temperature below T_N could we observe more than one peak in $(\partial M/\partial H)_T$. This is in contrast to $Ni(py)_2Cl_2$ where as many as three peaks in $\partial M/\partial H$ and two anomalies in the specific heat were observed.[37,42] Presumably such behavior implies an ordered state with more than two and perhaps as many as six sublattices.[34,39]

Discussion

From susceptibility and electron paramagnetic resonance data, we suggest that $Cu(4\text{-}Ph\text{-}py)_2Cl_2$ is a well-isolated antiferromagnetic linear chain whose *intrachain* exchange character is largely unchanged relative to other analogous complexes but whose *interchain* coupling is much smaller. Thus, the speculations advanced in the Introduction are at least partially fulfilled in this case. Also, this complex may lend itself to a more easily interpreted analysis of EPR line width and angular-variation studies such as Richards and co-workers have done for $Cu(py)_2Cl_2$.[16,24] A possible shortcoming of this suggestion may be due to the insolubility of $Cu(4\text{-}Ph\text{-}py)_2Cl_2$, but we note that McGregor and Soos[48] have recently been able to obtain reasonable results on powder samples of $Cu(ox)\cdot{}^1/_3H_2O$, another highly insoluble copper(II) compound.

We find that $Mn(4\text{-}Ph\text{-}py)_2Cl_2$ has *intrachain* exchange comparable to those of other manganese(II) complexes of simple pyridines, and *interchain* interactions (even at these suspected greater distances) or perhaps single-ion effects are noticeable. It should be of considerable interest to obtain low-temperature heat capacity experiments on this compound since Klaaijsen et al.[17,42] have shown that this experiment is particularly sensitive to both of these types of interactions while powder susceptibility data are not. Furthermore, a choice between single-ion and *interchain* effects may be made by performing EPR experiments on crystals of a magnetically dilute isomorphous compound containing manganese ions as guests. Such resonance methods are very sensitive to a single-ion anisotropy, and these parameters can be measured with very high precision.[50]

The observation that $Ni(4\text{-}Ph\text{-}py)_2Cl_2$ has a substantially larger *interchain* exchange and also larger single-ion anisotropy than its previously reported analogues is a surprising result. The fact that the ordering temperature, T_N, is nearly 1.5 K higher than that of the closest unsubstituted analogue[37,42] was unexpected. If one adheres to the accepted notion[1] that superexchange interactions are usually very short-ranged ($\sim r_{m\text{-}m}^{-10}$ dependence), then it is very difficult to propose a mechanism for enhanced *interchain* exchange unless a rather dramatic structural change occurs. Of course, it is possible that the very large anisotropy plays an intimate role in the above process or that long-range dipole–dipole effects are in some way implicated. At best, these effects are not well understood, and more examples of systems showing this type of behavior need to be studied.

Many of the above ideas are quite speculative in the absence of full crystallographic information on these substances, and such data are highly desirable. If these results were available, then additional experiments on single crystals would likely provide additional insight into the unusual properties of these complexes.

Acknowledgment. This research was supported by the National Science Foundation through Grant No. CHE77-09913. We are grateful for this continuing support.

Registry No. $Cu(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-56-6; $Ni(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-54-4; $Mn(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-52-2.

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(50) G. M. Wolterman and J. R. Wasson, *J. Phys. Chem.*, **78**, 45 (1974); *Inorg. Chem.*, **12**, 2366 (1973).

