extracted with methylene chloride. The extracts were stripped to dryness, and the residue was stirred with acetone, filtered, and dried, yielding 20.7 g (74%) of dichloro[3,6-bis(dipropylaminomethyl)-1,2-phenylene]dipalladium(II).

The identities of the two products were confirmed by conversion to the isomeric 2,2,6,6-tetramethyl-3,5-heptanedionato derivatives (see Table III).

The method used for preparing these and other derivatives listed in Table III consisted, in general, of warming a solution or suspension of the chloropalladio derivative with a slight excess of the chelating ligand (either as Tl or diisopropylethylammonium salt) in DMF for several hours, diluting with water, and extracting the product with methylene chloride. The products were purified by chromatography on alumina.

Crystallographic Data on 3,6-Bis(diethylaminomethyl)phenylenebis(2,4-pentanedionatopalladium) (14). Crystals of **14** are monoclinic with $a = 13.74$ Å, $b = 11.3$ Å, $c = 20.66$ Å, and $\beta = 118.8°$. The space group is $P2_1/c$ and there are four molecules per cell. The calculated density on this basis is 1.55 g/cm³. The observed density (flotation in a carbon tetrachloride–bromobenzene mixture) is also 1.55 g/cm³. There is no space group imposed molecular symmetry.

Registry No. *p*-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39022-99-6; *m*-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39023-00-2; *o*-$(CH_2)_4NCH_2C_6H_4CH_2N(CH_2)_4$, 39023-01-3; *m*-$Et_2NCH_2C_6H_4CH_2NEt_2$, 39023-02-4; *p*-$Pr_2NCH_2C_6H_4CH_2NPr_2$, 39023-03-5; Na_2PdCl_4, 13820-53-6; $[2\text{-}(Me_2NCH_2)C_6H_4PdL_2]$ L = AcAc, 39046-23-6; $[2\text{-}(Me_2NCH_2)C_6H_4PdL_2]$ L_2 = EAc, 39046-24-7; $[2\text{-}(Me_2NCH_2)C_6H_4PdL_2]$ L_2 = PIP, 39046-25-8; $[2\text{-}(Et_2NCH_2)C_6H_4PdL_2]$ L_2 = $(pyridine)_2PF_6$, 39151-88-7; $[2\text{-}(Et_2NCH_2)C_6H_4PdL_2]$ L_2 = DPM, 39046-26-9; $[2\text{-}(Me_2NCH_2)C_6H_4PdL_2]PF_6$ L = pyridine, 39046-30-5; $[3,6\text{-}(Et_2NCH_2)\text{-}1,2\text{-}C_6H_4(PdL_2)_2]$ L = DPM, 33394-24-0; $[3,6\text{-}(Et_2NCH_2)\text{-}1,2\text{-}C_6H_4(PdL_2)_2]$ L = TPL, 39046-32-7; $[3,6\text{-}(Pr_2NCH_2)\text{-}1,2\text{-}C_6H_4(PdL_2)_2]$ L = DPM, 39046-33-8; $[4,6\text{-}(Et_2NCH_2)\text{-}1,3\text{-}C_6H_4(PdL_2)_2]$ L = AcAc, 33394-25-1; $[4,6\text{-}(Et_2NCH_2)\text{-}1,3\text{-}C_6H_4(PdL_2)_2]$ L = TPL, 39046-35-0; $[4,6\text{-}(Et_2NCH_2)\text{-}1,3\text{-}C_6H_4(PdL_2)_2]$ L = pyridine, 33461-17-5; $[2,5\text{-}(Me_2NCH_2)\text{-}1,4\text{-}C_6H_4(PdL_2)_2]$ L = AcAc, 39046-36-1; $[2,5\text{-}(Et_2NCH_2)\text{-}1,4\text{-}C_6H_4(PdL_2)_2]$ L = AcAc, 33394-21-7; $[2,5\text{-}(Et_2NCH_2)\text{-}1,4\text{-}C_6H_4(PdL_2)_2]$ L = DPM, 39046-27-0; $[2,5\text{-}(Et_2NCH_2)\text{-}1,4\text{-}C_6H_4(PdL_2)_2]$ L = TPL, 39046-28-1; $[2,5\text{-}(Pr_2NCH_2)\text{-}1,4\text{-}C_6H_4(PdL_2)_2]$ L = DPM, 39046-29-2; 2-(1-pyrazolyl)phenylpalladium(II) chloride dimer, 39046-05-4; 2-(diethylaminomethyl)-4-methylphenylpalladium(II) chloride dimer, 39046-06-5; 2-(diethylaminomethyl)phenylpalladium(II) chloride dimer, 33571-42-5; 2-(dipropylaminomethyl)phenylpalladium(II) chloride dimer, 39046-08-7; 2-(*N*-*tert*-butylformimidoyl)phenylpalladium(II) chloride dimer, 39046-09-8; [2-(2-pyridyl)phenyl](tri-*p*-tolylphosphine)palladium(II) chloride, 39046-10-1; bis(benzylmethyl sulfide)palladium(II) dichloride, 39003-76-4; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(1-pyrazolyl)phenylpalladium(II), 29190-53-2; 1-(ethoxy-1,3-butanedionato)-2-(1-pyrazolyl)phenylpalladium(II), 39046-12-3; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(2-pyridyl)phenylpalladium(II), 39046-13-4; (2,2,6,6-tetramethyl-3,5-heptanedionato)-2-(3,5-dimethyl-1-pyrazolyl)phenylpalladium(II), 39046-14-5; (2,2,6,6-tetramethyl-3,5-heptanedionato)-8-(dimethylamino)naphthylpalladium(II), 39046-15-6; tetrakis(pyridine)palladium(II) bis(hexafluorophosphate), 39003-77-5; bis(pyridine)[2-(1-pyrazolyl)phenyl]palladium(II) hexafluorophosphate, 39046-16-7; bis(pyridine)[2-(diethylaminomethyl)-4-methylphenyl]palladium(II) hexafluorophosphate, 39046-17-8; dichlorobis(3,5-dimethyl-1-phenylpyrazole)palladium, 39003-78-6; bis(pyridine)[2-(3,5-dimethyl-1-pyrazolyl)phenyl]palladium(II) hexafluorophosphate, 39046-18-9; bis[(2-dimethylaminomethyl)phenyl]palladium(II), 23626-48-4; (2-dimethylaminomethylphenyl)(2-pyrazolylphenyl)palladium(II), 39046-20-3; dichloro-3,6-bis(diethylaminomethyl)-1,2-phenylenedipalladium(II), 33247-34-6; dichloro-2,5-bis(diethylaminomethyl)-1,4-phenylenedipalladium(II), 33247-33-5; *μ*-chloro-[3,6-bis(diethylamino)-1,2-phenylene]bis(pyridine)dipalladium(II) hexafluorophosphate, 33394-22-8; dichloro[3,6-bis(dipropylaminomethyl)-1,2-phenylene]dipalladium(II), 39046-45-2; dichloro[2,5-bis(dipropylaminomethyl)-1,4-phenylene]dipalladium(II), 39046-46-3; 3,6-(diethylaminomethyl)phenylenebis(2,4-pentanedionatopalladium(II), 33394-23-9.

