

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
DREXEL INSTITUTE OF TECHNOLOGY, PHILADELPHIA, PENNSYLVANIA 19104**Binuclear Chlorine-Bridged Complexes of Manganese(II) and Nickel(II) Chlorides with Pyridine N-Oxides<sup>1</sup>**

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The 1:1 complexes of manganese(II) and nickel(II) chlorides with pyridine N-oxides have been synthesized, under anhydrous experimental conditions. Far-infrared evidence revealed the presence of both terminal and bridging chlorine atoms and the new complexes were assigned a binuclear chlorine-bridged structure. The electronic spectra and magnetic moments of the Ni(II) binuclear complexes are suggestive of the presence of tetracoordinated Ni(II) ions and a symmetry intermediate between distorted tetrahedral and square planar for the  $\text{OCNiCl}_2$  groupings. Similarities in their X-ray powder diffraction patterns indicate that the Mn(II) and Ni(II) dimeric complexes are of nearly the same structure. The magnetic moments of the Mn(II) complexes are suggestive of possible spin-spin interaction. The new complexes are not attacked by relatively bulky ligand molecules, presumably due to steric hindrance, but are solvated by dry methanol.

**Introduction**

During recent studies of the metal complexes of 4-ethoxypyridine N-oxide (EPNO), we synthesized a water-free 1:1 complex of this ligand with  $\text{MnCl}_2$ .<sup>2</sup> This is the first example of a 3d metal halide analog of the extensively studied 1:1 complexes of copper(II) halides with aromatic amine oxides.<sup>3</sup> The latter complexes are dimeric in the solid state, possess oxygen-bridged structures, and exhibit subnormal and temperature-dependent magnetic moments.<sup>3</sup> The only other 1:1 complexes of pyridine N-oxides with 3d metal halides reported involve coordination of a molecule of a different ligand, *i.e.*, they are of the type  $\text{MLX}_2 \cdot \text{L}'$  ( $\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Mn(II)}, \text{and Cu(II)}$ ;<sup>4</sup>  $\text{L} = \text{pyridine N-oxide and derivatives}$ ;  $\text{L}' = \text{water, dimethyl sulfoxide, N,N-dimethylformamide}$ ;  $\text{X} = \text{Cl, Br}$ ).  $\text{MLX}_2$  complexes of pyridine N-oxides with other divalent metal halides appearing in the literature are those of  $\text{Sn(II)}$ ,<sup>7</sup>  $\text{Cd(II)}$ ,<sup>8</sup> and  $\text{Hg(II)}$ .<sup>8,9</sup> Schmauss and Specker assigned far-infrared bands of the  $\text{Cd(II)}$  and  $\text{Hg(II)}$  complexes to both terminal and bridging halogen-metal stretching vibrations and formulated these compounds as binuclear halogen bridged.<sup>8</sup> Pappas, Villa, and Powell concluded that only metal-terminal halogen stretching bands are present in the far-ir spectrum of  $\text{Hg}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2$  and assigned a binuclear oxygen-bridged structure to this complex.<sup>9</sup>

The water-free 1:1 complexes of EPNO with  $\text{MnCl}_2$  and  $\text{CuCl}_2$  exhibit similar solubility characteristics,<sup>2</sup> being insoluble in most organic solvents and sparingly soluble in dibromomethane and nitromethane.<sup>2</sup> They show relatively higher solubility in methanol or mixtures of methanol with halogenated hydrocarbons (*e.g.*, ethylene dichloride). These properties are suggestive of a bi- or polynuclear structure for both the Mn(II) and Cu(II) complexes. The synthesis and characterization of water-free 1:1 complexes of transition metal chlorides with a group of pyridine N-oxides was undertaken. The present paper reports on the preparation and properties of Mn(II) and Ni(II) complexes of the type  $\text{MLCl}_2$  ( $\text{L} = \text{pyridine N-oxide and 4-alkoxy derivatives}$ ).

**Experimental Section**

**Chemicals.**—Pyridine N-oxide (PNO), 4-methoxypyridine N-oxide (MPNO), and EPNO were obtained commercially and purified by recrystallization (PNO) or vacuum sublimation (MPNO,<sup>10</sup> EPNO<sup>2</sup>). The metal salts, dehydrating agents, and solvents utilized were the purest commercially available. Absolute methanol (Fisher) was further dehydrated<sup>11</sup> prior to its utilization as a solvent.

