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Low Hydrates of Bis(Pyridine carboxylate N-Oxide)·Metal(II) Complexes from N,N-Dimethylformamide*

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The standard preparative method for pyridinecarboxylate [1–3] and pyridine carboxylate N-oxide [4, 5] 3d metal complexes(ML_n) involves reaction of metal acetate or iron ammonium sulfate with either the free acid(LH) or the ammonium salt(NH_4L) of the ligand, in aqueous media. The complexes precipitated under these conditions contain a large number of water molecules, present in the form of aqua ligands and/or lattice water [1–9]. In the case of 3d metal pyridine carboxylates, lower hydrates or the anhydrous complexes can be obtained by heating the higher hydrates at 100–200 °C, under reduced pressure [1–3]. However, the corresponding nicotinate N-oxide (N-nicO) [5] and some of the picolinate N-oxide (N-pico) [4] 3d metal complexes cannot be dehydrated without decomposition under similar conditions.

During our recent studies on linear, polynuclear, hexacoordinated $[M(N\text{-nicO})_2(OH_2)_2]_n \cdot xH_2O$ complexes (M = Mn, Fe, Co, Ni, Cu, Zn; x = 2n or 3n), we attempted their dehydration by storage in a desiccator over P_4O_{10}, under a vacuum of 10^{-4} torr and at ambient temperature, for up to three weeks [5]. Complete dehydration was achieved only in the cases of Fe(II) and Co(II), while the Zn(II) complex yielded the monohydrate. $[Zn(N\text{-nicO})_2(OH_2)]_n$ was characterized as a linear, polynuclear, pentacoordinated compound, and the two $[M(N\text{-nicO})_2]_n$ complexes appeared to be cross-linked polymers, involving coordination number five (M = Fe) or six (M = Co) and participation of all the three ligand oxygens (N–O and COO) in coordination [5]. In the rest of the cases examined, no structural changes were brought about in the desiccator and only partial or complete elimination of the lattice water was observed, *i.e.*, the resulting complexes were found to be hexacoordinated of the type $[M(N\text{-nicO})_2(OH_2)_2]_n \cdot yH_2O$ (y = 0 for M = Mn; y = n for M = Ni, Cu) [5].

In view of the interesting structural characteristics of the dehydrated Fe(II), Co(II) and Zn(II) N-nicO complexes, we engaged in several synthetic attempts aimed at the precipitation of the Mn(II), Ni(II) and Cu(II) analogs from various organic solvents. In the most successful procedure developed, N,N-dimethylformamide(DMF), an excellent ionizing dipolar aprotic solvent [10], is used as the reaction medium. It should be noted at this point that West *et al.* have obtained $[M(N\text{-picO})_m]_n \cdot zH_2O$ (z = 0 for M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+}; z = 0.5 for M = Co^{2+}; z = 2 for M = Ni^{2+}, Zn^{2+}; m = 2 or 3) complexes, by allowing picolinic acid N-oxide (N-picOH) to interact with the hydrated metal acetate in methanol [11]. In the case of N-nicO and isonicotinate N-oxide (N-inicO), performance of the analogous reaction in DMF appears to lead to the best results, as far as precipitation of low hydrates or anhydrous 3d metal complexes is concerned.

Experimentally, 20 mmol nicotinic acid N-oxide (N-nicOH) were dissolved in water by adding NH_4OH dropwise, under stirring [5]. The resulting solution was then filtered, boiled to near dryness, 25 ml DMF were added and this mixture was heated to 70 °C. Subsequently, some water was added dropwise, under stirring, for complete dissolution of the $NH_4(N\text{-nicO})$ (approximate ratio of DMF to H_2O in the system, 9:2 (v/v)). 10 mmol metal(II) acetate (M = Mn, Ni, Cu) were dissolved separately at room temperature in 20 ml DMF, and the resulting solution was immediately added to the warm ligand solution, under stirring. Precipitation was immediate in all three cases. The new complexes were separated by filtration, washed with a warm 9:1 (v/v) mixture of DMF–H_2O, allowed to dry in the air for 1 hr, and placed in a desiccator over P_4O_{10} under a vacuum of 10^{-4} torr. Ni(II) and Cu(II) produced lower hydrates than those previously obtained [5], *viz.*: $Ni(N\text{-nicO})_2 \cdot H_2O$, bright green; analysis (C, H, N by Schwarzkopf, New York; metals by atomic absorption spectroscopy; water by Karl Fischer titration): Found (Calc.)%: C 40.35 (40.84); H 3.15 (2.86); N 8.27 (7.94); Ni 16.24 (16.63); H_2O 5.60 (5.10). $Cu(N\text{-nicO})_2 \cdot 2H_2O$, blue-green; analysis, %: C 38.86 (38.36); H 3.57 (3.22); N 7.82 (7.45); Cu 17.33 (16.91); H_2O 9.67 (9.59). However, in the case of Mn(II) the substitution of acetate with N-nicO ions was only partial and the final gold-colored product was of the type $Mn(CH_3COO)(N\text{-nicO}) \cdot 0.5H_2O$: analysis, %: C 37.19 (36.80); H 3.01 (3.09); N 5.45 (5.36); Mn 20.79 (21.04); H_2O 3.11 (3.45). In view of this anomaly we attempted the preparation of the

