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Sequence Distribution of Aluminum(3+) and Titanium(3+) Ions in β -Phase $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$

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For the first time, the sequence distribution concepts applied for understanding organic copolymer microstructures are used to determine the microstructure of an inorganic copolymer, β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$, consisting of TiCl_3 and AlCl_3 sequences or repeat units. Whereas organic copolymer sequence distributions are invariably determined from interpretation of ^{13}C NMR spectra, we have determined the TiCl_3 , AlCl_3 sequence distributions in this inorganic copolymer by magnetic methods (electron spin resonance spectroscopy and magnetic susceptibility) sensitive to unpaired electrons. The magnetic behavior of this material is consistent with a periodic sequence distribution in which Al^{3+} and Ti^{3+} ions have fixed, alternating runs of one and three units, respectively. This sequence distribution gives rise to 0.33 spin/Ti. Other sequence distributions that have longer Al^{3+} and/or Ti^{3+} runs and give rise to only 0–0.20 spin/Ti can be discounted.

Introduction

β -Phase TiCl_3 has the linear polymer structure² $[\text{TiCl}_6/2]_n^{\pm}$.³ The Ti–Ti distance in this compound is 2.91 Å. Lewis and co-workers⁴ reported β - TiCl_3 to exhibit very weak paramagnetism at room temperature and at 77 K. Drent et al.⁵ subsequently confirmed this observation and further reported that β - TiCl_3 gives a very weak electron spin resonance (ESR) signal, which accounts for only 1–2% of the spins associated with the total number of individual Ti^{3+} ions. It is reasonable to conclude the short Ti...Ti distance in this phase results, to a substantial degree, in either direct or ligand-mediated metal–metal bonds, which quench the paramagnetism of the individual centers.

The linear polymer structure of β - TiCl_3 can also be adopted by cocrystallized TiCl_3 and AlCl_3 having the stoichiometry $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$.⁶ Since the Al^{3+} ions substituting for Ti^{3+} ions contain only high-energy, unpopulated d orbitals and no unpaired electrons, the sequence distribution of the Al^{3+} ions along the polymeric metal(3+) chain is expected to have a marked impact on the magnetic properties of the alloy. Measurement and interpretation of the magnetic properties of β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ with respect to possible Al, Ti sequence distributions form the basis of this paper. Electron spin resonance (ESR) spectra were also recorded for β - TiCl_3 for comparison, as we have obtained this phase of TiCl_3 free from impurities.

Experimental Section

Pure β - TiCl_3 was prepared by γ radiation-induced (^{60}Co) reduction of TiCl_4 at 65–70 °C as previously described.⁷ The isolated brown solid analyzed as $\text{TiCl}_{2.99}$ and was crystallographically pure as indicated by its X-ray diffraction pattern.

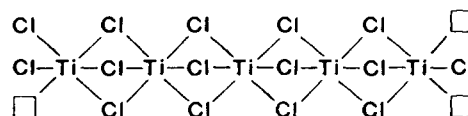
β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ was prepared by stoichiometric reduction of TiCl_4 with activated aluminum powder in benzene according to another published procedure.⁸ Since the β -form of this material is metastable at ambient temperature and has a tendency to be converted to the α - or γ -forms at temperatures above about 100 °C (or lower temperatures in the presence of TiCl_4) it is important to keep the reaction temperature well below this level. The use of refluxing benzene as the diluent meets this requirement. However, since the reaction of activated Al powder with TiCl_4 is vigorous and highly exothermic, local overheating may occur, unless special precautions are taken to prevent this from happening. In this particular preparation, a modestly activated Al powder was used and the reaction proceeded at a slow rate. Even so, rather weak

diffraction peaks corresponding to d spacings of about 5.84 and 2.48 Å were observed in the product. These peaks are close to the two major peaks in γ - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$, but they are even closer to the major diffraction peaks of AlCl_3 . On the basis of the known intensities of the diffraction peaks for these compounds, one can estimate the crystallographic impurity to correspond to about 3–4% of the total material. The composition of this impurity and its potential effect on the magnetic measurements will be discussed further in the next section.

