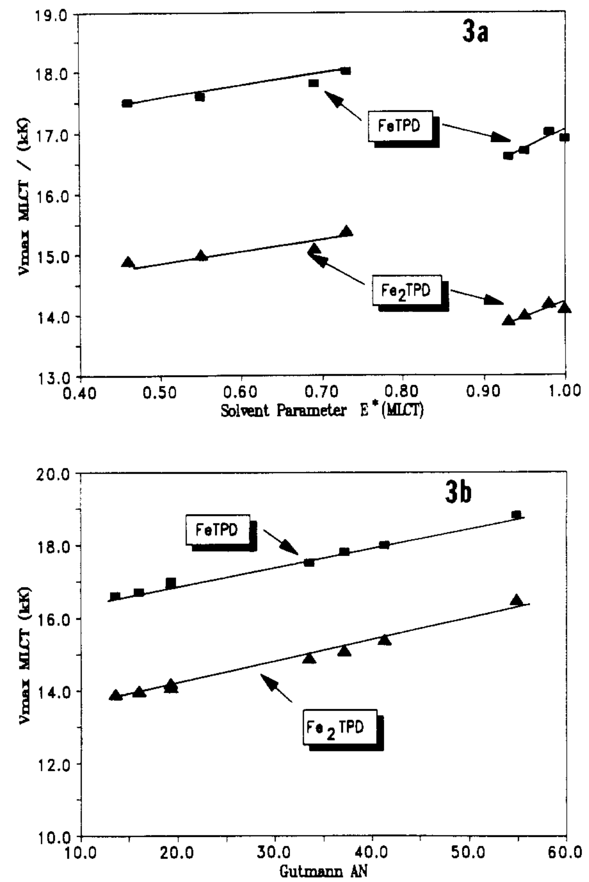

Figure 3. Plots of ν_{max} (kK = 10^3 cm^{-1}) for the lowest energy MLCT peak of $[Fe(CN)_3(tpd)]^-$ (■) and $[(Fe(CN)_3)_2(tpd)]^{2-}$ (▲) ions in various solvents vs (a) E^*_{MLCT} solvent parameter and (b) Gutmann AN.

of the lowest energy MLCT peaks for $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ vs the E^*_{MLCT} solvent parameters[30] for combined alcoholic and aliphatic solvents are nonlinear (Figure 3a). Separation of solvents produces two distinct linear solvatochromic behaviors for both mono- and bimetallic complexes. The discontinuity of $[Fe(CN)_3(tpd)]^-$ and $[(Fe(CN)_3)_2(tpd)]^{2-}$ plots may result from the fact that the E^*_{MLCT} solvent parameter was derived from solvent effects on neutral complexes and does not compensate for enhanced ground-state stabilization due to the polarizability of anionic metal complexes by the very polarizing alcoholic protons. The Gutmann acceptor number, a solvent parameter based on the hardness of the solvent in donor-acceptor interactions,[31] appears to be a more appropriate model for the $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ complexes. A plot of ν_{max} MLCT vs Gutmann AN (Figure 3b) is linear, suggesting that molecular polarizability of the metal complex plays an important role in solvatochromic behavior.[32]

