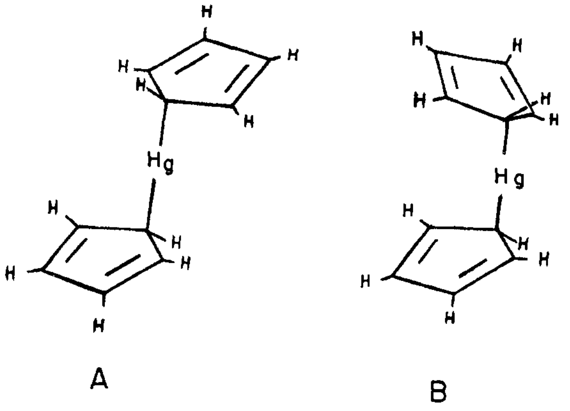

Figure 4.—The two extreme orientations of the C_5H_5 rings with respect to each other: transoid structure (A) and cisoid structure (B).

cyclopentadienyl rings about the C–Hg–C axis. Complete determination of the structure is difficult to make unless theoretical values of the dipole moment are calculated for each structure.

The Pmr Spectrum

As stated in the Introduction, the pmr spectrum of $(C_5H_5)_2Hg$ has been controversial. If the theory of valence tautomerism proposed by Piper and Wilkinson[5] is correct, the low-temperature pmr spectrum of $(C_5H_5)_2Hg$ should exhibit three peaks, with the expected intensity ratio of 2:2:1. Previously, Dvoryantseva, *et al.*,[20] measured the pmr spectrum of this compound in a tetrahydrofuran solution at −70°. Contrary to the expectation from valence tautomerism, they observed only a single peak at −70°. In order to confirm their results, the pmr spectrum of $(C_5H_5)_2Hg$ was measured in various solvents down to −70°. In triethylamine, only a single peak was observed. In CS_2, the peak was noticeably broadened as the temperature reached −70°. In SO_2 solution, however, three distinct peaks were observed.[21] These results have recently been questioned by Nesmeyanov, *et al.*,[22] who observed no splitting of the $(C_5H_5)_2Hg$ signal at −70°, using sulfur dioxide as the solvent. We are now carrying out a more careful study to confirm our results. Even admitting the correctness of their results, however, it is dangerous to draw the conclusion that there is no valence tautomerism on the basis of this negative evidence. The low-temperature pmr spectrum of $(C_5H_5)HgCl$ has also been studied, in the hope of observing a splitting at low temperatures. Tetrahydrofuran, diethyl ether, and sulfur dioxide were used as the solvents and the temperature was lowered to −70°. However, no change was observed in the pattern of the spectrum. The reason for this failure cannot be understood until a more elaborate theory is developed about the mechanism of valence tautomerism and the solvent effect on it.

Acknowledgment.—The compound $(C_5H_5)_2Mo(NO)I$ was very kindly supplied to us by Professor R. Bruce King of the University of Georgia, Athens, Ga.

(20) G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Sheinker, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **166**, 868 (1966).

(21) E. Maslowsky and K. Nakamoto, *Chem. Commun.*, 257 (1968).

(22) A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and F. S. Kochetova, *ibid.*, 105 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF YORK, YORK, ENGLAND

Raman Spectroscopic Studies of the Structure of the Lower Chlorides of Indium in the Molten State

BY J. H. R. CLARKE AND R. E. HESTER[1]

Received November 7, 1968

Raman spectra have been obtained over a range of temperatures for molten and solid $InCl_2$, molten and solid In_2Cl_3, and InCl dissolved in the molten LiCl–KCl eutectic. It is shown that $InCl_2$ has the constitution $In^+InCl_4^-$ in the liquid and probably also in the solid state. The spectra of molten In_2Cl_3 and molten $InCl \cdot 4(Li,K)Cl$ both show the presence of In(III) chloro complexes and it is concluded that there is disproportionation of In^+ in the presence of free chloride and that In^0 coordinates with $In^{III}Cl_4^-$ to form metal–metal bonds. A strong, polarized Raman band at *ca.* 170 cm^{-1} is assigned to an In–In stretching mode.

