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4-Ethoxypyridine N-Oxide Complexes of Metal Halides and Perchlorates

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Complexes of 4-ethoxypyridine N-oxide (EPNO) with metal halides and perchlorates were synthesized and characterized by means of spectral, magnetic, conductance and, in certain cases, X-ray powder diffraction studies. $Mn(EPNO)Cl_2$ and $Pd(EPNO)_2Cl_2$ are the first examples of pyridine N-oxide complexes of this type for these metal ions. $Co(EPNO)_2Cl_2$ shows differences in its solution spectra from analogous complexes of other substituted pyridine N-oxides. Although some metal perchlorates form analogous cationic complexes to those reported for pyridine N-oxides, those of Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} form pentacoordinated cationic complexes, of the type $[M(EPNO_5]$-$(ClO_4)_2$. The Mn^{II}, Co^{II} and Ni^{II} perchlorate complexes are of the high-spin type. The presence of both penta- and hexa-coordinated species in equilibrium in solutions of the Co^{II} and Ni^{II} perchlorate complexes containing excess free ligand has been established by means of spectral evidence. Satisfactory correlation of the N–O stretching vibration of EPNO and some of its metal complexes with the ν_{NO} of other 4-substituted pyridine N-oxides and their correspondig complexes has been observed in ν_{NO} vs. σ^+ plots.

Introduction

Several studies dealing with metal complexes of aromatic amine oxides have appeared in recent years.[1] Correlations of substituent constants with characteristic properties of substituted pyridine N-oxides and their metal complexes have been successfully attempted in a number of cases.[2-7] Thus, linear plots of the N–O stretching frequencies of 4-substituted pyridine N-oxides and their metal perchlorate[5,6] and TiF_4[7] complexes *vs.* the substituent σ^+ constants have been reported.[5-7]

In view of the numerous substituted pyridine and quinoline N-oxide complexes reported,[1] a study of the complexes of 4-ethoxypyridine N-oxide (EPNO), would not be expected, prima facie, to add much to the knowledge available in the field. Nevertheless, our preliminary experiments have revealed that certain 3d metal perchlorates form 1:5 complexes with EPNO and $MnCl_2$ forms a complex of the type $MLCl_2(L=EPNO)$. The latter is the first 3d metal ion analog of the extensively studied 1:1 $CuCl_2$-pyridine N-oxide complexes[1,8] to be reported. While this study was in progress a Co^{II} perchlorate complex with 2-picoline N-oxide (2-picNO), of the type $[Co(2\text{-}picNO)_5](ClO_4)_2$, was reported.[9] In all other cases appearing in the literature, 3d metal perchlorates form hexa- or tetra- coordinated cationic complexes with aromatic amine oxides.[1] Moreover, a satisfactory correlation is obtained in the ν_{NO} of a sample of EPNO, purified by vacuum sublimation, which occurs at 1209 cm^{-1} in Nujol mull, in the ν_{NO} *vs.* σ^+ plot for 4-substituted pyridine N-oxides.[6,7] It is noteworthy, in this connection, that controversial values for the ν_{NO} of 4-methoxypyridine N-oxide (MPNO) in Nujol mull appear in the literature (1207,[10] 1210,[4,5,11] 1213,[6] 1228[7] cm^{-1}). The value of 1228 cm^{-1} has been observed in a sample of MPNO purified by vacuum sublimation.[7] However, the fit of this value in the ν_{NO} *vs.* σ^+ plots for 4-substituted pyridine N-oxides is not as satisfactory as that of the values of 1210 and 1213 cm^{-1} observed by other research groups.[5,6]

The observations cited above and the fact that no EPNO metal complexes have been reported, prompted us to undertake a study in this direction. The present paper reports on the synthesis and characterization of EPNO metal complexes as well as the correlation of the ν_{NO} of the free ligand and some of its complexes with ν_{NO} values reported for other 4-substituted pyridine N-oxides, in ν_{NO} *vs.* σ^+ plots.

Experimental Section

Chemicals: The metal salts and solvents utilized were the purest commercially available. The commercial sample of EPNO was purified by vacuum

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Table I. Properties and Analytical Data of EPNO Metal Complexes