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2,2′-Bipyridine *N*-Oxide Chelates with Divalent 3d Metal Perchlorates

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Received October 3, 1972

Transition metal perchlorate chelates with the mono-*N*-oxide of 2,2′-bipyridine (*N*-bipyO) were synthesized and characterized by means of spectral (ir–electronic), magnetic, and conductance studies. The new chelates are of the types $[M(N\text{-bipyO})_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Zn) and $[Cu(N\text{-bipyO})_2](ClO_4)_2$, involving respectively hexa- and tetracoordinated complex cations. *N*-bipyO acts as a bidentate O,N-chelating agent and assumes a configuration close to that of the cis form in the new complexes. Each coordinated ligand molecule involves twisting of the two aromatic rings about the 2,2′ bond. In the uv–visible spectra of the complexes, ligand, charge-transfer, and d–d bands are observed. The calculated spectrochemical parameters for the new metal chelates suggest that *N*-bipyO is a stronger ligand than 2,2′-bipyridine *N,N*-dioxide and weaker ligand than 2,2′-bipyridine. The latter ligand forms a spin-paired cationic ferrous complex of the type $[FeL_3]^{2+}$, but the *N*-bipyO analog is spin free; the strength of the ligand field in $[Fe(N\text{-bipyO})_3]^{2+}$ is insufficient to produce a spin-paired Fe(II) complex. Finally, *N*-bipyO occupies a lower position than 2,2′-bipyridine in the nephelauxetic series.

Introduction

2,2′-Bipyridine (bipy) is among the most extensively studied chelating agents.[2,3] The metal complexes of this ligand (I) are characterized by five-membered chelate rings.[2,3] Metal chelates of 2,2′-bipyridine *N,N*-dioxide (*N,N*-bipyO$_2$)

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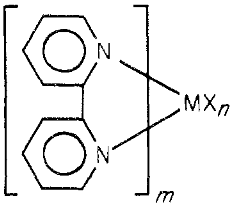
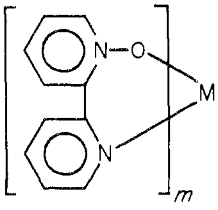
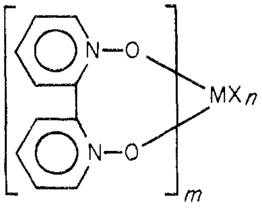
have also been reported in recent years.[4-9] Compounds of this type (III) involve seven-membered chelate rings and a staggered (gauche) configuration of the pyridine rings.[5] The mono-*N*-oxide of 2,2′-bipyridine (*N*-bipyO) would also be expected readily to form metal complexes, characterized by six-membered chelate rings (II). Although complex formation between *N*-bipyO and Fe^{3+} has been detected in solution[10] and a number of *N*-bipyO salts with mineral acids have been reported,[11] no crystalline metal chelates of this ligand were prepared. Some 3d metal chelates of an analogous ligand, the mono-*N*-oxide of 1,10-phenanthroline (*N*-phenO), were isolated but not fully characterized.[12] Synthetic and characterization studies of *N*-bipyO and *N*-phenO chelates with a variety of metal salts were recently undertaken by this laboratory. The present paper deals with *N*-bipyO complexes with divalent 3d metal perchlorates (Mn, Fe, Co, Ni, Cu, Zn).



