in intermolecular bonding to nickel atoms in different planes, on the basis of infrared studies. However, the infrared frequencies that were assigned to ν(Ni–S) are in the range which have been previously assigned to ν(Ni–N) in benzoxazole.[14] While ambidentate behavior might have been expected with a class b metal ion (Pt(II)), our data show that both class a and b metal ions only N bond to thiazole. This is presumably because the important resonance structures for thiazoles place a formal positive charge on the sulfur atom, which would retard π donation from the ligand.

Preliminary work indicates that the N-alkylated derivatives of substituted thiazoles, which could use metal–sulfur bonding, all form complexes of the form MX_2L_2. They appear, however, to involve $(MX_4{}^{2-})(L^+)_2$ rather than metal–sulfur coordination.

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Complexes of 1,8-Naphthyridines. III. Transition Metal–Perchlorate Complexes of 2,7-Dimethyl-1,8-naphthyridine[1]

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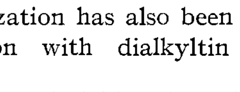
A number of transition metal–perchlorate complexes of the type $MI_3(ClO_4)_2$ (M = Fe, Cu, Ni, Co, Zn, and Cd), $HgI_2(ClO_4)_2$, and AgI_2ClO_4, where I = 2,7-dimethyl-1,8-naphthyridine, have been synthesized. Elemental analyses, molar conductances, magnetic moments, and infrared and electronic spectral data have been applied to the characterization of the compounds. The resulting ligand field parameters place the present ligand nearer pyridine than 1,10-phenanthroline and 2,2-bipyridine in the spectrochemical series. Since the latter two are very similar in basicity and synergic bonding to I, the resulting weak ligand field property is attributed to strain produced in the formation of a four-member chelate ring system.

Introduction

Complexes of transition metal salts with the nitrogen heterocycles 1,10-phenanthroline (phen), 2,2-bipyridine (bipy), and their numerous derivatives which form a five-member chelate ring system have long been known.[2] The strong crystal field properties of these ligands have been ascribed in part to their ability to participate in π bonding with the metal atom.[3,4] Previously Hendricker and Reed have reported stable complexes of the ligand 2,7-dimethyl-1,8-naphthyridine, I,



I

which forms a four-member chelate ring system.[5] From the CO stretching frequencies exhibited by group VIb metal carbonyl complexes of the type $M(CO)_4I$ they inferred that the π bonding of I is similar to that of phen. The ability of I to form stable complexes without π stabilization has also been demonstrated by adduct formation with dialkyltin dihalides.[6] The pK_a's of I, phen, and bipy are similar;[5] thus any variation in coordinating ability of the three ligands may not be attributed to differences in basicity. A comparison of the steric requirements of I with those of 2,9-dimethyl-1,10-phenanthroline is of interest in light of the documented inability of metal centers to accommodate three molecules of the latter.[7,8] Although reports of metal complexes involving various 1,5-, 1,6-, and 1,7-naphthyridines have appeared in the literature,[9–11] none of these ligands participates in chelation utilizing both heterocyclic nitrogens with the same metal center. Hence, as an integral part of our intensive studies involving a comparison of four- and five-member nitrogen heterocyclic chelate systems, we wish to report the preparation and characterization of some transition metal–perchlorate complexes of I.

Experimental Section

Materials.—Metal perchlorates were purchased from G. F. Smith Chemical Co., Columbus, Ohio, and used without further purification. Practical grade 2,2-dimethoxypropane (dmp) and Spectral grade acetonitrile and nitromethane were obtained from Eastman Chemicals. Purity of the ligand 2,7-dimethyl-1,8-naphthyridine, prepared by the method of Paudler and Kress,[12] was verified by pmr.

