4; IX, 50860-29-2; X, 51108-05-5; *closo*-1,6-$C_2B_4H_6$, 20693-67-8; 2,3-$C_2B_4H_8$, 21445-77-2; 2,4-$C_2B_5H_7$, 20693-69-0; $[(C_6H_5)_2PCH_2]_2NiCl_2$, 14647-23-5; $CH_3C_2B_4H_7$, 34228-46-1; $(CH_3)_2C_2B_4H_6$, 20741-68-8.

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# 2-, 3-, and 4-Picoline *N*-Oxide Complexes with Cobalt(II), Nickel(II), and Copper(II) Nitrates[1]

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Complexes of 2-, 3-, and 4-picoline *N*-oxides (picO) with cobalt(II), nickel(II), and copper(II) nitrates were prepared, by utilizing either 2:1 or 8:1 ligand to metal salt ratios during the synthetic procedure. Characterization studies of these complexes led to the following formulations: (a) complexes prepared by using 2:1 L to M ratios, $[M(2\text{-picO})_2(ONO_2)(O_2NO)]$ (M = Co, Ni), $[Cu(2\text{-picO})_2(ONO_2)_2]$, $[Co(3\text{-picO})_2(O_2NO)_2]$, $[Ni(L)_2(O_2NO)_2]$ (L = 3- or 4-picO), $[Cu(L)(O_2NO)_2]$ (L = 3- or 4-picO); for $Co(NO_3)_2\cdot(4\text{-picO})$ a binuclear structure of the type $[(ONO_2)_2Co(4\text{-picO})_2Co(O_2NO)_2]$ is considered as possible; (b) complexes prepared by using 8:1 L to M ratios, $[M(2\text{-picO})_4(ONO_2)](NO_3)$ (M = Co, Ni), $[Cu(2\text{-picO})_4](NO_3)_2$, $[Co(L)_6](NO_3)_2$ (L = 3- or 4-picO), $[Ni(4\text{-picO})_6](NO_3)_2$, $[Ni(3\text{-picO})_5(ONO_2)](NO_3)$, $[Cu(4\text{-picO})_4(ONO_2)](NO_3)$; finally, for $Cu(NO_3)_2\cdot 4(3\text{-picO})$ the overall evidence is compatible with either a monomeric ($[Cu(3\text{-picO})_4](NO_3)_2$) or a binuclear ($[(3\text{-picO})_3Cu(3\text{-picO})_2Cu(3\text{-picO})_3](NO_3)_4$) structure.

## Introduction

A variety of 3d metal nitrate complexes with pyridine *N*-oxide (pyO) and its substituted derivatives were reported in recent years.[2-11] pyO forms complexes of the following types with divalent 3d metal nitrates: $M(pyO)_2(NO_3)_2$ (M = Mn–Zn), $Cu(pyO)_4(NO_3)_2$, $M(pyO)_6(NO_3)_2$ (M = Mn, Co, Ni, Zn).[4] The 2:1 complexes are neutral, involving coordination of both $NO_3$ groups, while the 4:1 Cu(II) complex and the 6:1 M(II) complexes are cationic and involve exclusively ionic nitrate.[2-4] The presence of substituents on the pyridine ring may introduce steric effects and influence the nature of substituted pyridine *N*-oxide–metal nitrate complexes as well as the highest possible ligand-to-metal ratio attained. An extreme case was recently observed with 2,6-lutidine *N*-oxide (2,6-lutO), which yields only 2:1 complexes with $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn), regardless of the amounts of ligand utilized during the synthetic procedure.[8] $Cu(2,6\text{-lutO})_2(NO_3)_2$ involves monodentate nitrato ligands, while the $M(2,6\text{-lutO})_2(NO_3)_2$ (M = Mn, Co, Ni, Zn) complexes are pentacoordinated, containing one mono- and one bidentate coordinated nitrate.[8] Several divalent 3d metal nitrate–aromatic amine *N*-oxide complexes with unusual stoichiometries have also been reported in the literature, *i.e.*, $Co(NO_3)_2\cdot 3L$ (L = 4-ethoxypyridine *N*-oxide),[6] $Ni(NO_3)_2\cdot 4L$ (L = 2-ethylpyridine *N*-oxide), $Ni(NO_3)_2\cdot 4L$ (L = 2,4-lutidine *N*-oxide), and $Ni(NO_3)_2\cdot 3L\cdot 0.5H_2O$ (L = quinoline *N*-oxide).[5] It was of interest to us to investigate the nature of divalent 3d metal nitrate complexes with 2-, 3-, and 4-picoline *N*-oxides (2-, 3-, and 4-picO, respectively). The present paper reports on the synthesis and characterization of cobalt(II), nickel(II), and copper(II) nitrate complexes with these ligands.

## Experimental Section

**Chemicals.** The picoline *N*-oxides were obtained commercially (Aldrich or Baker products) and utilized without further purification. Reagent grade hydrated metal nitrates, triethyl orthoformate, and organic solvents were used.

**Synthetic Procedure.** During a series of experiments ligand and metal salt were mixed in 2:1 molar ratio, and during another in 8:1 molar ratio. The following synthetic procedure was employed in both cases. A 0.5–1-g sample of the hydrated metal salt was dissolved in *ca.* 50 ml of a 15:1 (v/v) mixture of triethyl orthoformate (a dehydrating agent[12])–acetone. The resulting solution was warmed at 50–60° for *ca.* 30 min, under stirring, and a 5% (w/w) solution of the ligand in triethyl orthoformate was subsequently added (ligand to metal molar ratio 2:1 or 8:1). The reaction mixture was stirred at 50–60° for 15 min, a large excess of ligroin (bp 63–75°) was then added, and the mixture was allowed to cool slowly, under continuous stirring, which is continued at room temperature for another 2–3 hr. During this period gradual precipitation of the $M(NO_3)_2$–picO complexes occurred. The complexes were then filtered, thoroughly washed with ligroin, and dried in an evacuated desiccator over phosphorus pentoxide. As shown in Table I, which gives analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.), complexes of the following stoichiometries were obtained during this work. Interaction of ligand and salt in 2:1 molar ratio yielded 2:1 complexes in most cases with the following exceptions: the $Co(NO_3)_2$–4-picO and $Cu(NO_3)_2$–3- or –4-picO interactions led to the formation of 1:1 complexes. On the other hand, interaction of ligand and salt in 8:1 molar ratio led to the formation of the following products: 6:1 complexes in the cases of 3- or 4-picO–$Co(NO_3)_2$ and 4-picO–$Ni(NO_3)_2$; a 5:1 complex between 3-picO and $Ni(NO_3)_2$; and 4:1 complexes in all other cases.

