could well experience an increase in polarization in going to the Ru(II) state since the added t_{2g} electron will be significantly delocalized around the aromatic rings, acting to increase their net charge density. This latter effect would yield a negative contribution to $\Delta S°_{rc}$ which will be roughly proportional to the number of pyridine rings. Therefore the stepwise replacement of ammine by bipyridine or pyridine ligands would result in an approximately linear decrease in $\Delta S°_{rc}$, as observed. For $Ru(bpy)_3^{3+/2+}$, these two effects presumably cancel, yielding $\Delta S°_{rc} \approx 0$. The small (or slightly negative) values of $\Delta S°_{rc}$ observed for Ru(III/II), Fe(III/II), and Os(III/II) polypyridine couples have been previously ascribed to the efficient shielding of the metal center from the solvent by these ligands.[10] This latter explanation seems less reasonable since the polypyridine ligands will allow some solvent molecules to approach close to the metal center along the open channels formed by the planar aromatic rings. Also, the markedly larger values of $\Delta S°_{rc}$ (22 eu) observed for both $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ [2] can be more easily understood on the basis of the present model. These Co(III) → Co(II) reactions involve the electronic conversion $t_{2g}^6 → t_{2g}^5e_g^2$ which should minimize the extent of electron delocalization in the reduced state and therefore discourage any increase in solvent polarization in the vicinity of the pyridine rings. This change in electronic configuration will also yield a marked expansion of the cobalt center[13] and hence an especially large decrease in the polarization of nearby water molecules.[3]

We have obtained further evidence that favors the present interpretation from the observation that the ferrocinium/ferrocene couple has a distinctly *negative* value of $\Delta S°_{rc}$ in aqeous media (–5 eu, Table I). Since this couple is of the charge type +1/0, the simple dielectric polarization model predicts a small positive value of $\Delta S°_{rc}$. Although the added electron will be substantially delocalized around the cyclopentadienyl rings in a manner similar to the polypyridine couples, the "sandwich" structure of the ferrocinium/ferrocene couple should largely prevent the close approach of solvent molecules to the metal center. Consequently in this case the predominant contribution to $\Delta S°_{rc}$ is anticipated to be the increased polarization of water molecules adjacent to the aromatic rings in the lower oxidation state, in accordance with the observed negative value of $\Delta S°_{rc}$. Negative values of $\Delta S°_{rc}$ have also been observed for some blue copper protein couples having the charge type +1/0 and have been interpreted in terms of hydrophobic effects in the vicinity of the copper redox center.[14]

The large values of $\Delta S°_{rc}$ typically observed for aquo couples have been attributed to field-assisted hydrogen bonding between the aquo ligands and surrounding water molecules.[2] As noted previously,[2] substitution of a single aquo ligand into $Ru(NH_3)_6^{3+/2+}$ yields a proportionately larger increase in $\Delta S°_{rc}$ than those which result from subsequent aquo substitutions (Table I). However, there is reasonable agreement between $\Delta S°_{rc}$ and $(\Delta S°_{rc})^{estd}$ for *cis*-$Ru(NH_3)_4(OH_2)_2^{3+/2+}$ (Table I). On the other hand, substitution of one bipyridine in $Ru(bpy)_3^{3+/2+}$ by two aquo ligands in either a cis or trans configuration[15] yields somewhat smaller values of $\Delta S°_{rc}$ compared with $(\Delta S°_{rc})^{estd}$ (Table I). It is possible that the extent of hydrogen bonding involving aquo ligands is very sensitive to the electrostatic and steric environment. It therefore may

be generally difficult to predict accurate values of $\Delta S°_{rc}$ for mixed-ligand couples containing aquo ligands.

Since a large number of complexes employed in redox kinetics contain anionic as well as neutral ligands, it is of interest to examine the stepwise changes in $\Delta S°_{rc}$ that occur as anions are substituted into the coordination sphere. Substantial and even qualitative changes in $\Delta S°_{rc}$ are generally expected from the Born model as well as from local solvation effects due to the variations in the overall charges of the complexes. Unfortunately, suitable data are extremely sparse. Table I contains data for three Fe(III/II) couples containing bipyridine and/or cyanide ligands. Again it is seen that the estimated values $(\Delta S°_{rc})^{estd}$ for the mixed-ligand couple $Fe(CN)_4bpy^{-/2-}$ is in reasonable agreement with the experimental value of $\Delta S°_{rc}$, whereas the Born model fails to provide adequate estimates of $\Delta S°_{rc}$ for all three couples.

