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# Isonicotinate N-Oxide Complexes with Dipositive 3d Metal Ions [1]

L. S. GELFAND, L. L. PYTLEWSKI and D. L. COSGROVE
*Department of Chemistry, Drexel University, Philadelphia, Pa. 19104*
C. M. MIKULSKI
*Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038*
A. N. SPECA
*USI Chemicals Co., Research Division, Cincinnati, Ohio 45237*
N. M. KARAYANNIS
*Amoco Chemicals Corporation, Naperville, Ill. 60540, U.S.A.*
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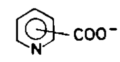
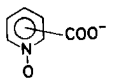
*Divalent 3d metal complexes with isonicotinate N-oxide (N-inicO), of the type* $M(N\text{-}inicO)_2\cdot xH_2O$ *(M = Mn–Zn; x = 6 for M = Fe, Co, Ni, Zn; x = 5 for M = Mn; x = 2 for M = Cu), were prepared by reaction of* $(N\text{-}inicO)NH_4$ *with the corresponding metal(II) acetates or ferrous ammonium sulfate in water. Desiccation of the preceding complexes over* $P_4O_{10}$*, under a vacuum of* $10^{-4}$ *torr, led to partial dehydration, affording the following lower hydrates: x = 5 for M = Ni; x = 1.5 for M = Co, Zn; x = 1 for M = Cu; x = 0.5 for M = Mn, Fe. Characterization of the new metal complexes, based on spectral and magnetic studies, and the insolubility of all the complexes in water and organic solvents, led to their formulation as polynuclear of the following types: Hexa- and penta-hydrates; hexa-coordinated,* $[M(N\text{-}inicO)_2(OH_2)_2]_n\cdot mH_2O$ *(m = 4n for M = Fe, Co, Ni, Zn; m = 3n for M = Mn, Ni), with the N-inicO ligands forming single bridges between adjacent metal ions and functioning as bidentate, coordinating through the N–O and one of the carboxylate oxygens; part of the non-coordinated COO oxygens are hydrogen-bonded to water, which is present in the form of both aqua ligands and lattice* $H_2O$*. The lower hydrates of the type* $[(N\text{-}inicO)_2M\text{-}(OH_2)\text{-}M(N\text{-}inicO)_2]_n\cdot$ *bridging aqua ligand per two metal ions, as well as bidentate bridging N-inicO, being pentacoordinated of the type* $[(N\text{-}inocO)_2M\text{-}(OH_2)\text{-}M(N\text{-}inico)_2]_n\cdot mH_2O$ *(m = 0 for M = Mn, Fe; m = 2n for M = Co, Zn). The dihydrate Cu(II) complex appears to be square-planar of the type* $[Cu(N\text{-}inicO)_2]_n\cdot 2nH_2O$*, with bidentate bridging N-inicO ligands and exclusively lattice and H-bonded water. The corresponding monohydrate* $([Cu(N\text{-}inicO)_2]_n\cdot nH_2O)$ *probably contains both tetra- and penta-coordinated* $Cu^{2+}$ *ions, with some N-inicO ligands acting as bidentate and some as tridentate (coordinating through the N–O and the two COO oxygens) bridging. N-inicO is a ligand of about the same strength as picolinate- and nicotinate-N-oxides.*

## Introduction

Considerable interest in metal complexes with pyridinemonocarboxylates (I) and their N-oxides (II) has been displayed in recent years. The picolinate (pic; Ia) ligand has the tendency to function as a bidentate N,O-chelating agent, forming five-membered chelate rings [2–9]. In some cases, participation of the same carboxylate oxygen of pic in chelation and in bridging between adjacent metal ions may occur [9]. In contrast, the nicotinate (nic; Ib) and isonicotinate (inic; Ic) ligands have little or no tendency to function as bidentate N,O-chelating agents; in fact, only $Ge(nic)_2Cl_2$ has been characterized as a chelate of this type [10]. In hydrated complexes of the type $ML_2\cdot 4H_2O$ (L = nic or inic), these ligands function as unidentate, either coordinating exclusively through the ring nitrogen (M = Co, Ni, Zn, Cd) [11, 12] or forming species involving coordination of one of the ligands through nitrogen and the other through one carboxylate oxygen, as in $Mg(inic)_2\cdot 4H_2O$ [13]. In lower hydrates or anhydrous $ML_2$ complexes (M = Mn, Co, Ni, Cu, Ag, Zn, Pb), both nic and inic show a pronounced tendency to act as bridging ligands, coordinating



(I)

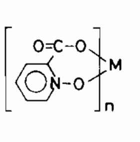


(II)

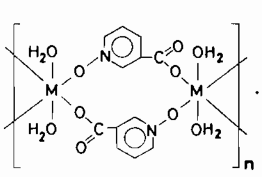
a. 2-carboxylate
b. 3-carboxylate
c. 4-carboxylate

through the ring nitrogen and one or both of the COO oxygens [2, 5, 6, 11, 14]. However, Cd(nic)$_2$ was characterized as a monomeric chelate, with the ligand coordinating exclusively through the two carboxylate oxygens [15]. For lanthanide(III) complexes with nic or inic, the proposed structures involve both chelating and bridging ligand groups, coordinated either through the two carboxylate oxygens [16] or as tridentate(N,O,O-ligands) [17]. Nicotinic and isonicotinic acid (nicH and inicH, respectively) have been found to function as unidentate, N-bonding, in most of their adducts with transition metal salts [18, 19]; nicH seems, nevertheless, to act as a bidentate N,O-chelating agent in its cationic Ln(III) complexes [20]. Finally, complexes involving coordination of both neutral and anionic pyridinecarboxylate ligands have been also reported, *e.g.*, Ag(pic)(picH)$\cdot$H$_2$O [21].

