J. Am. Chem. Soc. 1992, 114, 10384-10394

Magnetic Properties of Mixed-Valence Heteropoly Blues. Interactions within Complexes Containing Paramagnetic Atoms in Various Sites as Well as "Blue" Electrons Delocalized over Polytungstate Frameworks

Nieves Casañ-Pastor[†] **and Louis C. W. Baker***

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057.

Received August 3, 1992

Abstract: Magnetic behaviors are reported for 16 heteropoly blue tungstate anions and for their oxidized parent heteropoly complexes (isomorphs of the corresponding blue species). Ten of the reduced species and one of the oxidized ones are new compounds. Each blue complex contained either one or two added "blue" electrons delocalized over numerous W and O atoms of the heteropoly framework. Most of the species contained one or two paramagnetic atoms, substituted at specific octahedral and/or tetrahedral sites into the heteropoly frameworks as integral parts thereof. These isolated systems thus contained delocalized blue electrons and/or one or more paramagnetic atom(s) having localized unpaired electrons. The magnetic responses of such systems are reported and rationalized. Measurements on the solids were made at 5 000 G in a SQUID magnetometer over the range 4–300 K and on solutions at room temperature at 70 500 G by very accurate Evans method determinations. The complexes used were derivatives of the Keggin structure, α-$[XO_4W_{11}O_{35}ML]^{n-}$, in which various diamagnetic or paramagnetic heteroatoms, X, can occupy the central tetrahedral site and in which various diamagnetic or paramagnetic metal atoms, M, can substitute for a W in an octahedral site of the parent 12-tungsto Keggin structure. Belt- and cap-octahedral-site-substituted (α_1 and α_2) derivatives of the Wells–Dawson structure, $[(XO_4)_2W_{17}O_{53}ML]^{n-}$, were also used. These systems are intermediate between those which have been treated by classical magnetochemistry and those for which solid state treatments are necessary. They offer a special case of mixed-valence influence on magnetic properties of inorganic compounds showing electron delocalization. Uniquely, the atoms over which the electrons are delocalized do not include the paramagnetic atoms involved. The properties of the paramagnetic (1e) blue electron systems must be explained on the basis of electron delocalization, high covalency, and high distortion factors, in addition to the expected large spin–orbit coupling constants. Most of these parameters have values near the limits of what may be considered safe for the classical magnetochemical model to be appropriate. On the other hand, antiferromagnetism is observed in 1e blues between delocalized unpaired blue electrons and transition metal ions in the octahedral or tetrahedral sites in the structure. In these complexes such interactions follow the strength pattern M(tetrahedral)–blue e < M(octahedral)–blue e < blue e–blue e. Diamagnetic blue electrons in 2e tungstate blues are firmly and completely coupled antiferromagnetically, although at a given instant they do not necessarily reside on adjacent W atoms. That coupling shows no temperature or field dependence in the conditions studied, implying an unusually large antiferromagnetic interaction between short-lived W^V centers via multiroute superexchange. Nevertheless, such blue electron pairs modify substantially the magnetic moments of octahedrally substituted transition metal ions by eliminating or greatly decreasing their second order contributions, such as spin–orbit couplings or zero field splittings. The pairs of blue electrons, despite the fact that they carry no magnetic moment, also modify the exchange coupling between transition metal ions which were antiferromagnetically coupled in the oxidized precursors. These properties are interpreted as resulting from an increase of covalency upon reduction and/or delocalization of the blue electrons. Such a conclusion is strongly supported by variable temperature ^{183}W NMR studies of spin densities in paramagnetic 2e blue species. Ring currents in blue complexes contribute to diamagnetism, but the other effects in paramagnetic species far outweigh them.

This paper is one of a series[1-11] aimed at further elucidating the roles of delocalized ("blue") electrons and of unpaired electrons in determining properties and structures of heteropoly complexes and their blue reduction products. It reports an extensive initial study of the influence of paired and unpaired delocalized added electrons on the magnetic susceptibilities of heteropoly anion systems that also contain localized unpaired d electrons in transition metal atoms incorporated into the magnetically isolated complexes at different specific sites. The blue electrons are delocalized over numerous atoms of the polytungstate frameworks.[1] As far as we are aware, this study constitutes the first treatment of such a problem on a molecular level. The examples presented here represent limited systems intermediate in size between those which have been treated in classical mixed-valence coordination chemistry and those involving itinerant electron magnetism in the solid state, and thus they suggest the pertinence of further study.

Background

Heteropoly complexes resemble discrete fragments of metal oxide structures of definite sizes and shapes.[12-17] They maintain their identities in ionic crystals and in aqueous and non-aqueous solutions, thus permitting study by various spectroscopies. Magnetic susceptibilities of the discrete complexes involve minimal lattice interactions.[18,19] Many heteropoly complexes of known

---

[†] Present address: Instituto de Ciencia de Materiales de Barcelona, CSIC, Campus U.A.B., 08193 Bellaterra, Barcelona, Spain.

* Address correspondence and reprint requests to this author.

(1) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2748.

(2) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(3) Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 3159.

(4) Jorris, T. L.; Kozik, M.; Casañ-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402.

(5) Kozik, M.; Casañ-Pastor, N.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1988**, *110*, 7697.

(6) Casañ-Pastor, N.; Bas-Serra, J.; Coronado, E.; Pourroy, G.; Baker, L. C. W. *J. Am. Chem. Soc.*, preceding paper in this issue.

(7) Acerete, R.; Casañ-Pastor, N.; Bas-Serra, J.; Baker, L. C. W. *J. Am. Chem. Soc.* **1989**, *111*, 6049.

(8) Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 7604.

(9) Gomez-Garcia, C. J.; Casañ-Pastor, N.; Coronado, E.; Baker, L. C. W.; Pourroy, G. *J. Appl. Phys.* **1990**, *67*, 5995.

(10) Casañ-Pastor, N.; Gomez-Romero, P.; Jameson, G. B.; Baker, L. C. W. *J. Am. Chem. Soc.* **1991**, *113*, 5658.

(11) Casañ-Pastor, N.; Acerete, R.; Baker, L. C. W. *J. Am. Chem. Soc.*, submitted for publication.

(12) Baker, L. C. W. In *Advances in the Chemistry of the Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961; pp 608ff.

(13) (a) Souchay, P. *Polyanions et Polycations*; Gauthier-Villars: Paris, 1963. (b) *Ions Minêraux Condensês*; Masson: Paris, 1969.

(14) Evans, H. T., Jr. *Perspect. Struct. Chem.* **1971**, *4*, 1.

(15) Weakley, T. J. R. *Struct. Bonding (Berlin)* **1974**, *18*, 131.

(16) Tytko, K. H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239.

0002-7863/92/1514-10384$03.00/0

structures can be made that contain various individual d-transition metal atoms, or combinations thereof, at specific sites.[4,17,20,21] Often the complexes exist in isomorphous series, which decreases interpretive complications. The complexes may involve (1) only diamagnetic atoms, (2) single paramagnetic atoms, or (3) combinations of paramagnetic atoms. Further, numerous of these heteropoly complexes (Pope's "Type I")[17] can be reversibly reduced by addition of various specific odd or even numbers of electrons. The reduction products, which typically have minimal structural differences from their oxidized precursors,[10] are frequently deep blue in color, comprising a large and potentially very important group of complexes generally known as the "heteropoly blues". The added "blue" electrons are "delocalized", according to various time scales, over numerous addenda atoms[1,17,22] (e.g., W, Mo, or V) and the oxygen atoms which link them in the heteropoly structures.[10] Heteropoly blues are usually regarded as class II systems in the Robin and Day treatment[23] of mixed-valence compounds.

Elucidation of electronic structure in heteropoly complexes and heteropoly blues is especially valuable for understanding of numerous important areas of current interest,[10] e.g., catalysis, intermolecular and intramolecular electron transfer, mixed oxide conductivity, mechanisms and pathways for mixed-valence electron delocalization and for d electron spin delocalization, theory of multinuclear NMR chemical shifts, and anti-tumor and anti-viral agents.

Electron delocalization in heteropoly blue complexes is viewed as operating through two mechanisms: a thermally activated electron hopping process from one addendum (e.g., W or Mo) atom to the next and a ground state delocalization (gsd)[10,17] involving π bonding and the bridging oxygens. A preponderance of evidence indicates that when a heteropoly blue tungstate contains an even number of blue electrons, their spins are characteristically completely paired at room temperature via multiroute superexchange.

Introduction

The present paper focuses on 23 isomorphous tungstate derivatives of the α-Keggin structure[24,25] plus four derivatives of another isomorphous series having the α-Wells–Dawson structure[26] (see Figure 1). Ten of the reduced species and one of the parent species are new complexes, and several of the anions were obtained in ionic crystals for the first time. The susceptibilities of solid samples of salts of reduced and nonreduced species were measured in a SQUID magnetometer from 4 to 300 K at a field strength of 5 000 G, and solutions of the species were measured at room temperature at 70 500 G by a very accurate modification[5] of Evan's ^{1}H NMR susceptibility method.

The α-Keggin structure (Figure 1a), $[XO_4W_{12}O_{36}]^{n-}$, has a tetrahedrally coordinated heteroatom, X, at its center. X may be a diamagnetic atom (e.g., Si^{IV}) or a paramagnetic atom (e.g., Co^{II} or Fe^{III}). The octahedrally coordinated W^{VI} atoms are diamagnetic, and one of them can be replaced by another diamagnetic octahedrally coordinated atom (e.g., Zn^{II}) or by a paramagnetic atom (e.g., Co^{II}, Fe^{III}, Cr^{III}, V^{III}, or V^{IV})[20] (see Figure 1b). Complexes wherein more than two paramagnetic atoms substitute for W atoms can be made, but they are not included in the present report.

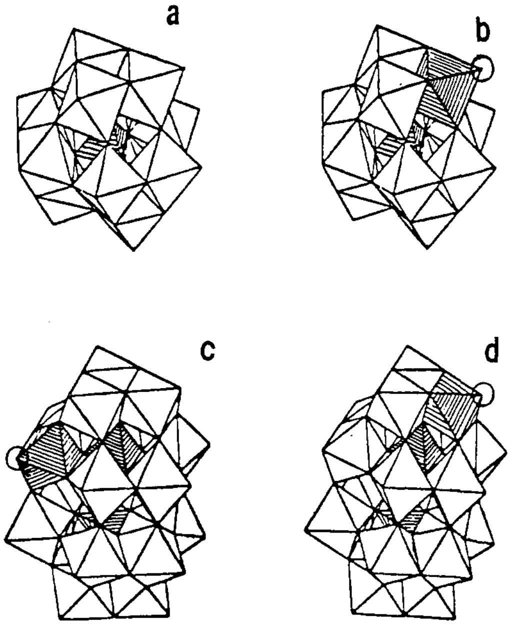

Figure 1. Structures of heteropoly complexes: (a) Keggin structure, α-$[XO_4W_{12}O_{36}]^{n-}$; (b) substituted Keggin structure, α-$[XO_4W_{11}O_{35}ML]^{n-}$; (c) belt-substituted Wells–Dawson structure, α_1-$[P_2W_{17}O_{61}ML]^{n-}$; (d) cap-substituted Wells–Dawson structure, α_2-$[P_2W_{17}O_{61}ML]^{n-}$. Each vertex locates the center of an oxygen atom, and each white octahedron contains a W atom, displaced far off-center toward its unshared O atom and away from the central tetrahedron. Each hatched tetrahedron contains a heteroatom, X (metal or non-metal), and each hatched octahedron contains a metallic heteroatom, M. Each circled vertex locates L, which is an O^{2-}, OH^-, or H_2O coordinated to M.