It therefore appears that the assumption that the reaction entropies for mixed-ligand couples arise from simple linear additive contributions from each ligand can provide a useful, albeit approximate, means of estimating $\Delta S°_{rc}$ under some circumstances. However, often one or both $\Delta S°_{rc}$ values for the corresponding pure ligand couples are unavailable. Inasmuch as the values of $\Delta S°_{rc}$ are often expected to depend chiefly on the ligands and the charge type of the redox couple,[2] the required reaction entropies could be inferred from those for other couples containing the same ligands. George et al.[4] have given empirical parameters for various ligands obtained from ionic entropy data that allow estimates of $\Delta S°_{rc}$ to be obtained for couples containing these ligands. We have pointed out that this approach has limitations since in some cases $\Delta S°_{rc}$ can be significantly dependent on the nature as well as the charges of the central metal ions.[2,3] Nevertheless, the method could be usefully employed, albeit with caution, to estimate the *changes* in $\Delta S°_{rc}$ resulting from minor alterations in ligand composition.

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Formation of Extrinsic (Pt^{3+}-Doped) Magnus' Green Salt in the Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

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Magnus' green salt (MGS), $Pt(NH_3)_4PtCl_4$, has long been of interest as a quasi-one-dimensional semiconductor.[1,2] This is because the alternate cation and anion stacking in the crystal structure[3] permits strong overlap of the Pt(II) d_{z^2} orbitals and

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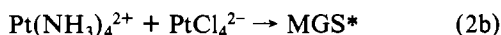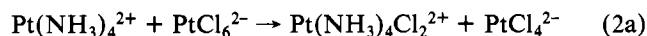
hence, highly anisotropic properties. The semiconducting properties of this salt, however, have been found to be impurity dominated.[4,5] By selective doping, we recently showed that the extrinsic behavior can be attributed to Pt(III)-like centers introduced into the Pt(II) chains by Pt(IV) impurities in the nominally "pure" solutions used to prepare Magnus' salt.[6,7] The Pt(III)-like "hole" states are charge-compensated by interstitial halide ions which bind them with an energy $E_b \approx 0.46$ eV,[8] or about twice the activation energy for electrical conductivity.[2,4] On the basis of the observed Pt^{195} superhyperfine structure in the electron spin resonance spectrum, it has been surmised that the hole extends over several Pt sites but does not interact with the ligands.[6,9]

The presence of Pt(IV) complexes during the preparation of $Pt(NH_3)_4PtCl_4$ leads to complex redox processes which apparently become "trapped" in the solid state.[6,7] In our original experiments, $K_2Pt(CN)_4Br_2$, $K_2Pt(CN)_4Cl_2$, and K_2PtCl_6 were used as oxidizing agents to introduce the impurity states into MGS powders. In those studies[7] aqueous $Pt(NH_3)_4Cl_2$ was permitted to react with K_2PtCl_4 solutions containing Pt(IV) anionic oxidizing agents. This approach was chosen because $PtCl_4^{2-}$ reacts very slowly compared to $Pt(NH_3)_4^{2+}$ with anionic Pt(IV). We have now investigated the redox doping reaction in greater detail and have isolated both the intermediate and final reaction products. In particular, we have examined the $Pt(NH_3)_4^{2+}/PtCl_6^{2-}$ couple more fully and have identified the reaction leading to the incorporation of Pt(III) hole states in MGS.

The rapid addition, with stirring, of 0.01 M aqueous solutions of $Pt(NH_3)_4Cl_2$ and K_2PtCl_6 resulted in the immediate precipitation of Magnus' green salt. The salt was filtered and the solution evaporated to dryness to crystallize the remaining products. Analysis of the products and stoichiometry indicated that the overall reaction for equimolar concentrations of reactants can be written

$$2Pt(NH_3)_4Cl_2 + 2K_2PtCl_6 \rightarrow$$
$$MGS^* + [Pt(NH_3)_4Cl_2]Cl_2 + K_2PtCl_6 + 2KCl \quad (1)$$
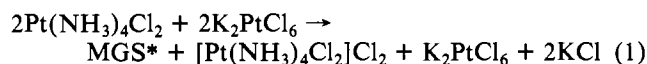
where the Magnus salt product is denoted MGS* to indicate its extrinsic (Pt^{3+}-doped) nature. We explicitly show in (1) that only half the K_2PtCl_6 is consumed because MGS* must be formed in the reaction of the tetrachloroplatinate(II) reduction product with tetraammineplatinum(II):

$$Pt(NH_3)_4^{2+} + PtCl_6^{2-} \rightarrow Pt(NH_3)_4Cl_2^{2+} + PtCl_4^{2-} \quad (2a)$$