Both of the β -phase products are highly air- and moisture-sensitive. Consequently, both were handled in a helium-containing drybox (Vacuum Atmospheres, equipped with recirculator). The moisture level was routinely monitored with a Panometrics moisture probe and was always below 1 ppm of water during sample manipulation. Variable-temperature ESR measurements were recorded over the temperature range 90–300 K on a Bruker/IBM 100D electron spin resonance spectrometer. Samples were flame-sealed in evacuated quartz tubes. For some spectra data were collected and processed on an IBM CS 9001 computer. Field settings were calibrated with a polyacetylene⁹ or diphenylpicrylhydrazyl (dpph) standard. All spectra were recorded with a modulation amplitude of 10G. Spin densities, determined by signal double integrations, were calibrated by using two spin standards: freshly prepared *fac*- $\text{TiCl}_3(\text{PMe}_3)_3$ dissolved in toluene and solid $\text{TiCl}_3(\text{PPhMe}_2)_2$.¹⁰ The resonance cavity tuned almost identically for the spin standards as for the samples. The magnetic susceptibility trace for $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ was recorded over the range 4–300 K on an automated Biomagnetics Technology (BTI, San Diego, CA) susceptometer. For this measurement, the sample was sealed in a dried 97%/3% Si/Al alloy can. Each susceptibility data point reported for a given temperature is the average of three separate determinations recorded at that temperature.

Results and Discussion

Electron spin resonance spectra for β - TiCl_3 recorded at 110 K and at room temperature are displayed in Figure 1. The room-temperature spectrum is exceedingly weak while that at 110 K is composed of a moderately intense apparent doublet centered at $g = 1.91$. The signal exhibits an unusually strong non-Curie temperature dependence. This has been attributed⁴ to excited-state relaxation by two different pathways. The highest spin population (still well below 1 spin/Ti) is detected at the lowest temperature used (110 K) for recording spectra. A spin density estimate, derived from the spectrum recorded at 110 K and calibrated by using established standards (see Experimental Section), gives a value of about 1 spin/1000 Ti^{3+} ions (accuracy $\pm 30\%$). Like Drent et al.⁵ we believe these residual spins are associated with chain-end, coordinatively unsaturated Ti^{3+} ions:



- (1) (a) Polyethylene & PVC Technology Division. (b) Elastomers Technology Division.
- (2) Natta, G.; Corradini, P.; Bassi, I. W.; Porri, L. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1958**, *24*, 121.
- (3) Jensen, W. B. *J. Chem. Educ.* **1977**, *54*, 277.
- (4) Lewis, J.; Machin, D. J.; Newnham, I. E.; Nyholm, R. S. *J. Chem. Soc.* **1962**, 2036.
- (5) Drent, E.; Emeis, C. A.; Kortbeek, A. G. T. *G. Chem. Phys.* **1975**, *10*, 313.
- (6) Tornqvist, E. G. M. *Ann. N.Y. Acad. Sci.* **1969**, *155*, 447–467.
- (7) Tornqvist, E. G. M. U.S. Patent 3 424 774, issued Jan 28, 1969, Esso Research and Engineering Co.
- (8) Example 5 in U.S. Patent 3 434 774; ref 7 above.

- (9) Snow, A.; Brant, P.; Weber, D. C.; Yang, N.-L. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 263.
- (10) Schmulbach, C. D.; Kolich, C. H.; Hinckley, C. C. *Inorg. Chem.* **1972**, *11*, 2841.

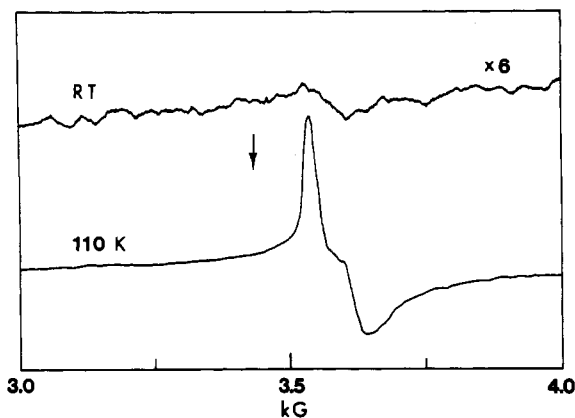


Figure 1. Electron spin resonance spectra of β - TiCl_3 recorded at room temperature (top) and 110 K (bottom). The arrow denotes the resonance position of the g value calibrant.