Similarly, octahedrally coordinated paramagnetic atoms can be substituted for a W^{VI} atom in one 6W belt or in one 3W cap of the α-Wells–Dawson structure (Figure 1, c and d).

The studies reported herein involve 1-electron (unpaired) and 2-electron (spin paired) heteropoly blue reduction products.

The first susceptibility measurements (77–300 K) on heteropoly species exhibiting magnetic exchange were carried out by Simmons[20,27] and later extended.[18,19,28] Nonreduced isostructural α-Keggin complexes, $[MO_4W_{11}O_{35}M'(H_2O)]^{n-}$ (Figure 1b), having two paramagnetic atoms, showed unusual antiferromagnetic properties. At low temperatures the susceptibilities followed Curie laws characteristic of the difference in the metals' spins (i.e., complete coupling); at high temperatures susceptibilities asymptotically approached Curie laws characteristic of the sum of the metals' spins (complete decoupling); in broad (~150 °C) intermediate temperature ranges only small changes in susceptibilities were exhibited. That was interpreted on the basis of very wide spans of magnetic states.[18,19]

Subsequently antiferromagnetism was observed (1) in a heteropoly complex containing three adjacent edge-sharing $V^{IV}O_6$ octahedra[29] and (2) in a complex containing three Cu^{II} atoms which were connected only through the heteropoly framework.[30] More recently, we have observed[6,31] ferromagnetic exchange in-

---

[17] Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

[18] Baker, L. C. W.; Baker, V. E. Simmons; Wasfi, S. H.; Candela, G. A.; Kahn, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5499.

[19] Baker, L. C. W.; Baker, V. E. Simmons; Wasfi, S. H.; Candela, G. A.; Kahn, A. H. *J. Chem. Phys.* **1972**, *56*, 4917.

[20] Baker, L. C. W.; Baker, V. E. Simmons; et al. *J. Am. Chem. Soc.* **1966**, *88*, 2329.

[21] For example: (a) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794. (b) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006. (c) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742, 2751. (d) Weakley, T. J. R.; et al. *J. Chem. Soc., Chem. Commun.* **1973**, 139. (e) Evans, H. T., Jr.; et al. *J. Chem. Soc. Dalton* **1986**, 2699.

[22] Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M. *J. Am. Chem. Soc.* **1983**, *105*, 6817.

[23] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 248.

[24] Keggin, J. F. *Proc. R. Soc. London* **1934**, *A114*, 75. Illingworth, J. W.; Keggin, J. F. *J. Chem. Soc.* **1935**, 575.

[25] D'Amour, H.; Allman, R. *Kristallogr. Z.* **1975**, *143*, 1.

[26] Wells, A. F. *Structural Inorganic Chemistry*, 1st ed.; Oxford University Press: Oxford, 1945; p 344. Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113. D'Amour, H. *Acta Crystallogr.* **1976**, *B32*, 729.

[27] Simmons, V. E. Doctoral Dissertation, Boston University, 1963; *Diss. Abs. Int.* **1963**, *24*, 1391.

[28] Wasfi, S. H. Doctoral Dissertation, Georgetown University, 1971; *Diss. Abs. Int.* **1971**, *33B*, 1050.

[29] Mossoba, M. M.; O'Connor, C. J.; Pope, M. T.; Sinn, E.; Hervé, G.; Tezé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864.

[30] Siedle, A. R.; Padula, F.; Baranowski, J.; Goldstein, C.; DeAngelo, M.; Kokoszka, G. F.; Azevedo, L.; Venturini, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 7447.

[31] Casañ-Pastor, N. Doctoral Dissertation, Georgetown University, 1988; *Diss. Abs. Inst.* **1989**, *50B*, 1397.

[32] Cox, P. A. *Chem. Phys. Lett.* **1980**, *69*, 340.

[33] Girerd, J. J. *J. Chem. Phys.* **1983**, *79*, 1766.

Table I. Analytical Results for Solid Samples,[a] Molecular Formulas Derived and Diamagnetic Corrections Applied on the Basis of the Analyses

compd	mol wt from W anal.	e^{*b}	no. of blue e	formula	dia. correction ×10^6 (emu/mol)
$SiW_{12}1e$	3178 (1)	0.83 (0)	0.83	$K_{4.83}[SiW_{12}O_{40}]\cdot 6.39H_2O$	−468
$SiW_{12}2e$	3382 (3)	1.86 (2)	1.86	$K_{5.86}[SiW_{12}O_{40}]\cdot 15.5H_2O$	−596
$Fe^{III}W_{12}$	3186 (18)		0	$K_5[Fe^{III}W_{12}O_{40}]\cdot 4.9H_2O$	−456
$Fe^{III}W_{12}1e$	3329 (6)	0.91 (0)	0.91	$K_{5.91}[Fe^{III}W_{12}O_{40}]\cdot 10.9H_2O$	−545
$Fe^{III}W_{12}2e$	3340 (18)	1.76 (1)	1.76	$K_{6.76}[Fe^{III}W_{12}O_{40}]\cdot 9.7H_2O$	−547
$Co^{II}W_{12}$	3196 (32)		0	$K_6[Co^{II}W_{12}O_{40}]\cdot 3H_2O$	−448
$Co^{II}W_{12}2e$	3384 (39)	1.77 (3)	1.77	$K_{7.7}[Co^{II}W_{12}O_{40}]\cdot 9.72H_2O$	−562
$SiW_{11}V^{IV}$	3272 (89)	1.00 (0)	0	$K_6[SiW_{11}V^{IV}O_{40}]\cdot 16.4H_2O$	−592
$SiW_{11}V^{III}$	3110 (60)	1.69 (1)	0	$[C(NH_2)_3]_{6.69}[SiW_{11}O_{39}V^{III,IV}(OH)]\cdot 1.44H_2O$	−523
$SiW_{11}V^{III}1e$	3296 (76)	3.06 (4)	1.06	$K_7[SiW_{11}O_{39}V^{III}(OH)]\cdot 15.6H_2O$	−604
$SiW_{11}V^{III}2e$	3371 (24)	4.03 (1)	2.03	$K_8[SiW_{11}O_{39}V^{III}(OH)]\cdot 17.6H_2O$	−647
$SiW_{11}Co^{II}$	3396 (20)		0	$Li_6[SiW_{11}O_{39}Co^{II}(H_2O)]\cdot 33.5H_2O$	−728
$SiW_{11}Co^{II}2e$	3191 (44)	1.80 (3)	1.80	$K_{7.8}[SiW_{11}O_{39}Co^{II}(H_2O)]\cdot 7.5H_2O$	−524
$Co^{II}W_{11}V^{IV}$	3315 (43)	0.68 (0)	0	$K_{7.68}[Co^{II}W_{11}V^{IV,V}O_{40}]\cdot 13.4H_2O$	−588
$Fe^{III}W_{11}Co^{II}2e$	3299 (12)	1.38 (0)	1.38	$K_{8.38}[Fe^{III}W_{11}O_{39}Co^{II}(H_2O)]\cdot 10.7H_2O$	−577
$Co^{II}W_{11}Co^{II}2e$	3285 (14)	1.38 (8)	1.38	$K_{9.38}[Co^{II}W_{11}O_{39}Co^{II}(H_2O)]\cdot 7.6H_2O$	−554

[a] All complexes are α isomers. [b] e* = number of electrons added per complex as shown by redox titrations.

volving four co-planar edge-sharing $Co^{II}O_6$ octahedra in a heteropoly complex. All of these previously-examined complexes were oxidized species, not involving delocalized blue electrons.

There have been relatively few magnetochemical studies of delocalized mixed-valence complexes, and in each of them one or, more usually, two paramagnetic atoms participate as recipient(s) of the "delocalized" electron. The situation pertaining in the present paper differs importantly from such cases in that the "blue" electrons are delocalized over a significantly larger number of atoms (W and O), and those atoms do not contain the localized unpaired electrons, although the paramagnetic atoms are intimately coordinated into the framework over which the blue electrons are delocalized. Thus the heteropoly blues containing paramagnetic atoms may present analogies, on a molecular level, to systems exhibiting itinerant electron effects on magnetic properties in the solid state (Kondo effect[35]) or to the random indirect coupling described by the RKKY model.[35] Of course the polytungstates' delocalized electrons do not behave as described by band theory (e.g., they do not show Pauli paramagnetism) since the electronic levels are still discrete. Nevertheless, in terms of sizes and nature of the systems, it appears that these complexes may link two extremes, classical magnetochemistry and solid state magnetism. The absence of bands, however, constrains us at present to deal with the effects in terms of classical magnetochemistry.

The unique magnetochemical systems described herein present a new sort of problem in coordination chemistry. The absence of extra localized unpaired electrons on atoms among which delocalized electrons move simplifies the situation somewhat, allowing a separation of contributions to magnetic properties.

Heteropoly tungstates were used in preference to polymolybdates or polyvanadates because the tungstates are generally more stable. The higher stability of 2e heteropoly blues over 1e blues resulted in a larger number of examples of the former.

In the remainder of this paper, an abbreviated notation will be used for the complexes. The abbreviated formulas omit oxygen atoms and anionic charges, and they specify the number of blue electrons as well as the pertinent oxidation states of transition metals (e.g., $[Fe^{III}W_{12}O_{40}]^{6-} = Fe^{III}W_{12}1e$, where e always represents blue electrons). For cases where there are two heteroatoms, the one written first corresponds to that in the tetrahedral site, and the last represents the metal substituted for W in an octahedral site (e.g., $[Fe^{III}O_4W_{11}O_{35}Co^{II}(H_2O)]^{9-} = Fe^{III}W_{11}Co^{II}2e$.

Experimental Section

Syntheses of Parent Oxidized Heteropoly Complexes. The syntheses of most of the parent oxidized complexes studied in this work[31] have been reported previously.[21a,d,27,28,36-48] All samples were recrystallized as described in the original preparative procedures. A new species, $[Co^{II}O_4W_{11}V^{IV}O_{36}]^{8-}$, was prepared by addition of $VOSO_4\cdot nH_2O$ to a concentrated solution of $[Co^{II}W_{11}O_{39}]^{9-}$ (in molar ratio ~2+:1) at pH 5. The lacunary $[Co^{III}W_{11}O_{39}]^{9-}$ was prepared by the method of Todorut and Baker.[46] The potassium salt of the new species was isolated by addition of KCl to the solution, followed by recrystallization.

In all cases complexes were identified in solution by their cyclic voltammograms[28,39,43,45,48-50] and, when possible, by their ^{183}W (and ^{31}P in the cases of phosphates) NMR spectra.[47,51,52] For paramagnetic samples, especially when no NMR could be observed, identification was also verified by UV-vis spectroscopy[27,53] and/or by the previously reported[18,19,27] magnetic moments at room temperature. For all of the compounds the fits of these identification methods, showing excellent purity, were perfect within the possible limits of observation.

