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Synthesis and Characterization of Transition Metal Complexes Containing a Pentadentate Macrocyclic Ligand

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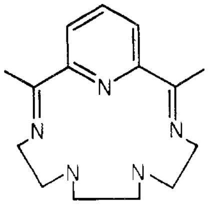
The transition metal complexes (Fe(III), Co(III), Ni(II), and Cu(II)) with the pentadentate macrocyclic ligand 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene (abbreviated as pyaneN_5), have been prepared and characterized by elemental analyses and by spectral, magnetic, conductance, and electrochemical measurements. In the cases of the Ni(II) and Co(III) complexes, the macrocycle is folded and one additional ligand is included in the coordination sphere to form six-coordinate complexes with approximate octahedral geometry: $[M(pyaneN_5)X]^{n+}$ ($M = Ni$, $X = I^-$, Br^-, Cl^-, NCS^-, CH_3CN, NH_3, H_2O, $n = 1$ or 2; $M = Co$, $X = I$, Br, Cl, NCS, N_3, NO_2, and $n = 2$). The average ligand field strengths ($Dq = 1124$ cm^{-1} for Ni(II) and 2520 cm^{-1} for Co(III)) are typical of those observed for hexaamminenickel(II) and -cobalt(III) systems and indicate that complexation involves little or no steric strain. The Fe(III) complexes are seven-coordinate with one bidentate or two monodentate ligands included in the coordination sphere in addition to the pentadentate ring. Oxidative dehydrogenation of the Fe(III) complexes by reaction with oxygen introduces imine linkages into the macrocyclic ligands. The Cu(II) complex is a five-coordinate species.

Introduction

The cyclic ligands 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (abbreviated pydieneN_5, structure I) and 2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1(21), 2,-15,17,19-pentaene (pydieneN_6, structure II) were the first macrocyclic ligands to be prepared which contained more than four donor atoms.[1] Complexes of ligand I have been prepared with iron(III)[2] and manganese(II)[3] and have been characterized as seven-coordinate, with the pentadentate macrocyclic ligand lying in a plane and with two monodentate anions occupying axial positions. This geometry has been confirmed by an X-ray crystal structure determination on the $Fe^{III}(pydieneN_5)(NCS)_2^+$ derivative.[4] The planar nature of the pyridine ring and adjacent imines contributes to the tendency toward planar coordination by this ligand with ions having spherical electron distributions such as high-spin iron(III) and manganese(II). A second class of pentadentate macrocyclic ligands has recently been prepared (structure III); however, it also favors planar chelation and only its Zn(II) and Cd(II) complexes have been characterized.[5] The study of pentadentate macrocyclic complexes of other transition metal ions, for example, those with electron distributions which favor an octahedral coordination geometry, requires a macrocyclic ligand which is flexible and large enough to fold in order to provide a nonplanar five-donor arrangement. Such a ligand and its metal complexes with several transition element ions (Fe(III), Co(III), Ni(II), Cu(II)) are reported here.



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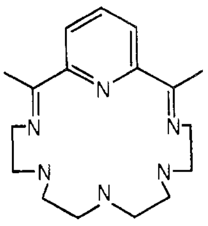

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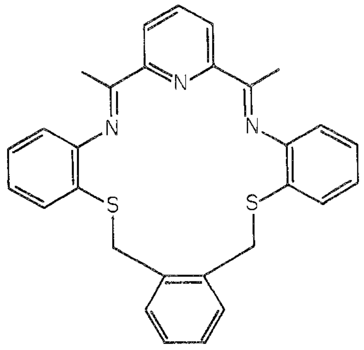


III

Results and Discussion

Preparation of the Ligand. The preparation of the new ligand 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene (structure IV, referred to as

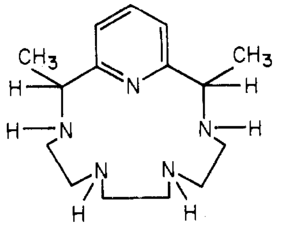
Table I. Analytical Data for the Nickel Complexes of the Cyclic Pentadentate Ligand

Complex	% found C	% found H	% found N	% found X	% calcd C	% calcd H	% calcd N	% calcd X
$[Ni(pyaneN_5)H_2O](PF_6)_2$	27.91	4.50	10.85	35.24 (F)	27.92	4.50	10.85	35.37 (F)
$[Ni(pyaneN_5)CH_3CN](PF_6)_2$	30.46	4.39	12.66	34.25 (F)	30.68	4.53	12.60	34.18 (F)
$[Ni(pyaneN_5)NCS](NCS)$	45.39	5.99	21.52	13.95 (S)	45.04	5.96	21.63	14.13 (S)
$[Ni(pyaneN_5)NH_3](PF_6)_2$	27.89	4.72	12.77	35.18 (F)	27.96	4.66	13.05	35.42 (F)
$[Ni(pyaneN_5)Cl]Cl\cdot2.5H_2O$	39.93	6.92	15.70	14.66 (Cl)	39.86	7.09	15.50	15.72 (Cl)
$[Ni(pyaneN_5)Br]Br\cdot2H_2O$	33.41	5.31	12.89	29.34 (Br)	33.86	5.83	13.17	30.07 (Br)
$[Ni(pyaneN_5)I]I\cdot H_2O$	29.41	4.78	11.53	39.58 (I)	29.63	4.77	11.52	41.78 (I)

Table II. Some Physical Properties of the Nickel Complexes of the Cyclic Pentadentate Ligand

Complex	Color	μ_{eff}, BM	Λ_M,[a] cm²/(ohm mol) [solvent]
$[Ni(pyaneN_5)(H_2O)](PF_6)_2$	Violet	3.13	125 [DMF]
$[Ni(pyaneN_5)(CH_3CN)](PF_6)_2$	Purple	3.14	261 [CH_3CN]
$[Ni(pyaneN_5)NCS]NCS$	Purple	3.15	80 [DMF]
$[Ni(pyaneN_5)(NH_3)](PF_6)_2$	Purple	3.09	288 [CH_3CN]
$[Ni(pyaneN_5)Cl]Cl\cdot2.5H_2O$	Blue	3.10	71 [CH_3NO_2]
$[Ni(pyaneN_5)Br]Br\cdot2H_2O$	Blue-gray	3.05	74 [CH_3NO_2]
$[Ni(pyaneN_5)I]I\cdot H_2O$	Gray	3.09	78 [CH_3NO_2]

[a] Measurements were made at room temperature on ~10^{-3} *M* solutions. For typical values for 1:1 and 2:1 electrolytes, see R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, 9, 1215 (1970).



