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Complexes of Transition Metal Chlorides with 2,2′-Bipyridine N-oxide[1]

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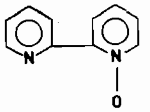
The synthesis and characterization of 3d metal chloride chelates with the mono-N-oxide of 2,2′-bipyridine (N-bipyO) is reported. The N-bipyO ligand acts generally as a bidentate O,N-chelating agent in the new complexes. The characterization of these compounds was based on spectral, magnetic and conductance studies. $[Cr(N\text{-}bipyO)_2Cl_2]Cl\cdot 4H_2O$ *involves a low symmetry hexacoordinated complex cation and one anionic chloride group.* $Fe(N\text{-}bipyO)Cl_3$ *was shown to be a high-spin complex of the type* $[Fe(N\text{-}bipyO)_2Cl_2][FeCl_4]$. *Complexes of the general formula* $[M(N\text{-}bipyO)Cl_2]\cdot C_2H_5OH$ *are tetrahedral and high-spin for M = Mn or Co, and square planar, partially spin-paired* ($S = 1, \mu_{eff} = 3.51$ *BM) for M = Fe.* $[Zn(N\text{-}bipyO)Cl_2]$ *is tetrahedral, while* $[Ni(N\text{-}bipyO)_2Cl_2]\cdot H_2O$ *is a low symmetry, hexacoordinated, high-spin compound. The latter complex dissociated in N,N-dimethylformamide, behaving as a 1:1 electrolyte.* $Cu(N\text{-}bipyO)Cl_2$ *is the only polynuclear complex of the series; its normal* μ_{eff} *(1.99 BM) suggests that chloride rather than N-bipyO bridges are present in this compound. The water or ethanol molecules present in certain new complexes, appear to be in the form of lattice rather than coordinated moieties on the basis of the ir evidence. The lattice ethanol is easily removed by treatment at 65° C under reduced pressure, but the water of crystallization is held rather tenaciously and can be only partially removed by similar treatment.*

Introduction

The synthesis and characterization of 2,2′-bipyridine mono-N-oxide (N-bipyO; I) chelates with 3*d* metal perchlorates[2] and nitrates[3] was recently reported by this laboratory.



(I)

These studies have been extended to include complexes of di- and tri-valent 3*d* metal chlorides. Following a preliminary presentation of our work in this direction,[1b] the present paper deals in some detail with synthetic and characterization studies of the N-bipyO–3*d* metal chloride complexes.

Experimental

Chemicals

N-bipyO was prepared by the method of Murase,[4] and its authenticity checked by elemental analysis and examination of its melting point (57–58° C) and ir spectrum.[4–6] Reagent grade hydrated 3*d* metal chlorides, triethyl orthoformate and organic solvents were utilized throughout this work.

Synthetic Procedure

3.2 mmol (0.55 g) N-bipyO were dissolved in *ca.* 10 ml of a 3/2 (v/v) ethanol–triethyl orthoformate mixture, and the resulting solution was warmed for 15–20 min at 50–60° C under stirring. 1 mmol of hydrated metal salt was treated separately in exactly the same manner. The ligand and salt solutions were subsequently combined. In all but one (Ni(II)) of the cases examined, precipitates formed immediately. In the case of the N-bipyO–$NiCl_2$ mixture, a color change occurred when the two solutions were mixed, and the new complex was precipitated by addition of anhydrous diethyl ether. The new complexes were filtered, washed with ethanol or ether (Ni(II) complex), and dried in an evacuated desiccator over phosphorus pentoxide. Identical complexes are obtained when the same general synthetic procedure is followed, but the ligand to metal salt molar ratio is changed to 1:2. Interactions at this ratio were investigated because 1,10-phenanthroline N-oxide (N-phenO) was found to form more than one complex with certain 3*d* metal chlorides and nitrates; thus, N-phenO yields 2 or 3:1 metal complexes when a 3:1 molar ratio is used during the synthesis, and 1:1 metal complexes when a 1:2 molar ratio is utilized.[1,3] Analytical data for the new complexes (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) are given in Table I. The new N-

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TABLE I. Analytical Data for the New N-bipyO(L)–Metal Chloride Complexes.