**Spectral, Magnetic, and Conductance Studies.** Infrared (Tables II and III, Figures 1 and 2) and electronic (Table IV, Figures 3 and 4) spectra and magnetic susceptibility and conductance measurements

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**Table I.** Analytical Data for picO Complexes with $M(NO_3)_2$ (M = Co, Ni, Cu)

| Complex | Color | % C |  | % H |  | % N |  | % metal |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| $Co(NO_3)_2 \cdot 2(2\text{-picO})$ | Pinkish mauve | 35.92 | 35.27 | 3.51 | 4.09 | 13.96 | 13.21 | 14.66 | 14.98 |
| $Co(NO_3)_2 \cdot 2(3\text{-picO})$ | Pink-orange | 35.92 | 35.14 | 3.51 | 3.52 | 13.96 | 13.37 | 14.66 | 14.07 |
| $Co(NO_3)_2 \cdot (4\text{-picO})$ | Deep rose | 24.67 | 24.46 | 2.41 | 3.12 | 14.38 | 13.96 | 20.17 | 19.69 |
| $Co(NO_3)_2 \cdot 4(2\text{-picO})$ | Purple | 46.53 | 47.16 | 4.55 | 4.87 | 13.56 | 13.13 | 9.51 | 9.82 |
| $Co(NO_3)_2 \cdot 6(3\text{-picO})$ | Dark brick red | 51.61 | 50.96 | 5.05 | 4.76 | 13.38 | 12.91 | 7.03 | 7.45 |
| $Co(NO_3)_2 \cdot 6(4\text{-picO})$ | Pink-orange | 51.61 | 51.08 | 5.05 | 5.43 | 13.38 | 13.23 | 7.03 | 7.67 |
| $Ni(NO_3)_2 \cdot 2(2\text{-picO})$ | Chartreuse | 35.94 | 35.02 | 3.52 | 4.11 | 13.97 | 13.40 | 14.64 | 15.14 |
| $Ni(NO_3)_2 \cdot 2(3\text{-picO})$ | Light green | 35.94 | 35.24 | 3.52 | 4.00 | 13.97 | 13.37 | 14.64 | 15.24 |
| $Ni(NO_3)_2 \cdot 2(4\text{-picO})$ | Chartreuse | 35.94 | 35.07 | 3.52 | 3.79 | 13.97 | 13.25 | 14.64 | 15.08 |
| $Ni(NO_3)_2 \cdot 4(2\text{-picO})$ | Yellow-green | 46.55 | 46.46 | 4.55 | 4.74 | 13.57 | 13.11 | 9.49 | 9.56 |
| $Ni(NO_3)_2 \cdot 5(3\text{-picO})$ | Yellow-green | 49.47 | 48.83 | 4.84 | 5.22 | 13.46 | 12.97 | 8.06 | 8.20 |
| $Ni(NO_3)_2 \cdot 6(4\text{-picO})$ | Light green | 51.63 | 50.99 | 5.05 | 5.11 | 13.40 | 13.04 | 7.01 | 7.47 |
| $Cu(NO_3)_2 \cdot 2(2\text{-picO})$ | Light blue | 35.50 | 35.14 | 3.47 | 3.62 | 13.79 | 13.30 | 15.65 | 15.68 |
| $Cu(NO_3)_2 \cdot (3\text{-picO})$ | Green | 24.34 | 25.06 | 2.38 | 2.53 | 14.22 | 13.78 | 21.45 | 20.87 |
| $Cu(NO_3)_2 \cdot (4\text{-picO})$ | Green | 24.34 | 24.23 | 2.38 | 2.81 | 14.22 | 14.00 | 21.45 | 21.32 |
| $Cu(NO_3)_2 \cdot 4(2\text{-picO})$ | Light green | 46.19 | 46.03 | 4.52 | 4.51 | 13.46 | 12.80 | 10.18 | 10.33 |
| $Cu(NO_3)_2 \cdot 4(3\text{-picO})$ | Bright green | 46.19 | 45.64 | 4.52 | 4.66 | 13.46 | 13.12 | 10.18 | 10.54 |
| $Cu(NO_3)_2 \cdot 4(4\text{-picO})$ | Light green | 46.19 | 45.95 | 4.52 | 5.08 | 13.46 | 12.82 | 10.18 | 9.89 |

**Table II.** Ir Bands Associated with Vibrational Modes of the $NO_3$ Group[a] and with $\nu_{M-O}$(nitrato) ($cm^{-1}$)[b]