Introduction

In addition to indium monochloride and trichloride a number of intermediate compounds have been characterized for the indium–chlorine system in the solid state.[2–5] The existence of $InCl_2$ as a definite compound was at one time called into doubt,[2] but careful reinvestigation[4] of the phase diagram has confirmed its existence in the solid state. The compound is diamagnetic[6] and it has been suggested[7] that it might consist of $InCl_2$ dimers, although the alternative mixed-valence structure $In^{I}In^{III}Cl_4$ seems more likely by analogy with the

---

(1) To whom requests for reprints should be addressed.

(2) R. J. Clark, E. Griswold, and J. Kleinberg, *J. Am. Chem. Soc.*, **80**, 4764 (1958).

(3) V. N. Fadeer and P. I. Fedorov, *Zh. Neorgan. Khim.*, **9**, 378 (1964).

(4) J. R. Chadwick, A. W. Atkinson, and B. G. Huckstepp, *J. Inorg. Nucl. Chem.*, **28**, 1021 (1966).

(5) A. W. Atkinson, J. R. Chadwick, and E. Kinsella, *ibid.*, **30**, 401 (1968).

(6) G. Brauer and H. Morawietz, *Z. Anorg. Allgem. Chem.*, **340**, 133 (1965).

(7) W. Klemm and W. T. Tilk, *ibid.*, **207**, 175 (1932).

corresponding gallium compound.[4] Other stable compounds include In_4Cl_5, In_4Cl_7, and In_2Cl_3, all of which can be formulated as mixed-valence compounds,[5] the last having the structure[2] $In^I_3In^{III}Cl_6$.

Discussions of the structures of these compounds in the solid and liquid states have been, up to now, rather speculative owing to a lack of direct experimental evidence. This Raman spectroscopic investigation was undertaken in order to obtain such information.

Experimental Section

Raman spectra were obtained using a Perkin-Elmer LR-1 spectrophotometer, with a Spectra Physics Model 125 He-Ne laser as the light source. The techniques for handling the molten salt samples are described elsewhere.[8] Raman frequency shifts are quoted with an accuracy of ±3 cm^{-1}.

Samples of the required composition were prepared by melting together weighed quantities of dry indium trichloride and indium metal. Postanalyses of samples for indium and chlorine were carried out as described previously.[8]

Results and Discussion

Figure 1 shows the Raman spectrum of molten $InCl_2$ at 300 and 500° and as a solid at room temperature. Four bands were observed for the liquid; at 317 cm^{-1} (polarized) and at 91, 116, and 349 cm^{-1} (all weaker and depolarized). The presence of the weak 349-cm^{-1} band was only revealed in the polarization experiments when observing scattered light polarized perpendicular to the electric vector of the exciting radiation. Within the limits of accuracy of measurement the band frequencies were the same at 300 and 500°. Owing to the high level of primary scattering from the solid, only the strongest band was observed, of frequency 316 cm^{-1} at 250°, decreasing to 312 cm^{-1} at 25°.

As outlined in the preliminary communication[9] the four-band spectrum of molten $InCl_2$ is satisfactorily explained as originating from the tetrahedral species $InCl_4^-$, a conclusion which is supported by the close similarity between the spectral pattern observed for the melt and that assigned to $InCl_4^-$ in ether solution at room temperature.[10] Furthermore, the spectrum of molten $InCl_2$ is essentially identical with that of molten $InCl_3 \cdot KCl$ (see Figure 1) which has recently been shown to contain $InCl_4^-$ ions.[8] From these comparisons it is clear that there is no strong interaction between In^+ and $InCl_4^-$ in molten $InCl_2$, nor is there any evidence to suggest appreciable dissociation of $InCl_4^-$ to $InCl_3$ and Cl^-. The frequency of the strongest band, due to the symmetric In–Cl stretching mode, is slightly lower in the case of the solid compound, which perhaps is indicative of stronger environmental interactions. Nevertheless, there seems little doubt that the proper formulation of $InCl_2$ in both the liquid and solid states is $In^+InCl_4^-$.