IV

pyaneN5), involves hydrogenation of the pentadentate macrocycle previously reported (I). The hydrogenated ligand has been isolated as the nitric acid amine salt $pyaneN_5\cdot4HNO_3$ and it is formed by the reduction of $Mn(pydieneN_5)Cl_2$ with a nickel–aluminum alloy under basic aqueous conditions, followed by the addition of cold concentrated nitric acid. Infrared and pmr data indicate reduction of the two Schiff base linkages, with the macrocyclic ligand remaining intact. The C=N stretching mode at 1650 cm^{-1} disappears and a new NH stretching band appears at ~3050 cm^{-1}, in the spectrum of the acid salt. The pmr spectrum of the free ligand in $CDCl_3$ has a methyl doublet at 1.39 ppm relative to TMS (relative intensity 6) and a quartet assigned to the methine proton at 3.75 ppm (2) with $J = 6.5$ Hz. An AB_2 pattern is observed for the pyridine protons at 7.2 ppm, and a broad multiplet assigned to the methylene proton occurs at 2.60 ppm (12). The appearance of a single methyl doublet is consistent with the presence of a single isomeric form of the pure ligand. This is further supported by the absence of evidence of diastereoisomers among the complexes.

Nickel Complexes. The reaction of the acid salts of the ligand with nickel acetate in water and subsequent addition of ammonium hexafluorophosphate yielded the purple complex $[Ni(pyaneN_5)(H_2O)](PF_6)_2$. Metathetical reactions produced other complexes $[Ni(pyaneN_5)X](PF_6)_n$, where X = NCS^-, NH_3, or CH_3CN and *n* = 1 or 2; and reaction of the free ligand $pyaneN_5$ with the appropriate dehydrated nickel halide salt in anhydrous methanol yielded the water-sensitive complexes $[Ni(pyaneN_5)X]X$, where X = Cl^-, Br^-, or I^-. The elemental analyses agree with the proposed stoichiometries of the complexes and are listed in Table I.

The infrared spectra of the complexes indicate that the macrocycle has remained intact upon complexation. A multiplet of medium intensity at ~3200 cm^{-1} is assigned to the four N–H stretching modes. The shape and position of this band varies with the nature of the other ligands in the complex. For the derivatives containing coordinated water and acetonitrile, ν_{N-H} is a sharp doublet and is observed near 3340 cm^{-1}, while for the thiocyanate, bromide, and iodide derivatives, the band is broadened and appears at somewhat lower frequencies (~3200 cm^{-1}). The ir spectra of all of the complexes display a sharp doublet (1600 and 1580 cm^{-1}) due to the unsaturation in the pyridine ring of the macrocycle, but no other bands appear in the region from 1700 to 1500 cm^{-1}. This indicates the absence of imine linkages, which would confirm incomplete reduction, or carbonyl functions that would suggest the presence of uncyclized ligand. The spectrum of the dithiocyanato complex has two C≡N stretching bands at 2050 and 2085 cm^{-1} and is characteristic of one N-coordinated and one free thiocyanate ion, respectively.[6] The C≡N stretching modes of the acetonitrile derivative are observed as a sharp doublet at 2300 cm^{-1}.

The molar conductances of the compounds (Table II) correspond to the coordination of only one donor ligand in addition to the macrocycle, the electrolyte types being AB_2 with neutral ligands and AB with anionic ligands. Room-temperature magnetic moments range from 3.05 to 3.15 BM (Table II). These moments are typical of compounds with two unpaired electrons in a high-spin (distorted) octahedral d^8 configuration. The electronic spectra also are characteristic of nickel complexes with octahedral symmetry (Table III). The lower energy bands, observed in the regions 10,500–11,500 and 18,000–19,000 cm^{-1}, respectively, are assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$. The third spin-allowed transition $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ is obscured in some of the spectra by charge-transfer bands but is observed as a shoulder in the case of X = H_2O, NCS, and NH_3 at ~29,500 cm^{-1}. An additional shoulder on the high-energy side of the first band is assigned to the spin-forbidden transition $^1E_g \leftarrow$

Table III. Electronic Spectra of the Nickel Complexes of the Cyclic Pentadentate Ligand[a]

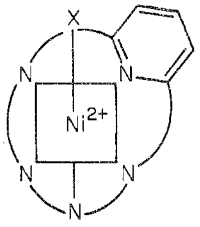
Complex	Solvent	$\nu(^3T_{2g} \leftarrow {}^3A_{2g})$, cm^{-1}	$\nu(^1E \leftarrow {}^3A_{2g})$, cm^{-1}	$\nu(^3T_{1g}(F) \leftarrow {}^3A_{2g})$, cm^{-1}	$\nu(^3T_{1g}(P) \leftarrow {}^3A_{2g})$, cm^{-1}
$[Ni(pyaneN_5)H_2O](PF_6)_2$	H_2O	11,360 (22)	12,660 sh	18,180 (6.6)	29,850 sh
$[Ni(pyaneN_5)CH_3CN](PF_6)_2$	CH_3CN	11,470 (32)		18,870 (12)	
$[Ni(pyaneN_5)NCS]NCS$	H_2O	11,170 (36)	11,700 sh	18,380 (20)	29,400 sh
$[Ni(pyaneN_5)NH_3](PF_6)_2$	CH_3CN	11,240 (27)		18,690 (11)	29,410 sh
$[Ni(pyaneN_5)Cl]Cl\cdot2.5H_2O$	CH_3NO_2	10,750	11,450 sh	18,180	
$[Ni(pyaneN_5)Br]Br\cdot2H_2O$	CH_3NO_2	10,200 (21)	11,600 sh	18,520	
$[Ni(pyaneN_5)I]I\cdot H_2O$	CH_3NO_2	10,200			

[a] Numbers in parentheses are the molar extinction coefficients; sh = shoulder.

Table IV. Analytical Data for the Cobalt(III) Complexes of the Cyclic Pentadentate Ligand

	% found				% calcd			
Complex	C	H	N	X	C	H	N	X
$[Co(pyaneN_5)Cl](ClO_4)_2$	32.11	4.68	11.94	19.71 (Cl)	31.51	4.73	12.25	18.64 (Cl)
$[Co(pyaneN_5)Br](ClO_4)_2$	29.34	4.51	11.25	12.85 (Br)	29.28	4.39	11.39	13.00 (Br)
$[Co(pyaneN_5)I](I)_2$	25.07	3.49	9.75	54.31 (I)	25.12	3.77	9.77	53.12 (I)
$[Co(pyaneN_5)NCS](ClO_4)_2$	32.09	4.69	13.53	5.52 (S)	32.28	4.55	14.17	5.41 (S)
$[Co(pyaneN_5)N_3](ClO_4)_2$	30.92	4.55	19.22	12.20 (Cl)	31.17	4.68	19.40	12.30 (Cl)
$[Co(pyaneN_5)NO_2](ClO_4)_2$	30.57	4.56	14.20	12.33 (Cl)	30.99	4.65	14.47	12.21 (Cl)

$^3A_{2g}$. The nature of the data indicates that the nickel complexes are pseudooctahedral with the macrocyclic ligand functioning as a pentadentate donor, folded in an approximate square-pyramidal array of nitrogen atoms. Molecular models indicate that the aromatic pyridine ring and its adjacent nitrogen linkages should be coplanar; therefore, one of the two nitrogen atoms opposite the pyridine nitrogen assumes an axial position. The sixth position of the octahedral complex is occupied by a monodentate ligand (structure V). While an approximate octahedral array of donor atoms is thus provided for the nickel ion, the overall symmetry of the complex is minimal, C_1.