In the case of the new species, $[Co^{II}W_{11}V^{IV}O_{40}]^{8-}$, the formulation is strongly supported by analogy to preparations of other isomorphous V^{IV} complexes,[17] and by the fact that the CV showed two quasireversible one-electron waves at positive potentials, with coulombic counts 1:1, corresponding to the known potential regions[48,50] for Co(III/II) and V(V/IV). It was possible to obtain in solution by controlled potential electrolysis the compounds containing $Co^{III}V^{V}$, $Co^{II}V^{V}$, and $Co^{II}V^{IV}$, and all the transformations were reversible. In addition, the visible spectra show absorptions characteristic of tetrahedrally coordinated Co(II) and of coordinated vanadyl ion,[27,53] at around 630 and 460 nm, respectively.

Each compound was prepared as a single batch product, and all measurements were made on samples from that batch. Those prepara-

---

(34) Borshch, S. A.; Kotov, I. N.; Bersuker, I. B. *Chem. Phys. Lett.* **1982**, *89*, 381. Drillon, M.; Pourroy, G.; Darriet, J. *Chem. Phys.* **1984**, *88*, 27.

(35) White, R. M. *Quantum Theory of Magnetism*; Springer-Verlag: Berlin, 1983.

(36) North, E. D. In *Inorganic Syntheses*; Booth, H. S., Ed.; McGraw-Hill: New York, 1939; Vol. I, p 129.

(37) Baker, L. C. W.; Pope, M. T. *J. Am. Chem. Soc.* **1960**, *82*, 4176.

(38) Reference 13b, p 106-107.

(39) Varga, G. M. Doctoral Dissertation, Georgetown University, 1968; *Diss. Abs. Int.* **1971**, *29B*, 926.

(40) Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935.

(41) Jorris, T. L. Doctoral Dissertation, Georgetown University, 1987; *Diss. Abs. Int.* **1989**, *49B*, 2639.

(42) Contant, R.; Ciabrini, J. P. *J. Chem. Res. (S)* **1977**, 222; *J. Chem. Res. (M)* **1977**, 2601.

(43) Tezé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999.

(44) Sanchez, C.; Livage, J.; Hervé, G. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2795.

(45) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186.

(46) Todorut, I.; Baker, L. C. W., in preparation.

(47) Acerete, R. Doctoral Dissertation, Georgetown University, 1981; *Diss. Abs. Int.* **1982**, *B42*, 3701.

(48) (a) Harmalker, S. P. Doctoral Dissertation, Georgetown University, 1982; *Diss. Abs. Int.* **1983**, *B43*, 2895. (b) Harmalker, S. P.; Pope, M. T. *J. Inorg. Biochem.* **1986**, *28*, 85.

(49) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547.

(50) Pope, M. T.; Varga, G. M. *Inorg. Chem.* **1966**, *5*, 1249.

(51) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267.

(52) Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

(53) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.

Table II. Reduction Potentials Applied and Conditions for Electrolyses for Obtaining Solid Salts for SQUID Measurements[a]

oxidized anion	concn, mol/L	medium	E_{appl}, V vs SCE	$Q_{\text{expt}}/Q_{\text{theo}}$	species formed
α-SiW$_{12}$	0.077	0.05 M H_2SO_4	−0.29	1.03	1e$^-$
	0.077	0.05 M H_2SO_4	−0.54	1.02	2e$^-$
α-Fe^{III}W$_{12}$	0.046	pH 4.5, 1 M LiOAc buffer	−0.43	0.95	1e$^-$
	0.046	pH 4.5, 1 M LiOAc buffer	−0.61	0.95	2e$^-$
α-Co^{II}W$_{12}$	0.05	pH 3, 1 M LiOAc buffer	−0.69	1.00	2e$^-$
α-SiW$_{11}$Co^{II}	0.025	pH 5.5, 1 M LiOAc buffer	−0.84	1.01	2e$^-$
α-SiW$_{11}$V^{IV}	0.019	pH 4.9	−0.84	1.0	V^{III}
	0.035	pH 7, 1 M Tris buffer	−0.83	1.0	V^{III} + 1e$^-$
	0.019	pH 4.8	−0.87	1.01	V^{III} + 2e$^-$
α-Fe^{III}W$_{11}$Co^{II}	0.01	pH 5.37, 1 M LiOAc buffer	−0.84	1.01	2e$^-$
α-Co^{II}W$_{11}$Co^{II}	0.01	pH 5.37, 1 M LiOAc buffer	−0.78	1.05	2e$^-$

[a] Compounds are shown with a contracted formula (e.g. α-[SiW$_{12}$O$_{40}$]$^{4-}$ is shown as α-SiW$_{12}$ and its two-electron blue as α-SiW$_{12}$2e$^-$). When two heteroatoms are present, the first occupies a tetrahedral site, while the second is substituted into an octahedral site.

tions of oxidized species that involved low yields were repeated several times, and the products were thoroughly mixed before any measurement or further treatment.

Electrolytic Preparation of Reduced Samples. Much care has to be taken during preparation and handling of heteropoly blues because most of them are decidedly sensitive to air oxidation.

Cyclic voltammograms for most of the anions studied had been previously reported,[28,39,43,45,48-50] but they were run again to determine the reduction potentials at the chosen conditions. A BAS CV 27 voltammograph with a supplementary ESC digital coulometer was used for CV and electrolysis experiments.

Preparation of solid salts (listed in Table I) was achieved by constant potential reductions, under the conditions shown in Table II. Reduced species for which susceptibilities were to be measured in solution were prepared at the same potentials as those used for the preparation of the corresponding reduced solids, but different concentrations of heteropoly complexes were used to prepare solids and to prepare samples for solution measurements (see Table III). The concentrations used in those cases, as well as the reference compounds used in such solution magnetic measurements, are given in Table III. That table also includes the conditions for those additional complexes the susceptibilities of which were measured only in solution. CV's of the reduced compounds were the same as those of the oxidized species, with two exceptions: α_1-[P$_2$W$_{17}$O$_{61}$Co^{II}(H$_2$O)]$^{8-}$, which shows a Co^{II} wave at very positive potentials, did not show it after reduction, probably owing to an increase in the reduction potential for the Co(III)/Co(II) pair. In the case of α-[SiW$_{11}$V^{III}O$_{40}$]$^{7-}$, three waves at positive potential are observed (related with V), while the V^{IV} precursor showed only one. This was interpreted in terms of the equilibrium existing between V^{III}–oxo, –hydroxo, and –aquo species, for the existence of which some proof exists.[48b] After reoxidation, the CV of the oxidized species returns in both cases. No evidence of heteropoly decomposition was observed, then, in any of the cases.

A double junction Ag/AgCl reference electrode with 1 M LiNO$_3$ solution in the outer compartment was used at all times to avoid precipitation of the not very soluble potassium salts, during electrolysis. Carbon cloth was always the working electrode, and platinum the auxiliary one, immersed in a half cell with the same supporting electrolyte. Before and during each electrolysis, a stream of nitrogen, deoxygenated by scrubbing through VCl$_2$ solution and then through water, was passed through the electrolysis solution. The method also ensures no evaporation of the solvent during the relatively long electrolyses (a consideration that proved very important when Evans susceptibility measurements were to be made on the blue solutions).

In most cases the proximity of higher reduction waves did not permit waiting for a current 1% of the original as a criterion for the end of the electrolysis. It was thus necessary to rely on the less sensitive methods of rest potential and number of coulombs expected theoretically. The overlap of the V^{IV}/V^{III} reduction wave with those of W did not prevent the preparation of the V^{III} derivative, although in this case the signal to stop the reduction had to be the coulomb count, which in turn coincided with the change in color to the typical blue of heteropoly blues.

For preparation of each solid salt, the electrolyzed solution was transferred to a Schlenck flask by applying pressure with argon or with the help of a gas-tight syringe and Teflon needle. The solid potassium salts were precipitated by the common ion effect upon addition of saturated deoxygenated solutions of KCl (transferred by gas-tight syringe) while stirring with an argon stream passing through the solution. The mixture was cooled with an ice bath and the solid filtered using a Schlenck setup, which also allowed washing with deoxygenated cold water. Afterwards the solid was dried in the same setup by passing a stream of argon over it for several hours. Guanidinium salts were obtained in cases where the potassium salts were very soluble.

Table III. Concentrations and Reference Compounds Used for Evans Measurements

compd	concn, mM	ref compd
SiW$_{12}$1e	15	SiW$_{12}$
SiW$_{12}$2e	11	SiW$_{12}$
Fe^{III}W$_{12}$	2.5	
Fe^{III}W$_{12}$1e	2.9	Fe^{III}W$_{12}$
Fe^{III}W$_{12}$2e	2.5	Fe^{III}W$_{12}$
Co^{II}W$_{12}$	15	
Co^{II}W$_{12}$1e	10	Co^{II}W$_{12}$
Co^{II}W$_{12}$2e	4.0	Co^{II}W$_{12}$
SiW$_{11}$Co^{II}	6.0	
SiW$_{11}$Co^{II}2e	6.0	SiW$_{11}$Co^{II}
Co^{II}W$_{11}$V^{IV}	6.0	
SiW$_{11}$V^{IV}	10	
SiW$_{11}$V^{III}	9.8	SiW$_{11}$V^{IV}
SiW$_{11}$V^{III}1e	9.8	SiW$_{11}$V^{IV}
SiW$_{11}$V^{III}2e	9.9	SiW$_{11}$V^{IV}
SiW$_{11}$Cr^{III}	2.4	
SiW$_{11}$Cr^{III}1e	2.4[a,f]	SiW$_{11}$Cr^{III}
SiW$_{11}$Cr^{III}2e	2.4[b,f]	SiW$_{11}$Cr^{III}
SiW$_{11}$Zn^{II}2e	10[c,f]	SiW$_{11}$Zn
α_1-P$_2$W$_{17}$Co^{II}	5.0	
α_1-P$_2$W$_{17}$Co^{II}2e	5.0[d,f]	α_1-P$_2$W$_{17}$Co^{II}
α_2-P$_2$W$_{17}$Ni^{II}	5.0	
α_2-P$_2$W$_{17}$Ni^{II}2e	5.0[e,f]	α_2-P$_2$W$_{17}$Ni^{II}
Fe^{III}W$_{11}$Co^{II}	3.6	
Fe^{III}W$_{11}$Co^{II}2e	3.6	Fe^{III}W$_{11}$Co^{II}
Co^{II}W$_{11}$Co^{II}	1.3	
Co^{II}W$_{11}$Co^{II}2e	1.3	Co^{II}W$_{11}$Co^{II}

[a] pH 7, 1 M Tris buffer, E_{appl} = −0.80 V. [b] pH 7, 1 M Tris buffer, E_{appl} = −0.99 V. [c] pH 4.9, 1 M LiOAc buffer, E_{appl} = −0.86 V. [d] pH 4.35, 1 M LiOAc buffer, E_{appl} = −0.45 V. [e] pH 5.0, 1 M LiOAc buffer, E_{appl} = −0.52 V. [f] Tris stands for tris(hydroxymethyl)aminomethane; OAc stands for acetate.

Most of the reduced samples were black solids (dark blue when ground). Attempts to prepare Wells–Dawson derivatives in the solid state always produced blue powders that were difficult to dry and extremely sensitive to traces of oxygen.

