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Chromium(III) and Iron(III) Perchlorate Chelates with the Mono-N-Oxides of 2,2′-Bipyridine and 1,10-Phenanthroline

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2,2′-bipyridine- and 1,10-phenanthroline-mono-N-oxide (bipyNO and phenNO, respectively) chelates with Cr(III) and Fe(III) perchlorates were synthesized and characterized by means of spectral, magnetic and conductance studies. The new complexes are of the types $[M(bipyNO)_3](ClO_4)_3 \cdot 2H_2O$ *and* $[M(phenNO)_3](ClO_4)_3$ *(M = Cr, Fe). The mono-N-oxides act as bidentate O,N-chelating agents. The bipyNO complexes contain lattice water. The UV bands of bipyNO exhibit larger shifts and splittings than those of phenNO, upon metal complex formation. BipyNO exists in the trans-form in the crystal and assumes a configuration close to the cis-form in its metal chelates, whereas free phenNO is rigidly held in the cis-form in the crystal, and has the same conformation in its chelates. The electronic spectra of the complexes are characterized by strong metal-to-ligand charge-transfer bands. Approximate Dq parameter calculations for the Cr(III) complexes indicate that bipyNO and phenNO are weaker ligands than the parent bases and stronger ligands than the corresponding N,N-dioxides. The Cr(III) complexes are magnetically normal, but the Fe(III) compounds exhibit temperature-dependent magnetic moments (3.02–3.67 BM for the bipyNO acid, 1.98–2.52 BM for the phenNO complex, over the temperature range 80–313° K), which were attributed to the existence of spin-free–spin-paired equilibria.*

Introduction

Recent work at this laboratory dealt with the synthesis and characterization of divalent 3d metal perchlorate chelates with the mono-N-oxides of 2,2′-bipyridine (bipyNO)[1] and 1,10-phenanthroline (phenNO).[2] These studies have now been extended to include the corresponding Cr(III) and Fe(III) complexes of the above ligands, reported in the present paper. Aside from this laboratory's work,[1,2] the only complexes of the above ligands reported in the literature are Co(II), Ni(II) and Cu(II) chloride–phenNO chelates[3] and salts of both bipyNO[4] and phenNO[5] with mineral acids. In addition, complex formation between Fe^{3+} and bipyNO has been detected in solution.[6]

Experimental

Chemicals

BipyNO and phenNO were prepared by the methods of Murase[6] and Corey *et al.*,[3] respectively, and their authenticity checked by means of elemental analyses and examination of their melting points (bipyNO 57–58° C,[6,7] phenNO 180–181° C[3,8]) and ir spectra.[4,5]. Reagent grade Cr(III) and Fe(III) perchlorates (hydrated), triethyl orthoformate and organic solvents were utilized.

Syntheses

3.2 mmoles of ligand and 1 mmole of metal salt were treated separately in *ca.* 10 ml of a 3/2 (V/V) ethanol–triethyl orthoformate mixture at 50–60° C for 15–20 min under stirring. The ligand and salt solutions were subsequently combined. In the case of phenNO, precipitates formed immediately. The bipyNO complexes precipitated in the form of viscous oils, which were hardened to solids upon anhydrous diethyl ether addition. These solids were ground into fine powders in a mortar under ether. The new complexes were filtered, thoroughly washed with ether and dried in an evacuated desiccator over phosphorus pentoxide. Analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.), given in Table I, suggest that they are of the types $M(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$ and $M(phenNO)_3(ClO_4)_3$ (M = Cr, Fe). These complexes are very sparingly soluble or insoluble in water, ethanol or chloroform, and soluble in nitromethane and dimethylsulfoxide.

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

Infrared (Table II), and electronic (Table III) spectra, magnetic susceptibility (Table III), conductance mea-

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TABLE I. Analytical Data for bipyNO and phenNO–Metal Perchlorate Complexes.

