state $(C_6H_5)_3S{\cdot}I{\cdot}$ decomposes by a nondiffusive pathway to diphenyl sulfide and iodobenzene and by a diffusive pathway to diphenyl sulfide and phenyl radicals which form benzene by reaction with solvent. Electroreduction of diphenyliodonium ion at a mercury electrode in water[7] proceeds by an initial one-electron reduction to form diphenyliodine radicals (eq 3). Diphenyliodine radicals can then decompose to give iodobenzene and phenyl radicals (eq 4), or they can be reduced in an irreversible process to iodobenzene and benzene at a more negative potential (eq 5). Yields of iodobenzene

$$(C_6H_5)_2I^+ + e^- \rightleftarrows (C_6H_5)_2I\cdot \tag{3}$$

$$(C_6H_5)_2I\cdot \rightarrow C_6H_5I + C_6H_5\cdot \tag{4}$$

$$(C_6H_5)_2I\cdot + H^+ + e^- \rightarrow C_6H_5I + C_6H_6 \tag{5}$$

and benzene[3] suggest that the photolysis of diphenyliodonium iodide also occurs by the formation of a charge-transfer radical pair $(C_6H_5)_2I{\cdot}I{\cdot}$ which decomposes by both diffusive (eq 4) and nondiffusive pathways.

The observed electroreduction at about −1.0 V (relative to sce) and the photoexcitation energy of about 4.2 V (296 nm) of $B_{10}H_9IC_6H_5^-$ ion suggest that the excited state should be capable of oxidizing water (potential required $\sim$+0.6 to +1.0 V), even allowing for considerable reorganization energy and changes in solvation energy. Decomposition of the one-electron reduction species $B_{10}H_9IC_6H_5{\cdot}^{2-}$ could take place either directly to $B_{10}H_9I^{2-}$ and a phenyl radical analogous to eq 4 or indirectly accompanied by an additional proton and electron transfer to $B_{10}H_9I^{2-} + C_6H_6$, analogous to eq 5. The observation of coulometric *n* values between 1 and 2 in acetonitrile and in water suggests that both pathways are possible in the electrolysis.

The photolysis of the $B_{10}H_9IC_6H_5^-$ produces a relatively "clean" product mixture for two apparent reasons. First, irradiation can be carried out at a wavelength at which the products are essentially transparent, so that no secondary photolysis of products occurs. Second, the irradiation produces a bound excited state capable of accepting an electron from the solvent, resulting in the formation of a reduced ion similar in properties to an excited charge-transfer complex which decomposes quite cleanly.

Experimental Section

A solution of 4.0 mmol of $CsB_{10}H_9IC_6H_5$ in 650 ml of water was irradiated with a medium-pressure mercury lamp fitted with a Corex filter (290-nm cutoff) for 4–5 hr, during which time the evolution gas was monitored with a gas buret. The reaction mixture was titrated with standardized sodium hydroxide solution to a pH of 7, and aqueous tetramethylammonium chloride was added. The resulting precipitate gave a 75% yield of white crystals of $Cs(CH_3)_4NB_{10}H_9I$ when recrystallized from an acetonitrile–water mixture. This double salt was converted to the more soluble $[(CH_3)_4N]_2B_{10}H_9I$ by ion exchange to the sodium salt and addition of tetramethylammonium chloride. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_9I$: B, 27.55; equiv wt 199.2. Found: B, 27.11; equiv wt (acid ion exchange) 200.

In order to be able to monitor the progress of the photolysis by ^1H nmr, 0.2 mmol of $CsB_{10}H_9IC_6H_5$ was converted to the sodium salt of $B_{10}H_9IC_6H_5^-$ by acid ion exchange and neutralization with sodium hydroxide. After evaporation of the solvent, the residue was transferred to an nmr sample tube with about 0.3 ml of water. Following addition of 0.3 ml of 2-propanol to the solution, the sample was irradiated in a Rayonet reactor fitted with 300-nm lamps for 2.5 hr. During this period, nmr spectra of the mixture were run at intervals of 0.5–1.0 hr. Integration of the nmr signals showed that benzene and acetone were formed in equivalent amounts and that the reaction was essentially complete in 2.5 hr.

About 50 ml of an acetonitrile–water mixture containing 2.0 mmol of $CsB_{10}H_9IC_6H_5$ was electrolyzed at a mercury pool electrode first at −1.5 V (relative to sce) and then at −2.2 V until 2.2 mequiv of current had passed. The addition of aqueous tetramethylammonium chloride caused the precipitation of 1.0 mmol of $Cs(CH_3)_4NB_{10}H_9I$, identified by its ir spectrum. Addition of more tetramethylammonium chloride afforded the recovery of 0.6 mmol of the starting material as $(CH_3)_4NB_{10}H_9IC_6H_5$. Concentration of the remaining solution led to the isolation of 0.1 mmol of $[(CH_3)_4N]_2B_{10}H_9I$.