$$Pt(NH_3)_4^{2+} + PtCl_4^{2-} \rightarrow MGS^* \quad (2b)$$

For simplicity, the reactions illustrated in eq 2 are considered separately, but in fact if (2a) and (2b) were to occur consecutively, as subsequently discussed, MGS would not be extrinsic.
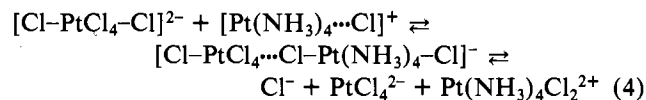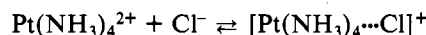
On warming of the reaction mixture (1), MGS* is found to rapidly dissolve, and as shown in (3), evaporation of the resulting solution leads to the isolation of only two products:

$$Pt(NH_3)_4Cl_2 + K_2PtCl_6 \xrightarrow{heat}$$
$$[Pt(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4] + 2KCl \quad (3)$$
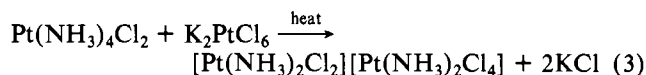
The mixed-valence Pt^{II}/Pt^{IV} product is a red-brown solid (red crystals) with orthorhombic lattice constants $a = 7.79$, $b = 7.37$, and $c = 10.54$ Å, based on complete X-ray powder pattern indexing. It is thus likely isomorphic with the analogous Pd^{II}/Pd^{IV} and Pd^{II}/Pt^{IV} salts.[10] The mixed-valence compound is composed of two neutral complexes which can also be viewed as forming from the initial reactants by ligand exchange rather than redox reaction. Nevertheless, the actual course involves a redox reaction and the formation of MGS* as an intermediate.

Confirmation of the extrinsic nature of the Magnus salt in (1) was obtained from EPR measurements, which showed a powder spectrum with $g_\parallel = 1.96$ and $g_\perp = 2.50$. These parameters are identical with those obtained in detailed powder and single-crystal studies.[6] Although it is difficult to establish a precise value, we estimate a maximum Pt(III)-doping level of 0.5 mol % in our samples from the EPR signal intensity.

Reaction 2a is clearly an example of a Pt(II)-catalyzed Pt(IV) substitution reaction.[7,11] Mechanistically, we can write

$$Pt(NH_3)_4^{2+} + Cl^- \rightleftarrows [Pt(NH_3)_4 \cdots Cl]^+$$

$$[Cl-PtCl_4-Cl]^{2-} + [Pt(NH_3)_4 \cdots Cl]^+ \rightleftarrows$$
$$[Cl-PtCl_4 \cdots Cl-Pt(NH_3)_4-Cl]^- \rightleftarrows$$
$$Cl^- + PtCl_4^{2-} + Pt(NH_3)_4Cl_2^{2+} \quad (4)$$

Reaction 4 involves a two-electron transfer from Pt(II) to Pt(IV) with the transinsertion of two Cl⁻ ligands into the coordination sphere of the tetraammineplatinum. Although this step is rapid, it is not likely to be faster than the precipitation reaction of $Pt(NH_3)_4^{2+}$ with $PtCl_4^{2-}$, for MGS* would not form otherwise. Hence (2a) and (2b) compete for the tetraammineplatinum(II) ion, resulting in the incorporation of "trapped intermediates" in MGS*. As previously proposed, these are Pt^{3+} centers with associated charge-compensating halide ions occupying interstitial sites.[6-9] Trapped Pt^{4+} centers are unstable relative to two Pt^{3+}, so that the holes must be mostly singly charged.[6,7]

The very slow rate of reaction 3 at room temperature makes it highly unlikely that ligand exchange can provide a facile route for the incorporation of charge-compensating halide ions into MGS*. This is consistent with our model based upon EPR experiments[6] and Coulomb energy arguments[8] which rule against charge compensators occupying platinum coordination sites (e.g., $Pt(NH_3)_3Cl^{2+}$).

Finally, since $PtCl_4^{2-}$ is generated in the redox reaction, its presence is unnecessary in the preparation of MGS*, unless other Pt(IV) complexes are used as dopants (i.e., $PtCl_6^{2-}$ serves as both an oxidizing agent and a $PtCl_4^{2-}$ source).[6,7] This suggests the possibility of producing even more unusual mixed-valence chain salts by combining other Pt(II)/Pt(IV) couples with favorable redox potentials.