I



II



III

(M = metal ion; X = anion)

Experimental Section

Chemicals. *N*-bipyO was prepared by the method of Murase[10] and its authenticity was established by examination of its melting point (57–58°) and ir spectrum.[10,11,13] Reagent grade transition metal perchlorates (hydrated), triethyl orthoformate, and organic solvents were utilized.

Synthetic Procedure. The hydrated metal perchlorate was dissolved in a 7:3 (v/v) mixture of ethanol and the dehydrating agent[14] triethyl orthoformate and the resulting solution was warmed for 20–30 min at 50–60° under stirring. *N*-bipyO was treated separately in exactly the same manner. The warm ligand and metal salt solutions were mixed (ligand to metal molar ratio 3:1). In all cases examined, a precipitate started forming immediately. The reaction mixture was maintained at 50–60° for 5–10 min, under stirring, and then allowed to cool slowly to room temperature. The new complexes were filtered, washed with ethanol, and dried in an evacuated desiccator over phosphorus pentoxide. The Cu(II) and Zn(II) complexes are insoluble in ethanol and chloroform, while the rest of the complexes reported are very sparingly soluble in these media. The new complexes are stable in the atmosphere and generally soluble in nitromethane and dimethyl sulfoxide (DMSO); nitromethane solutions of the complexes are of the same color as the solids, but the DMSO solutions exhibit pronounced color differences from the corresponding solid compounds. The yellow Mn(II) complex produces a colorless solution in water; this is most probably due to dissociation of the complex to uncoordinated *N*-bipyO and $[Mn(OH_2)_6]^{2+}$.[12] The rest of the new complexes exhibit limited solubility in water. Analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.), given in Table I, demonstrate that the complexes reported are of the types M(*N*-bipyO)$_3$(ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni, Zn) and Cu(*N*-bipyO)$_2$(ClO$_4$)$_2$.

Spectral, Magnetic, and Conductance Measurements. Infrared (Nujol and hexachlorobutadiene mulls; Table II, Figures 1 and 2) and electronic (Nujol mulls and nitromethane solutions; Table III, Figures 3 and 4) spectra and magnetic susceptibility and conductance measurements (Table IV) were obtained by methods described elsewhere.[15] No ir bands associated with coordinated water were detected in the spectra of the new complexes.

Discussion

Infrared and Conductance Data. The molar conductivities of the new complexes in nitromethane demonstrate that these compounds behave as 1:2 electrolytes[16] in polar solvents. The ir spectra of the complexes (Table II, Figures 1 and 2) suggest that the perchlorate groups are also ionic in the solid state. In fact, the ν_3 and ν_4 vibrational modes of T_d ClO_4^- appear as single bands in these spectra.[17] In the $\nu_1(ClO_4)$ region (*ca.* 940–920 cm^{-1}) a weak band is observed and is probably due to this vibration; in several metal complexes, exclusively involving ionic perchlorate, ν_1 is weakly ir active in their solid-state spectra.[17] The free ligand exhibits a rich spectrum in the 1620–200-cm^{-1} region; band assignments at 1620–650 cm^{-1} were recently reported by Dega-Szafran.[11] Table II shows pertinent ir data for the ligand and the new complexes, including ν_{N-O}, δ_{N-O}, ν_{M-O}, ν_{M-N}, and ν_{ClO_4} assignments and a number of ring vibrations of the pyridine and pyridine *N*-oxide fragments of the ligand,[11] undergoing characteristic frequency shifts upon metal complex formation. The assignments given in Table II were based on the latter work[11] and on comparisons of the spectra of free *N*-bipyO and its complexes to those of free and complexed *N*,*N*-bipyO$_2$ [5,8,9] and bipy.[18-24] Coordination through the N–O oxygen in the new complexes is clearly

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Table I. Analyses and Properties of *N*-bipyO–Metal Perchlorate Complexes

			Analysis							
			% C		% H		% N		% metal	
Complex	Color	Thermal stability, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Mn(N\text{-bipyO})_3](ClO_4)_2$	Deep yellow	240, darkens; 250, dec	46.77	47.01	3.15	3.13	10.91	11.36	7.13	6.88
$[Fe(N\text{-bipyO})_3](ClO_4)_2$	Scarlet red	195, dec	46.71	47.33	3.14	3.10	10.90	10.80	7.24	7.01
$[Co(N\text{-bipyO})_3](ClO_4)_2$	Bright orange	275, darkens; 290, dec	46.53	47.13	3.13	3.30	10.85	10.66	7.61	7.35
$[Ni(N\text{-bipyO})_3](ClO_4)_2$	Lime green	Stable to 300	46.54	46.84	3.13	3.16	10.86	11.36	7.58	7.29
$[Cu(N\text{-bipyO})_2](ClO_4)_2$	Light blue	Stable to 300	39.59	39.74	2.66	2.84	9.23	9.09	10.45	10.22
$[Zn(N\text{-bipyO})_3](ClO_4)_2$	White	265, dec	46.14	45.69	3.10	2.99	10.76	10.99	8.37	8.61

Table II. Pertinent Infrared Data for *N*-bipyO–Metal Perchlorate Complexes (cm^{-1})[d]

