$\rightarrow 0$, τ_M is the mean lifetime of an H_2O in the Co(II) first coordination sphere, $\Delta\omega_M$ is the resonance frequency difference between a free H_2O and one in $Co(H_2O)_6^{2+}$, and ΔW is the width of the resonance. Near the fast exchange limit $\tau_M^2\,\Delta\omega_M^2 << 1$, so the shift equation can be written as

$$\Delta\nu = \Delta\nu_\infty(1 - \tau_M^2\Delta\omega_M^2) = \Delta\nu_\infty(1 - \Delta W^2/\Delta\nu^2)$$

The slope of a plot of $\Delta\nu$ vs. P can be obtained with sufficient accuracy by regarding $\Delta\nu$ in the right-hand side as constant so that

$$\left(\frac{\partial\Delta\nu}{\partial P}\right)_T = -\frac{2\Delta\nu_\infty\Delta W}{\Delta\nu^2}\left(\frac{\partial\Delta W}{\partial P}\right)_T$$

The shift data at 72.3 and 83.0 °C were fit with a linear least-squares program and gave slopes of −0.010 ± 0.002 and −0.006 ± 0.002 Hz/MPa, respectively, whereas the slopes calculated from the above equation and the W vs. P data were −0.0103 and −0.0059 Hz/MPa, respectively. This shows that the very slight decrease in shift observed with increasing pressure can be entirely accounted for by the decrease in rate of exchange with pressure and allows one to conclude that A/h must have been constant within about ±0.1% over the 200 MPa pressure range.

In Figure 2 values of ln K_{eq} vs. P are shown for two temperatures for the solution 0.0675 *m* in Ni complex and 4.0 *m* in $NaClO_4$. The K_{eq} values are calculated for the process $Ni(H_2O)_2L \leftrightarrow NiL + 2H_2O$ from the fast-exchange relation[1] $K_{eq} = (8.0 - Q)/Q$ where 8.0 is the Q value expected for a solution containing 100% $Ni(H_2O)_2L$ and Q is the observed shift function, $Q \equiv T\Delta\nu[L]/[M]\nu_0$, where T is in K, $\Delta\nu$ is the observed frequency shift of bulk $^{17}OH_2$ in the Ni solution relative to a blank, ν_0 is the ^{17}O resonance frequency in the blank and [M] and [L] are defined above. We calculate ΔV° from $d\ln K_{eq}/dP = -\Delta V^\circ/RT$. The solution containing only the Ni complex at 0.0496 *m* yields $\Delta V^\circ = 3.1 \pm 0.3$ cm^3/mol at 56.8 °C; for the 0.0675 *m* Ni and 4.0 *m* $NaClO_4$ solution at 62 °C, $\Delta V^\circ = 2.53 \pm 0.08$ cm^3/mol, and at 45 °C, $\Delta V^\circ = 2.09 \pm 0.07$ cm^3/mol. The latter value may well be somewhat low as the water exchange rate is slowing down at 45 °C. Line broadening data were also obtained on the Ni solutions, but they are imprecise and difficult to interpret in any case, so they are not reported here.

Discussion

Whereas one might expect some increase in A/h as pressure on an aqueous ion increases (due to a slight compressibility), there is no significant effect observed in the pressure range to ca. 2 kbar (200 MPa). Thus, one can use ^{17}O shift measurements to study complex equilibria as a function of pressure to obtain ΔV° values.

The small positive ΔV° found for the Ni-2,3,2-tet system is similar to those found by Kitamura[3] using a spectral method (note that his values are given for the reverse of our equation). These small values are in contrast to the +10 cm^3/mol found by Merbach et al.[4] in the tetramethylcyclam case. Kitamura considers that the smaller size of the low-spin Ni complex accounts for the small ΔV° values (+36 cm^3/mol is expected if the high- and low-spin forms are of equal molal volume); i.e., a contraction occurs that offsets H_2O loss. As we discussed in our earlier paper,[1] we feel that ClO_4^- plays a specific role in the conversion to low-spin Ni. The ClO_4^- ion has a molal volume of ca. +36 cm^3/mol, and if ClO_4^- is removed from solution by some "complexing" in the low-spin form, the low ΔV° values can also be accounted for. Perhaps both factors are operative. Possibly steric effects prevent ClO_4^- from as close an approach in the tetramethylcyclam system, resulting in a larger ΔV°.

