chloromanganate systems, since the tetrachloroferrate salts are known to undergo transitions similar to the tetrachloromanganates, but at higher temperature (87 K).

Conclusion

This work has shown that MnPS$_3$ behaves as a two-dimensional antiferromagnet. Intercalation reduces the intra-

layer coupling because of the cationic character of the guest species. Anisotropy in the 2-D Hamiltonian is thus revealed, with the occurrence of weak ferromagnetism as a consequence.

Registry No. MnPS$_3$, 43000-56-2; I, 74346-92-2; II, 74346-93-3; III, 74346-94-4; IV, 74346-95-5.

Correspondence

Ferrocene as an Internal Standard for Electrochemical Measurements

Sir:

Electrochemistry is an increasingly popular technique for the characterization of new compounds. The basic thermodynamic quantity that is assigned to an electrode process is the standard or formal reduction potential ($E°$ or E^f). In aqueous solution the measurement of reduction potentials is facilitated by the use of reliable and universally accepted reference electrodes such as the normal hydrogen electrode (NHE) or the saturated calomel electrode (SCE).[1] In many instances electrochemical measurements in water are impossible due to insolubility or instability of the compound. Unfortunately, no universal reference electrode exists for nonaqueous solvents.[2,3]

Since a variety of reference electrode systems have been employed, the literature contains numerous reduction potentials which cannot be related to each other and which are, occasionally, difficult to reproduce. For example, two common methods for reporting nonaqueous potentials are vs. the SCE which inevitably includes unknown liquid junction potentials[2] and vs. pseudo reference electrodes such as a silver wire. We believe that the situation described above need not exist, and on the basis of concepts and data already in the literature, we suggest a simple method for reporting reduction potentials in nonaqueous solvents.

Internal Standard. During the course of our studies of copper–macrocyclic ligand complexes we have found that a practical approach to this problem is the use of the potential of the oxidation of ferrocene as an internal standard.[4-10] After the electrochemistry attributed to the compound of interest has been identified, ferrocene is added to the working compartment of the cell. The electrochemical experiment is repeated, and the position of the waves can be directly compared to the potential of the ferrocenium/ferrocene (Fc$^+$/Fc) couple. Figure 1a illustrates this method by showing a cyclic voltammogram of tris(acetylacetonato)ruthenium(III) in CH$_3$CN.
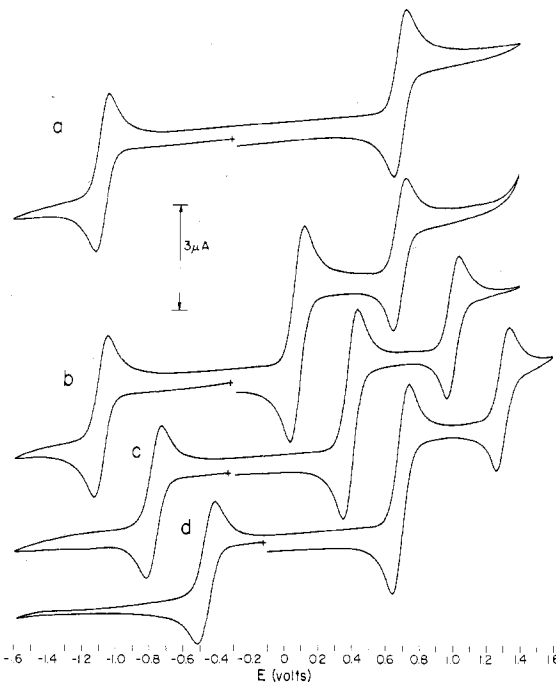
Figure 1. Platinum button cyclic voltammetry at 50 mV/s of 0.005 M Ru(acac)$_3$ in CH$_3$CN with 0.1 M tetrabutylammonium perchlorate: b, c, and d, ferrocene added; a and b, vs. Ag/AgNO$_3$ (0.01 M), TBAP (0.1 M), CH$_3$CN; c, vs. SCE; d, vs. Cu wire.

Figure 1b shows the same voltammogram after addition of a similar amount of ferrocene. Use of the formula $E^f = (E_{p(anodic)} + E_{p(cathodic)})/2$ allows calculation of formal potentials for the processes in Figure 1 of 0.602 and −1.157 V vs. E^f(Fc$^+$/Fc). An important advantage of this method is that choice of the reference electrode used to satisfy the three-electrode potentiostat (a Ag/Ag$^+$ electrode in Figure 1a,b) is reduced to a matter of experimental convenience. Parts c and d of Figure 1 were recorded under conditions identical with those for Figure 1b except that an SCE was used as a reference electrode for Figure 1c, while a copper wire was used for Figure 1d. From the values on the potential axis the waves appear to be shifted, but formal potentials relative to E^f(Fc$^+$/Fc) remain unchanged. Formal potentials obtained in the manner described above should be reproducible because variables such as type of reference electrode, liquid junction potentials, and reference electrode degradation are eliminated.[11]

The Fc$^+$/Fc couple ($E°$ = 0.400 V vs. NHE)[12] may be

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(11) Ferrocene as well as other materials has been used as an external standard to determine solvent and junction potential correction factors. One shortcoming of this external approach is junction potential variability from experiment to experiment.
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inappropriate as an internal standard for some systems due to overlapping waves. In these cases other compounds such as cobaltocene ($E° = -0.918$ V vs. NHE)[12] or any of a variety of aromatic compounds, comprising a virtual continuum of reduction potentials, can be substituted.[13] Potentials can still be related to $E^f(Fc^+/Fc)$ through a second experiment.

