conditions. All reactions were monitored by infrared spectroscopy following the growth of the absorbance at 1675 cm^{-1} due to the C═O stretch of the carbonate ligand. The rate constants are listed in Table II. Activation parameters of $\Delta S^{\ddagger} = -21$ eu and $\Delta H^{\ddagger} = 15$ kcal/mol were calculated. The negative entropy of activation is indicative of an ordered transition state, and the increasing rate with increasing solvent polarity is suggestive of a polar transition state. The dependence on carbon monoxide concentration, as shown in Figure 1, is typical of a rate law that involves a preequilibrium prior to carbon monoxide oxidation. The rate constants

$$\text{rate} = \frac{k_1 k_2[\mathrm{CH_3Ir(P(}p\text{-tolyl})_3)_2(\mathrm{CO})(\mathrm{O_2})][\mathrm{CO}]}{k_{-1} + k_2[\mathrm{CO}]}$$

are defined in Scheme I. A similar mechanism is seen for ligand substitution reactions in alkyl transition-metal complexes, where incoming ligand addition is preceded by a rapid preequilibrium that involves the formation of an acyl intermediate.[8]

The preequilibrium for the reaction between $(\mathrm{CH_3})\mathrm{Ir}(\mathrm{P}(p\text{-tolyl})_3)_2(\mathrm{CO})(\mathrm{O_2})$ and CO probably involves the rapid interconversion of the bonding of the dioxygen ligand from a bidentate to a monodentate form. The uncoordinated end of the dioxygen ligand could then attack free carbon monoxide. A peroxide attack on substrate has previously been implicated in oxidation reactions.[9] The proposed mechanism for this reaction is illustrated in Scheme I.

A similar preequilibrium involving a side to end-bonded dioxygen ligand has been previously suggested for other transition-metal dioxygen complexes, but this study provides the first tangible evidence for such a reaction. The preequilibrium step was considered but dismissed for the oxidation of hexafluoroacetone by reaction with a chloroiridium dioxygen complex.[10] Some of the observed reactivity of $\mathrm{MO_2}(t\text{-BuNC})_2$ complexes of nickel and palladium was attributed to this preequilibrium, but no data to substantiate the pathway were obtained.[11] Many proposed reaction pathways for oxygen atom transfer reactions of transition-metal complexes require coordination of the substrate prior to oxidation.[12,13] Our isotopic labeling studies demonstrate that the CO oxidized is not the CO initially coordinated to iridium and cast doubt on prior coordination as a requirement for oxidation by $(\mathrm{CH_3})\mathrm{Ir}(\mathrm{P}(p\text{-tolyl})_3)_2(\mathrm{CO})(\mathrm{O_2})$.[14] Another possible route involves loss of the dioxygen ligand before the carbon monoxide becomes oxidized. This route can also be rejected since this would result in formation of a 16-electron complex which, from earlier studies,[3] shows instantaneous reactivity with methyl iodide and toward CO exchange. CO exchange is not observed, and no reaction has been observed for the dioxygen complex with $\mathrm{CH_3I}$.

The mechanism shown in Scheme I provides the most reasonable explanation for the kinetic and isotopic labeling studies. The preequilibrium step is consistent with the observed rate law showing dependence on the [CO] only at low [CO]. A possible charge separation in the transition state could account for the increasing rate with solvent polarity. Presence of negative charge on the noncoordinated oxygen atom may facilitate attack on an external CO. Attack would be expected to occur at different rates for different substrates. This is observed with the order $\mathrm{SO_2} > \mathrm{PPh_3} > \mathrm{CO_2} > \mathrm{CO}$ for oxidation. After attack of the oxygen on CO, substantial rearrangement occurs leading to the stable bidentate carbonate. Studies are continuing to define the role of steric and electronic factors on the reactivity of this dioxygen complex.

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Preparation and Structure of $[(\mathrm{C_6H_5})_4\mathrm{P}]_3[\mathrm{NbTe_{10}}]{\cdot}\mathrm{DMF}$: A Soluble Tellurium Cluster Containing an Interstitial Transition-Metal Atom

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Zintl ions are isolated polyanionic clusters of main-group elements. They have been known to exist in solution for many years, but only the relatively recent use of cryptands to sequester the alkali metal counterion has facilitated their isolation.[1] This has resulted in the structural characterization of a wide variety of novel compounds. However clusters containing transition metals are rare. An iron carbonyl cluster containing a tetrahedron of bismuth atoms has been reported[2] as well as a solid-state compound in which a niobium atom is surrounded by an eight-membered arsenic ring.[3] In addition, there are several gold and mercury telluride clusters obtained by extraction of mixed phases in basic solvents.[4] There is also NMR evidence for a platinum phosphine complex becoming incorporated into a $\mathrm{Sn_9}^{4-}$ cluster in solution.[5] However, bare clusters containing transition metals incorporated into main-group frameworks have not yet been isolated.

