system with an aromatic amine.[14] In 50% ethanol, pyrrole hydrogen ionization in the mixed 1+ complex occurs with $\mathrm{p}K_a = 8.2$, slightly lower than the statistically adjusted value (see Discussion) from Table I for a nontetragonal complex. The visible absorption spectrum of the mixed complex is that of a tetragonal Cu(II) complex with the wavelength of maximum absorption shifting from 625 nm before pyrrole hydrogen ionization to 608 nm afterward. Spectra in the ultraviolet region are comparable to the 2:1 complexes presented above.

As for many mixed complexes of L-alaninate and Cu(II),[15] the visible circular dichroism (CD) of Cu(PH)(L-Ala)$^+$ exhibits a net negative sign. In water the CD extrema show $\Delta\epsilon = -0.03$ and $+0.01$ at 568 and 695 nm, respectively. Transfer to 50% ethanol and pyrrole hydrogen ionization result in increases in CD magnitudes within the same sign pattern. The mixed complexes of Cu(II), L-alaninate, and either bis(imdazolyl)methane[16] or bipyridyl in 50% ethanol yield a similar sign pattern. However, the mixed complex of Cu(II), L-alaninate, and bipyridyl in water yields a visible CD spectrum with two positive maxima[15] in contrast to the net negative CD for the mixed PH complex. These solvent effects which alter the sign of the CD deserve further investigation.

The magnetic susceptibility of the $\mathrm{Fe(PH)_3}^{2+}$ complex in $\mathrm{D_2O}$ at pH ~7 is 3.4 BM at 34°. This value is within the range observed for solid complexes at $\mathrm{Fe(PH)_3}^{2+}$ and a variety of anions which show a temperature-dependent susceptibility with a predominance of the low-spin form at room temperature.[17]

Discussion

Marked promotion of pyrrole hydrogen ionization in 2-(2′-pyridyl)imidazole, PH, upon chelation to transition metal ions is revealed by inspection of Table I. Saturation of metal ion coordination sites in tris complexes of the bidentate ligand indicates that pyrrole ionization is promoted by coordination of the metal ion across the imidazole ring and not by substitution of the pyrrole hydrogen by the metal ion. Pyrrole ionization in complexes of glycylhistidine is promoted by metal ion substitution and the system exhibits behavior different from that described in this paper.[18] Since there are three ligand molecules in the tris complexes of Table I, the successive intrinsic acidity constants are indicated by $\mathrm{p}K_1 + \log 3 = \mathrm{p}K_1 + 0.5$, $\mathrm{p}K_2$, and $\mathrm{p}K_3 - 0.5$. Chelation of the ligand PH in a dipositively charged transition metal ion complex results in promotion of the first pyrrole ionization by 5.1, 5.2, 4.7, 5.8, and 4.9 log units for the five tris complexes of first-row transition metal ions of Table I, respectively, and 7.9 log units for the Pd(II) complex. This last value is markedly greater than the promotion of 3.6 log units found for the pyrrole hydrogen ionization in Pd(en)(L-His)$^+$.[19] Though the $\mathrm{p}K_a$ of the unbound ligand is unknown, promotion of the pyrrole ionization in 2-(2′-pyridyl)benzimidazole by first-row transition metal ions in 50% dioxane follows the same order as above for PH.[20]

The ability of the metal ions to promote ionization of the pyrrole hydrogen shows marked differences from the stability constant order. Though its stability constant has not been determined, the Pd(II) complex of Table I is almost certainly the most stable, and it is also the one with the lowest $\mathrm{p}K_a$. For the first-row divalent transition metal ions the stability order as given by the first stability constant or as the product of the first two stability constants is Cu > Ni > Co > Zn > Fe.[5] If all three stability constants are considered, the positions of Cu and Ni are reversed. On the other hand the acidity of the complexes (Table I) as measured by $\mathrm{p}K_1$ or $\mathrm{p}K_1 + \mathrm{p}K_2$ is given by Cu > Co > Fe > Zn > Ni. If all three ionizations are considered, the order becomes Fe > Cu = Co > Zn > Ni. Considering its high position in the stability series and its bottom position in the acidity series, Ni(II) appears relatively ineffective in promoting pyrrole hydrogen ionization compared to the other metal ions. Co(II) and especially Fe(II) are markedly more effective in promoting pyrrole ionization than the stability series predicts. The Fe(II) complexes are at the bottom of the stability series, in the middle of the first acidity series, and at the top of the final acidity series. The near equality of the three successive stability constants[5] suggests a tendency for a low-spin complex in solutions of $\mathrm{Fe(PH)_3}^{2+}$. This conclusion is confirmed by the susceptibility determination with an intermediate result of 3.4 BM corresponding to about 57% low-spin Fe(II).[17] The marked promotion of Fe(II) from the bottom of the stability series to the top of the final acidity series suggests a mutal promotion of pyrrole hydrogen ionization and further stabilization of a low-spin form.

