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Mono- and Bi-dentate Nitrato and Cationic 4-Ethoxypyridine N-Oxide Complexes with Metal Nitrates

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Synthetic and characterization studies of 4-ethoxypyridine N-oxide (EPNO) complexes with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} nitrates are reported. The following structural assignments were made on the basis of spectral, magnetic and conductance studies: [$M(EPNO)_2(O_2NO)_2$] *(M = Co, Ni, Zn), essentially* O_h *symmetry with coordinated bidentate nitrato groups;* [$Cu(EPNO)_2(ONO_2)_2$]*, essentially planar symmetry;* [$Co(EPNO)_3(ONO_2)_2$]*, involves penta-coordinated Co^{II}; the last two complexes have coordinated monodentate nitrato groups;* [$M(EPNO)_6$](NO_3)$_2$ *(M = Co, Ni), distorted* O_h *symmetry;* [$Cu(EPNO)_4$](NO_3)$_2$*, essentially planar symmetry. Mono- and bi-dentate nitrato groups, as well as ionic* NO_3^-*, are easily distinguishable from the IR spectra of the new complexes. A* C_s *symmetry was assigned to the coordinated monodentate nitrato group, and a* C_{2v} *symmetry to the bidentate nitrato group.*

Introduction

Various studies dealing with complexes of metal nitrates with pyridine N-oxides have appeared in recent years.[1-9] Complexes of the types [$ML_2(NO_3)_2$] (M = Mn, Co, Ni, Cu, Zn, Hg; L = pyridine N-oxide and substituted derivatives),[1-7] [ML_6](NO_3)$_2$ (M = Mn, Co, Ni, Cu, Zn)[1-3] and [$ML_4(NO_3)$]$^{2+}$ (M = Y, Ln)[8] have been reported. Ni(NO_3)$_2$ yields with some 2-substituted pyridine N-oxides complexes of the type [$NiL_4(NO_3)_2$] and with quinoline N-oxide (QNO) the complex [$Ni(QNO)_3(NO_3)_2$] . 1/2H_2O.[7] The crystal structure determination of [$Cu(C_5H_5NO)_2(NO_3)_2$] revealed that this compound is dimeric, involving two bridging and two terminal pyridine N-oxide molecules, with the coordinated nitrate groups acting as monodentate ligands.[9] The Cu^{II} ion is in a distorted tetragonal pyramidal environment of five oxygen atoms.[9]

We have recently reported the complexes of 4-ethoxypyridine N-oxide (EPNO) with metal halides and perchlorates.[10] A number of divalent 3d metal perchlorates (Mn, Co, Ni, Zn) yield penta-coordinated cationic complexes with EPNO, while in the presence of excess ligand equilibria between the species [$M(EPNO)_5$]$^{2+}$ and [$M(EPNO)_6$]$^{2+}$ (M = Co, Ni) have been established by means of spectral studies.[10] Extension of our recent studies,[10] to include the complexes of 3d metal nitrates with EPNO, is herein reported. Of particular interest are the infrared spectra of the new complexes, which provide conclusive evidence on the nature of the nitrate group in each compound (*i.e.* ionic nitrate, monodentate and bidentate nitrato group). In addition, an unusual pentacoordinated complex of the type [$Co(EPNO)_3(NO_3)_2$] has been synthesized and characterized.

Experimental Section

Chemicals. EPNO was purified by vacuum sublimation, as described elsewhere.[10] The metal salts and solvents utilized were the purest commercially available.

Syntheses. Complexes of the type [$M(EPNO)_2(NO_3)_2$] (M = Co, Ni, Cu, Zn) were synthesized by mixing warm absolute ethanol solutions of ligand and hydrated salt (in molar ratio 2:1), allowing to cool, adding 2,2-dimethoxypropane in excess and leaving in the refrigerator for several days. For the precipitation of the Cu^{II} complexes addition of 2,2-dimethoxypropane is not necessary. Crystalline complexes were formed by this procedure. They were filtered, washed with ether and dried in an evacuated desiccator over magnesium perchlorate. The 3:1 to 6:1 crystalline complexes described below were treated in the same way.

Complexes with ligand to metal ratios higher than 2:1 were prepared as follows.