Among the corresponding N-oxide ligands, picolinate N-oxide (N-picO; IIa) has been rather extensively investigated [22–30]. This ligand acts, in most cases, as a bidentate O,O-chelating agent, coordinating through the N–O and one of the carboxylate oxygens, and yielding chelates of type (III) with alkaline earth, 3d metal, lanthanide, actinide and B(III) ions [22–24, 26–30]. Its function as unidentate, N–O oxygen-bonded [25], as chelating and at the same time bridging [29] or as simply bridging (in M(N-picO)$_3$ (M = Cr, Co) complexes, containing also two chelating N-picO ligands) [23] has been postulated in certain occasions. Picolinic acid N-oxide (N-picOH) may function either as unidentate, N–O oxygen-bonding [23, 31] or as a chelating agent in a fashion similar to that shown in (III) [30]. Nicotinate N-oxide (N-nicO; IIb) was recently shown by these laboratories to act as a bidentate bridging ligand, coordinating through the N–O and one of the carboxylate oxygens, in its complexes with dipositive 3d metal ions (M = Mn, Fe, Co, Ni, Cu, Zn), and affording linear, double-bridged, polynuclear species-(IV) [32]. In the Fe(III) analog, N-nicO seems to behave as tridentate bridging in a highly crosslinked polymeric structure [33]. Other N-nicO complexes reported include Ln(N-nicO)$_3\cdot$4H$_2$O (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Tm), in which the ligand also appears to coordinate through the N–O and one COO oxygen [34]; and Co(II), Mg(II) and Na(I) complexes, which were not adequately characterized [35]. Adducts of nicotinic acid N-oxide (N-nicOH) or its ethylester with CuX$_2$ (X = Cl, Br, ClO$_4$) [36], Fe(III) salts [37], MCl$_2$ (M = Co, Ni) [38] and UCl$_4$ [31] were also reported. In these adducts the ligand is unidentate, N–O oxygen-bonded.



(III)



(IV)

Metal complexes with isonicotinate N-oxide (N-inicO; IIc) have not been reported. Adducts of isonicotinic acid N-oxide (n-inicOH), its methyl- or ethyl-ester with CuX$_2$ (X = Cl, Br, ClO$_4$) [36], the [TiF$_5$]$^-$ anion [39], (*cis*-2-butene)PtCl$_2$ [40] and UCl$_4$ [31], involving unidentate N–O oxygen-bonded ligands, are the only literature citations of complexes with ligands closely related to the N-inicO anion. The lack of information on M(N-inicO)$_n$ complexes and the fact that, judging from the behavior of inic (as compared to nic) in polynuclear metal complexes, N-inicO would form single – rather than double – bridges between neighboring metal ions [2, 5, 6, 14, 16], suggested that synthetic and characterization studies of N-inicO metal complexes would be worthwhile. Accordingly, work in this direction was undertaken and the present paper reports on M(N-inicO)$_2\cdot$xH$_2$O (M = Mn, Fe, Co, Ni, Cu, Zn) complexes.

## Experimental

### *Synthetic Procedure*

Isonicotinic acid N-oxide (Reilly Tar & Chemical Corp.) was utilized as received. Reagent grade NH$_4$OH and metal salts were used. The new metal complexes were prepared by methods similar to those employed for the syntheses of the N-picO [23] and N-nicO [32] analogs. 20 mmol N-inicOH were dissolved in water by adding NH$_4$OH dropwise, under stirring, and the resulting ammonium isonicotinate N-oxide ((N-inicO)NH$_4$) solution was filtered and condensed to near dryness (to drive off excess NH$_3$). Then, the residue was allowed to interact with a warm (80–90 °C) solution of 10 mmol M(II) acetate (M = Mn, Co, Ni, Cu, Zn) or Fe(NH$_4$)$_2$(SO$_4$)$_2\cdot$9H$_2$O in 15 ml water, under stirring. Solid precipitates formed either immediately or (in the case of Ni$^{2+}$) after 2–3 minutes of stirring. The new metal complexes were separated by filtration, washed with water, allowed to dry in the atmosphere for 2–3 hr and stored in an evacuated desiccator over anhydrous calcium sulfate. Analytical data (C, H, N analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.; metal analyses by atomic absorption spectroscopy; water determinations by Karl Fischer titration ), given in Table I, indicate that the preceding new complexes are of the general type M(N-inicO)$_2\cdot$xH$_2$O (x = 6 for M = Fe, Co, Ni, Zn; x = 5 for M = Mn; x = 2 for M= Cu). Lower hydrates (*cf.* Table I; x = 5 for M = Ni; x = 1.5 for M = Co, Zn; x = 1 for M = Cu; x = 0.5 for M = Mn, Fe) of the same complexes were obtained by allowing the original precipitates to dry at ambient temperature, for a period of 3

TABLE I. Analytical Data for N-inicO (L) 3d Metal Complexes.