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Lower Valence Fluorides of Vanadium. 4. The Rutile-like Compounds VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and Opaque $VF_{2+\delta}$

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The rutile-like compounds VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and opaque $VF_{2+\delta}$ were studied. A solid solution $MgVF_4$ was prepared from equimolar amounts of VF_2 and MgF_2, and its lattice dimensions obey Vegard's rule. Lattice constants for trirutile $Li_{0.50}VF_3$ are a = 4.699 Å and c = 9.288 Å. The opaque rutile phase $VF_{2+\delta}$ is very close to VF_2 in composition with lattice dimensions a = 4.801 Å and c = 3.234 Å vs. those of VF_2 a = 4.804 Å and c = 3.236 Å. All four compounds order magnetically above 4.2 K. In these materials, all important magnetic interactions are antiferromagnetic except in trirutile $Li_{0.50}VF_3$ which appears to have ferromagnetic interactions as well. A small remnant moment $\sim 0.01\ \mu_B$ was observed for the solid solution $MgVF_4$. Magnetic constants for VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and $VF_{2+\delta}$ are T_N = 8, 25, 26, and 20 K, C_M = 1.82, 1.82, 1.24, and 1.76, and Θ = −88, −57, −3, and −80 K, respectively.

Introduction

Vanadium difluoride was first synthesized by Stout and Boo[1] and was verified by them to be isostructural with MnF_2, FeF_2, CoF_2, NiF_2, and ZnF_2. All of these compounds have the rutile structure, space group $P4_2/mnm\text{-}D_{4h}^{14}$. A significant difference was found in the low-temperature magnetic properties of VF_2 vs. those of the other divalent fluorides of the first transition series. Antiferromagnetic ordering of the A–B sublattice type was reported for MnF_2, FeF_2, CoF_2, and NiF_2 to occur at 67.30,[2] 78.25,[3] 37.70,[3] and 73.22 K,[4] respectively. VF_2, however, displays long-range order below 7 K and its ordered structure is reported to consist of spiraled chains directed along its c axis.[1,5] The reason for the difference is in the relative strengths of magnetic-exchange interactions

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(1) (a) J. W. Stout and W. O. J. Boo, *J. Appl. Phys.*, **10**, 966 (1966); (b) J. W. Stout and W. O. J. Boo, *J. Chem. Phys.*, **71**, 1 (1979).
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0020-1669/80/1319-0031$01.00/0

within the tetragonal unit cell. The two most important interactions have constants J_1 between nearest-neighboring metal atoms at the distance c and J_2 between next-neighbor metal atoms at the distance $(c^2 + 2a^2)^{1/2}$. In MnF_2, FeF_2, CoF_2, and NiF_2, J_2 is greater than J_1, but in VF_2, J_1 has the larger value.

Other instances in which the V^{2+} ion is located in a rutile-type lattice include solid solutions of VF_2 with diamagnetic MgF_2. If a 50:50 mol % mixture forms a random arrangement of V^{2+} and Mg^{2+} ions, the linear chains of magnetic ions along the c direction would be broken into very short lengths of a few, or even single, atoms. As each metal ion has eight second-nearest-neighboring metal ions, dilution by diamagnetic Mg^{2+} makes the second-nearest-neighbor interactions increasingly important. By dilution, the possibility of V^{2+} ions being nearest neighbors is reduced and, hence, constraints to long-range order are removed. In VF_2, 90% of the entropy associated with magnetic ordering occurs above T_N in the form of linear short-range ordering. In a solid solution of composition $MgVF_4$, one would expect some short-range ordering to occur above T_N. Even if linear chains along c were broken into dimers (pairs of V^{2+} ions), the entropy associated with short-range order would be 50% of the total magnetic entropy.

The trirutile compound $Li_{0.50}VF_3$ ($LiV^{II}V^{III}F_6$) offers another possibility for V^{2+} (and V^{3+}) in a rutile-type structure. Unlike $MgVF_4$ in which one would expect a random arrangement of V^{2+} and Mg^{2+}, the trirutile structure is ordered with respect to Li^+, although V^{2+} and V^{3+} are believed to be random. The arrangement of metal ions in the trirutile structure is such that nearest-neighboring V^{2+}–V^{3+} pairs have only Li^+ ions for common second nearest neighbors. This removes all constraints to long-range magnetic ordering. One would expect nearest-neighboring V^{2+}–V^{3+} ions to form ordered dimers at temperatures beginning about 100 K and three-dimensional long-range ordering to occur at a temperature considerably higher than 7 K, as in VF_2.