Compound	Color	M.p. °C	Analytical Data C% Calc.	C% Found	H% Calc.	H% Found	N% Calc.	N% Found	Metal% Calc.	Metal% Found
EPNO=L (purified)	White	124.5-126.5	60.42	60.14	6.52	6.80	10.06	10.02		
$[CaL_4](ClO_4)_2$	White	233-234	42.28	42.57	4.56	4.66	7.04	6.88	5.13	5.01
TiL_2F_4	White	168-170	41.81	41.44	4.51	4.48	6.96	6.78	11.91	12.62
$[CrL_6](ClO_4)_3$	Green	220-222	42.59	42.22	4.59	4.81	7.09	7.17	4.39	4.52
$[MnL_5](ClO_4)_2$	Yellow	177-179	44.37	44.29	4.77	4.93	7.37	7.65	5.75	5.30
$MnLCl_2$	Cream-white	253-255	31.72	32.58	3.42	3.67	5.28	5.16	20.73	20.64
$[FeL_6](ClO_4)_3$	Yellow	238-239	42.42	42.40	4.58	4.78	7.07	6.87	4.69	4.51
$[CoL_5](ClO_4)_2$	Deep rose	193-195	44.08	44.22	4.76	5.06	7.34	7.57	6.18	6.52
CoL_2Cl_2	Dark blue	146-148	41.19	41.31	4.44	4.98	6.86	6.67	14.41	14.26
$[NiL_5](ClO_4)_2$	Light green	182-183	44.09	44.08	4.76	5.06	7.34	7.18	6.16	6.30
PdL_2Cl_2	Beige-orange	176-178	36.90	36.71	3.97	4.03	6.14	5.73	23.35	23.65
$[CuL_4](ClO_4)_2$	Green-blue	150-152	41.06	40.79	4.43	4.49	6.84	6.90	7.76	7.95
$CuLCl_2$	Chartreuse	241-242	30.73	30.93	3.32	3.50	5.12	4.91	23.22	22.97
$[AgL_2]ClO_4 . L$	White	149-151	40.37	40.51	4.35	4.32	6.72	6.70	17.26	17.52
$[ZnL_5](ClO_4)_2$	White	162-164	43.78	43.82	4.73	4.76	7.29	7.25	6.81	7.04
ZnL_2Cl_2	White	164-166	40.55	40.43	4.37	4.53	6.75	6.40	15.77	15.30
$[CdL_6](ClO_4)_2$	White	192-193	44.01	44.05	4.72	4.78	7.35	7.98	9.91	9.98
SnL_2Cl_4	White	96-99	31.21	29.88	3.37	3.66	5.22	4.81	22.03	23.03

sublimation,[7] and the structure of the purified compound was confirmed by elemental analysis, melting point (124.5-126.5°, which agrees with reported values[12]), NMR[13] and infrared spectroscopy.

Synthesis: The EPNO complexes of the metal perchlorates, TiF_4, $CuCl_2$, $ZnCl_2$ and $SnCl_4$ were prepared by procedures analogous to those reported in the literature.[5-7,9,14-18] During the preparation of the metal perchlorate complexes by the method of Quagliano *et al.*[15] the ratio of ligand to salt was in excess of 6:1. Refrigeration induced the formation of crystalline percipitates. $AgClO_4$ formed a 1:3 complex, the perchlorates of Ca^{II} and Cu^{II} 1:4 complexes, those of Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} 1:5 complexes, and those of Cr^{III}, Fe^{III} and Cd^{II} 1:6 complexes. The Ca^{II}, Fe^{III}, Ni^{II} and Zn^{II} complexes were recrystallized from acetonitrile. All complexes were washed with ether and dried in vacuo over $Mg(ClO_4)_2$.

In the case of $CuCl_2$, regardless of the molar ratio of ligand to salt, the chartreuse $CuLCl_2$ was always precipitated $ZnCl_2$ and $SnCl_4$ produced precipitates of the 1:2 complexes upon mixing ethanolic solutions of ligand and salt. TiL_2F_4 was precipitated during the concentration of a dichloromethane solution of the reagents under reduced pressure. CoL_2Cl_2 was precipitated as an oil from a warm (50°) ethanolic solution of EPNO and $CoCl_2 . 6H_2O$ (molar ratio 3:1) by addition of 2,2-dimethoxypropane and subsequent refrigeration. This oil was gradually solidified to dark blue crystals. Pyridine N-oxide forms a 1:3 complex with $CoCl_2$,[14,15] but the bulkier N-oxides of 2,4- and 2,6-lutidine and 2,4,6-collidine form 1:2 complexes with this salt.[19]

The only Mn^{II} halide-pyridine N-oxide complex reported is the dibromobis-(pyridine N-oxide) Mn^{II}.[14] We have prepared $MnLCl_2$ as follows. A solution of anhydrous $MnCl_2$ in a 1:1 mixture of acetone-ethanol was added to an equimolar solution of EPNO in the same solvent and to the reaction mixture an equal volume of anhydrous ether was added. The mixture was gently heated for 15 min. and then refrigerated. After 24 hours a yellow oil separted, which was solidified to a cream white precipitate after 1-2 more days in the refrigerator. The complex was filtered, washed with ether and dried over phosphorus pentoxide in vacuo.

PdL_2Cl_2 was prepared by mixing acetone solutions of $PdCl_2$ and EPNO (molar ratio 1:2) and warming at 50°. A beige-orange precipitate was formed at this temperature and increased during refrigeration. The complex was filtered, washed with ether, recrystallized from acetone and dried in vacuo over magnesium perchlorate. This is the first example of a Pd^{II} complex with pyridine N-oxides. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Analytical data and properties of the complexes are given in Table I. All syntheses were repeated at least once.

Infrared Spectra: IR spectra (4000-750 cm^{-1}) of the ligand and its metal complexes were obtained on Nujol mulls between IRTRAN 2 (zinc sulfide) windows on a Perkin-Elmer 621 spectrophotometer. The spectra were, generally, characterized by the complete absence of water bands. Calibration of the spectra was effected by means of known frequency absorptions of polystyrene. The observed values of ν_{NO} and ν_3 of ClO_4^- are given in Table II.