| Complex | Color | Analysis | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | %C | | %H | | %N | | %Metal | | %Water | |
| | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| $MnL_2 \cdot 5H_2O$ | Bright yellow | 34.22 | 34.61 | 4.31 | 4.48 | 6.65 | 6.62 | 13.04 | 12.77 | 21.38 | 21.85 |
| $MnL_2 \cdot 0.5H_2O$ | Yellow-gold | 41.28 | 40.84 | 2.89 | 3.11 | 8.02 | 7.95 | 16.15 | 15.88 | 2.65 | 3.06 |
| $FeL_2 \cdot 6H_2O$ | Yellow | 32.75 | 32.62 | 4.58 | 4.80 | 6.36 | 6.57 | 12.69 | 12.90 | 24.56 | 24.95 |
| $FeL_2 \cdot 0.5H_2O$ | Light brown | 42.26 | 41.88 | 2.66 | 2.88 | 8.21 | 8.09 | 16.37 | 16.31 | 2.64 | 2.54 |
| $CoL_2 \cdot 6H_2O$ | Orange-pink | 32.51 | 32.64 | 4.55 | 4.49 | 6.32 | 6.44 | 13.30 | 13.80 | 24.38 | 24.26 |
| $CoL_2 \cdot 1.5H_2O$[a] | Grey-beige | 39.80 | 39.67 | 3.06 | 3.12 | 7.73 | 7.63 | 16.27 | 15.85 | 7.46 | 8.07 |
| $NiL_2 \cdot 6H_2O$ | Light blue-green | 32.53 | 32.77 | 4.55 | 4.65 | 6.32 | 6.31 | 13.25 | 13.02 | 24.40 | 24.94 |
| $NiL_2 \cdot 5H_2O$ | Light green | 33.91 | 34.14 | 4.27 | 4.31 | 6.59 | 6.37 | 13.81 | 13.50 | 21.19 | 21.39 |
| $CuL_2 \cdot 2H_2O$ | Dark blue | 38.36 | 38.66 | 3.22 | 3.16 | 7.45 | 7.18 | 16.91 | 16.43 | 9.59 | 9.23 |
| $CuL_2 \cdot H_2O$ | Light green | 40.29 | 39.94 | 2.82 | 2.87 | 7.83 | 8.08 | 17.76 | 17.51 | 5.04 | 4.74 |
| $ZnL_2 \cdot 6H_2O$ | White | 32.04 | 31.78 | 4.48 | 4.33 | 6.23 | 6.11 | 14.54 | 14.96 | 24.04 | 24.46 |
| $ZnL_2 \cdot 1.5H_2O$ | White | 39.26 | 39.09 | 3.01 | 3.26 | 7.60 | 7.42 | 17.73 | 17.36 | 7.33 | 7.73 |

[a] The crystals of $CoL_2 \cdot 1.5H_2O$ are characterized by a metallic (silvery) luster.

weeks, over $P_4O_{10}$ and under high vacuum ($10^{-4}$ torr). Attempts to obtain the completely anhydrous complexes by heating the partially dehydrated products at 70–100 °C, under reduced pressure, led to some decomposition, as was also the case with the corresponding $M(N\text{-nicO})_2$ complexes [32] and some $M(N\text{-picO})_3$ (M = Cr, Co) compounds [23]. The twelve new metal complexes are generally insoluble in water and all common organic solvents and soluble in aqueous mineral acid solutions.

### *Spectral, Magnetic and X-Ray Powder Diffraction Studies*

Infrared spectra (Table II) were obtained on KBr discs (4000–500 $cm^{-1}$) and on Nujol mulls of the complexes between high-density polyethylene windows (700–200 $cm^{-1}$) by using a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility measurements at 295 °K (Table III) and X-ray powder diffraction patterns were obtained by methods described elsewhere [41]. Studies of temperature variation effects on the magnetic properties of $Cu(N\text{-inicO})_2 \cdot H_2O$, obtained courtesy of Dr. A. B. P. Lever at York University, Toronto (Canada), gave the following results (each set of three numbers shows the temperature (°K), $10^6\chi_M^{cor}$ (cgs units) and (in italics) $\mu_{eff}(\mu B)$: 298.9, 1529, *1.92*; 297.8, 1555, *1.93*; 279.6, 1625, *1.91*; 260.4, 1745, *1.91*; 242.2, 1892, *1.92*; 223.4, 2037, *1.92*; 205.2, 2207, *1.91*; 187.6, 2402, *1.91*; 169.6, 2648, *1.90*; 152.0, 2917, *1.89*; 134.3, 3288, *1.89*; 117.2, 3735, *1.88*; 99.8, 4436, *1.89*; 81.0, 5310, *1.86*.

The X-ray patterns of the four hexahydrated complexes (M = Fe, Co, Ni, Zn) exhibit significant similarities, showing strong peaks at 1.86–1.99, 2.15–2.40, 3.46–3.58 and 7.74–7.89 Å and weaker peaks at 1.68–1.82 Å. However, each complex shows additional weak peaks, not necessarily present in the patterns of all the other hexahydrates, *e.g.*: Co(II): 4.57, 5.37; Ni(II): 2.35, 2.37, 5.43; Zn(II): 3.17, 3.75, 4.40 Å. Thus, these hexahydrates are of about the same structure, but cannot be characterized as isostructural. The pattern of the pentahydrated Ni(II) complex is very similar to those of the hexahydrates, showing the strongest peaks at 1.89, 2.37, 3.46 and 7.75 Å; $Mn(N\text{-inicO})_2 \cdot 5H_2O$ exhibits, nevertheless, a quite different pattern (main peaks at 2.84, 3.02, 3.37, 3.62, 4.80, 9.21 Å). The $M(N\text{-inicO})_2 \cdot 0.5H_2O$ (M = Mn, Fe) compounds are apparently of low crystallinity, showing a single peak at *ca.* 3.60 Å, whereas the two $M(N\text{-inicO})_2 \cdot 1.5H_2O$ complexes (M = Co, Zn) exhibit four to five peaks and rather similar patterns. Finally, the patterns of the two Cu(II) complexes are characterized by thirteen to fifteen peaks at 1.77–5.68 Å and are distinctly different from one another and from the patterns of the rest of the new complexes.

## Discussion

### *Infrared Evidence*

Initially, the $M(N\text{-inicO})_2$ complexes were obtained in the form of hexa-, penta- or di-hydrates, which yielded lower hydrates upon standing over $P_4O_{10}$ under a vacuum of $10^{-4}$ torr. Similar behavior has been observed in the case of the $M(N\text{-nicO})_2$ analogs [32], and many metal complexes with pyridinecarboxylate ligands [2, 3, 5, 6, 11–14, 42].