Complex	Color	Analysis							
		C%		H%		N%		Metal %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cr(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	Lilac	39.90	40.59	3.13	3.42	9.31	9.33	5.76	5.75
$Fe(bipyNO)_3(ClO_4)_2 \cdot 2H_2O$	Red–brown	39.73	40.86	3.12	3.48	9.27	9.62	6.16	6.17
$Cr(phenNO)_3(ClO_4)_3$	Light green	46.04	46.66	2.58	3.07	8.95	8.74	5.54	5.07
$Fe(phenNO)_3(ClO_4)_3$	Olive green	45.86	47.12	2.57	3.10	8.91	9.33	5.92	5.71

TABLE II. Pertinent Infrared Data for bipyNO, phenNO and their Cr(III) and Fe(III) Perchlorate Complexes (cm^{-1}).[a]
A. BipyNO Complexes

Compound	ν_{N-O}	δ_{N-O}	ν_{ClO_4} (ν_3, ν_4)	ν_{8a}, ν_{19a} ν_{10b}[b] and γ_{CH}[c]	ν_{M-O}	ν_{M-N}	ν_{Ligand} (450–200 cm^{-1})
bipyNO	1250 s 1232 s	855 vs	–	1575 m 1457 m 765 vs 770 vs	–	–	443 w 401 m–s 340 m 310 w 291 w 279 w 251 w 242 w 221 sh 200 m, b
$Cr(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	1241 m 1200 s	844 s	1075 vs, vb 620 vs	1593 s 1472 vs 769 vs 789 m, sh	412 s	376 m	430 s, sh 391 m–s 349 m 340 m 331 m 320 w, sh 300 w, b 290 m 278 m 266 m 244 m 200 m–w <200 vs
$Fe(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	1236 m 1201 s	850 s 839 s	1070 vs, vb 620 vs	1594 s 1470 s 767 vs 791 m–s	390 vs	359 m, sh	420 m 395 m–s, sh 340 w, sh 319 m–w 305 w 295 w 289 m–s 279 vs 266 m 243 m 220 m–w <200 vs

TABLE II. (Cont.)

B. PhenNO Complexes

Compound	ν_{N-O}	δ_{N-O}	ν_{ClO_4} (ν_3, ν_4)	1650–1540 cm^{-1} region	γ_{CH} modes	ν_{M-O}	ν_{M-N}	ν_{Ligand} (450–200 cm^{-1})
phenNO	1269 s 1249 s	811 sh 808 s	–	1612 w 1590 m 1588 sh 1550 m 1546 sh	854 s 835 vs 722 s 710 vs	–	–	445 w, b 407 sh 397 m 361 m 320 vw 289 m 278 m–s 265 w 241 m 220 m–s 208 m–s
$Cr(phenNO)_3(ClO_4)_3$	1235 m 1205 m	802 sh 798 m	1081 vs 623 vs	1630 w 1603 w 1577 m 1569 m, sh 1556 w, sh	849 vs 719 m 703 s	450 w–m, b	390 m	435 w 420 w–m 408 w 388 m, sh 375 w 366 w 338 w 320 w, b 300 w 280 m 268 w 242 m 222 m–w 208 m–s
$Fe(phenNO)_3(ClO_4)_3$	1258 m 1233 m 1207 m	816 m 796 m	1088 vs 621 s	1630 w 1602 w 1586 w, sh 1576 m 1565 m, sh 1560 m, sh	848 s–vs 723 m 708 s	439 m	386 m	420 m 377 w, sh 345 m 337 w, sh 320 w, b 290 w, sh 279 m–s 267 m 246 m 221 m–w 208 s

Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder. [a] Hexachlorobutadiene (4000–1300 cm^{-1}) and Nujol (1350–200 cm^{-1}) mull spectra. [b] Bands attributed to the pyridine fragment of bipyNO. [c] Bands attributed to the pyridine N-oxide fragment of bipyNO.

surements, and X-ray powder diffraction patterns were obtained by methods described elsewhere.[2,9] Temperature-dependence measurements (Table IV) of the magnetic susceptibility of the ferric complexes were performed by Professor A.B.P. Lever's laboratory, York University, Toronto, Ont., Canada. The molar conductivities of 10^{-3} M nitromethane solutions of the complexes at 25° C are as follows (Λ_M in Ω^{-1} cm^2 $mole^{-1}$): $Cr(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$, 263; $Fe(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$, 266; $Cr(phenNO)_3(ClO_4)_3$, 280; $Fe(phenNO)_3(ClO_4)_3$, 245. The X-ray powder patterns of the bipyNO complexes show that these compounds are amorphous. The phenNO analogs are crystalline, but not isomorphous, and exhibit the following patterns (d spacings in Å; relative intensities in parentheses): $Cr(phenNO)_3(ClO_4)_3$: 10.04(12), 9.93(8), 8.11(11), 5.90(22), 5.79(15), 5.37(26), 4.90(22), 4.09(100), 3.55(89), 3.42(78), 3.39(60), 3.24(45), 2.93(66), 2.44(18). $Fe(phenNO)_3(ClO_4)_3$: 6.23(34), 5.50(28), 4.55(34), 4.41(34), 4.21(68), 4.17(68), 3.98(72), 3.93(66), 3.81(81), 3.62(100), 3.52(68), 3.48(68), 3.40(50), 3.21(44), 3.01(25).