Electronic Spectra: The electronic spectra of solutions and Nujol mulls[6] of the complexes were obtained with a Cary Model 14 spectrophotometer and are given in Table III.

Magnetic Measurements: Magnetic susceptibilities were measured at room temperature (297 K) by the

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(13) See, A. R. Katritzky, and R. A. Y. Jones, *Proc. Chem. Soc.*, 313 (1960); A. R. Katritzky and J. M. Lagowski, *J. Chem. Soc.*, 43 (1961).

(14) K. Issleib and A. Kreibich, *Z. anorg. Chem.*, *313*, 338 (1961).

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Table II. Infrared Data (ν_{NO}, $\Delta\nu_{NO}$ and $\nu_3(ClO_4^-)$) of Nujol Mulls of EPNO Metal Complexes

Compound	ν_{NO}, cm^{-1}	$\Delta\nu_{NO}$, cm^{-1}	$\nu_3(ClO_4^-)$, cm^{-1}
EPNO (purified)	1209		
$[CaL_4](ClO_4)_2$	1220, 1202	+2 (av.)	1080
TiL_2F_4	1200	−9	
$[CrL_6](ClO_4)_3$	1197	−12	1070
$[MnL_5](ClO_4)_2$	1201, 1197 sh	−10 (av.)	1076
$MnLCl_2$	1198	−11	
$[FeL_6](ClO_4)_3$	1199	−10	1076
$[CoL_5](ClO_4)_2$	1200 sh		
	1192	−13 (av.)	1070
CoL_2Cl_2	1185	−24	
$[NiL_5](ClO_4)_2$	1204 sh		
	1198	−8 (av.)	1075
PdL_2Cl_2	1184	−25	
$[CuL_4](ClO_4)_2$	1196	−13	1087 (broad)
$CuLCl_2$	1202, 1184	−16 (av.)	
$[AgL_2]ClO_4 . L$	1196, 1179	−21.5 (av.)	1090
$[ZnL_5](ClO_4)_2$	1203 sh		
	1199	−8 (av.)	1068
ZnL_2Cl_2	1185	−24	
$[CdL_6](ClO_4)_2$	1201	−8	1078
SnL_2Cl_4	1190, 1170	−29 (av.)	

Table III. Electronic Spectra of 4-Ethoxypyridine N-oxide Metal Complexes [a]

Complex	Medium	ν max, cm^{-1} (ε max)
$[CrL_6](ClO_4)_3$	Nujol mull	16,130, 22,940, 29,410 sh
	4.3×10^{-3} *M* in CH_3NO_2	15,970 (81.8), 23,750 (154.7), 27,100 (198.4)
	0.78×10^{-3} *M* in CH_3CN	15,670 (94.9), 23,200 (141)
$[MnL_5](ClO_4)_2$	0.72×10^{-3} *M* in CH_3CN	20,920 (6.9), 22,940 sh, 26,950 (534.7)
$MnLCl_2$ [b]	in $CH_2Br_2+CH_3NO_2$	22,780, 27,800
$[FeL_6](ClO_4)_3$	in CH_3NO_2	>27,000
$[CoL_5](ClO_4)_2$	Nujol mull	12,800, 18,550, 19,530, 25,640
	9.6×10^{-3} *M* in CH_3NO_2	8,700 w, 12,720 (9.4), 13,280 (8.9), 17,590 sh, 18,250 (56.5), 19,380 (50.7)
	6.6×10^{-3} *M* in a 6.4×10^{-2} *M* EPNO solution in CH_3NO_2	8,280 (9.1), 13,280 (6.4), 15,500 sh, 18,590 (53.6), 20,080 sh
CoL_2Cl_2	5.2×10^{-3} *M* in CH_3NO_2	6,380 (50.6), 14,990 (365.4), 16,100 (347.1)
	5.2×10^{-3} *M* in absolute CH_3OH	7,050 (9.8), 17,550 sh, 19,630 (24.5)
$[NiL_5](ClO_4)_2$	Nujol mull	8,260, 9,170, 13,300, 18,980 sh, 22,880 sh, 26,950
	4.3×10^{-2} *M* in CH_3NO_2	7,210 sh, 8,060 (10.1), 8,730 sh, 12,020 sh, 12,580 sh, 13,760 (15.8), 18,250 sh, 26,960 (237.1)
	4.3×10^{-2} *M* in a 6.4×10^{-2} *M* EPNO solution in CH_3NO_2	7,140 sh, 7,930 (10.8), 8,700 sh, 10,420 w, 12,090 sh, 12,530 (13.8), 13,000 sh, 13,530 (14.9), 14,100 sh, 15,970 sh, 18,250 sh
PdL_2Cl_2	2.9×10^{-3} *M* in CH_3CN	25,580 (397.2)
$[CuL_4](ClO_4)_2$	3.1×10^{-3} *M* in CH_3NO_2	14,950 (114.7)
$CuLCl_2$ [b]	in $CH_2Br_2+CH_3NO_2$	12,740

sh: shoulder, w: weak. [a] The spectra of thc complexcs are generally characterized by an intense charge-transfer band in the UV, which trails into the visible.[16] In some cases the band at 25,000-28,000 cm^{-1} is either masked by this absorption or appearing as a shoulder. [b] Saturated solution.