Experimental Section

Vanadium difluoride and VF_3 were prepared from 99.9% vanadium metal. Optical grade LiF and MgF_2 were obtained commercially. Products were analyzed by Guinier-Hägg and Debye-Scherrer X-ray powder techniques and by polarized microscopy. X-ray data were reduced by computer using a least-squares program. A PAR Foner-type vibrating-sample magnetometer with rotating head, liquid-helium cryostat, gallium arsenide thermometer, and temperature controller was used to measure magnetic susceptibilities from 4.2 to 300 K.

Preparation of Materials

The method originally used for the preparation of VF_2 by Stout and Boo[1] was employed for this study and is essentially the best method available for obtaining stoichiometric material of good quality. Vacuum encapsulation by electron-beam welding was the method chosen for compound preparation. Pulverized and thoroughly mixed VF_2 and MgF_2 were encapsulated in V-lined Mo and reacted at 800 °C to form the solid solution $MgVF_4$; the resulting material was then melted at 1200 °C. The trirutile compound, $Li_{0.50}VF_3$, was prepared from equimolar amounts of LiF, VF_2, and VF_3 heated at 800 °C in Mo. Preparations of phases intermediate in composition between VF_2 and VF_3 were attempted by heating samples of the two materials encapsulated in Mo. The only change resulting from these experiments was the discoloration of the VF_2 phase. By optimization of the heating schedule, the rutile phase was made totally opaque even in very thin sections. The green VF_3 phase, however, showed no apparent change.

Results and Discussion

X-ray Diffraction. The lattice constants of VF_2, MgF_2, and $MgVF_4$ (shown in Table I) obey Vegard's rule. Both a and c of the three substances are linear with respect to composition. Unit cell dimensions of the trirutile $Li_{0.50}VF_3$ are also shown in Table I, along with those of the opaque rutile phase. This opaque phase has lattice dimensions only slightly smaller than blue VF_2.

Table I. Lattice Constants of Rutile-like Compounds

compd	a, Å	c, Å
VF_2	4.804 ± 0.001	3.236 ± 0.001
MgF_2	4.621 ± 0.001	3.050 ± 0.001
$MgVF_4$	4.722 ± 0.005	3.148 ± 0.005
LiV_2F_6	4.699 ± 0.001	9.288 ± 0.001
opaque rutile phase	4.801 ± 0.001	3.234 ± 0.001

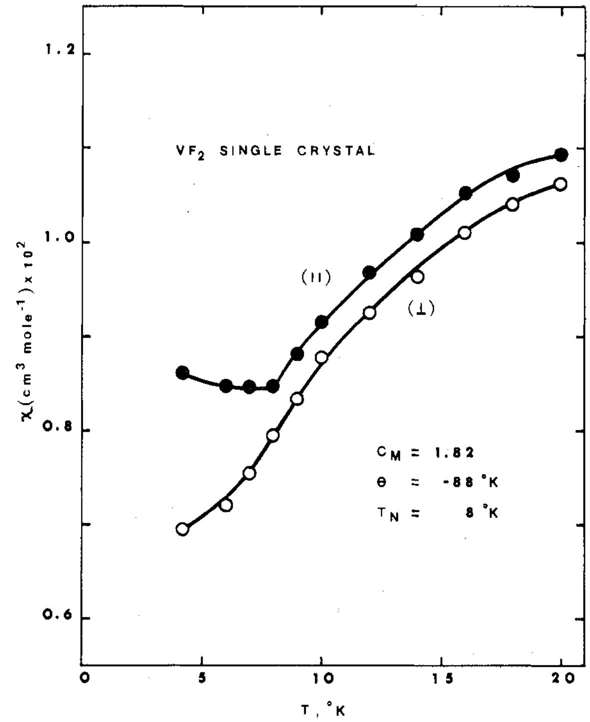

Figure 1. Magnetic susceptibilities vs. temperature of a single crystal of VF_2 oriented parallel and perpendicular to the magnetic field.