V

The position of the lowest energy transition in the electronic spectra of octahedral nickel complexes can be correlated with the overall field strength of the complexed ligands. Since the macrocycle remains constant in this series of complexes, the position of the first band should vary slightly with the field strength of the monodentate ligand. The observed order (Table III) I^-, $Br^- < NCS^-$, $< NH_3 < H_2O < CH_3CN$ corresponds only roughly to the usual spectrochemical series.[7]

The crystal field splitting parameter *Dq* for the NiN_6 system in $[Ni(pyaneN_5)NH_3]^{2+}$ is 1124 cm^{-1}, a value which is comparable to those of other $Ni^{II}N_6$ systems ($Ni(NH_3)_6{}^{2+}$, 1075 cm^{-1}; $Ni(en)_3{}^{2+}$, 1120 cm^{-1}).[8] The ligand field strength of the pentadentate macrocycle on nickel corresponds to that of an unstrained 15-membered tetradentate macrocycle[9] but is weaker than that of the well-known 14-membered ring cyclam ([14]aneN_4). The latter has been assigned *Dq* values greater than 1200 cm^{-1}.[9] The proximity of the value for the pentadentate complex to those for the noncyclic ligand derivatives (*e.g.*, en) and unstrained tetradentate rings suggests that the macrocycle has the necessary size and flexibility to coordinate to the nickel ion in a strain-free arrangement.

While many nickel macrocyclic complexes undergo ligand oxidative dehydrogenation in a reaction with oxidizing agents such as nitric acid,[10] no ligand dehydrogenation has yet been observed when the pentadentate nickel complexes are subjected to oxidizing conditions. The reaction of $[Ni(pyaneN_5)H_2O]^{2+}$ with concentrated nitric acid results in removal of the ligand from the metal ion and the nitric acid salt of the free reduced ligand can be isolated from such solutions.

The electrochemical oxidation of $[Ni(pyaneN_5)CH_3CN]^{2+}$ at a platinum electrode in acetonitrile discloses a reversible process at +0.78 ± 0.01 V *vs.* Ag–Ag^+ (0.1 *M*), which is interpreted as the Ni(II) → Ni(III) oxidation. This value is near the lower limit of those oxidation potentials observed for 14-membered, planar tetradentate macrocyclic nickel complexes, which range from 0.67 to 1.05 V.[11] The value is nearest those for complexes containing saturated [14]aneN_4 macrocyclic ligands. Conversely, the electrochemical reduction of $Ni(pyaneN_5)(CH_3CN)^{2+}$ occurs quasireversibly at −1.94 V *vs.* Ag–Ag^+ (0.1 *M*), a more cathodic value than the potential range observed for the reduction of the planar nickel macrocycles, −0.8 to −1.7 V.[11]

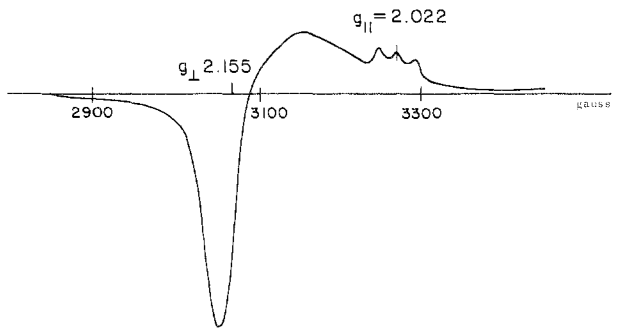


Figure 1. Epr spectrum of $[Ni(pyaneN_5)H_2O]^{3+}$ in MeOH at 77°K.

Chemical oxidation of $[Ni(pyaneN_5)H_2O]^{2+}$ with ammonium persulfate in aqueous solution produced a light green solution of $[Ni(pyaneN_5)(H_2O]^{3+}$ characterized by an anisotropic low-temperature (liquid N_2) solution esr spectrum, with $g_{\perp} = 2.155$ and $g_{\parallel} = 2.022$. This is typical of an octahedral low-spin d^7 Ni(III) system[11,12] (Figure 1). The absorption at $g_{\parallel}$ is split into a triplet by superhyperfine coupling ($A = 23$ G) of the unpaired electron with the axial nitrogen ($I = 1$) of the macrocycle. The spectrum provides further confirmation of the proposed folded configuration of the pentadentate ligand. The unpaired nickel electron in this high-spin tetragonally distorted octahedral field apparently is in an orbital primarily of d_{z^2} character. It appears to be insensitive to the lack of symmetry in the N_4 plane since the esr spectrum shows the two *g* values characteristic of a molecule with axial symmetry.

Cobalt(III) Complexes. A series of $[Co(pyaneN_5)X](ClO_4)_2$ compounds has been prepared, where X = I^-, Br^-, Cl^-, NCS^-, N_3^-, and NO_2^-, and these have also been characterized as octahedral complexes. The chloride and bromide derivatives were prepared by the reaction of the appropriate Co(II) salt with the macrocyclic ligand in acidic aqueous medium, followed by air oxidation of the resulting solution. Crystallization occurs upon the addition of excess sodium perchlorate. The other derivatives were prepared by metathesis reactions with the appropriate sodium salt. The stoichiometries of the cobalt complexes have been confirmed by elemental analyses (Table IV) and the molar conductance values are in the range expected for 2:1 electrolytes (Table V).