Table IV. Magnetic Moments of EPNO Metal Complexes at 297 K.

Complex	$\chi_M^{corr}\times10^6$	μ_{eff}, BM
$[CrL_6]ClO_4)_3$	6,183	3.85
$[MnL_5](ClO_4)_2$	15,035	6.00
$MnLCl_2$	12,842	5.54
$[FeL_6](ClO_4)_3$	14,994	5.99
$[CoL_5](ClO_4)_2$	8,809	4.60
CoL_2Cl_2	9.439	4.76
$[NiL_5](ClO_4)_2$	4,543	3.30
$[CuL_4](ClO_4)_2$	1,920	2.09
$CuLCl_2$	181	0.66

Table V. Molar Conductivities of 5×10^{-5} *M* Nitromethane Solutions of ENPO-Metal Perchlorate Complexes at 21°C.

Complex	Λ_M, ohm^{-1} cm^2 $mole^{-1}$
$[CaL_4](ClO_4)_2$	194.2
$[CrL_6](ClO_4)_3$	296.6
$[MnL_5](ClO_4)_2$	215.8
$[FeL_6](ClO_4)_3$	294.7
$[CoL_5](ClO_4)_2$	194.4
$[NiL_5](ClO_4)_2$	209.7
$[CuL_4](ClO_4)_2$	197.9
$[AgL_2]ClO_4 . L$	126.1
$[ZnL_5](ClO_4)_2$	186.8
$[CdL_6](ClO_4)_2$	193.2

Faraday method. Mercuric tetrathiocyanato-cobaltate(II) was used as the magnetic susceptibility standard. Pascal's constants were utilized for diamagnetic corrections.[20] Magnetic moments were calculated by use of the equation $\mu_{eff} = 2.84\sqrt{\chi_M^{corr} . T}$ and are shown in Table IV.

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[20] J. Lewis and R. G. Wilkins, « Modern Coordination Chemistry », Interscience Publishers, Inc., New York 1960, 403.

Conductance Measurements: The conductivities of $5\times10^{-5}\,M$ nitromethane solutions of the perchlorate complexes were measured at 21° by using a Wayne Kerr Universal bridge and a cell calibrated with aqueous 0.01 N potassium chloride. The results, shown in Table V, clearly indicate that the Ag^{I} complex is a 1:1 electrolyte, those of Ca^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} are 2:1 electrolytes and the Cr^{III} and Fe^{III} complexes 3:1 electrolytes.[9,21]

NMR Spectra: The proton NMR spectrum of the purified EPNO was recorded on a $CDCl_3$ solution with a Varian A-60 A Analytical NMR spectrometer. Tetramethylsilane was used as internal reference. This spectrum exhibits the chemical shifts and fine structure expected for the α and β protons of the pyridine ring and the CH_3 and CH_2 protons of the ethoxy group.[13] The absence of any other signal in the spectrum excludes the presence of any impurity in the purified ligand.

Discussion

Infrared Spectra: EPNO purified by vacuum sublimation, which is slightly hygroscopic, shows the ν_{NO} at 1209 cm^{-1} (Nujol mull), and a slight shoulder at 1240 cm^{-1}. Upon complex formation the 1209 cm^{-1}band is considerably shifted, while the band at 1240 cm^{-1} shows negligible frequency variations. The latter band has been assigned as CH in-plane deformation in pyridine N-oxide complexes.[22] Thus, there is no doubt as far as the assignment of the 1209 cm^{-1} band as ν_{NO} is concerned. The ν_{NO} of EPNO observed correlates satisfactorily with the ν_{NO} values of other 4-substituted pyridine N-oxides,[6,7] in the ν_{NO} *vs.* σ^+ plots as shown in Figure 1.

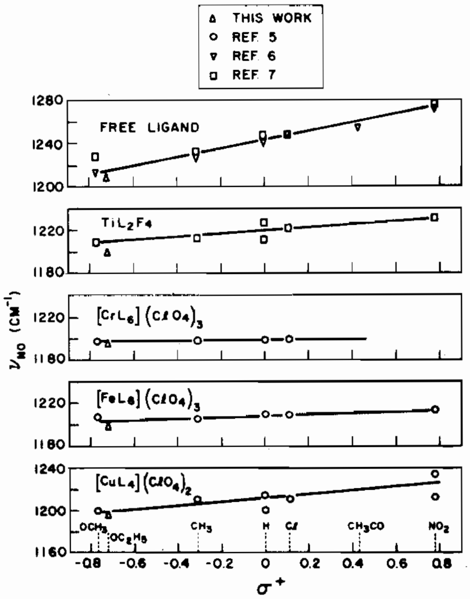

Figure 1. Correlation of N—O stretching vibrations of 4-ethoxypyridine N-oxide and some of its complexes to those of other 4-substituted pyridine N-oxides and their corresponding complexes, in ν_{NO} *vs.* σ^+ plots. Values of σ^+ taken from: R. O. C. Norman and T. Taylor, « Electrophilic Substitution in Benzenoid Compounds », Elsevier Publishing Co., Amsterdam, 1965, 287 for OC_2H_5; H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, *79*, 1913 (1957) for the other substituents.