Instrumentation.—The infrared spectra (4000–200 cm^{-1}) were

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TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA

	% calcd			% found				Conductivity[a] Λ(molar), cm² mho	Concn, $M \times 10^3$
	N	C	H	N	C	H	Color		
$Ni(C_{10}H_{10}N_2)_3(ClO_4)_2$	11.48	49.20	4.14	11.55	49.00	4.10	Blue-green	176	0.98
$Fe(C_{10}H_{10}N_2)_3(ClO_4)_2$	11.54	49.40	4.15	11.60	49.66	4.19	Yellow	176	0.21
$Co(C_{10}H_{10}N_2)_3(ClO_4)_2$	11.48	49.19	4.14	11.49	49.11	4.04	Pink	186	1.04
$Cu(C_{10}H_{10}N_2)_3(ClO_4)_2$	11.42	48.88	4.11	11.29	48.67	4.23	Brown	151	0.90
$Cd(C_{10}H_{10}N_2)_3(ClO_4)_2$	10.71	45.84	3.86	10.52	45.41	3.64	White	184	0.45
$Hg(C_{10}H_{10}N_2)_2(ClO_4)_2$	7.83	33.55	2.82	7.89	33.39	2.77	White	188	0.91
$Ag(C_{10}H_{10}N_2)_2ClO_4$	10.70	45.86	3.86	10.69	45.72	3.75	White	82	1.26
$Zn(C_{10}H_{10}N_2)_3(ClO_4)_2$	11.39	48.76	4.10	11.20	48.37	4.03	White	169	0.95

[a] All conductivity values were obtained in nitromethane solutions. The following compounds and their molar conductivities were used for comparison: $[(CH_3(CH_2)_3)_4N]Br$, 79; $[(CH_3(CH_2)_3)_4)N]NO_3$, 82; $[Co(diars)_2](ClO_4)_2$, 177.

obtained with a Perkin-Elmer Model 621 double-beam grating spectrometer on Nujol–Fluorolube mulls supported between sodium chloride or polystyrene windows. All spectra were calibrated with polystyrene film. Electronic absorption spectra were measured on acetonitrile solutions of the complex in matched 1-cm quartz cells using a Cary 14 recording spectrophotometer. An Industrial Instruments Model RC-16B2 conductance bridge was used to determine the conductivity of nitromethane solutions of the complexes. The Sargent Model 5-29885 cell was calibrated with a standard KCl solution prepared with conductance water. Magnetic moments were obtained using a Varian A-60 nmr instrument equipped with a variable-temperature probe. Carbon, hydrogen, and nitrogen contents were ascertained by combustion.

Preparations. **$Ni(C_{10}H_{10}N_2)_3(ClO_4)_2$.**—To 0.46 g (1.26 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 100 ml of absolute methanol was added with stirring approximately 15 ml of dmp and the resulting solution was refluxed for 6 hr. After the addition of 0.6 g (3.78 mmol) of I in 50 ml of absolute methanol and stirring for 4 days, the resulting light blue solution was concentrated under reduced pressure to approximately 15 ml and cooled. The blue-green product was filtered, recrystallized several times from absolute ethanol, washed with chloroform, and dried *in vacuo* at 110° over phosphorus pentoxide for several days.

$Fe(C_{10}H_{10}N_2)_3(ClO_4)_2$.—A solution of 0.12 g (0.33 mmol) of $Fe(ClO_4)_2 \cdot 6H_2O$ in 30 ml of absolute methanol and 3 ml of dmp was refluxed for 1 hr followed by the addition of 0.2 g (1.26 mmol) of I in 10 ml of absolute methanol. After 3 days, the resulting yellow solution was concentrated with warming under reduced pressure to one-third volume and 25 ml of chloroform was added. The bright yellow precipitate was filtered, washed with chloroform, and dried *in vacuo* at room temperature.

$Co(C_{10}H_{10}N_2)_3(ClO_4)_2$.—A solution of 0.074 g (0.202 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ in 50 ml of absolute methanol and 13 ml of dmp was refluxed for 1 day followed by the addition of 0.4 g (2.52 mmol) of I in 10 ml of absolute methanol. After 5 days, the resulting pink solution was concentrated with warming under reduced pressure to approximately 20 ml and cooled. The pink product was filtered, stirred in boiling ethyl acetate, filtered, washed with 20 ml of chloroform, and dried *in vacuo* at 110° for 5 days.