Acknowledgment. The authors thank the National Science Foundation (Grant No. CHE-831-3075) for support of this work.

Registry No. NiL^{2+}, 46365-93-9; $Ni(H_2O)_2L^{2+}$, 64616-26-8; ^{17}O, 13968-48-4; $Co(H_2O)_6^{2+}$, 15276-47-8; Co, 7440-48-4.

Contribution from the National Bureau of Standards,
Gaithersburg, Maryland 20899

Solid-State ^{13}C NMR Probe for Organotin(IV) Structural Polymorphism

Thomas P. Lockhart*[1a,b] and William F. Manders*[1a]

Received August 9, 1985

Two types of structural polymorphism are not uncommon in organotin(IV) chemistry: (A) where there is more than one structural modification present per unit cell[2–6] and (B) where two or more crystalline modifications of a single compound exist.[5–9] While single-crystal X-ray studies can readily reveal the former case, many instances of type B polymorphism may be presumed to go unnoticed in routine structural studies.

In contrast to X-ray diffraction studies carried out on single crystals, solid-state NMR spectra are acquired on bulk, polycrystalline samples of 0.1–0.4 g, which ensures more representative sampling of a material. In our structural investigations of methyltin(IV) compounds by solid-state ^{13}C NMR[8,10] we have found that ^{13}C chemical shifts of methyls bonded to tin are very sensitive to the local environment (which, unlike the case in solution, is generally static in the crystalline state). This sensitivity suggests that solid-state NMR can provide a convenient tool for revealing the presence of structural polymorphism in crystalline samples.[11] We describe below examples that confirm the general utility of the method for determining the occurrence and type of methyltin(IV) (and, by extension, other organometal) polymorphism.

Results and Discussion

Table I gathers solid-state ^{13}C NMR data obtained for three pure, polycrystalline methyltin(IV) compounds at 15.08 MHz with cross-polarization and magic-angle spinning (CPMAS) and high-power proton decoupling. Both hexacoordinated $Me_2Sn(S_2CNEt_2)_2$[6,8] and the tetracoordinated cyclic trimer $[Me_2SnS]_3$[9] are known from single-crystal X-ray diffraction studies to exist in two or more crystalline modifications. For each compound we have been able to isolate one of the characterized crystalline modifications in pure form and to obtain crops of crystals in which other forms are present in varying amounts. The presence of

---

(1) (a) National Bureau of Standards-National Research Council Associate, 1983–1985. (b) Present address: Central Research and Development Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE 19898.

(2) For a bibliography of organotin X-ray structures see: Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, *12*, 97.

(3) Harrison, P. G.; King, T. J.; Phillips, R. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2317. Harrison, P. G.; King, T. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *185*, 199. Webster, M.; Mudd, K. R.; Taylor, D. J. *Inorg. Chim. Acta* **1976**, *20*, 231.

(4) Theobald, F.; Trimaille, B. *J. Organomet. Chem.* **1984**, *267*, 143.

(5) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1970**, 490.

(6) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1979**, *9*, 13.

(7) Sheldrick, G. M.; Sheldrick, W. S.; Dalton, R. F.; Jones, K. *J. Chem. Soc. A* **1970**, 493. Yoshida, M.; Ueki, T.; Yasuoka, N.; Kasai, N.; Kakudo, M.; Omae, I.; Kikkawa, S.; Matsuda, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1113. Kimura, T.; Ueki, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2479. Pelizzi, C.; Pelizzi, G.; Tarasconi, P. *J. Organomet. Chem.* **1977**, *124*, 151. Pelizzi, G. *Inorg. Chim. Acta* **1977**, *24*, L31.

(8) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O.; Zuckerman, J. J. *J. Am. Chem. Soc.*, in press.