With the exception of the $Ca(ClO_4)_2$ complex, the coordination of the ligand to the metal ion through the oxygen of the N—O group is obvious from the negative ν_{NO} shifts (Table II). In $[CaL_4](ClO_4)_2$ the N—O stretch occurs as a doublet at 1220 and 1202 cm^{-1}. Alkaline earth perchlorate complexes with sulfoxides show the S—O stretch at higher frequencies than the corresponding transition metal perchlorate complexes.[23] On the other hand, the occurrence of the ν_{NO} in MPNO and, consequently, EPNO metal complexes at higher frequencies than would be expected, is discussed in detail by Herlocker *et al.*[6] It is, thus, not surprising that the Ca^{II} complex shows an average ν_{NO} of $+2$ cm^{-1}. Further, since Ca^{2+} has no d electrons available for metal-to ligand back-bonding,[6] a σ-donor strength toward Ca^{2+} and coupling of the N-oxide and metal-oxygen frequencies, as discussed by Herlocker *et al*,[6] can explain satisfactorily the high ν_{NO} observed. The above discussion accounts for the positive average ν_{NO} shift and coordination through the N—O oxygen can, therefore, be assumed for the Ca^{II} complex.

The ν_{NO} data of Table II are, generally, in agreement with the arguments of Herlocker *et al*[6] mentioned above. Thus, for example, in the EPNO-d^3-d^{10} metal perchlorate complexes $\Delta\nu_{NO}$ varies between -8 and -13 cm^{-1} and is considerably smaller than the $\Delta\nu_{NO}$ in the corresponding unsubstituted pyridine N-oxide complexes, which varies between -18 and -37 cm^{-1}.[15,24] Satisfactory correlations of the ν_{NO} of the Cr^{III}, Fe^{III} and Cu^{II} perchlorate-EPNO complexes with the ν_{NO} values reported for the corresponding complexes of other 4-substituted pyridine N-oxides[5] are obtained in ν_{NO} *vs.* σ^+ plots, as shown in Figure 1. However, the ν_{NO} of $Ti(EPNO)_2F_4$ does not correlate as well with the ν_{NO} reported for the corresponding TiF_4-pyridine N-oxide complexes.[7] In the IR spectra of the metal perchlorate complexes there is no indication of any deviation of the perchlorate ion from pure T_d symmetry. In fact, the ν_3 mode of ClO_4 occurs as a single rather broad band in the region of 1090-1068 cm^{-1}, which is characteristic of coordination compounds containing the perchlorate ion.[25]

Metal Halide Complexes: $CuLCl_2$ shows an abnormally low magnetic moment (0.66 BM) at room temperature, as expected.[1,8] The magnetic moment of $MnLCl_2$ (5.54 BM) is close to that observed for $Mn(C_5H_5NO)_2Br_2$ (5.62 BM).[14] Both these values are lower than the moments observed usually in high-spin Mn^{II} complexes (5.90 BM).[26] $CuLCl_2$ and $MnLCl_2$ show similar solubility characteristics, *i.e.* they are

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(21) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1187 (1964).

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

(23) P. W. N. M. van Leeuwen, *Rec. Trav. Chim.*, *86*, 201 (1967).

(24) Y. Kakiuti, S. Kida, and J. V. Quagliano, *Spectrochim. Acta*, *19*, 201 (1963).

(25) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961)

(26) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, *6*, 37 (1964).

insoluble in most organic solvents and very sparingly soluble in dibromomethane and nitromethane.

Their solubility in the latter solvents is insufficient for molecular weight determinations. The main interest in 1:1 complexes of Cu^{II} halides with aromatic amine oxides lies in their abnormally low and temperature-dependent magnetic moments.[1,8] These complexes have been found to be dimeric and possessing binuclear oxygen-bridged structures in the solid state.[8,27] The spectral and magnetic data available are not sufficient for the characterization of the Mn^{II} complex. Further work on the synthetic, structural and magnetic aspects of these complexes will be reported in a future publication, including the properties of some 1:1 Mn^{II} and Ni^{II} chloride complexes with pyridine N-oxide and MPNO.

CoL_2Cl_2 has the same ligand to salt molar ratio as the corresponding lutidine and collidine N-oxide complexes.[19] The magnetic moment (4.76 BM) and electronic spectra of this complex in nitromethane solution and Nujol mull clearly indicate a tetrahedral ligand-field symmetry. In methanol solution the complex is in an octahedral environment (Table III), as is also the case with the analogs mentioned above.[19] The difference between CoL_2Cl_2 and the latter complexes lies in their solution spectra in nitromethane, in which the di- or tri- methylpyridine N-oxide complexes appear to have a symmetry intermediate between T_d and centrosymmetric.[19] On the basis of the evidence reported here, CoL_2Cl_2 is assigned a T_d symmetry, which changes to octahedral in the presence of an excess of relatively non-bulky solvent molecules, such as methanol, by coordination of two molecules of the solvent to the metal ion.