The infrared spectra of the subject complexes have the expected bands in the ν_{N-H} region, 3200–3400 cm^{-1}, and the unsaturated region (doublet at 1600 cm^{-1}). The complexes $[Co(pyaneN_5)N_3]^{2+}$, $[Co(pyaneN_5)NCS]^{2+}$, and $[Co(pyaneN_5)NO_2]^{2+}$ all represent Co–N_6 systems, the N-bonded nature of the NCS^- and NO_2^- ligands being confirmed by infrared data. The C–S stretching mode of the N-bonded NCS^- is observed at 850 cm^{-1}; no band is observed around 700 cm^{-1} as would be expected for M–S–C–N.[13] Three bands at 1410 (ν_{as}), 1305 (ν_s), and 820 cm^{-1} (δ_{ONO}) are observed

Table V. Some Physical Properties of the Cobalt(III) Complexes of the Cyclic Pentadentate Ligand

Complex	Color	μ_{eff}, BM	Λ_M,^{a} cm^2/(ohm mol) [solvent]
$[Co(pyaneN_5)Cl](ClO_4)_2$	Red	0.59	122 [DMF]
$[Co(pyaneN_5)Br](ClO_4)_2$	Rose	0.77	130 [DMF]
$[Co(pyaneN_5)I](I)_2$	Brown	0.90	135 [DMF]
$[Co(pyaneN_5)(NCS)](ClO_4)_2$	Orange	0.60	146 [DMF]
$[Co(pyaneN_5)N_3](ClO_4)_2$	Brown	0.75	255 [CH_3CN]
$[Co(pyaneN_5)NO_2](ClO_4)_2$	Gold	0.76	130 [DMF]

[a] Measurements were made at room temperature on ~10^{-3} *M* solutions.

for the $[Co(pyaneN_5)NO_2]^{2+}$ salt.[14]

While the nmr spectra of the complexes are complicated, two overlapping doublets are observed in the methyl region (1.6 ppm). This is consistent with the presumed structure which involves nonequivalent methyl groups because of folding of the macrocyclic ligand.

The electronic spectra of the cobalt complexes (Table VI) generally can be interpreted in terms of the pseudooctahedral symmetry and involve the $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ transitions. The low-energy band is observed near 20,000 cm^{-1}, but for most of the complexes, charge-transfer bands obscure the second expected absorption. For an approximate C_{4v} site symmetry at the metal ion (in this approximate treatment the five nitrogens of the macrocycle are assumed equivalent) the tetragonal splitting is most often too small to be observed; but the field strength of the monodentate ligand in the halide derivatives is sufficiently different from that of the five nitrogen donors of the macrocycle to cause an observable tetragonal distortion. Only strong charge-transfer bands are seen in the spectrum of the iodide complex, but the chloride and bromide derivatives have three absorptions in the visible region (Figure 2). The octahedral low-energy transition is split to give two bands at ~19,000 cm^{-1} ($^1E \leftarrow {}^1A_1$) and ~22,000 cm^{-1} ($^1A_2 \leftarrow {}^1A_1$), and the high-energy transition is observed at ~28,000 cm^{-1}.

The equation $E = 10Dq - C$ applies to the transitions $^1T_{1g} \leftarrow {}^1A_{1g}$, in octahedral symmetry, and to $^1A_2 \leftarrow {}^1A_1$, in C_{4v} symmetry. If the Racah parameter C is assigned a value of 3800 cm^{-1},[15] the average Dq parameter for the three $Co^{III}N_6$ systems is 2520 cm^{-1}, a value very similar to those assigned to other $Co^{III}N_6$ systems ($Co(en)_3{}^{3+}$, 2530 cm^{-1};[15] $Co(NH_3)_6{}^{3+}$, 2490 cm^{-1} [15]). Again, this indicates that pyaneN5 can chelate in a pentadentate fashion with little steric strain.[9]

The equations $Dt = (4/35)(10Dq^{xy} - V_e - C)$ and $Dq^z = Dq^{xy} - (7/2)Dt$ apply to a Co(III) electronic spectrum of C_{4v} symmetry, as is approximated by the chloro and bromo derivatives. By using the average ν_A value of 21,490 cm^{-1}, Dt can be calculated as 279 and 339 cm^{-1} for the chloride and bromide derivatives, respectively. The Dq^z value for the axial Cl is, then, 1554 cm^{-1}; for Br$^-$, it is 1344 cm^{-1}. These values are comparable to those observed for the chloride and bromide derivatives of the formula $[Co(NH_3)_5X]^{2+}$ (Dq(Cl) = 1559 cm^{-1} and Dq(Br) = 1366 cm^{-1} [15]).

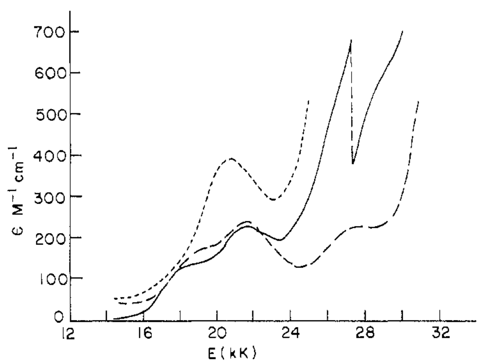


Figure 2. Electronic spectra of $[Co(pyaneN_5)X]^{2+}$ in DMF where $X^- = Cl^-$ (- - -) and Br^- (——) and in CH_3CN where $X^- = N_3{}^-$ (- - - - -).

Iron Complexes. An iron(III) complex of pyaneN5 was prepared by the reaction of the free ligand with an ethanol solution of anhydrous iron(II) chloride under an inert atmosphere followed by air oxidation and the addition of NH_4PF_6. The yellow crystalline material has been characterized as the seven-coordinate iron(III) complex $[Fe(pyaneN_5)(Cl)_2]PF_6$. Additional complexes of the type $[Fe(pyaneN_5)X_2]PF_6$, where X = Br$^-$, NCS$^-$, N$_3^-$, NO$_3^-$, and $^1/_2$ C_2O_4, were prepared by metathetical reactions. The elemental analyses are listed in Table VII.

The infrared spectra of the Fe(III) complexes have absorptions in the region 3200–3300 cm^{-1}, attributable to N–H stretching modes of secondary amines in the pentadentate ligand. Again, the imine region of the spectrum (1500–1700 cm^{-1}) has only the doublet around 1600 cm^{-1} associated with the pyridine ring. Absorptions at 1505, 1290, and 1000 cm^{-1} in the spectrum of $[Fe(pyaneN_5)(NO_3)_2]PF_6$ are similar to other systems with monodentate nitrate anions, although these data do not rule out a bidentate mode of coordination by each of the NO_3^- groups.[16] The spectrum of the oxalate derivative, with two strong absorptions centered at 1640 and 1300 cm^{-1}, appears characteristic of a symmetric bidentate oxalate complex.[17]

Conductance data (Table VIII), which indicate that the

Table VI. Electronic Spectra of the Cobalt(III) Complexes of the Cyclic Pentadentate Ligand^a

Complex	Solvent	$\nu(^1E_1 \leftarrow {}^1A_1)$, cm^{-1}	$\nu(^1A_2 \leftarrow {}^1A_1)$, cm^{-1}	$\nu(^1E_1 + {}^1B \leftarrow {}^1A_1)$, cm^{-1}
$[Co(pyaneN_5)Cl](ClO_4)_2$	DMF	18,520 sh	21,740 (245)	29,412 sh
$[Co(pyaneN_5)Br](ClO_4)_2$	DMF	19,050 sh	21,650 (209)	27,470 sh
$[Co(pyaneN_5)NCS](ClO_4)_2$	DMF		21,280 (475)	
$[Co(pyaneN_5)N_3](ClO_4)_2$	CH_3CN		20,580 (380)	
$[Co(pyaneN_5)NO_2](ClO_4)_2$	DMF		22,220 (436)	
$[Co(pyaneN_5)I](I)_2$	DMF		Charge transfer (5000)	

[a] Numbers in parentheses are the molar extinction coefficients; sh = shoulder.