Complex	Color	Analysis							
		C% Calc.	Found	H% Calc.	Found	N% Calc.	Found	Metal % Calc.	Found
$CrL_2Cl_3 \cdot 4H_2O$	Green	41.79	42.40	4.22	4.26	9.75	9.53	9.05	9.35
$MnLCl_2 \cdot C_2H_5OH$	Yellow-orange	41.88	42.22	4.10	3.77	8.14	8.41	15.96	15.74
$FeLCl_2 \cdot C_2H_5OH$	Red	41.77	42.06	4.10	3.92	8.12	8.37	16.19	15.98
$FeLCl_3$	Yellow	35.92	35.65	2.41	2.63	8.38	8.75	16.70	16.42
$CoLCl_2 \cdot C_2H_5OH$	Light green	41.40	41.11	4.06	3.80	8.05	7.79	16.93	17.04
$NiL_2Cl_2 \cdot H_2O$	Lime green	48.82	48.74	3.69	3.89	11.39	11.58	11.93	11.30
$CuLCl_2$	Turquoise	39.17	39.46	2.63	2.86	9.14	9.48	20.72	20.36
$ZnLCl_2$	White	38.93	39.33	2.62	2.92	9.08	9.37	21.19	20.85

bipyO metal complexes are stable in the atmosphere and soluble in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), except for the Cu(II) complex which is very sparingly soluble in these media. With some exceptions, mentioned in parentheses, they are insoluble in chloroform, ethanol (Mn(II), Ni(II)) and nitromethane (Fe(II), Co(II), Ni(II)). Some of the complexes dissolve in water with decomposition (color changes). Attempts at the recrystallization of the new complexes from suitable solvents (*e.g.*, Mn(II) or Ni(II) from ethanol, Co(II) or Ni(II) from nitromethane) led invariably to crystalline products containing substantial amounts of the solvent used.

Spectral, Magnetic, Conductance and X-ray Powder Diffraction Studies

Infrared (Table II) and electronic (Table III) spectra, magnetic susceptibility and conductance measurements (Table IV) and X-ray powder diffraction patterns (Table V) were obtained by methods described elsewhere.[7]

Discussion

Infrared, Conductance and X-ray Data

The function of N-bipyO as a bidentate O,N-ligand in the new complexes is established by shifts and/or splittings of several characteristic vibrational modes of the ligand and the occurrence of several metal-sensitive vibrations in the lower frequency ir region (Table II). Tentative ν_{M-O}, ν_{M-N} and ν_{M-Cl} assignments for the latter bands were based on our previous work with 3*d* metal perchlorate–N-bipyO chelates,[2] as well as ir studies of 2,2′-bipyridine (bipy),[8–12] its N,N-dioxide (N,N-bipyO$_2$),[13] aromatic amine N-oxide[14] and other ligand 3*d* metal halide complexes.[8,15–18] Coordination of N-bipyO through oxygen is clearly demonstrated by the negative frequency shifts of the ν_{N-O} bands,[2,13,14,19–21] whereas coordination through the nitrogen of the pyridine fragment of this ligand is suggested by frequency shifts and splittings of the ν_{8a}, ν_{19a} and ν_{10b} (γ_{CH}) modes[2,5,12,21–23] Table (II).

As suggested by the analytical (Table I) and ir (Table II) evidence, the Fe(III), Cu(II) and Zn(II) complexes are anhydrous, the Cr(III) and Ni(II) compounds contain water molecules, and the Mn(II), Fe(II) and Co(II) complexes contain ethanol molecules. The ir data suggest that lattice rather than coordinated water or ethanol is present in the latter complexes. In fact, the ν_{OH} in the hydrated complexes exhibits multiple splittings in the 3620–3200 cm^{-1} region. Absorption in this region is in favor of the presence of lattice water[2,24,25] rather than coordinated aquo ligands;[26] for instance, aqueous adducts of $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) exhibit a broad ν_{OH} band centered at 3225 cm^{-1} and bands attributable to the rocking mode[27] of the coordinated aquo ligand at 1000–700 cm^{-1}.[26] Comparison of the spectra of the new Cr(III) and Ni(II) complexes with the anhydrous Fe(III), Cu(II) and Zn(II) complexes in the 1000–600 cm^{-1} region, did not reveal additional bands in the case of the hydrated complexes. Hence, the water molecules in these complexes have negligible or no interaction with the central metal ion and most probably reside in "pockets" formed by the coordinated N-bipyO ligands, in a way analogous to that described by Jensen *et al.* for hydrated bipy and phen metal complexes.[28] As far as the ethanol-containing Mn(II), Fe(II) and Co(II) complexes are concerned, the ν_{OH} (ethanol) vibrational mode appears as a very broad band of medium intensity at 3550–3450 cm^{-1}. Comparison of these data with the ν_{OH} mode of coordinated ethanol, reportedly occurring as a broad band with a maximum at 3385 cm^{-1} in $[Ni(C_2H_5OH)_6](ClO_4)_2$,[29] is again in favor of the presence of lattice ethanol in the N-bipyO complexes. This assignment is further substantiated by the fact that the $[Co(N\text{-}bipyO)Cl_2]$ moiety is pseudotetrahedral (*vide infra*).