The extensively studied complexes of the type (A) $PtCl_2$ (pyridine N-oxide) (A = olefin, CO) are of square planar symmetry.[29] The Pt—O—N angle is 120° and the plane of the pyridine N-oxide ring is almost at right angle to the plane defined by the Pt atom and the four atoms bonded to it.[28] The electronic spectrum of PdL_2Cl_2 suggests a square planar symmetry.[29] This complex, which contains two EPNO molecules coordinated to Pd^{II} through the N—O oxygens, would, therefore, offer an interesting case for crystal structure determination.

An octahedral arrangement with the EPNO molecules occupying adjacent cis positions is assigned to TiL_2F_4,[30] and a distorted tetrahedral symmetry is assigned to ZnL_2Cl_2,[31] on the basis of structural determinations reported for corresponding complexes with other pyridineN-oxides.[30,31] For the only reported analog of SnL_2Cl_4, *i.e.* $Sn(C_5H_5NO)_2Br_4$, no structural assignment was made.[15]

Metal Perchlorate Complexes: The formulation of the metal perchlorate complexes as $[ML_n](ClO_4)_m$ is justified from the conductance measurements in nitromethane (Table V). The 1:3 Ag^I complex is formulated as $[AgL_2]ClO_4 . L$. This formulation was proposed by Schmauss and Specker for 1:3 $AgClO_4$ complexes with pyridine N-oxides on the basis of the occurrence of ν_{NO} as a doublet, which is indicative of two chemically inequivalent sets of ligands, and of the tendency of Ag^I to exhibit linear two-fold coordination.[18] In the IR spectrum of the EPNO complex, ν_{NO} occurs as a doublet (Table II).

$[CuL_4](ClO_4)_2$, $[CrL_6](ClO_4)_3$ and $[FeL_6](ClO_4)_3$ are analogous to the corresponding complexes of other 4-substituted pyridine N-oxides reported in the literature.[5,9,16,22,24] Nujol mull and solution electronic spectra of the Cr^{III} and Cu^{II} complexes are in satisfactory agreement. The electronic spectra of these complexes and the magnetic moments of the Fe^{III}, Cr^{III} and Cu^{II} complexes are in agreement with the spectral and magnetic data reported for the corresponding complexes of other 4-substituted pyridine N-oxides.[5,9] It is worth noting that he Cr^{III} complexes of EPNO (Table III, Figure 2) and MPNO have almost identical electronic spectra in the solid state and their spectrochemical parameters toward Cr^{III}[5] are, therefore, closely similar. $[CdL_6]^{2+}$ is assigned a similar ligand-field symmetry to that of $[CrL_6]^{3+}$ and $[FeL_6]^{3+}$ on the basis of the close resemblance of the X-ray powder diffraction patterns of their perchlorate complexes.

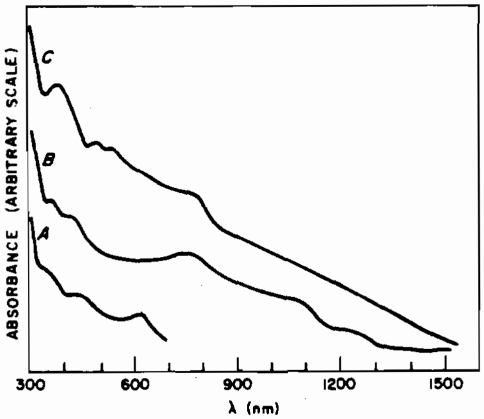

Figure 2. Solid state electronic spectra in Nujol mulls of (A) $[CrL_6](ClO_4)_3$, (B) $[NiL_5](ClO_4)_2$, (C) $[CoL_5](ClO_4)_2$.

As far as the ligand-field symmetries of 1:4 and 1:6 metal perchlorate (or tetrafluoroborate)-pyridine N-oxide complexes are concerned, D_{4h} and O_h configurations, respectively, have been generally assumed.[1] Nevertheless, a very recent study indicates that such symmetries can be assigned only to the MO_4 and MO_6 moieties, on the basis of a detailed examination of the vibrational and electronic (at −196°) spectra and magnetic moments of pyridine N-oxide-metal perchlorate complexes.[9] If the entire ligand molecule is considered the effective symmetries of the complex cations are lower than D_{4h} or O_h.[9] Multiple bands near 1200 cm^{-1} in the IR spectra of these complexes have been attributed to ν_{NO} frequencies and interpreted in terms of the symmetry lowering.[9] Examina-

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(27) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, *42*, 504 (1965).
(28) M. Orchin and P. J. Schmidt, *Coordin. Chem. Rev.*, *3*, 345 (1968).
(29) See, H. P. Fritz, I. R. Gordon, K. E. Schwarzhans and L. M. Venanzi, *J. Chem. Soc.*, 5210 (1965).
(30) D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966); *Inorg. Chem.*, *6*, 8 (1967).
(31) R. S. Sager and W. H. Watson, *ibid.*, *7*, 1358 (1968).

tion of the corresponding EPNO complexes, in the light of this recent evidence, reveals that the ν_{NO} bands of the Fe^{III} and Cd^{II} perchlorate complexes are quite sharp, but those of the Cr^{III} and Cu^{II} complexes are broader and the possibility of overlapping of two closely located absorptions cannot be excluded. In the case of the Ca^{II} complex the splitting of ν_{NO} in two bands occurs (Table II).