Table VII. Analytical Data for the Iron and Copper Complexes of the Cyclic Pentadentate Ligand

Complex	% found				% calcd			
	C	H	N	X	C	H	N	X
$[Fe(pyaneN_5)Cl_2](PF_6)$	33.10	4.94	12.91	13.24 (Cl)	32.80	4.92	12.75	12.92 (Cl)
$[Fe(pyaneN_5)Br_2]PF_6$	28.39	4.10	10.78		28.23	4.23	10.98	
$[Fe(pyaneN_5)(NO_3)_2]PF_6$	30.07	4.39	16.52		29.91	4.49	16.29	
$[Fe(pyaneN_5)(NCS)_2]PF_6$	33.93	4.45	15.83	10.61 (S)	34.34	4.55	16.51	10.79 (S)
$[Fe(pyaneN_5)(N_3)_2]PF_6$	32.35	4.85	26.73	20.86 (F)	32.03	4.80	27.43	20.29 (F)
$[Fe(pyaneN_5)C_2O_4]PF_6$ ·	34.94	4.87	12.07	19.75 (F)	34.94	4.97	11.99	19.53 (F)
$[Cu(pyaneN_5)](PF_6)_2$	28.90	4.26	11.09		28.55	4.28	11.10	

Table VIII. Some Physical Properties of the Iron and Copper Complexes of the Cyclic Pentadentate Ligand

Complex	Color	μ_{eff}, BM	Λ_M,[a] cm^2/(ohm mol)
$[Fe(pyaneN_5)Cl_2]PF_6$	Yellow	5.97	99
$[Fe(pyaneN_5)Br_2]PF_6$	Gold	5.81	83
$[Fe(pyaneN_5)(NO_3)_2]PF_6$	Yellow	5.80	84
$[Fe(pyaneN_5)(NCS)_2]PF_6$	Red	5.97	77
$[Fe(pyaneN_5)(N_3)_2]PF_6$	Orange	6.00	62
$[Fe(pyaneN_5)C_2O_4]PF_6 \cdot H_2O$	Yellow	5.96	84
$[Cu(pyaneN_5)](PF_6)_2$	Blue	1.90	200

[a] Measurements were made at room temperature on ~10^{-3} *M* solutions; solvent was CH_3NO_2.

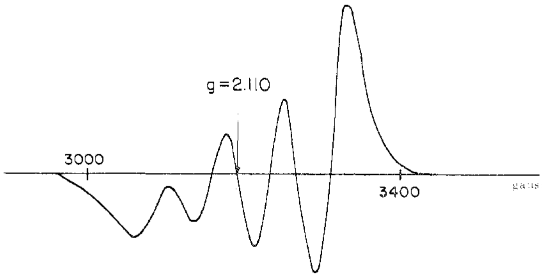


Figure 3. Epr spectrum of $[Cu(pyaneN_5)](PF_6)_2$ in CH_3OH–$CHCl_3$ at room temperature.

complexes are uni-univalent electrolytes, confirm the seven-coordinate nature of Fe(III). The magnetic moments of the complexes (Table VIII) are in the range expected for high-spin d^5 systems, 5.80–6.00 BM.

The electronic spectra of the complexes have strong charge-transfer bands in the wavelength region below 5000 Å which prevent observation of the very low-intensity spin-forbidden d–d transitions expected for the sextet state of Fe(III). The observed charge-transfer bands and extinction coefficients are listed in Table IX.

While seven-coordinate complexes of iron(III) are relatively uncommon,[2,18] the pentadentate nature of the uncharged macrocycle provides a favorable basis for formation of iron complexes with high coordination numbers. The nuclear charge on the high-spin Fe(III) ion combined with its relatively large radius and lack of octahedral crystal field stabilization energy are factors which favor the coordination of two additional monodentate anions. These ($pyaneN_5$) complexes of Fe(III) are similar in composition to the more unsaturated $[Fe^{III}(pydieneN_5)X_2]^+$ derivatives mentioned above (structure I).[2] The latter have been characterized as pentagonal-bipyramidal structures in which the macrocycle is planar and the two monodentate anions are in trans axial positions.[4] Such a strain-free arrangement might also be expected for the monodentate derivatives of the $Fe^{III}(pyaneN_5)$ series. Particularly in the cases of the dibromo and dinitrate derivatives, the bulky anions would be expected to be in axial positions in order to avoid steric interactions. However, the bidentate oxalate derivative obviously cannot assume a trans arrangement. Our failure to isolate an oxalate derivative with the unsaturated ($pydieneN_5$) macrocycle suggests that in $[Fe(pyaneN_5)ox]PF_6$, the more flexible ring is folded in order to accommodate the cis oxygen donors.

Oxidative dehydrogenation of the macrocycle in the $Fe^{III}(pyaneN_5)$ complexes to form $Fe^{III}(pydieneN_5)$ species can be effected by bubbling oxygen through an acetonitrile solution of the complex for a period of 4–6 hr. The isolated products are somewhat deeper in color than the starting materials and have infrared spectra characteristic of the oxidized complexes. A single sharp N–H stretching absorption is observed at 3270 cm^{-1}, and a new band at 1655 cm^{-1} is assigned to the azomethine linkages.[2] The process of oxidative dehydrogenation has been observed in several other iron complexes. The macrocyclic complex $[Fe([14]dieneN_4)]^{2+}$, for example, reacts with oxygen in solution to form $[Fe(1,4,11\text{-}trieneN_4)]^{2+}$ and $[Fe(1,4,8,11\text{-}tetraeneN_4)]^{2+}$.[19] However, oxidation of the pentadentate macrocycle represents the first reported observation of ligand dehydrogenation in a complex of high-spin Fe(III).

Copper Complex. A copper(II) complex was prepared by the reaction of copper acetate with the acid salt of $pyaneN_5$ in aqueous solution. The deep blue complex was crystallized by the addition of NH_4PF_6. The elemental analysis (Table VII) indicates that the compound has the composition $[Cu(pyaneN_5)](PF_6)_2$. The conductance value (Table VIII) is in the range expected for a di-univalent electrolyte and provides evidence for the five-coordinate nature of the complex.