| Complex | $\nu_1 + \nu_4$ | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_{M-O}$(nitrato) |
|---|---|---|---|---|---|---|
| $Co(NO_3)_2 \cdot 2(2\text{-picO})$ | 1773 w, 1760 sh, 1748 w, 1737 w | 988 m, b, sh | 819 m | 1449 s, sh, 1428 s, sh, 1312 s, 1304 s | 741 m, 725 m | 341 m, 290 m |
| $Co(NO_3)_2 \cdot 4(2\text{-picO})$ | 1747 m, 1731 w, 1723 w, sh | 1004 w, 996 m | 813 m | 1429 s, sh, 1352 vs, 1297 vs | 737 v, sh, 723 m, 704 m | 341 m, sh, 308 m, sh |
| $Ni(NO_3)_2 \cdot 2(2\text{-picO})$ | 1777 w, 1761 w, 1745 w, 1721 w | 1002 m, sh | 818 m, sh, 815 m | 1444 s, sh, 1437 s, sh, 1317 s, 1299 s, sh | 751 w, 722 m | 309 w, 298 w |
| $Ni(NO_3)_2 \cdot 4(2\text{-picO})$ | 1759 w, sh, 1742 w–m, 1722 w, sh | 1009 m, 994 m | 816 m | 1427 s, sh, 1350 vs, 1297 vs | 749 w, 728 m, 707 m–s | 339 w, sh, 307 w, sh |
| $Cu(NO_3)_2 \cdot 2(2\text{-picO})$ | 1753 w, b, 1717 w | 1009 s | 812 s, 807 s | 1451 s, 1287 vs | 722 m, 709 m–s | 358 s, 271 m |
| $Cu(NO_3)_2 \cdot 4(2\text{-picO})$ | 1749 w–m | 1000 w–m | 811 w | 1346 vs | 726 m |  |
| $Co(NO_3)_2 \cdot 2(3\text{-picO})$ | 1778 w, 1740 w, b | 1026 m, sh | 819 m, sh, 806 m, sh | 1438 vs, 1296 vs | 724 w, 712 w | 331 w, 309 w |
| $Co(NO_3)_2 \cdot 6(3\text{-picO})$ | 1746 w | 1019 m | 811 m | 1347 vs | 727 w, sh |  |
| $Ni(NO_3)_2 \cdot 2(3\text{-picO})$ | 1771 w, 1740 w, b | 1021 m | 812 s | 1438 vs, 1306 vs | 722 w, 717 w, sh | 311 m, 298 m |
| $Ni(NO_3)_2 \cdot 5(3\text{-picO})$ | 1748 w, 1744 w, 1726 w, sh | 1020 m–s, 999 m, sh | 821 m, sh, 811 m–s | 1447 s, sh, 1349 vs, 1306 m | 730 m, sh, 720 m, sh | 316 w, 297 w |
| $Cu(NO_3)_2 \cdot (3\text{-picO})$ | 1757 w, 1723 m | 1019 m–s | 808 m | 1444 vs, sh, 1294 vs | 717 w, b | 331 w, 375 w, b |
| $Cu(NO_3)_2 \cdot 4(3\text{-picO})$ | 1741 m | 1012 m | 806 m | 1337 vs | 721 m, sh |  |
| $Co(NO_3)_2 \cdot (4\text{-picO})$ | 1762 w–m, b, 1712 w | 1013 m, b | 809 m | 1441 s, sh, 1300 m, b | 742 w, sh, 728 m | 290 w, 276 w |
| $Co(NO_3)_2 \cdot 6(4\text{-picO})$ | 1743 w | 1008 w, sh | 820 w, sh | 1347 vs | 726 w–m |  |
| $Ni(NO_3)_2 \cdot 2(4\text{-picO})$ | 1778 w, 1740 w, 1708 w, sh | 1021 m, sh | 811 m | 1428 s, sh, 1299 s, b | 722 m | 309 w, 290 w, b |
| $Ni(NO_3)_2 \cdot 6(4\text{-picO})$ | *Ca.* 1750 w | 1020 w, sh | 814 w | 1348 m–s | 723 m |  |
| $Cu(NO_3)_2 \cdot (4\text{-picO})$ | 1753 vw, 1735 w, 1719 w | 1018 m, sh | 829 w, 812 m | 1440 vs, sh, 1288 vs | 729 m, sh, 727 m, sh | 350 m, sh, 318 w, sh |
| $Cu(NO_3)_2 \cdot 4(4\text{-picO})$ | 1781 w, 1741 w–m, 1721 w, 1717 w, sh | 1014 s | 829 m, 819 w | 1455 vs, b,[c] 1338 vs, 1297 vs | 724 m, 703 m | 308 s, sh, 299 s |

[a] $\nu_1$–$\nu_4$ assignments refer to the fundamental vibrational modes of ionic ($D_{3h}$) $NO_3^-$. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [c] Overlaps with Nujol absorption.

**Table III.** $\nu_{N-O}$, $\nu_{M-O}$(picO), and $\nu_{ligand}$ (500–250 cm$^{-1}$) Modes (cm$^{-1}$)$^a$

| Compd | $\nu_{N-O}$ | $\nu_{M-O}$(picO) | $\nu_{ligand}$ (500–250 cm$^{-1}$) |
|---|---|---|---|
| 2-picO | 1242 vs | | 469 m, 449 m, 336 m |
| Co(NO$_3$)$_2$·2(2-picO) | 1202 vs | 391 m, 377 m–s | 462 m, 450 w, sh, 335 w, sh |
| Co(NO$_3$)$_2$·4(2-picO) | 1219 vs, 1208 vs | 379 s | 473 m, 460 m, 336 m |
| Ni(NO$_3$)$_2$·2(2-picO) | 1208 vs | 377 m | 471 m, sh, 461 m, 341 m |
| Ni(NO$_3$)$_2$·4(2-picO) | 1210 vs | 380 s | 478 m, 461 m, 332 m |
| Cu(NO$_3$)$_2$·2(2-picO) | 1200 vs | 419 vs | 470 m, 450 w, sh, 335 w, sh |
| Cu(NO$_3$)$_2$·4(2-picO) | 1209 vs | 414 s | 467 m, 341 w |
| 3-picO | 1280 vs | | 493 m, 450 m, 418 w, sh, 306 w |
| Co(NO$_3$)$_2$·2(3-picO) | 1260 s | 375 m | 489 m, 445 m, 422 w, sh |
| Co(NO$_3$)$_2$·6(3-picO) | 1255 vs | 339 s | 492 s, 446 m, 420 w, sh, 310 w, b |
| Ni(NO$_3$)$_2$·2(3-picO) | 1262 s, sh | 381 m, 349 m | 498 m, sh, 449 m |
| Ni(NO$_3$)$_2$·5(3-picO) | 1262 s, sh, 1251 vs | 349 s | 491 s, 447 m, 422 w, sh, 310 w, sh |
| Cu(NO$_3$)$_2$·(3-picO) | 1259 s, 1250 s, sh | 410 m | 496 m, 480 w, sh, 425 w, sh |
| Cu(NO$_3$)$_2$·4(3-picO) | 1249 s | 409 s | 493 w, sh, 481 m, 460 w, sh, 310 w |
| 4-picO | 1228 vs | | 481 m, 468 m, 337 m, 320 w, sh |
| Co(NO$_3$)$_2$·(4-picO) | 1198 m, b | 386 m, sh | 486 m, 450 m, sh, 437 m–s |
| Co(NO$_3$)$_2$·6(4-picO) | 1214 s | 372 s | 484 s, 420 w, sh, 332 w |
| Ni(NO$_3$)$_2$·2(4-picO) | 1207 s | 388 m | 481 s, 419 m, 334 w |
| Ni(NO$_3$)$_2$·6(4-picO) | 1217 s | 378 m | 480 s, 413 m, 330 w, b |
| Cu(NO$_3$)$_2$·(4-picO) | 1209 s | 424 m, 408 m, sh | 480 m, b, 333 m, sh |
| Cu(NO$_3$)$_2$.4(4-picO) | 1210 vs | 397 s, 353 m | 482 s, 439 s, 331 m, 312 sh |