Compd	ν_{N-O}	δ_{N-O}	ν_{ClO_4} (ν_3, ν_1, ν_4)[a]	ν_{8a}, ν_{19a}, ν_{10b}[b] and γ_{CH}[c]	ν_{M-O}	ν_{M-N}	ν_{ligand}[c]
N-bipyO = L	1250 s, 1232 s	855 vs		1575 m, 1457 m, 765 vs, 770 vs			401 ms, 340 m, 310 w, 279 w, 251 w
$[MnL_3](ClO_4)_2$	1220 sh, 1213 vs	842 s	1085 vs, vb, 930 w, 621 vs	1595 vs, 1571 vs, 1471 vs, 770 vs, 778 vs	355 m	265 m	329 mw, 279 m, 271 m, 251 m
$[FeL_3](ClO_4)_2$	1219 sh, 1208 vs	849 s, 839 s	1086 vs, 935 w, b, 623 vs	1599 vs, 1574 s, 1473 vs, 769 vs, 779 vs	370 mw	269 mw	341 mw, 279 mw, 254 mw
$[CoL_3](ClO_4)_2$	1215 m, sh, 1207 s	847 s, sh, 839 s	1080 vs, 941 w, 622 vs	1599 vs, 1574 vs, 1471 vs, 767 vs, 771 vs, 778 vs	371 ms, 369 sh	295 sh	343 m, 310 vw, 279 m, 263 mw, 251 w
$[NiL_3](ClO_4)_2$	1220 m, sh, 1211 vs	850 s, sh, 843 vs	1085 vs, 941 w, 623 vs	1600 vs, 1577 vs, 1475 vs, 768 vs, 779 vs, 782 vs	382 ms, 375 sh	295 m, b	350 m, 280 m, 268 m, 260 m, 252 m
$[CuL_2](ClO_4)_2$	1204 s	851 s, sh, 841 vs	1070 vs, b, 932 w, 621 vs	1600 vs, 1573 sh, 1478 vs, 770 vs, 774 vs, sh	398 s	315 m, b	371 m, 276 m, 266 w, 251 m
$[ZnL_3](ClO_4)_2$	1230 vs, 1213 vs	850 vs, 842 vs	1090 vs, vb, 932 w, 628 vs	1601 vs, 1578 vs, 1478 vs, 769 vs, 779 vs, 785 vs, sh	369 m	256 w	340 m, 295 w, b, 281 m, 270 w, 249 w

[a] The weak bands at 941–930 cm^{-1} might be due to the $\nu_1(ClO_4)$ mode[17] (see text). [b] Bands attributed to the pyridine fragment of the ligand.[11] [c] Bands attributed to the pyridine *N*-oxide fragment of the ligand.[11] [d] Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder. [e] 400–250 cm^{-1}.

Table III. Electronic Spectra of *N*-bipyO and Its Metal Perchlorate Complexes[a]

Compd	Medium	λ_{max}, nm (ϵ_{max})
N-bipyO	Nujol	239 vs, 281 vs, 293 sh, 344 s, sh
$[Mn(N\text{-bipyO})_3](ClO_4)_2$	Nujol	235 vs, b, 303 vs, 366 vs, 421 vs, b, 527 ms, sh
	6×10^{-4} *M* in CH_3NO_2	371 (1052), 432 (881), 441 (859), 488 (402), 530 b, sh (168)
$[Fe(N\text{-bipyO})_3](ClO_4)_2$	Nujol	224 vs, sh, 263 vs, b, 300 vs, b, 360 vs, b, sh, 515 s, vvb, 650 m, b, sh, 700 m, sh, 820 m, vb, sh
	6×10^{-4} and 3×10^{-3} *M* in CH_3NO_2	369 (2911), 375 (2982), 378 (2982), 466 (1750), 481 (1911), 493 (1752), 505 sh (1684), 862 (48), 1140 sh
$[Co(N\text{-bipyO})_3](ClO_4)_2$	Nujol	219 vs, 253 vs, sh, 265 s, sh, 314 vs, 365 s, 441 ms, 535 m, sh, 850–1050 w, vvb
	7×10^{-4} and 7×10^{-3} *M* in CH_3NO_2	370 (1068), 414 (661), 477 sh (323), 529 sh (81), 979 sh (26), 1010 (26), 1100 sh (24)
$[Ni(N\text{-bipyO})_3](ClO_4)_2$	Nujol	227 vs, 261 vs, 315 vvs, 349 vs, 417 s, sh, 435 s, sh, 454 s, 547 mw, sh, 971 w, sh
	8×10^{-4} and 8×10^{-3} *M* in CH_3NO_2	367 (746), 416 sh (373), 425 (391), 431 (393), 435 sh, 572 (20), 792 sh (22), 962 (29), 1044 sh (24)
$[Cu(N\text{-bipyO})_2](ClO_4)_2$	Nujol	236 vs, 249 vs, 300 vs, b, 360 vs, 541 s, 586 s, 625 s, sh, 724 m, sh
	9×10^{-4} and 2×10^{-3} *M* in CH_3NO_2	367 (923), 426 sh (129), 593 (128), 765 sh (86)
$[Zn(N\text{-bipyO})_3](ClO_4)_2$	Nujol	221 vs, sh, 245 vs, 264 vs, 306 vs, b, 347 s, sh