The infrared spectrum of $[Cu(pyaneN_5)](PF_6)_2$ has four bands between 3250 and 3230 cm^{-1} attributable to the four nonequivalent secondary amine groups in a folded macrocyclic structure. If the geometry of the $[Cu(pyaneN_5)]^{2+}$ cation is assumed to have approximate C_{4v} symmetry, three d–d transitions are expected in the electronic spectrum: $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{z^2}$, and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$. However, only two bands, which occur at 11,490 cm^{-1} (72) and 16,670 cm^{-1} (175), are resolved. This is the type of spectrum often observed for a Cu(II) complex with an intermediate tetragonal distortion from octahedral symmetry.[20] The two transitions $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ are similar in energy, in this case, and fall under a single band. The position of this absorption is expected at, or above, 16,130 cm^{-1} for ligands with nitrogen donor atoms.[20] The visible spectrum was unchanged as the solvent was varied from nitromethane to water.

The esr spectrum of the copper complex in $MeOH$–$CHCl_3$ solution at room temperature is split into four equally spaced absorptions (Figure 3). Interaction with the Cu(II) nucleus ($I = {}^3/_2$) causes the hyperfine splitting of the isotropic signal ($g = 2.110$). The hyperfine coupling constant A is calculated to be 74.3 G. When the solution is frozen at liquid nitrogen temperatures, an esr spectrum characteristic of axial symmetry is observed (Figure 4). Overlap of the signals, both split by hyperfine coupling with Cu(II), makes interpretation of the spectrum difficult without comparison with a computer-simulated curve. Approximate parameters are $g_\parallel = 2.21$, $g_\perp = 2.09$, and $\langle g \rangle = 2.13$ where $\langle g \rangle = (g_\parallel + 2g_\perp)/3$.

In contrast to the $[Ni(pyaneN_5)]^{3+}$ esr spectrum, no superhyperfine splitting by the nitrogen atoms of the macrocycle is observed in the copper spectra. The ground state of the Ni(III) ion has a large amount of d_{z^2} character, permitting interaction of the unpaired electron with the nucleus of the

Table IX. Electronic Spectra of the Iron Complexes of the Cyclic Pentadentate Ligand

Complex	Solvent	Transitions,[a] cm^{-1}		
$[Fe(pyaneN_5)Cl_2]PF_6$	MeOH	29,400 sh	38,900 (9000)	
$[Fe(pyaneN_5)C_2O_4]PF_6$	MeOH	29,400 sh	38,800 (11,100)	42,500 sh
$[Fe(pyaneN_5)(NO_3)_2]PF_6$	MeOH	29,400 sh	38,500 (11,000)	46,500 (9100)
$[Fe(pyaneN_5)Br_2]PF_6$	MeOH	29,400 sh	39,000 (8900)	
$[Fe(pyaneN_5)(N_3)_2]PF_6$	CH_3NO_2	21,300 (5000)		
$[Fe(pyaneN_5)(NCS)_2]PF_6$	CH_3NO_2	20,800 (11,200)		

[a] Numbers in parentheses are the molar extinction coefficients; sh = shoulder.

Table X. Electrochemical Data for Some Complexes Containing a Pentadentate Cyclic Ligand[a]

Complex	$E_{1/2}$, V Reductn	Oxidn
$[Ni(pyaneN_5)(CH_3CN)](PF_6)_2$	−1.94	+0.78[b]
$[Co(pyaneN_5)Cl](ClO_4)_2$	−0.41, −2.2[c]	
$[Fe(pyaneN_5)Cl_2]PF_6$	−0.56	
$[Cu(pyaneN_5)](PF_6)_2$	−0.94	+1.30[c]

[a] All measurements were carried out in acetonitrile with 0.1 *M* $(n\text{-}Bu)_4NBF_4$ as supporting electrolyte. $E_{1/2}$ values, given *vs.* the Ag–Ag$^+$ (0.1 *M*) reference electrode, were measured from curves obtained by a rotating platinum electrode and from the mean of the peak voltages produced by cyclic voltammetry using a platinum wire electrode. In all cases, the $E_{1/2}$ values computed by the two methods agreed. All processes were quasireversible with $\Delta p > 60$ mV unless otherwise noted. [b] Electrochemically reversible, $\Delta p = 60$ mV. [c] Completely irreversible.

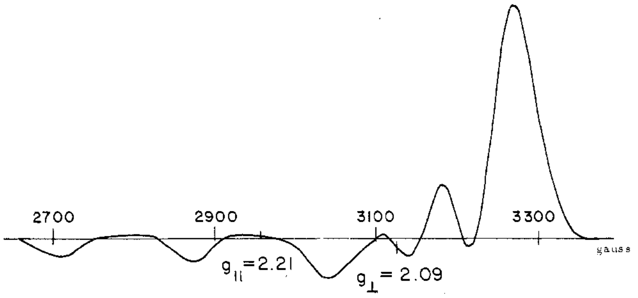


Figure 4. Epr spectrum of $[Cu(pyaneN_5)]^{2+}$ in MeOH–$CHCl_3$ at 77°K.

unique axial nitrogen. However, with the $d_{x^2-y^2}$ ground state of the Cu(II) ion in a tetragonal structure, resolution of splitting by the four nitrogen atoms in the *xy* plane is not observed.

Experimental Section

Materials. 2,6-Diacetylpyridine was obtained from Aldrich and from K and K Chemical Co. and was recrystallized from water–ethanol. Technical grade triethylenetetramine from Aldrich Chemical Co. was used without purification. All other solvents and chemicals were reagent grade.

Physical Measurements. Visible and near-infrared absorption spectra were obtained on solutions in matched silica cells using a Cary Model 14-R recording spectrophotometer. Perkin-Elmer Models 337 and 457 recording spectrophotometers were used to obtain the infrared spectra by a mull technique. The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. Measurements were taken at room temperature at 1000 Hz on solutions that were $\sim 10^{-3}$ *M*.

Solid-state magnetic moments were measured at room temperature under 35 mm of helium gas by the Faraday method. The system was equipped with a Cahn electrobalance.[21] Diamagnetic corrections for the ligands and counterions were made using Pascal's constants.[22] The esr spectra were recorded on a Varian V-4500 Model EPR spectrophotometer operating in the X band. The instrument is equipped with a dual davity; a sample of DPPH was placed in the reference cavity and its *g* value was taken to be 2.0037. The *g* values were calculated by the approximate method of Kneubühl[23] and most are accurate to ±0.005.