Despite the existence of a 1e wave at pH 5 for [Co^{II}W$_{12}$O$_{40}$]$^{6-}$, and the proofs of the existence of the 1e species in solution (magnetic moment at room temperature), isolation of Co^{II}W$_{12}$1e as a solid salt proved impossible. Although the solution was deep blue after reduction and the current had decreased smoothly during the electrolysis, addition of saturated KCl solution always yielded a black solid, later analyzed as the 2e blue, and a green solution corresponding to the oxidized species. Such disproportionation also always occurred when attempts were made to precipitate the 1e anion with various other counterions.

Analyses. Each solid sample to be measured in the SQUID magnetometer was analyzed for W. When vanadium was absent, W analysis was performed by EDTA back-titration of excess Pb^{II} after decomposition of the heteropoly anion by base and precipitation of lead tungstate with standardized Pb^{II} solution.[54] In cases where other transition metals were present, they had to be separated as the metal hydroxide(s) of the oxidized metal(s) after decomposition of the complex with excess strong base.[27] For complexes containing vanadium, W was determined gravi-

---

(54) Hayashi, H.; Moffat, J. B. *Talanta* **1982**, *29*, 943.

metrically with 8-hydroxyquinoline.[55]

The number of electrons which had been added to each reduced complex in the solid samples was determined by redox potentiometry. The sample of reduced compound was dissolved in excess standard deaerated $K_2Cr_2O_7$ solution, and the excess dichromate was back-titrated with standardized Mohr's salt solution.

The purpose of the analyses was to provide a best overall formula for each solid. The effective molecular weight of each salt was calculated from the most accurate analysis available (W). The formulas of the oxidized complexes were taken as correct based on the analyses which accompanied their original preparations and on the cleanness of the identifying experiments cited above. Since many of the waters of crystallization in heteropoly salts are zeolytic, the W analyses are necessary to fix the molecular weights of differently dried samples. The excellent precision of the triplicate analyses is indicated by the deviations shown in the calculated molecular weights in Table I.

In the cases of the heteropoly blues, the reductions were generally less than complete owing to the method of determining the end-points of the electrolyses and possibly slight electrolysis of solvent and/or, more probably, slight involvement of the next reduction wave. Again, the excellent precision of the triplicate redox analyses is shown in Table I. The solids were then taken to be mixtures (probably solid solutions of the isomorphous complexes) containing small proportions of oxidized complex in large proportions of the reduced species. This, with the W analyses, enables calculation of the formulas given in Table I from the redox titrations. Consequently, diamagnetic corrections and separations of the molar susceptibilities of the fully reduced form and of the oxidized impurity can be made, thus yielding the desired susceptibilities for the reduced species, as detailed below.

Susceptibility Measurements in Solution. All determinations of magnetic susceptibilities in solution for oxidized species were done at room temperature by the Evans method[56,57] using deaerated sample and reference solutions having densities that were accurately measured in a 2-mL pycnometer.[31] The ^1H NMR-active solute was *tert*-butyl alcohol, which does not interact with heteropoly species.[5] A Bruker AM-300WB NMR spectrometer, operating at 7.05 T (300.13 MHz for protons) and equipped with an Aspect 3000 computer, was used. For a superconducting magnet of usual geometry with a field parallel to the sample,[57] the Evans equation becomes

$$\chi_u - \chi_r = (3/(4\pi m))(\nu_u - \nu_r)/\nu_0 + \chi_0(d_r - d_u)/m \qquad (1)$$

where subscripts u and r refer to unknown and reference solutions, ν_0 represents the spectrometer frequency, d's are the solution densities, χ's are in gram susceptibilities, m is grams of unknown per milliliter of solution, and χ_0 is the gram susceptibility of the solvent. The solvent was a solution of the same buffer as that in which the complex was separately reduced. The method was checked by measuring the susceptibilities of several well-known simple species and two heteropoly anions, $Fe^{III}W_{12}$ and $Co^{II}W_{12}$, for which accurate literature values are available.[18,19,27,28,39] All results were within <1% of the literature values. Diamagnetic corrections, described below, were applied.

All determinations of magnetic susceptibilities of reduced species in solution at room temperature were made by the very sensitive and accurate modification of Evan's method which we have described in detail previously.[5] This method avoids the determinations of densities by experimentally canceling the last term in eq 1. It avoids any errors in estimating diamagnetic corrections and the necessity for problematic and less accurate matching of solution concentrations. It uses as reference solution the parent solution of the oxidized species and yields directly the difference between the susceptibilities of the reduced and oxidized forms.

When *diamagnetism* is being measured, the concentration needed to produce a ^1H NMR signal splitting considered significant (i.e., about 1 to 2 Hz) is approximately 10 mM. However, when a paramagnetic ion is present, especially if that ion possesses an orbitally nondegenerate ground state (e.g., Fe^{III} tetrahedral or octahedral), a large line broadening can prevent observation of resolved NMR peaks. For example, the upper limit of concentration for $Fe^{III}W_{12}$, for good results, lies at about 3 to 4 mM when the 1e blue is measured against the oxidized form.

The concentrations and reference compounds used for all of the solution measurements are listed in Table III.

Susceptibility Measurements on Solids. Magnetic measurements on solid samples were made on an SHE VTU Model 905 SQUID magnetometer, with an applied magnetic field of 5 000 G. Since the complexes retain their structures in solution and in the solid state, comparison of the SQUID measurements at 5 000 G with the Evans results for solutions t 70 500 G provides information about field dependence at room temperature, which is necessary for understanding the phenomena involved.

For SQUID measurements, especially on magnetically dilute samples such as heteropoly salts, it is essential to select a sample holder having a center of gravity that coincides with that of the sample. A description of this problem and the potential artifacts involved has been presented in another paper.[58]

After each dried reduced solid sample was prepared as described above, portions were transferred under argon into glass ampules, which were then sealed. Several ampules were made for each preparative batch. For a given compound, analyses were performed taking samples from different ampules to check for possible heterogeneity. If the extent of reduction for a specific compound was found to oscillate more than the small experimental error expected for such analyses, or if it suffered very fast oxidation upon being exposed to air, it was eliminated from the set of samples run in the SQUID. That was the case for all tetrabutylammonium salts and for the potassium salts of Wells–Dawson derivatives. For such samples, only the solution magnetic data are given in this paper.

For each compound an ampule containing it was broken in an argon-purged glovebag and the sample was tightly packed in the SQUID's preweighed aluminum–silicon sample bucket which was closed with the top and the adjusting and supporting cotton thread. Then each sample in the closed holder was weighed in air (a process that took less than 2 min and resulted in no oxidation detectable by analysis) and introduced into the sample chamber. The chamber was then purged with successive vacuum (to less than 100 mTorr) and helium treatments. The sample holder was preweighed for every run, full of argon. The difference in weight caused by the density of argon was calculated to be negligible.

After the magnetic data had been acquired, the samples (now containing He) were quickly resealed in ampules after purging with argon in a glovebag. They were later analyzed again by the redox methods described above. No appreciable changes in extents of reduction were observed.

Blank samples of the reduced compounds were weighed before and after purging in the magnetometer sample chamber, and no appreciable changes in weight (which might have come from dehydration at a pressure of 100 mTorr) were observed.

A number of corrections had to be applied to the raw data obtained from the SQUID, taking into account the exact number of added electrons. First, the contribution from the sample holder, as empirically determined by measuring it at many temperatures, was subtracted. Molecular weights obtained from the W analyses were used to calculate the average molar susceptibilities. These molecular weights and molar susceptibilities correspond to the mixtures of reduced and oxidized compounds which comprised the samples, as explained above. At this point diamagnetic corrections based on these average molecular formulas were applied. See Table I.

The diamagnetic corrections, which were also used for the oxidized compounds measured by the Evans method, are based on the value reported by Simmons[27] for $K_4[SiW_{12}O_{40}]\cdot 11H_2O$, which is -507×10^{-6} emu/mol. Corrections for changes in heteroatoms, number of tungstens, counterion numbers and type, and numbers of water molecules were based on Pascal constants.[59] A correction for the number of W^V atoms was also based on Pascal constants. The total diamagnetic corrections for all compounds are given in Table I.

Although not improbable, protonation of some of the heteropoly blue species was not taken into account in the average molecular formulas, the purpose of which was to estimate diamagnetic corrections. If protonation occurs, it decreases the number of counterions; but, since the molecular weight determination remains unchanged, more waters would have to be included in the formula. Thus the changes in diamagnetic corrections involved largely cancel each other. Protonation would increase the diamagnetic corrections modestly (~2.5% per proton) and, in the worst case, decrease the magnetic moment by a maximum of ~1.5% per proton at room temperature. The change in diamagnetic correction becomes so much less important at low temperatures that magnetic moments are essentially unchanged. The results from the Evans room temperature solution measurements are, of course, independent of calculated diamagnetic corrections for the blue species since the method itself cancels them out. In any case the changes are insufficient to affect significantly the conclusions of this study.

Excess diamagnetism attributable to ring currents[5] is not included in the diamagnetic corrections for heteropoly blues since its behavior with

---

(55) Erdey, L. *Gravimetric Analysis*, Part II; Pergamon Press: Oxford, 1965; p 552.

(56) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(57) Becker, E. D. *High Resolution NMR. Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980; p 44.

(58) Casañ-Pastor, N.; Gomez-Romero, P.; Baker, L. C. W. *J. Appl. Phys.* **1991**, *69*, 5088.

(59) Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; John Wiley and Sons: New York, 1976.

Table IV. Room Temperature Magnetic Moments (μ_B)

	SQUID (5000 G, solid)		EVANS (^{1}H NMR) (70 500 G, solution)
$SiW_{12}1e$	1.48		1.30
$SiW_{12}2e$	the complex is diamagnetic; see Table V		
$SiW_{11}Zn^{II}2e$	the complex is more diamagnetic than its oxidized parent; see Table V		
$Co^{II}W_{12}$	4.30		4.28
$Co^{II}W_{12}1e$			4.37 (max 4.4)[a]
$Co^{II}W_{12}2e$	4.38		4.24
$Fe^{III}W_{12}$	5.85		5.88
$Fe^{III}W_{12}1e$	5.65	≪	6.09 (max 6.09)[a]
$Fe^{III}W_{12}2e$	5.82		5.89
$SiW_{11}V^{IV}$	1.76		1.75
$SiW_{11}V^{III}$	2.55		2.58
$SiW_{11}V^{III}1e$	2.18	≪	2.70 (max 2.9)[a]
$SiW_{11}V^{III}2e$	2.82		2.83 (max 2.6)[a]
$SiW_{11}Co^{II}$	5.27	<	5.37
$SiW_{11}Co^{II}2e$	4.88	<	5.10
$SiW_{11}Cr^{III}$			3.87
$SiW_{11}Cr^{III}1e$			3.87 (max 4.1)[a]
$SiW_{11}Cr^{III}2e$			3.87
α_1-$P_2W_{17}Co^{II}$			4.93
α_1-$P_2W_{17}Co^{II}2e$			4.00
α_2-$P_2W_{17}Ni^{II}$			3.01
α_2-$P_2W_{17}Ni^{II}2e$			2.81
$Co^{II}W_{11}V^{IV}$	4.80	<	4.90 (max 4.6)[a]
$Fe^{III}W_{11}Co^{II}$	6.14	≪	6.45 (max 7.7)[a]
$Fe^{III}W_{11}Co^{II}2e$	6.36	≪	6.63 (max 7.7)[a]
$Co^{II}W_{11}Co^{II}$	6.30	≪	6.80 (max 6.8)[a]
$Co^{II}W_{11}Co^{II}2e$	6.31	≪	6.63 (max 6.8)[a]

[a] The max value is the estimated expected value if no magnetic coupling is present.