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TABLE I. Characterization Data for N-nicO and N-inicO 3d Metal Complexes.

Electronic spectrum, λ_{max}, nm[a]	$Mn(CH_3COO)(N\text{-}nicO) \cdot 0.5H_2O$	$Ni(N\text{-}nicO)_2 \cdot H_2O$	$Cu(N\text{-}nico)_2 \cdot 2H_2O$	$Mn(N\text{-}inicO)_2$
	217vvs, 257vvs, 268vvs, sh, 278vvs, 305vs, sh, 365s, vb, 392s, b	215vs, 277vs, vb, 302s, 405m, 422m, 448m, sh, 690m, sh, 760m, b, 1660w, b, 1910mw, b	209vvs, 222vvs, b, 277vs, b 309s, sh, 335s, sh, 363m, sh, 685m, b, 802mw, sh	204vvs, 219vvs, 278vs, sh, 294vs, b, 310s, sh, 345ms, b, 425ms, vb
$10^6 \chi_M^{cor}$, cgsu	15,562	4732	1322	15.345
μ_{eff}, MB	6.09	3.36	1.77	6.04
Infrared Data, cm^{-1}				
ν_{OH}	3450ms	3325vs	3300vs, vvb	3450vvw, b[b]
ν_{CO_2}(asym)[c]	1665vs, 1620vs, vvb	1625vs	1628vs	1650svs, sh, 1600vs
ν_{CO_2}(sym)[c]	1400vs, vb, 1360vs, vb	1390vs, b	1385vs, b	1404vs, 1380vs, b
ν_{N-O}[c]	1219vs	1222vs	1228vs	1240vs
ν_{M-O}(aqua)	431ms	466ms, sh	455m	–
ν_{M-O}(N–O)	362ms, sh	409m, b	408mw	361m
ν_{M-O}(COO)	335s, b, 320svs, 295ms, sh	313m, sh	320w, 287w	291m, 270ms

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

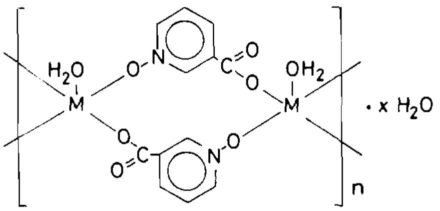
[a] Electronic spectra of the ligands (aqueous solutions), nm: N-nicOH; 220, 260, 306sh; N-inicOH: 216, 280 [29]. [b] Due to traces of residual water (see text). [c] Ligand ir bands, cm^{-1}: N-nicOH: $\nu_{C=O}$ 1710vs; ν_{C-O} 1436vs; ν_{N-O} 1270vs. N-inicOH: $\nu_{C=O}$ 1720vs, 1708vs; ν_{C-O} 1439vs; ν_{N-O} 1290vs [14].

Mn(II) analog with N-inicO (it is worth mentioning that $Mn(CH_3COO)_2$ and NH_4(N-inicO) react to yield $Mn(N\text{-}inicO)_2 \cdot 5H_2O$ from aqueous solution, and this complex is dehydrated to the hemihydrate under a vacuum of 10^{-4} torr, over P_4O_{10} [12]). By following the synthetic procedure described above (substituting N-inicOH for N-nicOH) we obtained from DMF the practically anhydrous golden yellow $Mn(N\text{-}inicO)_2$ complex; analysis, %: C 43.11 (43.53); H 2.56 (2.44); N 8.73 (8.46); Mn 16.60 (16.59); H_2O 0.35 (0.00). All the new metal complexes are insoluble in water and all common organic solvents; this is suggestive of polymeric configurations.