The conductance of the new Cr(III) complex in DMF (Table IV) is within the range of Λ_M values reported for 1:1 electrolytes in this solvent.[30] This

TABLE II. Pertinent Infrared Data for Metal Chloride–N-bipyO Complexes (cm^{-1}).*

Compound	ν_{N-O}	δ_{N-O}	$\nu_{8a}, \nu_{19a}, \nu_{10b}$** and γCH***	ν_{M-O}	ν_{M-N}	ν_{M-Cl}	ν_{Ligand}(450–200 cm^{-1})
N-bipyO = L	1250s, 1232s	855vs	1575m, 1457m, 765vs, 770vs				443w, 401m-s, 340m, 310w, 291w, 279w, 251w, 242w, 221sh, 200m, b
$CrL_2Cl_3 \cdot 4H_2O$	1235m, 1194vs	849s, 838s	1592s, 1466vs, 770vs, 784s, sh	432m-s, 401vs	385m, sh, 346m	363s, 328m, b	432m, 300w, 289m, 277w, 263m, 250w, 241w, 218m, sh
$MnLCl_2 \cdot C_2H_5OH$	1241m, sh 1208s	846m, sh, 840m-s	1588s, 1468s, 768vs, 789m, sh	367m, 360m, 355m	271m-s	329m, 324m	450w, 426w, 410m-s, 396m, 380w, 308w, 288m-s, 261m, 247m, sh, 239s, 219s
$FeLCl_2 \cdot C_2H_5OH$	1237m, 1206m-s	850s, 840m, sh	1596s, 1470s, 767s, 791m	373s, sh, 359vs	303s, sh	308s	450w, 420m, 383s, sh, 290s, sh, 278m, 262w, 248m, sh, 241m, 218m, b
$FeLCl_3$	1234m, 1203s	850m-s, 839s	1592s, 1470vs, 765vs, 788s	390s	381s, sh, 361s	377vs, 355s, sh, 311s****	448m, 420m, 291s, 278s, 262w, 248m, sh, 229s, 220s
$CoLCl_2 \cdot C_2H_5OH$	1222m, sh, 1201s	847m, sh, 837s	1594s, 1469vs, 768vs, 784s, sh	373m, 369m	300m-s	330m, 313m	418m, 388w, sh, 289s, 279s, 261m, 245m, b, 229m, 221m
$NiL_2Cl_2 \cdot H_2O$	1227m, sh, 1202vs	838vs	1591vs, 1465s, 770vs, b, 778s, sh	379m, 341m	279vs	243m	423m, 384m, sh, 320w, 293m, sh, 288s, 260m, 237m, sh, 220m
$CuLCl_2$	1239m, 1210m	849m	1595s, 1465m, 770vs, 783m, sh	343m-w, 330m-w	284s	298vs, 240s	440w, b, 410m, 391w, 380w, 370w, 363w, 275m, sh, 261m, 215m, 205m
$ZnLCl_2$	1247m, 1208m, b	850m, 831m	1599vs, 1470vs, 764vs, 791m	362m	317vs	322vs, 300m, sh	422w, sh, 410s, 382w, b, 270m, 261m, 240m, 219m, 209m

