a range of monocarbon carborane cage systems. In particular, I was found to undergo cage closure and cage capping reactions similar to those that had previously been observed for 9-SMe$_2$-7-[(Me$_3$Si)$_2$CH]CB$_{10}$H$_{11}$.[6,7]

Thus, reaction of I with NaH results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the known *closo*-CB$_{10}$H$_{11}^-$ anion IVa. Likewise, thermolysis of I was found to result in hydrogen loss to yield a single product, *closo*-4-SMe$_2$-2-CB$_{10}$H$_{10}$ (III) in high yield. On the basis of the similarity of its spectral data with that obtained for *closo*-4-SMe$_2$-2-[(Me$_3$Si)$_2$CH]-CB$_{10}$H$_{10}$, III is proposed to adopt a structure based on a dodecahedron in which the dimethyl sulfide is bound at the 4-boron position.

$$\textit{nido}\text{-8-Me}_2\text{S-7-CB}_{10}\text{H}_{12} + \text{NaH} \rightarrow \textit{closo}\text{-2-CB}_{10}\text{H}_{11}^- + \text{H}_2 + \text{SMe}_2 \qquad (6)$$

$$\textit{nido}\text{-8-Me}_2\text{S-7-CB}_{10}\text{H}_{12} \xrightarrow{\Delta} \textit{closo}\text{-4-SMe}_2\text{-2-CB}_{10}\text{H}_{11} + \text{H}_2 \qquad (7)$$

In a reaction related to that previously found for 7-Me$_3$N-7-CB$_{10}$H$_{12}$,[12a] the dehydro capping of the open face of I was accomplished by reacting the carborane with tributylphosphine–borane to yield the known closo anion CB$_{11}$H$_{12}^-$ in 80% yield (eq 8). Likewise, the reaction (eq 9) of I with cyclopentadienylnickel

$$\text{8-SMe}_2\text{-7-CB}_{10}\text{H}_{12} + (n\text{-C}_4\text{H}_9)_3\text{P}\cdot\text{BH}_3 \rightarrow [\text{LH}]^+[\text{CB}_{11}\text{H}_{12}]^- + \text{H}_2 + \text{SMe}_2 \qquad (8)$$

$$\text{8-SMe}_2\text{-7-CB}_{10}\text{H}_{12} + \tfrac{1}{2}[(\eta\text{-C}_5\text{H}_5)\text{NiCO}]_2 \rightarrow \text{2-}(\eta\text{-C}_5\text{H}_5)\text{-2,1-NiCB}_{10}\text{H}_{11} + \text{CO} + \tfrac{1}{2}\text{H}_2 + \text{SMe}_2 \qquad (9)$$

carbonyl dimer resulted in the formation of the known[11] metallacarborane 2-(η-C$_5$H$_5$)-2,1-NiCB$_{10}$H$_{11}$.

The formation of V may be envisioned via a dehydro insertion of the (η-C$_5$H$_5$)Ni onto the open face of carborane I, followed by dissociation of the dimethyl sulfide bound to the cage, to produce the formal RCB$_{10}$H$_{10}^{3-}$ ligand.

Acknowledgment. We thank the National Science Foundation for the support of this work. We also thank Drs. George Furst and Pat Carrol for their assistance in obtaining the NMR and X-ray crystallographic data.

Supplementary Material Available: Tables of anisotropic temperature factors, bond angles, and least-squares planes (6 pages); a listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Influence of Electronic Configuration on the Structure and Optical Properties of KSnOPO$_4$