(9) (a) Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291. (b) Jacobsen, H.-J.; Krebs, B. *J. Organomet. Chem.* **1977**, *136*, 333.

(10) (a) Manders, W. F.; Lockhart, T. P. *J. Organomet. Chem.* **1985**, *297*, 143. (b) Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 4546. (c) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1985**, *107*, 5863.

(11) A few isolated reports of the resolution of different crystalline structural isomers by solid-state NMR (of varying levels of documentation) have appeared: Ripmeester, J. A. *Chem. Phys. Lett.* **1980**, *74*, 536. Diesveld, J. W.; Menger, E. M.; Edzes, H. T.; Veeman, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 7935. Balimann, G. E.; Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *Philos. Trans. R. Soc. London, A* **1981**, *No. 299*, 643. Hill, H. D. W.; Zens, A. P.; Jacobus, J. *J. Am. Chem. Soc.* **1979**, *101*, 7090. See also unpublished data cited in: Harris, R. K.; Packer, K. J.; Reams, P. *Chem. Phys. Lett.* **1985**, *115*, 16.

Table I. Solid-State ^{13}C NMR Data for Polymorphic Methyltin(IV) Compounds

compd	cryst modification(s)	Sn–Me ^{13}C chem shifts, ppm[a]
$[Me_2SnS]_3$	tetragonal	7.5, 8.3, 12.2
	mixture[b]	2.2, 4.6, 7.5, 8.3, 12.2, 13.8
$Me_2Sn(S_2CNEt_2)_2$	orthorhombic	15.17, 16.47
	mixture of orthorhombic, monoclinic, triclinic[c]	15.17, 16.47, 18.25, 19.71[d]
$MeSnPh_3$	nd[e]	−8.8, −6.9

[a] Chemical shifts of $Me_2Sn(S_2CNEt_2)_2$ relative to linear polyethylene (33.63 ± 0.03 ppm at 1.4 T); others relative to Delrin (89.1 ± 0.3 ppm). [b] From sublimation; contains tetragonal form (identified by NMR, microscopic examination). [c] Presence of monoclinic, triclinic crystalline modifications determined by X-ray unit cell analysis. [d] Region between 12 and 15 ppm obscured by large, broad methyl ligand resonance. [e] Not determined (see Experimental Section).

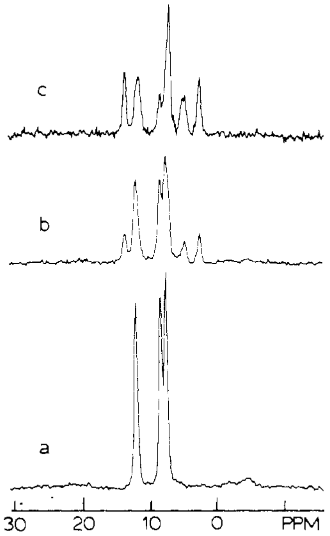

Figure 1. Solid-state ^{13}C NMR spectra (15.08 MHz) of $[Me_2SnS]_3$ at 28 °C: (a) pure tetragonal modification; (b) mixtures of tetragonal and other crystalline modifications from sublimation; (c) sample from low-temperature recrystallization.

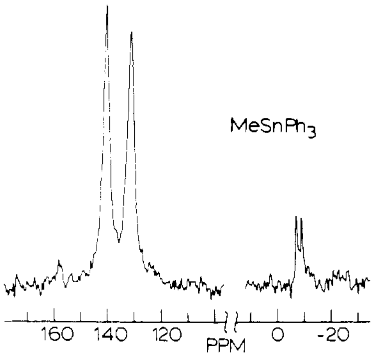

Figure 2. Solid-state ^{13}C NMR spectrum of crystalline $MeSnPh_3$ at 28 °C. Fused ^{117}Sn, ^{119}Sn satellites are visible around the downfield aromatic resonance $[^1J(^{117,119}Sn,^{13}C) = 510$ Hz]. Small, broad resonances to the right of the methyl signal (−10 to −25 ppm) arise from spinning sidebands (ca. 2300 Hz) of aromatic resonances.

additional crystalline modifications is clearly indicated by the appearance of new tin–methyl resonances in the NMR spectra of the mixed crops (Table I). The compositional identity of the different crystalline forms was established by melting point and solution ^{13}C NMR. Additionally, recrystallization of the mixed crops under appropriate conditions yielded back the pure crystalline modification.