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

demonstrated by the negative frequency shifts of the ν_{N-O} bands,[4-9,25] while coordination through the nitrogen of the pyridine fragment of the ligand is suggested by frequency shifts and splittings of the ν_{8a}, ν_{19a}, and ν_{10b} (γ_{CH}) modes of this fragment.[22-26] Shifts of the δ_{N-O} and γ_{CH} bands of the pyridine *N*-oxide fragment of the ligand were also observed, as expected.[5,25,26] Tentative ν_{M-O} and ν_{M-N} assignments, given in Table II, are generally in satisfactory agreement with values reported for analogous *N,N*-bipyO$_2$[5] and bipy[18-22] 3d metal chelates, respectively. On the basis of the ir and conductance evidence the new complexes are formulated as $[M(N\text{-bipyO})_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Zn) and $[Cu(N\text{-bipyO})_2](ClO_4)_2$. The ligand acts as a bidentate O,N-chelating agent in these metal complexes.

Ultraviolet Spectra. The 200-300-nm region of the *N*-bipyO spectrum is characterized by two main peaks at 239 and 281 nm (Table III, Figure 3), assigned as the π_2 and π_1 bands ($\pi \rightarrow \pi^*$ transitions), after Nakamoto,[27] and a shoulder at 293 nm, which may be due to an n → π^* transition.[28]

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Table IV. Magnetic Properties (300°K)[a] and Molar Conductivities (10^{-3} *M* Nitromethane Solutions at 25°) of *N*-bipyO–Metal Perchlorate Complexes

Complex	$10^6 \chi_M{}^{cor}$, cgsu	μ_{eff}, BM	Λ_M, Ω^{-1} cm^2 mol^{-1}
$[Mn(N\text{-bipyO})_3](ClO_4)_2$	13,549	5.73	196
$[Fe(N\text{-bipyO})_3](ClO_4)_2$	12,285	5.45	191
$[Co(N\text{-bipyO})_3](ClO_4)_2$	9,777	4.86	192
$[Ni(N\text{-bipyO})_3](ClO_4)_2$	4,656	3.36	182
$[Cu(N\text{-bipyO})_2](ClO_4)_2$	1,382	1.83	170
$[Zn(N\text{-bipyO})_3](ClO_4)_2$	Diamagnetic		191

[a] Error limits in the μ_{eff} values given are of the order of ±1.5%.

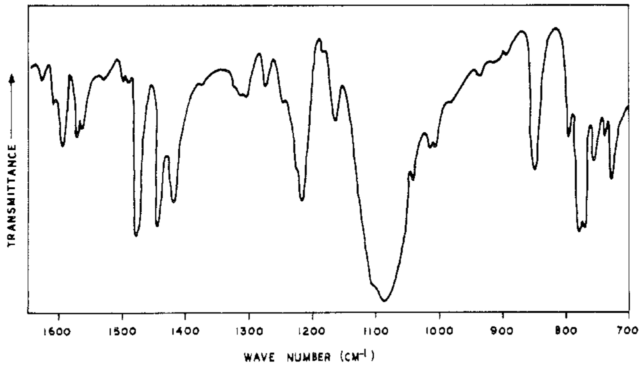
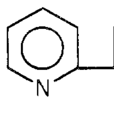
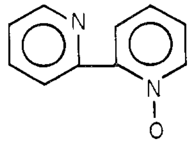


Figure 1. Infrared spectrum (1650–700 cm^{-1}) of $[Mn(N\text{-bipyO})_3](ClO_4)_2$: 1650–1400 cm^{-1}, hexachlorobutadiene mull; 1400–700 cm^{-1}, Nujol mull, between Irtran 2 windows.

bipy exists in the trans form in the crystal[29] but assumes the cis configuration in its metal chelates.[27,30] The uv spectra of bipy metal chelates are characterized by red shifts of the π_1 and π_2 bands and, quite often, splittings of π_1.[27,28,31] These splittings are vibrational in origin.[31] In the uv spectra of the new *N*-bipyO metal chelates, similar red shifts and splittings of π_1 are observed. Furthermore, π_2 also appears as a split band in most cases (Table III, Figure 3). The overall uv evidence suggests that free *N*-bipyO, which most



IV



V

probably exists in the trans form (IV) in the crystal,[11] assumes a configuration, which is of necessity close to that of the cis form (V)[2] but involves twisting to a certain extent of the two aromatic rings about the 2,2′ bond in each coordinated ligand.[27,31,32] It should be noted that the bipy ligand is also nonplanar in many metal chelates,[30] whereas in the case of *N,N*-bipyO_2 metal chelates, the deviation of the ligand from planarity is apparently pronounced.[5]

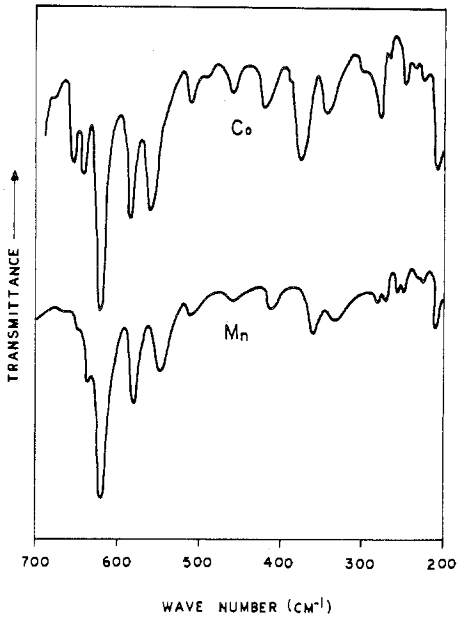


Figure 2. Infrared spectra (700–200 cm^{-1}) of $[Mn(N\text{-bipyO})_3](ClO_4)_2$ and $[Co(N\text{-bipyO})_3](ClO_4)_2$ (Nujol mulls between high-density polyethylene windows).