$^a$ Spectra of ligands and complexes obtained on Nujol mulls. Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

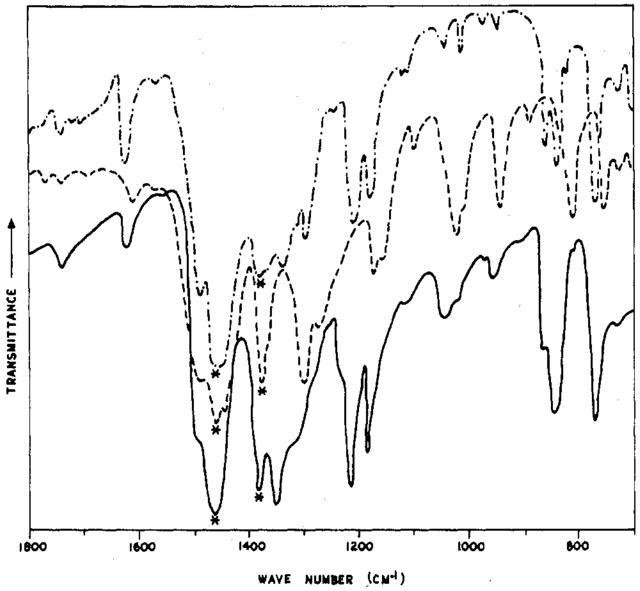

**Figure 1.** Representative ir spectra (1800–700 cm$^{-1}$): —, Co(NO$_3$)$_2$·6(4-picO), a complex involving exclusively ionic NO$_3$; - - -, Ni(NO$_3$)$_2$·2(3-picO), a complex involving exclusively coordinated NO$_2$; -·-·-, Cu(NO$_3$)$_2$·4(4-picO), a complex involving both ionic and coordinated NO$_3$. The asterisks indicate Nujol absorptions.

(Table V) were obtained by methods described elsewhere.[13]

## Discussion

**Infrared and Conductance Evidence.** The presence of ionic or coordinated nitrate can be generally established by examination of ir spectra.[14-17] The exclusive presence

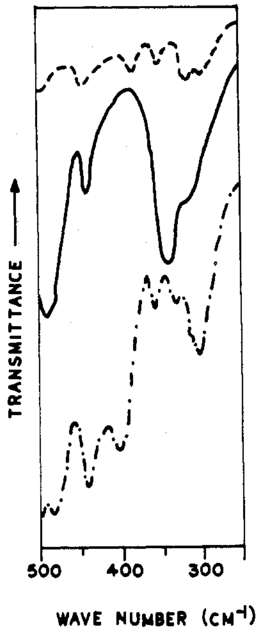

**Figure 2.** Low-frequency ir spectra (500–250 cm$^{-1}$) of the complexes of Figure 1.

of ionic nitrate in all the 6:1 complexes and the 4:1 complexes of 2- and 3-picO with Cu(NO$_3$)$_2$ is clearly indicated from their ir spectra (Table II, Figure 1). In fact, the spectra of these compounds are characterized by four bands attributable to the fundamental vibrational modes of ionic ($D_{3h}$) nitrate[14,15] and a single $\nu_1 + \nu_4$ combination band in the 1800-1700-cm$^{-1}$ region.[16,17] Furthermore, no bands associated with $\nu_{M-O}$ (nitrato) modes[18] were observed in the ir spectra (Table II, Figure 2). Complexes with both ionic and coordinated nitrate are the 4:1 2-picO–M(NO$_3$)$_2$ (M = Co, Ni) and 4-picO–Cu(NO$_3$)$_2$ and the 5:1 3-picO–Ni(NO$_3$)$_2$ complexes. In these cases ir bands corresponding to the fundamental vibrational modes of both ionic and coordinated nitrate (*e.g.*, in Ni(NO$_3$)$_2$·5(3-picO) the $\nu_3$ absorption at 1349 cm$^{-1}$ is due to ionic NO$_3$; and the bands