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Introduction

Potassium titanyl phosphate (KTiOPO$_4$, or KTP) has become the material of choice for second-harmonic generation (SHG) from Nd:YAG laser light at 1.064 μm and has also demonstrated considerable utility for nonlinear optical (NLO) and electrooptical (EO) applications such as sum and difference frequency mixing (SFG), optical parametric oscillation (OPO), and electrooptic switching.[1] The KTP structures is acentric and consists of one-dimensional chains of TiO$_6$ octahedra linked by phosphate tetrahedra to give a three-dimensional network. The cations lie in channels parallel to the [001] direction. In the chain, the TiO$_6$ groups share corners to link up alternately as cis and trans with respect to the central Ti atom. These Ti–O bonds are alternately short (<1.75 Å) and long (>2.10 Å) through the chain, and each short Ti–O bond is trans to a long bond.[2] The long–short nature of the bridging Ti–O bonds leads to a picture of the TiO$_6$ unit as a distorted octahedron in which the Ti atom has been displaced from the geometric center. Several theories point to distortion of the MO$_6$ unit from perfect octahedral symmetry as the source of second-order nonlinearity in KTP and other metal oxide systems with distorted octahedral geometries such as perovskites, LiNbO$_3$, and tungsten bronzes. In all models, the degree of distortion of the MO$_6$ group strongly influences NLO susceptibility.[3]

In a study of phase-matching properties of crystals with the general formula KTi$_{1-x}$Sn$_x$OPO$_4$, Jarman and Grubb determined that KSnOPO$_4$ has no measurable SHG intensity.[4] It was postulated that the "second-order Jahn–Teller" effect responsible for MO$_6$ distortion in KTP is weakened or nullified by the d^{10} electronic configuration of tin(IV), eliminating any net contribution to the bulk susceptibility tensor $\chi(2)_{ijk}$ from the Sn–O bonds.[4] However, it is not immediately apparent whether this electronic influence should merely result in a loss of short M–O bonds, as is the case in the compound KGaPO$_4$F$_{0.7}$(OH)$_{0.3}$,[5] or if substitution results in crystallization in a centric space group, as is the case in the high-temperature ($T > T_c$) form of TlTiOPO$_4$.[6]

In this work, the effects of d^{10} metal substitution on the electronic and structural properties of KTP are examined by using X-ray crystallography, SHG intensities, and UV spectral data. Changes in band energies and in the degree of mixing of bonding (valence band) and antibonding (charge-transfer band) MOs are used to explain the resulting structural and optical properties.

Experimental Section

Synthesis. Crystals of KSnOPO$_4$ were grown from a phosphate flux with a K:P ratio of 1.33:1, prepared by fusing 0.067 mol of KH$_2$PO$_4$ (Fisher) and 0.033 mol of K$_2$HPO$_4$·3H$_2$O (Mallinckrodt). To this was added 0.010 mol of SnO$_2$ (Alfa), and the mixture was heated at 1125 °C in a Pt crucible. The SnO$_2$ reacted swiftly with the phosphate flux to yield KSnOPO$_4$, which was allowed to remain in contact with the flux for 10 days to ensure its saturation. The resulting melt was poured off from the undissolved KSnOPO$_4$, reheated to 1125 °C and then cooled to 750 °C over 24 h. Small KSnOPO$_4$ crystals precipitated from the melt. After the flux was poured off, the crystals were washed with hot water and recovered by filtration. The crystals were colorless pinacoidal prisms, typically 0.2–0.5 mm on edge. Many crystals contained flux inclusions; yield was 0.028 g. KSnOPO$_4$ that had not dissolved in the initial melt was worked up in identical fashion, resulting in powder consisting of white grains approximately 50 μm in diameter.

A finer grained KSnOPO$_4$ powder was obtained via a gel synthesis technique in which 1.00 g of K$_2$SnCl$_6$[7] was treated with 2.74 g of K$_2$HPO$_4$·3H$_2$O in 5.0 mL of H$_2$O to form a hydrogel, which was sealed in a Teflon bag and autoclaved at 200 °C at autogenous pressure for 5 days. After cooling, the resulting suspension was filtered and air-dried. KSnOPO$_4$ powder was obtained in quantitative yield. This material consisted of tetragonal microcrystals approximately 4 μm long and 2 μm wide, both as individual pieces and in clusters.