Coulometry was carried out at a mercury pool electrode at −1.2 V in millimolar solutions of $CsB_{10}H_9IC_6H_5$ in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate, using a Wenking potentiostat with a Hewlett-Packard voltage-to-frequency converter and electronic counter. Coulometric *n* values for two solutions were 1.2 and 1.4.

When electrolysis was carried out on a 0.04 *M* solution of $CsB_{10}H_9IC_6H_5$ in a 50:50 (by volume) mixture of acetonitrile and water, *n* values of 1.6 based on recovery of starting material and 2.0 based on isolated product yield were obtained.

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Registry No. $CsB_{10}H_9IC_6H_5$, 12551-04-1; $[(CH_3)_4N]_2B_{10}H_9I$, 39436-16-3.

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Electron Paramagnetic Resonance Spectra of Oxides of Titanium. Effective Magnetic Moments of Ti^{3+} Ions

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We have previously reported epr and magnetic susceptibility studies on several discrete phases of the titanium-oxygen system described by Ti_nO_{2n-1},[1-12] as have a number of other investigators.[13-16] Goodenough recently has reviewed the properties of several transition metal oxide systems, including the Ti-O system.[17,18]

In all of the epr studies the spectra observed at 77 K have been attributed primarily to the Ti^{3+} $(3d^1)$ ion. Shannon[19]

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has found that the presence of hydrogen and/or water vapor favors the oxygen vacancy (V_o) mechanism of defect production during reduction of TiO_2, while the formation of Ti interstitials dominates the kinetics of vacuum reduction. Reduction of TiO_2 with Ti in an inert atmosphere gives rise to a defect having two associated spin-degenerate levels separated by a finite energy.[20] As pointed out by Goodenough[17] this is suggestive of oxygen vacancies (V_o centers) having two associated Ti^{3+} ions with a finite separation between the first and second ionization energies. Oxygen vacancies are expected to dominate in the samples under investigation here. We therefore anticipate one of three types of defect centers to predominate.

I. $(Ti^{3+}\text{-}V_o\text{-}Ti^{3+})^0$, which at low temperatures would most likely involve a homopolar bond between the cations and therefore be epr "inactive." Although the existence of a corresponding triplet has been suggested, the magnetic susceptibility results[2,6] in this low-temperature region do not support this contention.

II. $(Ti^{3+}\text{-}V_o\text{-}Ti^{4+})^+$, which would consist of an electron localized on or about an oxygen vacancy with possible charge transfer between the two associated Ti sites. This center would be paramagnetic and should be observable by epr.

III. $(Ti^{4+}\text{-}V_o\text{-}Ti^{4+})^{2+}$, which represents a doubly ionized electron trap and would be most prevalent at high temperatures. It too would be epr "inactive."

Thus, it is expected that the observed epr spectra arise from "localized" electrons at a $(Ti^{3+}\text{-}V_o\text{-}Ti^{4+})^+$ center.

In this note we shall show that the effective magnetic moments obtained from the observed spectra are consistent with the effective magnetic moment, μ_{eff}, calculated for the Ti^{3+} ion on the basis of crystal field theory. We shall rely on the conceptual approximations of the crystal field theory to describe the electronic structures of these phases—at least in the "localized" states of the cations—since the band picture for these oxides in the semiconducting and metallic regions is imperfectly understood at present.

The samples were prepared by a borate flux method under controlled oxygen fugacities as discussed elsewhere.[21] These were characterized as indicated below. The compositions of the samples were checked by measurement of the weight gained upon reoxidation to TiO_2 in air. The phase homogeneity was determined by comparison of X-ray diffraction patterns with those of Andersson and Magneli.[22] Field dependence studies of the static magnetic susceptibility indicated no detectable ferromagnetic impurities.

The epr spectra of the polycrystalline samples were recorded at 77 K on a Perkin-Elmer ESR-1 spectrometer at a frequency of 8550 MHz.

The resulting spectra are found to be reasonably well described by assuming axial symmetry,[23-27] $S = {}^1/_2$ and $I = 0$, where S and I represent the electronic and nuclear spins of the system, respectively.