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**Table IV.** Electronic Spectra of Picoline *N*-Oxide-Metal Nitrate Complexes[a]

| Complex | Medium | $\lambda_{max}$, nm ($\epsilon_{max}$) |
|---|---|---|
| Co(NO$_3$)$_2$·2(2-picO) | Nujol | 498 s, 527 s, sh, 650 m, sh, 752 m, 815 m, sh, 1008 w, sh |
| | 5 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 498 sh (122), 513 sh (138), 524 (141), 739 (17), 820 sh (15), 1035 (16) |
| Co(NO$_3$)$_2$·4(2-picO) | Nujol | 544 s, 576 s, sh, 713 m, 808 m, b, sh, 1030 w |
| | 4.8 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 526 (206), 755 sh (24), 803 sh (21), 1050 b (22) |
| Co(NO$_3$)$_2$·2(3-picO) | Nujol | 502 s, 552 s, b, 862 m, sh, 1200 m, sh |
| | 1.4 × 10$^{-2}$ *M* in CH$_3$NO$_2$ | 505 sh (88), 521 (94), 800 m, b (9), 1218 b (14) |
| Co(NO$_3$)$_2$·6(3-picO) | Nujol | 483 s, sh, 539 s, sh, 551 s, sh, 702 m, sh, 800 m–w, b, sh, 1150 w, b |
| | 1.3 × 10$^{-2}$ *M* in CH$_3$NO$_3$ | 502 sh (85), 528 (88), 680 sh (9), 1178 b (12) |
| Co(NO$_3$)$_2$·(4-picO) | Nujol | 529 s, b, 584 s, sh, 679 w, sh, 1150 m, b |
| | 6.8 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 506 (131), 648 sh (19), 1146 b (17) |
| Co(NO$_3$)$_2$·6(4-picO) | Nujol | 492 s, 530 s, b, 702 w, sh, 1160 w, b |
| | 4.8 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 503 sh (183), 530 (200), 1190 b (10) |
| Ni(NO$_3$)$_2$·2(2-picO) | Nujol | 399 s, 460 s, sh, 516 m, sh, 665 m, b, 723 m, sh, 890 w, 1130 w, b |
| | 1.5 × 10$^{-2}$ *M* in CH$_3$NO$_2$ | 390 sh (25), 480 sh (30), 667 (26), 749 sh (20), 1137 b (10) |
| Ni(NO$_3$)$_2$·4(2-picO) | Nujol | 389 s, 440 s, sh, 652 m, 690 m, 720 m, sh, 785 m, sh, 1190 w, sh |
| | 1.3 × 10$^{-2}$ *M* in CH$_3$NO$_2$ | 385 sh (88), 479 sh (39), 699 (22), 766 sh (18), 1190 b (9) |
| Ni(NO$_3$)$_2$·2(3-picO) | Nujol | 381 s, 603 m, b, 1150 w, b |
| | 10$^{-2}$ *M* in CH$_3$NO$_2$ | 389 sh (69), 473 sh (6), 673 (17), 761 sh (13), 1168 b (8) |
| Ni(NO$_3$)$_2$·5(3-picO) | Nujol | 400 s, sh, 480 s, sh, 560 s, sh, 615 m, b, 645 m, sh, 1250 w, sh |
| | 9.6 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 395 sh (204), 499 sh (32), 697 (19), 760 sh (15), 1240 b (9) |
| Ni(NO$_3$)$_2$·2(4-picO) | Nujol | 396 s, 660 m, b, 1170 w, b |
| | 10$^{-2}$ *M* in CH$_3$NO$_2$–(CH$_3$)$_2$CO | 396 (37), 500 sh (5), 672 (8), 720 b, sh (7), 1158 b (5) |
| Ni(NO$_3$)$_2$·6(4-picO) | Nujol | 383 s, 695 m, 760 m, sh, 1250 m, b |
| | 2.4 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 383 (50), 468 b, sh (14), 660 b (12), 740 sh (10), 1220 b (8) |
| Cu(NO$_3$)$_2$·2(2-picO) | Nujol | <300 vs, 615 s, b |
| | 4.9 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 694 (90) |
| Cu(NO$_3$)$_2$·4(2-picO) | Nujol | <300 vs, 674 s, b |
| | 3.2 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 708 sh (122), 733 (125), 1165 sh (48) |
| Cu(NO$_3$)$_2$·(3-picO) | Nujol | <300 vs, 640 s, b, 671 s |
| | 1.7 × 10$^{-2}$ *M* in CH$_3$NO$_2$–CH$_3$OH | 698 sh (85), 707 (87) |
| Cu(NO$_3$)$_2$·4(3-picO) | Nujol | 360 vs, 702 s, b, 827 m |
| | 3.2 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 722 b (115), 903 sh (25) |
| Cu(NO$_3$)$_2$·(4-picO) | Nujol | <300 vs, 737 s, b, 1015 m, sh |
| | 4.8 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 670 (137), 696 sh (135) |
| Cu(NO$_3$)$_2$·4(4-picO) | Nujol | 326 vs, 400 vs, sh, 499 s, 528 s, sh, 650 s, b, 755 s, 820 s, sh |
| | 3.2 × 10$^{-3}$ *M* in CH$_3$NO$_2$ | 720 (81), 960 sh (31) |

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

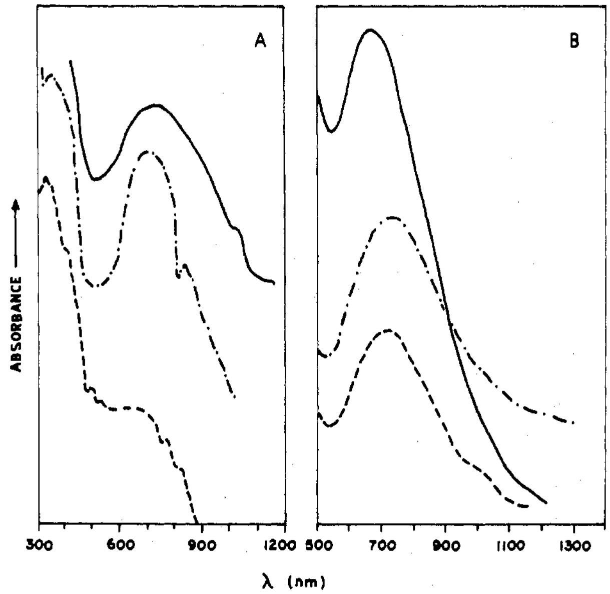

**Figure 3.** Electronic spectra: —, Cu(NO$_3$)$_2$·(4-picO); - - -, Cu(NO$_3$)$_2$·4(4-picO); - · -, Cu(NO$_3$)$_2$·4(3-picO); A, mull spectra; B, CH$_3$NO$_2$ solution spectra.