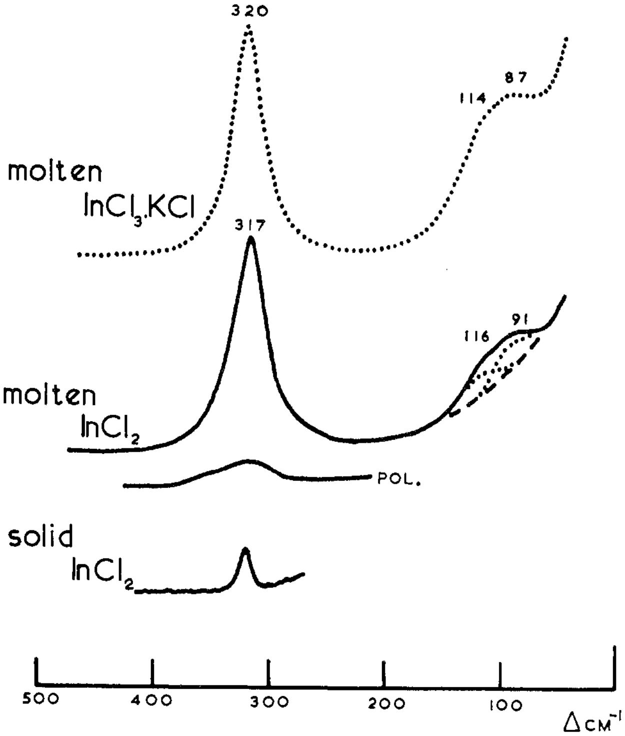

Figure 1.—Raman spectra of $InCl_4^-$ in molten $InCl_3 \cdot KCl$, molten $InCl_2$, and solid $InCl_2$. The intensity scales of individual spectra are not comparable. POL indicates trace obtained with the polarizer in the scattered beam and transmitting only light of an electric vector perpendicular to that of the exciting light.

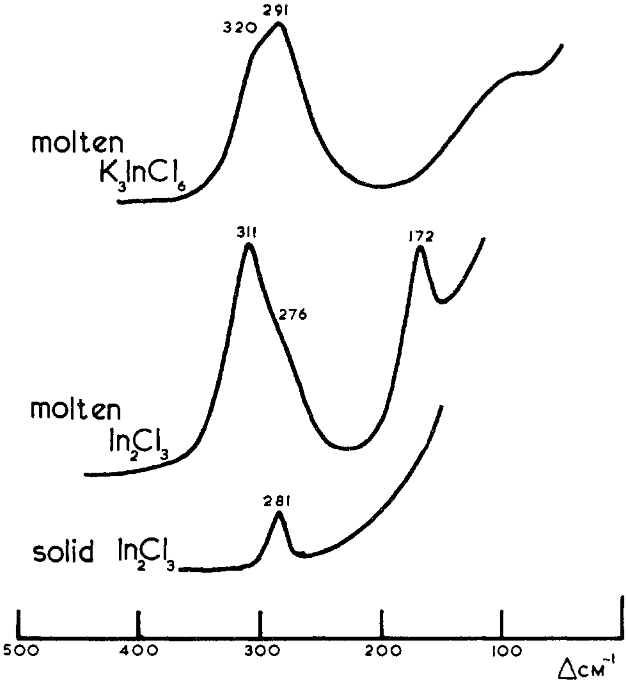

Figure 2.—Raman spectra of molten K_3InCl_6, molten In_2Cl_3, and solid In_2Cl_3. Intensity scales are not comparable.

The spectrum of molten In_2Cl_3 just above its melting point (314°) is shown in Figure 2. The color of the melt was claret red at 320° but deepened markedly on raising the temperature, causing extensive absorption of exciting light. However, it was established that over the temperature range 320–360° the essential features of the spectrum remained unchanged. Three strong and highly polarized bands were observed at 311, 276, and 172 cm^{-1}. The spectrum of the solid, deter-

---

(8) J. H. R. Clarke and R. E. Hester, *J. Chem. Phys.*, in press.