These points are illustrated in greater detail for $[Me_2SnS]_3$ (Figure 1). The pure tetragonal modification was obtained from slow recrystallization of a cyclohexane solution at room temperature; mixed crops were obtained both from use of lower recrystallization temperatures and by sublimation. In the tetragonal form $[Me_2SnS]_3$ adopts a twist-boat conformation.[9a] The presence of an approximate C_2 symmetry axis relating three pairs of methyls gives rise to three ^{13}C resonances of equal area.[10a] The numerous new resonances in the mixed crop (a total of at least six ^{13}C resonances can be distinguished) indicate the presence of one or more additional crystalline forms.[12] In fact, a second modification (in which $[Me_2SnS]_3$ again adopts a twist-boat geometry) has been characterized by X-ray, and evidence for a third form has been produced.[9b] The relative intensities of the new resonances in the spectra of the mixed material vary from crop to crop in a way that appears consistent with the presence of two additional forms (with apparent coincidental overlap of resonances at 7.5 and 12.2 ppm). Complete analysis has been hindered by our inability to obtain pure crops of the other forms (or to separate by hand enough crystals for NMR analysis).

$MeSnPh_3$ provides an example of polymorphism of type B. The solid-state ^{13}C NMR spectrum of this compound after recrystallization from hydrocarbon or alcohol solvents shows the presence of two narrow, partially resolved methyl resonances of equal size (Figure 2). Only a single methyl resonance is observed in the solution ^{13}C NMR spectrum, in complete agreement with that reported.[13] The presence of two methyl resonances in the spectrum of a pure crystalline compound containing a single methyl per molecule *requires* the presence of more than one structural modification of $MeSnPh_3$ in the polycrystalline sample. The simple integer ratio (1:1) of the methyl resonances suggests that they result from the presence of two distinct molecules of $MeSnPh_3$ in a single crystalline modification (type B polymorphism); the invariance of the ratio from recrystallization crop to crop in spite of changes in solvent and temperature of recrystallization provides evidence against (though it does not strictly rule out) the possibility that they arise from two crystalline modifications. Support for this analysis is available in the recent X-ray structure of vinyltriphenyltin, $(CH_2{=}CH)SnPh_3$, which was found[4] to adopt two almost enantiomeric forms in the crystal. (See Note Added in Proof.)

On the basis of these examples we propose a few guidelines that may aid in the use of solid-state ^{13}C NMR to identify structural polymorphism of methyltin(IV) compounds or other organometals. For pure polycrystalline methyltin(IV), observation of a larger number of ^{13}C resonances than there are methyls in the molecule,[14] or a ratio of methyl resonance areas inconsistent with the number of methyls in the molecule, indicates the presence of more than one structural modification (it is assumed that the purity of the crystalline sample has been established). For type A polymorphism, the ratio of methyl resonances must be constant, within experimental error, for different crystalline crops and will indicate a (small) integer ratio of isomeric forms in the crystalline modification (1:1 ratios of different structural modifications seem to be most common; large ratios are uncommon or unknown).[15] Routine single-crystal X-ray diffraction studies are capable of

---

(12) Interestingly, we observed only a single ^{13}C resonance for this compound in acetone-d_6 down to temperatures of 185 K, indicating facile interconversion of positions in the twist-boat ring in solution.

(13) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177.

(14) Because of the sensitivity of the ^{13}C chemical shift to slight differences in environment we have generally observed one ^{13}C resonance for each methyl bonded to tin except in cases where the methyls are symmetry-related. See ref 10 and: Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.* **1985**, *107*, 7451.