$Cu(C_{10}H_{10}N_2)_3(ClO_4)_2$.—A solution of 0.14 g (0.42 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 30 ml of absolute methanol and 8 ml of dmp was refluxed for 6 hr followed by the addition of 0.2 g (1.26 mmol) of I in 10 ml of absolute methanol. After 1 day, a light brown precipitate was obtained on cooling. The product was filtered, recrystallized several times from absolute methanol, filtered, washed with chloroform, and dried *in vacuo* at 110° for 1 day.

$Cd(C_{10}H_{10}N_2)_3(ClO_4)_2$.—A solution of 0.35 g (0.84 mmol) of $Cd(ClO_4)_2 \cdot 6H_2O$ in 60 ml of absolute methanol and 10 ml of dmp was refluxed for 5 hr followed by the addition of 0.4 g (2.52 mmol) of I in 15 ml of absolute methanol. After 7 days, the resulting clear colorless solution was concentrated with warming under reduced pressure to approximately 20 ml and cooled. The white product was filtered, recrystallized twice from absolute ethanol, and dried *in vacuo* at 110° for 6 days.

$Hg(C_{10}H_{10}N_2)_2(ClO_4)_2$.—To a solution of 0.24 g (0.42 mmol) of $Hg(ClO_4)_2 \cdot 9H_2O$ in 50 ml of absolute methanol was added with stirring 0.2 g (1.26 mmol) of I in 15 ml of absolute methanol. An immediate white precipitate was obtained. The flask was wrapped with aluminum foil and the solution was stirred for 4 days. The product was filtered under an inert atmosphere, washed with absolute methanol and pentane, and dried *in vacuo*.

$Ag(C_{10}H_{10}N_2)_2ClO_4$.—To a solution of 0.1 g (0.48 mmol) of anhydrous $AgClO_4$ in 30 ml of absolute methanol was added with stirring 0.16 g (1.01 mmol) of I in 15 ml of absolute methanol. An immediate white precipitate was obtained. The flask was wrapped with aluminum foil and the solution was stirred for 2 days. The product was filtered under an inert atmosphere, recrystallized twice from absolute methanol, and dried *in vacuo*.

$Zn(C_{10}H_{10}N_2)_3(ClO_4)_2$.—A solution of 0.47 g (1.26 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 100 ml of absolute methanol and 25 ml of dmp was refluxed for 3 hr followed by the addition of 0.6 g (3.78 mmol) of I in 50 ml of absolute methanol. After 5 days, the resulting clear colorless solution was concentrated under reduced pressure with heat to approximately 20 ml. The white precipitate which formed on cooling was filtered, recrystallized twice from an absolute ethanol–methanol mixture (3:1), and dried *in vacuo*.

Magnetic Moments.—Solution magnetic moments were determined by the method of Evans.[13] The temperature was calculated by the difference of the chemical shift (in hertz) between the CH_3 and the OH group in methanol.[14] Diamagnetic corrections were calculated from Pascal's constants[15] with a value of 110×10^{-6} (g-atom)$^{-1}$ approximated for I. This approximation was based on the similar bipy and phen ligands which are given values of 105×10^{-6} and 128×10^{-6} (g-atom)$^{-1}$, respectively.[15] The last correction term in expression 1, involving the densities of solution, was neglected as suggested by Evans.[13]

$$\chi = \frac{3\delta v}{2\pi v_0 m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad (1)$$

Discussion

The analytical and physical data for the newly prepared complexes are reported in Table I. The divalent and monovalent metal compounds exhibit conductivity values appropriate for three- and two-ion salts, respectively.[16] The similarity in color to hydrated metal perchlorates suggests weak-field complexes. The obtained magnetic moments in Table II agree well with the spin-free experimental moments for octahedral first-row transition metals,[15] 2.8–3.50 BM for Ni^{2+}, 5.10–5.70 BM for Fe^{2+}, and 4.30–5.20 BM for Co^{2+}, thus