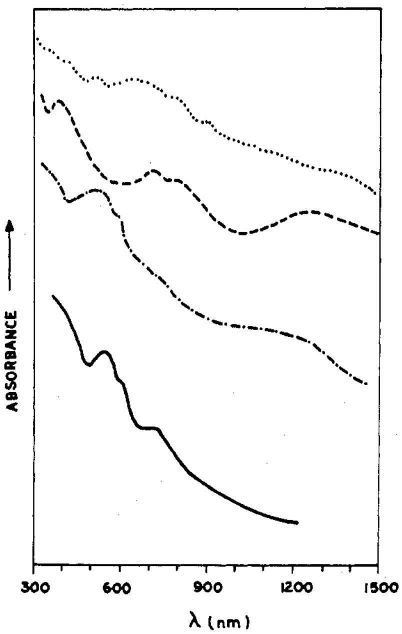

**Figure 4.** Solid-state (Nujol mull) electronic spectra: —, Co(NO$_3$)$_2$·4(2-picO); - · -, Co(NO$_3$)$_2$·(4-picO); - - -, Ni(NO$_3$)$_3$·6(4-picO); · · · ·, Ni(NO$_3$)$_2$·2(2-picO).

at 1447 and 1306 cm$^{-1}$ are due to the split $\nu_3$ mode in the lower symmetry coordinated nitrato group;[14,15] *cf.* Table II) are observed. In addition the 1800-1700-cm$^{-1}$ region is characterized by three or four absorptions[16,17] while $\nu_{M-O}$ (nitrato) modes[18] (tentatively assigned) appear below 345 cm$^{-1}$.

Distinction between mono- and bidentate nitrato ligands, on the basis of ir evidence, is usually difficult, as, in most cases, the coordinated –ONO$_2$ and –O$_2$NO groups have the same local site symmetry ($C_{2v}$).[14,15] In the 1800-1700-cm$^{-1}$ region, two bands are observed in both mono- and bidentate nitrato metal complexes; the separation of these two absorp-

**Table V.** Magnetic Moments (293°K) and Molar Conductivities ($10^{-3}$ *M* Nitromethane Solutions at 25°) of Metal Nitrate–picO Complexes

| Complex | $10^6\chi_M^{cor}$, cgsu | $\mu_{eff}$, BM | $\Lambda_M$, $\Omega^{-1}$ $cm^2$ $mol^{-1}$ |
|---|---|---|---|
| $Co(NO_3)_2 \cdot 2$(2-picO) | 8,804 | 4.56 | 29 |
| $Co(NO_3)_2 \cdot 4$(2-picO) | 8,930 | 4.59 | 49 |
| $Ni(NO_3)_2 \cdot 2$(2-picO) | 4,912 | 3.41 | 30 |
| $Ni(NO_3)_2 \cdot 4$(2-picO) | 5,102 | 3.47 | 52 |
| $Cu(NO_3)_2 \cdot 2$(2-picO) | 1,587 | 1.94 | 42 |
| $Cu(NO_3)_2 \cdot 4$(2-picO) | 1,492 | 1.88 | 32 |
| $Co(NO_3)_2 \cdot 2$(3-picO) | 9,303 | 4.69 | 31 |
| $Co(NO_3)_2 \cdot 6$(3-picO) | 9,275 | 4.68 | 64 |
| $Ni(NO_3)_2 \cdot 2$(3-picO) | 4,661 | 3.31 | 41 |
| $Ni(NO_3)_2 \cdot 5$(3-picO) | 4,444 | 3.24 | 56 |
| $Cu(NO_3)_2 \cdot$(3-picO) | 1,702 | 2.00 | 57 |
| $Cu(NO_3)_2 \cdot 4$(3-picO) | 1,617 | 1.95 | 70 |
| $Co(NO_3)_2 \cdot$(4-picO) | 9,022 | 4.62 | 36 |
| $Co(NO_3)_2 \cdot 6$(4-picO) | 10,079 | 4.88 | 47 |
| $Ni(NO_3)_2 \cdot 2$(4-picO) | 4,511 | 3.26 | 40 |
| $Ni(NO_3)_2 \cdot 6$(4-picO) | 4,379 | 3.22 | 59 |
| $Cu(NO_3)_2 \cdot$(4-picO) | 1,666 | 1.98 | 58 |
| $Cu(NO_3)_2 \cdot 4$(4-picO) | 1,631 | 1.96 | 52 |

tions is generally smaller for the mono- rather than the bidentate nitrato ligand complexes.[16,17] The above-mentioned complexes, which involve both ionic and coordinated nitrate, exhibit combination bands (1800-1700 $cm^{-1}$) corresponding to both these types of $NO_3$; it is, thus, rather difficult to draw any conclusions regarding the nature of the coordinated nitrato group, and structural assignments were based on their electronic spectra (*vide infra*). The 2:1 2-picO complexes of Co(II) and Ni(II) clearly involve two types of coordinated nitrate (*i.e.*, mono- and bidentate), as is also the case with the corresponding 2,6-lutO complexes.[8] In fact, four bands are observed at 1800-1700 $cm^{-1}$ (Table II) in the spectra of these compounds,[16,17] while in the fundamental vibrational mode regions several absorptions attributable to coordinated $NO_3$ are split (*e.g.*, the two components of the split $\nu_3$ mode are also split as shown in Table II).[14-17] The rest of the complexes reported contain exclusively one type of coordinated nitrate, these are the three 1:1 and the following 2:1 complexes: 2-picO-$Cu(NO_3)_2$, 3-picO-$M(NO_3)_2$ (M = Co, Ni), and 4-picO-$Ni(NO_3)_2$. The spectra of these compounds exhibit bands typical of $C_{2v}$ coordinated nitrate;[14-17] the separations of the bands at 1800-1700 $cm^{-1}$ (between 31 and 70 $cm^{-1}$) in the spectra of these complexes are in favor of the presence of bi- rather than monodentate nitrate.[16,17] The low-frequency ir spectra of all the new complexes involving coordinated nitrate exhibit bands attributable to $\nu_{M-O}$(nitrato) modes;[18] tentative assignments are given in Table II (see also Figure 2).