Proton NMR spectra of $[(Fe(CN)_3)_{1,2}(tpd)]^{-,2-}$ were recorded in D_2O (Table III). The bimetallic complex spectrum shows two doublets and two triplets, as expected from the symmetrically coordinated tpd ligand. The two sets farthest downfield at 8.95 and 8.66 ppm are doublets that must be assigned to $H_{6'}$ and $H_{3'}$ on coordinated pyridine rings. In accordance with previous assignments for cyanoiron(II) complexation to pyridine,[33] and tpd when symmetrically coordinated to two metals,[24] the doublet at 8.95 ppm is assigned to $H_{6'}$ and the 8.66 ppm doublet to $H_{3'}$. The triplets at 7.92 and 7.54 ppm are assigned to $H_{4'}$ and $H_{5'}$, respectively, also in agreement with previous assignments. It is of interest to note that, for the $[(Fe(CN)_3)_2(tpd)]^{2-}$ ion, the $H_{3'}$ doublet is shifted downfield with respect to the $H_{4'}$ and $H_{5'}$ triplets, in contrast with the previously reported $[(Ru(tpy))_2(tpd)]^{4+}$ ion, where $H_{3'}$ reported further upfield from $H_{4'}$ and $H_{5'}$ triplets. The downfield shift observed for $H_{3'}$ in the bimetallic cyanoiron(II) complex must be due to increased π-withdrawing effects of the CN^- vs tpy ligand on the metal center. The monometallic complex displays four sets of doublets and four sets of triplets, as expected from protons on the coordinated and noncoordinated rings. Two sets of doublets at 8.82 and 8.74 ppm are assigned to the protons in the coordinated rings as $H_{6'}$ and $H_{3'}$. Doublets at 8.04 and 6.98 ppm are assigned to H_6 and H_3 on the uncoordinated rings. As previously noted for the monometallic ruthenium complex,[23] when the coordinated pyridine and diazine rings are held coplanar, the uncoordinated pyridine ring presumedly rotates out of plane, resulting in an upfield shift of the uncoordinated protons. The observation of H_3 in the $[Fe(CN)_3(tpd)]^-$ complex to be shifted upfield to 6.98 ppm appears to support the previous rationale.

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(30) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825.
(31) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.
(32) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306.
(33) Malin, J. M.; Schmidt, C. F.; Toma, H. E. *Inorg. Chem.* **1975**, *14*, 2924.

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Reformulation of the Hexafluorooctadecatungstate Anion as a Heteropoly Sodate Complex: $[H_2F_6NaW_{18}O_{56}]^{7-}$[†]

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Chauveau, Doppelt, Lefebvre, et al.[1-11] published an elegant and valuable series of papers (1974-1983) on fluoroisopolytungstate complexes, chiefly derivatives of the metatungstate ($[H_2W_{12}O_{40}]^{6-}$) structure, wherein F^- ions replaced various interior isoelectronic O^{2-} ions. In the course of that work they reported[4] the preparation and structure of "$[H_2F_6W_{18}O_{56}]^{8-}$", which is grossly isostructural with the well-known Wells-Dawson[12-14] species α-$[P_2W_{18}O_{62}]^{6-}$ but wherein the P atoms have been replaced by H's and the six most central O atoms have been replaced by F atoms. Their structure proof was based on chemical analyses, similarities of X-ray powder patterns and CV data with those of known Wells-Dawson derivatives, ultracentrifugation, and especially ^1H and ^{19}F NMR spectroscopy.

The present paper modifies their conclusion by showing that a nonexchanging Na^+ ion is enclosed at the very center of the complex, in trigonal-prismatic coordination to its six nearest-neighbor F atoms. (See Figure 1.) So far as we are aware, this is the first case of trigonal-prismatic coordination by hard ligands. We have been unable to form the complex in the absence of Na^+.

In 1973 our laboratory reported[15] the first polytungstate complexes containing fluoride ions substituted for oxide ions. We subsequently unequivocally established[16-18] those complexes and others as comprising a series of isomorphous heteropoly d,l-α_1-aquometalloheptadecatungstopolyfluorosodates, d,l-α_1-$[(H_2O)M^{n+}O_5H_2F_6NaW_{17}O_{50}]^{(11-n)-}$, wherein M^{n+} = Co^{2+}, Co^{3+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, or Mn^{3+}. The detailed structure proof was based primarily on ^{23}Na, ^{19}F, ^1H, and ^{183}W NMR spectroscopy, a complete X-ray structure, and isotope-exchange studies. That proof is contained in a dissertation[16] and has been presented at an international heteropoly symposium.[18] It will be the subject of a forthcoming detailed major paper. The 18-tungstohexafluorosodate complex which is the subject of this paper turned out to be an isomorph of the α_1-aquometalloheptadecatungsto-

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[†] Abstracted from a portion of the Ph.D. dissertation of Thomas L. Jorris, Georgetown University, 1987.