TABLE III. Electronic Spectra and Magnetic Properties (300° K) of Cr(III) and Fe(III) Perchlorate Complexes with bipyNO and phenNO.

Compound	Electronic Spectra		Magnetic Properties	
	Medium	λ_{max} nm(ε max)	χ_M^{cor} cgsu	μ_{eff} BM
bipyNO	Nujol	239 vs	–	–
		281 vs		
		293 sh		
		344 s, sh		
$Cr(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	Nujol	204 vs	5806	3.73
		220 vs, sh		
		224 vs, sh		
		234 vs, sh		
		245 s–vs		
		259 s–vs		
		282 s–vs		
		317 vs, vb		
		340 s–vs, sh		
		378 s, sh		
		456 m, sh		
		512 m, sh		
		551 m		
	$76 \times 10^{-5} M$ in CH_3NO_2	<400(>600)		
		459 sh(128)		
		500(79)		
		543 sh(50)		
		604 sh(16)		
$Fe(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	Nujol	205 vs	5565	3.66
		222 s, sh		
		265 vs, sh		
		274 vs, b		
		320 vs, vb		
		355 vs, vb		
		465 s, vb, sh		
	$25 \times 10^{-5} M$ in CH_3NO_2	<400(>2700)		
		480(2090)		
		512(2070)		
phenNO	Nujol	216 vs		
		243 vs		
		274 vs		
		325 s, b, sh		
		380 m–s, sh		
		434 m, sh		
$Cr(phenNO)_3(ClO_4)_3$	Nujol	207 vs	5982	3.79
		222 vs		
		240 s		
		288 vs, b		
		336 s, sh		
		371 s		
		398 s, sh		
		527 m, b		
	$66 \times 10^{-5} M$ in DMSO	<400(>700)		
		505 sh(47)		
$Fe(phenNO)_3(ClO_4)_3$	Nujol	218 s, sh	2565	2.51
		248 vs		
		284 vs, b		
		312 s, sh		
		378 s, b, sh		
	$35 \times 10^{-5} M$ in DMSO	377(2330)		
		610 sh(330)		

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

TABLE IV. Magnetic Susceptibility Variation with Temperature for the Ferric Perchlorate Complexes with bipyNO and phenNO.

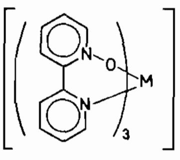
Complex	Temp. °K	$10^6\chi_g$ cgsu	$10^6\chi_m$ sgsu	μ_{eff} BM
$Fe(bipyNO)_3(ClO_4)_3 \cdot 2H_2O$	80.2	15.16	14198	3.02
	85.0	14.69	13771	3.06
	101.2	12.68	11944	3.10
	118.5	11.12	10533	3.16
	135.4	10.02	9537	3.21
	152.4	9.18	8774	3.27
	170.1	8.47	8126	3.33
	187.7	7.90	7612	3.38
	205.8	7.41	7164	3.44
	224.0	6.97	6765	3.48
	242.5	6.60	6433	3.53
	260.4	6.27	6133	3.57
	278.8	5.96	5850	3.61
	297.2	5.70	5617	3.66
	312.6	5.44	5384	3.67
$Fe(phenNO)_3(ClO_4)_3$	81.4	5.92	6025	1.98
	98.3	5.16	5304	2.04
	111.2	4.67	4846	2.08
	127.6	4.18	4388	2.12
	144.7	3.81	4035	2.16
	162.8	3.50	3745	2.21
	178.9	3.26	3515	2.24
	195.5	3.04	3306	2.27
	211.2	2.91	3182	2.32
	229.1	2.75	3036	2.36
	247.3	2.60	2890	2.39
	265.7	2.46	2764	2.42
	283.8	2.35	2659	2.46
	297.4	2.33	2641	2.51
	301.7	2.26	2576	2.49
	313.3	2.22	2535	2.52