All polarographic studies were carried out in acetonitrile in a Vacuum Atmospheres enclosure equipped with a Dri Train and using an argon atmosphere. The apparatus used for the electrochemical measurements has been previously described.[10c] A silver wire immersed in a 0.1 *M* $AgNO_3$–CH_3CN solution was used as a reference electrode. The platinum wire electrodes were pretreated by oxidation of the surface with $K_2Cr_2O_7$–H_2SO_4 and subsequent reduction with $Fe(NH_4)_6SO_4$. The electrode surface was periodically tested for reproducible behavior with a standard compound. Spectroquality acetonitrile, obtained from Eastman Kodak, was purified by distillation from CaH_2 and deoxygenated by repeated vacuum-line pumping. Tetra-*n*-butylammonium tetrafluoroborate, used as supporting electrolyte, was obtained from Southwestern Analytical and dried by heating *in vacuo* at 80° for 48 hr.

Preparation of the Ligand Acid Salt. Ten grams of NaOH and 10 g of Ni–Al alloy were added alternately in small portions to 50 g of $Mn(pydieneN_5)Cl_2 \cdot H_2O$[3] dissolved in 250 ml of H_2O. The basic solution was kept under an inert atmosphere of nitrogen or argon during the reduction. After stirring for 3 hr, the purple solution was filtered and acidified with nitric acid to pH 8 in order to precipitate $Al(OH)_3$. The hydroxide was filtered, and the filtrate was reduced in volume to ~150 ml and cooled in an ice bath. Addition of 50 ml of cold concentrated nitric acid resulted in precipitation of white crystals of the nitric acid salt of the reduced ligand $pyaneN_5 \cdot 4HNO_3$. The ligand was washed with ethanol and acetone and dried over P_4O_{10} in a vacuum desiccator. The yield was ~60%. *Anal.* Calcd for $C_{15}H_{31}N_9O_{12}$: C, 34.0; H, 5.91; N, 23.8. Found: C, 34.2; H, 6.15; N, 24.0.

$[Ni(pyaneN_5)H_2O](PF_6)_2$. Four grams (7.5 mmol) of $pyaneN_5 \cdot 4HNO_3$ dissolved in 25 ml of water was added to an aqueous solution of 1.86 g (7.5 mmol) of $Ni(OAc)_2 \cdot 4H_2O$. The blue solution was stirred at 60° for 20 min; then 2.43 g (1.5 mmol) of NH_4PF_6 was added. The volume of the solution was reduced to 20 ml and cooled until blue crystals of $[Ni(pyaneN_5)H_2O](PF_6)_2$ formed. The complex can be recrystallized from hot water.

$[Ni(pyaneN_5)(CH_3CN)](PF_6)_2$ and $[Ni(pyaneN_5)NH_3](PF_6)_2$. $[Ni(pyaneN_5)H_2O](PF_6)_2$ was dissolved in acetonitrile. Evaporation of the solvent to a few milliliters caused crystallization of purple $[Ni(pyaneN_5)CH_3CN](PF_6)_2$. Addition of 5–10 ml of concentrated NH_4OH solution to an aqueous solution of $[Ni(pyaneN_5)H_2O](PF_6)_2$ (1 g) yielded purple crystals of $[Ni(pyaneN_5)NH_3](PF_6)_2$.

$[Ni(pyaneN_5)NCS]NCS$. Excess NaNCS was added to an aqueous solution of $[Ni(pyaneN_5)(CH_3CN)](PF_6)_2$. The solution was cooled to precipitate $[Ni(pyaneN_5)NCS]PF_6$. The crystallization was repeated until no PF_6^- was detected by infrared spectroscopy.

$[Ni(pyaneN_5)X]X$ where X = Halide. Two grams of $pyaneN_5 \cdot 4HNO_3$ (3.8 mmol) was slurried in 30 ml of MeOH. To this was added 15.2 mmol of sodium methoxide in methanol. The resulting neutralized solution of free ligand and $NaNO_3$ was evaporated to dryness and extracted with chloroform. The chloroform was evaporated to yield the anhydrous free ligand in the form of a yellow oil. A methanol solution of $NiCl_2 \cdot 6H_2O$ (0.83 g, 3.5 mmol), which had been dehydrated by stirring with 21.0 mmol of 2,2-dimethoxypropane at 60°, was added to a methanol solution of the free ligand and stirred at 60° for 30 min. The deep blue solution was evaporated to dryness and taken up in dichloromethane, from which blue crystals formed. The other halide derivatives were formed in a similar way using the appropriate nickel halide. Preparation of the iodide derivative required reflux of the methanol reaction mixture. The products were washed with acetone or dichloromethane and protected from moisture by storing in a vacuum desiccator.

$[Co(pyaneN_5)Cl](ClO_4)_2$. To an aqueous mixture of $CoCl_2 \cdot 6H_2O$ (0.45 g, 1.9 mmol) and $pyaneN_5 \cdot 4HNO_3$ (1 g, 1.9 mmol) heated on a steam bath was added 0.30 g (7.6 mmol) of NaOH. The solution immediately turned dark brown. Approximately 2–3 ml of concentrated HCl was added and air was bubbled through the solution for 1 hr. Upon addition of a concentrated aqueous solution of $NaClO_4$, red crystals of $[Co(pyaneN_5)Cl](ClO_4)_2$ formed. The complex can be recrystallized from a hot aqueous $NaClO_4$ solution.

$[Co(pyaneN_5)Br](ClO_4)_2$. The procedure reported for $[Co(pyaneN_5)Cl](ClO_4)_2$ was followed except that $CoBr_2 \cdot 6H_2O$ and HBr (48%) were used.

$[Co(pyaneN_5)I](I)_2$. A procedure similar to that given for the other halide derivatives was followed except that a solution of free ligand (0.53 g, 1.9 mmol) in methanol was added to 0.47 g of $Co(OAC)_2 \cdot 4H_2O$ (1.9 mmol) in methanol. HI was the acid used. The deep brown crystals which formed after oxidation were recrystallized from hot water with some HI added.

$[Co(pyaneN_5)N_3](ClO_4)_2$. Excess NaN_3 dissolved in water was added to a solution of $[Co(pyaneN_5)Cl]^{2+}$ and the solution was filtered. A concentrated aqueous solution of $NaClO_4$ was added to the filtrate and after several hours dark red-brown crystals of $[Co(pyaneN_5)N_3](ClO_4)_2 \cdot H_2O$ formed. Recrystallization from hot water and drying over P_4O_{10} yielded $[Co(pyaneN_5)N_3](ClO_4)_2$.

$[Co(pyaneN_5)NCS](ClO_4)_2$. A procedure similar to that given for the azide derivative was followed. Deep blue crystals of $[Co(pyaneN_5)NCS][Co(NCS)_4]$ formed upon addition of the NaNCS. These were recrystallized from an aqueous solution of $NaClO_4$ to yield orange crystals of $[Co(pyaneN_5)NCS](ClO_4)_2$.