Magnetic Measurements. VF_2. A small, elongated, single crystal of VF_2 grown from the vapor phase and weighing approximately 26 mg was mounted in a sample holder on the end of the vibrating-sample magnetometer rod such that the c axis of the crystal could be oriented (∥) or (⊥) to the magnetic field by rotating the magnetometer head. The crystal was cooled to 4.2 K in a field of 10 kG in the (∥) position. It was also rotated in the field at 4.2 K. A maximum moment was observed for the (∥) position and a minimum moment observed when the crystal was oriented (⊥) to the field. Field-dependent measurements were made at 4.2 K with the crystal oriented both (∥) and (⊥), but no spontaneous moment was found.

Measurements of $\chi(\parallel)$ and $\chi(\perp)$ were made in a 10-kG field from 4.2 to 300 K. These results are in agreement with anisotropy measurements reported by Stout and Lau.[6] The susceptibilities vs. temperature of the two orientations from 4.2 to 20 K are shown in Figure 1. The small anisotropy apparent on this plot begins above 100 K. This is consistent with heat capacity measurements[1] which indicate that short-range magnetic ordering begins at these temperatures. A maximum in magnetic susceptibility near 40 K and the maximum in specific heat near 28 K correspond to the increase in short-range ordering. At lower temperatures, both functions decrease because ordering of linear chains is nearly complete. A λ-shaped maximum in the heat capacity[1] at 7 K marks the beginning of three-dimensional long-range ordering, and neutron diffraction experiments[5] indicate that incommensurate modulations set in at this temperature as spiraled chains along

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(6) J. W. Stout and H. Y. Lau, *J. Appl. Phys.*, **38**, 1472 (1967).

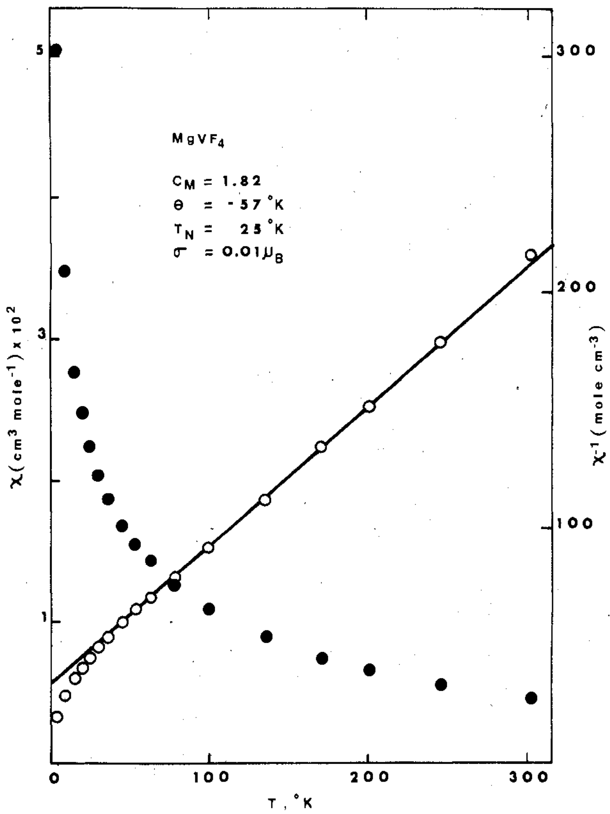

Figure 2. Magnetic susceptibility and inverse susceptibility vs. temperature of a powder sample of $MgVF_4$.

the *c* axis. The magnetic susceptibility shown in Figure 1 shows a sharp anomaly in $\chi(\|)$ near 8 K which coincides with the onset of three-dimensional magnetic ordering. Below 8 K, $\chi(\|)$ remains approximately constant and $\chi(\perp)$ decreases which supports the conclusion that ordered spins are perpendicular to the *c* axis.