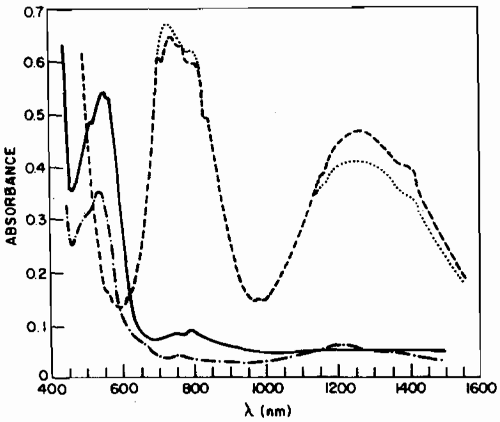

Figure 3. Solution spectra of: (——), $[CoL_5](ClO_4)_2$, 9.6×10^{-3} *M* in nitromethane; (. . .), $[NiL_5](ClO_4)_2$, $4.3\times\times10^{-2}$ *M* in CH_3NO_2(700-800,1100-1500 nm); (—.—), $[CoL_5](ClO_4)_2$, 6.6×10^{-3} *M* in a 6.4×10^{-2} *M* solution of EPNO in nitromethane; (- - -), $[NiL_5](ClO_4)_2$, 4.3×10^{-2} *M* in a 6.4×10^{-2} *M* solution of EPNO in nitromethane.

The pentacoordinated complexes of the type $[ML_5](ClO_4)_2$ (M = Mn, Co, Ni, Zn) are of interest, since only one complex of this type, namely $[Co(2\text{-}PicNO)_5](ClO_4)_2$, has been reported.[9] The Nujol mull and nitromethane solution electronic spectra of the Co^{II} complex (Figure 2 and 3) are in satisfactory agreement and they show close similarity to the spectra of $[Co(2\text{-}PicNO)_5](ClO_4)_2$.[9] The latter complex has been assigned a trigonal bipyramidal configuration,[9] on the basis of the resemblance of its spectrum to the spectra of pentacoordinated Co^{II} complexes of this configuration, reported by Ciampolini and Nardi.[32]

The Nujol mull spectrum of $[NiL_5](ClO_4)_2$ (Figure 2) shows also similarity to reported Ni^{II} complexes of trigonal bipyramidal or lower symmetry.[32-34] Its nitromethane solution spectrum (Table III, Figure 3) also resembles the spectra of pentacoordinated Ni^{II} complexes in solution.[33,35] If free ligand is added to nitromethane solutions of the Co^{II} and Ni^{II} complexes dramatic spectral changes occur (Figure 3), clearly indicating the existence of pentacoordinated-hexacoordinated equilibria in solution. In fact, the intensity of the doublet at 12,720 and 13,280 cm^{-1}, which is characteristic of the pentacoordinated Co^{II} complex, is considerably lowered while a new broad band with its maximum at 8,280 cm^{-1} appears. Further, a shoulder appears at 15,500 cm^{-1} and the bands at 18,250 and 19,380 cm^{-1} show a blue shift. All these characteristics are indicating the presence of both $[CoL_5](ClO_4)_2$ and $[CoL_6](ClO_4)_2$ in a nitromethane solution of the pentacoordinated complex containing excess free ligand. It should be noted, in this connection, that the solid state spectrum of $[Co(MPNO)_6](ClO_4)_2$ shows absorption maxima at 8,333, 14,930, 18,180 and 20,000 cm^{-1}.[5] $[NiL_5](ClO_4)_2$, under similar conditions, shows two additional bands at 13,000 and 14,100 cm^{-1} and a considerable decrease in the intensity difference between the bands at 12,000-14,000 cm^{-1} and 7,000-9,000 cm^{-1}. $[Ni(MPNO)_6](ClO_4)_2$ shows the following absorption maxima (cm^{-1}) in nitromethane solution (ε_{max} in parentheses): 8,000 (12.2), 12,820 (12.5), 14,045 (13.9), 25,975 (450).[6] Thus, the changes observed in a nitromethane solution of the Ni^{II} complex containing excess free ligand are fully consistent with the presence of $[NiL_5]$ $(ClO_4)_2$ and $[NiL_6](ClO_4)_2$ in equilibrium.

The magnetic moments of the Co^{II} (4.60 BM), Ni^{II} (3.30 BM) and Mn^{II} (6.00 BM) complexes are within the range observed for highspin pentacoordinated complexes of these metal ions.[9,32-36] The structural similarity of the Mn^{II} and Zn^{II} perchlorate complexes, for which structural assignments cannot be made on the basis of electronic spectra, to those of Co^{II} and Ni^{II}, is obvious from the close resemblance of the X-ray powder diffraction patterns of the four complexes. These patterns are distinctly different from those of the tetra- and hexa- coordinated metal perchlorate complexes reported. Moreover, the N—O stretching vibrations of the pentacoordinated complexes occur as doublets (Table II). Due to the small separation of the maxima of these bands (4-8 cm^{-1}), the lower intensity absorption appears as a shoulder. A similar doublet (1208 and 1196 cm^{-1}) has been observed in $[Co(2\text{-}PicNO)_5](ClO_4)_2$.[9] Supporting evidence concerning pentacoordination is provided by the analytical data. The Ni^{II} and Zn^{II} complexes were analyzed after double recrystallization from acetonitrile. The Mn^{II} complex, which obtains a darker color during storage as in the case of $[Mn(C_5H_5NO)_6](ClO_4)_2$,[16] and that of Co^{II} could not be recrystallized from acetonitrile or a number of other solvents. Finally, coordination of one $OClO_3$ group to the metal ion, in the crystal or in solution, which would lead to hexacoordination, is excluded on the basis of the already discussed vibrational and electronic spectral data and conductance measurements.

