of the K_a evaluation) activity coefficients vary to a degree in each set of multicomponent systems, even though extraordinary care is taken to maintain the ionic strength of the media at 0.100.

Conclusions

The current results are more acceptable from a theoretical viewpoint than the earlier data. In particular, the K_1 and K_3 values are lower and the K_2 values are higher than those reported by Thompson;[2] thus the new K_1/K_2 ratios are smaller and the K_2/K_3 values are larger than those obtained from data reported previously, while both sets of ratios show improved internal consistency. The new average K_1/K_2 value (3.7 ± 0.3) is definitely less than the S_{12} value (4.92) required in the case of tridentate ligandcy but greater than the S_{12} value (3.27) required for bidentate ligandcy. The K_2/K_3 ratios also satisfy the requirements for bidentate bonding of the ligand to a nine-coordinate cation; *i.e.*, in general, $K_2/K_3 > S_{23} = 3.06$. The rising trend of K_2/K_3 noted with the heavier rare earths is consistent with the mounting steric hindrance expected when several bulky ligand anions are grouped about cations of smaller and smaller dimensions.

It is seen that the new data, particularly the $\bar{n}$ values exceeding 3.0, confirm the contention of Thompson[2] that the 2-picolinate anion functions bidentately in bonding to lanthanide cations. Monodentate behavior can be discounted in view of the large magnitudes of the step formation constants. Our data in no way discredit the likelihood that the coordination number of the lighter elements of the series (La^{3+}–Nd^{3+}) may be 10 rather than 9. Data of Spedding, *et al.*,[11–14] demonstrate rather conclusively that the lighter rare earth cations in dilute aqueous media are more highly hydrated than the smaller, heavier ones.

The data confirm, in a general way, the hypothesis of Devine[3] that the activity coefficient correction for K_1/K_2 at 0.1 M ionic strength tends to cancel the electrostatic term T of Bjerrum[5] which has been estimated by Manning[6] to have a value of about 1.5 when K_1 and K_2 are the successive step formation constants of the LnL^{2+} and LnL_2^+ species. A value of $T \simeq 1.5$ is certainly reasonable in view of the fact that an L^- species closely interacting with an Ln^{3+} species should tend to reduce the effective attracting charge from 3+ to 2+. The deviations of K_1/K_2 and K_2/K_3 from S_{12} and S_{23} are attributable, most likely, to steric hindrance, arising from the bulk and relative inflexibility of the picolinate anion. Recent work by Matkovich[7] in this laboratory has shown, in the case of the α-hydroxyisobutyrate anion, that $^*K_1/^*K_2 \simeq 1.5S_{12}$ with both neodymium (to which α-HIB[3] and HCPC[4] attach tridentately) and thulium (to which α-HIB[3] and HCPC[4] bond bidentately) at ionic strength 0. The work of Matkovich[7] supports the magnitude of the electrostatic factor estimated by Manning[6] and the hypothesis by Devine[3] that this electrostatic term is largely negated by a compensating ionic strength factor in 0.1 M media.

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The Metallic Nature of Osmium Dioxide

BY J. E. GREEDAN,[1a] D. B. WILLSON,[1b] AND T. E. HAAS

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The temperature-independent paramagnetic susceptibility of OsO_2, $\chi_M = 119 \times 10^{-6}$ cgsu in the range 77–500°K, is atypically low for Os(IV) compounds[2] and suggests that it may be best not to consider this material as an ordinary coordination compound. In order to characterize OsO_2 and to investigate its electronic structure we undertook to grow single crystals of this material and to make electrical-transport measurements on these crystals.

Experimental Section

Crystal Growth.—Single crystals of osmium dioxide were grown by chemical transport using osmium tetroxide as the transporting agent under conditions similar to those described by Schäfer[3] with modifications in procedure adapted from the transport of WSe_2 and $NbSe_2$ as described by Kershaw, Vlasse, and Wold.[4] Osmium metal was prepared by the reduction of hydrated osmium dioxide in a stream of hydrogen at 400–500°. OsO_4 was used as received from Alfa Inorganics, Inc. Osmium metal (0.60 g, 0.0032 g-atom) and OsO_4 (0.85 g, 0.0033 mol) were placed in a Vycor tube of 10-mm i.d. which had been sealed off at one end. The tube was frozen, evacuated, and filled with oxygen. This operation was repeated four times. The Vycor tube was then sealed off to a length of 20 cm and placed in the crystal-growing furnace.