**Syntheses.**—The syntheses of  $\text{Mn(EPNO)Cl}_2$  and  $\text{Cu(EPNO)Cl}_2$  have been reported elsewhere.<sup>2</sup> As the synthetic procedure for  $\text{Mn(EPNO)Cl}_2$  was rather tedious, other methods of preparation were sought. By adding triethyl orthoformate, instead of ether,<sup>2</sup> to acetone-ethanol solutions of equimolar amounts of hydrated salt and ligand, the 1:1 complexes of MPNO with  $\text{MnCl}_2$  and  $\text{NiCl}_2$  were immediately precipitated.  $\text{Mn(EPNO)Cl}_2$  can also be obtained by this procedure, but we have been unable to prepare a  $\text{NiCl}_2$ -EPNO analog. The complexes synthesized in this way contained some residual water, which was completely removed after prolonged vacuum desiccation over  $\text{P}_2\text{O}_5$ .

The PNO complexes of manganese(II) and nickel(II) chlorides were precipitated by addition of a triethyl orthoformate-ethanol or 2,2-dimethoxypropane-ethanol solution of the ligand to an equimolar solution of the hydrated salt in the same solvent mixture. The precipitates contained some residual water, which was completely removed after vacuum desiccation over  $\text{P}_2\text{O}_5$ .  $\text{FeCl}_2$  and  $\text{CoCl}_2$  complexes with PNO in 1:1 molar ratio were also obtained by this procedure. However, these complexes

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(2) N. M. Karayannis, J. V. Minkiewicz, L. L. Pytlewski, and M. M. Labes, *Inorg. Chim. Acta*, **3**, 129 (1969).

(3) R. Whyman and W. E. Hatfield, *Inorg. Chem.*, **6**, 1859 (1967), and references therein.

(4) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

(5) A. J. Pappas, F. A. Osterman, Jr., and H. B. Powell, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn. April 13-18, 1969, No. INOR 83.

(6) (a) G. F. Kokoszka, H. C. Allen, Jr., and G. Gordon, *J. Chem. Phys.*, **46**, 3013 (1967); (b) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(7) J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.*, **29**, 393 (1967).

(8) G. Schmauss and H. Specker, *Z. Anorg. Allgem. Chem.*, **363**, 113 (1968).

(9) A. J. Pappas, J. F. Villa, and H. B. Powell, *Inorg. Chem.*, **8**, 550 (1969).

(10) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *ibid.*, **6**, 1099 (1967).

(11) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

TABLE I  
 PROPERTIES AND ANALYTICAL DATA ON METAL CHLORIDE-PYRIDINE N-OXIDE COMPLEXES

Complex	Color	% C		% H		% N		% metal	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Mn(PNO)Cl <sub>2</sub>	Cream white	27.18	26.64	2.28	2.56	6.34	5.91	24.86	24.02
Co(PNO)Cl <sub>2</sub> ·xH <sub>2</sub> O <sup>a</sup>	Blue	26.70	27.49	2.24	2.74	6.22	6.40	26.20	25.62
Ni(PNO)Cl <sub>2</sub>	Yellow	26.73	26.15	2.24	2.53	6.23	5.80	26.13	26.18
Sn(PNO)Cl <sub>2</sub>	White	21.09	20.00	1.77	1.84	4.92	4.62	41.69	40.85
Mn(MPNO)Cl <sub>2</sub>	Cream white	28.71	28.02	2.81	2.99	5.58	5.27	21.89	21.81
Ni(MPNO)Cl <sub>2</sub>	Pale yellow	28.29	28.32	2.77	2.78	5.49	5.48	23.04	23.12
Mn(EPNO)Cl <sub>2</sub>	Cream white	31.72	32.58	3.42	3.67	5.28	5.16	20.73	20.64
Cu(EPNO)Cl <sub>2</sub>	Chartreuse	30.73	30.93	3.32	3.50	5.12	4.91	23.22	22.97

<sup>a</sup> Calculated analytical data refer to the anhydrous complex Co(C<sub>5</sub>H<sub>5</sub>NO)Cl<sub>2</sub>.