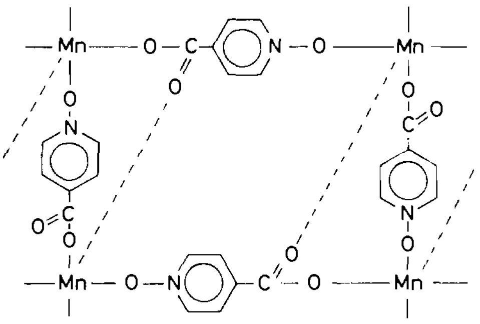
Characterization of the metal complexes was based on infrared and solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements (at 295 °K), obtained by methods previously described [5, 13]. Pertinent data are given in Table I. The infrared spectra clearly demonstrate coordination of the N-oxide ligands through both N–O and COO oxygens. In fact, the $\nu_{C=O}$, ν_{C-O} and ν_{N-O} bands of the free acid ligands [14] show characteristic negative frequency shifts, which are due to the presence of coordinated carboxylate (ν_{CO_2} asymmetric and symmetric modes) [4, 5, 11, 15] and N–O [4, 5, 11] groups. The ν_{CO_2} splittings in $Mn(N\text{-}inicO)_2$ may arise from the presence of two types of coordinated carboxylate groups, *i.e.*, some coordinating through only one of the oxygens (bands at 1650, 1380 cm^{-1}) and some through both oxygen atoms (1600, 1405 cm^{-1}) [4, 5, 11, 15]. Whereas the splittings of the corresponding bands in $Mn(CH_3COO)(N\text{-}nicO) \cdot 0.5H_2O$ are primarily due to the presence of two different carboxylate ligands, *i.e.*, N-nicO [4, 5, 11] and aceto [16]; again, some carboxylate groups seem to function as unidentate (1665, 1360 cm^{-1}) and some as bidentate (1620, 1400 cm^{-1}). The presence of the acetato ligand in this compound is also suggested by absorptions at 3000–2920 cm^{-1} (ν_{CH} (aliphatic) in addition to the ν_{CH} (ring) bands, which appear at 3130–3050 cm^{-1} in the spectra of all the new complexes [5]), 1335, 1030 (CH_3 bands), 938 (C–C stretch) cm^{-1} [16, 17], as well as three absorptions attributable to ν_{Mn-O}(COO) (Table I). The water present in three of the new complexes shows ν_{OH} bands at 3450–3300 cm^{-1}, characteristic of aqua ligands [5, 18]. In the case of the Cu(II) complex the ν_{OH} absorption is very broad, covering the whole 3600–3200 cm^{-1} region; this is probably due to the simultaneous presence of aqua ligands and lattice water [5, 18, 19]. $Mn(N\text{-}inicO)_2$ also exhibits a very weak ν_{OH} band, owing to traces of residual water (*ca.* 0.05 mol H_2O/mol of the complex, on the basis of the analytical results). The three N-nicO complexes show significant absorption at 2900–1800 cm^{-1} (most prominent bands at *ca.* 2750, 2450, 2350 and 1970 cm^{-1}), attributable to ν_{OH} modes arising from hydrogen-bonding between water and non-coordinated COO oxygens [20]; H-bonding of this type seems to be quite common in hydrated metal complexes of the pyridinecarboxylate ligands [3, 6–9, 21, 22] and their N-oxides [4, 5, 11].