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TABLE II
MAGNETIC DATA

Compound	$10^6\chi_{\text{measd}}$, cgsu	$10^6\chi_{\text{cor}}$, cgsu	Temp, °K	μ_{eff}, BM
$NiI_3(ClO_4)_2$	4.36	3,586	294	2.90[a]
$FeI_3(ClO_4)_2$	15.85	11,954	291	5.28[b]
$CoI_3(ClO_4)_2$	11.92	9,127	307	4.74[b]

[a] Data obtained in TMS–acetonitrile solutions. [b] Data obtained in 1% *t*-butyl alcohol–methanol solutions.

illustrating the weak ligand field properties of I. The compounds are indefinitely stable on exposure to air. *Melting points were not determined due to the violent explosion of* $FeI_3(ClO_4)_2$ *which occurred at 170°.* It is interesting to note that, in heating at 110° *in vacuo* for 3 days, this compound undergoes a color transformation from yellow to black with no alteration of chemical composition or infrared spectra. Similar color changes reported for $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ are accompanied by the loss of 1 mol of ligand.[17]

TABLE III
SELECTED INFRARED ABSORPTIONS (4000–200 CM^{-1})[a]

Band	L	CdL_3^{2+}	ZnL_3^{2+}	FeL_3^{2+}	CoL_3^{2+}	NiL_3^{2+}	CuL_3^{2+}	HgL_2^{2+}	AgL_2^{+}
I	1532 s	1563 m	1570 m	1560 s	1568 m	1564 m	1550 m	1565 m	1558 m
II	1360 s	1377 m	1380 m	1375 s	1380 m	1372 m	1370 s	1380 m	1377 m
III	1240 m	1250 w	1255 w	1255 m	1255 m	1250 m	1252 vw	1257 w	1250 vw
IV	1205 m	1212 w	1218 w	1220 m	1216 m	1212 m	1218 s	1225 m	1217 m
V	...	1110 vs, br	1095 vs, br	1090 vs, br	1090 vs, br	1090 vs, br	1085 vs, br	1095 vs, br	1088 vs, br
VI	848 s	857 m	868 w	870 s	867 m	860 m	855 s	870 s	856 s
VII	807 s	...	853 w	852 s	851 s	845 m	810 w	820 s	...
VIII	778 vs	800 s	803 m	802 vs	800 vs	797 vs	797 vs	793 vs	798 s
IX	440 m	450 w	453 w	452 vw	454 m	448 w	455 w	453 w	450 vw
X	343 s	353 w	356 w	356 w	356 m	376 m	350 w	373 w	364 w
XI	240 s	260 w	267 m	272 w	278 s	280 m	300 m	275 w	266 w
XII	...	...	...	...	211 m	217 m	250 m	...	...

[a] See text for various band assignments.

We recorded and analyzed (4000–200 cm^{-1}) the infrared spectra of the reported complexes. In Table III the ligand modes which suffer substantial (>10 cm^{-1}) change on complexation are given. Bands I–VIII except V are assigned using the parent ligand 1,8-naphthyridine as a model.[18] The assignments are: I, skeletal stretch; II, combination skeletal stretch and CH symmetrical bend;[19] III, CH in-plane bend; IV, unassigned; V, perchlorate anion;[20] VI, skeletal stretch and CH out-of-plane bend; VII and VIII, CH out-of-plane bend. Absorbances IX–XII have not previously been reported and are tentatively assigned in the following manner: IX, ring CH_3 bend; X–XII, ring deformation modes.[19]

The free ligand modes observed at 1532, 848, and 240 cm^{-1} shift significantly toward higher energy on complexation. Similar behavior is noted in complexes of the type R_2SnCl_2I where R = Cl, alkyl, or phenyl.[6] For all the complexes exhibiting octahedral geometry except CuI_3^{2+}, the frequency of the 240-cm^{-1} band increases with decreasing size or increasing polarizing ability of the metal ion: Cd < Zn < Fe < Co < Ni.