 TABLE II  
 INFRARED DATA (CM<sup>-1</sup>) OF METAL CHLORIDE COMPLEXES WITH PYRIDINE N-OXIDES<sup>a</sup>

Compound	$\nu_{\text{NO}}$	$\Delta\nu_{\text{NO}}$	$\delta_{\text{NO}}$	$\nu_{\text{MO}}$	$\nu_{\text{M-Cl}}$	Other far-ir bands
PNO	1243 vs		462 vs			541 s, 518 s, 233 m
Mn(PNO)Cl <sub>2</sub>	1190 vs	-53	449 s	395 sh	370 s, sh (t), 344 vs (t), 313 sh (b), 243 s (b)	543 vs
Co(PNO)Cl <sub>2</sub> ·xH <sub>2</sub> O	1193 vs	-50				
Ni(PNO)Cl <sub>2</sub>	1200 vs	-43	437 s, sh	402 vs	375 s, sh (t), 342 s, sh (t), 300 s (b), 242 s (b)	563 vs, 512 sh
Cu(PNO)Cl <sub>2</sub> <sup>b</sup>	1203 vs	-40	461 s	397 m	330 w, sh, 311 vs	234 w
Sn(PNO)Cl <sub>2</sub>	1192 vs <sup>c</sup>	-51	454 sh	440 s	382 vs (t), 323 vs (t), 297 vs (b), 236 m (b)	560 vs, 514 sh
MPNO	1213 s		463 m			522 m, 407 w, 372 vw, 232 m
Mn(MPNO)Cl <sub>2</sub>	1194 s	-19	438 m, sh	380 s, b <sup>d</sup>	380 s, b (t), <sup>d</sup> 345 s, sh (t), 298 vs (b), 254 vs (b)	563 s, 525 m, 499 vs
Ni(MPNO)Cl <sub>2</sub>	1192 s	-21	435 s	390 s	370 s, sh (t), 340 s, b (t), 288 s, b (b), 254 vs (b)	565 s, b, 525 m, 482 m, b
Cu(MPNO)Cl <sub>2</sub> <sup>b</sup>	1197 s	-16	459 m	417 m	324 vs	546 w, 502 s, 315 m, sh, 236 w
EPNO	1209 s		463 m, b			540 m, 515 m, 332 m, 358 m, 232 m
Mn(EPNO)Cl <sub>2</sub>	1198 s	-11	435 w, b	390 s	386 s (t), 323 s, <sup>e</sup> 246 vs (b)	525 m, 518 m, 481 vs
Cu(EPNO)Cl <sub>2</sub>	1202 s, 1184 m	-16 (av)	457 m	420 m, sh	374 m, 336 s, 310 sh, 298 vs	570 m, 485 s, 242 w

<sup>a</sup> With the exception of Co(PNO)Cl<sub>2</sub>·xH<sub>2</sub>O, the ir spectra of the 1:1 complexes are characterized by the complete absence of water bands. Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder; (t), terminal chlorine; (b), bridging chlorine. <sup>b</sup> Data (down to 300 cm<sup>-1</sup>) and assignments from ref 3 and from Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Japan*, **39**, 58 (1966). <sup>c</sup> A value of 1195 cm<sup>-1</sup> has been reported for the  $\nu_{\text{NO}}$  of Sn(PNO)Cl<sub>2</sub>.<sup>7</sup> <sup>d</sup> Coupling of  $\nu_{\text{MO}}$  and  $\nu_{\text{M-Cl}}$ . <sup>e</sup> May be assigned either as  $\nu_{\text{M-Cl}}$  or as  $\nu_{\text{M-Cl}}$ .

contained water which could not be removed by drying over P<sub>2</sub>O<sub>5</sub> *in vacuo*. The Fe(II) complex is relatively unstable and was not further studied. The Co(II) complex is bright blue and is gradually transformed to the violet Co(PNO)Cl<sub>2</sub>·H<sub>2</sub>O<sup>4</sup> when exposed to atmospheric moisture. Sn(PNO)Cl<sub>2</sub> was also prepared by this method. This complex has been synthesized by Morrison and Haendler in tetrahydrofuran solution.<sup>7</sup>

All syntheses were repeated several times with good reproducibility. The solubility characteristics of the new Mn(II) and Ni(II) complexes are similar to those of Mn(EPNO)Cl<sub>2</sub>. These complexes are high melting (mp >250°) and stable in the presence of atmospheric moisture. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and are given in Table I.