Crystal growth was carried out in a two-zone furnace. The zone temperatures were maintained by separate heaters. An 11-cm length of the tube rested in the reaction or hot zone and 9 cm rested in the cold or growth zone. At the start of the experiment the growth zone temperature was raised to 960° while the reaction zone was kept at about 250°. The reaction zone temperature was then raised to 960°, while the growth zone was held at the same temperature. Finally, the growth zone temperature was lowered at a rate of 1–5°/hr to 900°. These transport conditions were maintained for 7 days.

About 12 crystals of a coppery metallic luster were recovered, most of them in the form of elongated rectangular parallelepipeds. The crystals ranged in size from about 7 × 5 × 3 mm to those only a few tenths of 1 mm on a side. Three larger crystals were especially well formed, and these were chosen for electrical-transport experiments. A typical size for these crystals was about 5 × 2 × 1 mm.

OsO_2 crystals were analyzed by hydrogen reduction at 350–380°. *Anal.* Calcd: Os, 85.6. Found: Os, 85.5.

The density of OsO_2 was calculated from the unit cell param-

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eters $a_0 = 4.51$ Å and $c_0 = 3.19$ Å assuming the rutile structure.[5] If a precision of 0.5% is assumed for the crystallographic parameters, the calculated density is 11.4 ± 0.2 g/cm^3. The density of OsO_2, determined by displacement of CCl_4, was 11.5 ± 0.2 g/cm^3.

Conductivity Measurements.—These were done by the potential probe method.[6] All contacts were pressure contacts. The voltage probes were made of silver-brazed wire ground to a knife edge and fixed in a Bakelite block. The temperature-dependence measurements were carried out with the sample in an evacuable tube immersed in a series of temperature baths down to liquid N_2 temperatures. Sample temperature was measured by a copper–constantan thermocouple imbedded in the sample holder about 1 mm from the crystal. All measurements were done either under vacuum or in a dry nitrogen atmosphere. Direct current was supplied by a Harrison 6200A regulated power supply and measured with a Simpson ammeter. Voltages were measured using a Keithley 148 nanovoltmeter. Measurements were taken with both current polarities in order to eliminate thermoelectric effects. Three different crystals were used in compiling the data and agreement to within about 15% was obtained.

Hall Effect Measurements.—Hall voltage measurements were attempted using a dc technique with a mismatch potentiometer.[7] Current was supplied by Cd–Ni alkali batteries and voltages measured with a Keithley nanovoltmeter. Magnetic fields were generated with a standard electromagnet and power supply. All contacts to the sample were firmly held pressure contacts using phosphor bronze strips for the current and no. 26 tinned Cu wire for the voltage contacts. All circuit leads were of shielded wire cable. The major problem with the Hall experiment appeared to be temperature fluctuations which gave rise to small fluctuating emf's causing signal drift of about 0.3 μV.

Results and Discussion

The electrical conductivity of OsO_2 in the *c*-axis direction (identified by the crystal habit) of a representative crystal is shown in Figure 1. Both the high room-temperature conductivity and the negative temperature coefficient strongly suggest that this material is intrinsically metallic. The close agreement of the chemical analysis with the calculated Os content as well as the high carrier density observed also tend to support an intrinsic metallic model. Furthermore, a semiquantitative Seebeck coefficient measurement using a hot-probe technique showed a negative emf on the order of microvolts per degree. All of the above information can be used to argue for the intrinsic metallic nature of OsO_2 and against the possibility that OsO_2 is a grossly nonstoichiometric degenerate semiconductor. On one crystal of sufficient size, room-temperature conductivity measurements were made in a direction perpendicular to the *c* axis and the results showed that the *c*-axis conductivity was slightly larger, by about a factor of 2. We do not interpret this difference as showing marked anisotropy.