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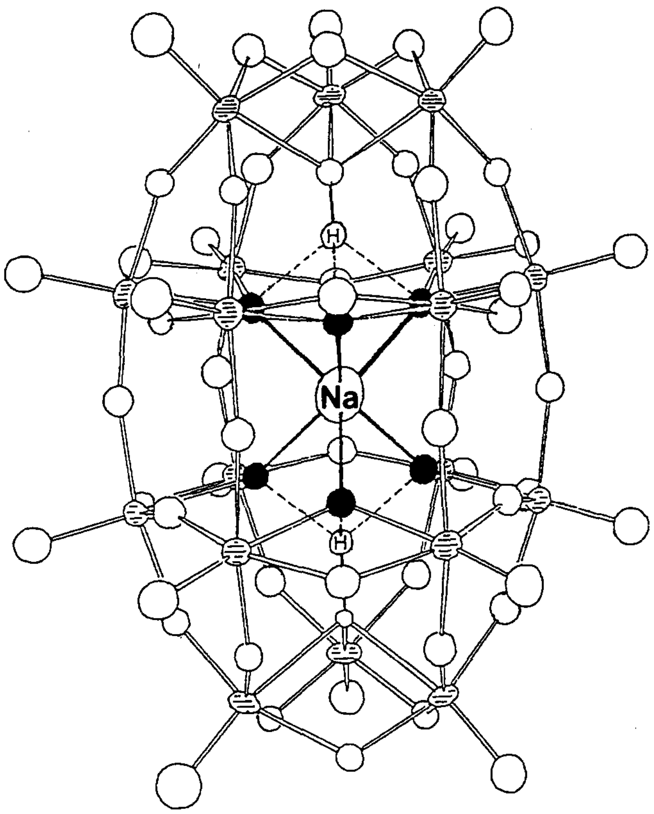

Figure 1. Structure of the $[H_2F_6NaW_{18}O_{56}]^{7-}$ complex. Open circles locate centers of O atoms, shaded circles locate centers of W atoms, and blackened circles locate centers of F atoms. The trigonal prism of F atoms surrounding the Na is indicated, and an H atom is located over each end of the prism.

polyfluorosodates. Therefore the X-ray results, ^{23}Na NMR spectroscopy, and ^{22}Na-exchange studies on those heteropoly species substantiate and confirm the present report.

Experimental Section

Preparation and Purification. Preparation of the potassium salt of the 6-fluoro-18-tungsto complex was fundamentally by the method worked out by the French authors.[4] An aqueous mixture of HF and HCl solutions is heated with a solution of Na_2WO_4. The mixture is cooled and filtered, and more of the two halogen acids is added. A Drechsel ether extraction at 0 °C gives an ether solution from which the free acid of the complex crystallizes upon evaporation. It is recrystallized three or four times from water. Addition of concentrated KCl or $N(CH_3)_4Cl$ solution to a solution of recrystallized free acid precipitates the potassium or tetramethylammonium salt of the complex. These products were *not* recrystallized in the original work.

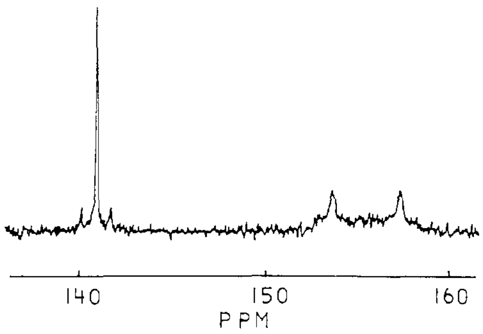

Figure 2. ^{183}W NMR spectrum of $Li_7[H_2F_6NaW_{18}O_{56}]$ solution in D_2O. Standard frequency = 12.505 MHz; no. of scans = 2065; sweep width = 830.6 Hz.

Our ^{19}F NMR spectrum of the four-times-recrystallized free acid in D_2O shows primarily the single intense peak reported earlier,[4] but our spectrum covers a moderately broader chemical shift range than that originally shown[4] and clearly reveals a number of lines (collectively of substantial intensity) attributable to one or more impurities.

Recrystallization of the precipitated potassium salt results in separation of a white crystalline impurity from the crystals of the desired light greenish product. The white crystals comprise about 10% of the product. Impurities could still be detected in a D_2O solution of the once-recrystallized light green crystals by use of high amplification of the ^{19}F NMR spectrum. Further recrystallization of the greenish product was necessary to obtain pure material showing only the single resonance.

Since the Li salt of the complex is more soluble than the other salts mentioned, all the NMR spectra discussed below were obtained with solutions of the Li salt, prepared by metathesis from a solution of the purified K salt by addition of a 2-fold excess of $LiClO_4$.