The position of ν_{M-N} for these complexes is of considerable interest if one wishes to compare the stability of four- and five-member chelate ring systems. Certainly ν_{M-N} will lie below these modes assigned by Nakamoto in metal–ammine complexes (419–509 cm^{-1}).[21] Metal–nitrogen stretching frequencies in the region of 264–300 cm^{-1} have been reported by Inskeep for Co(II), Cu(II), and Zn(II) complexes of phen and bipy.[22] McWhinnie has attributed the 286-cm^{-1} band in Cu(bipy)$_3$(ClO$_4$)$_2$ to ν_{M-N};[23] however, Clark and Williams contended that this is an activated ligand mode since no bands which can be ascribed to ν_{M-N} are observed for analogous trivalent metal complexes.[24,25] One would expect increasing the oxidation state of the central metal to yield an increase in ν_{M-N}. Assignment of ν_{M-N} in $SnCl_4I$,[6] $SnCl_4$phen,[26] and $SnCl_4$bipy[26] to absorbances at 207, 202, and 181 cm^{-1}, respectively, leads to the conclusion that in complexes of the type $MI_3(ClO_4)_2$, $MI_2(ClO_4)_2$, and MI_2ClO_4 this mode lies below 200 cm^{-1} and thus was not detected in the present study.

Varying the metal center of the complex does not produce significant differences in the frequency of modes VII and VIII assigned to the CH out-of-plane bend. In benzene derivatives this mode has been demonstrated to change markedly as the π-electron density of the ring system is altered.[27] That modes VII and VIII are relatively consistent for most complexes may imply a similar π-electron density on the ligand in these complexes. As suggested for phen, bipy, and pyridine complexes,[28] a mechanism for this would be the participation of the ligand with the metal center in π bonding. In metal–carbonyl complexes, I has been found to π

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bond to a degree similar to phen and bipy.[5] However, since positively charged metal ions would require a lesser degree of π stabilization than zerovalent metals and various metal cations would not be expected to participate in π interaction to the same degree, the consistency of modes VII and VIII may be the result of several factors.

Ligand modes which are not appreciably altered on coordination and their assignments are: 3050 and 3000 cm^{-1}, CH stretch;[19] 2981 cm^{-1}, CH stretch;[19] 2018, 1980, 1780, and 1698 cm^{-1}, combination and overtones of out-of-plane CH bend[29] (this pattern is in good agreement with that expected for a 1,2,3,4-substituted benzenoid[30] type); 1598 and 1500 cm^{-1}, skeletal stretch;[18] 1437 cm^{-1}, combination skeletal stretch[18] and CH bend;[19] 1310 and 1285 cm^{-1}, CH in-plane bend;[19] 1145 and 1128 cm^{-1}, skeletal bend including C–CH$_3$ stretch;[18,19] 1008 and 988 cm^{-1}, skeletal stretch;[18] 720, 676, 622, 582, 540, and 478 cm^{-1}, skeletal modes[19] with 1033 and 948 cm^{-1} unassigned.[18] Coordination has greatly enhanced the intensity of the 582- and 540-cm^{-1} absorptions.

The broad, very strong 1090-cm^{-1} and strong 620-cm^{-1} absorptions are typical for the asymmetric stretch and asymmetric bending modes of ionic perchlorate.[31] Although a very sharp ligand mode also appears at 620 cm^{-1}, the spectra of the complexes show a broad band in this region suggesting a combination of perchlorate and ligand absorptions. The absence of bands in the 900–930-cm^{-1} region and the lack of splitting of the 1090-cm^{-1} band substantiate the presence of a noncoordinated anion.[31] Only in the spectra of CdI$_3^{2+}$ was evidence for the presence of a trace amount of water detected.

The electronic spectra of the free ligand and complexes in which the metal ion has fewer than ten d electrons are recorded in Table IV. Although we have assumed octahedral geometry for interpretation of the spectra, it is obvious from molecular models that some distortion does exist. The relatively broad and unsymmetrical character of bands obtained in the spectra of the iron and cobalt salts further supports the contention that the system is somewhat distorted.