(9) J. H. R. Clarke and R. E. Hester, *Chem. Commun.*, 1042 (1968).

(10) L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 4473 (1960).

mined just below the melting point and also at room temperature, showed the presence of only one band at 281 cm^{-1}, in the range 150–400 cm^{-1}.

It has been suggested[2,5] that In_2Cl_3 has the structure $In^{I}_3In^{III}Cl_6$, *i.e.*, that it is formed by the reaction $3InCl + InCl_3 \rightarrow 3In^+ + InCl_6^{3-}$. On this basis the Raman spectrum should be quite similar to that of K_3InCl_6, which probably contains[5] $InCl_6^{3-}$. For comparison, therefore, the spectrum[8] of molten K_3InCl_6 is also included in Figure 2. Only a single band was found in the solid K_3InCl_6 spectrum.

Despite the incompleteness of the spectra, it was seen that both solid compounds did give similar strong Raman bands, at 281 cm^{-1} for In_2Cl_3 and 290 cm^{-1} for K_3InCl_6, both of which may be assigned[8,11] to the symmetric In–Cl stretching mode (ν_1) of $InCl_6^{3-}$, though the latter frequency actually lies closer to that reported for the pentachloro species,[12] $InCl_5^{2-}$. In contrast, it is clear that the spectra of the liquids are quite different.

It has been shown previously[8] that the solid K_3InCl_6 partially decomposes on melting into $InCl_4^-$ and Cl^- ions. The extent of this dissociation is indicated by the relative intensities of the 320-cm^{-1} band of $InCl_4^-$ and the 291-cm^{-1} band of the higher chloro complex (see Figure 2), both of these bands being assigned to In–Cl stretching modes. It has also been shown[8] that changes in the degree of dissociation on substituting Cs^+ or Li^+ for K^+ in the melt can be rationalized in terms of the different polarizing powers of the cations. Since the ionic radius of In^+ must be quite close[5] to that of K^+, similar extents of dissociation might be expected to accompany the fusion of K_3InCl_6 and $In^{I}_3In^{III}Cl_6$, and unless there is some specific interaction between In^+ and other compounds of the melt, similar spectra would be expected of the two liquids. The fact that the two spectra are quite different suggests that some such specific interaction *is* present.

As expected, bands attributable to the In–Cl stretching modes of both $InCl_4^-$ and $InCl_6^{3-}$ are observed for molten In_2Cl_3 at 311 and 276 cm^{-1}, respectively. However, comparison of their relative intensities with those of the similar bands observed for molten K_3InCl_6 is indicative of a much greater extent of dissociation in the former case, and it must be concluded that this effect is caused by an associative reaction between In^+ and Cl^- ions. The simplest possibility is that there is some coordination of Cl^- to In^+ to form an In^{I} chloro complex; the strong and polarized band at 172 cm^{-1} could then be assigned to the symmetric In–Cl stretching mode of such a species (by analogy with $InCl_4^-$ and $InCl_6^{3-}$ this type of mode would be expected to have by far the greatest intensity in the Raman spectrum). However, this is not a reasonable assignment; as compared with $\nu_1(InCl_4^-)$ at *ca.* 320 cm^{-1}, 170 cm^{-1} is a very low value to assign to such a mode, even after taking account of the change in oxidation state.[13] Furthermore, Raman spectroscopic evidence for Ga^{I} chloro complexes in aqueous and ether solutions has been presented,[14] and in this case a frequency of 233 cm^{-1} is reasonably assigned to Ga^{I}–Cl stretching. As compared with $\nu_1(GaCl_4^-)$, this represents a 33% decrease, whereas a frequency of 172 cm^{-1} represents nearly a 50% decrease on $\nu_1(InCl_4^-)$.