[*Co(EPNO)$_3$(NO$_3$)$_2$*]. This complex was prepared by mixing equimolar solutions of Co(NO_3)$_2$. 6H_2O

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Table I. Properties and Analyses of 4-Ethoxypyridine N-Oxide-Metal Nitrate Complexes

Complex	Color	M.p. °C	Analysis C% Calc.	C% Found	H% Calc.	H% Found	N% Calc.	N% Found	Metal % Calc.	Metal % Found
$[Co(EPNO)_2(O_2NO)_2]$	Rose	102-103	36.46	36.65	3.93	4.25	12.15	11.93	12.78	12.30
$[Ni(EPNO)_2(O_2NO)_2]$	Light green	150-151	36.47	36.29	3.94	3.77	12.15	11.80	12.73	12.37
$[Zn(EPNO)_2(O_2NO)_2]$	White	125-126	35.95	35.57	3.88	3.93	11.98	11.61	13.98	14.10
$[Co(EPNO)_3(ONO_2)_2]$	Garnet	126-128	42.00	41.59	4.53	4.68	11.67	11.29	9.82	9.73
$[Cu(EPNO)_2(ONO_2)_2]$	Green	129-131	36.10	35.93	3.89	3.99	12.03	11.77	13.64	13.88
$[Co(EPNO)_6](NO_3)_2$	Brick red	144-145	49.56	49.72	5.35	5.77	11.01	10.71	5.79	5.45
$[Ni(EPNO)_6](NO_3)_2$	Yellow	146-148	49.57	49.88	5.35	5.55	11.01	10.67	5.77	5.66
$[Cu(EPNO)_4](NO_3)_2$	Blue green	61-62	45.19	44.63	4.88	5.13	11.29	10.92	8.54	8.32

Table II. Ligand NO Stretching Vibration[a] and Nitrate IR Bands in EPNO-Metal Nitrate Complexes (cm^{-1})

Complex	ν_{NO}	$\Delta\nu_{NO}$						
			Bidentate Nitrate (C_{2v})[b]					
			ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$[Co(EPNO)_2(O_2NO)_2]$	1199 vs	−10	1408 vs	972 m-s	815 m-s	1318 vs	740 m, sh	688 w
$[Ni(EPNO)_2(O_2NO)_2]$	1194 vs	−15	1400 vs	970 m-s	812 m-s	1321 vs	720 m	682 w
$[Zn(EPNO)_2(O_2NO)_2]$	1201 vs	−8	1406 vs	971 m-s	819 m-s	1323 vs	728 m	695 w, sh
			Monodentate Nitrate (C_s)[b]					
			ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$[Co(EPNO)_3(ONO_2)_2]$	1196 vs	−13	1282 vs	1020 vs	730 m, sh	1475 vs	720 m, sh	812 m
$[Cu(EPNO)_2(ONO_2)_2]$	1188 vs, b	−21	1275 vs	1013 vs	740 m-s	1485 vs	713 m, sh	805 m
			Ionic Nitrate (D_{3h})[b]					
			ν_1		ν_2		ν_3	ν_4
$[Co(EPNO)_6](NO_3)_2$	1195 vs	−14	[c]		816 m, sh		1360 vs	718 m, sh
$[Ni(EPNO)_6](NO_3)_2$	1201 vs	−8	[c]		813 m, sh		1350 vs	705 m, sh
$[Cu(EPNO)_4](NO_3)_2$	1203 vs	−6	[c]		825 m, sh		1355 vs	725 m, sh

Abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very. [a] ν_{NO} in free EPNO occurs at 1209 cm^{-1}.[10] [b] Labelling of vibrational modes of ionic (ν_{1-4}) and coordinated (ν_{1-6}) nitrate after Addison and Simpson.[13a] [c] IR inactive.

Table III. Electronic Spectra of EPNO-Metal Nitrate Complexes

Complex	Medium	ν_{max}, cm^{-1} (ε_{max})	Onset of charge transfer cm^{-1}
$[Co(EPNO)_2(O_2NO)_2]$	Nujol mull	29,330 vs, 19,490 s, 16,130 sh, 8,140 m.	22,700
	13×10^{-3} *M* in CH_3NO_2 + acetone	18,720 (48.5), 8400 (7.8).	23,000
$[Ni(EPNO)_2(O_2NO)_2]$	Nujol mull	26,180 s, sh, 15,315 m, b, 13,020 sh, 8,330 w.	20,000
$[Cu(EPNO)_2(ONO_2)_2]$	Nujol mull	13,610 s, b.	21,300
	12×10^{-3} *M* in CH_3NO_2	13,480 (125.0).	22,700
$[Co(EPNO)_3(ONO_2)_2]$	Nujol mull	27,470 vs, sh, 19,920 s, 19,090 s, sh, 14,660 m, b, 11,110 w, b.	22,200
	2×10^{-3} *M* in CH_3NO_2	19,305 sh, 18,180 (30.0), 17,990 sh, 8,330 (3.0).	22,700
$[Co(EPNO)_6](NO_3)_2$	Nujol mull	25,975 vs, 19,800 sh, 18,380 s, 15,725 sh, 8,330 m.	22,200
	42×10^{-3} *M* in CH_3NO_2	18,800 (27.4), 8,590 (3.6).	22,200
$[Ni(EPNO)_6](NO_3)_2$	Nujol mull	25,310 vs, sh, 13,810 m, 12,780 m, 8,000 w, b.	21,300
	2.5×10^{-3} *M* in CH_3NO_2	$>$26,300 ($>$190), 13,930 (20.0), 12,690 sh, 8,410 (15.2).	21,300
$[Cu(EPNO)_4](NO_3)_2$	Nujol mull	13,480 s, b.	19,600
	5×10^{-3} *M* in CH_3NO_2	13,810 (144.7)	21,500

