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 $\sim$1.7-1.8 μ_B.[34] When a v of 5000 cm^{-1} and $v/\lambda_0 \simeq 33$ are assumed, a μ_{eff} of $\sim$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 $v \simeq 5000$ cm^{-1}, $\mu_{\text{eff}} \simeq 1.71$ 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 $\sim$0.01% of the total Ti^{3+} in Ti_3O_5 to $\sim$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

[1] Taken from the thesis of L. McK., submitted in partial fulfillment of the requirements for the M.S. degree at Georgetown University, 1972.

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[8] See, for example, D. R. Wexell and M. T. Pope, *Chem. Commun.*, 886 (1971).

Mo^{VI} to W^{VI} results in a halving of intensity at most.[9] An alternative explanation for the 18-kK band, that the reduced complex is a heteropoly blue containing Ce^{IV}, Mo^{V}, and Mo^{VI} does not seem likely in view of the rather positive reduction potential at which it is produced.[10]

The electronic structure of the species present in reduced solutions of 12-molybdocerate is therefore of interest, particularly in connection with the validity of the type I-type II rationalization of heteropoly blue formation. We report here results of an electrochemical investigation of the reduction of this anion.

Results and Discussion

Cyclic voltammograms of a solution of ammonium 12-molybdocerate(IV) in 1 *M* sulfuric acid using a wax-impregnated graphite electrode (wige) showed a well-defined reduction peak at +0.45 V *vs.* sce. The corresponding oxidation peak appeared at a potential 77 mV more positive. The reduction was shown to be a one-electron process by comparing the peak height with that shown at 0.80 V for the established[11] one-electron oxidation of $Co^{II}W_{12}O_{40}{}^{6-}$ to $Co^{III}W_{12}O_{40}{}^{5-}$, using the same electrode and instrument settings. The effects of supporting electrolyte and pH upon the reduction of 12-molybdocerate are summarized in Table I.

The reduction potential in 1 *M* sulfuric acid is consistent with that reported by Peacock and Weakley for hydrochloric acid solutions, but there is a strong pH dependence showing that protonation accompanies reduction. There is also a small effect of ammonium ions on E_p. Some solutions for voltammetry were made from the free 12-molybdoceric(IV) acid, prepared by ion exchange;[4] the reduction peak potentials were then observed to be some 40 mV more positive than indicated in Table I. Occasionally, the voltammograms showed two small reductions at *ca* +0.3 and +0.15 V and these were also seen on the anodic sweep. These peaks were eventually traced to an isopolymolybdate impurity, since solutions of ammonium heptamolybdate in 0.1 *M* sulfuric acid gave voltammograms with reductions at these potentials. The molybdate impurity could be removed by thoroughly washing the initial precipitate of ammonium 12-molybdocerate[4] before recrystallizing it twice from sulfuric acid.

The results in Table I clearly show that the reduction is reversible only in 1 *M* acid solution and that the reduced complex is either rapidly decomposed or is otherwise unoxidizible at pH 5. Solutions of the reduced complex were prepared by controlled-potential electrolysis of a 0.01 *M* solution in 1.0 *M* sulfuric acid. Voltammograms taken during the course of the reduction remained unchanged, except for the anticipated anodic displacements. At the end of the reduction a rotating platinum electrode polarogram showed the wave at +0.4 V to be fully anodic. Absorption spectra of solutions taken during the electrolysis showed a well-defined isosbestic point at 450 nm and the spectrum of the fully reduced (brown-orange) solution showed a single broad shoulder at *ca.* 450 nm, $\epsilon \sim 100\ M^{-1}\ cm^{-1}$. This spectrum is in marked contrast to that reported by Peacock and Weakley; see below.

Table I. Voltammetric Reduction of Ammonium 12-Molybdocerate(IV) at wige[a]

Supporting electrolyte	E_{pc}, V	ΔE, mV	i_{pc}, μA	i_{pa}/i_{pc}
1 *M* H_2SO_4	+0.45	77	3.00	1.08
0.1 *M* HNO_3	+0.35	127	1.56	0.89
Bisulfate buffer, pH 2	$+0.22_7$	138	1.92	0.93
pH 3	$+0.11_5$	173	1.68	0.59
Acetate buffer, pH 4	− 0.50	223	1.20	0.66
pH 5[b]	− 0.75	*c*	2.72	*c*

[a] Depolarizer concentration 0.30 *mM*; voltage sweep rate 0.5 V min^{-1}; E_{pc} is cathodic peak potential; $\Delta E = E_{pc} - E_{pa}$; i_{pc} is cathodic peak current. [b] No ammonium ion present (see text). [c] No anodic peak observed.