We have recently found that polytelluride and polyselenide anions prepared from the elements and an alkali metal in liquid ammonia are convenient reagents for the generation of a variety of metal polychalcogenides.[6] Recently our attention has focused on the reactions of polychalcogenides with high-valent transition-metal salts. Reaction of Te_n^{2-} or Se_n^{2-} ($n = 2$–4) with $\mathrm{CrCl_3}$ in DMF produces $\mathrm{Cr_3Te_{24}}^{3-}$ and $\mathrm{Cr_3Se_{24}}^{3-}$, respectively.[7] Reaction of $\mathrm{MoCl_5}$ or $\mathrm{WCl_6}$ with Te_x^{2-} in DMF generates $[\mathrm{MOTe_8}]^{2-}$ with the oxygen atom apparently derived from the solvent.[8] Previous to our work, Krebs prepared $\mathrm{Fe_2Se_{12}}^{2-}$,[9] and Ibers reported $\mathrm{V_2Se_{13}}^{2-}$[10] as well as several tungsten polyselenide anions.[11] However, further work in this area has been scarce.[12] In this communication we report the preparation and structure of $\mathrm{NbTe_{10}}^{3-}$ which is the first Zintl ion containing an interstitial transition-metal atom.

The title compound was synthesized by the reaction of $\mathrm{NbCl_5}$ and 2 equiv of $\mathrm{K_2Te_4}$, in DMF, followed by the the addition of

$$\mathrm{NbCl_5} + 2\mathrm{Te_4}^{2-} \xrightarrow[(\mathrm{C_6H_5})_4\mathrm{PBr}]{\mathrm{DMF}} [(\mathrm{C_6H_5})_4\mathrm{P}]_3[\mathrm{NbTe_{10}}]$$

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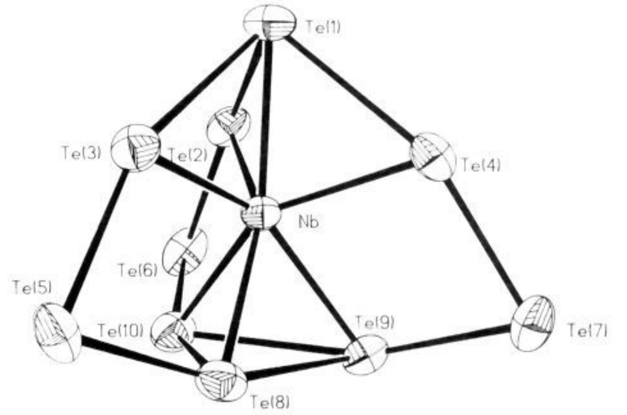

Figure 1. ORTEP view of the $NbTe_{10}^{3-}$. Some selected bond distances are (in Å) as follows: Nb–Te1 2.857 (2), Nb–Te2 2.757 (2), Nb–Te3 2.768 (2), Nb–Te4 2.770 (2), Nb–Te8 2.824 (2), Nb–Te9 2.848 (2), Nb–Te10 2.845 (2), Te1–Te2 3.067 (2), Te1–Te3 3.142 (2), Te1–Te4 3.148 (2), Te2–Te6 2.906 (2), Te3–Te5 2.866 (2), Te4–Te7 2.873 (2), Te5–Te8 2.820 (2), Te6–Te10 2.825 (2), Te7–Te9 2.818 (2), Te8–Te9 3.132 (2), Te8–Te10 3.161 (2), Te9–Te10 3.154 (2).

$(C_6H_5)_4PBr$ to the red brown solution. The product was isolated as large black crystals, with the formula $[(C_6H_5)_4P]_3[NbTe_{10}]\cdot DMF$, by the slow addition of THF and storage at 4 °C overnight.

The crystal structure[13] of the compound reveals three well-separated $[(C_6H_5)_4P]^+$ groups and a badly disordered DMF molecule in addition to the binary niobium telluride cluster. The presence of the DMF was also confirmed by an IR spectrum of the bulk sample. The anion consists of a niobium atom sitting at the center of an unusual ten-membered tellurium cluster which has an unprecedented structure (see Figure 1). It can best be described as an extended birdcage structure similar to P_4S_3 but having two atoms instead of one bridging tetrahedral edges. The niobium atom sits at the center of this cage and is coordinated to seven of the tellurium atoms. This would generate C_3 symmetry under ideal conditions, but since the molecule crystallizes in a triclinic space group it only contains pseudo-C_3 symmetry (see Figure 2).[14] Seven-coordinated niobium is not uncommon, but it is almost invariably pentagonal bipyramidal.[15] The geometry in this compound might be best thought of as a distorted capped trigonal prism.