All NMR spectra were obtained on a Bruker AM300 WB NMR spectrometer.

Although it has been suggested[19] that NaBr solutions be used as the chemical shift standard for ^{23}Na NMR spectroscopy, other studies[20,21] have shown that considerable effects of solvent, concentration, and anion on chemical shift were most pronounced in the cases of large anions such as I^- and Br^-. These studies showed that the ^{23}Na NMR chemical shifts for solutions of $NaClO_4$ in D_2O were least subject to these variations. Accordingly, the ^{23}Na NMR spectra of the polyfluoropolytungstate complexes were recorded in D_2O by the sample replacement method with 2 M $NaClO_4$ in D_2O as the external chemical shift reference standard.

Results and Discussion

The above-described evidence of impurities accounts for the incorrect analyses in the original paper,[4] which appeared to show 8.0 H^+ or K^+ or $N(CH_3)_4{}^+$ per 18 W atoms. The same incorrect proportion of cations had probably carried through from impurities in the free acid.

^{183}W NMR Spectroscopy. Our ^{183}W NMR spectrum (Figure 2) is consistent with the spectrum described by Chauveau in the text of her 1986 review,[11] but the spectrum shown for this complex in that review (Figure 8) was evidently accidentally replaced by the spectrum of a different compound. Our ^{183}W NMR spectrum exhibits a sharp ($\Delta\nu_{1/2} < 1$ Hz) six-tungsten signal (occurring at −141.0 ppm and showing 20-Hz W–W satellites) originating from the six structurally equivalent W's in the two W_3O_{13} caps at the ends of the Wells–Dawson-type structure of $[H_2F_6NaW_{18}O_{56}]^{7-}$. (See Figure 1.) Those W's are relatively distant from the F atoms. In addition, there is a twelve-tungsten signal from the twelve structurally equivalent belt W's (integration ratio to the six-tungsten peak = 1.99). Each of those belt W's has one F atom as one of its nearest neighbors, so that the signal is split into peaks at 153.6 ppm and at 157.3 ppm ($^1J_{WF}$ = 46 Hz). A notable feature

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(1) Chauveau, F.; Souchay, P. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1761.
(2) Launay, J.-P.; Boyer, M.; Chauveau, F. *J. Inorg. Nucl. Chem.* **1976**, *38*, 243.
(3) Chauveau, F.; Doppelt, P.; Lefebvre, J. *J. Chem. Res., Synop.* **1978**, 130; *J. Chem. Res., Miniprint* **1978**, 1727.
(4) Chauveau, F.; Doppelt, P.; Lefebvre, J. *Inorg. Chem.* **1980**, *19*, 2803.
(5) Chauveau, F.; Doppelt, P.; Lefebvre, J. *J. Chem. Res., Synop.* **1981**, 155; *J. Chem. Res., Miniprint* **1981**, 1937.
(6) Doppelt, P.; Lefebvre, J. *Nouv. J. Chim.* **1981**, *5*, 463.
(7) Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589.
(8) Chauveau, F.; Doppelt, P.; Lefebvre, J. *Polyhedron* **1982**, *1*, 263.
(9) Sanchez, C.; Livage, J.; Doppelt, P.; Chauveau, F.; Lefebvre, J. *J. Chem. Soc., Dalton Trans.* **1982**, 2439.
(10) Chauveau, F.; Doppelt, P.; Lefebvre, J. *Bull. Soc. Chim. Fr.* **1983**, 197.
(11) Chauveau, F. *Bull. Soc. Chim. Fr.* **1986**, 199.
(12) Wells, A. F. *Structural Inorganic Chemistry*, 1st ed.; Oxford University Press: Oxford, U.K., 1945; p 344.
(13) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113.
(14) D'Amour, H. *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 729.
(15) Baker, L. C. W. *Proc. Int. Conf. Coord. Chem. 15th* **1973** (portion of plenary lecture, on work by L. C. W. Baker and I. Todorut).
(16) Jorris, T. L. Doctoral Dissertation, Georgetown University, 1987.
(17) Marcu, Gh.; Ciogolas, I.; Todorut, I. *Rev. Roum. Chim.* **1979**, *24*, 715.
(18) Baker, L. C. W.; Jorris, T. L.; Todorut, I.; Jameson, G. B. *Abstracts of Papers presented at the Symposium on Heteropolyanions and Their Catalytic Properties*, Third Chemical Congress of the North American Continent, Toronto, 1988.
(19) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981.
(20) Line, J. D.; Popov, A. *J. Am. Chem. Soc.* **1981**, *103*, 3773.
(21) Detellier, C.; Laszlo, P. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1081.