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

Table IV. Magnetic Moments at 300°K and Molar Conductivities of 10^{-3} *M* Nitromethane Solutions at 24°C of EPNO-Metal Nitrate Complexes

Complex	$\chi_M^{corr}\times10^6$	μ_{eff}, BM	Λ_M, ohm^{-1} cm^2 $mole^{-1}$
$[Co(EPNO)_2(O_2NO)_2]$	10,075	4.93	13
$[Ni(EPNO)_2(O_2NO)_2]$	3,557	2.93	[a]
$[Cu(EPNO)_2(ONO_2)_2]$	1,672	2.01	26
$[Zn(EPNO)_2(O_2NO)_2]$	Diamagnetic		23
$[Co(EPNO)_3(ONO_2)_2]$	8,768	4.58	48
$[Co(EPNO)_6](NO_3)_2$	8,567	4.56	71
$[Ni(EPNO)_6](NO_3)_2$	4,770	3.39	72
$[Cu(EPNO)_4](NO_3)_2$	1,704	2.03	77

[a] $[Ni(EPNO)_2(O_2NO)_2]$ is insoluble in nitromethane, acetone, alcohols, *p*-dioxane and halogenated hydrocarbons.

and EPNO in isopropanol.[2] A purple oil separated after 24 hrs., which yielded a crystalline precipitate after 1 day in the refrigerator.

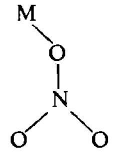
$[Cu(EPNO)_4](NO_3)_2$, $[Ni(EPNO)_6](NO_3)_2$, $[Co(EPNO)_6](NO_3)_2$. These complexes were prepared by exactly the same method employed for the 2:1 complexes, by mixing solutions of ligand and salt in a 7:1 molar ratio. $Zn(NO_3)_2$ yielded the 2:1 complex under these conditions. Attempts to prepare the corresponding Mn^{II} complexes by the above synthetic procedure were unsuccessful. Analyses of the new complexes were performed by Schwarzkopf Microanalytical Laboratory and are given in Table I.

Spectral, Magnetic and Conductance Measurements. Infrared spectra (Table II), electronic spectra (Table III), magnetic moments and electrical conductivities (Table IV) of the new complexes were obtained as described elsewhere.[10]

Discussion

Infrared and Conductance Data. The spectral, magnetic and conductance data provide sufficient evidence for structural assignments. Coordination of EPNO to the metal ion through the NO oxygen is demonstrated by the negative ν_{NO} shifts (Table II).[11] The IR spectra of the new complexes are characterized by the absence of water bands. Free EPNO exhibits a very rich IR spectrum in the 1650-800 cm^{-1} region, as follows (cm^{-1}):[12] 1636 m, 1491 s, 1476 s, 1448 m, 1398 m, 1292 s, 1209 s (ν_{NO}),[10] 1169 m, 1114 m, 1102 w, 1088 w, 1029 s, 925 s, 855 m, 838 s. Despite this fact, distinction between ionic and coordinated monodentate and bidentate nitrate groups can be easily made from the IR spectra of the EPNO complexes (Table II). In the cases of overlap of ligand and nitrate vibrations the presence of the nitrate band was confirmed by comparison of the relative intensity of the absorption in the region examined to that of ligand bands unaffected by complex formation (*e.g.* the ligand bands at 1636 and 855 cm^{-1}).[11,12]