**Magnetic and Spectral Measurements.**—Infrared spectra (Table II), electronic spectra (Table III), and magnetic moments (Table IV) were obtained as described elsewhere.<sup>2</sup> Far-ir spectra were recorded on Nujol mulls of the ligands and complexes between high-density polyethylene windows on a Perkin-Elmer 621 spectrophotometer. *The absence of water in the new Mn(II), Ni(II), and Cu(II) complexes is established by the fact that no absorptions are observed in the  $\nu_{\text{OH}}$  (3550–3200 cm<sup>-1</sup>) and  $\delta_{\text{H-O-H}}$  (1630–1600 cm<sup>-1</sup>) regions. Medium  $\nu_{\text{OH}}$  and weak  $\delta_{\text{H-O-H}}$  bands are observed in the ir spectrum of Co(PNO)Cl<sub>2</sub>·xH<sub>2</sub>O, while Co(PNO)Cl<sub>2</sub>·H<sub>2</sub>O and Ni(PNO)Cl<sub>2</sub>·H<sub>2</sub>O exhibit strong  $\nu_{\text{OH}}$  and medium  $\delta_{\text{H-O-H}}$  bands.<sup>12</sup> The magnetic moments of the*

(12) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

 TABLE III  
 ELECTRONIC SPECTRA OF METAL  
 CHLORIDE-PYRIDINE N-OXIDE COMPLEXES

Complex	Medium <sup>a</sup>	$\lambda_{\text{max}}$ , nm
Mn(PNO)Cl <sub>2</sub>	CH <sub>3</sub> OH–C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	366, <300
Mn(MPNO)Cl <sub>2</sub>	CH <sub>3</sub> OH–C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	355 sh, <300
Mn(EPNO)Cl <sub>2</sub>	CH <sub>2</sub> Br <sub>2</sub> –CH <sub>3</sub> NO <sub>2</sub>	439, 360, <300
Co(PNO)Cl <sub>2</sub> ·xH <sub>2</sub> O	Nujol	680, 615, 540 sh, 360
Ni(PNO)Cl <sub>2</sub>	CH <sub>3</sub> OH–C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1578, 669, 603, 542, 370
	Nujol	1230, 740, 422, 370
Ni(MPNO)Cl <sub>2</sub>	CH <sub>3</sub> OH–C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1250, 763, 683 sh, 408
	Nujol	1230, 755, 425, 355
Cu(EPNO)Cl <sub>2</sub>	CH <sub>3</sub> OH–C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1240, 781, 690 sh, 411
	CH <sub>2</sub> Br <sub>2</sub> –CH <sub>3</sub> NO <sub>2</sub>	785

<sup>a</sup> Solution spectra recorded on saturated solutions.

 TABLE IV  
 MAGNETIC DATA ON METAL CHLORIDE-PYRIDINE  
 N-OXIDE COMPLEXES AT 297°K

Complex	10 <sup>3</sup> $\chi_{\text{M}}^{\text{cor}}$ , cgsu	$\mu_{\text{eff}}$ , BM	Complex	10 <sup>3</sup> $\chi_{\text{M}}^{\text{cor}}$ , cgsu	$\mu_{\text{eff}}$ , BM
Mn(PNO)Cl <sub>2</sub>	13,131	5.60	Ni(PNO)Cl <sub>2</sub>	5107	3.49
Mn(MPNO)Cl <sub>2</sub>	12,187	5.40	Ni(MPNO)Cl <sub>2</sub>	4632	3.33
Mn(EPNO)Cl <sub>2</sub>	12,842	5.54	Cu(EPNO)Cl <sub>2</sub>	181 <sup>a</sup>	0.53

<sup>a</sup> N<sub>α</sub> (TIP correction) is assumed to be 60 × 10<sup>-6</sup> cgsu.<sup>6b</sup>

Mn(II) complexes show a small decrease with temperature variation over the range 77–300°K. Thus, Mn(PNO)Cl<sub>2</sub> exhibits magnetic moments of 5.60 BM at 297°K, 5.57 BM at 201°K, and 5.49 BM at 77°K. Ni(PNO)Cl<sub>2</sub> shows moments of 3.49 BM at 297°K, 3.44 BM at 201°K, and 3.42 BM at 77°K.