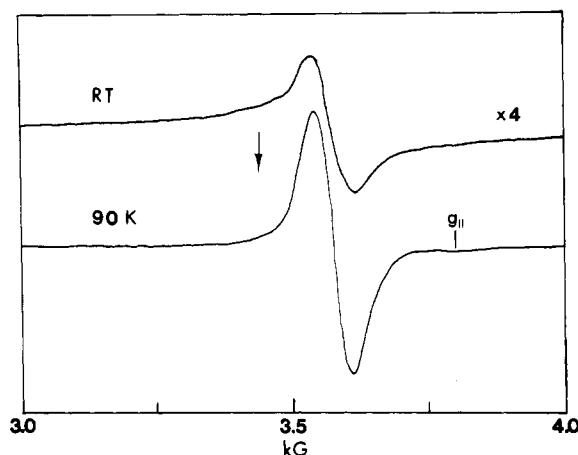


Figure 2. Electron spin resonance spectra of β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ recorded at room temperature (top) and at 90 K (bottom). The arrow denotes the position of the g value calibrant.

The reduced symmetry and different coordination numbers (four or five) of such sites are consistent with the complexity of the signal. We further believe the spins are associated only with $(\text{Ti}^{3+})_n$ chains where n is odd. Even-membered chains should be diamagnetic. On average then, an unpaired electron is associated with only one chain end in four. The experimental results, combined with our reasoning, suggest that in our material the average number of monomer units per chain is approximately 500.

β -Phase $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ gives a much stronger ESR signal than the parent β - TiCl_3 (Figure 2) even though there are 25% fewer Ti^{3+} ions in the cocrystallized material. At room temperature, we detect only a symmetric singlet with a g value of 1.9218 and peak-to-peak width of 79 G. The signal follows approximately Curie behavior down to 90 K, as determined from spectra recorded at six different temperatures. As the temperature decreases, the signal line shape changes from strongly Lorentzian to more nearly Gaussian and the line width decreases from 79 to 71 G. In addition, a new, very weak line is evident at $g = 1.816$. Since the Ti^{3+} ions in the chain possess D_{3d} symmetry, it is likely that the $g = 1.9218$ and $g = 1.816$ signals are g_{\perp} and g_{\parallel} respectively. The very weak g_{\parallel} signal is typical of powdered samples. Spin density estimates from room-temperature ESR spectra of β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ give 0.15–0.25 spin/ Ti^{3+} ion. Our analysis of the data indicates that Al^{3+} chain substitutions are responsible for the large increase in spin density in the cocrystalline material. This results because the Al^{3+} ion substitutions constitute diamagnetic chain termini along the metal(3+) backbone. The ESR signal arises only from those $(\text{Ti}^{3+})_n$ segments where n is odd. The simplicity of the β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ ESR signal results from the higher symmetry (D_{3d}) associated with internal, fully coordinated Ti^{3+} ions compared with the lower symmetry and possibility of

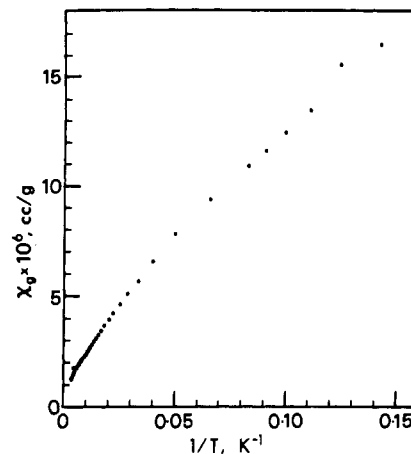


Figure 3. Magnetic susceptibility trace (χ_g vs. $1/T$) for β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ recorded over the temperature range 4.2–300 K.

two or more different environments for coordinatively unsaturated chain-end ions in β - TiCl_3 .

The spin density estimated by ESR for β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ suggests a fairly random distribution of Al^{3+} ions along the M^{3+} chain. A more accurate and independent assessment of the spin density in β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ can be obtained from its magnetic susceptibility. The magnetic susceptibility trace for this compound is shown in Figure 3. The susceptibility is found to follow Curie–Weiss behavior [$\chi = C/(T - \Theta)$],¹¹ where $C = 4.3 \times 10^{-4} \text{ cm}^3 \text{ K/g}$, and $\Theta = -60 \text{ K}$. The fit of the data to this equation is very good over the temperature range 40–300 K.