TABLE II. Pertinent Infrared Data ($cm^{-1}$) for $M(N\text{-inicO})_2 \cdot xH_2O$ Complexes.

| N–inicOH | M = Mn x = 5 | M = Mn x = 0.5 | M = Fe x = 6 | M = Fe x = 0.5 | M = Co x = 6 | M = Co x = 1.5 | M = Ni x = 6 | M = Ni x = 5 | M = Cu x = 2 | M = Cu x = 1 | M = Zn x = 6 | M = Zn x = 1.5 | Band Assignment |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3490mw | | | | | | | | | | | | | $\nu_{OH}$ (hydroxyl) |
| | 3360vs[a] | 3300s[b] | 3380vs[a] | 3320s[b] | 3390vs[a] | 3290s[a] | 3400vs[a] | 3400vs[a] | 3200vs, vb | 3190vs, sh | 3390vs[a] | 3300s[a] | $\nu_{OH}$ (water) |
| 3120vs | 3120vs | 3107vs | 3116vs | 3105vs | 3110vs | 3107vs | 3105vs | 3110vs | 3150–2950 | 3105vs | 3115vs | 3110vs | $\nu_{CH}$ |
| 3112vs | 3090vs, sh | | 3075vs[b] | 3065vs | 3080vs | 3075vs | 3065vs, sh | | vs, vvb | | 3075vs | 3070vs | |
| 3064m | 3058vs | 3060vs | | | | | | 3055vs, vb | | 3055vs, vb | | | |
| 3033m | 3030vs | 3037vs | 3040vs, sh | 3028vs | 3030vs | 3035vs, sh | 3025vs, sh | | | | 3030vs | 3040vs | |
| 1720vs | 1662vs[b] | 1643vs, sh | 1655vs[b] | 1646s, sh | 1648vs[b] | 1640s, sh | 1665vs | 1665vs | 1630vs | 1627vs | 1652vs[b] | 1638vs[b] | $\nu_{CO_2}$ (asym)[b] |
| 1708vs | 1630vs | 1618vs | 1619vs | 1616vs | 1615vs, sh | 1617vs | 1618vs | 1614vs | 1616vs | 1619vs | 1614vs | 1620vs[b] | |
| | 1637vs, sh | c | 1625s, sh | c | c | 1628s, sh | 1628s, sh | 1629s, sh | c | c | 1632s, sh | c | $\delta_{H-O-H}$ |
| 1608vs | 1606vs, b | 1601vs | 1592vs | 1600vs[b] | 1590vs[b] | 1588vs | 1598vs, b | 1595vs, b | 1603vs | 1605vs, sh | 1590vs | 1595vs[b] | $A_g + B_{2u} + B_{3u}$ ($\nu_{CC} + \nu_{CN}$) |
| 1562s, sh | 1553vs | 1550s | 1543s | 1549vs | 1544vs | 1540vs | 1547vs | 1545vs | 1550s | 1553s | 1543vs | 1550vs[b] | |
| 1473ms | 1483s | 1480s | 1482m | 1487m | 1481m | 1489m | 1483m | 1482s | 1490s | 1490sm | 1418m | 1480s | |
| 1439vs[d] | 1441ms | 1441m | 1434mw | 1438m | 1432w | 1437s, sh | 1432w | 1432m | 1440vs | 1478sm | 1433mw, sh | 1439vs | |
| | | | | | | | | | | 1430s | | | |
| 1439vs[d] | 1379vs, b | 1398vs, b | 1381vs, b | 1393vs, b | 1380vs, b | 1420vs | 1378vs, b | 1380vs, b | 1360vs, b | 1365vs, b | 1385vs, b | 1400vs | $\nu_{CO_2}$ (sym)[e] |
| | | | | | | 1385vs | | | | | | 1380vs[b] | |
| 1303vs, sh | | | | | | | | | | | | | OH in-plane def. + COOH |
| 1230m, b | | | | | | | | | | | | | |
| 1290vs | 1227vs, b | 1228vs, b | 1230vs | 1230vs, b | 1229vs | 1228vs | 1230vs | 1229vs | 1219vs, b | 1216vs | 1230vs | 1225vs[b] | $\nu_{N-O}$ |
| 867s | 868vs | 862vs | 865s | 869s | 868s, b | 866s | 856s, b | 858s, b | 870vs | 869vvs | 868s | 867vs[b] | $\delta_{N-O}$ |
| 852s | 861vs | | | 867s | | 860s | | | 862vs | | | | |
| 460ms | 479s | 468vs | 467ms, sh | 475ms, sh | 471m | 478m, sh | 470ms, sh | 469ms, sh | 479s | 479s | 460ms | 477s | $\nu_{Ligand}$ (500–230 $cm^{-1}$) |
| 440m, sh | 458s, sh | 459vs, sh | 460ms | 460ms | 463m, sh | 464m | 461ms | 464ms | 466s, sh | 462m, sh | 458ms | 468s | |
| 382mw | 422w | 383m, sh | 430w, sh | 421w, sh | 419w, sh | | 422w | 420w | | 420m, sh | 425vw, sh | 424w, sh | |
| 360mw | 386m | 362m, sh | 368m | 383w, sh | 384m, sh | | | | | 382m, sh | 370m | 375m[b] | |
| 331w | 358m | 316mw, sh | 311m | 370m | 372m | 370m, sh | 375ms | 377m | 378m, sh | 370w, sh | 361m | | |
| 319vw | 311ms | | 306ms | 310m | 312m | 317mw | 313ms | 315m | | 319m, sh | 316m, sh | 318w | |
| 298vw | 307m, sh | | | | 304m, sh | | 307m, sh | 309m, sh | 308m, sh | 307w, sh | 308m | | |
| 288vw | 300vw | 300vw | 300vw | 297s, sh | | | 293w | 295w | 296m, sh | | 293vw | | |
| 238vw | | 285w, sh | 290vw | | 288w | | | | 245vs | 240vs | 281vw | | |
| 230w | 232vs | 234vs | 230vs | 230vs | 232vs | 230vs | 238vs, b | 238vs, b | 230vs | 237vs | 228s[b] | 242s[b] | |
| | 390m | 407m, vb | 384m | 418m, vb | 394m | 431m | 396m | 396m | – | – | 381m | 420ms | $\nu_{M-O}$ (aqua) |
| | 342m, b | 355m, b | 340m | 363m | 352m | 378m | 364m | 364m | 426m | 439s, 396m | 338m, 319m | 357m, sh | $\nu_{M-O}$ (N–O) |
| | 257m | 273m, 263s | 260m | 280w, 263m | 270m, 258s | 292m, 276m | 274ms | 277ms | 340m, 280s | 332s, 328m | 259s | 291w, 275m, | $\nu_{M-O}$ (COO) |
| | | | | | | 262m | | | | 300s, 281s | | b | |