Tentative ν_{M-O} band assignments for thd aqua [5, 18], N-oxide [5, 23, 24] and carboxylate [5, 25] ligand sites generally favor coordination numbers lower than six. This is also in agreement with the d–d transition spectra of the Ni(II) and Cu(II) complexes. Thus, the Cu(II) complex exhibits the main d–d band maximum at 682 nm, as compared to two bands at 709, 747 nm in the previously reported hexacoordinated Cu(N-nicO)$_2$·4H$_2$O complex [5], and three maxima at 592–650 nm in the recently prepared square-planar Cu(N-inicO)$_2$·2H$_2$O [12]. Hence, both the electronic spectral [26, 27] and the low frequency ir [24] evidence are in favor of coordination number five for the new Cu(II) complex. Likewise, the d–d spectrum of the Ni(II) complex is atypical of hexacoordinated Ni^{2+}, and most probably due to a pentacoordinated configuration (several maxima at 400–1910 nm) [28]. The location of the ν_{M-O} (M = Ni or Mn) bands is also consistent with coordination number five [24]. in the UV region, the $\pi \rightarrow \pi^*$ (216–280 nm) and $n \rightarrow \pi^*$ (300–310 nm) ligand transitions [29] undergo small shifts and/or splittings upon metal complex formation, as expected [5]; furthermore, strong metal-to-ligand charge-transfer absorption, originating in the UV and trailing off into the visible (maxima at 345–425 nm) is also observed [4, 5]. In the case of Mn(CH$_3$COO)(N-nicO)·0.5H$_2$O, an additional UV band (257 nm) is probably due to the acetato ligand [30]. The magnetic moments of the new complexes are generally normal for spin-free d^5 and d^8 compounds and for the d^9 configuration; it is worth noticing that the μ_{eff} of the Ni(II) complex (3.36 μB) is in the same region as the moments of other pentacoordinated Ni^{2+} compounds [28].

On the basis of the overall evidence, the Ni(II) and Cu(II) complexes appear to be of type (I) (x = 0 for M = Ni; x = $n/2$ for M = Cu), *i.e.*, linear, polynuclear, involving double N-nicO bridges (as was also the case with the corresponding higher hydrates [5]) and coordination number five. Mn(N-inicO)$_2$ is apparently also polynuclear, with single rather than double N-inicO bridges (steric considerations suggest that double N-inicO bridges are highly improbable); a likely structure for this pentacoordinated complex is (II), in which some carboxylate groups coordinate through one and some through both oxygens [1]. Finally, the polymeric structure (III), involving alternating acetato and N-nicO double bridges is considered as likely for the Mn(CH$_3$COO)(N-nicO)·0.5H$_2$O complex; in this strcuture, the aqua ligands act as bridges between Mn^{2+} ions of adjacent linear, polymeric units. It should be mentioned that double bridges are not uncommon for either the acetato [30, 31] or the N-nicO [5] ligand.



(I)



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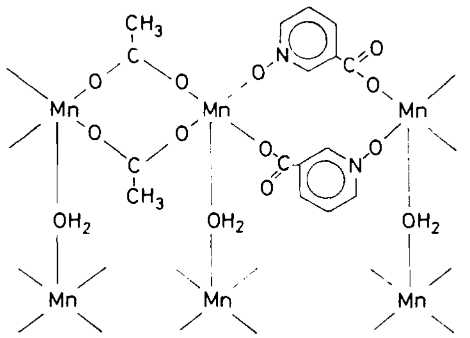

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References

1 A. Kleinstein and G. A. Webb, *J. Inorg. Nucl. Chem., 33,* 405 (1971).

2 G. D'Ascenzo and W. W. Wendlandt, *Anal. Chim. Acta, 50,* 79 (1970).

3 A. Anagnostopoulos, R. W. Matthews and R. A. Walton, *Can. J. Chem., 50,* 1307 (1972); A. Anagnostopoulos, *Inorg. Nucl. Chem. Lett., 10,* 525 (1974).

4 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.,* 5262 (1962); W. Byers, B. Fa-Chun Chou, A. B. P. Lever and R. V. Parish, *J. Am. Chem. Soc., 91,* 1329 (1969).

5 A. N. Speca, L. S. Gelfand, L. L. Pytlewski, C. Owens and N. M. Karayannis, *Inorg. Chem., 15,* 1493 (1976); *J. Inorg. Nucl. Chem., 39,* 537 (1977).

6 H. Loiseleur, G. Thomas, B. Chevrier and D. Grandjean, *Chem. Commun.,* 182 (1967); P. Lumme, G. Lundgren and W. Mark, *Acta Chem. Scand., 23,* 3011 (1969).

7 M. Biagini-Cingi, P. Domiano, C. Guastini, A. Musatti and M. Nardelli, *Gazz. Chim. Ital., 101,* 455 (1971); M. Biagini-Cingi, A. Gaetani-Manfredotti, C. Guastini, A. Musatti and M. Nardelli, *ibid., 101,* 815 (1971).

8 M. Biagini-Cingi, A. Chiesi-Villa, C. Guastini and D. Viterbo, *Gazz. Chim. Ital., 104,* 1087 (1974); A. Chiesi-Villa, C. Guastini, A. Musatti and M. Nardelli, *ibid.. 102,* 226 (1972).