Structure Solution. A single crystal devoid of inclusions with approximate dimensions 0.5 × 0.4 × 0.15 mm was mounted on a glass fiber with epoxy prior to data collection on an automated Huber four-circle X-ray diffractometer (graphite-monochromated Mo Kα radiation, λ =

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Table I. Crystallographic Data for $KSnOPO_4$

formula of asymmetric unit: $K_2Sn_2P_2O_{10}$	fw: 537.51
a = 13.170 (2) Å	space group: $Pna2_1$ (No. 33)
b = 6.5387 (9) Å	T = 22 °C
c = 10.745 (1) Å	λ = 0.71069 Å
$\alpha = \beta = \gamma$ = 90°	ρ_{calc} = 3.86 g/cm^3
cell vol = 925.24 Å^3	μ = 67.0 cm^{-1}
Z = 8	$R(F_o)$ = 3.05%, $R_w(F_o)$ = 3.08%
transm coeff: 0.0830–02096	

Table II. Final Atomic Positional and Thermal Parameters for $KSnOPO_4$

atom	x/a	y/b	z/c	U(iso), Å^2
K(1)	0.3757 (2)	0.7771 (3)	0.3135 (4)	0.0193
K(2)	0.1091 (2)	0.6937 (4)	0.0718 (4)	0.0247
Sn(1)	0.37295 (3)	0.49790 (9)	0.0111 (3)	0.0064
Sn(2)	0.24874 (5)	0.2540 (1)	0.2616 (3)	0.0067
P(1)	0.5011 (2)	0.3413 (3)	0.2619 (5)	0.0077
P(2)	0.1759 (1)	0.5009 (4)	0.5142 (6)	0.0077
O(1)	0.487 (1)	0.487 (1)	0.149 (1)	0.0082
O(2)	0.515 (1)	0.478 (2)	0.378 (1)	0.0130
O(3)	0.4074 (5)	0.205 (1)	0.2842 (8)	0.0109
O(4)	0.5927 (5)	0.201 (1)	0.2400 (8)	0.0121
O(5)	0.1056 (5)	0.316 (1)	0.5369 (8)	0.0099
O(6)	0.1079 (6)	0.687 (1)	0.4901 (9)	0.0120
O(7)	0.2440 (9)	0.531 (2)	0.628 (1)	0.0117
O(8)	0.2495 (9)	0.471 (2)	0.405 (1)	0.0114
O(9)	0.272 (1)	0.484 (2)	0.149 (1)	0.0136
O(10)	0.2348 (9)	0.033 (2)	0.387 (1)	0.0096

0.71069 Å), interfaced to a DEC MicroVAX-II computer with Crystal Logic stepping motor controllers. The orthorhombic unit cell constants were determined from 22 centered reflections and refined by least squares to final values of a = 13.169 (2), b = 6.5387 (8), and c = 10.745 (1) Å. Intensity data were collected at 22 °C by using the θ–2θ scan method with a scan rate of 6°/min, from 1.3° below Kα_1 to 1.6° above Kα_2. All reflections were in the octant $+h,+k,+l$. Measurements were made out to 65° in 2θ, giving a total of 2011 reflections. Systematic absences indicated two possible space groups: acentric $Pna2_1$, as found for other KTP isostructures, or centric $Pnam$. Three reflections monitored every 100 observations showed no systematic trends. During data reduction, the observations were corrected for absorption by using the method of Busing and Levy[8] (μ = 67.0 cm^{-1}). A total of 1685 independent reflections were considered observed on the basis of the criterion $I > 3\sigma(I)$. The KTP structure was used as a starting model in the space group $Pna2_1$, and the final anisotropic refinement on F converged to give agreement values of R = 3.05% (R_w = 3.08%) for 147 parameters. The polarity of the structure was established unambiguously by including the Flack polarity parameter in the final cycles of refinement.[9] No chemically reasonable starting model could be established in the centric space group. All least-squares and subsidiary calculations were performed by using the Oxford CRYSTALS system.[10] A Larson-type isotropic secondary extinction correction (refined value 341) was included in the final cycles of refinement.[11] A list of crystallographic data for $KSnOPO_4$ is presented in Table I, and final observed and calculated structure factors are available as supplementary material.