[a] These complexes are also characterized by a very broad weak continuous absorption, covering the 3600–3200 $cm^{-1}$ region; the values given in the Table refer to the maximum of the relatively sharp $\nu_{OH}$(aqua) band (see text). [b] $\nu_{C=O}$ in N-inicOH. [c] Overlap between $\nu_{CO_2}$(asym) and $\delta_{H-O-H}$. [d] Overlap between $\nu_{CO_2}$(sym) and $B_{3u}(\nu_{CC} + \nu_{CN})$ in the spectrum of N-inicOH. [e] $\nu_{C-O}$ in N-inicOH. Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.

TABLE III. Solid-State (Nujol Mull) Electronic Spectra and Magnetic Properties (295 K) of N-inicO (L) 3d Metal Complexes.

| Compound | $\lambda_{max}$, nm | $10^6 \chi_M^{cor}$, cgsu | $\mu_{eff}$, $\mu$B |
|---|---|---|---|
| N-inicOH[a] | 218vs, sh, 261vvs, sh, 284vvs, b, 311vvs, sh | | |
| (N-inicO)$NH_4$ | 209vs, 216vs, b, 230vs, sh, 264s, 287s, 305m, vb | | |
| $MnL_2 \cdot 5H_2O$ | 208vvs, 224vvs, 287vvs, sh, 299vvs, 314vs, 412s, b | 16,078 | 6.18 |
| $MnL_2 \cdot 0.5H_2O$ | 207vvs, sh, 232vvs, 276vs, sh, 297vs, 310s, sh, 345s, b, 423s, b | 15,763 | 6.12 |
| $FeL_2 \cdot 6H_2O$ | 218vs, sh, 283vvs, sh, 306vvs, b, 314vvs, sh, 362vvs, 433vs, 610m, 860mw, vb, 1020mw, b | 12,356 | 5.42 |
| $FeL_2 \cdot 0.5H_2O$ | 202vvs, 224vvs, 286vs, sh, 304vs, 312vs, sh, 350vs, vb, 400vs, sh, 435svs, b, 505s, sh, 615s, sh, 680m, 748m, sh, 835m, 904mw, b, 980mw, sh, 1075w, b | 10,587 | 5.02 |
| $CoL_2 \cdot 6H_2O$ | 200vs, 214vs, 284vs, sh, 305vvs, 312vs, sh, 423m, b, 449m, b, 504m, 1160w, b | 10,271 | 4.94 |
| $CoL_2 \cdot 1.5H_2O$ | 200vvs, 217vvs, 228vs, 287vs, sh, 303vs, b, 311vs, sh, 370svs, sh, 419 s, b, 438s, sh, 525m, vb, 553m, sh, 712mw, sh, 760mw, b, 1100w, vvb | 8998 | 4.63 |
| $NiL_2 \cdot 6H_2O$ | 204vs, 217vs, vb, 283vs, sh, 306vvs, 313vs, sh, 388s, b, 417m, sh, 642m, 712m, 1085w, b | 3774 | 2.98 |
| $NiL_2 \cdot 5H_2O$ | 204vvs, 219vs, 288vs, b, 303vs, 311vs, sh, 388s, b, 415m, sh, 644m, 711m, 1085w, b | 3598 | 2.93 |
| $CuL_2 \cdot 2H_2O$ | 200vvs, 220vvs, b, 277vs, 293vs, b, 308s, sh, 362s, sh, 592s, 621s, 650s, 784m, sh, 945w, sh | 1534 | 1.91 |
| $CuL_2 \cdot H_2O$ | 202vvs, 220vvs, 280vs, 297vs, b, 310s, sh, 365s, sh, 416s, b, 574m, sh, 640m, vb, 775m, sh, 812mw, sh, 970w, sh | 1555 | 1.93[b] |
| $ZnL_2 \cdot 6H_2O$ | 203vvs, 221vvs, 280s, 297vs, b, 313s, sh | Diamagnetic | |
| $ZnL_2 \cdot 1.5H_2O$ | 205vvs, 223vvs, 282vs, 300vs, b, 314vs, sh | Diamagnetic | |

[a] UV spectra of N-inicOH in solution, nm: in water: 212, 272–273 [56b, c]; corrected for the ionic species at equilibrium: 216, 280 [56a]; in ethanol: 220, 287–289 [56b, c]; in *p*-dioxane: 308.5 [56b]. [b] Magnetic susceptibility determined at 298 K for Cu(N-inicO)$_2 \cdot H_2O$. Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.

