dize maleate ion, but not acetate or benzoate.

Diperiodatocuprate(III) does not appear to be an attractive oxidant for alcohols from a synthetic point of view since the products inhibit further reaction. This kinetic study does shed significant light upon the chemistry of Cu(III). Since monoperiodatocuprate(III) is a much more active oxidant than diperiodatocuprate(III), the periodate ligand must have some stabilizing effect upon the Cu(III). Since the copper complexes are diamagnetic and square planar, it is not a steric effect but electronic.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; benzyl alcohol, 100-51-6; allyl alcohol, 107-18-6; $Cu(IO_6)_2{}^{7-}$, 36202-28-5.

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Complexes of 1,8-Naphthyridines. VII. Eight-Coordinate Transition Metal Perchlorate Complexes of 1,8-Naphthyridine[1]

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The syntheses of a number of transition metal complexes of the type $M(napy)_4(ClO_4)_2$ where M = Mn, Fe, Co, Ni, Cu, Zn, Pd, and Cd and napy = 1,8-naphthyridine are described. Elemental analyses, molar conductances, magnetic moments, molecular weights, and powder X-ray, infrared, electronic, and pmr spectral data have been applied to the characterization of the compounds. The arrangement of the eight nitrogen atoms around the metal in the Fe(II) complex is best described as a dodecahedron. The geometry of the other complexes in the solid state is discussed in terms of a dodecahedron with the shape parameters r_a and r_b becoming more divergent as the metal is changed from Mn to Cu. Solution spectral data for several complexes indicate a different geometry than is found in the solid state. A comparison with other eight-coordinate transition metal complexes where the metal has more than two d electrons is made.

Introduction

Although eight-coordination is common for the lanthanides, transition metal complexes of this type are extremely rare unless the electronic configuration of the metal ion is d^0, d^1, or d^2.[3] Bergman and Cotton have shown that $[As(C_6H_5)_4]_2[Co(NO_3)_4]$ contains eight-coordinate cobalt(II) in which the nitrate groups are bidentate and located in a dodecahedral geometry distorted relative to the cobalt atom.[4] Drummond and Wood[5] have shown that the nitrate groups are also bidentate in the tetraphenylarsonium salt of the dodecahedral $Mn(NO_3)_4{}^{2-}$ ion while preliminary data suggest that $Zn(NO_3)_4{}^{2-}$ is also eight-coordinate. Recently, King, *et al.*, have shown that $Fe(NO_3)_4{}^-$ also contains four bidentate nitrate groups yielding an eight-coordinate Fe(III).[6] Eight-coordination has been found for both Cd(II) and Cu(II) in the compound $Ca[M(O_2CCH_3)_4]\cdot 6H_2O$, where M = Cd or Cu.[7] Other possible eight-coordinate transition metal complexes in which the metal ion contains more than two d electrons are discussed by Lippard.[3]

Recently we reported the first known example of an eight-coordinate iron(II) complex.[8] The compound, tetrakis(1,8-naphthyridine)iron(II) perchlorate, has been shown to possess a distorted dodecahedral geometry.[9,10] We have also reported partial synthetic and physical data for the other transition metal complexes of stoichiometry $M(napy)_4(ClO_4)_2$ where M = Mn, Co, Ni, Cu, Zn, Pd, and Cd and napy = 1,8-naphthyridine.[11] It is the purpose of this paper to present and examine in detail the syntheses and physical and chemical data of the transition metal complexes of stoichiometry $M(napy)_4(ClO_4)_2$.

Experimental Section

Materials. Metal perchlorates were purchased from G. F. Smith Chemical Co. and used without further purification. Potassium tetrachloropalladate(II) was prepared according to the method of Grube.[12] Commercially available ethyl acetate, dried before use,[13] and absolute methanol and ethanol were used in the preparation of the metal complexes. Practical grade 2,2-dimethoxypropane (dmp) and spectral grade acetonitrile and nitromethane were obtained from Eastman Chemicals. Purity of the ligand 1,8-naphthyridine, prepared by the method of Paudler and Kress,[14] was verified by pmr spectroscopy.