The $KSnOPO_4$ powder was characterized by X-ray powder diffraction using a Scintag automated θ–θ powder diffractometer and Cu Kα radiation (λ = 1.5418 Å). The pattern was indexed on the basis of the single-crystal unit cell constants, and refined lattice parameters and esd's were obtained by using Scintag routines.

Optical Measurements. SHG intensity data were obtained on powder samples at room temperature with 1.064-μm pump radiation by using a system similar to that described by Dougherty and Kurtz.[12] Data were obtained from samples of uniform crystallite size; both the powder and 50-μm crystals were tested. Visible light resulting from sample irradiation was collected in transmittance, and the intensity of the second-harmonic light from the sample was measured relative to the SHG intensity at the reference channel. A Kigre MK-367 Nd:YAG laser was the source of the 1.064-μm light, producing 20-mJ, 4-ns pulses in the single-shot mode. Intensities were measured by using a Tektronix 2467B 400-MHz oscilloscope with a DCS01 digitizing camera system. UV spectra data were recorded on powder samples with a Cary 14 UV–visible–IR spectrophotometer operating in the diffuse-reflectance mode.

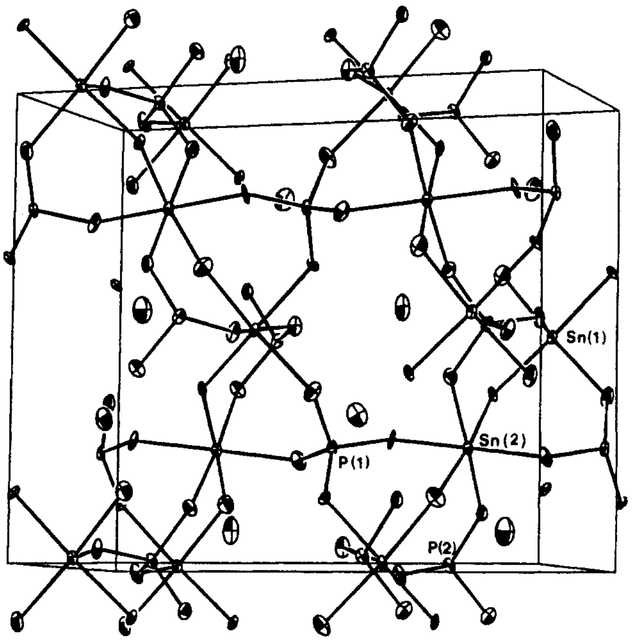

Figure 1. Oblique view of the $KSnOPO_4$ (010) plane showing SnO_6 chains along [011] and [0$\bar{1}$1].

Table III. Selected Bond Distances (Å) and Angles (deg) for $KSnOPO_4$

Sn(1)–O(1)	2.113 (8)	Sn(1)–O(6)	2.061 (5)
Sn(1)–O(2)	2.069 (9)	Sn(1)–O(9)	1.980 (9)
Sn(1)–O(5)	2.114 (5)	Sn(1)–O(10)	1.974 (8)
Sn(2)–O(3)	2.126 (5)	Sn(2)–O(8)	2.087 (9)
Sn(2)–O(4)	2.089 (5)	Sn(2)–O(9)	1.963 (8)
Sn(2)–O(7)	2.054 (9)	Sn(2)–O(10)	1.974 (8)
P(1)–O(1)	1.552 (9)	P(1)–O(3)	1.540 (5)
P(1)–O(2)	1.54 (1)	P(1)–O(4)	1.531 (5)
P(2)–O(5)	1.543 (5)	P(2)–O(7)	1.535 (9)
P(2)–O(6)	1.538 (5)	P(2)–O(8)	1.532 (9)
K(1)–O(1)	2.984 (8)	K(1)–O(7)	3.041 (9)
K(1)–O(2)	2.768 (9)	K(1)–O(8)	2.780 (8)
K(1)–O(3)	2.847 (6)	K(1)–O(9)	2.95 (1)
K(1)–O(5)	3.003 (6)	K(1)–O(10)	2.611 (7)
K(2)–O(1)	2.754 (8)	K(2)–O(7)	2.992 (8)
K(2)–O(3)	3.112 (7)	K(2)–O(8)	3.163 (9)
K(2)–O(4)	3.159 (6)	K(2)–O(9)	2.677 (8)
K(2)–O(5)	2.853 (6)	K(2)–O(10)	3.055 (9)
O(9)–Sn(1)–O(10)	91.8 (2)	Sn(1)–O(9)–Sn(2)	127.1 (4)
O(9)–Sn(2)–O(10)	175.1 (5)	Sn(1)–O(10)–Sn(2)	127.6 (4)