$MgVF_4$. A plot of χ vs. T and χ^{-1} vs. T of a randomly oriented powder sample of $MgVF_4$, over the temperature range 4.2–300 K in a field of 10 kG, is shown in Figure 2. There is no indication of a second-order phase transition from this plot. A small remnant moment of magnitude 0.01 μ_B, detected by extrapolation to zero field, was observed to disappear at approximately 25 K, giving evidence that long-range magnetic ordering occurs in $MgVF_4$ with $T_N \approx 25$ K. The fact that Θ is slightly smaller for $MgVF_4$ than for VF_2 is a dilution effect. The inverse susceptibility does not deviate significantly from the Curie law above 50 K which is an indication that V^{2+} and Mg^{2+} ions are well mixed and relatively few V^{2+} ions have other V^{2+} ions for nearest neighbors. The χ^{-1} vs. T curve deviates negatively from linearity at low temperatures as is characteristic of materials having small spontaneous magnetic moments.

$Li_{0.50}VF_3$. The magnetic susceptibility of $Li_{0.50}VF_3$ was measured from 4.2 to 300 K on a randomly oriented powder sample in a 10-kG field. A plot of χ vs. T, shown in Figure 3, indicates that long-range ordering occurs at 26 K. The inverse susceptibility vs. T shows that deviation from paramagnetic behavior begins near 100 K. In the calculation of χ and χ^{-1}, corrections were made for temperature-independent paramagnetism in V^{3+}. The value 6×10^{-4} emu/mol reported by Gossard et al.[7] was used.

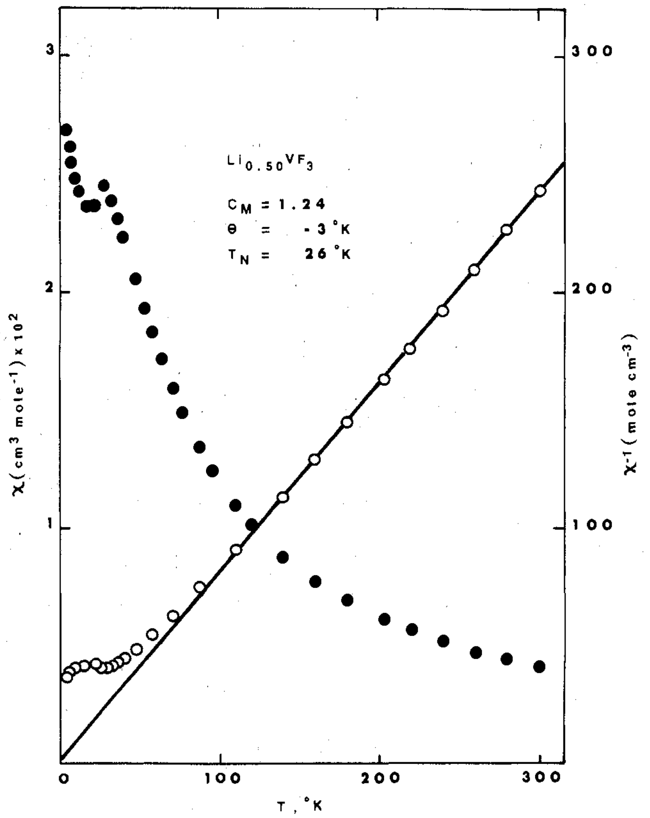

Figure 3. Magnetic susceptibility and inverse susceptibility vs. temperature of a powder sample of $Li_{0.50}VF_3$.