Instrumentation. The infrared (4000–200 cm^{-1}) and solution (CH_3CN) electronic absorption spectra, conductivities, and carbon, hydrogen, and nitrogen contents were obtained as previously described.[15] Diffuse reflectance spectra were measured on finely ground pure solids with a Beckman DU spectrophotometer fitted with a Beckman Model 2500 reflectance attachment using magnesium carbonate as the reference. Solid electronic absorption spectra were recorded using a Cary Model 14 recording spectrophotometer with the samples mulled with Nujol or hexachlorobutadiene and supported on

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Table I. Analytical Data and Physical Properties of $M(napy)_4(ClO_4)_2$ Complexes[a]

Compd	% calcd			% found			Color	Conductivity data[b]	
	C	H	N	C	H	N		Λ (molar), cm^2 mho	Concn × 10^3, *M*
$Mn(C_8H_6N_2)_4(ClO_4)_2$	49.63	3.13	14.47	49.71	3.08	14.57	Light yellow	178	0.71
$Fe(C_8H_6N_2)_4(ClO_4)_2$	49.56	3.13	14.45	49.58	3.08	14.34	Red-orange	183	1.03
$Co(C_8H_6N_2)_4(ClO_4)_2$	49.37	3.12	14.40	49.30	2.95	14.21	Pink	184	1.03
$Ni(C_8H_6N_2)_4(ClO_4)_2$	49.38	3.11	14.40	49.33	3.09	14.21	Blue-green	185	0.90
$Cu(C_8H_6N_2)_4(ClO_4)_2$	49.08	3.09	14.31	48.86	3.09	14.42	Blue	185	1.03
$Zn(C_8H_6N_2)_4(ClO_4)_2$	48.96	3.09	14.28	48.88	3.16	13.85	White	185	0.61
$Pd(C_8H_6N_2)_4(ClO_4)_2$	46.53	2.93	13.57	46.82	2.77	13.53	Yellow	177	1.01
$Cd(C_8H_6N_2)_4(ClO_4)_2$	46.20	2.91	13.47	46.26	2.94	13.56	White	187	1.02

[a] napy = 1,8-naphthyridine. [b] Values obtained in nitromethane solutions at 25°. The following compounds and their conductivities were used for comparison: $[(CH_3(CH_2)_3)_4N]NO_3$, 82; $[Co(2,7\text{-}Me_2napy)_3][ClO_4]_2$, 186.

Whatman's No. 2 filter paper. A Varian Model HA-100 nmr spectrometer was used to obtain the pmr spectra of saturated nitromethane solutions of the complexes with TMS as the internal standard. Magnetic moments were obtained at 24.5° using the Faraday apparatus described by DuBois and Meek.[16] Diamagnetic corrections for the metal and perchlorate ions were calculated from Pascal's constants[17] with a value of -86.8×10^{-6} cgsu measured for napy. Powder X-ray diffraction patterns were obtained using a Norelco water-cooled X-ray diffractometer, Model 12045. The finely ground samples were packed in 0.05-mm capillary glass tubes and mounted in a Philips Debye-Scherrer X-ray powder camera of diameter 57.3 mm. The film was exposed to nickel-filtered copper radiation (λ 1.539 Å) for 10-15 min at 50 kV and 25 mA. In the case of the cobalt complex, several thickness of aluminum foil were employed to shield the film from fluorescent radiation. Intensity plots from the films were obtained by the use of a Joyce and Loebel Mark III-CS automatic recording microdensitometer. Molecular weights were obtained using a Mechrolab vapor pressure osmometer, Model 301-A, calibrated with methanol.

Preparations. *Caution! Since the completion of this work, explosions during the dehydration of* $Mn(ClO_4)_2 \cdot 6H_2O$ *and* $Ni(ClO_4)_2 \cdot 6H_2O$ *with 2,2-dimethoxypropane have been reported.*[18,19] We have not encountered any difficulties for any of the hydrated metal perchlorates. However, caution should be employed.