### Discussion

With the exception of Sn(PNO)Cl<sub>2</sub>, which has been tentatively characterized as monomeric and involving tricoordinated Sn(II),<sup>7</sup> the water-free complexes of the type M(PNO)X<sub>2</sub> (M = Cu, Cd, Hg) have been assigned binuclear structures with the metal ion exhibiting coordination number 4.<sup>3,8,9</sup> Quite recently, Sager, Williams, and Watson have described more accurately the crystal structure of Cu(PNO)Cl<sub>2</sub> as consisting of oxygen-bridged dimers held together in infinite chains by weak chloride bridges.<sup>13</sup> Each cupric ion is in a distorted square-pyramidal environment, where the two bridging oxygen atoms and the two chloride ions form the distorted square base, and a chloride ion from an adjacent dimer is situated at the apex.<sup>13</sup> In 1:1 d<sup>5</sup>-d<sup>10</sup> metal halide-pyridine N-oxide complexes, the central metal ion satisfies a coordination number higher than 3 either through dimerization<sup>3,8,9</sup> or by coordination to a nonbulky ligand molecule, such as water.<sup>4-6</sup> Complexes of the type M(PNO)Cl<sub>2</sub>·H<sub>2</sub>O (M = Mn, Co, Ni) are dehydrated at elevated temperatures (130–250°), yielding similar complexes to those reported here.<sup>5,14</sup> The isolation of water-free Mn(II) and Ni(II) complexes during the present work is attributed to the anhydrous experimental conditions. Molecular association is, presumably, favored in compounds of the type M(PNO)Cl<sub>2</sub> (M = transition metal ion). Attack of these oligomers by relatively bulky ligands is sterically hindered. Nevertheless, "small" ligands (*e.g.*, water) can obviously reach the first coordination sphere of the metal ion. This is substantiated by the fact that the new Mn(II) and Ni(II) complexes exhibit considerable solubility in dry methanol but are insoluble in bulkier ligands (*e.g.*, ethanol and acetone). This interaction may be interpreted in terms of coordination of the nonbulky ligand molecule, leading either to dissociation of the oligomer and formation of a monomeric tetracoordinated complex or to formation of an oligomeric 1:1 adduct. The product may be formulated as [M(PNO)-Cl<sub>2</sub>B]<sub>n</sub> (B = H<sub>2</sub>O, CH<sub>3</sub>OH; n = 1, 2, ...).

**Infrared Studies.**—Coordination through the N-O oxygen is clearly indicated by the negative shifts of the N-O stretching vibration frequency,<sup>4,12</sup> observed in all of the new complexes reported (Table II). Conclusions concerning the structure of the new complexes may be drawn from their far-ir spectra. Thus, ν<sub>M-O</sub> absorptions are of considerably greater intensity in dimeric complexes involving terminal pyridine N-oxide groups (*e.g.*, [Cu(MPNO)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>) than in binuclear oxygen-bridged complexes of these ligands (*e.g.*, [Cu(MPNO)-

Cl<sub>2</sub>]<sub>2</sub>).<sup>3</sup> Chlorine-bridged dimeric transition metal complexes exhibit ν<sub>M-Cl</sub> at *ca.* 350 cm<sup>-1</sup> for terminal (t) chlorine atoms and below 320 cm<sup>-1</sup> for bridging (b) chlorine atoms (*e.g.*, (CH<sub>3</sub>)<sub>2</sub>SeClPdCl<sub>2</sub>PdClSe(CH<sub>3</sub>)<sub>2</sub> exhibits the following ν<sub>Pd-Cl</sub> bands (cm<sup>-1</sup>): 350 (t), 306 (b), 286 (b)).<sup>15</sup> An interesting observation is that in complexes involving only terminal pyridine N-oxide groups the N-O bending mode shows shifts of the order of 15–30 cm<sup>-1</sup> (*e.g.*, [Cu(MPNO)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>,<sup>3</sup> SnCl<sub>4</sub>·2PNO<sup>16</sup>), while in oxygen-bridged 1:1 complexes with copper(II) halides this band occurs at about the same frequency as in the free ligand.<sup>3</sup>