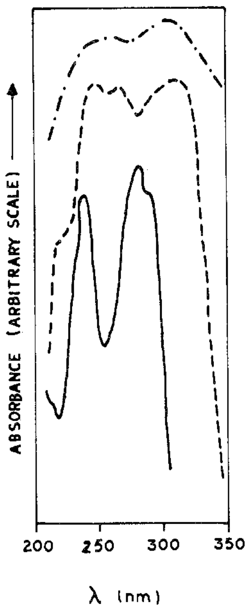


Figure 3. Ultraviolet spectra (Nujol mulls): ——, *N*-bipyO; - - -, $[Zn(N\text{-bipyO})_3](ClO_4)_2$; — · — ·, $[Mn(N\text{-bipyO})_3](ClO_4)_2$.

Charge-Transfer and Ligand Field Spectra. Ferrous complexes with bipy and related N,N bidentate ligands are intensely colored; the absorption responsible for this color results from a Laporte-allowed transition of the $t_{2g} \rightarrow \pi^*$ (metal to ligand) type, occurring in the 500-nm region.[33-40] Additional bands at 330–490 nm, in the spectra of these complexes, are also charge-transfer bands;[35,38] metal to ligand charge-transfer processes are considerably more

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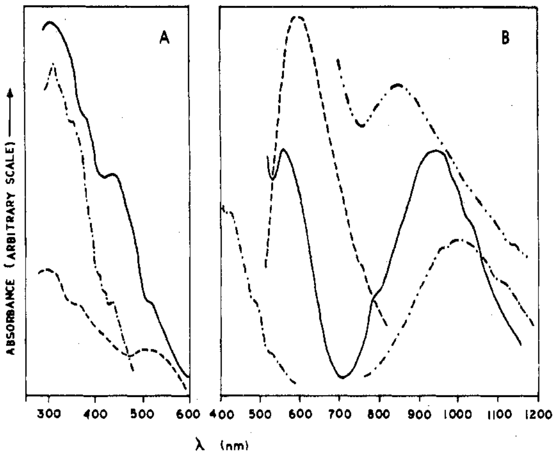

Figure 4. A. Nujol mull electronic spectra (250–600 nm) of [M(*N*-bipyO)$_3$](ClO$_4$)$_2$: ——, Mn; – – –, Fe; – · –, Ni. B. Nitromethane solution electronic spectra (400–1200 nm): ——, [Ni(*N*-bipyO)$_3$](ClO$_4$)$_2$, 8×10^{-3} *M*; – – –, [Cu(*N*-bipyO)$_2$](ClO$_4$)$_2$, 2×10^{-3} *M*; – · –, [Co(*N*-bipyO)$_2$](ClO$_4$)$_2$, 2×10^{-3} *M*; – · –, [Co(*N*-bipyO)$_3$](ClO$_4$)$_2$, 7×10^{-4} *M* at 400–600 nm and 7×10^{-3} *M* at 700–1200 nm; – · · –, [Fe(*N*-bipyO)$_3$](ClO$_4$)$_2$. An optical cell with a 5-cm path length was utilized.

important for Fe(II)-bipy complexes, than for the complexes of this ligand with the rest of the metal ions under study.[36] Pyridine *N*-oxide 3d metal complexes on the other hand show intense metal-to-ligand charge-transfer bands[41,42] ($t_{2g} \rightarrow \pi^*$ in hexacoordinated Fe(II), Co(II), and Ni(II) complexes and $e_g \rightarrow \pi^*$ in the corresponding Mn(II) and Cu(II) complexes[42]). [Fe(*N*-bipyO)$_3$](ClO$_4$)$_2$ exhibits charge-transfer bands similar to those of the corresponding bipy complexes (Table III, Figure 4); the strong band at 515 nm is assigned as $t_{2g} \rightarrow \pi^*$. The Fe(II)-*N*-bipyO complex is, however, of the high-spin type (Table IV), whereas the bipy analog is diamagnetic.[33-40] This is obviously due to the fact that *N*-bipyO gives rise to a weaker ligand field than bipy (*vide infra*). Metal-to-ligand charge-transfer bands are also observed in the spectra of the rest of the paramagnetic metal chelates of *N*-bipyO (Table III, Figure 4). Thus, the deep yellow color of the Mn(II) complex results from the charge-transfer bands at 421 and 527 nm; bands in the same region have been observed in Mn(II) complexes with pyridine *N*-oxides.[41,42] Visible charge-transfer absorptions appear also in the spectra of the Co(II), Ni(II), and Cu(II) complexes and interfere with certain d–d transitions. Thus the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition in the Ni(II) complex is obscured by the charge-transfer absorption.[37,43]