Although distinction between ionic and coordinated nitrate by means of IR spectroscopy is simple, only in some cases differences in the spectra of compounds with monodentate and bidentate nitrato groups have been reported.[13,14] Ferraro *et al.* have assigned a structure involving bidentate nitrato groups to a number of lanthanide nitrate-tri-n-butyl phosphate complexes on the basis of Raman spectra.[15] In many cases, however, the IR spectrum of the bidentate nitrato group exhibits roughly the same frequencies to that of the monodentate.[16] An interesting feature of the present study is, therefore, the possibility of distinguishing between mono- and bi-dentate nitrato groups in the complexes reported. The bands assigned to nitrate vibrations in Table II are in agreement with the assignments of Addison and Simpson,[13a] with the exception of the ν_1 (NO stretch) mode of bidentate nitrate. This mode occurs at 1410-1400 cm^{-1} (Table II) in the complexes reported here and at 1630 cm^{-1} in $Sn(NO_3)_4$.[13a] The high frequency of ν_1 in the latter compound and in $Ti(NO_3)_4$ has been attributed to the influence of the high oxidation number of the metal ion,[13] however. In a series of complexes of trivalent lanthanide nitrates the same vibrational mode has been assigned to a group of bands in the 1550-1490 cm^{-1} region.[15] It is thus, not surprising that ν_1 occurs at 1410-1400 cm^{-1} in the bidentate nitrato EPNO complexes, in view of the oxidation state of the metal ions and the metal to amine oxide $d\pi$–$p\pi$ back-bonding, which has been established in 3d metal ion (including Zn^{2+}) complexes with pyridine N-oxides.[17] The difference in the IR spectra of mono- and bi-dentate nitrate observed during the present study may be interpreted in terms of different symmetries of these groups.[18] In fact, the monodentate (C_s) and bidentate (C_{2v}) carbonato groups are easily distinguishable.[18] In many cases a C_{2v} symmetry has been established or assumed for monodentate nitrato metal compounds.[18] In the case of $[Cu(C_5H_5NO)_2(ONO_2)_2]_2$, however, Scavnicar and Matkovič established that the Cu–O–N (nitrato) grouping forms an angle, and the nitrato group is, therefore, of C_s symmetry:[9]



We assign a similar symmetry to the monodentate nitrato groups in the complexes of EPNO (Table II).

The conductances (Table IV) of the 2:1 EPNO-metal nitrate complexes clearly indicate that these compounds are neutral, involving only coordinated nitrato groups. The 3:1 Co^{II} complex exhibits a partial dissociation in nitromethane (Table IV). Its IR and electronic spectra and magnetic moment (Tables II-IV) are consistent with a penta-coordinated configuration. The 4:1 and 6:1 complexes behave as 1:1 electrolytes in nitromethane, but their IR spectra do not indicate any coordination of NO_3. A similar behavior has been reported for hexakis-(isoquinoline N-oxide)Ni^{II} nitrate and was attributed to the displacement of the amine oxide by nitrate groups in solution.[7]

The EPNO-metal nitrate complexes are formulated as follows, on the basis of the IR and conductance data: $[M(EPNO)_2(O_2NO)_2]$ (M = Co, Ni, Zn); $[Cu(EPNO)_2(ONO_2)_2]$; $[Co(EPNO)_3(ONO_2)_2]$; $[Cu(EPNO)_4](NO_3)_2$; $[M(EPNO)_6](NO_3)_2$ (M = Co, Ni).

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These formulations are substantiated by the electronic spectra and magnetic moments of the complexes (vide infra).