To investigate further the interaction of In^+ and Cl^- ions, an attempt was made to obtain the Raman spectrum of indium monochloride dissolved in the molten LiCl–KCl eutectic. A mixture of LiCl–KCl eutectic with $InCl_3$ and In metal corresponding to the composition $InCl\cdot 4(Li,K)Cl$ formed a deep red melt at 370°, leaving *ca.* 15% of the metal undissolved. After removal of the excess metal, the melt, of composition $InCl_{1.2}\cdot 4(Li,K)Cl$, gave the spectrum shown in Figure 3. Three bands were observed, all strongly polarized, at 315, 281, and 169 cm^{-1}. There is a marked similarity with the spectrum of In_2Cl_3, and although the relative intensities of the three bands in the two spectra are different, there seems to be little doubt that the two melts must contain similar species. Studies of more concentrated solutions or of InCl itself were precluded by the deep red-black color of the melts.

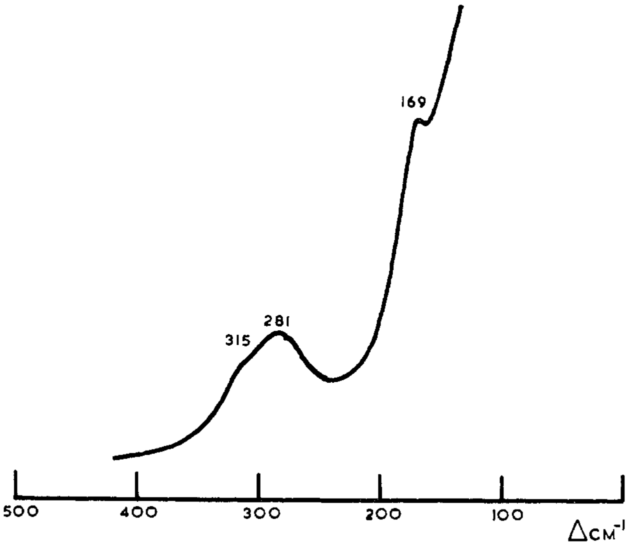

Figure 3.—Raman spectrum of the molten mixture $InCl\cdot 4(Li,K)Cl$ at 370°.

The failure of sufficient In metal to dissolve to produce the InCl stoichiometry could be explained by the tendency of In^+ to disproportionate according to the equation $3In^{I} \rightarrow 2In^0 + In^{III}$ in the presence of excess chloride. Spectral features characteristic of In^{III} complexes in this melt add support to this proposal. Since the spectra of $InCl_2$ show that In^+ is apparently quite stable in the absence of "free" chloride ions, it seems reasonable to suppose that the driving force for this reaction is the high relative stability of the In^{III} chloro complexes produced. The stabilization of higher oxi-

(11) T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *J. Chem. Soc., A*, 1810 (1967).

(12) I. Wharf and D. F. Shriver, *Chem. Commun.*, 526 (1968).

(13) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 48.

(14) L. A. Woodward and M. J. Taylor, *J. Inorg. Nucl. Chem.*, **27**, 737 (1965).

dation states by complex formation in molten salts has been discussed previously.[15] Evidence for retention of some In^0 in solution in the melt was provided by the fact that indium metal separated out from the solid on cooling. The question remains as to the state of combination of the In^0 in solution; we suggest that this may be coordinated to In^{III} or, more likely, to $InCl_4^-$. The strong, polarized Raman band at *ca.* 170 cm^{-1} observed for both molten In_2Cl_3 and molten $InCl_{1.2}\cdot 4(Li,K)Cl$ could then be explained as due to the stretching mode of an In–In bond; In^{3+} is isoelectronic with Cd^{2+}, and the latter has been shown to coordinate with Cd^0 to form Cd_2^{2+} in the molten state. The Cd–Cd stretching frequency was found[15] at 183 cm^{-1}, quite close to the above-mentioned band in these indium-containing melts. Association of In^0 with In^I seems improbable since it was shown in separate experiments that there is no appreciable solubility of indium metal in molten $InAlCl_4$, which contains only In^I.