For the calculation of the room-temperature magnetic moment a diamagnetic correction of $65 \times 10^{-6} \text{ cm}^3/\text{mol}$ was applied to the measured susceptibility.¹² From the corrected susceptibility, we calculate a room-temperature moment of $0.86 \mu_B/(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ unit. As has been observed for other pseudooctahedral Ti^{3+} complexes,^{13–15} the moment decreases with decreasing temperature (for example, it is $0.45 \mu_B$ at 10 K). Room-temperature moments for magnetically dilute pseudooctahedral Ti^{3+} complexes are typically in the range 1.50 – $1.70 \mu_B$ ^{13–17} so the 0.86 - μ_B moment translates into 0.31 – 0.36 spin/ $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ unit.

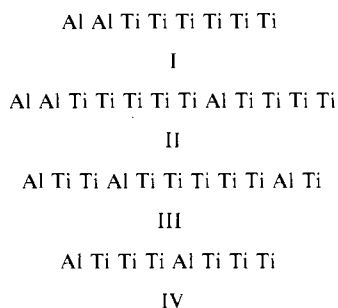
Alternatively, one can approximate independently the number of spins/ Ti^{3+} by comparing the Curie constant C_M^{obsd} derived from the fit of the data with the calculated Curie constant C_M^{calcd}

$$C_M^{\text{calcd}} = N_A(g_{\text{av}})^2[S(S+1)/3k_B]\mu_B^2 \quad (1)$$

where N_A is Avogadro's number, g_{av} is 1.887, $S = 1/2$ (assumes 1 spin/ Ti), μ_B is the Bohr magneton, and k_B is the Boltzmann constant. Inserting all these values into eq 1, we obtain a value for C_M^{calcd} of $0.334 \text{ cm}^3 \text{ K/mol}$ of Ti . Our observed Curie constant is 0.085, so by this method we calculate 0.254 spin/ $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ unit, in reasonable agreement with the 0.31 – 0.36 spin derived from the room-temperature moment.

The number of spins present in β - $(\text{TiCl}_3)(\text{AlCl}_3)_{0.33}$ should be determined by the sequence distributions of Al^{3+} and Ti^{3+} ions along the chain. The different sequence distributions considered (I–IV) are

- (11) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.
- (12) Diamagnetic corrections used (values in cm^3/mol ; cgs units): AlCl_3 (60×10^{-6}), TiCl_3 (45×10^{-6}). These were estimated from the values for BCl_3 (59.9×10^{-6}), GaCl_3 (63×10^{-6}), PCl_3 (63.4×10^{-6}), and TiCl_4 (54×10^{-6}). All data taken from: Foex, G. *Tables de Constantes et Donnees Numerique*; Masson: Paris, 1957; Vol. 7. Constantes Selectionnees Diamagnetisme et Paramagnetisme.
- (13) Nasiff, P. J.; Cauch, T. W.; Hatfield, W. E.; Villa, J. F. *Inorg. Chem.* **1971**, *10*, 368.
- (14) Giggenbach, W.; Brubaker, C. H. *Inorg. Chem.* **1969**, *8*, 1131.
- (15) Ameis, R.; Kremer, S.; Reinen, D. *Inorg. Chem.* **1985**, *24*, 2751.
- (16) Richardson, J. T.; Brant, P.; Tornqvist, E. G. M., unpublished results.
- (17) McDonald, G. D.; Thompson, M.; Larsen, E. M. *Inorg. Chem.* **1968**, *7*, 648.



Structure I is a block copolymer, with all the Ti^{3+} ions in one block and all the Al^{3+} ions in another along a given M^{3+} chain. Structure II represents a completely random distribution of both Ti^{3+} and Al^{3+} . Structure III has all Al^{3+} ions as single, dispersed units, while the Ti^{3+} ions exist in runs of random length for which the average length is three. Finally, structure IV has both Al^{3+} and Ti^{3+} in alternating runs of fixed length: one for Al^{3+} and three for Ti^{3+} .

Given that the substitution of Al^{3+} ions for Ti^{3+} ions in the chains affects the magnetic properties in the manner suggested above, then one can calculate the expected magnetic susceptibility values for the different arrangements from the respective Ti^{3+} sequence distributions. These distributions can be calculated by using the monomer reactivity ratio method for binary copolymers developed by Natta et al.¹⁸ or the run number method developed for monomer distributions in copolymers by Harwood and Ritchey.¹⁹ However, direct calculation is also simple.