The Mn(II) and Ni(II) complexes reported here exhibit (Table II): (a) two or three strong to very strong bands in the 405–340-cm<sup>-1</sup> region; (b) strong to very strong absorptions below 255 cm<sup>-1</sup>; (c) considerable shifts of the N-O bending mode, which occurs at 462–463 cm<sup>-1</sup> in the free ligands.<sup>16</sup> These features are not observed in the oxygen-bridged [Cu(PNO)Cl<sub>2</sub>]<sub>2</sub> and [Cu(MPNO)Cl<sub>2</sub>]<sub>2</sub>. Thus, the far-ir evidence is in favor of a binuclear chlorine-bridged structure for the new Mn(II) and Ni(II) complexes.<sup>3,8,15,16</sup> Tentative assignments of the far-ir bands of these complexes as ν<sub>M-O</sub> and ν<sub>M-Cl</sub> (terminal and bridging) are shown in Table II. The bands assigned as ν<sub>Mn-O</sub> or ν<sub>Ni-O</sub> show a trend to occur at lower frequency upon substitution of H with electron-releasing alkoxy groups at the 4 position of the pyridine ring. This would be expected since metal to ligand back-bonding decreases with increasing electron-releasing character of the substituent in transition metal complexes involving terminal pyridine N-oxide groups.<sup>17</sup>

A chlorine-bridged bi- or polynuclear structure may be assigned to the Mn(II) and Ni(II) complexes on the basis of the far-ir spectral assignments. Polymeric distorted octahedral complexes of the type MLC<sub>2</sub> (M = Mn, Ni; L = pyridine, quinoline, imidazole, and derivatives) have been reported.<sup>18,19</sup> Ni(II) complexes of this type exhibit magnetic moments in the same range as those of the NiCl<sub>2</sub> complexes of pyridine N-oxides.<sup>18</sup> Far-ir evidence rules out such a structure for the complexes reported here. If the coordination number of each metal ion was 6, the ν<sub>M-Cl</sub> bands should be observed at lower frequencies than those reported in Table II.<sup>8,20</sup> In fact, hexacoordinated polymeric 1:1 complexes of imidazole with manganese(II) and nickel(II) chlorides do not exhibit bands in the 400–280-cm<sup>-1</sup> region.<sup>19</sup> Absorptions at 280–250 cm<sup>-1</sup> in the spectra of these compounds have been assigned to a metal-ligand stretching vibration and the ν<sub>M-Cl</sub> bands occur below 260 cm<sup>-1</sup>.<sup>19</sup> Thus, the far-ir evidence points to a binuclear chlorine-bridged structure for the

(15) J. R. Allkins and P. J. Hendra, *ibid.*, A, 1325 (1967).

(16) Y. Kawasaki, M. Hori, and K. Uenaka, *Bull. Chem. Soc. Japan*, **40**, 2463 (1967).

(17) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

(18) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

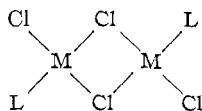
(19) D. M. L. Goodgame, M. Goodgame, P. J. Hayward, and G. W. Rayner-Canham, *Inorg. Chem.*, **7**, 2447 (1968).

(20) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

(13) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **8**, 694 (1969).

(14) D. H. Brown, D. Kenyon, and D. W. A. Sharp, *J. Chem. Soc.*, A, 1474 (1969).

new Mn(II) and Ni(II) complexes, which are formulated as



The oxygen-bridged 1:1 complexes of  $\text{CuCl}_2$  with PNO and MPNO exhibit medium-intensity  $\nu_{\text{Cu-O}}$  bands and one or two strong  $\nu_{\text{Cu-Cl}(t)}$  bands in the 330–310- $\text{cm}^{-1}$  region (Table II).<sup>3</sup>  $\text{Cu}(\text{EPNO})\text{Cl}_2$  also exhibits a medium-intensity  $\nu_{\text{Cu-O}}$  absorption (Table II) and a subnormal magnetic moment (Table IV). Nevertheless, four bands in the 375–295- $\text{cm}^{-1}$  region may be assigned to  $\nu_{\text{Cu-Cl}}$  vibrational modes (Table II). Although the magnetic properties of this complex indicate an oxygen-bridged structure, the very strong band at 298  $\text{cm}^{-1}$  may represent fairly strong intermolecular bridging chlorine to copper bonds.<sup>18,21</sup> Unambiguous characterization of this compound should be based on a complete crystal structure determination. The bands assigned as  $\nu_{\text{Cu-O}}$  in the complexes discussed occur at higher frequency with increasing bulkiness of the 4 substituent (Table II). This is in agreement with the increase of the metal to ligand bond strength with increasing steric effect of the substituent in binuclear oxygen-bridged complexes of copper(II) halides with pyridine N-oxides, discussed by Muto, *et al.*<sup>22</sup> With the exception of a medium band at 236  $\text{cm}^{-1}$ , the far-ir spectrum of  $\text{Sn}(\text{PNO})\text{Cl}_2$  shows considerable similarity to those of the Mn(II) and Ni(II) analogs.<sup>21</sup> Thus, this complex may also have a binuclear chlorine-bridged structure. Tentative assignments of  $\nu_{\text{Sn-O}}$  and  $\nu_{\text{Sn-Cl}}$  bands are given in Table II.