The 10Dq values for the Ni(II), Fe(II), and Co(II) complexes are 9.56 ± 0.05 (β = 0.90 ± 0.04), 10.10 ± 0.05, and 9.67 ± 0.05 kK (β = 0.81 ± 0.01), respectively. The secular equations for Ni(II) (d^8) and Co(II) (d^7) were solved in the weak-field formalism using matrices given by Drago[32] for Ni(II) and Ballhausen[33] for Co(II). The values of Dq for Ni(II) and Fe(II) were taken directly from the lowest energy, spin-allowed absorption band.

TABLE IV
ELECTRONIC ABSORPTION SPECTRA[a]

λ, mμ	ν, kK	ϵ_{max}, M^{-1} K^{-1}	Assignment
		NiI$_3^{2+}$	
1046	9.56	6.8	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$
791	12.64	0.2	$^1E_g(D) \leftarrow {}^3A_{2g}(F)$
635	15.75	10.9	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$
(327)	(30.6)	2,680	CT
317	31.6	34,900	CT
309	32.4	30,800	CT
304	32.9	31,000	CT
(297)	(33.7)	21,800	CT
(292)	(34.3)	16,200	CT
264	38.0	15,100	CT
		FeI$_3^{2+}$	
990	10.10	6.0	$^5E_g(D) \leftarrow {}^5T_{2g}(D)$
315	31.8	25,700	CT
307	32.6	24,300	CT
303	33.1	21,200	CT
(295)	(33.9)	14,700	CT
(290)	(34.5)	10,400	CT
260	38.5	7,530	CT
		CoI$_3^{2+}$	
1170	8.55	5.9	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$
520	19.23	25.0	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
315	31.8	24,900	CT
307	32.6	24,200	CT
302	33.1	22,500	CT
(296)	(33.8)	16,900	CT
(290)	(34.5)	12,500	CT
(282)	(35.5)	8,500	CT
252	39.7	11,500	CT
		CuI$_3^{2+}$	
(552)	(18.1)	53.0	CT
315	31.8	22,700	CT
308	32.5	22,300	CT
302	33.1	20,800	CT
(296)	(33.8)	15,300	CT
(290)	(34.5)	10,900	CT
(284)	(35.2)	7,280	CT
254	39.5	10,100	CT
		I	
315	31.8	9,130	CT
308	32.5	8,600	CT
303	33.1	8,250	CT
(297)	(33.7)	6,150	CT
(291)	(34.4)	4,800	CT
(285)	(35.1)	3,450	CT
248	40.3	5,300	CT

[a] Parentheses designate shoulders; CT, charge transfer.

Although $\nu_1(^3T_{2g}(F) \leftarrow {}^3A_{2g}(F))$ and $\nu_3(^3T_{1g}(P) \leftarrow {}^3A_{2g}(F))$ are usually used in calculating Dq for Ni(II) complexes,[34] the NiI$_3^{2+}$ complex exhibits only ν_1 and $\nu_2(^3T_{1g}(F) \leftarrow {}^3A_{2g}(F))$. Using ν_1 and ν_2, ν_3 is calculated to be at 27.2 kK which is in the ligand charge-transfer region. A ligand charge-transfer band also obscures ν_3 in the spectra of Ni(phen)$_3^{2+}$ and Ni(bipy)$_3^{2+}$, a situation which has been associated with significant ligand–metal π interaction[35] and is characteristic of nitrogen heterocycles.[36] The range given for Dq and β in NiI$_3^{2+}$ is a result of the relatively broad ν_1 at maximum absorption.

The Dq range for FeI$_3^{2+}$ is due to the broad (unsym-

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metrical on the low-energy side) $^5E_{2g}(D) \leftarrow {}^5T_{2g}(D)$ transition. The unsymmetrical behavior is believed to result from a lifting of the twofold degeneracy of the $^5E_g(D)$ state by a low-symmetry ligand field component.[34]

In the CoI_3^{2+} spectrum $\nu_2(^4A_{2g}(F) \leftarrow {}^4T_{1g}(F))$ is calculated to occur at 18.2 kK using $\nu_1 = 8.55$ and $\nu_3 = 19.23$ kK. It is known that ν_2 is a two-electron transfer and therefore should have a very low intensity.[33] The spectrum does not clearly show the position of this transition. The higher energy band, ν_3, is nearly gaussian and attempts to resolve it to show ν_2 were unsuccessful. However a slight shoulder can be observed in the calculated region of ν_2. It should be noted that in the calculation of ν_2, the third transition was considered to arise only from ν_3.