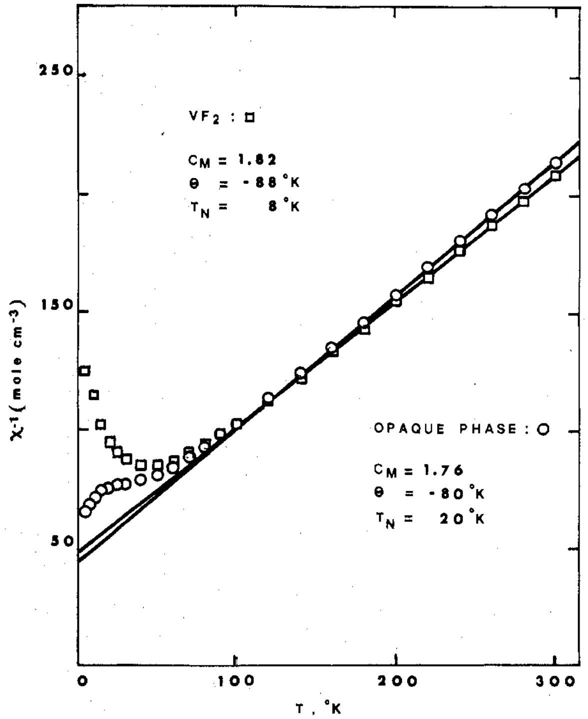

Figure 4. Inverse susceptibilities vs. temperature of VF_2 and the opaque rutile phase.

The Curie constant indicates the orbital moment of V^{3+} is largely quenched. An interesting feature not found in VF_2 or $MgVF_4$ is the very small Θ value. It is very close to zero. The magnetic susceptibility was measured at 4.2 K in fields from 1 to 10 kG with no display of field dependence. Although no spontaneous moment was observed, the very small Θ value suggests that at least one of the magnetic-exchange interactions is ferromagnetic. In all likelihood, this is a V^{2+}–V^{3+} interaction.

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(7) A. C. Gossard, H. H. Guggenheim, F. S. L. Hsu, and R. C. Sherwood, *AIP Conf. Proc.*, No. 5, 302 (1971).

The Opaque Rutile Phase. The magnetic susceptibility of the opaque rutile phase was measured from 4.2 to 300 K. No remnant moment was found at 4.2 K. In Figure 4, χ^{-1} vs. T of the opaque phase is compared with that of VF_2. In calculating χ^{-1} for this plot, the formula weight of VF_2 was used for the opaque phase. From the plot, one sees the slope of the opaque phase is greater than that of VF_2, indicating a smaller average magnetic moment per unit mass. This is consistent with the conclusion that the opaque material has stoichiometry close to VF_2 but between VF_2 and VF_3. The formula for the opaque phase should therefore be written $VF_{2+\delta}$ $(V^{II}_{1-\delta}V^{III}_{\delta}F_{2+\delta})$. Assuming the orbital moment of V^{3+} is quenched and average g values of 1.97 and 1.80[8] for VF_2 and VF_3, respectively, we can make an estimate of δ. The theoretical Curie constants for V^{2+} and V^{3+} should be $C_{(2+)} = 1.82$ and $C_{(3+)} = 0.81$. The Curie constant of $VF_{2+\delta}$, calculated from the paramagnetic region of the χ^{-1} vs. T plot, is 1.76. Since $C_M = (1 - \delta)C_{(2+)} + \delta C_{(3+)}$, a first approximation value for δ is 0.06. A second approximation is obtained by replotting χ^{-1} vs. T of $VF_{2+\delta}$ using the formula weight of $VF_{2.06}$. This gives values of $C_M = 1.78$ and $\delta = 0.04$. The value 0.04 may still be high as a consequence of possible contamination by finely divided VF_3. At any rate, δ is small and would be difficult to establish by conventional chemical analysis.

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Registry No. VF_2, 13842-80-3; MgF_2, 7783-40-6; $MgVF_4$, 71749-59-2; $Li_{0.50}VF_3$, 56092-96-7.