Structure I has all the Ti^{3+} present as if it were a separate phase, though diluted on a weight basis by the $AlCl_3$ present. Thus, it should have the same molar susceptibility as pure $\beta-TiCl_3$ having the same number average sequence length, $(TiCl_3)_n$. There would be one spin for every $2n$ $TiCl_3$ sequences, as only the Ti^{3+} blocks of odd parity contribute spins. For large values of n , e.g. 500, the susceptibility becomes vanishingly small.

The random distribution in structure II would produce both Ti^{3+} and Al^{3+} sequences of varying length, beginning with single isolated units. From the ratio $Ti/Al = 3$, one can easily recognize that the frequency ratio between sequences containing $(n + 1)$ and n Ti^{3+} units, respectively, will be $3/4$. Thus the fractions containing 1, 2, 3, ..., n Ti^{3+} sequences can be represented as a , $a(3/4)$, $a(3/4)^2$, ..., $a(3/4)^{n-1}$. Summation and normalization give $a = 1/4$ and, as a consequence the average sequence length for Ti^{3+} will be 4. Since only $(TiCl_3)_n$ sequences where n is odd should contribute spin, those exhibiting spin will be represented by the fractions $1/4$, $(1/4)(3/4)^2$, $(1/4)(3/4)^4$, Those not exhibiting spin will be represented by $(1/4)(3/4)$, $(1/4)(3/4)^3$, $(1/4)(3/4)^5$, The sum of the second series is only $3/4$ of the first one, thus $4/7$ of the total number of sequences will exhibit spin. Since the average sequence length is four we find that $1/7$, or 0.143, spin/ Ti^{3+} will be expected for structure II.

In structure III, where the Al^{3+} ions are dispersed as single units, we know that the average length of the Ti^{3+} sequences must be three. As soon as an Al^{3+} has been added to the chain, we know that a Ti^{3+} must follow. However, after the Ti has been added, either one or more Ti^{3+} or a single Al^{3+} can follow. For the average Ti^{3+} sequence length to be three, the probability of another Ti adding must be twice that for Al . This leads to a distribution of Ti^{3+} sequence lengths similar to that for structure II, but with the $3/4$ replaced by $2/3$. Thus the fractional distribution of Ti sequences of 1, 2, 3, ..., n units will be $1/3$, $(1/3)(2/3)$, $(1/3)(2/3)^2$, ..., $(1/3)(2/3)^{n-1}$. Again, only odd-numbered sequences will contribute any spin. They comprise $3/5$ of the total number of sequences. It follows that $[(3/5)/3] = 1/5$ spin/ Ti^{3+} can be expected for structure III.

Table I. Magnetic Properties Expected for Different Al, Ti Sequence Distributions in $\beta-(TiCl_3)(AlCl_3)_{0.33}$

sequence distribution structure ^a	spin/ Ti^{3+}	magnetic moment, μ_B
I	approach zero	0
II	0.144	0.47–0.55
III	0.200	0.57–0.65
IV	0.333	0.80–0.88
exptl		
from rt moment	0.31–0.36	0.86
from eq 1 ^a	0.25	

^aSee text for explanation.

For structure IV, where the length of all Ti^{3+} sequences is three, it is obvious that the spin number per Ti^{3+} will be $1/3$. The spins/ Ti^{3+} ion values determined for the four different sequence distribution models are compared with the spins/ Ti^{3+} value measured experimentally and given in Table I. We see here that the experimental results (spins determined from both the room-temperature magnetic moment and from eq 1) agree best with the value expected for structure IV. However, the calculated values are lower limits based on infinite chain models (except in the case of structure IV, which maintains the same spin density, regardless of chain length). Consequently, it is worth considering for a moment whether we can reconcile the sequence distribution model that yields the next highest spins per titanium value, structure III, with the experimental result by shortening the chains associated with this distribution. If we make the reasonable assumption that the $Ti^{3+}:Al^{3+}$ stoichiometry of all chains is fixed at 3:1, we calculate that structure III cannot yield the number of spins measured experimentally, unless uniformly restricted to the three shortest possible chains— $(TiCl_3)_3(AlCl_3)-(TiCl_3)_9-(AlCl_3)_3$. As the chain length increases, the spin density declines rapidly toward structure III's infinite chain value of 0.20. For example, after just five $(TiCl_3)_3(AlCl_3)$ repeat units it falls to 0.224. Since diffraction data suggest chain lengths approaching just two or three repeat units are not likely and since there is no clear reason why the condensation reaction should terminate after just two or three repeat units, we rule out the possibility that short chain lengths can alter our assignment. However, the assignment could still be altered due to the effect on the magnetic measurements of the crystallographic impurity corresponding to an estimated 3–4% of the total (see Experimental Section).