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.
* ν_{OH} of C_2H_5OH in the Mn(II), Fe(II) and Co(II) complexes appears as a medium, very broad band at 3550–3400 cm^{-1}; ν_{OH} of water: Cr(III) complex: 3611m-s, 3560s, sh, 3510s, b, 3485s, 3380vs, b, 3315s, b, 3250s, b, 3200s, sh; Ni(II) complex: 3610m-s, 3440vs, 3405vs, 3360vs, 3340vs, 3285s, 3220s; the δ_{H-O-H} in the latter two complexes occurs at *ca.* 1630(m). ** Bands attributable to the pyridine fragment of the ligand. *** Band attributed to the pyridine N-oxide fragment of the ligand.[5] **** The band at 377 cm^{-1} is assigned as $\nu_3(FeCl_4^-)$, and those at 355 and 311 cm^{-1} as ν_{Fe-Cl} in the $[Fe(N\text{-}bipyO)_2Cl_2]^+$ cation (see text).

compound is, therefore, formulated as $[Cr(N\text{-}bipyO)_2Cl_2]Cl \cdot 4H_2O$; it is worth noting at this point that bipy[31] and N,N-bipyO_2[13] also form complexes of the type $[CrL_2Cl_2]Cl$. The ν_{CrCl} assignments for the new Cr(III) complex are in good agreement with the corresponding assignments in $CrCl_3 \cdot 3$pyridine.[8] For the Fe(III) complex, the analytical data are consistent with the empirical formula Fe(N-bipyO)Cl_3. The lower frequency ir evidence involves a very strong absorption at 377 cm^{-1}. This band is attributed to the ν_3 mode of the tetrachloroferrate(III) anion.[15,16] Several 2:1 unidentate aromatic amine N-oxide-$FeCl_3$ complexes are reportedly formulated as $[FeL_4Cl_2][FeCl_4]$;[18] Fe(bipy)Cl_3 also appears to be of this type.[32] The formulation of the new Fe(III) complex as $[Fe(N\text{-}bipyO)_2Cl_2][FeCl_4]$, involving both hexa- and tetra-coordinated Fe(III), is justified by the identification of $\nu_3(FeCl_4)$,[15,16,18] the occurrence of ir bands attributable to the

TABLE III. Electronic Spectra of N-bipyO–Metal Chloride Complexes.[a]

Compound	Medium	λ_{max}, nm (ε_{max})
N-bipyO = L	Nujol	239vs, 285vs, 293sh, 344s, sh
$CrL_2Cl_3 \cdot 4H_2O$	Nujol	218s, sh, 239vs, 267vs, 277vs, 323vs, 415s, b, 635m-s, b
	$7 \times 10^{-4} M$ in DMSO	418(80), 440(70), 603sh(50), 630(59)
$MnLCl_2 \cdot C_2H_5OH$	Nujol	203vs, 247vs, 278s, 293s, b, 325s-m, 435m-s, sh
	$27 \times 10^{-4} M$ in DMSO	411(52)
$FeLCl_2 \cdot C_2H_5OH$	Nujol	213s, 253s, sh, 278s, sh, 324vs, b, 395vs, b, 546vs, b, 700m-s, sh, 835m, b, 940m, vb
	$2 \times 10^{-4} M$ in CH_3NO_2	492sh(1250), 524(1390), 770(10), 962(18)
$FeLCl_3$	Nujol	210s, 256vs, 279vs, 313vs, b, 375s, b
	$3.4 \times 10^{-4} M$ in DMSO	<400(>1900)
$CoLCl_2 \cdot C_2H_5OH$	Nujol	212s, 244vs, b, 276vs, b, 300vs, sh, 352vs, 370vs, b, 392vs, 419s-vs, b, 616s, 635s, b, 677s, vb, 700s, 1380m, 1450m, sh
	$13 \times 10^{-4} M$ in CH_3NO_2	407(155), 594(176), 647(185), 677(214), 1365sh(29), 1387(40), 1406(50), 1449sh(27)
$NiL_2Cl_2 \cdot H_2O$	Nujol	210vs, 235s, sh, 278s, 324s, b, 380m, sh, 413m, 438m, 576m-w, sh, 950w, 980w, sh
	$6.6 \times 10^{-4} M$ in CH_3NO_2	420(182), 590(10), 630vb(12), 961(26)
$CuLCl_2$	Nujol	209vs, 226s, 241s, b, 281s, b, 333vs, sh, 360vs, b, 718s-m, vb
	$16 \times 10^{-4} M$ in DMSO	741b(87), 757(98)
$ZnLCl_2$	Nujol	221vs, 235vs, sh, 282s, vb, 360m-s

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

TABLE IV. Magnetic Properties (300° K)[a] and Molar Conductivities ($10^{-3} M$ N,N-dimethylformamide Solutions at 25° C) of N-bipyO(L)–Metal Chloride Complexes.