not explained by Chauveau is the broadening of the peaks of the twelve-tungsten signal ($\Delta\nu_{1/2}$ = 5.2 Hz for each). (See Figure 2.) We attribute this otherwise unexplained broadening to the proximity of these W's to the quadrupolar ^{23}Na atom within the complex. The same effect of broadening of belt W signals was observed in the diamagnetic $[(H_2O)ZnO_5H_2F_6NaW_{17}O_{50}]^{9-}$ complex, which undoubtedly contains a central Na^+ ion as explained below. No such broadening of signals from belt W's is observed for conventional Wells-Dawson complexes.[22-25]

^{19}F and ^1H NMR Spectroscopy. Our ^{19}F and ^1H NMR spectra and their interpretations confirmed those given by Chauveau et al.[4] The six structurally equivalent F atoms are at the vertices of the interior trigonal prism. The two F_3O tetrahedra, each formed by the three coplanar F atoms of one end of the F_6 prism and the one remaining interior O atom at the same end of the complex, contain one H atom apiece. See Figure 1. In each F_3O tetrahedron we conclude that the single H is covalently bonded to the O and H-bonded to F. At a given instant the H is probably preferentially H-bonded to a given F, but the exchange of the H's position relative to the three F atoms is rapid, and the resulting ^{19}F NMR signal coalesces to a single resonance (split by H-F coupling to a doublet). The ^1H NMR signal is a quartet owing to the presence of the three neighboring F atoms adjacent to each H. The quartet collapses to a singlet when F is decoupled.

Since each F atom is a nearest neighbor of the quadrupolar Na atom, the ^{19}F NMR signal is markedly broadened. The H-decoupled ^{19}F NMR spectra reported by Chauveau et al. show $\Delta\nu_{1/2} \cong 20$ Hz[4] for the 18-tungstosodate, but $\Delta\nu_{1/2}$ is only ~2 Hz[3] for the F's in $[HF_3OW_{12}O_{36}]^{4-}$, which contains no Na but has the F's in the same sort of HF_3O tetrahedron. This additional previously unexplained difference in line widths also substantiates the presence and location of the Na atoms. The H-decoupled ^{19}F spectrum of the 12-tungsto complex shows clearly resolved W-F coupling.[3] The W-F coupling is undetectable in the H-decoupled ^{19}F NMR spectrum of the 18-tungstosodate[4] owing to the broadening of the signal.

^{23}Na NMR Spectroscopy. ^{23}Na NMR spectroscopy in general exhibits only a very small relative chemical shift range (about 30 ppm). ^{23}Na, being quadrupolar, produces a broad NMR line when the Na atom is in an unsymmetrical environment and a sharp line when it is in a centrosymmetric site (as is the case for hydrated simple Na^+ in water).

Since a trigonal prism is not centrosymmetric, the ^{23}Na NMR signal from the $[H_2F_6NaW_{18}O_{56}]^{7-}$ complex consists of a single symmetrical broad peak ($\Delta\nu_{1/2} \cong 2500$ Hz) centered at 4.2 ppm. This was not detectably different from the ^{23}Na signal for the Zn-substituted isomorph, α_1-$[(H_2O)ZnO_5F_6NaW_{17}O_{50}]^{9-}$, at the same concentration. Addition of simple $^{23}Na^+$ to the solution produces a relatively sharp spike ($\nu_{1/2}$ = 25 Hz) superimposed on the broad signal and centered at 0.19 ppm. The area of the sharp spike is proportional to the concentration of simple $^{23}Na^+$ present.