Table III (see also Figures 1 and 2) shows the $\nu_{N-O}$, $\nu_{M-O}$(picO) (tentatively assigned), and low-frequency ligand bands. The $\nu_{N-O}$(*N*-oxide) mode of the free ligands[19,20] is shifted toward lower frequencies upon metal complex formation, as is generally the case for complexes of $R_nNO$ ligands, involving coordination of the oxygen to the metal ion.[19-22] The positions of the $\nu_{M-O}$(picO) modes were, in many cases, used in combination with the electronic spectral evidence for the formulation of the new complexes and are discussed in the next section.

The molar conductivities (Table V) of the new complexes in nitromethane (Table V) do not provide any useful information concerning the nature of the complexes in the solid state. The $\Lambda_M$ values suggest that certain new complexes behave as nonelectrolytes ($\Lambda_M = 29\text{–}40\ \Omega^{-1}\ cm^2\ mol^{-1}$), while other complexes exhibit intermediate behavior between 1:1 and nonelectrolytes ($\Lambda_M = 41\text{-}70\ \Omega^{-1}\ cm^2\ mol^{-1}$) in $10^{-3}$ *M* nitromethane solution.[23] For complexes containing exclusively ionic nitrate, $\Lambda_M$ values corresponding to 1:2 electrolytes would be expected, *prima facie.* Nevertheless, several hexakis(aromatic amine *N*-oxide)metal(II) or -metal(III) nitrate complexes, reported in the past, behave as 1:1 electrolytes in nitromethane.[5,6,8] This has been attributed to the displacement of *N*-oxide by nitrato ligands in solution.[5,6,8] On the other hand, certain complexes, presumably neutral as suggested by their ir spectra, but exhibiting unexpectedly high $\Lambda_M$ values (*e.g.*, $Cu(NO_3)_2 \cdot$(4-picO)), are apparently dissociated in nitromethane.

**Electronic Spectra and Magnetic Susceptibilities.** The magnetic moments of the new complexes (Table V) are generally normal for high-spin configurations of the metal ions under study.[24] The electronic spectra of some Cu(II) complexes are illustrated in Figure 3. $Cu(NO_3)_2 \cdot 2$(2-picO) exhibits the d-d transition at 615 nm (Table IV) and is, most probably, tetracoordinated and monomeric, involving monodentate nitrato ligands, *i.e.*, $[Cu(2\text{-picO})_2(ONO_2)_2]$. In fact, the 2,6-lutO analog, which is also monomeric, shows the d-d band at 605 nm,[8] while the corresponding binuclear, pentacoordinated pyO compound[10] exhibits a split d-d band with maxima at 719 and 850 nm.[4] Steric hindrance introduced by the presence of the 2-methyl substituent does apparently impede the formation of the dimer in the case of $Cu(NO_3)_2 \cdot 2$(2-picO). The occurrence of $\nu_{Cu-O}$(2-picO) at 419 $cm^{-1}$ in this complex is in support of the above formulation.[20] The 1:1 $Cu(NO)_3$-3- or -4-picO complexes exhibit splittings of the d-d transition (Table IV). These spectra are probably suggestive of pentacoordinated monomeric configurations,[4,25,26] involving two bidentate nitrato ligands, *i.e.*, $[Cu(L)(O_2NO)_2]$ (L = 3- or 4-picO). A hexacoordinated structure for these compounds may be ruled out, since the $\nu_{Cu-O}$(picO) modes occur at too high frequencies (Table III) for hexacoordinated Cu(II) compounds with aromatic amine *N*-oxides,[8,27] while coordination number 6 would also result in a considerable shift of the d-d band toward lower energy.[28] The occurrence of the d-d transition at higher wavelength in the 3- rather than the 4-picO complex is, presumably, due to the fact that 3-picO is a weaker ligand than 4-picO.[22] $Cu(NO_3)_2 \cdot 4$(2-picO) is obviously of the type $[Cu(2\text{-picO})_4](NO_3)_2$, as suggested by the single character of the d-d band and the location of $\nu_{Cu-O}$(2-picO). The other 4:1 Cu(II) complexes exhibit split d-d bands (Table IV). For $Cu(NO_3)_2 \cdot 4$(4-picO), which contains both ionic and coordinated nitrate (*vide supra*), the formulation $[Cu(4\text{-picO})_4(ONO_2)](NO_3)$, involving pentacoordinated Cu(II) and a monodentate nitrato ligand, is considered as most probable. $Cu(NO_3)_2 \cdot 4$(3-picO) is, however, char-

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acterized by exclusively ionic nitrate; the d–d splitting in this case might be interpreted in terms of either a low-symmetry[28] tetracoordinated configuration ($[Cu(3\text{-picO})_4](NO_3)_2$) or a binuclear, *N*-oxide-bridged structure of the type $[(3\text{-picO})_3Cu(3\text{-picO})_2Cu(3\text{-picO})_3](NO_3)_4$, with coordination number 5 for the central $Cu^{2+}$ ions. The normal $\mu_{eff}$ (1.95 BM) of this complex does not preclude the latter possibility; in fact, although binuclear, *N*-oxide-bridged copper(II) halide-*N*-oxide complexes are usually magnetically subnormal,[29] analogous $Cu(NO_3)_2$-*N*-oxide compounds exhibit normal paramagnetism(the electronic spin–spin interaction in the $[Cu(pyO)_2(NO_3)_2]_2$ dimer yields a triplet ground state, as reported recently).[9,10]