#### Magnetic Susceptibilities and Electronic Spectra.—

The magnetic moments of the Mn(II) complexes at 297°K (5.40–5.60 BM) (Table IV) are considerably lower than the spin-only value of 5.92 BM. Measurements at lower temperatures, down to 77°K (see Experimental Section), revealed small decrease in the moments of these complexes with decreasing temperature. Spin–spin coupling up to a certain extent possibly occurs over the range 77–300°K. Measurements at temperatures below this range should show a greater spin–spin interaction.<sup>23</sup> Similar behavior has been observed with anhydrous bis(acetylacetonato)manganese(II) ( $\mu_{\text{eff}} = 5.68$  BM at 290°K), which shows slight magnetic moment variations over the tempera-

ture range 128–418°K.<sup>23</sup> Structural assignments cannot be made on the basis of the solution electronic spectra of the Mn(II) complexes. Tetrahedral manganese(II) chloride complexes with some monodentate oxo ligands (*e.g.*, phosphine oxides) are light green, fluorescent, and triboluminescent.<sup>24</sup> The cream-white complexes reported here do neither fluoresce nor triboluminesce and show similarity in these respects to  $\text{Mn}((\text{C}_6\text{H}_5)_3\text{PO})_4^{2+}$ , which has been assigned a symmetry intermediate between distorted tetrahedral and square planar.<sup>24</sup>

The solid-state electronic spectra and magnetic moments of the Ni(II) complexes (Tables III and IV) show great similarity to those observed for  $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_4](\text{ClO}_4)_2$ , which has been assigned a  $D_{2d}$  symmetry.<sup>25</sup> X-Ray powder diffraction patterns of the new Mn(II) and Ni(II) complexes with the same ligand (*e.g.*, PNO), though not identical, exhibit considerable similarities and are distinctly different from those of the Cu(II) and Sn(II) complexes. Each metal ion is most probably tetracoordinated in the Mn(II) and Ni(II) binuclear complexes and the symmetry of the  $\text{OCIMCl}_2$  groupings is intermediate between distorted tetrahedral and square planar. Weak chlorine to metal bridging between adjacent dimers, similar to that established for the dimeric  $\text{Cu}(\text{PNO})\text{Cl}_2$ <sup>13</sup> and leading to pentacoordination, cannot be ruled out, however. *The electronic spectra of dry methanol–ethylene dichloride solutions of the Ni(II) complexes may be interpreted in terms of either a symmetry close to  $D_{2d}$  or an octahedral configuration (vide supra).* The electronic spectrum of the hydrated Co(II) complex is indicative of an essentially tetrahedral symmetry.

In conclusion, water-free binuclear 1:1 complexes of manganese(II) and nickel(II) chlorides with pyridine N-oxides are isolated under anhydrous experimental conditions. In contrast to their oxygen-bridged Cu(II) analogs, the Mn(II) and Ni(II) compounds are chlorine bridged. Nonbulky ligands (*e.g.*,  $\text{CH}_3\text{OH}$ ), when in excess, form adducts with the new complexes. The coordination number of each metal ion in the binuclear Mn(II) and Ni(II) complexes is, most probably, 4 and the symmetry of the  $\text{OCIMCl}_2$  groupings is intermediate between distorted tetrahedral and square planar. The magnetic moments of the Mn(II) complexes are suggestive of a possible spin–spin interaction.

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(22) Y. Muto, M. Kato, H. B. Jonassen, and L. C. Cusachs, *Bull. Chem. Soc. Japan*, **42**, 417 (1969).

(23) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

(24) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 3735 (1961).

(25) F. A. Cotton and E. Bannister, *ibid.*, 1873 (1960).