(15) In the extreme case, bonding interactions between monomeric species in the crystalline state could give rise to dimers (or oligomers). If each of the methyltin(IV) moieties adopts a unique conformation, then there will be a greater number of methyl ^{13}C resonances than expected from the formula of the monomer. As for type A polymorphism, the ratio of methyl ^{13}C resonances should be invariant with recrystallization; single-crystal X-ray diffraction will readily distinguish this type of polymorphism. We have observed such a case for $[Me_2Sn(OAc)]_2O$, which exists as a dimer in the solid state (Lockhart, T. P.; Manders, W. F.; Holt, E. M., submitted for publication).

providing a complete analysis of this case. In contrast, if the ratio of signals varies with crystallization conditions or indicates unusual ratios of methyltin(IV) compounds present in the sample, then the presence of more than one crystalline modification (type B polymorphism) is strongly indicated; isolation of the individual crystalline forms for characterization (by NMR, X-ray, etc.) would provide absolute confirmation of this analysis.

Experimental Section

$[Me_2SnS]_3$ and $MeSnPh_3$ were obtained from commercial sources. $Me_2Sn(S_2CNEt_2)_2$ was prepared according to the published procedure.[6] The purity of different recrystallization crops of these compounds was established by melting point and/or solution ^{13}C NMR. Small, colorless hexagonal plates (orthorhombic modification[8]) of $Me_2Sn(S_2CNEt_2)_2$ were obtained from slow evaporation of a $CHCl_3/EtOH$ solution at room temperature. Mixed crops containing the orthorhombic and the known monoclinic and triclinic modifications were obtained from recrystallizing at reduced temperature or by adding water to the recrystallization solution. Their presence in the mixtures was demonstrated by single-crystal X-ray unit cell determinations. Under no conditions were we able to obtain pure the other crystalline modifications.

Slow crystallization of $[Me_2SnS]_3$ from cyclohexane solution at room temperature gave well-formed octagons which match the description[9a] of the tetragonal form. Recrystallization of *n*-hexane solutions at low temperatures (+5 to −70 °C) gave variable, mixed crops containing small amounts of octagonal crystals (as little as ca. 10%) and larger amounts of small needles and plates. Mixed crops of very small crystals were also obtained by sublimation.[9b] The small size of these crystals prevented separation by hand of amounts (0.1–0.4 g) sufficient for NMR analysis of the individual modifications.

$MeSnPh_3$ as obtained commercially gave a slightly broadened NMR spectrum in which two distinct Me resonances were present. Recrystallization from hydrocarbon solvents gave microcrystalline powders; clear, colorless crystals were obtained upon very slow crystallization from methanol or isopropyl alcohol. Twinning of the crystals prevented successful X-ray analysis.

NMR spectroscopic equipment and methods have been described elsewhere.[10c]

Note Added in Proof. The X-ray structure of allyltriphenyltin has just appeared (Ganis, P.; Furlani, D.; Marton, D.; Tagliavini, G.; Valle, G. *J. Organomet. Chem.* **1985**, *293*, 207). This compound also crystallizes with two independent, though structurally nearly identical molecules in the unit cell.

Registry No. $[Me_2SnS]_3$, 16892-64-1; $Me_2Sn(S_2CNEt_2)_2$, 19413-37-7; $MeSnPh_3$, 1089-59-4.

Contribution from Ames Laboratory
and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Complexes of Rare-Earth Elements with 1,3-Diamino-2-hydroxypropane-*N,N,N′,N′*-tetraacetic Acid

Jack E. Powell,* Daren R. Ling, and Pui-Kwan Tse

Received January 7, 1985

There has appeared a literature summary dealing with 1,3-diamino-2-hydroxypropane-*N,N,N′,N′*-tetraacetic acid (DHPTA) and its complex formation with various metal ions.[1] Thompson et al.,[2] in particular, determined the stabilities of some divalent metal complexes formed with the DHPTA anion at 25 °C and $I = 0.1$ (KNO_3). Their results showed that both normal and protonated complex species existed and that neglect of the latter had contributed to the widely discordant results previously published for alkaline-earth metals. The values obtained were compared with results for trimethylenediamine-*N,N,N′-N′*-tetraacetic acid (TMDTA), and it was concluded that in such complexes, with the possible exception of those of strontium and barium, there is no participation of the OH group in the coordination sphere.