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Coordination Compounds of Indium. 34. Preparative and Spectroscopic Studies of InX_3Y^- and $InX_2Y_2^-$ Anions ($X \neq Y$ = Cl, Br, I)

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The oxidation of indium(II) complexes $In_2X_6^{2-}$ (X = Cl, Br, I) with halogen (Y_2; Y = Cl, Br, I) yields the anionic mixed-halogeno complexes InX_3Y^-. Similar oxidations of the indium(I) anions InX_2^- furnish $InX_2Y_2^-$ anions, all as salts with tetraalkylammonium cations. The far-infrared and Raman spectra establish that the anions are indeed the mononuclear mixed-ligand species, and force constant calculations, using a modified valence force field method, confirm the vibrational assignments. The reaction mechanism and some trends in the force constants are discussed.

Introduction

In a recent paper,[1] the preparation of the first unambiguous indium(II) complexes was reported, in the form of the salts tetrabutylammonium hexahalogenodiindate(II). Vibrational spectroscopy and some simplified force constant calculations showed that these anions contain an indium–indium bond linking two InX_3^- units. We have now begun to investigate the chemical properties of these substances. One obvious reaction is oxidation, in which one might expect cleavage of the indium–indium bond to give X_3InY^- compounds. By way of a preliminary study of the generality of such reactions, we have carried out the oxidation of all three $In_2X_6^{2-}$ anions with other halogens in benzene to give the anionic mixed-halogeno complexes InX_3Y^-. At the same time, the availability of InX_2^- salts[2] allowed us to study the oxidation of these compounds under similar conditions, when the products are $InX_2Y_2^-$ anions. The preparation of these compounds and the infrared and Raman spectra to 50 cm^{-1} are now reported, together with some force constant calculations which serve to establish that the products are indeed the anions in question.

There have been no previous reports on the preparation or properties of such mixed-halide complexes of indium, but several anionic complexes in which thallium(III) is bonded to two different halides have been reported. Preparative work,[3,4] vibrational spectroscopy,[4,5] electronic spectroscopy,[6] and X-ray powder methods[6] have established the existence of these mononuclear complexes, although there is some dispute as to whether or not dissociation in solution gives rise to mixtures of the appropriate TlX_4^- and TlY_4^- anions.[5,6]

Experimental Section

Starting Materials (General). The tetra-*n*-butylammonium salts of hexahalogenoindate(II) anions were prepared via InX_2 as described in the previous paper.[1] Tetraethylammonium salts of dihalogenoindate(I) anions were obtained from the reaction of the appropriate $(C_2H_5)_4NX$ + HX species with cyclopentadienylindium(I).[2]

Solvents and analytical methods were as in the previous work.[1,2]

Preparations. (a) $InCl_3I^-$, $InBr_3I^-$, $InCl_3Br^-$, InI_3Br^-, $InCl_2I_2^-$, $InBr_2I_2^-$. Weighted quantities (approx 2 mmol) of bromine and iodine were dissolved in benzene (50 cm^3), the solution was heated to boiling, and the calculated amount of the appropriate $((C_4H_9)_4N)_2In_2X_6$ or $((C_2H_5)_4N)InX_2$ salt was added in small portions over about 5 min. The color of the halogen discharged progressively during the addition, and the final colorless solution was allowed to cool to room temperature, when a brownish oil settled out. The benzene layer was decanted and the oil taken up in hot ethanol (20 cm^3); the solution was filtered hot and allowed to crystallize on cooling.

(b) $InBr_3Cl^-$, InI_3Cl^-, $InBr_2Cl_2^-$. A solution of chlorine in benzene was prepared, and the concentration was determined titrimetrically with $Na_2S_2O_3$ after addition of excess KI. Calculated quantities of salts of $In_2X_6^{2-}$ (X = Br, I) or $InBr_2^-$ were then added to approximately 50 cm^3 of a solution containing 2–4 mmol of Cl_2 at room temperature, and the product was isolated as described above.

The order of addition of reagents was found to be critically important, since if one adds a halogen Y_2 to a solution of

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