Among the new complexes, those involving 6,5 or 1.5 water molecules exhibit two types of $\nu_{OH}$ ir bands, *viz.*: A relatively sharp maximum at 3400–3290 cm$^{-1}$ and a weaker, very broad, continuous absorption at 3600–3200 cm$^{-1}$; these bands are, respectively, attributable [32] to the simultaneous presence of aqua ligands [43] and lattice water [44]. The M(N-inicO)$_2 \cdot 5H_2O$ (M = Mn, Fe) complexes show only a relatively sharp $\nu_{OH}$ band 3320–3200 cm$^{-1}$, indicative of the exclusive presence of aqua ligands, whereas the two Cu(II) compounds exhibit a very strong broad band at *ca.* 3200 cm$^{-1}$. The latter absorption can be attributed to the presence of exclusively lattice and hydrogen-bonded water; similar $\nu_{OH}$ absorptions were reported for $WO_3 \cdot H_2O$, which also involves lattice, H-bonded water [44b], and for KLn(N-picO)$_4$ complexes, containing lattice, H-bonded methanol and water [30]. It is worth noticing that additional weak $\nu_{OH}$ bands, indicative of H-bonding between water and non-coordinated carboxylate oxygens, are present in the spectra of all of the new metal complexes at 2950–1800 cm$^{-1}$ (most prominent bands at *ca.* 2740, 2450, 2360 and 1950 cm$^{-1}$) [6, 30, 45]. Similar weak absorptions are observed in the same region of the ir spectrum of N-inicOH; in this case, intermolecular H-bonding presumably occurs between –COOH hydrogen and N–O oxygen atoms [45, 46].

In the 1800–800 cm$^{-1}$ region, N-inicOH exhibits the characteristic $\nu_{C=O}$ (1720, 1708 cm$^{-1}$), $\nu_{C-O}$ (1439 cm$^{-1}$), $\nu_{N-O}$ (1290 cm$^{-1}$) and $\delta_{N-O}$ (867, 852 cm$^{-1}$) absorptions [47]. The new metal complexes generally show doublets in the $\nu_{CO_2}$ (asymmetric) region (1662–1614 cm$^{-1}$) and one or two $\nu_{CO_2}$ (symmetric) bands at 1420–1360 cm$^{-1}$. These features are in favor of the participation of carboxylate oxygens in coordination [23, 29, 32, 33, 48]. On the other hand, coordination of the ligand through the N–O oxygen is demonstrated by shifts of the $\nu_{N-O}$ mode to lower wavenumbers and small $\delta_{N-O}$ shifts [23, 29, 32, 33, 49] (Table II). Regarding the function of the carboxylate groups in the metal complexes, the presence of two $\nu_{CO_2}$(asym) and either one broad or two distinct $\nu_{CO_2}$(sym) absorptions in all of the new compounds suggests that some COO groups act as unidentate, coordinating through only one of the available oxygens (higher frequency $\nu_{CO_2}$(asym) bands), whilst other carboxylate groups either function as bidentate, bridging between adjacent metal ions or are bonded to a metal ion through one oxygen and H-bonded to water through the second oxygen [23, 32, 48]. Other ligand bands at 1800–800 cm$^{-1}$, such as the $A_g + B_{2u} + B_{3u}\nu_{CC} + \nu_{CN}$ modes [50], are not affected by coordination as much as the $\nu_{CO_2}$ and $\nu_{N-O}$ modes (Table II).

In the lower frequency ir region several metal-sensitive bands are observed. Tentative $\nu_{M-O}$ (aqua, N–O and COO) assignments (Table II) were based on similar assignments for the N-nicO analogs [32], and various aqua [43], aromatic amine N-oxide [51, 52] and carboxylato [53] 3d metal complexes. These assignments are suggestive of coordination number six for the hexa- and penta-hydrates, and five for the complexes involving 1.5 or 0.5 molecules of water per metal ion [32, 43, 51–53]. The two Cu(II) compounds do not exhibit any bands identifiable as $\nu_{Cu-O}$(aqua); the $\nu_{Cu-O}$(N–O and COO) modes occur at substantially higher wavenumbers than the corresponding bands in the rest of the new complexes, and are suggestive of coordination number four [52]. The $\nu_{Cu-O}$ splittings, observed in the spectrum of the monohydrated complex may be interpreted in terms of either chemically non-equivalent sets of N-inicO ligands [54] or both tetra- and pentacoordinated $Cu^{2+}$ ions (*vide infra*).

### *Electronic spectra and Magnetic Moments*

The magnetic moments of the new metal complexes (Table III) are generally normal for high-spin compounds of the metal ions under study [23, 32, 54]. In view of the $\nu_{Cu-O}$ splittings, occurring in the ir spectrum of the monohydrated Cu(II) complex, it seemed appropriate to investigate the possibility that this compound may involve N–O oxygen bridging sites (*i.e.*, Cu–O(N)–Cu bridges), which are common in cupric complexes with aromatic amine N-oxides and give rise, in most cases, to anomalous magnetic properties [36, 55]. The $\mu_{eff}$ and $\chi_g$ variations with temperature for Cu(N-inicO)$_2$·$H_2O$ (*cf.* experimental section) indicate that it is a magnetically normal compound. Thus, Cu–O(N)–Cu bridging is rather unlikely for this complex.