Discussion

Infrared and Conductance Data

The molar conductivities of the new complexes in nitromethane are characteristic of 1:3 electrolytes.[10] The infrared spectra of the complexes suggest that the perchlorate is also exclusively ionic in the solid state.[11] In fact, the ν_3 and ν_4 vibrational modes of ionic (T_d) ClO_4 appear as single bands in the spectra of these complexes, while ν_1 is ir-inactive[11] (Table II). The phenNO complexes are devoid of ir bands associated with ν_{OH} and δ_{H-O-H} (water) modes. The bipyNO complexes exhibit strong ν_{OH} absorption at 3600–3450 cm^{-1} (Cr(III) complex: 3610 sh, 3575 s, 3540 s, 3515 s, 3478 s, sh, 3450 m, sh; Fe(III) complex: 3620 sh, 3580 s, 3540 s, b, 3510 s, b, 3460 s–m, b, sh) and weak to medium δ_{H-O-H} bands at 1670–1660 and *ca.* 1630 cm^{-1}. Furthermore, the ν_3 and ν_4 (ClO_4) bands in the bipyNO complexes are broader than the corresponding absorptions in the phenNO complexes. The ir evidence is in favor of the presence of lattice watter[2,12] rather than coordinated aquo ligands.[13] In fact 1,10-phenanthroline metal complexes, involving coordinated water, reportedly exhibit the ν_{OH} bands at 3325–3200 cm^{-1}, and bands attributable to the rocking mode of the coordinated aquo ligand[14] at 1000–700 cm^{-1}.[13] The ir spectra of the $M(ClO_4)_3$(M = Cr, Fe)–bipyNO complexes in the latter region are virtually identical to those of the water-free $[M(bipyNO)_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Zn) and $[Cu(bipyNO)_2](ClO_4)_2$ chelate, previously reported.[1]

The free ligands exhibit two ν_{N-O} bands in the 1300–1200 cm^{-1} region.[4,5] These bands are shifted towards lower frequencies upon metal complex formation (Table II); this is suggestive of coordination through the N–O oxygen.[1,2,15,16] The δ_{N-O} ligand mode also exhibits small shifts in the spectra of the metal complexes, as expected.[1,2,15,16] Coordination through the nitrogen atom of the pyridine fragment of the ligands is suggested by frequency shifts of several ir bands associated with vibrations of this fragment[1,2,4,5,17–19] (examples are shown in Table II). In the lower frequency infrared region metal-sensitive bands were tentatively assigned to ν_{M-O} and ν_{M-N} modes (Table II); these assignments were based on our previous work,[1,2] and ir studies of Cr(III) and Fe(III) chelates with 2,2′-bipyridine, 1,10-phenanthroline[20] and 2,2′-bipyridine N,N-dioxide.[16] The overall ir spectral and conductance evidence suggests that the new complexes are of the types $[M(bipyNO)_3](ClO_4)_3 \cdot 2H_2O$ and $[M(phenNO)_3](ClO_4)_3$ (M = Cr, Fe), involving tris-chelate complex cations; bipyNO and phenNO act as bidentate O,N-chelating agents, forming six-membered chelate rings (I and II, respectively). $[ML_3]^{3+}$ complex cations are also common in the cases of 2,2′-bipyridine, 1,10-phenanthroline[21,22] and 2,2-bipyridine N,N-dioxide[16,23] complex with Cr(III) and Fe(III) salts.



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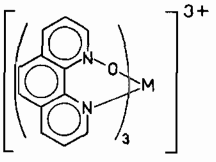

II

Electronic Spectra and Magnetic Moments

The Cr(III) complexes are magnetically normal (Table III) as is generally the case with monomeric, hexacoordinated compounds of this metal ion.[24] The Fe(III) compounds, however, show μ_{eff} values intermediate between those reported for high-spin and low-spin ferric complexes.[24] $[FeL_3](ClO_4)_3$ complexes are of the low-spin type for L = 2,2′-bipyridine or 1,10-phenanthroline (μ_{eff} = *ca.* 2.40 BM)[22,25] and of the high-spin type for L = 2,2′-bipyridine N,N-dioxide