If the impurity is $AlCl_3$, 3–4% of the total mass of product would correspond to 12–16% of the $AlCl_3$ present. Independent of the type of sequence distribution for Ti^{3+} and Al^{3+} found in $\beta-(TiCl_3)(AlCl_3)_{0.33}$, the removal of some $AlCl_3$ from the chains must result in a decrease in the overall magnetic susceptibility. The only sequence distribution structure that could accommodate a decrease in spins and still yield a spins per titanium value close to the experimental values is structure IV.

Whenever a single $AlCl_3$ unit is removed from structure IV, a six-unit Ti^{3+} sequence is formed from two three-unit sequences with the attendant loss of two spins, since an even-numbered sequence is formed from two odd ones. However, the subsequent removal of $AlCl_3$ units will not necessarily result in loss of two spins. For example, if an $AlCl_3$ sequence separating $(TiCl_3)_3$ and $(TiCl_3)_6$ sequences is removed, then a nine-unit $TiCl_3$ sequence is formed with no loss of spin. If we assume that the removal of $AlCl_3$ from the $\beta-(TiCl_3)(AlCl_3)_{0.33}$ is random, as will be the case if the $AlCl_3$ molecules are removed by extraction when present at the ends of growing M^{3+} chains, we can readily calculate the number and type of Ti^{3+} sequences formed in a manner similar to that used previously for the determination of the Ti^{3+} sequence length distributions for structures II and III. For removal of 15% of the $AlCl_3$, the quotient between the number of sequences having $n + 1$ and n , beginning with $n = 1$, "adjacent" $AlCl_3$ molecules removed will be 0.15. The number of Ti^{3+} sequences having 6, 9, 12, etc. members can now be calculated if we remember that such sequences will be formed from the removal of 1, 2, 3, etc. $AlCl_3$ molecules, respectively. The calculation of the loss of spins

(18) Natta, G.; Mazzanti, G.; Valvassori, A.; Sartori, G.; Morero, D. *Rubber Chem. Technol.* **1963**, *39*, 1583.

(19) Harwood, H. J.; Ritchey, W. M. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 601. For the interested reader, the appropriate run numbers, calculated according to the method of Harwood and Ritchey, for structures II–IV are 37.5, 50, and 50, respectively.

is simplified if we remember that each member in the pair of sequences 6 and 9, 12 and 15, 18 and 21, etc. leads to the loss of the same number of spins, namely, in order, 2, 4, 6, and so on. We find then, that 26–30% of the original, magnetically active Ti^{3+} sequences will become magnetically inactive, given removal of 12–15% of the $AlCl_3$ from $\beta-(TiCl_3)(AlCl_3)_{0.33}$. On the basis of this scenario, the spins per titanium now expected for structure IV would be suppressed to only 0.23–0.24. Once again structure IV, modified for contribution from this crystalline impurity, yields the best agreement with experiment from among the four structures considered.

On the other hand, as we mentioned, the impurity could also be $\gamma-(TiCl_3)(AlCl_3)_{0.33}$. This phase of the cocrystallized $TiCl_3$ and $AlCl_3$ has a layer-lattice structure and, at room temperature, gives 1 spin/ Ti^{3+} .¹⁵ If 4% of the material examined is in the γ -phase, then the effect will be to raise the spin/ Ti^{3+} value for any of the sequence distribution structures I–IV by 0.02–0.03. This being the case, the best fit with experiment again is clearly obtained with sequence distribution structure IV.

After consideration of all the sequence distribution structures, and the effects of chain lengths and impurities on the experimental

results, we conclude that only structure IV is consistent with these results.

Conclusion

For the first time, the sequence distribution concepts originally applied for detailed understanding of organic copolymer microstructure have been used to interpret the magnetic behavior of an inorganic copolymer, $\beta-(TiCl_3)(AlCl_3)_{0.33}$. The magnetic properties are best matched by using a sequence distribution model consisting of fixed, alternating runs of Al^{3+} ions and Ti^{3+} ions of lengths one and three, respectively. This newly gained sequence distribution information can provide insight into the growth mechanism for such chains, a subject we intend to discuss in a forthcoming paper.