The ultraviolet spectrum of N-inicOH shows two $\pi \rightarrow \pi^*$ (218 and a split band at 261, 284 nm in the solid-state spectrum) and one $n \rightarrow \pi^*$ (311 nm) transition band [56]. In the corresponding spectra of the metal complexes or the ammonium salt (Table III) the high energy $\pi \rightarrow \pi^*$ transition appears as split in most cases, while the bands at 261 and 284 nm are shifted to lower energies and the $n \rightarrow \pi^*$ transition occurs at 305–311 nm. Similar trends were previously observed in the UV spectra of the N-nicO 3d metal complexes [32]. The hexa-, penta- and di-hydrated M(N-inicO)$_2$ complexes (M = Mn–Cu) exhibit one metal-to-ligand charge-transfer band, quite common in aromatic amine N-oxide 3d metal(II) complexes [23], at 362–433 nm (increasing order of energies Fe < Co < Ni < Mn < Cu). The lower hydrates show more than one maximum in the same region. The analogous charge-transfer absorptions in M(N-picO)$_2$·$2H_2O$ (M = Mn–Cu) and Cu(N-picO)$_2$ occur at 363–475 nm and show the same order of increasing energies [23] as that observed for the new N-inicO complexes. In the case of the M(N-nicO)$_2$·$4H_2O$ (M = Mn–Cu) complexes, the charge transfer maxima appear at 337–363 nm, while their energies increase along the series Fe < Mn < Ni < Co < Cu [32]. The fact that the N-nicO 3d metal complexes exhibit the charge-transfer bands at significantly higher energies relative to their N-picO analogs was attributed to the function of the N–O and COO ligand sites as richer and poorer, respectively, electron-donating groups in N-nicO metal complexes, in comparison to their function as donor groups in the N-picO complexes [32]. The N–O group in N-inicO is reportedly under the influence of a substantially stronger electron-withdrawing substituent relative to N-nicO ($\sigma_{pyNO}$ substituent constants: 4-COOH 0.608; 3-COOH 0.335) [57]. Hence, it is not surprising that the charge-transfer bands in the spectra of the new metal complexes occur at about the same region as those of the N-picO analogs and at considerably lower energies than the charge-transfer bands in the M(N-nicO)$_2$·$4H_2O$ complexes.

The d–d transition spectra of the M(N-inicO)$_2$·$6H_2O$ (M = Fe, Co, Ni) and Ni(N-inicO)$_2$·$5H_2O$ complexes are characteristic of hexacoordinated configurations. The $^5T_{2g} \rightarrow {}^5E_g$ transition in the Fe(II) complex is split into three bands at 610–1020 nm and indicative of a low effective ligand-field symmetry [54]. In view of the similarities of the X-ray patterns of the higher hydrates (*cf.* experimental section), it is most likely that all the hexacoordinated complexes are characterized by effective symmetries lower than $O_h$. The d–d transition maxima in the spectra of the hexacoordinated Co(II) and Ni(II) complexes are assigned as follows (for pure $O_h$ symmetry), nm: [32, 58] Co(N-inicO)$_2$·$6H_2O$: $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 449; $^4A_{2g}(F)$ 504; $^4T_{2g}(F)$ 1160; Ni(N-inicO)$_2$·$6H_2O$: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 388; $^3T_{1g}(F)$, $^1E_g(D)$ 642, 712; $^3T_{2g}(F)$ 1085; Ni(N-inicO)$_2$·$5H_2O$: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 388; $^3T_{1g}(F)$, $^1E_g$ (D) 644, 711; $^3T_{2g}(F)$ 1085. It should be noted at this point that the assignment of the band at 388 nm in the $Ni^{2+}$ complexes as a d–d transition and the maximum at 415–417 nm as a charge-transfer band is considered as reasonable, in view of the fact that the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition occurs at 395 nm in Ni(N-nicO)$_2$·$4H_2O$ [32]. Approximate spectrochemical parameter calculations for the preceding Co(II) and Ni(II) N-inicO complexes gave the following values: Co(II) complex: Dq = 1040 cm$^{-1}$; $\beta$ = 0.87; Ni(II) complexes: Dq = 922 cm$^{-1}$; $\beta$ = 0.85. The corresponding Dq values (cm$^{-1}$) for the M(N-picO)$_2$·$2H_2O$ and M(N-nicO)$_2$·$4H_2O$ complexes are: N-picO: Co(II) 1030; Ni(II) 935 [23]; N-nicO: Co(II) 1026; Ni(II) 926 [32]. It appears, therefore, that the strengths of the ligand fields generated by N-picO, N-nicO and N-inicO are of about the same magnitude.

Fe(N-inicO)$_2$·$0.5H_2O$ and Co(N-inicO)$_2$·$1.5H_2O$

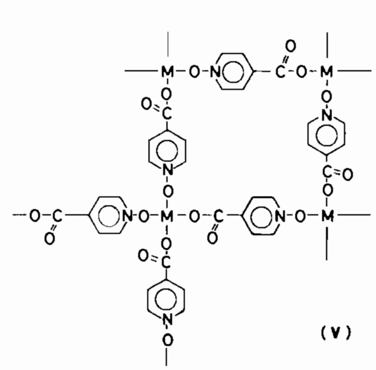
are characterized by considerably richer d–d band spectra, relative to the hexahydrated analogs. These features are consistent with pentacoordinated configurations [54, 59], which are also favored by the $\nu_{M-O}$ assignments for these compounds, and, for the Co(II) complex, by the presence of d–d transition maxima at 712 and 760 nm [54]. The Mn(II) and Zn(II) lower hydrates can also be characterized as pentacoordinated, by analogy to the corresponding Fe(II) and Co(II) complexes, as well as on the basis of their low frequency ir spectra (*vide supra*).

The d–d spectrum of Cu(N-inicO)$_2$·2H$_2$O may be attributed to a square-planar CuO$_4$ moiety, but a low effective ligand-field symmetry, arising from the nonplanarity of the whole complex molecule [54, 60]. In fact, the main d–d transition maxima occur at 592–650 nm in this complex, while the corresponding bands in the hexacoordinated Cu(N-nicO)$_2$·4H$_2$O were observed at 709 and 747 nm [32] (*i.e.*, at about 3000 cm$^{-1}$ lower energies) [54, 60]. As far as the Cu(N-inicO)$_2$·H$_2$O complex is concerned, the d–d band is very broad, showing its main maximum at 640 nm; this small shift to lower energy (by *ca.* 500 cm$^{-1}$), relative to the d–d transition spectrum of the dihydrate, may be due to the simultaneous presence of tetra- and penta-coordinated Cu$^{2+}$ ions [60] in the monohydrate (also suggested by the $\nu_{Cu-O}$ splittings).