Other Evidence. The X-ray crystal structure determination of α_1-$(NH_4)_9[(H_2O)ZnO_5H_2F_6NaW_{17}O_{50}]\cdot 9H_2O$ revealed electron density at the center of the complex corresponding to one Na^+. Since that was a special crystallographic position, which might conceivably have accumulated errors to produce the apparent electron density as an artifact, a refinement based on omitting the Na^+ was run. This resulted in significant increase of *R*, substantiating the reality of the electron density.

The potassium salt of the Zn-substituted isomorph was prepared in the presence of radioactive $^{22}Na^+$ and purified. Precipitation of the radioactive complex with excess guanidinium ion resulted in all of the radioactivity, in the expected amount, being found in the precipitate. Exchange of $^{22}Na^+$ in the dissolved complex with excess $^{23}Na^+$ in solution for various time periods and at various temperatures was attempted. Even after the complex was allowed to stand for 1 week with excess $^{23}NaCl$ in solution at 60 °C, all of the radioactivity was still found in the complex after its precipitation.

Because the diamagnetic Zn-substituted complex is an isomorph of the subject $[H_2F_6NaW_{18}O_{56}]^{7-}$, these experiments taken with the identical broad ^{23}Na NMR spectra and the identical broadening of the signals from the belt W's substantiate the presence of one Na^+ at the center of each complex.

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(22) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267; **1982**, *104*, 5384.

(23) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478.

(24) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777.

(25) Jorris, T. L.; Kozik, M.; Casañ-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402.

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Unusual Addition of the Indium-Butyl Bond to Organotin Oxides. Preparation and Characterization of Novel Dibutylindio- or Butyl(propionyloxy)indio-Substituted Stannoxanes

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Many organotin oxides are known to form μ-oxo-bridged aggregates[1] and are useful as reagents or catalysts in the field of synthetic chemistry.[2] Modification of these organometallic polymers or oligomers by replacing some of the tin atoms in the chains with other metallic species might lead to more sophisticated reagents, catalysts, and especially precursors for ceramics and electronics.[3] Several metallorganic polymers have been extensively studied for this purpose.[4] Here we describe the modification of organotin oxides by treating with tributylindium or dibutylindium propionate (**1**), aiming to prepare an effective precursor for highly conductive and transparent indium-tin oxide thin films.

Experimental Section

Analysis. IR and ^1H and ^{13}C NMR spectra were recorded on a Hitachi 260-30 spectrophotometer, and on a Hitachi R90H FT spectrometer, respectively. Fast-atom-bombardment (FAB) and electron-impact (EI) mass spectra were obtained with a JEOL JMS-DX303 instrument with a JEOL JMA-DA5000 data processing system (Faculty of Engineering, Osaka University). Molecularity was measured by using a Corona 117 type vapor pressure osmometer (VPO) calibrated by benzil. Contents of indium and tin in the indiostannoxanes were determined with a Rigaku ultratrace 0600 X-ray fluorescence analyzer. Thermal analysis was done by means of a SEIKO TG-DTA 20 type analyzer.

Materials. All organotin oxides were from commercial sources. Solvents and other reagents were used after distillation or recrystalliza-

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(1) Davies, A. G.; Smith, P. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1980; Vol. 2, pp 573-577.

(2) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 297-299. (b) Molloy, K. C. *Chemistry of Tin*; Harrison, P. G. Ed.; Blackie: London, 1989; pp 191-192, 199-202.

(3) Wynne, K. J. *Inorganic and Organometallic Polymers*; Zedlin, M, Wynne, K. J., Allcock, H. R., Ed.; American Chemical Society: Washington DC, 1988; pp 1-4.

(4) The generally so-called "Sol-gel process" uses partially hydrolyzed metal alkoxides as starting materials; see, for example: (a) Dislich, H. *Angew. Chem.* **1971**, *83*, 428. (b) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893. (c) Fischer, J.; Kress, J.; Osborn, J. A.; Ricard, L.; Wesolek, M. *Polyhedron* **1987**, *6*, 1839. (d) Chisholm, M. H. *J. Organomet. Chem.* **1987**, *334*, 77. (e) Hirashima, Y.; Nishiwaki, K.; Miyakoshi, A.; Tsuiki, A.; Ueno, A.; Nakabayashi, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1945. (f) Sharma, H. K.; Kapoor, P. N. *Polyhedron* **1988**, *7*, 1389.

0020-1669/90/1329-4586$02.50/0