The rest of the triplet state d–d bands in the Ni(II) chelate are assigned as follows (Table III, Figure 4): $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ at 547 nm and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ at 971 nm. *Dq* is, therefore, 1029 cm^{-1}. Comparison of this *Dq* value with those of bipy (1279 cm^{-1})[37] and *N,N*-bipyO$_2$ (857 cm^{-1})[6] for the tris-chelate Ni(II) cationic complexes leads to the spectrochemical series bipy > *N*-bipyO > *N,N*-bipyO$_2$, as expected. The Racah parameter *B* cannot be determined accurately for the new Ni(II) complex, in view of the overlap of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition with charge-transfer absorptions.[43] It should be noted at this point that the symmetry of the hexacoordinated cationic *N*-bipyO complexes (*i.e.*, Mn(II), Fe(II), Co(II), Ni(II), Zn(II)) is lower than pure O_h. [Ni(bipy)$_3$]$^{2+}$, for instance, has D_{3h} symmetry[37] while even [ML$_6$]$^{2+,3+}$ complexes with aromatic monodentate ligands (*e.g.*, pyridine *N*-oxides) have effective symmetries lower than O_h.[44] In the case of *N*-bipyO, an unsymmetrical bidentate ligand, the highest possible symmetry for the [M(*N*-bipyO)$_3$]$^{2+}$ cation is C_3. The d–d band assignments made during this work and the calculated spectrochemical parameters are based on pure O_h symmetry and are, therefore, approximate.

The solid-state electronic spectrum of the Co(II) chelate exhibits poor resolution. The corresponding nitromethane solution spectrum (Figure 4) does not exhibit dramatic differences from that in the solid state, at least as far as the d–d transitions are concerned, and may be used for the calculation of the spectrochemical parameters. By assigning the bands at 1010 and 529 nm as the transitions from the ground state ($^4T_{1g}(F)$) to excited states $^4T_{2g}(F)$ and $^4T_{1g}(P)$, respectively, a *Dq*/*B* value of 1.63 is obtained. This value corresponds to the following progression of energy levels: $^4T_{1g}(F) < {}^4T_{2g}(F) < {}^4T_{1g}(P) < {}^4A_{2g}(F)$.[45] The calculated values for the spectrochemical parameters of the *N*-bipyO relative to hexacoordinated Co(II) are $Dq = 1113$ cm^{-1}, $B = 683$ cm^{-1}, and $\beta = 0.60$. *N*-bipyO occupies, therefore, a lower position than bipy in both the spectrochemical and nephelauxetic series (bipy values in [Co(bipy)$_3$]$^{2+}$: $Dq = 1267$ cm^{-1}, $B = 791$ cm^{-1}).[37] From the above *Dq* and *B* values for *N*-bipyO the energy of the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition is calculated to be 21,370 cm^{-1} (468 nm). The absorption at 477 nm in the actual spectrum of the complex in nitromethane is, thus, assigned to this transition.

In the case of the high-spin Fe(II) complex, a split d–d band ($^5T_{2g} \rightarrow {}^5E_g$) is observed in both the solid-state and solution spectra, as is usually the case with hexacoordinated ferrous compounds.[45] From the maximum of this absorption in the solution spectrum (862 nm, Figure 4) a *Dq* value of 1160 cm^{-1} is calculated. *Dq* values reported for the low-spin [Fe(bipy)$_3$]$^{2+}$ analog are substantially higher; *i.e.*, Madeja and Konig reported a value of 1330 cm^{-1} for the latter compound,[46] but, more recently, Palmer and Piper concluded that this value is at least 1400 cm^{-1} and most likely in the range 1650–1900 cm^{-1}.[37] A *Dq* value of 1160 cm^{-1} is, presumably, insufficient to induce spin pairing; it is noteworthy, in this connection, that Robinson, *et al.*, have estimated the critical *Dq* value for spin pairing in the 1160–1340-cm^{-1} region;[43] *N*-bipyO, which has the lowest value in this region is, thus, one of the stronger known ligands producing spin-free ferrous complexes.

Cu(ClO$_4$)$_2$ yields under the experimental conditions a 1:2 complex with *N*-bipyO. For bipy and *N,N*-bipyO$_2$ both 1:2 and 1:3 complexes with various cupric salts have been reported.[2,3,5,6,47,48] [Cu(*N,N*-bipyO$_2$)$_2$](PtCl$_4$) involves apparently a tetracoordinated complex cation. In the case of 1:2 Cu(II)-bipy complexes, pentacoordinated complex cations of the type [Cu(bipy)$_2$X]$^+$ (X = ClO$_4$, Cl, Br, I, etc.) are formed in most cases.[2,3,48] Nevertheless, Cu(II)- and Ag(II)-bipy compounds involving tetracoordinated cationic complexes have also been reported, *viz.*, [Cu(bipy)$_2$](SO$_4$)$_2$,[47b]

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$[Cu(bipy)_2](PF_6)_2$,[48] and $[Ag(bipy)_2](S_2O_8)$.[49] The new Cu(II) complex has been formulated as $[Cu(N\text{-}bipyO)_2](ClO_4)_2$ on the basis of the ir and conductance evidence (*vide supra*). The electronic spectral evidence is also in support of this assignment. In fact, the d-d transition appears split[48-50] and shows a pattern (Table III, Figure 4) quite similar to that of $[Cu(bipy)_2](PF_6)_2$ (λ_{max} for this complex: 590 and 700 nm).[48] $[Cu(N\text{-}bipyO)_2]^{2+}$ is, therefore, tetracoordinated and probably involves square-planar CuO_2N_2 moieties, but an overall symmetry lower than D_{4h}.[44,49,50]