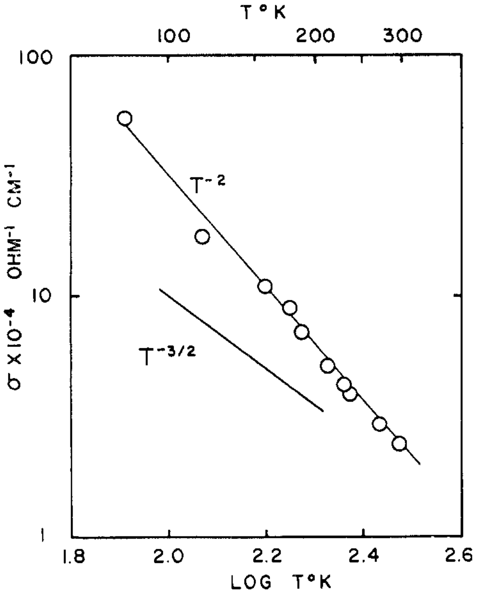

Figure 1.—Temperature dependence of the electrical conductivity of OsO_2 parallel to the *c* axis.

Since, for a metallic conductor, the carrier density, *n*, is constant with temperature, any temperature dependence of the conductivity, σ, is due to the temperature variance of μ, the mobility, as $\sigma = n|e|\mu$. Assuming $\mu \propto T^{-a}$, the data of Figure 1 indicate that $a \approx 2$. This is greater than $a = {}^3/_2$ expected for purely acoustical phonon scattering and suggests the admixture of optical mode scattering in this temperature range.

Hall effect measurements were undertaken in order to determine the carrier density, using currents up to 1 A and fields up to 4500 G. However, to within experimental error no Hall voltage could be detected. Assuming $R_H = 1/(n|e|c)$ and given the sensitivity of the measuring equipment, it was estimated that the smallest detectable Hall voltage would correspond to $n \approx 10^{22}$ cm^{-3}. This number fixes the lower limit for the actual carrier density. A reasonable value for an upper limit can be set by recognizing that Os(IV), a d^4 system, cannot contribute more than 4 electrons/OsO_2 unit to any conduction band. These considerations lead to an upper limit of $n \approx 10^{23}$ cm^{-3}.

These limits on *n* serve to set bounds on the room-temperature carrier mobilities as follows: $1.5 \leq \mu \leq 15$ cm^2 V^{-1} sec^{-1}. A mobility in the upper part of this range would place this compound in a nearly free electron class along with materials like the tungsten bronzes which have mobilities in the range 10–20 cm^2 V^{-1} sec^{-1} and ratios of the effective mass, m^*, to the electronic rest mass, m_0, on the order of 1 or 2.[8] A mobility in the lower part of this range would suggest the presence of carriers in a narrow conduction band.

In the event that a nearly free electron picture is valid, one would expect that the magnetic susceptibility would be well described by the Pauli–Peierls equation[9]

$$\kappa = \frac{4\mu_0{}^2 m^*}{h^2}(3\pi n^2)^{1/3}\left\{1 - {}^1/_3\left[\frac{m_0}{m^*}\right]^2\right\}$$

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where κ is the volume susceptibility, μ_0, the Bohr magneton, n, the electron density, and h, Planck's constant.

After the corrections for the diamagnetism of O^{2-} and Os^{4+} according to Selwood,[10] one calculates $\chi_M = 172 \times 10^{-6}$ cgsu. Assuming a rutile structure for OsO_2 with $a_0 = 4.51$ Å and $c_0 = 3.19$ Å,[5] a value of $\kappa = 8.6 \times 10^{-6}$ cgsu cm^{-3} is calculated. Using this value of κ and as a first approximation taking $m^* = m_0$ in the Landau term for the collective electron diamagnetism, we obtain the calculated value of $n = 2.03 \times 10^{26}$ cm^{-3}, an absurd result. A value of $m^*/m_0 > 8$ is required to bring n into the range defined by the Hall effect results. Such a large value of m^*/m_0 is more characteristic of narrow-band carriers, as are encountered in the transition metals themselves,[11] than of nearly free carriers.