$Mn(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.140 g (0.387 mmol) of $Mn(ClO_4)_2 \cdot 6H_2O$ in 30 ml of methanol and 2 ml of dmp was refluxed for 30 min followed by the addition of 0.200 g (1.52 mmol) of napy in 10 ml of methanol. After 4 days, the clear, colorless solution was concentrated to approximately one-fourth volume by warming under reduced pressure. Twenty-five milliliters of an ethanol-methanol (3:1) mixture was added and the solution was reconcentrated to approximately one-fourth volume by warming under reduced pressure. The light yellow crystals, which resulted when the solution was cooled in a refrigerator for 3 days, were collected by filtration and dried *in vacuo* for 1 week. Analytical data for this and the following complexes may be found in Table I.

$Fe(C_8H_6N_2)_4(ClO_4)_2$. A solution containing 0.138 g (0.380 mmol) of $Fe(ClO_4)_2 \cdot 6H_2O$, 5 ml of dmp, and 15 ml of ethanol was refluxed for 1 hr followed by the addition of 0.200 g (1.52 mmol) of napy in 12 ml of ethyl acetate. The cloudy solution was stirred for 15 min and filtered. The red-orange product was washed with 5 ml of ethanol and dried *in vacuo* for 3 days.

$Co(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.556 g (1.26 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ in 100 ml of methanol and 15 ml of dmp was refluxed for 1 day followed by the addition of 0.600 g (4.46 mmol) of napy in 40 ml of methanol. After 3 days, the pink solution was concentrated to approximately 30 ml by warming under reduced pressure, and 100 ml of chloroform was added. The pink product was collected by filtration, recrystallized twice from ethanol, and dried *in vacuo* at 110° over phosphorus pentoxide for 1 week.

$Ni(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.417 g (1.14 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 50 ml of ethanol and 5 ml of dmp was refluxed for 30 min followed by the addition of 0.600 g (4.56 mmol) of napy in 10 ml of methanol. After 2 days, the blue-green solution was concentrated to approximately 10 ml by warming under reduced pressure. The product obtained by filtration of the cooled solution under an inert atmosphere was stirred in 75 ml of hot ethyl acetate and collected by filtration under an inert atmosphere. The blue-green product was recrystallized from ethanol and dried *in vacuo* at 110° over phosphorus pentoxide for 1 week.

$Cu(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.282 g (0.761 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 50 ml of ethyl acetate and 7 ml of dmp was stirred at room temperature for 20 min followed by the addition of 0.400 g (3.04 mmol) of napy in 10 ml of ethyl acetate and 4 ml of chloroform. After 9 days, the blue product was collected by filtration, recrystallized twice from ethanol, and dried *in vacuo* at 110° over phosphorus pentoxide for 1 week.

$Zn(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.556 g (1.52 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 100 ml of methanol and 20 ml of dmp was refluxed for 8 hr followed by the addition of 0.600 g (4.56 mmol) of napy in 15 ml of methanol. After 4 days, the clear, colorless solution was concentrated to approximately 20 ml by warming under reduced pressure and cooled. The white product was collected by filtration under an inert atmosphere, recrystallized twice from an ethanol-methanol (1:1) mixture, and dried *in vacuo* for 3 days.

$Pd(C_8H_6N_2)_4(ClO_4)_2$. To 0.495 g (1.52 mmol) of K_2PdCl_4 in 70 ml of boiling water was added with stirring 0.200 g (1.52 mmol) of napy in 60 ml of hot water. After 5 min, the brown cloudy solution was filtered, and the product was washed with 100 ml of boiling water. The brown precipitate was stirred in 200 ml of boiling water followed by the addition of 0.400 g (3.04 mmol) of napy. After 500 ml of water was added, the solution was boiled for 15 min and filtered. To the light yellow filtrate was added with stirring 0.400 g (3.04 mmol) of napy in 60 ml of hot water. After 10 min, 0.450 g (3.83 mmol) of NH_4ClO_4 in 30 ml of warm water was added and the resulting solution was cooled for several hours at 0° with occasional stirring. The yellow product was collected by filtration and dried *in vacuo* at 110° over phosphorus pentoxide for 3 days.