The results reported here for the complexes of 2-(2′-pyridyl)imidazole indicate that metal ion induced pyrrole hydrogen ionization may be a feature of many systems containing imidazole and derivatives as ligands.

Registry No. $\mathrm{Fe(PH)_3}^{2+}$, 18745-06-7; $\mathrm{Co(PH)_3}^{2+}$, 18973-12-1; $\mathrm{Ni(PH)_3}^{2+}$, 18745-07-8; $\mathrm{Cu(PH)_3}^{2+}$, 20219-48-1; $\mathrm{Zn(PH)_3}^{2+}$, 18745-08-9; Pd(en)PH^{2+}, 51052-18-7; PH, 18653-75-3; Cu(PH)(L-Ala)$^+$, 51108-14-6.

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Application of Magnetic Measurements to Complex Formation in Fused Salts

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Magnetic susceptibility measurements on transition metal complexes are routine for the investigation of structure and are complementary to ligand field spectral studies. In investigating transition metal ions in fused-salt solutions, spectroscopy has been widely used, but only a handful of reports of magnetic work have appeared in this area.[1-5] The

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Table I. Magnetic Data for Co(II) and Ni(II) in Salt Melts and Glasses

System	Magnetic moment, BM	Probable coord geometry (from spectroscopic results)
KSCN melt at 180°: Co(II)	4.64	Tetrahedral[9]
Ni(II)	3.05	Octahedral[8]
KNO_3 melt at 140°: Co(II)	4.74	Eight-coordinate[15]
KNO_3–$Ca(NO_3)_2$ glass (3:2): Co(II)	4.72	Eight-coordinate[12,13]
Ni(II)	3.29	Octahedral[12]
$NaCH_3CO_2$–$LiCH_3CO_2$ glass (3:4): Co(II)	4.74	Eight-coordinate[12,14]
Ni(II)	3.30	Octahedral[14]
K_2SO_4–$ZnSO_4$ glass (2:3): Co(II)	5.18	Octahedral[10,11]
Ni(II)	3.40	Octahedral[10]
$ZnCl_2$ glass: Co(II)	4.50	Tetrahedral[10]

method is particularly adapted to following processes in which the spin state of the ion in question changes, and in certain cases the magnetic moment can provide information on coordination geometries.

One example of behavior of interest in fused salts is complex formation. Ni(II) in fused KCNS forms a complex with added CN^- ions which has been studied spectroscopically by Henion, *et al.*,[6] who reported a p*K* value of 19.5 (without, however, specifying the units).

The analogous reaction in aqueous solution produces the square-planar, diamagnetic $[Ni(CN)_4]^{2-}$ ion which is apparently the same species formed in the melt. Investigation of the magnetic changes in this system forms the major portion of this report.

Results and Discussion

The magnetic moment of Ni(II) in molten KSCN at 180° (Table I) was 3.05 BM, within the range normally encountered for octahedral coordination geometry for this ion (2.9-3.3 BM).[7] Spectroscopic results have earlier established octahedral coordination here.[8] Addition of KCN resulted in partial decomposition as Harrington and Sundheim reported[9] to produce a black precipitate shown by X-ray diffraction to be a NiS phase. The filtered melt was yellow-green, golden yellow with excess CN^-. The electronic spectrum showed no shifts in the nickel bands as the KCN content was increased–only a decrease in intensity. This is in agreement with earlier results[6] and suggests negligible formation of mixed thiocyanate–cyanide complexes.

The magnetic behavior of this system is shown in Figure 1. The susceptibility changes from the octahedral paramagnetic values to diamagnetism at a small excess of CN^- over Ni(II), confirming the formation of the square-planar cyanide complex in the melt. The moment decreases linearly with increasing CN^-:Ni ratio, although decomposition problems produce some scatter. At ratios above 5, a constant diamagnetic susceptibility was found. If the reaction is written $Ni(II) + 4CN^- \rightarrow [Ni(CN)_4]^{2-}$, a formation constant can be evaluated from

$$K = [a - ca]/[ca][ba - 4ac]^4$$

were a = total Ni(II) concentration, $b = CN^-$:Ni(II) ratio, and $c = \chi_A(\text{obsd})/\chi_A(\text{no } CN^-)$. The value obtained is about $2 \times 10^5 \ M^{-4}$.