No d–d transition was observed for CuI_3^{2+} due to extreme tailing of the ligand charge-transfer band in the appropriate region.

From the spectra of NiI_3^{2+}, FeI_3^{2+}, and CoI_3^{2+} the position of I in the spectrochemical series may be established. The $10Dq$ value of I in NiI_3^{2+}, 9.56 ± 0.05 kK, corresponds more closely with that observed for Ni(II) complexes of pyridine, 9.85 kK, than of phen, 12.70 kK, or bipy, 12.65 kK.[35] Similarly a $10Dq$ value for FeI_3^{2+} of 10.10 ± 0.05 kK suggests a ligand field strength more like pyridine than phen or bipy.[34] If one compares the Dq values of I in the Ni(II), Fe(II), and Co(II) complexes, the correct order of metals in the spectrochemical series, $Fe^{2+} > Co^{2+} > Ni^{2+}$, is observed.[34]

Busch and coworkers[37] have shown that polyamine ligands which exhibit $10Dq$ values for Ni(II) complexes of less than 11.20 kK produce spin-free Fe(II) complexes. Nelson and Rodgers[35] have more recently shown that spin pairing in Fe(II) complexes occurs if the $10Dq$ value for the corresponding Ni(II) complexes exceeds 11.70 kK. In view of these observations and the Ni(II) $10Dq$ value of 9.56 ± 0.05 kK for I, a spin-free FeI_3^{2+} is predicted. Our inability to obtain a pmr spectrum of FeI_3^{2+} in nitromethane solution and the magnetic moment of 5.28 BM indicate that this is a spin-free complex.

The uv absorption bands appear to arise primarily from the ligand π-electron states. Little spectral change from the free to complexed form of I is noticed except for the 248-mμ band which is shifted toward lower energy. Shoulders appear in the nickel and copper spectra which apparently do not exist in the free ligand spectrum. The origin may be due to complexation producing more allowed electronic transitions within the ligand system or, as suggested by Jørgensen for $Ni(phen)_3^{2+}$ systems, a charge transfer from the central metal to an unoccupied ligand orbital.[38]

A reviewer suggested that the present six-coordinate complexes may possess trigonal-prismatic rather than the assigned octahedral geometry. Molecular models of the present complexes indicate a D_{3h} trigonal-prismatic ligand arrangement produces extreme steric interaction between methyl groups on adjacent ligands, whereas in an octahedral arrangement there is virtually no steric interaction. Wentworth compared trigonal-prismatic with octahedral geometry and concluded that neither electronic absorption spectra nor magnetic moment data would distinguish one spatial form from the other.[39] However, the crystal field stabilization energy of all octahedral complexes (except of course for d^0, d^5, and d^{10} systems) is greater than that of the trigonal-prismatic type.[39] Because of energy and steric considerations, we feel that the six-coordinate complexes reported herein possess octahedral geometry.

Conclusions

The reported compounds add to the growing number of examples of stable four-member chelate ring systems. The presence of methyl groups on the carbons adjacent to the nitrogen atoms of I does not prevent three molecules from coordinating to a metal center as is the case with 2,9-dimethyl-1,10-phenanthroline which is unable to form such complexes. Since I, phen, and bipy are similar in π-bonding ability and have nearly the same pK_a's, the large differences in the respective ligand field properties lead us to the conclusion that there is significant strain in the four-member chelate ring. It should be pointed out that in I the electron pairs are extended in a parallel manner from the chelate and separated by approximately 2.2 Å whereas in phen the lone nitrogen pairs are not parallel but subtend an angle of ~85° at 2.00 Å[40] from the metal center. The presence of methyl groups on the naphthyridine does appreciably alter the coordination characteristics when compared with the unsubstituted ligand.[41] Further studies of the coordination behavior of various 1,8-naphthyridines with other metal salts are presently being completed.

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