$Cd(C_8H_6N_2)_4(ClO_4)_2$. A solution of 0.160 g (0.383 mmol) of $Cd(ClO_4)_2 \cdot 6H_2O$ in 30 ml of methanol and 3 ml of dmp was refluxed for 2.5 hr followed by the addition of 0.200 g (1.52 mmol) of napy in 10 ml of methanol. After 2 weeks, the clear, colorless solution was concentrated to approximately one-third volume by warming under reduced pressure. The white product obtained by filtration of the cooled solution was recrystallized twice from ethanol, stirred in boiling chloroform, and dried *in vacuo* at 110° over phosphorus pentoxide for 4 days.

Results and Discussion

The physical and analytical data for the complexes reported in Table I indicate that in the three-ion salts, 4 mol of napy is associated with each metal ion. The compounds are stable with respect to exposure to air. Melting points were not determined because of the presence of perchlorate.

Infrared spectral data (4000-200 cm^{-1}) consisting of selected ligand modes which change on complexation, fundamental frequencies of the perchlorate groups, and new absorptions in the low-frequency region are recorded in Table II. Absorptions due to napy from 1600 to 650 cm^{-1} have been previously assigned[20] while those below 650 cm^{-1} are attributed to ligand deformation modes. The change in the position of napy skeletal modes of the free ligand with respect to the complexes indicates coordination to the metal.

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Table II. Selected Infrared Absorptions for 1,8-Naphthyridine and $M(napy)_4(ClO_4)_2$ Complexes

	M								
napy	Mn	Fe	Co	Ni	Cu	Zn	Pd	Cd	Assignment[a]
1558 s	1580 m	1580 m	1575 m	1571 m	1561 m	1576 m	1565 m	1584 m	Skel str
1228 s	1135 s	1139 s	1140 s	1140 s	1142 s	1137 s	1137 s	1134 s	Skel bend
1105 w	1100 vs, br	1105 vs, br	1103 vs, br	1089 vs, br	1088 vs, br	1085 vs, br	1095 vs, br	1102 vs, br	ν_3' and skel bend
1045 w	1072 s	1075 s	1072 s	1061 sh	1058 sh			1074 s	Ligand
760 s	775 s	780 s	782 s	775 m	784 m	783 s	788 s	777 s	Skel bend and CH str
600 m	616 s	618 s	620 s	621 s	621 s	620 s	620 s	617 s	ν_4' and ligand
403 s	415 s	419 s	424 s	415 s	419 s	422 s	415 m	415 s	Ligand
	215 s	230 s	232 s	245 s	268 s	218 s	286 s		ν_{M-N}

[a] See text and ref 20 for various assignments.

No evidence of noncoordinated napy is found in any of the spectra of the complexes. All the complexes exhibit the broad, very strong 1090-cm^{-1} and strong 620-cm^{-1} absorptions which are typical for the asymmetric stretching and bending modes, respectively, of ionic perchlorate (T_d).[21] Only in the Zn and Pd complexes is evidence for a trace amount of water detected.

Only one new low-frequency band above 200 cm^{-1} appears in the spectra of the $M(napy)_4(ClO_4)_2$ complexes. This band, which follows the Irving-Williams order of stability ($Mn < Fe < Co < Ni < Cu > Zn$)[22] as would be expected for ν_{M-N}, is assigned to such a vibration. The metal isotope technique of Nakamoto, *et al.*, has provided unambigous assignments of metal-ligand vibrations of coordination compounds.[23] Hutchinson has recently completed such a study of the $M(napy)_4(ClO_4)_2$ complexes and has established that this low-energy band is properly assigned to ν_{M-N}.[24]

Solution stability is demonstrated for the Cd(II) complex by its pmr spectrum in nitromethane. Relative to TMS, the chemical shifts (ppm) of the complex and free napy are as follows: Cd(II), 9.17, 8.62, 7.77; napy, 9.04, 8.32, 7.54, for 2,7-H, 4,5-H, 3,6-H, respectively. The coupling constants in the heterocyclic ring system of the complex are the same as in the free base.[25] The deshielding of the ligand protons on complexation indicates electron donation from the heterocyclic ring to the metal ion. The experimental molecular weight of the Cd(II) complex, 822, assuming a three-ion salt, agrees well with the theoretical weight, 832. Molecular weight measurements on the other complexes were not made.