Complex	$10^6\chi_m^{cor}$, cgsu	μ_{eff}, BM	Λ_M, Ω^{-1} cm^2 mol^{-1}
$CrL_2Cl_3 \cdot 4H_2O$	6274	3.88	62
$MnLCl_2 \cdot C_2H_5OH$	15271	6.08	39
$FeLCl_2 \cdot C_2H_5OH$	4950	3.46	28
$FeLCl_3$	13727	5.76	70
$CoLCl_2 \cdot C_2H_5OH$	9002	4.67	28
$NiL_2Cl_2 \cdot H_2O$	4647	3.34	59
$CuLCl_2$	1642	1.99	b
$ZnLCl_2$	Diamagnetic	–	13

[a] Magnetic susceptibilities were determined by the Faraday method. [b] Insoluble in most organic solvents.

ν_{FeCl} modes in the $[Fe(N\text{-bipyO})_2Cl_2]^+$ complex cation,[17,18] and the fact that this complex behaves as a 1:1 electrolyte in DMF.[30]

$NiCl_2$ forms a 1:2 complex with N-bipyO, but the rest of the MCl_2 complexes investigated involve 1:1 molar ratios. It is noteworthy in this connection that hexacoordinated $[ML_2X_2]$ chelates with bipy and phen (X = halide ion) are easily prepared by conventional synthesis,[33] while the tetracoordinated $[MLX_2]$ chelates with these ligands are scarcer and generally ob-

TABLE V. Main Bands in the X-ray Powder Diffraction Patterns of N-bipyO(L)–Metal Chloride Complexes.[a]

Complex	*d* Spacings, Å (I in parentheses)
$CrL_2Cl_3 \cdot 4H_2O$	10.04(22), 8.04(19), 6.02(19), 4.17(100), 3.78(19), 3.53(14), 3.31(14), 3.08(30), 2.28(50)
$MnLCl_2 \cdot C_2H_5OH$	9.81(16), 9.40(11), 8.26(30), 8.11(20), 5.57(25), 4.72(43), 4.62(39), 3.74(27), 3.20(100), 2.67(36), 2.64(27), 2.33(43)
$CuLCl_2$	9.28(4), 7.96(34), 5.68(7), 4.55(30), 3.93(9), 3.75(7), 3.65(17), 3.28(100), 3.14(12), 2.63(14), 2.47(15), 2.29(20), 1.92(9)
$ZnLCl_2$	10.04(6), 8.34(13), 8.19(16), 7.69(7), 7.25(5), 5.90(26), 5.27(31), 5.09(22), 4.95(11), 4.19(100), 3.86(17), 3.77(25), 3.71(22), 3.29(75), 3.17(23), 2.98(17), 2.95(22), 2.37(11), 2.30(10), 1.99(15)

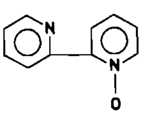
[a] The Fe(II), Fe(III), Co(II) and Ni(II) complexes are amorphous.

tained by thermal decomposition of tris- or bis-bipy or phen chelates.[33,34] It is, thus, of interest that N-bipyO forms 1:1 complexes with most of the M(II) chlorides investigated and with $FeCl_3$ under conventional synthetic conditions. The Ni(II) complex appears to be hexacoordinated on the basis of the low frequency ir[2,8,13–15,35] and electronic spectral evidence (*vide infra*). Although this compound behaves as a 1:1 electrolyte in DMF, other evidence suggests that it is a neutral complex of the type $[Ni(N\text{-}bipyO)_2Cl_2] \cdot H_2O$ in the solid state, and dissociates in DMF to yield cationic species such as $[Ni(N\text{-}bipyO)_2Cl(DMF)]^+$ or $[Ni(N\text{-}bipyO)_2Cl(OH_2)]^+$. In fact, Harris and McKenzie report similar behavior upon dissolution for neutral complexes of the type $[NiL_2X_2]$, where L = bipy or phen, and X = Cl, Br, I, NCS, *etc.*[36].