The electronic spectra of the Co(II) and Ni(II) complexes (Table IV, Figure 4) are suggestive of penta- or hexacoordinated configurations. The 2-picO complexes of these metal ions exhibit electronic spectra suggestive of coordination number 5. In fact, the absorptions at 700–820 nm are considerably stronger than that at 1008–1030 nm in the solid-state spectra of the Co(II)-2-picO complexes,[28,30] while the Ni(II) analogs show multiple splittings of the d–d band.[25,31] The location of the $\nu_{M-O}$(2-picO) bands and $\mu_{eff}$ values (Tables III, V) for these complexes are also in support of pentacoordinated structures.[20,25,31] This evidence, in combination with the information concerning the nature of the $NO_3$ groups, derived from the ir spectra (*vide supra*) of these compounds, leads to the following formulations: $[M(2\text{-picO})_2(ONO_2)(O_2NO)]$ (*i.e.*, identical with the 2,6-lutO analogs[8]) and $[M(2\text{-picO})_4(ONO_2)](NO_3)$, involving one monodentate coordinated nitrate (M = Co, Ni). The 1:1, 2:1, and 6:1 3- or 4-picO–$Co^{II}$ or -$Ni^{II}$ complexes exhibit electronic spectra compatible with hexacoordinated structures of low symmetry;[28] the magnetic moments of these Ni(II) complexes are within or just slightly above the limits of the "octahedral" region (2.83–3.30 BM)[24] for this metal ion. The $\mu_{eff}$ of the hexacoordinated Co(II) complexes are also within the range of values reported for distorted octahedral complexes of this metal ion with aromatic amine *N*-oxides.[28] The 2:1 and 6:1 complexes are, therefore, of the same types as the pyO analogs,[4] *i.e.*, $[M(L)_2(O_2NO)_2]$ (for M = Co, L = 3-picO; for M = Ni, L = 3- or 4-picO), with bidentate nitrato ligands, and $[M(L)_6](NO_3)_2$ (for M = Co, L = 3- or 4-picO; for M = Ni, L = 4-picO). A possible structure for $Co(NO_3)_2\cdot(4\text{-picO})$ is $[(ONO_2)_2Co(4\text{-picO})_2Co(O_2NO)_2]$, *i.e.*, binuclear with bidentate $NO_3$ ligands and bridging *N*-oxide groups. Finally, the electronic spectrum of $Ni(NO_3)_2\cdot 5(3\text{-picO})$ might be interpreted in terms of either a pentacoordinated or a low-symmetry hexacoordinated configuration.[25,28,31] The $\mu_{eff}$ (3.24 BM) of this compound and the fact that ir evidence suggests that one nitrate group is coordinated in this complex are definitely in favor of a hexacoordinated structure. Hence, this compound is formulated as $[Ni(3\text{-picO})_5(ONO_2)](NO_3)$.

The types of complexes isolated during the present study demonstrate that interactions of divalent 3d metal nitrates with aromatic amine *N*-oxides may lead to complexes with various stoichiometries. In fact, $M(NO_3)_2\cdot nL$ complexes, where $n$ = 1–6 (inclusive), between metal salts and ligands of the above types, have been reported during the present or previous[5,6] works. As is the case with $MX_2\cdot nL$ (M = 3d metal ion, X = halide ion, L = aromatic amine *N*-oxide) complexes, for which compounds with $n$ = 0.5 and 1–6 (inclusive) have been isolated,[2,3,32] the nature of the complex precipitated during the interaction of a given divalent 3d metal nitrate with a given aromatic amine *N*-oxide is apparently determined by the synthetic procedure followed. Comparisons of the nature of the Co(II) and Ni(II) complexes of the three ligands under study clearly show the steric hindrance introduced by the presence of the 2-methyl substituent in 2-picO. This hindrance is, nevertheless, not as severe as that observed with 2,6-lutO.[8] In fact, the latter ligand forms only $M(2,6\text{-lutO})_2(NO_3)_2$ (M = 3d metal ion) complexes, regardless of the ligand to metal ratio utilized during the synthetic procedure,[8] while 2-picO forms both 2:1 and 4:1 complexes with $M(NO_3)_2$. The second methyl substituent in 2,6-lutO has apparently a decisive effect in preventing the formation of complexes in molar ratios higher than 2:1.

**Registry No.** $Co(NO_3)_2\cdot 2(2\text{-picO})$, 49634-38-0; $Co(NO_3)_2\cdot 4(2\text{-picO})$, 49634-39-1; $Ni(NO_3)_2\cdot 2(2\text{-picO})$, 49634-40-4; $Ni(NO_3)_2\cdot 4(2\text{-picO})$, 49634-41-5; $Cu(NO_3)_2\cdot 2(2\text{-picO})$, 49634-42-6; $Cu(NO_3)_2\cdot 4(2\text{-picO})$, 49634-43-7; $Co(NO_3)_2\cdot 2(3\text{-picO})$, 49634-44-8; $Co(NO_3)_2\cdot 6(3\text{-picO})$, 49634-45-9; $Ni(NO_3)_2\cdot 2(3\text{-picO})$, 49654-94-6; $Ni(NO_3)_2\cdot 5(3\text{-picO})$, 49654-95-7; $Cu(NO_3)_2\cdot(3\text{-picO})$, 49654-96-8; $Cu(NO_3)_2\cdot 4(3\text{-picO})$, 49654-97-9; $Co(NO_3)_2\cdot(4\text{-picO})$, 49654-98-0; $Co(NO_3)_2\cdot 6(4\text{-picO})$, 49654-99-1; $Ni(NO_3)_2\cdot 2(4\text{-picO})$, 49655-00-7; $Ni(NO_3)_2\cdot 6(4\text{-picO})$, 49655-01-8; $Cu(NO_3)_2\cdot(4\text{-picO})$, 49655-02-9; $Cu(NO_3)_2\cdot 4(4\text{-picO})$, 49655-03-0.

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