Goodenough[12] has suggested that, in transition metal oxides with the rutile structure, conduction bands can be formed from direct overlap of t_{2g} orbitals on adjacent metal atoms along the c axis, giving rise to a metallic conductivity in a d band only along the c axis, and/or from overlap of t_{2g} orbitals on the metal with oxygen p–π orbitals, giving rise to a nearly isotropic conductivity in a π^* band. In this scheme the metal d band would contain 2 electrons/OsO_2 unit while the π^* band would have a capacity of 4 electrons/OsO_2 unit. These two bands are expected to lie close in energy and may overlap. Three situations can be imagined: (1) the top of the π^* band lies below the bottom of the d band; (2) the top of the d band lies below the bottom of the π^* band; (3) the two bands overlap appreciably.

The first of these possibilities can be ruled out as OsO_2 has exactly 4 valence electrons/OsO_2 unit and these would just fill the π^* band and give rise to nonmetallic behavior. Possibilities (2) and (3) are compatible with the observed metallic behavior. In case (2) the d band would be filled and the π^* half-filled, whereas in case (3) the 4 electrons would inhabit a composite band with total capacity of 6 electrons/OsO_2 unit. The carrier densities predicted by these two models are also consistent with the Hall data and the narrow band picture as case (2) predicts $n = 6 \times 10^{22}$ cm^{-3}, $\mu = 2.5$ cm^2 V^{-1} sec^{-1}, and case (3) predicts $n = 1.2 \times 10^{23}$ cm^{-3}, $\mu = 1.5$ cm^2 V^{-1} sec^{-1}.

In summary, we submit that the available, albeit scant, data on OsO_2 can be consistently rationalized on the basis of a wholly collective electron approach such as that suggested by Goodenough and involving the concepts of narrow bands and high density of states which are quite commonly encountered in the transition metals and their compounds.

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Mass Spectra of Hexachlorotriphosphonitrile and Octachlorotetraphosphonitrile

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Until recently no electron-impact studies of phosphorus–nitrogen polymers had been reported. Our results complement the mass spectral study of the bromophosphonitriles[1] and fluorophosphonitriles[2] and add important details to the abbreviated summary of spectral data for chlorophosphonitrile oligomers.[3] Together these studies provide a comprehensive description of the behavior of phosphonitriles to electron impact.

Results

The line spectrum of octachlorotetraphosphonitrile is shown in Figure 1. The relative abundances of ions in the mass spectra of the trimer and the tetramer are recorded in Tables I and II, respectively. The abundances are reported as a percentage of the total ion abundance. The measured intensities of the multiply charged ions were divided by the charge on the ion to provide comparability with the singly charged ions. Several ions not reported earlier[3] have been observed in low abundance.

Discussion

Certain characteristic behaviors of the chlorophosphonitriles to electron impact are evident from the relative abundance data. As noted previously,[3] the $P_nN_nCl_{2n-1}^+$ ion is the most abundant in both spectra. The phosphonitrile ring appears to be cleaved to a very great extent upon electron impact. The P_4N_4 ions in the tetramer spectrum account only for 25.0% of the total ions and the P_3N_3 ions in the trimer spectrum make up 32.4% of the total ions. Fragments which contain the P_3N_2 and P_2N backbone and are presumed to have a linear structure[3] appear to be stable. These fragments make up 19.8% of the total ions both in the tetramer and in the trimer.

The dominance of even-electron ions over odd-electron ions is striking. Of the ions which contain both phosphorus and nitrogen and are present in amounts greater than 0.1% in the trimer, 46.5% are even-electron ions and 17.3% are odd-electron ions. In the tetramer spectrum the figures are 46.8 and 15.1%, respectively. Two correlations are evident when the relative abundances of odd- and even-electron P_3N_3 and P_4N_4 ions of identical stoichiometry are compared. The data in Table III show that the relative abundance of an even-electron ion is always greater than the odd-electron ion of the same stoichiometry except for the

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