The Cu(II) complex is insoluble or very sparingly soluble in organic solvents and a conductivity measurement was not possible. Its solubility characteristics may be taken as suggestive of a bi- or poly-nuclear structure. This is substantiated by the positions of the ν_{CuX} (X = O, N, Cl) bands[2,8,13–15,35] and the fact that the electronic spectrum of this complex is compatible with a hexacoordinated configuration (*vide infra*). The rest of the new complexes (Mn(II), Fe(II), Co(II) and Zn(II)) behave as nonelectrolytes in DMF, and their far-ir spectra are suggestive of coordination numbers lower than six. Actually, this evidence favors tetracoordinated structures based on the following evidence. The bands assigned as $\nu_{M\text{–}Cl}$ (M = Mn, Co, Zn) modes occur at about the same frequencies as the corresponding absorptions in tetrahedral complexes of these metal chlorides,[8,16] whereas ν_{FeCl} appears at a higher frequency than ν_{FeCl} in the tetrachloroferrate(II) anion.[37] Electronic spectral evidence is also in support of tetracoordinated configurations as discussed below. Finally, the X-ray powder patterns of the crystalline complexes (Cr(III), Mn(II), Cu(II) and Zn(II); *cf.* Table V) are distinctly different from one another. Among these complexes, only those of Cu(II) and Zn(II) are isostoichiometric; the difference in their X-ray patterns lends additional support to our assignments, *i.e.*, a polynuclear, hexacoordinated structure for the Cu(II) complex, and a tetrahedral, monomeric configuration for the Zn(II) compound.

Electronic Spectra and Magnetic Moments

The uv spectrum of N-bipyO exhibits two main peaks at 239 and 281 nm (Table III) due to $\pi \rightarrow \pi^*$ transitions[38] and two shoulders at higher wavelengths (probably due to $n \rightarrow \pi^*$ transitions[39]). The $\pi \rightarrow \pi^*$ bands undergo considerable shifts and splittings upon metal complex formation (Table III). These shifts and splittings were previously interpreted in terms of a change in the configuration of N-bipyO from the *trans*-form (II) in the free ligand[5] to the *cis*-form (I) upon complexation.[2]



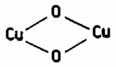
(II)

As is the case with N,N-bipyO$_2$[13,40] and bipy[38,41] metal chelates, the chelated N-bipyO molecules involve twisting to a certain extent of the two aromatic rings about the 2,2'-bond.[2] The electronic spectra of the new N-bipyO metal chelates are characterized by strong metal-to-ligand charge-transfer bands (Table III), as is also the case with the corresponding 3*d* metal perchlorate[2] and nitrate[3] chelates, as well as bipy[42–45] and aromatic amine N-oxide metal complexes.[46,47] These charge-transfer bands are responsible for the more intense than usual colors of the manganous, ferrous and ferric chloride–N-bipyO complexes. They also mask or interfere with several low wavelength (*d–d*) transitions, such as those of the tetrahedral $[FeCl_4]^-$ anion and Mn(II) complex,[48] the $^4A_{2g}(F) \to {}^4T_{1g}(F)$ transition of the Cr(III) complex, and the $^3A_{2g}(F) \to {}^3T_{1g}(P)$ transition of the Ni(II) complex[44,49] (based on pure O_h symmetry).