There has been a great deal of discussion concerning the factors which influence the formation of high-coordinate complexes.[26] The high formal charge, relatively large eight-coordinate metal radius, and the small energy difference between the (n−1)d, ns, and np orbitals of the central metal are important. In addition, chelating agents in which the intraligand distance ("bite") is constrained to a small distance favor high-coordinate complexes. Bergman and Cotton suggested that ideally the "bite" should be less than 2.2 Å[4] as was found in NO_3^- and O_2^-.[26]

Examination of the structure of $Fe(napy)_4(ClO_4)_2$ seems to indicate that a high formal charge of the central metal is not absolutely necessary. The same conclusion can be reached from consideration of the $Mn(NO_3)_4^{2-}$, $Co(NO_3)_4^{2-}$, and $Zn(NO_3)_4^{2-}$ structures.[4,5] The estimated eight-coordinate radius for Fe(II) of ~1.32 Å can be obtained by multiplying the known octahedral radius of 1.23 Å[27] by the factor 1.07.[28] Although this value is lower than normally found for other metals, 1.4-1.6 Å,[26] it is consistent with the eight-coordinate radii of the $M(NO_3)_4^{2-}$ series.

Table III. Magnetic Susceptibility Data[a]

Compd	$10^6\chi_{measd}$, cgsu	$10^6\chi_{cor}$, cgsu	$[n(n+2)]^{1/2}$	μ_{eff}(exptl), BM
$Fe(napy)_4(ClO_4)_2$	14.41	11,173	4.90	5.25
$Co(napy)_4(ClO_4)_2$	11.58	9,016	3.87	4.74
$Ni(napy)_4(ClO_4)_2$	5.49	4,274	2.83	3.35
$Cu(napy)_4(ClO_4)_2$	1.95	1,528	1.70	2.15
$Zn(napy)_4(ClO_4)_2$	−0.60	−411	0.0	b

[a] Data obtained at 24.5°; all values independent of field strength. [b] Compound is diamagnetic.

Apparently the availability of (n − 1)d orbitals is not a necessary requirement for σ bonding in eight-coordinate complexes since these orbitals are occupied by metal d electrons (*vide infra*) and are not available for such bonding. The small "bite" of the chelating agent appears to be the most important factor. The intraligand nitrogen-nitrogen distance of 2.26 Å in the iron complex[10] and 2.32 Å in the free ligand[29] is well within the range of other bidentate ligands which form eight-coordinate complexes.[26]

Powder pattern data suggest that the Mn, Co, Ni, Cu, and Pd complexes are isomorphous with $Fe(napy)_4(ClO_4)_2$.[1,30] The Zn and Cd compounds, although similar, have many more interplanar spacings which, in the Cd complex, is a result of a doubling of the unit cell in the "c" direction (~40 Å) as shown by single-crystal photographs.[30] Thus a dodecahedral geometry in the solid state may be expected for most all the complexes.

Although the shape parameter ratio r_a/r_b for this polyhedron is ideally 1.0, observed values cover the range of 0.67-1.42.[3] Since the value for $Fe(napy)_4(ClO_4)_2$ is 1.12,[10] it is reasonable to expect this value for the Mn complex to be closer to unity with the values for the Cu and Pd complexes being more divergent.

Magnetic data for the $M(napy)_4(ClO_4)_2$ complexes where M = Fe, Co, Ni, Cu, and Zn are recorded in Table III. The susceptibilities, corrected for diamagnetism of the metal ion, ClO_4^-, and napy, were obtained only at 24.5° and thus the dependence on temperature and the temperature-independent paramagnetism are not known. The complexes with less than 10 d electrons are spin free.

