine coupling constants are reflected by these values. It does appear though that the bridging halogen frequencies are less sensitive to substitution at indium, most of the effect of which appears to be felt by the remaining terminal halogens. (Also, the bridging and terminal chlorine nqr frequencies in monoalkylaluminum dichlorides[4,5] occur closer together than those in gallium trichloride.[27])

The reasons for this lower sensitivity of the nqr frequencies of the bridging halogens to substitution at the metal atom are not entirely clear. It may simply reflect the fact that the terminal metal-halogen bounds are shorter than the bridging metal-halogen bonds in these systems.[22,28] Another rationale for low sensitivity of halogen nqr frequencies to inductive effects is (p-d)π bonding[1,2] but there appears to be little evidence of this factor playing a *relatively* greater role in bridging than in terminal halogen in these systems.

The iodine frequencies of the tetraiodoindate anion (compound **6**, Table II) should represent an upper limit to bridging iodine frequencies in these compounds and this is indeed the case. Those of both ethylindium diiodide dimer and indium triiodide dimer are lower than the doublet of the anion. Coordination of two of the iodines of the anion to a positive center should result in a net σ-electron flow from the other two iodines to the indium and thus an increase in their nqr frequency. The terminal iodines in indium triiodide dimer are thus at substantially higher nqr frequency than the doublet of the anion and even those of ethylindium diiodide dimer are higher than those of the anion despite the lowering due to the alkyl group.

Proceeding on to the dimethylindium halides, a sharp drop in the nqr frequency of the remaining halogens is encountered. This drop is greater than that observed between monoalkylaluminum dichlorides and dialkylaluminum chlorides.[4,5] Furthermore, the ^{35}Cl nqr frequency of dimethylindium chloride is only 88% of the average of three dialkylaluminum chlorides[4,5] although in the dimeric trihalides[11,22,24-26] the halogen nqr frequencies of the aluminum compounds are substantially lower than those of the corresponding indium compounds (perhaps because of greater (p-d)π bonding in the aluminum compounds[2]). There thus appears to be a greater drop in the halogen nqr frequencies of the dimethylindium halides than would be expected merely from the inductive effect of the second alkyl group. These low halogen resonances, like the high metal ones, emphasize the low amount of electron transfer to the p_x and p_y orbitals of the linear dimethylindium cations in these systems.

Acknowledgment. We are grateful to G. E. Peterson for his continuing interest in this work.

Registry No. ^{115}In, 14191-71-0; ^{35}Cl, 13981-72-1; ^{79}Br, 14336-94-8; I_2, 7553-56-2; Me_2InOAc, 14799-87-2; Me_2InF, 50830-73-4; Me_2InCl, 14629-99-3; Me_2InBr, 14799-84-9; Me_2InI, 14799-83-8; $Me_2In[InI_4]$, 39042-62-1; $MeInBr_2$, 33393-06-5; $EtInI_2$, 39047-13-7; $InBr_3$, 26016-65-9; InI_3, 18897-69-3.

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(27) G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, **51**, 238 (1969).

(28) G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).