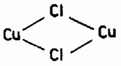
The *d–d* band spectra of the Cr(III) and Ni(II) complexes are consistent with the hexacoordinated configurations postulated (*vide supra*). The broad character of the $^4A_{2g}(F) \to {}^4T_{2g}(F)$ transition in the Cr (III) complex (635 nm) and the splitting of the $^3A_{2g}(F) \to {}^3T_{2g}(F)$ transition in the Ni(II) complex (950, 980 nm; $^3A_{2g}(F) \to {}^3T_{1g}(F)$ occurs as a shoulder at 576 nm) are typical of low symmetry hexacoordinated configurations for these complexes.[50] The magnetic moments (Table IV) are also within the range of values reported for low symmetry, high-spin, hexacoordinated Cr(III) and Ni(II) metal complexes.[2,32,50,51] The magnetic moments of the Mn(II), Fe(III), Co(II) and Cu(II) complexes are also normal for high-spin compounds of these metal ions, while that of the Fe (II) complex is subnormal.[32] It is of interest to note that Fe(bipy)Cl_3, which is presumably of the same type as its N-bipyO analog[32] (*vide supra*), is of the high-spin type,[32,52] while $[Fe(N\text{-bipyO})_3](ClO_4)_3 \cdot 2H_2O$ (μ_{eff} = 3.66 BM at 300° K) is characterized by spin-free (S = 5/2)–spin-paired (S = 1/2) equilibria.[2] On the other hand, the Fe(II) complex exhibits a μ_{eff} (3.46 BM) suggestive of the presence of two unpaired electrons (S = 1). Since $[Fe(N\text{-bipyO})_3](ClO_4)_2$ is a high-spin complex[2] the spin-pairing observed in Fe(N-bipyO)$Cl_2 \cdot C_2H_5OH$ is more likely due to the stereochemistry of the complex rather than the strength of the N-bipyO ligand. In fact, several square-planar ferrous complexes with half-quenched spin involving both strong (phthalocyanine, diethylphenylphosphine)[53] and weaker (2,6-lutidine N-oxide)[7b] ligands have been reported. N-bipyO is a stronger ligand towards O_h M(II) or M(III) ions than 2,6-lutidine N-oxide (the spectrochemical series bipy > N-bipyO > 2,6-lutidine N-oxide > N,N-bipyO_2 has been previously established),[2] but not strong enough to induce spin-pairing in $[Fe(N\text{-bipyO})_3]^{2+}$.[2] Hence, a square planar configuration for the $FeCl_2$ complex is the most compatible with the overall evidence. The location of the lowest energy *d–d* band (940 nm) is also in agreement with a square planar configuration. This band does not occur at a lower energy than that anticipated for the higher energy component of the split $^5T_{2g} \to {}^5E_g$ transition in low symmetry hexacoordinated Fe(II) complexes with ligands of strength similar to the N-bipyO and chloro ligands[54] (*e.g.*, hexacoordinated Fe(phen)$_2Cl_2$, which involves a substantially stronger ligand than N-bipyO, shows two *d–d* bands at 951 and 1181 nm[55]). Likewise, the square planar $[FeL_4](ClO_4)_2$ complex with 2,6-lutidine N-oxide exhibits the *d–d* transition at a substantially higher energy (961 nm)[7b] than the *d–d* bands in $[FeL_6](ClO_4)_2$ complexes with other pyridine N-oxides (above 1050 nm).[50,51a] The lower frequency ir evidence also favors a tetracoordinated configuration, as previously discussed. On the other hand, temperature dependence studies of the magnetic susceptibility of the new Fe(II) complex, recently performed by Professor A.B.P. Lever's laboratory (York University, Toronto, Ont., Canada; for a description of the fully automated Faraday magnetic balance system used see ref. 56), gave the following results (each set of three numbers gives the temperature (°K), $10^6\chi_M$(cgsu) and (in italics) the μ_{eff}(BM) values):
302.3, 4890, *3.44*; 287.8, 5085, *3.42*; 270.8, 5345, *3.40*; 257.5, 5578, *3.39*; 239.2, 5929, *3.37*; 221.4, 6318, *3.35*; 211.5, 6591, *3.34*; 198.1, 6980, *3.33*; 185.8, 7396, *3.32*; 169.1, 8032, *3.30*; 151.0, 8849, *3.27*; 134.1, 9848, *3.25*; 117.2, 11133, *3.23*; 100.3, 12833, *3.21*; 85.8, 14647, *3.17*.
These data (μ_{eff} increase of 0.27 BM in the 86–302° K temperature range) favor a S = 1 spin state. In fact, in square planar,[53,57] as well as octahedral[58] ferrous complexes with a half-quenched spin, μ_{eff} increases of 0.1–0.4 BM have been observed in the same temperature range. Whereas, in ferrous complexes involving spin-free (S = 2)–spin-paired(S = 0) equilibria ($^5T_2$–$^1A_1$ crossover), magnetic moment increases of 2.0–4.5 BM are almost invariably observed in the 80–300° K region.[59] One exception is $[Fe(bipy)_2(NCSe)_2]$, which is a 2:1 mixture of the spin-paired and spin-free isomers and shows a magnetic moment increase of 0.41 BM in the same temperature range[60]. Thus, the formulation of the Fe(II) complex as $[Fe(N\text{-bipyO})Cl_2] \cdot C_2H_5OH$, involving a square planar $FeONCl_2$ moiety, but an overall symmetry lower than D_{4h}, with a half-quenched spin (S = 1) is justified on the basis of the overall evidence.