The reduced solution was not stable and its spectrum and voltammogram decayed in a few hours. Addition of cesium ion to a freshly reduced solution yielded a pale pink-brown precipitate which could not be redissolved for recrystallization. The infrared spectrum of this material was essentially identical with that of ammonium 12-molybdocerate(IV) in the metal-oxygen vibrational region (1000–400 cm^{-1}); the spectrum was not similar to those of other polymolybdates.

If the reduced molybdocerate solutions were allowed to stand for 24–30 hr (no cesium ion added), they would occasionally deposit small quantities of well-formed dark rectangular blocks. The yield never exceeded 25% of the solute in the original solution, and the colors of different products varied from maroon to brown, although they were all isomorphous by X-ray powder diffraction.[12] Solutions of these crystals in 1.0 *M* sulfuric acid, when freshly prepared, gave optical spectra and voltammograms characteristic of the fully reduced electrolyzed solution and the infrared spectra of solid samples were identical with that of the oxidized material. The crystals therefore undoubtedly contain the $CeMo_{12}O_{42}{}^{9-}$ ion, but also, according to chemical analysis[13] of one sample, extra cerium, presumably cationic. The formula $(NH_4)_{2.5}Ce_{1.5}H_2[CeMo_{12}O_{42}]\cdot 9H_2O$ could account for the analytical results. *Anal.* Calcd: N, 1.47; Ce, 14.7; Mo, 48.3. Found: N, 1.62; Ce, 14.65; Mo, 48.47. It is likely that the differently colored products contained different amounts of cerium(III). As is common with heteropoly salts, variable cation stoichiometries can be accommodated in isomorphous series of crystals since the structures are frequently dominated by anion-packing arrangements.[14]

Electron spin resonance measurements on the freshly reduced solution and on the two solids described above, at ambient and liquid nitrogen temperatures, revealed no signals apart from small traces of a Mo(V) impurity present in the solids. The impurity was also present in the oxidized heteropoly salt. The absence of a signal proves that the reduced complex should be formulated as $H_nCe^{III}Mo_{12}O_{42}{}^{(9-n)-}$ rather than $H_nCe^{IV}Mo^{V}Mo_{11}O_{42}{}^{(9-n)-}$ since the extremely short spin-lattice relaxation time of cerium(III) prevents detection of a signal at temperatures much above 4°K. All monomeric molybdenum(V) complexes, however, including mixed-valence species such as $PMo^{V}Mo_{11}O_{40}{}^{4-}$, give strong esr signals that are narrow enough for easy detection at 77°K.[15] Other evidence for the Ce(III) formulation is (1) the value of the reduction potential, + 0.45 V (a dropping mer-

(9) *E.g.*, $V^{IV} \rightarrow W^{VI}$ in $PVW_{11}O_{40}{}^{5-}$, $\epsilon_{max} \sim 750$; $V^{IV} \rightarrow Mo^{VI}$ in $PVMo_{11}O_{40}{}^{5-}$, $\epsilon_{max} \sim 1400$: D. P. Smith, H. So, J. Bender, and M. T. Pope, *Inorg. Chem.*, 12, 685 (1973); R. A. Prados, H. So and M. T. Pope, in preparation.

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(12) The reduced material was not isomorphous with ammonium 12-molybdocerate(IV), however.

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cury electrode polarogram of a freshly reduced solution of 12-molybdocerate in 1.0*M* sulfuric acid showed no further reductions prior to −0.1 V, at which point a complex multielectron process occurred), and (2) the absence of an intense $Mo^{V} \rightarrow Mo^{VI}$ intervalence transition (observed in all mixed-valence molybdates at 800-1000 nm[16]). Direct spectroscopic observation of Ce(III) is difficult owing to the weakness and position of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (*ca.* 2250 cm^{-1}). A considerable, but unsuccessful, effort was made to detect this transition in the solids described above using Nujol mulls (at ambient and liquid nitrogen temperatures), KBr disks, and attenuated total reflectance of undiluted powdered material. In every case residual OH absorption obscured the region of interest. The observed transition at 450 nm in the spectrum of the freshly reduced solution can be assigned as a $Ce^{III} \rightarrow Mo^{VI}$ charge transfer, and its position and intensity are consistent with the arguments presented in the introduction.