It should be pointed out that neither the spectral nor the magnetic data available can be considered as definitive criteria for assigning a configuration to the pentacoordinated complex cations. Furlani stresses the point that pure, regular trigonal bipyramids (D_{3h}) or square pyramids(C_{4v}) practically never occur, and that a continuous variation between these two limiting geometries is possible and can actually occur by a normal vibration of either structure.[37] He also discusses the difficulties encountered in assigning a ligand-field symmetry to pentacoordinated complexes from spectral data, because of the close similarity of the

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(32) M. Ciampolini and N. Nardi, *ibid.*, *5*, 41 (1966).
(33) L. Sacconi, I. Bertini, and R. Morassi, *ibid.*, *6*, 1548 (1967).
(34) M. Ciampolini and N. Nardi, *ibid.*, 445.
(35) L. Sacconi and I. Bertini, *ibid.*, *7*, 1178 (1968).
(36) M. Ciampolini and N. Nardi, *ibid.*, *5*, 1150 (1966).
(37) C. Furlani, *Coordin. Chem. Rev.*, *3*, 141 (1968).

energy level diagrams of the D_{3h} and C_{4v} configurations and the presence of lower symmetry components leading to deviations from these idealized symmetries.[37] Magnetic moments observed for high-spin pentacoordinated complexes of Co^{II} and Ni^{II} halides with multidentate ligands, having trigonal bipyramidal, distorted square pyramidal or intermediate crystal structures established by X-ray studies,[38] do not show significant variations, *i.e.*: Trigonal bipyramidal (C_3 symmetry); Co^{II} 4.45-4.60 BM; Ni^{II} 3.10-3.42 BM;[32,39] distorted square pyramidal: Co^{II} $<$4.70 BM, Ni^{II} 3.30 BM;[40] intermediate between D_{3h} and C_{4v}: Co^{II} 4.60-4.80 BM; Ni^{II} 3.38 BM.[41]

Thus, in the absence of X-ray structural studies, the only criterion available in favor of a configuration close to trigonal bipyramidal for the structurally similar pentacoordinated EPNO complexes is the close similarity of the electronic spectrum of $[Co(EPNO)_5]^{2+}$ to that of $[Co(2\text{-}picNO)_5]^{2+}$, which is believed to be trigonal bipyramidal.[9] Complexes characterized by the MnO_5, CoO_5, and NiO_5 moieties have been recently reported.[9,42] However, Zn^{II} complex is the first example of a compound with five identical monodentate oxygen ligands for this ion.

Conclusion

The most interesting feature of the present study is the synthesis of complexes with unusual ligand to metal salt ratios, such as the pentacoordinated metal perchlorate complexes and $MnLCl_2$. The latter complex, which is the first example of a 3d metal ion analog of $CuLCl_2$, is the subject of structural studies currently in progress. Though 2-substituted pyridine N-oxides have been shown to form lower coordinated complexes than 3- or 4-substituted pyridine N-oxides,[9,19] presumably due to steric hindrance, this would not be expected from 4-substituted compounds. In fact 4-substituted pyridine N-oxides, including MPNO, and even 4- and 6-substituted quinoline N-oxides invariably form 1:6 complexes with 3d metal perchlorates, with the exception of Cu^{II}.[1,43] For the latter metal ion, the 1:4 complex is generally formed and only in the case of the unsubstituted pyridine N-oxide have both $[Cu(C_5H_5NO)_4]^{2+}$ and $[Cu(C_5H_5NO)_6]^{2+}$ been reported.[5,16]

The isolation of 1:5 complexes of EPNO with some divalent 3d metal perchlorates was therefore quite unexpected. However, spectral evidence shows that penta- and hexa- coordinated species are in equilibrium in solutions of $[CoL_5](ClO_4)_2$ and $[NiL_5](ClO_4)_2$ containing excess free ligand. It is, therefore, obvious that this is an analogous case to that of the 1:4 and 1:6 complexes of $Cu(ClO_4)_2$ with pyridine N-oxide. The conditions favoring the precipitation of $[ML_6](ClO_4)_2$ (M = Mn, Co, Ni, Zn) remain to be determined, as we have not been able to prepare these complexes by modifying the synthetic procedure. Work in this direction and toward the isolation of 1:5 complexes of the same salts with other 4-substituted pyridine N-oxides is currently in progress.

Acknowledgement. Thanks are due to Mr. C. M. Paleos for the purification of the ligand.

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