The bond distances in this novel molecule warrant discussion. All seven tellurium atoms which are bonded to the central niobium atom are well within the normal bond distance of niobium tellurides in solid-state compounds. (To our knowledge there have been no previous reports of molecular niobium tellurium complexes structurally characterized.) The bond distances range from 2.757 (2) to 2.857 (2) Å versus 2.784 (1) to 2.880 (1) Å for solid-state compounds such as $Nb_2Te_2X_6$ where X = Br and I.[16]

The Te–Te bonds exhibit considerable variation throughout the cluster, ranging from 2.818 (2) to 3.161 (2) Å. All bonds to the apical tellurium as well as all the bonds in the three-membered tellurium ring at the base of the cage are long (3.067 (2) to 3.161 (2) Å), whereas those bridging the apex to the base are shorter (2.818 (2) to 2.906 (2) Å). The shorter distances are comparable to that of elemental tellurium (2.835 Å[17]) and are also typical of those observed for Te–Te bonds in chains coordinated to metal centers. For example, Te–Te distances range from 2.686 (2) to 2.838 (2) Å in $[MoOTe_8]^{2-}$ and from 2.703 (1) to 2.764 (1) Å in $[W(CO)_4Te_4]^{2-}$. The longer distances can also be considered to be within bond distance. This aspect has been discussed in some detail previously for metal clusters like $Cp_2Mo_2Fe(\mu_3\text{-}Te)_2(CO)_7$, and it was concluded that distances in the range of 3.14 Å are chemically significant and constitute a bonding interaction.[18]

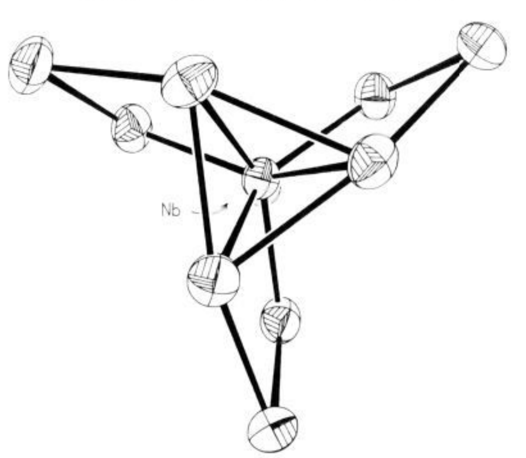

Figure 2. View of $NbTe_{10}^{3-}$ from below the three-membered tellurium ring, showing the pseudothreefold symmetry of the molecule.

The compound is diamagnetic in the solid state, but this does not clarify the formal oxidation state of the central niobium atom. The bonding in the molecule is not simple but may be approached by using valence bond theory. The cluster contains a total of 68 valence electrons. However, it can be assumed that a lone pair of electrons is localized on each tellurium vertex as is the case with virtually all main-group clusters.[19] In addition, it can be assumed that a second lone pair is localized on the divalent Te(5), Te(6), and Te(7). This leaves 42 electrons available for cluster bonding. The cluster contains 19 bonds between all atoms, suggesting that it is electron rich by four electrons. A valence bond analysis of Te_6^{4+} suggests that tellurium–tellurium distances of 3.14 Å actually have a bond order of 2/3.[18,20] Thus it may be postulated that one of the extra electron pairs is delocalized among the apical tellurium atoms, and the other pair is delocalized in the three-membered tellurium ring at the base of the cage. Each extra electron pair would cause the breaking of one bond overall resulting in the weakening of three Te–Te bonds.

It should be noted that there has been another compound characterized which contains a three-membered tellurium ring coordinated to a tungsten atom, in which the Te–Te bonds are considerably shorter than those reported here.[21] Thus, it would seem that the bond lengthening observed in this case is electronic in origin, since there appears to be no ring size or strain effects.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles of all atoms, anisotropic thermal parameters, and H atom coordinates for $[(C_6H_5)_4P]_3[NbTe_{10}]$ (8 pages); table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for $[(C_6H_5)_4P]_3[NbTe_{10}]\cdot DMF$: triclinic, $P\bar{1}$, $Z = 2$, $d = 1.97$ g/cm^2, $\mu = 36.90$ cm^{-1}, $a = 13.117$ (4) Å, $b = 14.488$ (4) Å, $c = 23.783$ (5) Å, $\alpha = 82.10$ (2)°, $\beta = 102.94$ (2)°, $\gamma = 109.14$ (2)°, $V = 4151.1$ (18) Å^3, $T = 24$ °C, 11 494 reflections read to 2θ(Mo Kα) = 45° with $R = 0.0584$ for 6517 reflections of $F_o^2 > 3\sigma(F_o^2)$.

[14] The TRACER program was used to confirm that the molecule does not contain crystallographic threefold symmetry but crystallizes in the $P\bar{1}$ space group.

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