Table I. Epr and Optical Spectral Parameters

	g_{obsd}	$10^2\delta g^a$	$10^{-4}\Delta$, cm^{-1}	v, cm^{-1}	λ, cm^{-1}	K_λ
Ti_3O_5	1.968	3.50	2.00	5000	87.6	0.570
Ti_4O_7	1.962	4.06	1.55	~5000	93.0	0.604
Ti_5O_9	1.965	3.76	1.48	~5000	84.5	0.550
Ti_6O_{11}	1.967	3.56	1.43	~5000	79.5	0.515
Ti_7O_{13}	1.966	3.62	1.39	~5000	79.3	0.515
Ti_8O_{15}	1.962	4.06	1.35	~5000	87.8	0.572
Ti_9O_{17}	1.966	3.62	1.32	~5000	79.3	0.515
$Ti_{10}O_{19}$	1.961	4.12	1.28	~5000	87.0	0.565

[a] $\delta g = g_e - g_{obsd}$, where g_e is the electron free-spin g factor, 2.0023.

In addition, Porter, *et al.*,[28,29] have reported the results of a diffuse reflectance spectroscopy study of these phases which suggest a trigonal distortion, v, of 5000 cm^{-1} in the case of Ti_3O_5. It was not possible to resolve any distortions of the other phases from Porter's data, but estimates of the $10Dq$ splitting (Δ) of the E_g and T_{2g} terms by the cubic ligand field of the oxygen anions were obtained and are given in Table I.

The average g values for the phases Ti_nO_{2n-1} for $n = 3\text{-}10$ are also listed in Table I. It can be seen that they are nearly equal at ~1.96-1.97 and are in general agreement with the results of Votinov and Klubnikin.[30]

From this result, as well as variable-temperature studies of the epr peak-to-peak line widths, δH, which indicate that the spin-lattice relaxation times (T_1) are approximately the same for all phases, it appears that the axial distortions of the phases are of the same magnitude as that for Ti_3O_5, *i.e.*, ~5000 cm^{-1}. (In addition, recent X-ray studies[31,32] of Ti_4O_7 indicate a large distortion of the TiO_6 octahedra.)

To describe this system (at least to first order) we may write a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_{crystal} + \mathcal{H}_{spin\text{-}orbit} + \mathcal{H}_{magnetic} \tag{1}$$

or

$$\mathcal{H} = \mathcal{H}_{cubic} + \mathcal{H}_{axial} + \vec{S}\cdot\vec{L} + |\beta|\vec{L}\cdot\vec{H} + g|\beta|\vec{S}\cdot\vec{H}$$

By applying standard perturbation techniques to eq 1, it can be shown that in the case of a large axial distortion (*i.e.*, $v \gg \lambda$) the spin-orbit coupling constant, λ, is given by [33]

$$\lambda = \frac{g - g_{av}}{\dfrac{4}{3v} + \dfrac{8}{3\Delta}} \tag{2}$$

Since g_{av}, v, and Δ are all known for Ti_3O_5, we may calculate the spin-orbit coupling constant. It is found to be ~88 cm^{-1}. From this we can obtain K_λ, the spin-orbit coupling constant reduction factor, defined by

$$K_\lambda = \lambda/\lambda_0 \tag{3}$$

where λ_0 is the spin-orbit coupling constant for the free ion, 155 cm^{-1}. For Ti_3O_5, $K_\lambda \simeq 0.57$.

With the assumption that the axial distortions of the other phases are of the same magnitude as that of Ti_3O_5, similar calculations have been made for all the phases and are recorded in Table I.

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The considerable reduction of the spin-orbit coupling constant reflected in the K_λ values is indicative of significant delocalization of the electrons around the Ti^{3+} sites.

A consideration of the effects of spin-orbit coupling and the first- and second-order Zeeman effects on the T_{2g} ground term in Van Vleck's expression[34] for the magnetic susceptibility leads to eq 4 for the Ti^{3+} ion in a perfect octahedral

$$\mu_{\text{eff}}^2 = \frac{8 + \left(\frac{3\lambda}{kT} - 8\right)\exp\left(\frac{-3\lambda}{kT}\right)}{\frac{\lambda}{kT}\left[2 + \exp\left(\frac{-3\lambda}{2kT}\right)\right]} \tag{4}$$

field. This equation gives a μ_{eff} for Ti^{3+} at 77°K of ~1.14 μ_B.