Table V. Differences between Corrected Molar Susceptibilities of Blue Species and Oxidized Species at Room Temperature, at 70 500 and 5 000 G

compd	$[X_M(2e^-) - X_M(0e^-)] \times 10^{-6}$ emu/mol: 70 500 G	$[X_M(2e^-) - X_M(0e^-)] \times 10^{-6}$ emu/mol: 5 000 G
α-SiW_{12}	−180	−83[a]
α-$SiW_{11}Zn$	−140	
α-$Fe^{III}W_{12}$	<|200|	−147[a]
α-$Co^{II}W_{12}$	−160	292
α-$SiW_{11}V^{III}$	569	610
α-$SiW_{11}Co^{II}$	−1190	−1660
α-$SiW_{11}Cr^{III}$	<|200|	
α_1-$P_2W_{17}Co^{II}$	−3500	
α_2-$P_2W_{17}Ni^{II}$	−990	
α-$Fe^{III}W_{11}Co^{II}$	990	1160
α-$Co^{II}W_{11}Co^{II}$	−961	53[a]

[a] The experimental error is larger than these numbers. The errors in the modified Evans method are much smaller than those in the SQUID method.

Table VI. Curie Law Parameters for Oxidized and Blue Species (Regression Coefficients Range from 0.999 to 0.9999)

compd	*C*, emu K/mol	θ	10^{-6}TIP, emu/mol	S_{eff}
$SiW_{11}V^{IV}$	.365		155	0.98/2
$Fe^{III}W_{12}$	4.335			4.89/2
$Fe^{III}W_{12}1e$	3.950			4.71/2
$Fe^{III}W_{12}2e$	4.335			4.89/2
$Co^{II}W_{12}$	2.330			3.43/2
$Co^{II}W_{12}2e$	2.310			3.41/2
$Co^{II}W_{11}V^{IV}$	2.820		870	3.86/2

temperature, although probably constant except at very low temperatures, is really unknown, and because it is probably not constant from compound to compound (even in isostructural cases). These points will be discussed.

The small temperature-independent paramagnetism (TIP) corrections for Co ions were also not included since the main focus of interest is in the behavior of blue species relative to their oxidized parents.

Calculation of the magnetic properties of the heteropoly blue species in a case where the number of electrons added was not integral requires a mathematical separation of the magnetic contributions involved.

If a 1e sample is considered to be a mixture of the oxidized and 1e blue compounds, the charge balance requires that the number of added electrons, n, is related to the mole fraction, x, of the 1e blue by $n = 1x + 0(1 - x) = x$. Then the molar susceptibility of the 1e blue is $\chi_{Mblue} = (\chi_{Msample} - (1 - x)\chi_{Moxid})/x$ (all χ's having been corrected for diamagnetism). χ_{Moxid} is the separately determined molar susceptibility of the oxidized parent.

In the case of a 2e sample there are two possibilities. It could be a mixture of 2e and oxidized compound or a mixture of 2e and 1e compounds. For the 2e + oxidized mixture, $n = 2x + 0(1 - x)$; and so the mole fraction of 2e blue is $x = n/2$. A calculation similar to that described for the preceding case will yield $\chi_{M2e\,corr}$. For the case of a 2e + 1e mixture, $n = 2x + 1(1 - x)$ and $x = n - 1$. Then χ_{M2e} can be calculated if χ_{M1e} is known.

The decision about the type of mixture present in the 2e blue samples is based on the internal consistency of the set of data for the group of heteropoly blues derived from the same oxidized species. As a first approach, the non-existence of 1e waves in the cyclic voltammograms at the pH of preparation is a good indicator that the mixture will be 2e + 0e, assuming that equilibrium between species in different oxidation states would be more difficult in the solid. The total non-existence of a 1e wave at any pH can be considered a stronger indication of the instability of the 1e species.

Taking the $Fe^{III}W_{12}$ series of compounds as an example, if the corrections are made assuming that the 2e sample is a mixture of 1e and 2e blues, then the 2e blue comes out to be more paramagnetic than the 1e or the oxidized species. While this is certainly a remote possibility, it does not agree with the value obtained for the 2e species when measured vs the oxidized species in the Evans experiments. One might also suppose that the 1e sample has really disproportionated into a mixture of 2e and 0e. In that case the 2e blue comes out much more diamagnetic than the oxidized species but very different from the results obtained for the real 2e sample and from Evans measurements. Therefore we may safely conclude that the 2e blue sample is a mixture of 2e and 0e and that the 1e sample is a mixture of 1e and 0e. On that basis the results come out consistent and reasonable.

If the same type of reasoning is applied to all samples, all 2e samples not showing a one-electron wave at the pH of preparation come out to be mixtures of 0e and 2e. Two-electron SiW_{12}, which shows a one-electron wave, is 1e + 2e. $Co^{II}W_{12}$, which also shows a one-electron wave, however, is 2e + 0e, probably owing to the low stability of the 1e versus the 2e species, consistent with the previously described disproportionation of the 1e species upon precipitation.

Results and Discussion

Overview. The general overall conclusions of this study are summarized in the Abstract; their substantiation is explained below.

Data. Table IV lists the corrected room temperature magnetic moments determined (1) in the SQUID magnetometer at 5 000 G and (2) in solution by the Evans method at 70 500 G. Since these stable heteropolytungstate complexes in solution retain the same structures as in the solid state, these data provide useful information about field dependences. Table V shows the differences between corrected molar susceptibilities of blue species and their oxidized parents at room temperature at the two field strengths. The magnetic data for solid $Fe^{III}W_{12}$, $Fe^{III}W_{12}1e$, $Fe^{III}W_{12}2e$, $Co^{II}W_{12}$, $Co^{II}W_{12}2e$, $SiW_{11}V^{IV}$, and $Co^{II}W_{11}V^{IV}$ all followed Curie laws down to 4 K, with the parameters given in Table VI. The following figures represent the magnetic data (4–300 K) for the following solids: Figure 2, $SiW_{12}1e$; Figure 3, $SiW_{11}V^{III}$, $SiW_{11}V^{III}1e$, and $SiW_{11}V^{III}2e$; Figure 4, $SiW_{11}Co^{II}$ and $SiW_{11}Co^{II}2e$; Figure 5, $Fe^{III}W_{11}Co^{II}$ and $Fe^{III}W_{11}Co^{II}2e$; Figure 6, $Co^{II}W_{11}Co^{II}$ and $Co^{II}W_{11}Co^{II}2e$. The estimated errors for μ_{eff} range from 0.1 μ_B for the most magnetically dilute species at the higher temperatures down to 0.01 μ_B for species that contain Fe^{III}.

Blue Species without Paramagnetic Atoms. The magnetic behavior of diamagnetic 2e heteropoly blues was the subject of a recent publication by our group[5] based on accurate measurements, by our modified Evans method, of the differences in

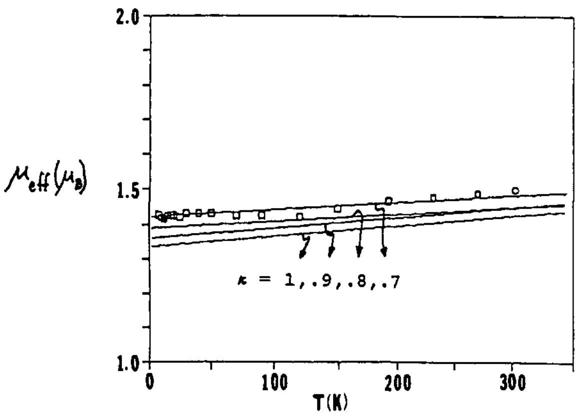

Figure 2. Effective magnetic moment vs T for $SiW_{12}1e$. Squares are experimental points and lines are trial fits for $\lambda = 1000\ cm^{-1}$, $\nu = \Delta/\lambda = 3$, $\kappa = 1, 0.9, 0.8, 0.7$. The upper line is the best fit. See text.

susceptibilities between reduced species and their oxidized precursors. In all the cases studied the 2e species were more diamagnetic than the corresponding oxidized complexes. The diamagnetic susceptibilities are not field dependent[5,31] in the range $H = 7$–12 T nor temperature dependent down to 6 K. The excess diamagnetisms in the 2e species are attributable to ring currents, which explains the direct dependence of that excess diamagnetism (1) on the radius of the loop of addenda octahedra through which the blue electrons circulate, (2) on the number of circulating blue electrons, and (3) on geometrical factors affecting the average orientation of the conduction loop.[5] For $SiW_{12}2e$, wherein all the W atoms participate equally in the electron delocalization on the NMR time scale[1] so that electron circulation is not restricted by the complex's orientation in the magnetic field, the excess diamagnetism is -180×10^{-6} emu/mol. That value yields, via Langevin's equation,[60,61] a loop of radius 5.4 ± 0.2 Å, which coincides well with the crystal structures of Keggin tungstates. It is also possible in these systems to induce localization of one of the added electrons by substitution of Mo for one W in the structure,[5] in which case the excess diamagnetism observed is half of the value for two blue electrons. XPS,[4] ESR,[22] and NMR[1] studies have shown the coexistence of only +6 and +5 oxidation states for W addenda atoms in 1e and 2e heteropoly blues. Thus, the two blue electrons in 2e polytungstates are strongly antiferromagnetically coupled, while still being delocalized through the structure.

As shown in Figure 2, $SiW_{12}1e$ appears to approximate a Curie law despite the big spin–orbit coupling expected for W^V (~3500 cm^{-1} for the free ion[62]) and the fact that the magnetic moment remains near 1.4–1.5 μ_B, distinctly lower than the spin-only value, over the entire temperature range. Even correction for the excess diamagnetism (ring current effect) raises the moment by only 0.1 μ_B. At 5 000 G the room temperature moment is higher than at 70 500 G (1.48 and 1.30μ_B respectively). This field dependence must derive from a large splitting of the ground state[63] originating in the considerable positive spin–orbit coupling constant. At high fields the high energy levels, having lower J multiplicity, are more accessible for thermal population, thus lowering the effective moment. The same effect, but with opposite sign, is observed for the compounds containing octahedral Co^{II}, to be explained below.

The temperature depencence of μ_{eff} for $SiW_{12}1e$ (Figure 2) approximates a straight line but with a small depression around 125 K, as if the behavior would shift from a Curie–Weiss law above 125 K to a Curie law at lower temperatures. Although this small depression seems to be real, no attempt was made to explain it in view of the number of variables already involved.

The main factors contributing to magnetic behavior of a d electron in a W^V atom, which has orbitally degenerate ground states, are (1) the spin–orbit coupling constant, λ, for each W^V, (2) the considerable distortion, Δ, of the WO_6 unit from ideal octahedral symmetry (which splits the T ground state into A and E states for a case of axial distortion), and (3) a covalency factor, κ, that represents the degree of molecular orbital formation or the degree of electron delocalization (related to covalency). Both the crystal field distortion and the covalency factor lower the spin–orbit constant.[63-65]

The value of κ may vary between 0 and 1 in theory, but in practice no values smaller than 0.7 are obtained. Any value too different from 1 is considered a sign of non-validity of the theory of perturbation being used since the perturbation would already be too large.[65] As κ decreases the moment approaches the spin-only value, and linearity of the μ_{eff} vs T plot increases.