Results

Structure. Final atomic positions with isotropic temperature factors are reported in Table II. The structure of $KSnOPO_4$ is quite similar to that of KTP, with SnO_6 chains parallel to [011] and [0$\bar{1}$1] linked by PO_4 tetrahedra (Figure 1). There are two $KSnOPO_4$ formula units in the asymmetric unit and four asymmetric units per unit cell. The two Sn atoms share O(9) and O(10) in the chain, with the O(9)–Sn(1)–O(10) bond approximately cis and the O(9)–Sn(2)–O(10) bond nearly trans (Table III). The other eight oxygen atoms are involved in Sn–O–P links with either of the crystallographically independent PO_4 groups. The potassium atoms coordinate irregularly with the framework oxygen atoms, with K(1) 8-coordinate within 3.2 Å and K(2) 9-coordinate within

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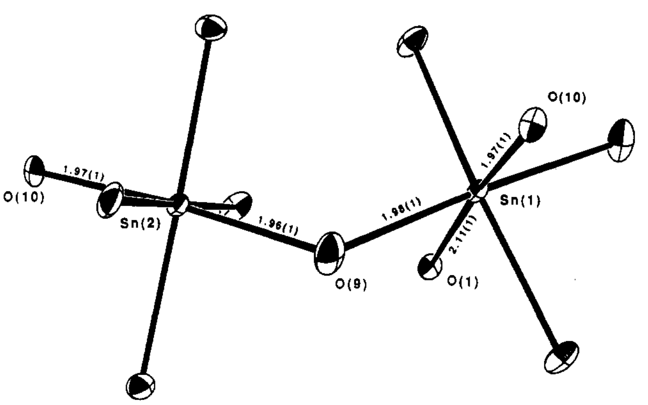

Figure 2. Sn coordination environment in the $KSnOPO_4$ asymmetric unit.

the same radius. The cation–framework interaction is therefore very similar to that seen in KTP, in which coordination numbers of 8 and 9 for K(1) and K(2), respectively, are also seen.

Unlike the case of KTP, the bridging Sn–O distances are nearly identical, and no short Sn–O bonds exist (Figure 2). Some degree of asymmetry in the Sn coordination environment exists, however, and it is evident that $KSnOPO_4$ adopts the less distorted MO_6 coordination environment typified in the compound $KGaPO_4F_{0.7}(OH)_{0.3}$, rather than crystallizing in a centric modification of the KTP structure such as the high-temperature $TlTiOPO_4$ phase.

Optical Properties. The SHG intensity of $KSnOPO_4$ powder from flux is less than that of quartz, though the presence of spurious light induced by laser damage precluded precise measurement, even at low power levels. The powder samples obtained from hydrogels, however, were not damaged even at moderate powder levels. These samples yielded SHG intensities of approximately half that of quartz ($\approx 10^{-4}$ × KTP's intensity). This result reveals the presence of nonzero $\mathbf{d}_{ijk}$ tensor coefficients in $KSnOPO_4$, which indicates our selection of the acentric starting model during structure refinement is justified.

The UV spectrum of $KSnOPO_4$ shows an absorption edge at 225 nm, corresponding to a ligand-to-metal charge-transfer (LMCT) transition with an E_g of 5.5 eV. In contrast, KTP's absorption edge lies at 350 nm or 3.5 eV. The difference in band gap is due to the presence in KTP of empty 3d orbitals of e_g symmetry into which ligand-to-metal charge transfer may occur. In $KSnOPO_4$, all of the 4d orbitals are filled, and the charge-transfer band consists mainly of 5d orbital character.