Unfortunately the present results do not provide sufficient information to deduce the actual structure of the proposed In^0–In^{III} species, and more extensive Raman studies were severely hindered by the deep red color of the melts. The presence of the strong band at 281 cm^{-1} may be indicative of competitive coordination of $InCl_4^-$ by free Cl^- to form $InCl_5^{2-}$ and $InCl_6^{3-}$, but broadness of the band suggests that it may also contain contributions from the In–Cl stretching modes of a complex of the type $(InCl_4In^0)^{2-}$. It is worth noting at this stage that in the molten Bi–$BiCl_3$ system which, like InCl and In_2Cl_3, is very deeply colored, there is strong evidence[17] to substantiate the existence of such moieties as Bi_5^{3+}, which probably are further coordinated to chloride ligands.

We should point out that although the above conclusions may be speculative, the evidence for disproportionation of In^I in the presence of free chloride is quite strong, and if further studies of the indium chloride melts confirm the existence of metal–metal bonds, then this is an entirely novel feature of the chemistry of indium.

Since the preparation of this work for publication, another paper offering Raman evidence for the formulation of molten $InCl_2$ as $In^+InCl_4^-$ has appeared.[18] However, the spectra in this paper are much less complete than ours, and the authors failed to observe the important new band at *ca.* 170 cm^{-1} in their spectra on addition of excess chloride. We have observed this band for molten mixtures of $InCl_2$ and KCl, thus confirming our conclusion that it is a feature typical of melts containing In^+ and excess chloride.

---

[15] J. D. Corbett, W. J. Burkhard, and L. F. Druding, *J. Am. Chem. Soc.*, **83**, 76 (1961).

[16] J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

[17] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *ibid.*, **6**, 1162 (1967).

[18] J. T. Kenney and F. X. Powell, *J. Phys. Chem.*, **72**, 3094 (1968).

CONTRIBUTION FROM THE AIR FORCE MATERIALS LABORATORY,
WRIGHT-PATTERSON AIR FORCE BASE, DAYTON, OHIO 45433, AND THE
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH 84112

A Fluorine-19 Nuclear Magnetic Resonance Study of Some Titanium Tetrafluoride–Substituted Pyridine 1-Oxide Adducts[1]

BY DANIEL S. DYER[2a,b] AND RONALD O. RAGSDALE[2c]

Received November 26, 1968

A fluorine-19 nmr study of several substituted pyridine 1-oxide adducts of titanium tetrafluoride is reported. Evidence for the existence of a number of *trans*-$TiF_4\cdot 2$(donor) complexes is presented and discussed. Mixed adducts of TiF_4 in which the donor molecules are oriented *trans* to each other in solution are reported for the first time. The factors which determine the stereochemistry of the $TiF_4\cdot 2$(donor) complexes are discussed. It appears that *trans*-$TiF_4\cdot 2$(donor) is formed only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximize $p\pi$–$d\pi$ bonding.

Introduction

Recently several reports of research on transition metal complexes of substituted pyridine 1-oxides have appeared in the literature. Of particular interest was the infrared study of some diadducts of titanium tetrafluoride with *para*-substituted pyridine 1-oxides ($TiF_4\cdot 2(4\text{-}ZC_5H_4NO)$).[3] The N–O and Ti–O stretching modes of this series of $TiF_4\cdot 2D$ (D = donor) complexes were investigated as a function of the *para* substituent. The observed linear correlation of these two vibrational modes with the substituent constant σ^+ was used to elucidate the nature of the titanium–ligand bonds. The present paper describes an ^{19}F nmr study of $TiF_4\cdot 2(4\text{-}ZC_5H_4NO)$ and other titantium tetrafluoride–substituted pyridine 1-oxide complexes.

Previous ^{19}F nmr studies of the $TiF_4\cdot 2D$ adducts include the work of Muetterties[4] and of Ragsdale, *et al.*[5,6]

---

[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] (a) Abstracted in part from the Ph.D. thesis of D. S. D. submitted to the University of Utah. (b) Wright-Patterson Air Force Base. (c) Chemistry Department, University of Utah.

[3] F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.*, **6**, 1099 (1967).

[4] E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

[5] R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).

[6] D. S. Dyer and R. O. Ragsdale, *ibid.*, **6**, 8 (1967).