The magnetic moment for the dodecahedral $Co(NO_3)_4^{2-}$ is 4.67 BM;[31] however, no range of moments for this basic

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Table IV. Electronic Spectral Data[a]

Compd	Soln[b]		Solid
	ν, kK	$\epsilon, M^{-1}\ \mathrm{K}^{-1}$	ν, kK
$\mathrm{Fe(napy)_4(ClO_4)_2}$	9.71	10	10.5
	(23.2)	385	20.8
	32.8	22,500	
	33.2	23,500	
	(34.0)	21,200	
	39.2	17,600	
$\mathrm{Co(napy)_4(ClO_4)_2}$	9.42	34	9.35
	18.5	239	18.5
	(19.4)	195	(20.4)
	32.7	19,300	
	33.2	20,000	
	33.9	18,100	
	39.2	15,800	
$\mathrm{Ni(napy)_4(ClO_4)_2}$	9.52	8	8.0
	16.2	14	15.4
	32.6	19,100	
	33.1	19,800	
	33.9	18,000	
	39.2	15,700	
$\mathrm{Cu(napy)_4(ClO_4)_2}$	15.8	77	16.8
	32.5	23,700	
	33.2	25,800	
	(33.7)	25,100	
	(36.4)	18,100	
	37.6	18,300	
$\mathrm{Zn(napy)_4(ClO_4)_2}$	32.5	23,400	
	33.3	24,400	
	33.8	21,500	
	38.2	15,500	
$\mathrm{Mn(napy)_4(ClO_4)_2}$	32.7		
	33.2		
	33.9		
	39.2		
$\mathrm{Cd(napy)_4(ClO_4)_2}$	32.5	26,500	
	33.2	23,800	
	33.9	22,800	
	38.2	16,800	
$\mathrm{Pd(napy)_4(ClO_4)_2}$	32.4	21,700	
	33.7	27,600	
	(34.7)	27,100	
	35.2	27,800	
napy	32.7	5,170	
	33.2	5,300	
	34.0	4,760	
	39.2	4,270	

[a] All absorptions greater than 30 kK are assigned as ligand $\pi^* \leftarrow \pi$ bands. All other absorptions except the 23.2-kK metal–ligand charge-transfer band in the Fe complex are d–d transitions. [b] Data obtained at $\nu_{\max}$ in acetonitrile; parentheses indicate a shoulder.

geometry has been established. For spin-free Co(II) complexes a moment of ~4.5 BM is expected for tetrahedral geometry while ~5.1 BM is common for an octahedral environment.[32] Though the moment of $\mathrm{Co(napy)_4(ClO_4)_2}$ of 4.74 BM is quite similar to that of $\mathrm{Co(NO_3)_4}^{2-}$, it also is within the upper limits expected of tetrahedral geometry. For Ni(II) complexes, octahedral and tetrahedral geometries yield moments of ~3.3 and ~3.8 BM, respectively.[32] In the absence of any known data for dodecahedral Ni(II) complexes, the $\mathrm{Ni(napy)_4(ClO_4)_2}$ data best fit an octahedral configuration.

The electronic absorption and reflectance spectral data for $\mathrm{M(napy)_4(ClO_4)_2}$ (M = Fe, Co, Ni, Cu) are recorded in Table IV. The absorption data were recorded for acetonitrile solutions between 1800 and 200 $\mathrm{m}\mu$ and the solid data indicate all absorptions from 2500 to 400 $\mathrm{m}\mu$. Although assignment of the 301- and 255-$\mathrm{m}\mu$ bands to the first and second $\pi^* \leftarrow \pi$ transition, respectively, has been justified on a theoretical bases,[33] the exact nature of the vibrational interactions which produce the 305- and 294-$\mathrm{m}\mu$ bands has not been elucidated. Thus, all absorptions within the heterocyclic ring system have been assigned as ligand $\pi^* \leftarrow \pi$ bands (Table V).