Variation of effective magnetic moments for a d^1 or d^9 system with an octahedral ground state $^2T_{2g}$, as a function of different Δ/λ ratios, has been well studied by Figgis and Lewis.[66] For λ values of the order of 200 cm^{-1} (a typical value for first transition series ions), the usual temperature range studied, 2–300 K, corresponds to a kT/λ range between 0 and 1 (that is, λ is of the me order of magnitude as kT). However, if λ is around 1000 cm^{-1}, the same temperature range is related to a kT/λ between 0 and 0.2 (that is, kT never reaches the value of λ). Therefore, as λ reaches very large values, the behavior of μ_{eff} becomes more linear in the usual temperature range (4–300 K).

Nevertheless, fitting of $SiW_{12}1e$ data was not possible by taking into account λ and Δ only. κ needed to be introduced in order to obtain a reasonable fit. Figure 2 shows different trial fits based on Figgis's tabulation.[67] Different combinations of those parameters with λ values between 500 and 1500 cm^{-1}, κ values between 0.7 and 1, and Δ values between 3 and 4 times the value of λ were tried for this sample. Although only a few of these are shown in Figure 2, the best fit corresponds to the following set of values: $\lambda = 1000\ cm^{-1}$, $\Delta/\lambda = 3$ ($\rightarrow \Delta = 3000\ cm^{-1}$), and $\kappa = 0.7$. Although the goodness of this set of parameters (not necessarily unique) needs to be taken with caution, it is evident that a good fit is achieved only with extreme values for all parameters involved, implying the doubtful applicability of classical theories in these systems. It is worth noting that a correction for excess diamagnetism arising from ring current effects leads to no appreciable change in the fit.

Among the few W^V compounds investigated in the past, we have found only one,[68] (quinolinium)$WOCl_4$, the magnetic behavior of which indicates similar parameters ($\Delta = 1800\ cm^{-1}$, $\kappa = 0.8$, and $\Delta/\lambda = 3$). However, it is not possible to check the influence of electron delocalization since to our knowledge the structure has not yet been reported.

ESR studies of 1e blues show that the blue electron becomes localized on a W in a rhombic site at very low temperatures (ca. 10 K for tungstates).[17,22,69] The e localization process for 1e blues (decrease of hopping rates as temperature falls at low T's) suggests that the electronic parameters λ, κ, and Δ might also be temperature dependent in the region of T where increasing localization is significant. It is, however, evident that there is no strong modification of these factors in such temperature ranges capable of changing the behavior of μ_{eff} vs T. Electron localization is not modifying substantially the covalency parameter or the distortion of the octahedron, and thus the magnetic properties may be more directly related to the ground state delocalization scheme than to the thermal e hopping, and the gsd may be responsible for the

---

(60) Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977; p 413.

(61) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 673.

(62) Casey, A. T.; Mitra, S. In *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; John Wiley: New York, 1976.

(63) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London (Halsted Press: New York), 1973.

(64) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill, Inc.: London, 1979; p 69.

(65) Gerloch, M.; Miller, J. R. *Prog. Inorg. Chem.* **1968**, *10*, 1.

(66) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.

(67) Figgis, B. N. *Trans. Faraday Soc.* **1961**, *57*, 198.

(68) Brisden, B. J.; Edwards, D. A.; et al. *J. Chem. Soc.* **1967A**, 1825.

(69) Launay, J. P.; Fournier, M.; Sanchez, C.; Livage, J.; Pope, M. T. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 257.

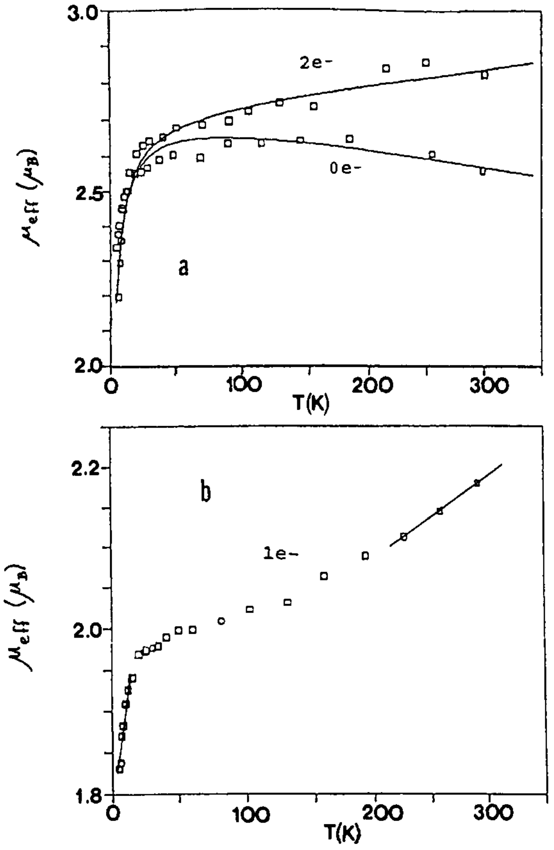

Figure 3. Effective magnetic moments versus temperature: (a) $SiW_{11}V^{III}$ and $SiW_{11}V^{III}2e$ (solid lines represent polynomial fits without physical meaning) and (b) $SiW_{11}V^{III}1e$ (solid lines indicate Curie–Weiss law fits).

extreme values of κ. Apart from the ring current effects, no special properties are observed that can be directly related to the thermal e hopping.

Parent Oxidized Compounds. $[Fe^{III}W_{12}O_{40}]^{5-}$, $[Co^{II}W_{12}O_{40}]^{6-}$, $[Fe^{III}W_{11}Co^{II}(H_2O)O_{39}]^{7-}$ and $[Co^{II}W_{11}Co^{II}(H_2O)O_{39}]^{8-}$ had been studied and interpreted before.[18,19,27,70] For the last two, antiferromagnetic coupling between transition metals was observed, as described in the Introduction section above. Only the field dependence will be described here.

All complexes containing a single paramagnetic ion (Table I) follow at least qualitatively the expected behavior for their number of electrons and geometry. Co^{II}, distorted octahedral[27,71] high spin d^7 (3d shell more than half filled) with a big negative spin–orbit coupling constant (-180 cm^{-1} for the free ion[62]), has as expected a magnetic moment higher than the spin-only value of 3.87 μ_B (Table IV) and a nonlinear dependence of μ_{eff} on temperature (see Figure 4). V^{III}, distorted octahedral d^2 (3d shell less than half filled) with a smaller positive spin–orbit constant (about 100 cm^{-1} for the free ion[62]), shows, at room temperature, a moment smaller than the spin-only value. The moment also changes nonlinearly with temperature (see Figure 3). Neither the Co^{II} nor the V^{III} could be fitted exactly to the existing models for axial distortion,[63] although they did qualitatively agree. Fe^{III}, regular tetrahedral high spin d^5 in $Fe^{III}W_{12}$, follows, as expected, a Curie law (Table VI) with a magnetic moment somewhat smaller than the spin-only value (5.88 μ_B observed vs 5.92 μ_B for spin-only). The small difference may be owing to a small zero field splitting (which in fact has been observed[70] for $Fe^{III}W_{12}$). Co^{II}, regular tetrahedral in $Co^{II}W_{12}$, fits well (Table VI) without considering its small TIP. Although the TIP value in the 2e blue is unknown, it is probably very similar to that in the oxidized species, and no attempt was made to include it in treating either compound.

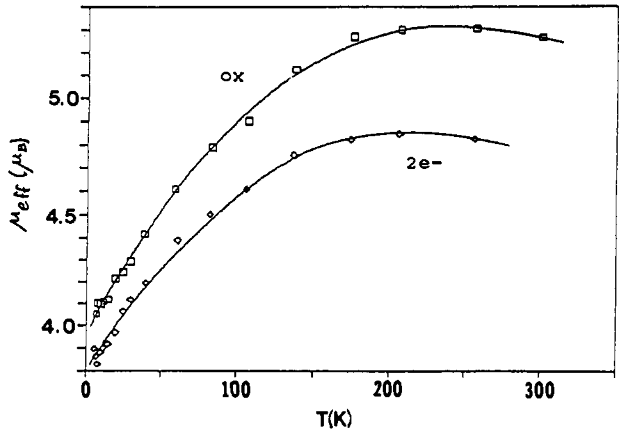

Figure 4. Effective magnetic moments versus T for $SiW_{11}Co^{II}$ and $SiW_{11}Co^{II}2e$. Solid lines represent polynomial fits without physical meaning.

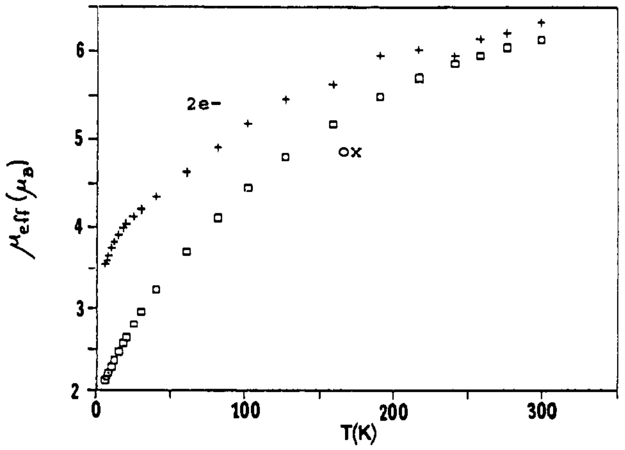

Figure 5. Effective magnetic moments vs T for $Fe^{III}W_{11}Co^{II}$ (□) and $Fe^{III}W_{11}Co^{II}2e$ (+).

$[Co^{II}W_{11}V^{IV}O_{40}]^{8-}$, taken as an example of a localized 1e case, showed a moment at room temperature higher than the sum expected for non-interacting Co^{II} tetrahedral (as measured in $Co^{II}W_{12}$) plus distorted octahedral V^{IV} (as measured in $SiW_{12}V^{IV}$). The temperature dependence showed very small interaction, if any. The Co^{II} and/or the V^{IV} contribution must therefore be underestimated by the assumptions that the irregular $Co^{II}O_4$ tetrahedron in $Co^{II}W_{11}V^{IV}$ has the same moment as the regular $Co^{II}O_4$ tetrahedron in $Co^{II}W_{12}$ and that the V^{IV} has the same moment as in $SiW_{11}V^{IV}$. The data fit two different Curie–Weiss laws:

$$\text{low } T\text{: } \chi = 0.356/(T + 0.1) \qquad S_{eff} = 3.9/2$$

$$\text{high } T\text{: } \chi = 0.353/(T + 11.0) \qquad S_{eff} = 3.9/2$$

where the S_{eff} obtained at low and high temperature are both high (corresponding to about 4e) and equal, implying no interaction. In addition, the fact that the Weiss constant is so large for the high-temperature fit implies that the model describing the system does not need to include coupling but a TIP instead, which will be 870 cm^{-1}, with the same S_{eff} of 3.9/2. The slight field dependence at room temperature (Table IV) may represent a very small coupling not detectable in the Curie plots. Table VI shows the parameters for the final Curie law fit.