For the Co(II) complex the electronic spectrum ($^4A_2(F) \to {}^4T_1(P)$ split into four bands at 616–700 nm and $^4A_2(F) \to {}^4T_{1g}(F)$ at 1380 and 1450 nm; ε_{max} in the solution spectrum up to 214 for the former and up to 50 for the latter transition[49,54]) and magnetic moment (4.67 BM)[32] are suggestive of a pseudotetrahedral configuration. On the basis of this evidence and the lower frequency ir data previously discussed, the Co (II), Mn(II) and Zn(II) complexes are characterized as pseudotetrahedral and formulated as follows: $[M(N\text{-bipyO})Cl_2] \cdot C_2H_5OH$ (M = Mn, Co) and $[Zn(N\text{-bipyO})Cl_2]$. Finally, the Cu(II) complex appears to be polynuclear and hexacoordinated on the basis of the ir evidence (*vide supra*). This assignment is supported by the electronic spectral evidence. In fact, the *d–d* band, which occurs at 718 nm, is observed at considerably lower energy than that of the tetracoordinated $[Cu(N\text{-bipyO})_2](ClO_4)_2$ complex (maximum at 586 nm).[2] Moreover, the corresponding 1:1 $CuCl_2$–phen complex which was also considered as polynuclear and hexacoordinated, exhibits a broad *d–d* band at

690 nm.[61] Hence, the polynuclear structure $[Cu(N\text{-}bipyO)Cl_2]_x$ seems to be most likely for the new Cu (II) complex. The normal magnetic moment of this compound (1.99 BM) is in favor of the presence of chloride ion rather than N-bipyO bridges.[62] In fact, bridges of the type



in Cu(II) complexes with uni- or bi-dentate aromatic amine N-oxide ligands lead almost invariably to subnormal magnetic properties owing to magnetic exchange between neighboring Cu^{2+} ions.[14,62,63] Two magnetically normal,[64] N-oxide bridged 1:2 $Cu(NO_3)_2$ binuclear complexes with the pyridine and quinoline N-oxides, involving a tetragonal pyramidal symmetry,[65] and a triplet ground state,[66] are the only exceptions reported. On the other hand



bridges in Cu(II) complexes with the same ligands lead generally to normal paramagnetism.[14,62,63] The latter possibility is considered as more likely for $[Cu(N\text{-}bipyO)Cl_2]_x$, in view of its normal μ_{eff}, and since the presence of both terminal and bridging chloride ligands in this complex is also suggested by ν_{CuCl} bands at 298 (terminal) and 240 (bridging) cm^{-1}.[15,67] A bi- or poly-nuclear structure involving N-oxide bridges would undoubtedly lead to subnormal paramagnetism. In fact, although there is the precedent of the magnetically normal, N-oxide-bridged, Cu(II) nitrate complexes mentioned above, $[Cu(N,N\text{-}bipyO_2)Br_2]$ reportedly exhibits a subnormal magnetic moment, and is N-oxide-bridged.[62] Hence, if the corresponding N-bipyO–$CuCl_2$ complex involved bridging of the same type, it would be certainly expected to show a subnormal μ_{eff}.

Note Added on July 27, 1975

At the suggestion of two referees the possibility of removal of the lattice ethanol or water from the new complexes, by heat treatment under reduced pressure, was explored. Ethanol is indeed easily removed from the Mn(II), Fe(II) and Co(II) complexes by treatment at 65° C and 60 mm Hg for 24 hr. In fact, the ir spectra of the treated chelates do not any more exhibit the ν_{OH} mode of lattice ethanol, while the rest of the ir bands of these complexes were not affected by this treatment. In contrast, similar treatment of the hydrated chelates(Cr(III), Ni(II)) leads to only small decreases (by 20–30%) of the intensity of the ν_{OH} (water) absorptions. The water of crystallization appears, thus, to be held rather tenaciously in these chelates. Strong association of lattice water is common in metal chelates of bipy and other α,α-diimines.[26,28,68–70]

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