There remains the discrepancy between our spectrum and that reported by Peacock and Weakley. Although these workers determined the reduction potential by stannous chloride titration, the spectral measurements were made on material that had been prepared by electrolysis of a neutral solution using a mercury cathode.[17] The potential was unspecified and presumably uncontrolled. Since we have observed that molybdocerate(III) solutions are unstable and that the reduction of molybdocerate(IV) becomes less and less reversible as the pH is raised, it seems probable that the material examined by Peacock and Weakley did not contain the 12-molybdocerate(III) anion. We have not examined this further but have noted that if 1 equiv of $SnCl_2$ is added to 12-molybdocerate(IV), the resulting solution has the color and spectrum of 12-molybdocerate(III) as reported here. Addition of excess Sn(II) caused the color of the solution to darken, and such solutions showed no voltammogram characteristic of 12-molybdocerate.[18]

Experimental Section

Ammonium 12-molybdocerate was prepared by the method of Baker, *et al.*[4]. *Anal.* Calcd for $(NH_4)_6H_2CeMo_{12}O_{42}\cdot 9H_2O$: N, 3.76; Mo, 51.50; $H_2O + NH_3$, 14.23. Found: N, 3.26; Mo, 51.74; $H_2O + NH_3$, 14.70. Voltammetric measurements were made with wax-impregnated graphite and rotating platinum electrodes (wige and rpe) as described elsewhere.[11] Cary 14 and Perkin-Elmer 225 instruments were used for optical and vibrational spectroscopy. Electron spin resonance measurements were made on powdered samples of the reduced compound at 77°K using a JEOL MES-3X spectrometer. X-Ray powder diffraction was carried out as described elsewhere.[19]

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Registry No. Ammonium 12-molybdocerate(IV), 12185-82-9; 12-molybdocerate(III) anion, 39465-42-4.

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Kinetics of the Permanganate Ion-Potassium Octacyanomolybdate(IV) Reaction

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The reactions of multiequivalent oxidizing reagents have stimulated the interest of chemical researchers for some time. Espenson has presented a review of the reaction of the chromate ion, CrO_4^{2-}, with a number of inorganic ions.[1] He showed the variety of reaction pathways and the mechanistic implications of the rate laws. The permanganate ion, MnO_4^-, like CrO_4^{2-}, is a multielectron-transfer reagent that has been extensively utilized in analytical chemistry for its oxidizing capacity with both organic and inorganic substances. The bulk of information concerning the mechanistic behavior of permanganate ion oxidations has been provided by organic systems.[2] Inorganic ions have found only limited examination. One such attempt by Rosenheim,[3] the oxidation of potassium octacyanomolybdate(IV), $K_4Mo(CN)_8$, by potassium permanganate, $KMnO_4$, was complicated by the photosensitivity of the oxidation product, potassium octacyanomolybdate(V), $K_3Mo(CN)_8$. The reaction product is easily reduced in light back to $Mo(CN)_8^{4-}$.[4,5]

The permanganate ion, unlike Ce(IV), is capable of reacting *via* one- or two-electron pathways and the reaction of MnO_4^- with $Fe(CN)_6^{4-}$ [6] and $Fe(phen)_3^{2+}$ [7] has been studied in an attempt to detect the existence of a two-electron step in the pathway. The study of the oxidation by Ce(IV) of a variety of iron(II)-phenanthroline complexes by Dulz and Sutin[8] showed the existence of a common mode of reaction. It would be of interest to obtain information on a reaction system in which the free energy of reaction, $\Delta G°$, varies over a wider range.

The $Mo(CN)_8^{4-}$ ion was chosen since both it and MnO_4^- are kinetically inert complexes, allowing the application of Marcus' theory,[9] and because the one-electron reduction pathway of the permanganate ion by $Mo(CN)_8^{4-}$, unlike the MnO_4^--$Fe(CN)_6^{4-}$ reaction, is thermodynamically unfavorable.

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$ $E° = 0.56$ V[10] (1)

$Mo(CN)_8^{3-} + e^- \rightarrow Mo(CN)_8^{4-}$ $E° = 0.80$ V[11] (2)

However, the 2-equiv reduction of the permanganate ion ($MnO_4^- + 2e^- \rightarrow MnO_4^{3-}$) is favorable, as it is in the MnO_4^--$Fe(phen)_3^{2+}$ system.

Experimental Section

$K_4Mo(CN)_8\cdot 2H_2O$ was prepared by the method of Van der Poel

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