Interpretation of absorption spectra for eight-coordinate complexes of D_{2d} symmetry has been mostly qualitative.[34,35] Based on its electronic absorption spectrum and magnetic moment, the $\mathrm{Co(NO_3)_4}^{2-}$ anion was originally designated as containing tetrahedral Co(II)[34] but later as being of a dodecahedral geometry.[4] The "tetrahedral-like" spectrum was explained by the approximate electronic environment imposed on the cobalt ion. The angles between the lines joining each midpoint of the intraligand O· · ·O and the cobalt ion (~107°) were very close to those describing a regular tetrahedron (109°). Although only qualitative, the approximation seemed to correlate the spectrum with the observed structure. However, in the Fe complex of napy such a "tetrahedral-like" approximation gives four angles which are close to 98° and two which are close to 135°.[10] If the approximation made for $\mathrm{Co(NO_3)_4}^{2-}$ can be generalized, then it is not to be expected that $\mathrm{Fe(napy)_4}^{2+}$ should yield a "tetrahedral-like" spectrum.

Garner and Mabbs[36] have recently determined that the relative energies of the d orbitals in eight-coordinate complexes of D_{2d} symmetry are functions of the geometrical parameters r_a, r_b, θ_A, and θ_B and the crystal field parameters Dq and Cp. The authors point out that it is only fortuitious that the electronic spectrum of $\mathrm{Co(NO_3)_4}^{2-}$ resembles that of a tetrahedron and that, in general, it is not valid to interpret the spectra of D_{2d} eight-coordinate complexes using a T_d model. Using the equations for the energies of the d orbitals given by Garner and Mabbs, the order of these orbitals for $\mathrm{Fe(napy)_4(ClO_4)_2}$ is $\mathrm{d}_{xy} > \mathrm{d}_{x^2-y^2} > \mathrm{d}_{xz}, \mathrm{d}_{yz} > \mathrm{d}_{z^2}$.

The spectrum of $\mathrm{Fe(napy)_4(ClO_4)_2}$ in the solid state exhibits a well-defined, intense band at 20.8 kK in addition to a weak band at 10.5 kK; while in solution, a shoulder at *ca.* 23.2 kK on a ligand charge-transfer band and a very broad, poorly defined band at *ca.* 9.7 kK (ϵ 10) are observed. Thus it appears that the complex does not retain the same structure in solution as in the solid. This contention is substantiated by the recent report that $\mathrm{Fe(napy)_4(ClO_4)_2}$ in acetonitrile gives $\mathrm{Fe(napy)_4(CH_3CN)_4}^{2+}$ while exposure to moist air yields $[\mathrm{Fe(napy)_4(H_2O)_4}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$.[37] A tetrahedral geometry for $\mathrm{Fe(napy)_4(ClO_4)_2}$ in the solid state or in

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solution may be ruled out due to the absence of a broad, sometimes split, very intense band in the 4-6-kK region.[38] As previously discussed, such a spectrum for the solid is not expected on the basis of X-ray data. The intense red color of many Fe(II) complexes of unsaturated diimines is due to a metal-ligand charge-transfer absorption in the region 20-25 kK.[38] Even though napy is not a diimine, it is an unsaturated heterocycle and therefore capable of π bonding.[39] Thus the band at 20.8 kK in the solid spectrum is tentatively assigned as a Fe → napy charge-transfer absorption.

The spectrum of $Co(napy)_4(ClO_4)_2$ in solution is very similar to the solid spectrum. In addition to the usual ligand absorptions, the solution spectrum exhibits a broad band in the near-infrared region at 9.5 kK (ϵ 35) and a more intense band in the visible region at 18.5 kK (ϵ 239) with a shoulder on the high-energy side at 19.2 kK (ϵ 195). Interpretation of this spectrum using a tetrahedral model in the same manner as originally applied to the similar spectrum of $Co(NO_3)_4{}^{2-}$ is possible.[31,34] However, since it has been established that the coordination in $Co(NO_3)_4{}^{2-}$ is dodecahedral[4] and theoretical work has shown that the electronic spectra of dodecahedral species may coincidentally appear similar to those of tetrahedral species,[36] a dodecahedral $Co(napy)_4{}^{2+}$ is consistent with the data. A pseudooctahedral environment for the cobalt may be ruled out from the magnitude of the extinction coefficients.