9 M. G. B. Drew, R. W. Matthews and R. A. Walton, *J. Chem. Soc., A,* 2959 (1971).

10 V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York (1968); p. 152; P. K. Chattopadhyay and B. Kratochvil, *Can. J. Chem.*, *55*, 3449 (1977).

11 T. J. Delia, M. A. Little and D. X. West, *J. Inorg. Nucl. Chem.*, *35*, 1400 (1973); S. A. Boyd, R. E. Kohrman and D. X. West, *ibid.*, *38*, 607 (1976).

12 C. M. Mikulski, L. S. Gelfand, L. L. Pytlewski, A. N. Speca and N. M. Karayannis, *Abstracts, the 2nd Joint Chem. Inst. Can./Am. Chem. Soc. Conference,* Montreal Canada, May 29–June 2 (1977); No. INOR 73; to be published.

13 A. N. Speca, N. M. Karayannis and L. L. Pytlewski, *J. Inorg. Nucl. Chem.*, *35*, 3113 (1973).

14 G. Costa and E. Pauluzzi, *Univ. Studi Trieste, Fac. Sci., Ist. Chim., Pubbl. 12* (1956); *Chem. Abstr.*, *51*, 4823b (1957).

15 K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, *79*, 4904 (1957); K. Nakamoto, Y. Morimoto and A. E. Martell, *ibid.*, *83*, 4528 (1961).

16 J. D. Donaldson, J. F. Knifton and S. D. Ross, *Spectrochim. Acta*, *21*, 275 (1965); D. Hibdon and J. H. Nelson, *Inorg. Chim. Acta*, *7*, 629 (1973).

17 K. Ito and H. J. Bernstein, *Can. J. Chem.*, *34*, 170 (1956); E. Spinner, *J. Chem. Soc.*, 4217 (1964); F. Vratny, C. N. R. Rao and M. Dilling, *Anal. Chem.*, *33*, 1455 (1961).

18 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, *20*, 429 (1964); K. Ichida, Y. Kuroda, D. Nakamura and M. Kubo, *ibid.*, *28A*, 2433 (1972).

19 M. Hass and G. B. B. M. Sutherland, *Proc. Roy. Soc., London*, *236A*, 427 (1956).

20 S. Yoshida and M. Asai, *Chem. Pharm. Bull.*, *7*, 162 (1959); R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 1005 (1962).

21 G. W. A. Fowles, R. W. Matthews and R. A. Walton, *J. Chem. Soc. A*, 1108 (1968).

22 S. C. Chang, J. K. H. Ma, J. T. Wang and N. C. Li, *J. Coord. Chem.*, *2*, 31 (1972).

23 A. D. van Ingen Schenau, W. L. Groeneveld and J. Reedijk, *Spectrochim. Acta*, *30A*, 213 (1974); A. T. Hutton and D. A. Thornton, *J. Mol. Struct.*, *39*, 33 (1977).

24 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem.*, *33*, 3185 (1971).

25 K. Nakamoto, P. J. McCarthy and B. Miniatas, *Spectrochim. Acta*, *21*, 379 (1965); M. Cadene and A. M. Vergnoux, *ibid.*, *28A*, 1663 (1972).

26 I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968); A. A. G. Tomlinson and B. J. Hathaway, *ibid.*, *A*, 1685 (1968).

27 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.*, *7*, 1835 (1968); C. Petitfaux, J.-P. Barbier and J. Faucherre, *Bull. Soc. Chim. France*, 3441 (1970).

28 L. Sacconi and I. Bertini, *Inorg. Chem.*, *7*, 1178 (1968); C. M. Mikulski, L. S. Gelfand, L. L. Pytlewski, J. S. Skryantz and N. M. Karayannis, *Inorg. Chim. Acta*, *21*, 9 (1977).

29 H. H. Jaffé, *J. Am. Chem. Soc.*, *77*, 4451 (1955); L. R. Caswell, F. C. Lee and L. T. Creagh, *J. Heterocycl. Chem.*, *9*, 551 (1972).

30 S. Yamada, K. Nakamura and R. Tsuchida, *Bull. Chem. Soc. Japan*, *31*, 303 (1958); B. J. Edmondson and A. B. P. Lever, *Inorg. Chem.*, *4*, 1608 (1965); L. Dubicki and R. L. Martin, *ibid.*, *5*, 2203 (1966).

31 F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).