Table I. Anion Protonation Constants of DHPTA and TMDTA at 25 °C and $I = 0.1$ (KNO_3)

	log K_n				
K_n	definition	DHPTA	1	2	TMDTA[9]
K_1	$[HL]/[H][L]$	9.49	9.49	9.49	10.46 − 0.2
K_2	$[H_2L]/[H_2][H]$	7.04	6.36	6.96	8.02 − 0.1
K_3	$[H_3L]/[H_2L][H]$	2.62	2.52	2.60	2.57 + 0.1
K_4	$[H_4L]/[H_3L][H]$	1.47	1.6	∼1.6	1.88 + 0.1

On examining the available literature, we found that someone had been interested in the stabilities of Ln(DHPTA) complexes[2] and that others[3] professed to have studied the complex behavior of DHPTA with rare-earth metals, but we were unable to find any published data.

Experimental Section

Reagents and Apparatus. 1,3-Diamino-2-hydroxypropane-*N,N,N′,N′*-tetraacetic acid was obtained from Aldrich Chemical Co. Approximately 0.1 M $Ln(NO_3)_3$ solutions were prepared by dilution of previously prepared[4] stock solutions and carefully analyzed prior to use.[5] All other chemicals used were of AR grade and all solutions were prepared from deionized water.

A Corning pH meter 130 was used for the pH_c measurements and was calibrated as described elsewhere.[6]

Anion Protonation Constants. The anion's four protonation constants were obtained from pH_c measurements on a series of independently prepared solutions of the ligand acid and carbonate-free KOH. In the final determinations, exactly enough KNO_3 was added to adjust the ionic strength to 0.100 M.

Stability Constants of the Chelate Species. The individual formation constants of the Ln- and Y(DHPTA) species were determined by the usual potentiometric method employed in this laboratory[6] at 25.0 °C and $I = 0.100$ (KNO_3).

Results and Discussion

Anion Protonation Constants. The anion protonation constants obtained are listed in Table I along with data sets reported by two other groups.[1,2] The values coincide well with each other. Comparison of the DHPTA protonation constants with corresponding values for the analogous ligand, trimethylenediamine-*N,N,N′,N′*-tetraacetate (TMDTA), which differs only by having a hydrogen atom in place of the OH, reveals that DHPTA is definitely the more readily dissociated acid.

Stability Constants. A summary of the data obtained in this work is given (along with data for TMDTA and EDTA) in Table II and plots of log K_{ML} vs. crystal ionic radius[7] are compared for DHPTA, TMDTA, EDTA, EEDTA, and BPETA in Figure 1.

As known, the neutralization of DHPTA in the presence of an equivalent amount of rare-earth metal cation indicates release of four protons at a relatively low pH, but a much higher pH is required to release the hydroxyl proton. We are concerned only with complex formation at low pH values, which are ambient in the application of polyamino polycarboxylates to cation-exchange elution separations. Thus DHPTA can be considered to be a tetraprotic acid. Only one species, LnL^-, is prevalent at pH 3–5. For lanthanum, the rare earth having the least affinity for the DHPTA anion, the value of the calculated complex formation constant was observed to vary somewhat with pH, and subsequent

---

(1) Klausen, K. S.; Ruud, O. E. *Anal. Chim. Acta* **1971**, *57*, 351.

(2) Thompson, L. C.; Kundra, S. K. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2945.

(3) Dyatlova, N. M.; Seliverstova, I. A.; Yashunskii, V. G.; Samoilova, O. I. *Zh. Obshch. Khim.* **1964**, *34*, 4003.

(4) Adolphson, M. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1969.

(5) Pribil, R. "Applied Complexometry"; Pergamon Press: Oxford, England, 1982.

(6) Miller, J. H.; Powell, J. E.; Burkholder, H. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1595.

(7) Templeton, D. H.; Dauben, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 5237.

0020-1669/86/1325-0585$01.50/0