Discussion

In the octahedral MO_6 unit, such as that found in KTP isostructures, oxygen pπ and metal dπ orbitals mix to form bonding, nonbonding, and antibonding orbitals of g, u, and g symmetries, respectively. The existence of long–short metal–oxygen bonding in KTP can be understood as a stabilization of a distorted ground state formed by mixing orbitals of g and u symmetries. This mixing results in incorporation of a certain amount of charge-transfer excited-state character into the valence-bond orbitals, the amount of which is defined by the mixing coefficients, which are influenced by the magnitudes of E_g and of the overlap integrals. These mixing coefficients determine not only the degree of distortion but the molecular hyperpolarizability β_{ijk} of the MO_6 unit as well.[13,14] On substitution of a d^{10} species, the metal dπ (e_g) orbitals are filled. Thus, the ground-state orbitals can now mix only with the excited-state metal dπ orbitals of the next highest quantum number (5d, in the case of $KSnOPO_4$).[4] The band gap energy is increased, and the degree of mixing and thus the charge-transfer character in the ground state are reduced. Less stabilization of the ground state is thus attained on distortion. Consequently, all Sn–O bonds are nearly of the same length, and contribution of the MO_6 unit to $\chi^{(2)}_{ijk}$ is drastically reduced.

In the compound $KSnOPO_4$, all of these predictions of the effects of d^{10} metal ion substitution are realized. The band gap energy E_g is increased, reducing the mixing coefficient between the ground and excited states. As a direct result, the stabilization attained on asymmetric distortion is less, and the Sn–O bonding is much more regular than it is in KTP. Furthermore, the increased band gap results in diminished mixing of excited-state character in the ground-state SnO_6 bonding orbitals, and the optical nonlinearity of the medium is sharply attenuated.

Note Added in Review. Voronkova and Yanovskii have recently reported an anomaly in the dielectric susceptibility of $KSnOPO_4$ between 900 and 1000 °C, which can be explained by a second-order ferroelectric-to-paraelectric phase transition with a Curie temperature between 1040 and 1100 °C.[15] The ferroelectric behavior of $KSnOPO_4$ is further evidence that this compound crystallizes in the acentric space group $Pna2_1$, and not in either $Pnam$ or $Pnan$.

Acknowledgment. This work was supported by the National Science Foundation. We also thank a reviewer for helpful suggestions concerning the structure refinement.

Supplementary Material Available: Listings of anisotropic thermal parameters and all bond distances within 3.3 Å (2 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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Isocyanocobalt(III) Species: Identification of the Elusive $[(NH_3)_5Co\text{–}NC]^{2+}$ Ion

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Cyanide ion binds metal ions through its carbon atom almost without exception.[1] Binding through nitrogen is rarer, but nonetheless well-established—for the bridging mode (where it is essentially enforced)[2,3] and for the terminally bound NC^-.[4] The latter isocyano ions can be synthesized by kinetic routes for the inert transition-metal ions by using CN^- blocked at carbon with, for example, H^+,[6] BR_3 and BH_3 in particular,[6-8] and Ag^+.[4] They can also be prepared in favorable cases by inner-sphere electron transfer with CN^- bridge transferral.[5]

The C- and N-bonded linkage isomers for pentacyanocobalt(III),[9] pentaaquachromium(III),[5] and pentaammineruthenium(II)[6] have been described. Of these, the N-bonded CN^- mode seems secure for Cr(III)[5] and Ru(II),[6] but there is controversy for the Co(III) system.[9,10] This note is concerned with the stability and lability of cyanide N-bonded to cobalt(III).

The existence of the transient $[(CN)_5Co\text{–}NC]^{3-}$ ion was originally reported for the $[(CN)_5)Co]^{2-}$ ion reduction of

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