Magnetic Moments. The magnetic moments of the new metal chelates are, in most cases, within the range of values reported for square-planar Cu(II) and octahedral M(II) (M = Mn, Fe, Co) compounds.[51] Only in the case of the Ni(II) chelate is the μ_{eff} (3.36 BM) slightly higher than the upper limit (3.30 BM) of the "octahedral" Ni(II) region;[51] various low-symmetry hexacoordinated cationic Ni(II) complexes (*e.g.*, complexes with pyridine *N*-oxide, dialkyl and diaryl sulfoxides, and sulfinamide) reportedly exhibit μ_{eff} values in the 3.30-3.40-BM region.[44,52] Finally, it should be mentioned that several geometrical and optical isomers and diastereoisomers of the new chelates are possible.[7,53] During the work reported here, no attempts at establishing the existence of isomeric forms of these chelates have been made. Studies in this direction are planned for the future by this laboratory.

Registry No. $[Mn(N\text{-}bipyO)_3](ClO_4)_2$, 38708-72-4; $[Fe(N\text{-}bipyO)_3](ClO_4)_2$, 38708-73-5; $[Co(N\text{-}bipyO)_3](ClO_4)_2$, 38708-74-6; $[Ni(N\text{-}bipyO)_3](ClO_4)_2$, 38708-75-7; $[Cu(N\text{-}bipyO)_2](ClO_4)_2$, 38708-76-8; $[Zn(N\text{-}bipyO)_3](ClO_4)_2$, 38708-77-9.

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Further Studies of the Coordination of Ethylenediaminedisuccinic Acid, an Isomer of Ethylenediaminetetraacetic Acid

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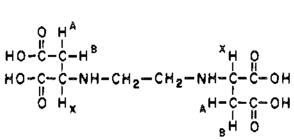
Received August 23, 1972

New complexes of ethylenediaminedisuccinic acid derived from (*S*)-aspartic acid, *S,S*-$EDDS^{4-}$, are reported with Rh(III) and Ni(II). The rhodium complex, $[Rh(S,S\text{-}EDDS)]^-$, is shown by analogy with the corresponding cobalt complex, $[Co(S,S\text{-}EDDS)]^-$, to contain hexadentate *S,S*-$EDDS^{4-}$ in which both aspartate moieties are in identical environments. The compound $[(CH_3)_4N]_2[Ni(S,S\text{-}EDDS)]$ has been isolated and it is proposed that the complex anion of this salt also contains hexadentate *S,S*-$EDDS^{4-}$. Infrared spectra of solutions of the Co(III), Rh(III), and Ni(II) complexes exhibit two separate bands in the 1560-1640-cm^{-1} spectral region. One is attributed to the asymmetric stretching vibration of the COO^- group of the six-membered chelate ring of *S,S*-$EDDS^{4-}$, and the other to that same vibration of the five-membered chelate ring.

Introduction

We previously reported the preparation and characterization of the cobalt(III) complex of (*S,S*)-*N,N'*-ethylenediaminedisuccinic acid[1] (hereafter *S,S*-H_4EDDS)[2] prepared from the reaction of *S,S*-$H_4EDDS\cdot H_2O$ with $Na_3[Co(CO_3)_3]\cdot 3H_2O$. In that report *S,S*-$EDDS^{4-}$ was shown to function as a stereospecific ligand for Co(III). Since that initial study, other complexes have been synthesized from *S,S*-H_4EDDS,[3] oxygen nmr studies of the Ni(II)–*S,S*-EDDS–H_2O system have been conducted,[4] the rate of CN^- replacement of *S,S*-$EDDS^{4-}$ coordinated to Ni(II) has been investigated,[5] and a single-crystal X-ray diffraction study of a hydrate of $NH_4[Co(S,S\text{-}EDDS)]$ has been performed.[6] In this paper we discuss in detail the synthesis and characterization of Ni(II)[3] and Rh(III)[3] complexes of *S,S*-$EDDS^{4-}$ as well as the synthesis of the ammonium salt of $[Co(S,S\text{-}EDDS)]^-$. For the latter



H_4EDDS

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(2) Since the EDDS used in this study is prepared[1] from (*S*)-aspartic acid and $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ in aqueous base, it is unlikely that racemization of the asymmetric carbon atoms of the (*S*)-aspartate moiety takes place during the synthesis. We have no evidence from fractional crystallizations of the cobalt(III) complex of EDDS or from ion-exchange chromatography of the complex that more than one species is formed. All samples of the complex prepared and isolated by whatever means exhibit the same circular dichroism spectrum. We are left to conclude that complete (100%) inversion of the asymmetric carbon atoms of the (*S*)-aspartate ion takes place in the synthesis of the ligand or that *no* inversion takes place. The latter choice seems warranted in terms of the organic chemistry involved. Thus, we designate the product of (*S*)-aspartic acid and $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ as *S,S*-EDDS.

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