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Absorption Spectrophotometric and X-ray Diffraction Studies of the Trichlorides of Berkelium-249 and Californium-249^{1a}

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Absorption spectrophotometric and X-ray powder diffraction methods have been applied to a study of the trichlorides of ²⁴⁹Bk and ²⁴⁹Cf and their relationship through the β decay of ²⁴⁹Bk. $BkCl_3$ has been prepared for the first time in the $PuBr_3$ -type orthorhombic modification by quenching from the melt. Each of the crystal forms (UCl_3 -type hexagonal and $PuBr_3$ -type orthorhombic) of $BkCl_3$ and $CfCl_3$ has been characterized on the basis of its solid-state absorption spectrum. The orthorhombic forms of $BkCl_3$ and $CfCl_3$ are the high-temperature modifications with respect to the hexagonal phases, with the apparent transition temperatures near the melting points of $BkCl_3$ (876 K) and $CfCl_3$ (818 K). Orthorhombic $BkCl_3$ transmutes to orthorhombic $CfCl_3$ and hexagonal $BkCl_3$ transmutes to hexagonal $CfCl_3$. Thus, it was found that both the oxidation state and the crystal structure of the parent ²⁴⁹Bk compound were retained by the daughter ²⁴⁹Cf compound through β decay in the bulk phase solid state.

Introduction

The first preparations of berkelium trichloride and californium trichloride were reported almost 20 years ago.^{2,3} From the analysis of X-ray powder diffraction data, both compounds were found to exhibit the UCl_3 -type hexagonal structure. Their average, room-temperature lattice parameters were determined to be $a_0 = 0.7382$ (2) nm and $c_0 = 0.4127$ (3) nm for $BkCl_3$ ² and $a_0 = 0.7393$ (40) nm and $c_0 = 0.4090$ (60) nm for $CfCl_3$.³ In each case a list of observed and calculated diffraction lines was presented along with a comparison of the observed and calculated intensities of the diffraction lines. Comparison of the similarly calculated trivalent ionic radii of the lanthanides and actinides that exhibit the UCl_3 -type hexagonal structure and the fact that the crystal structure of the lanthanide trichlorides changes between gadolinium (UCl_3 -type hexagonal) and terbium ($PuBr_3$ -type orthorhombic) led to the prediction that a crystal structure change

should occur in the actinide trichlorides heavier than $CfCl_3$.²

Single crystals of californium trichloride were grown from the melt on the microgram scale and used to establish the existence of the $PuBr_3$ -type orthorhombic phase ($o-CfCl_3$) for this compound, as well as to refine the structures of both the known UCl_3 -type hexagonal phase ($h-CfCl_3$) and this newly discovered orthorhombic phase.⁴ The room-temperature lattice parameters determined from the single crystal of each form were $a_0 = 0.7379$ (1) nm and $c_0 = 0.40900$ (5) nm for $h-CfCl_3$ and $a_0 = 0.3869$ (2), $b_0 = 1.1748$ (7), and $c_0 = 0.8561$ (4) nm for $o-CfCl_3$. Although the melting point of $CfCl_3$ was established as 818 ± 5 K, the temperature relationship between the hexagonal and orthorhombic phases could not be determined.⁴

In the present work we have utilized a microscope-spectrophotometer of local design to obtain solid-state absorption spectra from microgram-sized samples of $BkCl_3$ and $CfCl_3$. We have (1) prepared $BkCl_3$ in the previously unknown $PuBr_3$ -type orthorhombic modification ($o-BkCl_3$), (2) characterized spectrophotometrically the orthorhombic and hexagonal forms of both $BkCl_3$ and $CfCl_3$, (3) determined the chemical and physical consequences of the β decay of both crystal forms of ²⁴⁹ $BkCl_3$, and (4) deter-

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(2) Peterson, J. R.; Cunningham, B. B. *J. Inorg. Nucl. Chem.* **1968**, *30*, 823.
(3) Green, J. L.; Cunningham, B. B. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 343.

(4) Burns, J. H.; Peterson, J. R.; Baybarz, R. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1171.