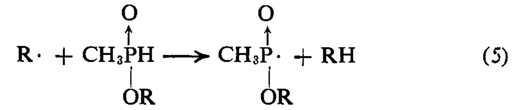
CH_3P), 4.93 (m, 1, $J = 6$ Hz, CH), 7.53 (m, 5, Ar). *Anal.* Calcd for $C_{10}H_{15}PO_2S$: C, 52.16; H, 6.57; P, 13.45; O, 13.90; S, 13.93. Found: C, 52.0; H, 6.5; P, 13.4; S, 15.4. This experiment would lead to the conclusion that in the presence of a source of radicals, a phosphino radical with seven electrons in the valence shell of the phosphorus atom is formed by the abstraction of a hydrogen atom from phosphinate (eq 5).



$$R\cdot + CH_3\underset{\underset{OR}{|}}{\overset{\overset{O}{\uparrow}}{P}}H \longrightarrow CH_3\underset{\underset{OR}{|}}{\overset{\overset{O}{\uparrow}}{P}}\cdot + RH \qquad (5)$$

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Intraconfigurational Spin-Forbidden Transitions in Chromium(III), Manganese(II), and Nickel(II) Complexes in Aqueous Glass Solutions at 77°K[1]

Sir:

The spin-forbidden, Laporte-forbidden intraconfigurational transitions of transition metal ions in complexes constitute the weakest light absorption processes in such ions. Such weak bands are usually obscured by stronger and more diffuse absorption bands of the ion. In a few cases they have been observed as narrow shoulders on broader bands, or occasionally have been studied in low-temperature crystal spectra as very sharp weak bands.

We have found that 77°K aqueous glasses are suitable as a medium for a spectral resolution of these transitions. Inorganic salts in water afforded a very suitable medium for the formation of aqueous glasses; *e.g.*, $MgCl_2\cdot 6H_2O/H_2O$ in weight ratio 0.9/1 constitutes one of our most useful solutions. Solubility of metal ion complexes is favored in these over that in traditional organic solvent glass solutions, as is the possibility of using perdeuterated solvent. In a few cases we utilized ethylene gycol/water in a 1/2 volume ratio.

We have studied the low-temperature (77°K) aqueous glass solution absorption spectra of some first series transition metal ions in a variety of ligand field environments. However, some intraconfigurational spin-forbidden transitions should be nearly independent of ligand field,[2] and in most cases very narrow bands have been observed and found to occur at wavelengths only slightly affected by the ligand.

Cr(III) (d^3) in an octahedral field has a $^4A_{2g}$ ($t_{2g}{}^3$) ground state, with intraconfigurational transitions to ^2E_g, $^2T_{1g}$, and $^2T_{2g}$ states. In the 15,000-cm^{-1} region in room-temperature aqueous solutions of Cr(III) complexes, some very weak poorly resolved peaks are observed, *e.g.*, in $Cr(en)_3{}^{3+}$ (en = ethylenediamine). However, 77°K absorption and emission studies[3] of this complex have yielded a very sharp though weak band at this position, assigned as the $^4A_{2g} \rightarrow {}^2E_g$ transition, accompanied by considerable vibrational structure (partially resolved). Our studies of $Cr(en)_3{}^{3+}$ in $MgCl_2$–H_2O glass shown in Figure 1 (top) essentially duplicate these results, with the principal peak at 14,907 cm^{-1} identified as the $^4A_{2g} \rightarrow {}^2E_g$ intraconfigurational electronic transition. The Cr(III) case is the easiest to study since the intraconfigurational transition is in a long-wavelength region clear of other bands. In $Cr(ox)_3{}^{3-}$ in $MgCl_2$–water glass at 77°K transitions from $^4A_{2g}$ to ^2E_g (14,357 cm^{-1}), $^2T_{1g}$ (15,082 cm^{-1}), and $^2T_{2g}$ (20,512 cm^{-1}) states are observed as resolved peaks.