Monosubstituted complexes do not show any field dependence with the exception of the complexes containing distorted octahedral Co^{II}, which show a very small dependence. In those Co^{II} compounds the spin–orbit coupling splits the ground state, giving rise to levels with different effective spins (see Figure 7). Different level occupation occurs since λ is of the same order of magnitude as the thermal energy ($kT = 206$ cm^{-1} at 297 K). A perturbing applied field makes accessible the higher energy states, consequently raising the magnetic moment.[63,72]

---

[70] So, H.; Pope, M. T. *J. Chem. Phys.* **1971**, *55*, 2786.

[71] Figgis, J. S. F. Doctoral Dissertation, Georgetown University, 1970; *Diss. Abs. Int.* **1970**, *31B*, 2537.

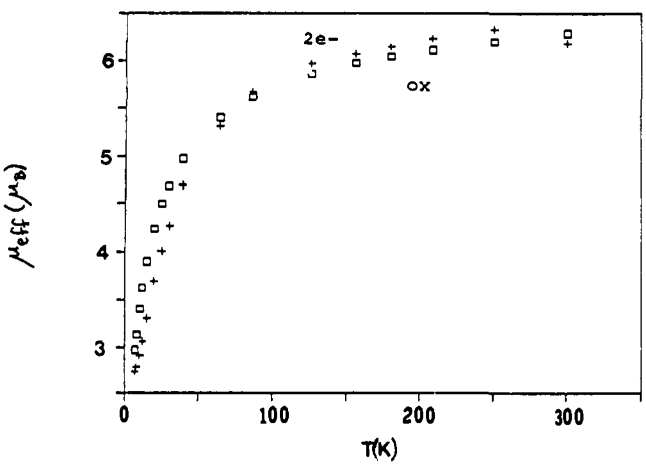

Figure 6. Effective magnetic moments vs T for $Co^{II}W_{11}Co^{II}$ (□) and $Co^{II}W_{11}Co^{II}2e$ (+).

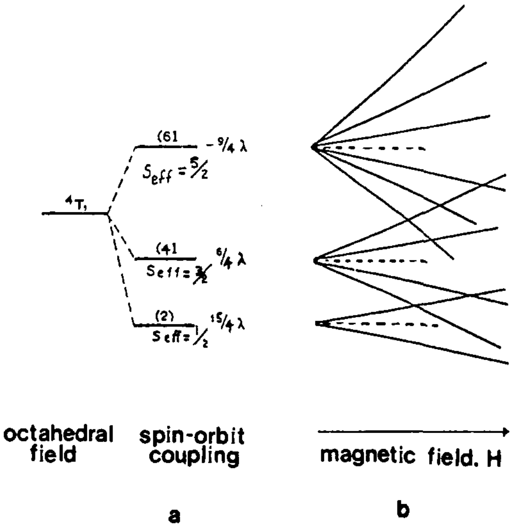

Figure 7. Splitting diagram produced by (a) spin–orbit coupling and (b) applied field for Co^{2+} ($\lambda = -180\ cm^{-1}$ for free ion, approximate thermal energy at room temperature).

On the other hand, oxidized complexes containing two paramagnetic transition metals (with the exception of $CoW_{11}V^{IV}$, treated above) show a large field dependence. Specifically, the compounds become more paramagnetic at higher fields, of the order of 7 T. The diagram shown in Figure 8 pertains to a simple d^1–d^1 system coupled antiferromagnetically, thus presenting a singlet ground state ($S = 0$) and a triplet excited state ($S = 1$). In the presence of a high field, the m_s levels from $S = 1$ can become the lowest in energy, and so the coupling is partially broken.

The values given as "max" in Table IV correspond to expected moments if the coupling is completely broken, as calculated from data for isomorphous complexes containing each individual ion. The field dependence where the moment increases with field is, then, an indication of antiferromagnetic coupling and of its relative strength.

With respect to $Fe^{III}W_{11}Co^{II}$ and $Co^{II}W_{11}Co^{II}$, the latter shows a complete break of coupling at high field while the former does not. This agrees with the values of J reported[18,19] previously: −50 and $-6\ cm^{-1}$, respectively.

Mixed Systems: Blues Containing Paramagnetic Transition Metals. (a) One-Electron Blues. Simmons[27] calculated, on theoretical grounds, that 1e or 2e reduction of Keggin structure complexes containing Fe^{III} would not result in formation of any Fe^{II} species. That was subsequently experimentally verified by Varga.[39]

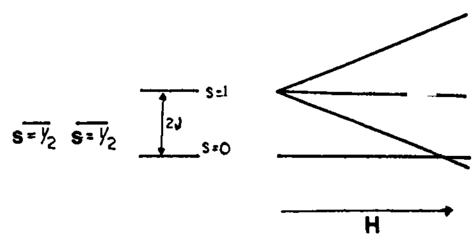

Figure 8. Splitting diagram for an antiferromagnetically coupled d^1–d^1 system.

The field dependence may be used as a diagnostic indication of coupling. The room temperature values of μ_{eff} for $Fe^{III}W_{12}1e$ and for $Co^{II}W_{12}1e$ correspond to the maximum expected moments at 70 500 G, respectively 6.09 and 4.37 μ_B (Table IV), while the iron complex has a moment at 5 000 G lower than the oxidized complex's moment. This indicates that antiferromagnetic coupling exists between Fe(III) and the blue electron, and it is strong even at room temperature, but it is broken completely by a field of 70 500 G. $Co^{II}W_{12}1e$ may well have the same type of coupling, but disproportionation upon crystallization prevented measurements of the solid 1e complex at 5 000 G. On the other hand $SiW_{11}Cr^{III}1e$ (for which the analyses also showed disproportionation during precipitation) has, nevertheless, a moment in solution at room temperature at 70 500 G, equal to the moment of the oxidized complex. This can be explained by postulating that the antiferromagnetic coupling is weak or, less probably, by postulating a very slow but complete disproportionation even in solution.

Despite the fact that no coupling seems to exist between Co^{II} in the tetrahedral site and the one electron localized on a V^{IV} in $Co^{II}W_{11}V^{IV}$ (the oxidized species), the coupling between inner tetrahedral heteroatoms and outer delocalized electrons is possible, as the $Fe^{III}W_{12}1e$ case shows. The existence of such coupling in the case of the Fe^{III} complex suggests that the electron delocalization facilitates the antiferromagnetic exchange. From structural data[10] it is known that the bonds between W atoms and the O atoms of the central tetrahedron get measurably longer and weaker upon 2e reduction. On the other hand, spin density analyses of $Co^{II}W_{12}$[7] and $Co^{II}W_{12}2e$[11] based on variable temperature ^{183}W NMR data show a notable increase in contact contribution to the isotropic shift of ^{183}W upon reduction (while the dipolar contributions decrease substantially). An increase in covalency between the Co^{II} and the heteropoly framework is thus occurring upon reduction. Tungsten, having much more diffuse orbitals than vanadium, can show a better overlap with the bridging oxygens connecting it with other tungstens or heteroatoms, a fact that also aids the delocalization of electrons and participation of the bridging oxygens in the gsd scheme. The superexchange mechanism is clearly more effective in the case of tungsten.

While the coupling in $Fe^{III}W_{12}1e$ is completely broken at 70 500 G, that in $SiW_{11}V^{III}1e$ is only partially broken, and the coupling of the blue electrons in $SiW_{12}2e$ remains complete for the same field strength. This suggests the following sequence of coupling strengths for 1e blues:

$$\text{M(tetrahedral)–blue e} < \text{M(octahedral)–blue e} < \text{blue e–blue e}$$

It is clear that this follows the order of orbital overlaps, including the bigger size of the tungsten orbitals as compared with first row transition metals.

Besides exhibiting antiferromagnetic coupling at room temperature and 5000 G, as explained above, $Fe^{III}W_{12}1e$ closely approximates Curie law behavior as summarized in Table VI. The coupling at room temperature may not be complete. However, the big magnetic response of high spin d^5 Fe^{III} would be expected largely to conceal the small changes in χ_M caused, as the temperature is lowered, by the coupling with the blue electron.

The effective moment vs temperature plot for $SiW_{11}V^{III}1e$ (Figure 3) shows a typical case of antiferromagnetic coupling. At room temperature and 5000 G it shows an effective moment much lower than its oxidized V^{III} precursor: 2.55 μ_B for $SiW_{11}V^{III}$

---

(72) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986.

vs 2.18 μ_B for $SiW_{11}V^{III}1e$. As the temperature is lowered the moment keeps decreasing until it reaches a plateau at around 100 K, considered as reaching complete coupling. The lowering of the moment at lower temperatures is clearly related to the orbital contribution from V^{III}. The data can be fitted to two different Curie–Weiss laws, one at high temperatures and the other at low temperatures (see Figure 3b) with regression coefficients of 0.9997 and 0.99997 respectively:

	C	Θ	S_{eff}
high T	0.768	−86	1.7/2
low T	0.514	−1.3	1.3/2

This shows a large coupling constant (between the two unpaired electrons from V^{III} and the one blue electron) even at high temperature. Classical models not considering orbital contribution[73] cannot even approach a fit to the data in order to obtain a value of J.

(b) Two-Electron Blues. An unexpected result was finding that 2e blues are more interactive than they seem from studies done on systems containing no paramagnetic atoms.[17] The type of interaction between a 2e delocalized system and the transition metals in the structure seems to be heavily related to electron delocalization rather than just to classical antiferro- or ferromagnetic exchange.

Considering first the field dependence, at room temperature, of the 2e blues containing a paramagnetic transition metal, the reduced species are found to follow the same tendency as their oxidized precursors. That is, in general the 2e blues do not show a field depencence unless octahedral Co^{II} is present or the species contains two paramagnetic atoms.

Nevertheless, the behaviors of the 2e blue species, at either 70 500 or 5 000 G, differ from those of their oxidized precursors.

The difference in susceptibilities observed by the Evans method between $Co^{II}W_{12}2e$ and $Co^{II}W_{12}$ (Table V) corresponds very well to the ring current excess diamagnetism observed in diamagnetic substituted 2e blue Keggin species.[5] The difference in susceptibilities between $Fe^{III}W_{12}2e$ and $Fe^{III}W_{12}$ appears to behave in the same way, as the room temperature values of the moments at 5000 G indicate, but in this case the behavior could not be quantitatively evaluated by the Evans method because the sizable line widths of the very close NMR peaks from the solutions containing respectively oxidized and reduced species prevented clear resolution of the lines. The same limitation applied to the case of $SiW_{11}Cr^{III}2e$ versus $SiW_{11}Cr^{III}$. However, for these Fe and Cr systems these high-field results do give an upper limit of -200×10^{-6} emu/mol for the differences in the susceptibilities, again consistent only with a ring current effect. Thus, for these three 2e reduced complexes no interaction of any type was observed between the completely coupled mixed valence system and the localized unpaired electrons on the paramagnetic atoms.

On the other hand, 2e blues exist (Table V) which are either much more diamagnetic than their oxidized precursors (those containing octahedral Co^{II} or octahedral Ni^{II}) or much more paramagnetic than their oxidized parents (those containing octahedral V^{III}).