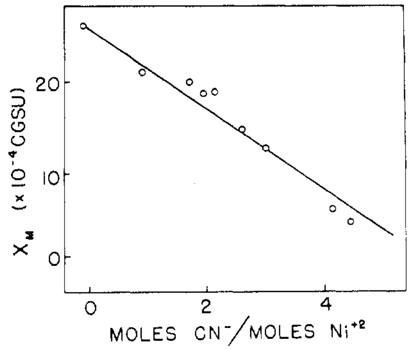

Figure 1. Magnetic susceptibility of the Ni^{II}–SCN^-–CN^- melt as a function of the CN^- to Ni(II) ratio at 180°.

Table I shows some magnetic moments determined for Ni(II) and Co(II) in several salt melts and glasses. Although single-temperature magnetic data are of limited structural value, it is seen that the values are consistent with the ranges anticipated for magnetically dilute systems from spectroscopic results[8-15] (octahedral Ni(II), 2.9-3.4 BM; octahedral Co(II), 4.7-5.2 BM; tetrahedral Co(II), 4.4-4.8 BM). In particular, for the three oxy anion systems where Co(II) gives an intermediate value, the best interpretation of the spectrum requires an effectively eight-coordinate structure where each Co(II) is surrounded tetrahedrally by four bidentate nitrate ions. This is the structure for $[Co(NO_3)_4]^{2-}$ in its solid compounds, where it exhibits a magnetic moment of 4.67 BM.[16] This is very close to the melt value.

Experimental Section

All magnetic susceptibility measurements were made by the Gouy technique, using closed Pyrex sample tubes. Melt samples were placed in a noninductively wound tubular furnace between the poles of the electromagnet (Varian 4 in.). Glasses were measured at room temperature. Diamagnetic corrections for the solvent salts were measured directly. Magnetic measurements at room temperature are believed to be accurate to within ±0.05 BM and at melt temperatures to ±0.1 BM, although in the latter decomposition can introduce larger errors.

All salts were reagent grade, recrystallized when necessary and vacuum-dried. In nitrate and thiocyanate media, the appropriate anhydrous salt or the anhydrous chlorides were used, giving indistinguishable results. Anhydrous nitrates and acetates were prepared by reported methods;[17,18] the chlorides and sulfates were obtained commercially.

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Solutions were prepared by melting the salt mixture under a stream of dry N_2 and adding the appropriate metal salt. After dissolution, the solution was filtered through a glass frit, cooled, and handled in a drybox; the sulfate and zinc chloride systems were not filtered, however. Formation of the various glasses has been described by Duffy and Ingram.[12,19] Concentrations used were varied for each system and were limited by solubility. Generally, they were of the order 1% metal ion by weight.

In the mixed SCN^-–CN^- system, separate melts of Ni(II) in KSCN and KCN in KSCN were made up, mixed in various proportions and then filtered. This procedure minimized decomposition reactions which have previously been noted.[9]

Metal concentrations were determined by EDTA titration or by atomic absorption spectroscopy. CN^- content of the SCN^-–CN^- mixture was obtained by adding a known excess of NaCN to prevent formation of insoluble $[Ni(H_2O)_6][Ni(CN)_4]$ and titrating with $NiSO_4$ using a diphenylcarbazone indicator.

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Registry No. Co(II), 22541-53-3; Ni(II), 14701-22-5; KSCN, 333-20-0; KNO_3, 7757-79-1; $Ca(NO_3)_2$, 10124-37-5; $NaCH_3CO_2$, 127-09-3; $LiCH_3CO_2$, 546-89-4; K_2SO_4, 7778-80-5; $ZnSO_4$, 7733-02-0; $ZnCl_2$, 7646-85-7.

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Reductive Fluoride Elimination Syntheses of Transition Metal Fluorides. Synthesis of Molybdenum Pentafluoride and Molybdenum Tetrafluoride[1]

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Previous methods for preparing second- and third-row transition metal pentafluorides MF_5 and tetrafluorides MF_4 include the direct fluorination of the metal, halogen exchange with a corresponding chloride, and decomposition or chemical reduction of a higher oxidation state metal fluoride.[2] In particular, molybdenum pentafluoride has been reported to be a product of reactions between $Mo(CO)_6$ and F_2,[3] $Mo(CO)_6$ and MoF_6,[4] $W(CO)_6$ and MoF_6,[4] Mo and F_2,[4] Mo and MoF_6,[4] and MoF_6 and PF_3.[5] More simply, MoF_4 has only been reported as a product from the reaction of MoS_2 and SF_4[6] and from the thermal decomposition of MoF_5.[3,4]

In our hands, most of these syntheses have been found to give poor yields and impure products and to be generally unreliable. In addition, no one reaction has been reported to be generally applicable to the synthesis of both metal pentafluorides and tetrafluorides. Since a comprehensive application of these interesting compounds to new synthetic systems has been impeded by preparative problems we have attempted to develop a simple, convenient, and general synthetic method for the preparation of second- and third-row transition metal pentafluorides and tetrafluorides. We report here two simple, novel reductive-fluoride elimination routes to MoF_5 and MoF_4.