The spectra of $Ni(napy)_4(ClO_4)_2$ in solution and in the solid state are similar in that only two bands are observed in addition to the usual ligand absorptions in the uv region. The solid spectrum exhibits a very broad, weak band in the near-infrared region at an energy lower than 8.9 kK. The mull spectrum indicates that the band maximum is in the region 7.9-8.0 kK. A well-defined band is also observed in the spectrum at 15.4 kK. The solid-state spectrum is not consistent with either tetrahedral or square-planar Ni(II).[38] The spectrum in solution exhibits two similar bands at somewhat greater energies with the low-energy band at 9.5 kK and the higher energy band at 16.2 kK. The positions and extinction coefficients of these bands are similar to those expected for an octahedral complex.

The electronic spectrum of $Cu(napy)_4(ClO_4)_2$ in the solid state exhibits, in addition to ligand absorptions, only one very broad (half-width at half-height $\simeq$3.5 kK), unsymmetrical to low energy band above 5kK. The shift in position of this band from 16.8 kK in the solid state to 15.8 kK (ϵ 77) when the complex is dissolved in acetonitrile suggests a change in geometry occurs. This solid-state spectrum is nearly identical with that reported for tetrakis(6-aminohexanoic acid)copper(II) diperchlorate and similar to that of calcium copper acetate hexahydrate.[40-42] Crystallographic studies indicate that in both of the above complexes the copper atoms experience a similar coordination geometry.[7,43] Although on preliminary examination the copper appears to be basically four-coordinate planar with four other oxygens located ~0.9 Å further away, single-crystal electronic and esr spectral studies as well as magnetic data indicate that both molecules are best described as distorted dodecahedrons.[40-42] It is interesting that $Cu(napy)_2Cl_2$ which has been reported to have a square-planar geometry (monodentate napy) exhibits a band at 14.3 kK (ϵ 15) and a second band at 27.2 kK (ϵ 26).[44] Hence, the spectrum of $Cu(napy)_4(ClO_4)_2$ is more consistent with a distorted dodecahedral structure.

The positions of the lowest two $\pi^* \leftarrow \pi$ transitions in the free ligand do not change on complexation except for the Pd and Cu complexes. In both of these cases, shifts in the position of the second $\pi^* \leftarrow \pi$ absorption are noted. The spin-allowed transitions known to occur in Pd(II) complexes are usually found above 20 kK[38] which is very close to the ligand adsorptions in $Pd(napy)_4(ClO_4)_2$. Therefore, the shoulder observed for the Pd complex of napy at *ca.* 25 kK probably has some d-d contribution. Other d-d transitions are probably hidden under the ligand adsorptions and thus produce the dissimilar spectrum. The uv spectra of $Ag(napy)(ClO_4)$ which is postulated to contain monodentate napy[1] and $Cu(napy)_2Cl_2$[45] which has been reported to possess monodentate napy[44] are similar to the uv spectra of the other $M(napy)_4{}^{2+}$ complexes. Thus, the spectral differences are not the result of mono- rather than bidentate coordination.

Registry No. $Mn(C_8H_6N_2)_4(ClO_4)_2$, 36312-67-1; $Fe(C_8H_6N_2)_4(ClO_4)_2$, 34343-65-2; $Co(C_8H_6N_2)_4(ClO_4)_2$, 12576-59-9; $Ni(C_8H_6N_2)_4(ClO_4)_2$, 36202-33-2; $Cu(C_8H_6N_2)_4(ClO_4)_2$, 12576-60-2; $Zn(C_8H_6N_2)_4(ClO_4)_2$, 36202-34-3; $Pd(C_8H_6N_2)_4(ClO_4)_2$, 36202-35-4; $Cd(C_8H_6N_2)_4(ClO_4)_2$, 12576-58-8.

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