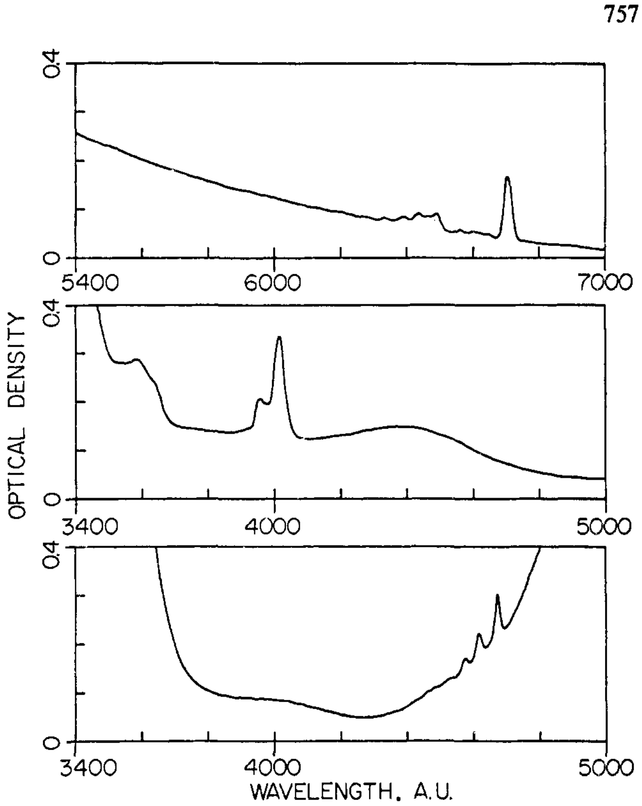

Figure 1. Intraconfigurational spin-forbidden transitions in Cr(III), Mn(II), and Ni(II) complexes in aqueous glass solutions at 77°K: (top) $Cr(en)_3{}^{3+}$ in $MgCl_2$–H_2O glass; (middle) $Mn(H_2O)_6{}^{2+}$ in ethylene glycol–H_2O glass; (bottom) $Ni(en)_3{}^{2+}$ in $MgCl_2$–H_2O glass (Cary 14 spectrometer).

Mn(II) (d^5) in an octahedral environment has a $^6A_{1g}$ ($t_{2g}{}^3e_g{}^2$) ground state, with low-lying intraconfigurational transitions to $^4A_{1g}$ and ^4E_g states. These transitions have also been observed previously,[4-6] with the $^6A_{1g} \rightarrow {}^4E_g$ transition appearing as a scarcely resolved shoulder in the room-temperature spectra (but as well-resolved peaks in a 20°K MnF_2 crystal[5]). Our spectrum of $Mn(H_2O)_6{}^{2+}$ in ethylene glycol–water glass at 77°K (Figure 1, center) shows two clearly resolved peaks, the $^6A_{1g} \rightarrow {}^4A_{1g}$ absorption appearing at 24,876 cm^{-1} and the $^6A_{1g} \rightarrow {}^4E_g$ absorption at 25,242 cm^{-1}. Also there appears a poorly resolved absorption peak at 27,861 cm^{-1} (ascribed[5] to $^6A_{1g} \rightarrow {}^4T_{2g}$) with a shoulder at 27,450 cm^{-1}.

Ni(II) (d^8) in an octahedral environment has a $^3A_{2g}$

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[1] This work was supported by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission and the Florida State University.

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[6] L. J. Heidt, G. F. Koster, and A. M. Johnson, *J. Am. Chem. Soc.*, **80**, 6471 (1958).

($t_{2g}^6e_g^2$) ground state, with intraconfigurational transitions to ^1E_g and $^1A_{1g}$ states. The $^3A_{2g} \rightarrow {}^1E_g$ transition is observed as a shoulder in $Ni(H_2O)_6^{2+}$ at 15,400 cm^{-1}; we observed this transition at 13,114 cm^{-1} for $Ni(en)_3^{2+}$ as a resolved peak at 77°K in $MgCl_2$–aqueous glass solution. The $^3A_{2g} \rightarrow {}^1A_{1g}$ transition has been assigned to some weak bands observed[7,8] at 4°K for $NiSiF_6 \cdot 6H_2O$ crystal in the region 24,330–24,450 cm^{-1}. At 80°K in $Ni(dipy)_3Br_2 \cdot 6H_2O$ crystal, this transition was assigned[9] to a shoulder at 20,960 cm^{-1}. For $Ni(en)_3^{2+}$ in $MgCl_2$–aqueous glass solution at 77°K we observed a series of extremely well-resolved peaks at 21,372, 21,623, and 21,817 cm^{-1} (Figure 1, bottom). These peaks must correspond to the 0, 0 and vibrational components of the $^3A_{2g} \rightarrow {}^1A_{1g}$ intraconfigurational transition. Five complexes of Ni(II) were studied in our work, with aniline, gly$^-$, en, dipy, and *o*-phen as ligands, showing a relative insensitivity of this transition to ligand field strength. The broad band centered on 25,000 cm^{-1} (Figure 1, bottom) probably corresponds to the $^3A_{2g} \rightarrow {}^1T_{2g}$ transition.