Consider first the Keggin monosubstituted complexes containing octahedral Co^{II} and V^{III}, $SiW_{11}Co^{II}$ and $SiW_{11}V^{III}$. Both Co^{II} and V^{III} have significant spin–orbit coupling constants, but they are of opposite sign (−180 and +100 cm^{-1}, respectively, for the free ions[62]). This produces, at room temperature in the oxidized complexes, a moment for Co^{II} which is higher than the spin-only value and a moment which is lower than the spin-only value for V^{III}. Upon reducing the systems to $SiW_{11}Co^{II}2e$ and $SiW_{11}V^{III}2e$, the moment of each becomes closer to its spin-only value. The only way both changes are possible, if the causation is the same for each, is by a major reduction of the spin–orbit coupling of each substituted metal upon 2e reduction.

The moment of the d^2 V^{III} complex rises to the spin-only value (2.82 μ_B), and the moment of the Co^{II} falls substantially but not all the way to the spin-only value (3.87 μ_B). These changes are very much larger than those attributable to any ring current effects.

If decrease of spin–orbit coupling upon reduction is responsible for the susceptibility changes in the Co^{II} and V^{III} complexes, as argued in the preceding two paragraphs, then Fe^{III} and Cr^{III}, which are typical spin-only ions, should show no changes upon reduction of their respective complexes, and indeed they do not.

Tetrahedral Co^{II} in $Co^{II}W_{12}$ and $Co^{II}W_{12}2e$ also possesses an orbitally nondegenerate ground state, but mixing with nonpopulated excited states which are more paramagnetic raises its moment above the spin-only value.[62] No contribution from spin–orbit coupling is involved, and only the ring-current effect is observed upon reduction. This might have been taken to indicate that the 2e pair does not interact at all with the inner tetrahedron. However, the fact that coupling is observed in $Fe^{III}W_{12}1e$ between the inner Fe^{III} and the blue electron says that that type of interaction is at least possible. Taken together, these observations support the interpretation that only ions sensitive to the interaction mechanism (that is, those where a change in spin–orbit coupling is possible) will show changes. Those ions not having spin–orbit coupling may experience an interaction but not show any changes in moment. The Ni^{II} cap-substituted Wells–Dawson derivative provides additional support for the above-described hypothesis. Ni^{II} has an orbitally nondegenerate ground state when octahedral, but zero field splitting of the ground state coming from spin–orbit coupling present in excited states[62] raises the moment above the spin-only value in the oxidized species. The Ni^{II} complex is also strongly affected by the 2e reduction, its moment falling to the spin-only value. The difference between the 2e and oxidized susceptibilities is about five times that expected from a ring current effect.

The Co^{II} belt-substituted Wells–Dawson complexes show parallel behavior to that of substituted Keggin $SiW_{11}Co^{II}$, but the magnitude of the change observed between 2e and oxidized species is three times bigger in the Wells–Dawson complex. It is worth noting here that α_1-$P_2W_{17}Co^{II}$ shows the largest isotropic shift in ^{31}P NMR signals among all the NMR spectra of paramagnetic samples studied to date.[4]

All octahedrally substituted ions studied which have an important contribution of spin–orbit coupling in the oxidized complexes are affected by the 2e reduction, in the direction consistent with lowering of that coupling, and the lack of a similar effect with tetrahedral heteroatoms is not necessarily caused by increased isolation[10] of the central tetrahedron from the tungsten framework.

The lowering of the spin–orbit couplings of octahedrally coordinated metals by the 2e reductions is most probably the result of increases in the covalency factor.[10,63–69] This interpretation receives strong support from variable temperature ^{183}W NMR studies of spin densities in $Co^{II}W_{12}$ and $Co^{II}W_{12}2e$[7,11] described above. It is also consistent with the discussion given above for $SiW_{12}1e$.

It is known that the added electrons get progressively more localized (i.e., hop between W's less and less frequently) as the thermal energy to overcome the activation energy for hopping[22] becomes progressively less available. It is noted that the difference between the moments of the oxidized and reduced species (Figures 3 and 4) become smaller as temperature is lowered, and these decreases are most prominent in the temperature ranges where electron localization increases. Metals with spin–orbit couplings might therefore be used as probes to indicate the temperatures at which blue electron localization becomes prominent for 2e blues. Observation by ESR of such localization has been limited to 1e blues.

Complexes Containing Two Paramagnetic Transition Metal Atoms. These present an additional variable since the two blue electrons may also modify coupling which exists in the oxidized species between the paramagnetic metals.

The magnetic moments for both oxidized and 2e reduced species ($Fe^{III}W_{11}Co^{II}$, $Fe^{III}W_{11}Co^{II}2e$, $Co^{II}W_{11}Co^{II}$, and $Co^{II}W_{11}Co^{II}2e$) show field dependences which are greater than expected from the fact that octahedral Co^{II} is present in all of them. Any effect that

---

(73) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

breaks the antiferromagnetic coupling will increase the moment, while lowering λ will tend to decrease the moment since all these complexes contain octahedral $\mathrm{Co^{II}}$. Both of these effects are operative in these compounds.

The differences in magnetic moments between the 0e and 2e blue species vary depending on the field. If no coupling is present (as is the case in $\mathrm{Co^{II}W_{11}Co^{II}}$ at 70 500 G where the antiferromagnetic coupling has been completely broken, giving the maximum expected moment of 6.80 μ_B), the 2e reduction should affect the tetrahedral and octahedral Co atoms independently. That is indeed the result observed in $\mathrm{Co^{II}W_{11}Co^{II}}$2e at 70 500 G since the moment is decreased considerably upon reduction as would be expected for an isolated octahedral $\mathrm{Co^{II}}$ (see Table IV). At 5000 G, however, the moment remains practically constant upon reduction. Since the Co–Co magnetic coupling is known to be operative at this field,[18,19,27] an invariant moment implies cancellation of two effects: (1) a lowering of the moment upon reduction because of decreased orbital contribution from octahedral $\mathrm{Co^{II}}$ and (2) an increase of the moment owing to the partial or total breaking of the magnetic coupling between the cobalts.

This interpretation is supported by the $\mathrm{Fe^{III}W_{11}Co^{II}}$ case, which shows an increase in moment upon reduction at both fields, suggesting that the effect of breaking the coupling (itself larger than in the Co–Co case)[18,19] by the 2e reduction is greater than the effect of lowering the spin–orbit coupling of octahedral $\mathrm{Co^{II}}$.

As expected from the fact that the $\mathrm{Fe^{III}}$–$\mathrm{Co^{II}}$ interaction is stronger than the $\mathrm{Co^{II}}$–$\mathrm{Co^{II}}$ interaction, the 70 500 G field does not break completely the antiferromagnetic coupling in the former, changing μ_{eff} only from 6.14 to 6.45 μ_B (vs a 7.7 μ_B maximum) in the oxidized form and from 6.36 to 6.63 μ_B in the 2e blue.

The temperature dependences in the cases of $\mathrm{Co^{II}W_{11}Co^{II}}$2e and $\mathrm{Co^{II}W_{11}Co^{II}}$ (Figure 6) show that at high temperatures the blue is slightly more paramagnetic than the oxidized complex, while at low temperatures the reverse is true. This shows that the temperature dependences of variation in spin–orbit coupling and in degree of breaking of the antiferromagnetic coupling are not the same. In fact, the breaking of the Co–Co coupling in the 2e blue must be the larger factor above about 100 K at this applied field, while the lowering of λ by the reduction must be the larger factor below about 100 K.

$\mathrm{Fe^{III}W_{11}Co^{II}}$2e shows, over the whole temperature range, greater paramagnetism than its oxidized parent, having therefore a lower $\mathrm{Fe^{III}}$–$\mathrm{Co^{II}}$ coupling at all times. However, the difference between the oxidized and 2e blue increases with temperature, which may be explained by the lowering of the antiferromagnetic coupling being greater than the lowering of λ despite the fact that both effects may be decreasing as the temperature is lowered.

It is interesting to note from comparison of the Fe–Co and Co–Co cases that the M–M coupling is lowered more effectively upon reduction in the case for which $|J|$ was much larger before reduction. It is probable that the ring currents in the blue species modify superexchange pathways in specific directions and that this modifies effective J's.

It will be highly desirable to extend this study to other species to cover a broader range of effects. Complexes containing (1) two ions with positive λ values, (2) more than one paramagnetic atom in octahedral sites, or (3) ferromagnetically coupled atoms are among the possibilities.

Acknowledgment. We thank Prof. Ekkehard Sinn for making available the SHE SQUID magnetometer at UVA and Dr. Thitinant N. Thaniasiri for help in its use. This research was supported by NSF Grant No. CHE-8406088, by an instrument grant from the W.M. Keck Foundation, by the U.S.–Spain Joint Committee for Scientific Cooperation through Grant No. CCB-8504039, and through a fellowship for N.C.-P.

β-Migratory Insertion Reactions of $(\eta^5\text{-}C_5R'_5)Rh(L)(C_2H_4)R^+BF_4^-$ ($R' = H, CH_3$; $R = H, C_2H_5$; $L = P(OMe)_3, PMe_3$). Comparison of the Energetics of Hydride versus Alkyl Migration

Maurice Brookhart,* Elisabeth Hauptman, and David M. Lincoln

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290. *Received June 18, 1992. Revised Manuscript Received September 14, 1992*

Abstract: Protonation of the rhodium ethylene complexes $C_5R_5(L)Rh(C_2H_4)$, **1a,b** and **2a,b** (**1** $R = CH_3$, **2** $R = H$, **a** $L = P(OMe)_3$, **b** $L = PMe_3$), with $HBF_4\cdot Me_2O$ in CH_2Cl_2 yields the four corresponding ethylene hydride complexes $C_5R_5(L)Rh(C_2H_4)H^+$, **3a,b** and **4a,b**. NMR techniques were used to measure the rates of migratory insertion for these species. Values for the free energies of activation were found to be 12.2 (**3a**), 12.1 (**3b**), 15.0 (**4a**), and 15.0 (**4b**) kcal/mol. Eyring plots based on rate constants measured over the −20 to +20 °C range established $\Delta S^{\ddagger} = 0$ for these migratory insertions. Treatment of **3a,b** and **4a,b** with excess ethylene gave the ethyl ethylene complexes $C_5R_5(L)RhCH_2CH_3(C_2H_4)^+$, **7a,b** and **8a,b**, whose structures were established by ^1H and ^{13}C NMR spectroscopy. These complexes function as ethylene dimerization catalysts; NMR spectroscopic analysis of the catalytic systems shows that **7a,b** and **8a,b** are the catalyst resting states. The turnover-limiting step is the β-migratory insertion reaction of the ethyl ethylene complexes. The $\Delta G^{\ddagger}$ values for β-migratory insertion calculated from turnover rates were found to be 22.4 (**7a**), 23.4 (**7b**), 23.4 (**8a**), and 24.7 (**8b**) kcal/mol. The $\Delta\Delta G^{\ddagger}$ values for H versus CH_2CH_3 migration for these systems thus lie in the range of 8.5–11 kcal/mol, which corresponds to relative migratory aptitudes k_H/k_{Et} of 10^6–10^8 at 23 °C.

The β-migratory insertion of transition metal olefin hydride complexes is a fundamental transformation of importance in several catalytic processes, including olefin hydrogenations, hydroformylations, and isomerizations. The analogous β-migratory insertion reaction of metal alkyl olefin complexes is the key carbon–carbon bond forming step in metal-catalyzed olefin polymerization reactions and related oligomerizations and dimerizations.[1]

0002-7863/92/1514-10394$03.00/0