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Photoelectron Spectra of Biferrocenylene and Biferrocene

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and Dwaine O. Cowan[1c]

Biferrocenylene (**1**), biferrocene (**2**), and the various charged
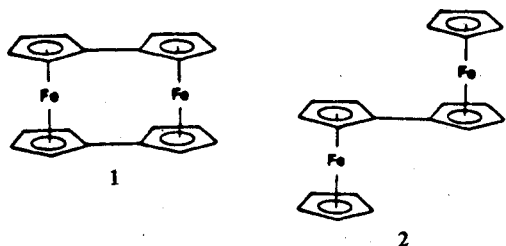
ions derived from **1** and **2** have found increasing interest in
recent years from both experimental[2] and theoretical[3] points
of view. The experimental data available indicate a difference
between **1** and **2** insofar as in **1**$^+$ there is a considerable in-
teraction between the two iron sites while in **2**$^+$ both Fe atoms
have integral oxidation states leading to a formal Fe^{II}, Fe^{III}
system with trapped valences.[4] In order to contribute to the
discussion concerning the bonding in **1** and **2**, we have recorded
the He I photoelectron (PE) spectra of **1** and **2**. This mea-
surement provides direct insight into the various hole states
of **1**$^+$ and **2**$^+$.[5]

Due to large relaxation effects in transition-metal com-
pounds[6] (breakdown of Koopmans' theorem[7]), we performed
calculations on the various hole states of **1**$^+$ and **2**$^+$ by using
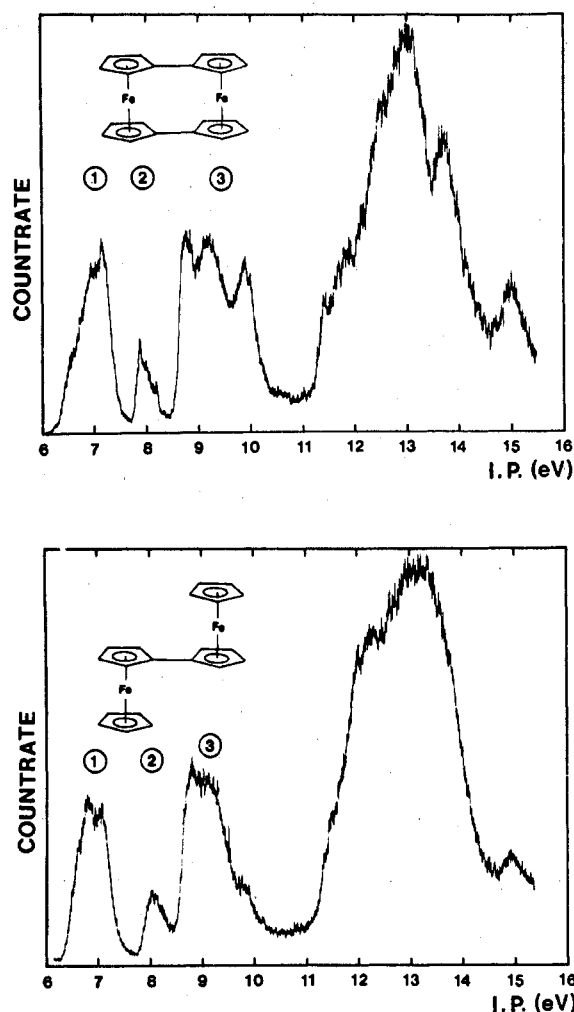the ΔSCF[8] and the TOM[9] procedures[10] on the basis of a

Figure 1. PE spectra of **1** and **2**.

recently developed INDO method for organometallic com-
pounds.[5]

In Figure 1 the PE spectra of **1** and **2** are displayed.[11] By
comparison with the PE spectrum of ferrocene[12] it is evident
that the first band in both spectra corresponds to ionization
events from the six MO's with mainly 3d character (see Table
I), mainly the g and u combinations of $3d_{z^2}$, $3d_{x^2-y^2}$ and $3d_{xy}$
orbitals. Inspection of Table I shows the anticipated consid-
erable electronic relaxation in the radical cation. The ex-
perimental values are only reproduced satisfactorily if the
ΔSCF and TOM calculations were performed without the
restriction that the Fe 3d MO's should be symmetry adapted.
Both model calculations lead to localized Fe 3d hole states,
meaning that the electron has been removed from one of the
two iron sites of the molecule. Similar results have been found
for the 1s hole states of O_2^{+}[13] and N_2^{+}.[14] In all cases it is
computed that the relaxation energy of a localized hole con-
tributes twice as much as that of a delocalized one.[15] The

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(10) Both methods of calculation reproduce satisfactorily the PE bands of
ferrocene.[12] Experimental: 6.88 (e$_{2g}$), 7.23 (a$_{1g}$), 8.72 (e$_{1u}$), 9.38 (e$_{1g}$).
ΔSCF: 7.85 (a$_{1g}$), 8.48 (e$_{2g}$), 9.27 (e$_{1u}$), 10.41 (e$_{1g}$). TOM: 6.27 (a$_{1g}$),
7.08 (e$_{2g}$), 8.88 (e$_{1u}$), 10.06 (e$_{1g}$).

(11) The He I PE spectra were recorded on a PS18 spectrometer of Per-
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