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The Existence of the Nickel(IV) Dication Derived from Nickelocene and a Cationic Boron Hydride Analog

Sir:

The exceptional stabilities of the d^6 bis(cyclopentadienyl)metallocenes, iron(II) ferrocene, $(\pi\text{-}C_5H_5)_2Fe$, and the cobalt(III) cobalticinium ion, $(\pi\text{-}C_5H_5)_2Co^+$, have been attributed to the retention of the inert gas configuration about the metal atom. Although nickelocene can be oxidized to a formal nickel(III) ion, $(\pi\text{-}C_5H_5)_2Ni^+$, further oxidation to the "electronically stable" d^6 nickel(IV) species, $(\pi\text{-}C_5H_5)_2Ni^{2+}$, has not been previously observed.[1–3] Wilkinson, Pauson, and Cotton found that complete disruption of the molecule occurred during an attempted electrochemical oxidation in an ethanolic electrolyte solution.[1] At room temperature we have observed similar results using cyclic voltammetry in acetonitrile solution; however, upon cooling the electrolyte, two reversible redox couples for the nickelocene system could be obtained. The voltammogram at −40° is presented in Figure 1. The nickel(II)–(III) couple (reduction peak potential at −0.09 V *vs.* sce) has been investigated previously by polarography.[1] The appearance of a reversible nickel(III)–(IV) couple at +0.77 V shows that the formal d^6 nickel(IV) ion, $(\pi\text{-}C_5H_5)_2Ni^{2+}$, actually does exist. No attempt was made to isolate this strongly oxidizing species, inasmuch as it rapidly decomposed in the electrolyte solution at temperatures above 0°.

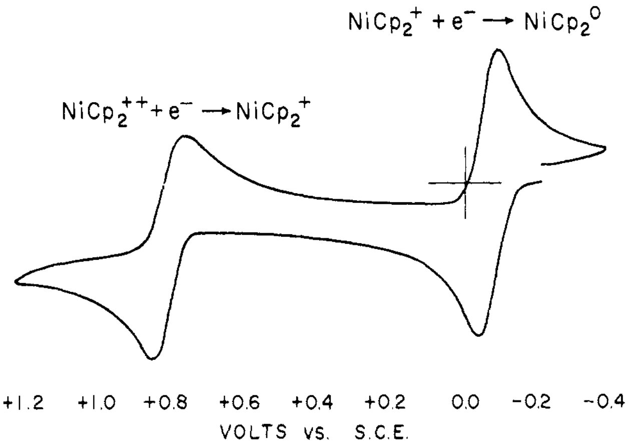

Figure 1. Cyclic voltammogram of the $(\pi\text{-}C_5H_5)_2Ni$ system; run in acetonitrile solution at −40°; anodic scan began at −0.2 V at 0.05 V/sec.

The much more stable bis(dicarbollyl)nickel(IV) analog, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni$,[4,5] exhibited redox properties similar to the nickelocene system, *i.e.*, two reversible one-electron couples by cyclic voltammetry. The reduction peak potentials are given in Table I.

Table I. Reduction Peak Potentials of the π-Cyclopentadienyl, π-(3)-1,2-Dicarbollylnickel Complexes[a]

Compounds	$M^{IV} + e^- \rightarrow M^{III}$	$M^{III} + e^- \rightarrow M^{II}$
$(C_5H_5)_2Ni$[b]	Dication $\xrightarrow{+0.77}$ cation	Cation $\xrightarrow{-0.09}$ neutral
$(C_5H_5)Ni(B_9C_2H_{11})$	Cation $\xrightarrow{+0.46}$ neutral	Neutral $\xrightarrow{-0.52}$ anion
$Ni(B_9C_2H_{11})_2$	Neutral $\xrightarrow{+0.18}$ anion	Anion $\xrightarrow{-0.56}$ dianion

[a] Obtained by cyclic voltammetry in acetonitrile solution at room temperature; 0.1 *N* tetraethylammonium perchlorate supporting electrolyte; measured in volts *vs.* sce. [b] Run at −40°.

Intermediate in stability to the bis-ligand systems above is the mixed sandwich species, $(\pi\text{-}C_5H_5)Ni[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ (**1**). This newly discovered formal nickel(III) complex was prepared in low yield from the reaction of a 5:1 mixture of sodium cyclopentadienide and disodium (3)-1,2-dicarbollide[5] with $NiBr_2 \cdot 2C_2H_4(OCH_3)_2$[6] in tetrahydrofuran. The initially formed nickel(II) complex was air-oxidized in water to the neutral nickel(III) derivative. **1** is brown-green [$\lambda_{\max}^{CHCl_3}$ (ϵ) 327 (22,200) and 434 mμ (2600)] and paramagnetic (μ_{eff} = 1.99 BM in $CHCl_3$ solution) as expected for a d^7 configuration. *Anal.* Calcd for

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[1] G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, 76, 1970 (1954).

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[3] Oxidation or reduction steps in these types of metal complexes cannot be attributed exclusively to the metal atom, inasmuch as electrons are removed from (or added to) *molecular* orbitals; however, for convenience, we have assigned fixed formal charges for the ligands and denoted redox steps of the complexes by changes in the formal oxidation states of the metal atoms.

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