(μ_{eff} = 6.13 BM).[16] The mono-N-oxides under study are stronger ligands than the corresponding N,N-dioxides and weaker ligands than the parent bases[1,2] (see also below). The room temperature magnetic moments (2.51–3.66 BM) of the ferric chelates may be interpreted in terms of either spin-free(S = 5/2)–spin-paired (S = 1/2) equilibria ($^6A_1$–$^2T_2$ crossover situation)[26,27] or the existence of a ^3T ground state involving three unpaired electrons (S = 3/2) and a strongly tetragonally distorted octahedral symmetry.[28] The data of Table IV demonstrates that we have a case of spin-free–spin-paired equilibria in the complexes under discussion. In fact, μ_{eff} variations with temperature shown in Table IV indicate that the new ferric complexes behave in the same manner as the corresponding N,N-dialkyldithiocarbamato chelates, which reportedly involve equilibria of this type.[26] In the latter complexes, μ_{eff} substantially increases (up to 2.5 BM) as the temperature is increased from 85° K to 315° K,[26] while in the case of ferric complexes with a half-quenched spin (S = 3/2), μ_{eff} is relatively insensitive (increases of about 0.1 BM) to temperature variation, in the same temperature range.[28,29] It should be noted that in the case of ferric N,N-dialkyldithiocarbamates the possibility of existence of a mixed-spin state of variable character, instead of the simultaneous existence of two almost equienergetic ground states, has been advanced,[30a] but not as yet substantiated by unequivocal experimental evidence.[30b]

The ultraviolet (200–350 nm) spectra of the free ligands are characterized by two or three strong bands, which are due to $\pi \rightarrow \pi^*$ transitions,[1,2,31,32] and shoulders at lower energies (probably due to $n \rightarrow \pi^*$ transitions[32]) (Table III). The $\pi \rightarrow \pi^*$ transitions of bipyNO undergo larger shifts and splittings than the corresponding phenNO bands, upon metal complex formation (Table III).[1,2] This is largely due to the fact that bipyNO, as is also the case with 2,2′-bipyridine,[21,31,33,34] apparently exists in the *trans*-form in the crystal[4], but assumes a configuration, which is of necessity close to that of the *cis*-form in its metal chelates.[1] This configuration involves twisting to a certain extent of the two aromatic rings about the 2,2′-bond.[16,21,31,34] PhenNO, on the other hand, would be expected to be rigidly held in the *cis*-configuration in the crystal and function as an essentially planar chelating agent,[2,5] as is also the case with 1,10-phenanthroline.[21,31,35] It should be mentioned at this point that several geometrical and optical isomers, and, in the case of bipyNO, which is probably non-planar, diastereoisomers of the new metal chelates are possible.[36–38] No attempts at establishing the existence of isomeric forms of these complexes were made during the present work.

Aromatic diimine[21,31,39–42] and amine-N-oxide[43,44] transition metal complexes are generally characterized by strong metal-to-ligand charge-transfer bands in the UV and part of the visible spectrum. As is the case with divalent 3d metal perchlorate chelates with bipyNO[1] and phenNO[2], the new complexes reported exhibit strong metal-to-ligand charge-transfer absorptions (Table III), which are responsible for the color of the ferric complexes. These bands overlap with the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition (in pure O_h symmetry) in the spectra of the Cr(III) complexes. The $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition is probably split (512,551 nm) in $[Cr(bipyNO)_3](ClO_4)_3 \cdot 2H_2O$, but appears as a single band (521 nm) in the Cr(III)–phenNO chelate. The highest possible symmetry in the new cationic complexes is C_3; if a pure O_h symmetry was assumed, the Dq parameter for phenNO towards octahedral Cr(III) would be 1919 cm^{-1}. The corresponding Dq value for bipyNO would be in the 1800–1900 cm^{-1} region. The position of the new ligands in the spectrochemical series, relative to 1,10-phenanthroline and 2,2′-bipyridine N,N-dioxide is (for octahedral Cr(III)): 1,10-phenanthroline (Dq = 2350 cm^{-1})[37] > phenNO > bipyNO > 2,2′-bipyridine N,N-dioxide (Dq = 1495–1585 cm^{-1}).[23] As already mentioned, 2,2′-bipyridine N,N-dioxide forms a high-spin $[FeL_3]^{3+}$ complex,[16,23] and 1,10-phenanthroline or 2,2′-bipyridine form low-spin $[FeL_3]^{3+}$ complexes.[22,25] The existence of spin-free–spin-paired equilibria in the mono-N-oxide ferric complexes was, therefore, expected, especially in view of the intermediate strength of these ligands, relative to the parent bases and the corresponding N,N-dioxides, and the fact that similar behavior has been reported for cationic Fe(III) complexes with weaker ligands (Dq towards octahedral Cr(III): N,N-diethyl-dithiocarbamate 1560 cm^{-1};[45] 2,6-lutidine N-oxide 1686 cm^{-1} [9]) than the mono-N-oxides under study.[26,27]

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