Electronic Spectra and Magnetic Moments. The electronic spectra (Table III) of the 2:1 and 6:1 Co^{II} and Ni^{II} complexes clearly indicate an essentially octahedral ligand field symmetry for the metal ions. A symmetry lower than O_h has been recently established for pyridine N-oxide cationic complexes of the type $[ML_6]^{2,3+}$,[19] and a similar assignment is made for the $[M(EPNO)_6]^{2+}$ (M = Co, Ni) complex cations. This assignment is corroborated by the fact that the magnetic moments (Table IV) of these complexes are beyond the limits of the octahedral region for Co^{II} and Ni^{II}.[19] If a pure O_h symmetry was assumed for $[M(EPNO)_6]^{2+}$, the (d–d) spectral bands (in cm^{-1}) would be assigned as follows (Table III):[17a,20] $[Co(EPNO)_6]^{2+}$: ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ 8330, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ 18,380, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 19,800; $[Ni(EPNO)_6]^{2+}$: ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ 8000, ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$ 12,780, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ 13,810, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 25,310. On the basis of these assignments, the following ligand field parameters are calculated for EPNO: toward Co^{II}: Dq = 949 cm^{-1}, B(Racah parameter) = 825 cm^{-1}; toward Ni^{II}: Dq = 800 cm^{-1}, B = 925 cm^{-1}. The Dq and B values are very close, as expected, to those reported for 4-methoxypyridine N-oxide toward Co^{II}[20] and Ni^{II}.[17a] The $[M(EPNO)_2(O_2NO)_2]$ (M = Co, Ni) complexes exhibit magnetic moments within the octahedral region for Co^{II} and Ni^{II}, and are, thus, assigned a symmetry closer to pure O_h than that of the $[M(EPNO)_6]^{2+}$ complexes. A similar symmetry is assigned to $[Zn(EPNO)_2(O_2NO)_2]$. The formation of $[Cu(EPNO)_4]^{2+}$ was anticipated, since cationic complexes of this type are formed with all substituted pyridine N-oxides.[21] Only the unsubstituted pyridine N-oxide forms both $[Cu(C_5H_5NO)_4]^{2+}$ and $[Cu(C_5H_5NO)_6]^{2+}$.[21,22] $[Cu(EPNO)_4]^{2+}$ is assigned a distorted planar structure.[19] This complex cation is most probably monomeric, since it exhibits one (d–d) band (Table III) at some 1500 cm^{-1} higher in energy than that reported for $[Cu(C_5H_5NO)_6]^{2+}$.[7,19]

$[Cu(EPNO)_2(ONO_2)_2]$ exhibits the (d–d) band at 13,610 cm^{-1} in the solid state spectrum and at 13,480 cm^{-1} in nitromethane (Table III). The dimeric $[Cu(C_5H_5NO)_2(ONO_2)_2]_2$, which involves pentacoordinated Cu^{II} shows the following bands (cm^{-1}) in the same region:[3] solid state: 13,890, 11,760; in CH_3CN 11,430; in N,N-dimethylformamide 12,900. The electronic spectrum of $[Cu(EPNO)_2(ONO_2)_2]$ is, thus, in favor of a monomeric structure, involving an essentially planar symmetry.[19] $[Co(EPNO)_3(ONO_2)_2]$ exhibits a solid state electronic spectrum and magnetic moment characteristic of high-spin pentacoordinated Co^{II} compounds.[10,19,23] The differences in the (d–d) band positions in the spectra of this complex and $[Co(EPNO)_5]^{2+}$,[10] may be attributed to a change in the ligand-field symmetry[24] arising by substitution of two EPNO molecules with two nitrato groups. In solution, this complex is dissociated, as indicated by its conductance which is intermediate between those of a « non »- and a 1:1 electrolyte (Table IV), yielding a hexacoordinated Co^{II} species (Table III). Finally, the electronic spectra of the Co^{II}, Ni^{II} and Cu^{II} complexes exhibit the characteristic charge-transfer bands, which invariably occur in pyridine N-oxide complexes with metal perchlorates, nitrates and halides.[3,22,25] These bands have been recently interpreted in terms of metal-to-ligand charge transfer ($t_{2g} \rightarrow \pi^*$ transitions in Fe^{II}, Co^{II} and Ni^{II} complexes and $e_g \rightarrow \pi^*$ transitions in Mn^{II} and Cu^{II} complexes).[25] The onset of the charge transfer bands in the complexes reported is given in Table III.

In conclusion, a number of complexes of EPNO with 3d metal nitrates were synthesized and characterized during the present work. The IR spectra of these complexes allow distinctions between mono- and bi-dentate nitrato groups, as well as ionic nitrate. The fact that the spectra of mono- and bi-dentate nitrato groups are distinguishable has been interpreted in terms of C_s symmetry, involving bent M–O–N groupings, for the monodentate, and C_{2v} symmetry for the bidentate nitrate. Co^{II} and Ni^{II} nitrates yield cationic complexes of the type $[M(EPNO)_6]^{2+}$, while the corresponding perchlorates form $[M(EPNO)_5]^{2+}$ complexes.[10] It appears that pyridine N-oxides may generally yield crystalline complexes with metal salts in various ligand to metal ratios, and the type of complex stabilized in the crystalline state depends on the synthetic procedure. In support of this statement is the fact that complexes of metal halides with pyridine N-oxides in ligand to metal ratios varying between 0.5:1 and 6:1 have been reported.[1,2,21,26] Further, in addition to the 2:1 and 6:1 complexes of EPNO with $Co(NO_3)_2$, which are analogous to the corresponding C_5H_5NO complexes,[3] a 3:1 EPNO–$Co(NO_3)_2$ complex was also isolated during this study.

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