Employing a redox couple as an internal standard in electrochemical experiments can be compared to the use of internal standards in nuclear magnetic resonance spectroscopy. For example, in proton NMR spectroscopy tetramethylsilane is commonly used to reference chemical shifts of other protons but is sometimes replaced by chloroform or other materials to avoid overlapping signals. As with NMR standards, an ideal electrochemical internal standard should not interact with other species in solution. Ferrocene adequately fills this criterion.

Use of ferrocene as an internal standard demands the observation of reversible electrochemistry for the Fc^+/Fc couple. Reversible behavior has been observed in a wide variety of solvents with the following limitations: (a) in water and alcohols the instability of the ferrocenium ion causes reduction potentials measured by potentiometry to differ from values measured by faster techniques; (b) cyclic voltammetry at slow scan rates (10–50 mV s^{-1}) results in reversible behavior, while faster scan rates (>1 V s^{-1}) reveal quasi-reversible behavior.[14-16]

Cyclic voltammetric peak separations, ΔE_p, serve as one criterion for electrochemical reversibility. For example, a one-electron process ($n = 1$) is expected to have $\Delta E_p = 59$ mV. High solution resistance, especially in nonaqueous solvents, can result in large peak separations, complicating wave shape analysis.[17,18] State of the art electrochemical instrumentation provides a capability for compensating for IR drop in an attempt to overcome solution resistance contributions to the shapes of cyclic voltammetric waves. Unfortunately some instrumentation permits overcompensation, sometimes resulting in meaningless results. For example, we have been able to obtain peak separations of 40–50 mV for both the Fc^+/Fc and $Ru(acac)_3/Ru(acac)_3^-$ couples by using instrumental IR compensation. In practice we do not use instrumental IR compensation, but simply compare ΔE_p for the couple of interest with that of the Fc^+/Fc couple under the same conditions. It should be emphasized that, while wave shape comparisons may be useful, reproducibility of reduction potential measurements is the key advantage of the ferrocene referencing system.

Thermodynamic Significance. The notion of ferrocene as an internal reference couple stems in part from attempts by others to compare redox potentials obtained in different solvents. The potential scale in water is established by assigning the potential of the hydrogen half-reaction as zero. Since the activity of the proton is not necessarily the same in all solvents, a similar convention establishes a different scale in each solvent. The problems associated with measuring and comparing reduction potentials on the same scale in a wide variety of solvents has received considerable attention through attempts to estimate free energies of transfer of single ions, ΔG_{tr}.[19]

These estimates require the use of an extrathermodynamic assumption. One such assumption is that the activity of a univalent, large, symmetrical ion, with the charge deeply buried, is the same as the activity of an uncharged molecule of the same size and structure in all solvents. Strehlow proposed that Fc^+/Fc fits the requirements and as such is a solvent-independent redox couple.[12] Thus $E°$ (Fc^+/Fc) in any solvent is assumed to be the same as measured in water, i.e., 0.400 V vs. NHE, and potentials vs. the Fc^+/Fc couple are directly comparable between solvents. Alternatively, tabulations of $\Delta G_{tr}(Ag^+)$ based on other assumptions[14,20] can be used to calculate the potential of Ag/Ag^+ reference electrodes (Pleskov electrodes) vs. NHE in water.[21]

It is not obvious which of the extrathermodynamic assumptions used to interrelate electrochemical potentials measured in various solvents is more valid, and we do not presume in principle to favor any one assumption over another. In practice, reproducibility of potentials vs. the Ag/Ag^+ Pleskov electrode are adversely affected by the insolubility of silver salts in some solvents like dichloromethane,[3] by reactions of Ag^+ with some solvents such as acetone and *N,N*-dimethylformamide,[3] or by trace impurities such as water which interact strongly with Ag^+.[14] Likewise, reference electrodes containing known concentrations of Fc and Fc^+ are unstable due to decomposition of ferrocenium ion.[14,15] Instead, we prefer the *internal* use of ferrocene because it is convenient, is reproducible, provides a basis for judging electrochemical reversibility, and allows for a quantitative comparison of reduction potentials measured in various solvents.

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(22) Contribution No. 6139.

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Transferability of Ligand Field Parameters and Nonlinear Ligation in Chromium(III) Complexes

Sir:

In a previous paper[1] we have demonstrated that transferable ligand field parameters of an additive field quite satisfactorily could account for our experimental spectral results for a series of *trans*-tetraammine- and tetrakis(pyridine)chromium(III) complexes. We used the angular overlap model to describe the chromium(III)–pyridine bond and obtained a negative $\Delta'_{\pi py}$ for pyridine.

This latter result has acted as an impetus for a recent paper in this journal by Smith[2] in which this result is questioned, partly by reviewing our paper in a fashion which we find unsatisfactory. The present paper is an attempt to clarify and extend certain points in our previous paper and also to discuss

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