Figgis and Lewis[35] have pointed out that the ligand field on the Ti^{3+} ion departs considerably from cubic symmetry in many of the complexes studied. Thus, Figgis[36] has modified eq 4 to take axial distortions into account. Figgis' approach indicates that an axial distortion tends to bring the effective magnetic moment to the "spin-only" value of 1.73 μ_B, *via* a quenching of the orbital moment; thus μ_{eff} in a large number of compounds is ~1.7-1.8 μ_B.[34] When a v of 5000 cm^{-1} and $v/\lambda_0 \approx 33$ are assumed, a μ_{eff} of ~1.73 μ_B is estimated for Ti^{3+} from Figure 1 of Figgis' paper.[36]

Figgis, *et al.*,[35,37] have related μ_{eff} to the axial distortion v and the epr parameter K_λ as in eq 5. (In our notation, v

$$\mu_{\text{eff}}^2 = 3\left(1 - \frac{2K_\lambda\lambda_0}{v}\right) + \frac{8K_\lambda^2 KT}{v} \tag{5}$$

corresponds to Δ, and K_λ corresponds to K in the nomenclature of Figgis and Lewis.[35])

Thus, for Ti_3O_5 at 77 K where $K_\lambda = 0.57$ and $v \approx 5000$ cm^{-1}, $\mu_{\text{eff}} \approx 1.71$ μ_B. Nearly the same value of μ_{eff} is obtained from eq 5 for all the phases studied. Thus we see that the value 1.71 μ_B obtained from the experimental K_λ values is consistent with that expected for the Ti^{3+} ion.

Considering that we have used Δ and λ_0 values corresponding to room temperature measurements and the observation that our g value does not change over a wide range of temperature,[1] the μ_{eff} thus obtained may be said to correspond to room temperature. Indeed, a closer examination of Figure 1 of Figgis' paper[36] revelas that μ_{eff} remains nearly constant over a wide range of kT/λ_0. Thus within the limitations of the crystal field theory approach, the epr spectra are shown to be consistent with those expected from Ti^{3+}.

These results pertain only to the noninteracting, localized Ti^{3+} ions and not to the total number of Ti^{3+} ions. The number of such ions ranges from ~0.01% of the total Ti^{3+} in Ti_3O_5 to ~40% of the total Ti^{3+} in $Ti_{10}O_{19}$.[38]

The remainder of the Ti^{3+} ions are believed to be involved in homopolar bonds within specific groups of Ti^{3+} ions.[17,32] (This was termed "constrained" antiferromagnetism in previous papers.[2,6])

Finally, it should be noted that the μ_{eff} reported by Danley and Mulay[2,6] represents a value averaged over all Ti^{3+} ions, whereas the μ_{eff} values obtained above correspond to the actual μ_{eff} of the unpaired, localized spins on Ti^{3+}.

These results are thus consistent with those of Danley and Mulay[2,6] and, in fact, justify their use of the spin-only formulation in the determination of the number of localized and delocalized electrons in the various phases.

Registry No. Ti_3O_5, 12065-65-5; Ti_4O_7, 12143-55-4; Ti_5O_9, 12065-98-4; Ti_6O_{11}, 12143-56-5; Ti_7O_{13}, 12143-58-7; Ti_8O_{15}, 12143-59-8; Ti_9O_{17}, 12143-60-1; $Ti_{10}O_{19}$, 12143-61-2.

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Reduction of the 12-Molybdocerate(IV) Anion. Optical Spectrum of 12-Molybdocerate(III)[1]

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We have recently pointed out that the reducibility of heteropoly and isopoly anions to isostructural mixed-valence "blues"[2] may be rationalized in terms of the site symmetries of the Mo^{VI}, W^{VI}, or V^V atoms in these anions. Structures that we have classified as "type II" (*i.e.*, those with cis MO_2 groups) are predicted not to be reducible to blues. One such type II polyanion is 12-molybdocerate(IV), first reported by Barbieri.[3] Baker, *et al.*,[4] on titrimetric evidence, argued that the anion must contain a minimum of 42 oxygen atoms (empirical formula $CeMo_{12}O_{42}^{8-}$), a conclusion that was confirmed with the structure reported by Dexter and Silverton.[5] An unusual feature of this structure is the arrangement of six pairs of face-shared MoO_6 octahedra which produces a regular icosahedral environment of oxygen atoms for the central cerium atom.

There have been two reports[6,7] of a one-electron reduction of 12-molybdocerate to a dark brown complex. Peacock and Weakley[7] reported a reduction potential of +0.70 V in 0.1 *M* HCl and an intense absorption (ϵ 3000) at 18.0 kK in the spectrum of the reduced solution. The quite reasonable assignment was made that this band corresponded to a $Ce^{III} \rightarrow Mo^{VI}$ ("metal-to-ligand") charge transfer, but the intensity of the band seemed puzzling to us for two reasons. First, it implied that molybdenum should be fairly easily reducible in this anion,[8] a point that was inconsistent with the hypothesis mentioned above. Second, bands assigned as $Ce^{III} \rightarrow W^{VI}$ charge transfer in the spectra of tungstocerates(III)[7] were one-sixth to one-tenth the intensity of the presumed $Ce^{III} \rightarrow Mo^{VI}$ band. In our experience, changing the "acceptor" atom from

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