Experimental Section

The manipulation of the volatile compounds was accomplished in a Monel vacuum line[7] fitted with auxiliary Kel-F reaction tubes.[8] The molybdenum hexafluoride was purchased from Ozark-Mahoning Co., Tulsa, Okla., and was purified by trap to trap vacuum distillation. Hydrogen fluoride was purchased from Matheson Co. The crude HF was purified by trap to trap distillation. The resulting liquid was stored over K_2NiF_6. The mass spectra were recorded with a modified Bendix Model 12 time-of-flight spectrometer using a solids-probe attachment. Thin-film infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer (4000–400 cm^{-1}). The Raman spectra were recorded with a Cary 82 spectrometer using 6471-Å Kr^+ laser excitation. The Raman samples were contained in sealed thin-wall 5-mm glass nmr tubes.

Syntheses of MoF_5. In a typical one-electron reduction reaction 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were condensed into a Kel-F reaction tube containing 30.8 mg (1.1 mmol) of pure silicon powder frozen in 5 ml of HF. *Caution! Metal hexafluorides should not be condensed directly into silicon powder without solvent present. Explosions may result.* After 1 hr at 23° the reaction is complete as evidenced by the disappearance of the silicon powder and the cessation of gas (SiF_4) evolution. Vacuum evaporation of the volatile products (HF, SiF_4, excess MoF_6) afforded 0.84 g (100%, based on Si) of bright yellow MoF_5. By a second method, 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were condensed into a Kel-F reaction tube. The tube was warmed to room temperature and hydrogen gas (2.3 mmol, P_0 = 2000 Torr) was added to the stirred solution. After 3 days the volatile products (HF, unreacted MoF_6) were vacuum evaporated leaving about 0.60 g (68%, based on H_2) of MoF_5.

Synthesis of MoF_4. In a typical two-electron reduction reaction, 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were combined with 64.4 mg (2.3 mmol) of silicon powder and 5 ml of HF in a Kel-F reactor. Three days of stirring at 23° resulted in a green oil from which MoF_5 could be sublimed at 90–100°. A pale yellow-green, nonvolatile powder, MoF_4 (0.19 g, 22% based on Si), remained. In a second, more satisfactory reaction, 1.0 g (5.23 mmol) of MoF_5 isolated above, 34.0 mg (1.2 mmol) of silicon powder and 10 ml of HF were combined in a Kel-F reactor. The silicon powder disappeared from the stirred solution in 6–12 hr. Vacuum evaporation of the volatile products afforded 0.9 g (97%, based on Si) of yellow-green MoF_4.

Characterization of Products. MoF_5. The yellow, moisture-sensitive, crystalline MoF_5 was found to sublime at *ca.* 50° and melt at 63°. The mass spectrum of the vapors above the solid (25°) was recorded at 70 eV, and the principal ions are as follows [*m/e* (assignment) relative intensity]: 193 ($^{98}MoF_5^+$) 20, 174 ($^{98}MoF_4^+$) 100, 155 ($^{98}MoF_3^+$) 47, 136 ($^{98}MoF_2^+$) 24, 117 ($^{98}MoF^+$) 10. Ion envelopes corresponding to $Mo_3F_x^+$ and $Mo_2F_x^+$ were easily detected, but individual ion resolution at *m/e* >300 was not possible. The ions listed above are for ^{98}Mo only; ions due to ^{92}Mo, ^{95}Mo, and ^{96}Mo also could be easily discerned. The infrared absorptions (cm^{-1}) from a cold (77°K) sublimed thin-film sample (Figure 1) are 765 (w), 739 (m), 691 (s), 654 (vs, sh), and 521 (m). The Raman data (cm^{-1}), recorded at 30° from a premelted, rapidly cooled sample are 747 (s, pol), 701 (w, pol), 228 (w), and 200 (w). The yellow solid is soluble without decomposition in anhydrous HF.

MoF_4. The pale yellow-green, moisture-sensitive MoF_4 obtained from the one-electron reduction of MoF_5 and from the thermal decomposition of the green oil was found to be insoluble in anhydrous HF. *Anal.* Calcd for MoF_4: F, 44.2. Found: F, 44.0. Powder X-ray diffraction data are d_{obsd} = 8.1 (vw), 6.9 (vw), 5.5 (w), 4.7 (m, br), 4.4 (m), 4.0 (m), 3.8 (s), 3.55 (br, s), 3.17 (w), 3.13 (w),

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