$[Co(pyaneN_5)(NO_2)](ClO_4)_2$. Addition of 1 equiv of $NaNO_2$ to an aqueous solution of $[Co(pyaneN_5)Cl]^{2+}$ followed by addition of a concentrated $NaClO_4$ solution produced orange-gold crystals which were recrystallized from hot water.

$[Fe(pyaneN_5)(Cl)_2]PF_6$. To 0.74 g (3.8 mmol) of anhydrous iron(II) chloride dissolved in ethanol under an inert atmosphere was added 1.1 g (3.8 mmol) of free ligand in ethanol. The reaction mixture was heated for 15 min at 60° and then exposed to air. The solution changed in color from yellow to yellow-green within minutes. One equivalent (0.62 g) of NH_4PF_6 was added and the solution was filtered to remove any iron oxides. The volume of the filtrate was reduced until the yellow product began to form. The crystals were washed with ethanol and dried *in vacuo* at 60°.

$[Fe(pyaneN_5)(Br)_2]PF_6$. The same procedure as given above for the dichloro derivative was followed, except that anhydrous iron(II) bromide was used.

$[Fe(pyaneN_5)(NCS)_2]PF_6$ and $[Fe(pyaneN_5)(N_3)_2]PF_6$. Two equivalents of LiNCS or LiN_3 dissolved in ethanol was added to a slurry of $[Fe(pyaneN_5)(Cl)_2]PF_6$ in ethanol. As the solution was heated, all of the solid dissolved to form a deep red solution. Upon reduction of volume and cooling, red crystals of $[Fe(pyaneN_5)(NCS)_2]PF_6$ or orange crystals of $[Fe(pyaneN_5)(N_3)_2]PF_6$ formed. The products were dried *in vacuo* at 60°.

$[Fe(pyaneN_5)(NO_3)_2]PF_6$. Two equivalents of $AgNO_3$ was added to an acetonitrile solution of $[Fe(pyaneN_5)(Cl)_2]PF_6$. The precipitate AgCl was filtered and the filtrate was reduced in volume until yellow crystals of $[Fe(pyaneN_5)(NO_3)_2]PF_6$ formed.

$[Fe(pyaneN_5)C_2O_4]PF_6$. One equivalent of $Li_2C_2O_4$ dissolved in water was added to an acetonitrile solution of $[Fe(pyaneN_5)Cl_2]PF_6$. Reduction of the solution volume induced precipitation of $[Fe(pyaneN_5)C_2O_4]PF_6 \cdot nH_2O$ which was dried *in vacuo* to give $[Fe(pyaneN_5)C_2O_4]PF_6 \cdot H_2O$.

$[Cu(pyaneN_5)](PF_6)_2$. Addition of 0.76 g (3.8 mmol) of $Cu(OAc)_2 \cdot H_2O$ to 2.0 g (3.8 mmol) of $pyaneN_5 \cdot 4HNO$, in water resulted in a deep blue solution. Addition of 1.24 g (7.6 mmol) of NH_4PF_6 induced crystallization of the deep blue product which was washed with ethanol and dried *in vacuo*.

Registry No. $[Ni(pyaneN_5)H_2O](PF_6)_2$, 54325-58-5; $[Ni(pyaneN_5)CH_3CN](PF_6)_2$, 54325-60-9; $[Ni(pyaneN_5)NCS](NCS)$, 54325-62-1; $[Ni(pyaneN_5)NH_3](PF_6)_2$, 54325-64-3; $[Ni(pyaneN_5)Cl]Cl$, 54325-65-4; $[Ni(pyaneN_5)Br]Br$, 54325-66-5; $[Ni(pyaneN_5)I]I$, 54325-67-6; $[Co(pyaneN_5)Cl](ClO_4)_2$, 54325-69-8; $[Co(pyaneN_5)Br](ClO_4)_2$, 54325-71-2; $[Co(pyaneN_5)I](I)_2$, 54325-72-3; $[Co(pyaneN_5)NCS](ClO_4)_2$, 54325-40-5; $[Co(pyaneN_5)N_3](ClO_4)_2$, 54325-42-7; $[Co(pyaneN_5)NO_2](ClO_4)_2$, 54325-44-9; $[Fe(pyaneN_5)Cl_2](PF_6)$, 54325-46-1; $[Fe(pyaneN_5)Br_2]PF_6$, 54340-23-7; $[Fe(pyaneN_5)(NO_3)_2]PF_6$, 54325-48-3; $[Fe(pyaneN_5)(NCS)_2]PF_6$, 54325-50-7; $[Fe(pyaneN_5)(N_3)_2]PF_6$, 54325-52-9; $[Fe(pyaneN_5)C_2O_4]PF_6$, 54325-54-1; $[Cu(pyaneN_5)](PF_6)_2$, 54325-56-3; $pyaneN_5 \cdot 4HNO_3$, 54293-31-1; $Mn(pydieneN_5)Cl_2$, 27577-84-0; $[Ni(pyaneN_5)H_2O]^{+3}$, 54325-32-5.

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Synthesis and Electrical Properties of Transition Metal Mercaptides of 1,4-Dimercaptobenzene[1]

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The synthesis of a number of new transition metal mercaptides of the ligand 1,4-dimercaptobenzene is reported. Several of these mercaptides, which are regarded as S-bridged polymers, behave like semiconductors within the temperature range investigated. An interesting result of the study is the relatively low electrical resistivity (ρ = 40 ohm cm at 25°) of the Cu(I) complex of composition $[CuSC_6H_4SCu]_n$. Copper thiophenolate, $[C_6H_5SCu]_n$, is also found to behave like a semiconductor, with an electrical resistivity of 5.1×10^4 ohm cm at 25°. The reaction of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with Cu(I) complexes cleaves the Cu–S bonds and leads to the formation of the Cu(I) salt of the TCNQ radical anion, $Cu^+TCNQ\cdot^-$.

Introduction

Extensive studies of the coordination chemistry of unsaturated or aromatic 1,2-dithiol ligands have been reported,[2–5] and semiconductor behavior has been noted for transition metal complexes of α-dithiodiketones, dithiooxamide (rubeanic acid), and N-substituted dithiocarbamates.[6–8] However, no information is available concerning 1,4-dimercaptobenzene and other aromatic polythiols as potential ligands. We became interested in these ligands and their coordination polymers with the object of finding new thermally stable materials having semiconducting properties. The ligands chosen meet the requirements to form complexes with these properties. First, they are thermally stable and possess donor atoms separated by an aromatic ring. Second, each ligand can bind two metal atoms, and substantial back-coordination of the metal d electrons to the ligand-based antibonding orbitals as well as the formation of sulfur-bridged metal chains could facilitate electron transport. In this paper, we report the synthesis and the chemical and electrical properties of a number of new polymeric mercaptides of 1,4-dimercaptobenzene having the