### *Nature of the New Metal Complexes*

As was the case with the polynuclear N-nicO analogs [32, 33], the N-inicO 3d metal complexes are insoluble in water or organic solvents (including N,N-dimethylformamide, hexamethylphosphoramide, dimethyl sulfoxide). In contrast, the corresponding N-picO monomeric metal chelates have been found to dissolve in water and/or methanol [23]. Thus, the solubility characteristics of the new metal complexes are definitely in favor of polynuclear structures, which are also supported by the fact that, although N-inicO does not have the ability to chelate through the N–O and one carboxylate oxygen (since these groups are *para*- to each other), its coordination through both N–O and COO oxygens was amply demonstrated by the ir evidence. Moreover, in none of the ir spectra of the new complexes has there been any indication of the presence of non-coordinated N–O or carboxylate sites. Thus, the most likely basic structural unit (V) for the N-inicO 3d metal complexes is similar to that proposed for polynuclear metal complexes with the parent base (inic) [2, 5, 14]. As mentioned in the introduction, N-inicO would be expected to form single- rather than double-bridged polymeric metal complexes, in view of the fact that inic also forms single bridges [2, 5, 6, 14, 16], and especially of the steric interference between two para-substituted pyridine N-oxide ligands in a double-bridged polynuclear structure [61].

Coordination number six in the hexa- and pentahydrated new complexes is attained by the presence of two aqua ligands per metal ion in structure (V); the rest of the water is obviously of the lattice type. Hence, the higher hydrates are formulated as [M(N-inicO)$_2$(OH$_2$)$_2$]$_n$·4nH$_2$O (M = Fe, Co, Ni, Zn) and [M(N-inicO)$_2$(OH$_2$)$_2$]$_n$·3nH$_2$O (M = Mn, Ni). For the lower hydrates of the preceding M(N-inicO)$_2$ complexes, the presence of bridging aqua ligands between metal ions of two parallel units of type (V) is compatible with coordination number five and the correspondence of 0.5 or 1.5 water molecules to one metal ion. The two hemihydrates are probably of the type [(N-inicO)$_2$M-(OH$_2$)-M(N-inicO)$_2$]$_n$ (M = Mn, Fe), involving exclusively coordinated water, while the other two complexes (M = Co, Zn) contain also lattice water, and seem to be of the [(N-inicO)$_2$-M-(OH$_2$)-M(N-inicO)$_2$]$_n$·2nH$_2$O type. Regarding the $\nu_{CO_2}$ splittings observed in the ir spectra of all the preceding complexes (M = Mn, Fe, Co, Ni, Zn), they are most probably due to exclusively unidentate COO ligand groups, some of which are H-bonded to water, whilst other are not.


(V)

Cu(N-inicO)$_2$·2H$_2$O is tetracoordinated and contains exclusively lattice, H-bonded water, on the basis of the overall evidence. Its formulation as [Cu(N-inicO)$_2$]$_n$·2nH$_2$O (structure V) is, thus, reasonable. The corresponding monohydrate may involve both tetra- and penta-coordinated Cu$^{2+}$ ions, as already discussed. Such an arrangement might arise by coordination of C=O oxygens not involved in H-bonding to a neighboring Cu$^{2+}$ ion, resulting in the formation of Cu–O–C–O–Cu bridges between two parallel units of type (V). This single carboxylate bridge between two Cu(II) ions would not necessarily cause anomalous paramagnetism; in fact, the magnetically subnormal dimeric Cu(II) carboxylates reportedly involve a quadruple carboxylate bridge between the two copper atoms [62]. Thus the magnetically normal monohydrated Cu$^{2+}$ compound can be tentatively formulated as [Cu(N-inicO)(*N-inicO*)]$_n$·nH$_2$O, with half of the N-inicO ligands acting as bidentate bridging (in the manner shown in V, with the C=O oxygens H-bonded to water), and the other half of the ligands (shown in italics in the preceding proposed formula) functioning as tridentate bridges between three $Cu^{2+}$ ions.

A final point of interest is that both N-nicO [32, 33] and N-inicO behave in a similar manner as their parent amine ligands (nic and inic) [2, 5, 6, 11, 14], in that they form polynuclear anhydrous or lowly hydrated metal complexes. Nevertheless, in the case of the corresponding higher hydrates, those with the two N-oxide ligands are also polynuclear, whereas those with the parent amines are usually monomeric. Thus, $ML_2 \cdot 4H_2O$ (L = nic or inic) complexes with transition metal ions (M = Co, Ni, Zn, Cd) are non-classical zwitterions, with the two amine ligands functioning as unidentate, N-bonding, and coordination number six being attained by the presence of four aqua ligands [11, 12]. The Mg(II) analog with inic is also monomeric with four coordinated aqua groups, but involves one N-bonded and one carboxylate O-bonded unidentate inic ligand [13]. In general, the coordination site of pyridinecarboxylate ligands seems to largely depend on the affinity of the metal ion toward N- or O-ligand sites (in addition to the preceding examples, it should be mentioned that the lanthanide(III) nic and inic complexes involve either exclusively [16] or at least mainly [17] O-bonded ligands). The situation is quite different with N-nicO and N-inicO, since both potential coordination sites in these ligands involve oxygen atoms. Furthermore, N-oxides are significantly weaker electron-pair donors than their parent amines [61, 63]. Thus, the competition between N–O and COO groups for the inner coordination sphere of a metal ion is much more severe than that between aza and COO groups, and results in a more frequent function of N-nicO or N-inicO as a bridging ligand. Prior to concluding, it should be mentioned that, most recently, we prepared anhydrous $Mn(N\text{-}inicO)_2$ by reaction between $(N\text{-}inicO)NH_4$ and Mn(II) acetate in N,N-dimethylformamide; characterization studies of this complex suggest that it is pentacoordinated, polynuclear single-bridged, with some carboxylate groups coordinating through one oxygen and some through both the COO oxygens [64].

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