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Picolinic Acid N-Oxide Interactions with 3d Metal Perchlorates [1]

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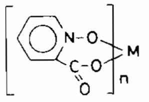
Interactions of picolinic acid N-oxide(LH) with 3d metal perchlorates in ethanol–triethyl orthoformate lead to the partial or complete substitution of perchlorate with anionic picolinate N-oxide(L) groups. Complexes of the following types were isolated and characterized: $[ML(LH)(OH_2)_2](ClO_4)$ *(M = Mn, Zn), with both L and LH functioning as bidentate chelating O,O-ligands, coordinating through the N-O and one of the COO oxygens;* $[CrL_2(LH)(OH_2)](ClO_4)\cdot 4H_2O$, $[FeL(LH)_2(OH_2)_2](ClO_4)\cdot 2H_2O$, $[ML(LH)(OH_2)_3](ClO_4)\cdot xH_2O$ *(M = Co, Ni; x = 0 for M = Co; x = 2 for M = Ni), with bidentate chelating L and unidentate N-O oxygen-bonded LH ligands;* $[FeL_2(OH_2)_3](ClO_4)\cdot H_2O$, *with one bidentate chelating and one unidentate N-O oxygen-bonded L ligand (all the preceding new complexes are low symmetry hexacoordinated); and the previously reported square-planar* $[CuL_2]$ *bis-chelate.*

Introduction

Metal chelates with the picolinate N-oxide(N-picO) anionic ligand (I) have been rather extensively studied in recent years [2–14]. This ligand acts in most cases as a bidentate O,O-chelating agent, coordinating through the N-O and C-O oxygens and yielding chelates of type (I) with alkaline earth, 3d metal, lanthanide, actinide and B(III) ions [2–6, 8–14]. Its function as unidentate, N-O or C-O oxygen-bonded [4, 7], as chelating and, at the same time, bridging [12] or as simply bridging (in $M(N\text{-picO})_3$ (M = Mn, Fe) complexes, also involving two chelating N-picO ligands per metal ion) [4] has been postulated in certain occasions. In contrast to N-picO metal complexes, only a few complexes with the corresponding neutral ligand, namely picolinic acid N-oxide (N-picOH; II), have been reported in the literature [4, 13, 15]. These include the ferric complex $Fe(N\text{-picO})_3(N\text{-picOH})$, which appears to involve two bidentate chelating N-picO ligands, with the third N-picO and the N-picOH groups acting as unidentate [4]; $[Ln(N\text{-picO})_2(N\text{-picOH})_2](ClO_4)\cdot xH_2O$ (Ln = La, Pr, Sm, Dy, Ho, Er, Yb; x = 0 - 3) complexes, with exclusively bidentate N-picO and N-picOH O,O-ligands [13]; and $UCl_4(N\text{-picOH})_n$ (n = 1 or 2) complexes, with the ligand functioning as unidentate, N-O oxygen bonded [15]. These laboratories have studied 3d metal complexes with analogous ligands; earlier work concerned the complexes with the anionic nicotinate [16, 17] and isonicotinate [18] N-oxide(N-nicO and N-inicO, respectively) ligands. Recently, our work was extended to include adducts of $CuCl_2$ with the neutral nicotinic(N-nicOH) and isonicotinic(N-inicOH) acid N-oxide ligands, a $NiCl_2$ adduct with N-nicOH and mixed ligand (N-nicOH-N-nicO or N-inicOH-N-inicO) complexes with Mn^{2+}, Co^{2+} and Ni^{2+} chlorides [19]. These recent studies have been now further extended to the interactions of the three pyridinemonocarboxylic acid N-oxides with 3d metal perchlorates [1], and the present paper deals with the complexes formed by interaction of ethanol–triethyl orthoformate(teof) solutions of N-picOH and various $M(ClO_4)_n$ (M^{n+} = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) salts.



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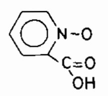


(II)

TABLE I. Analytical Data for Metal Complexes with N-picOH(LH) and N-picO(L).

Complex	Color	C%		H%		N%		Metal%		Cl%		Water%[a]	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$CrL_2(ClO_4)\cdot LH\cdot 5H_2O$	Dark blue green	32.92	32.45	3.53	3.60	6.40	6.71	7.92	8.17	5.40	5.91	13.82	13.40
$MnL(ClO_4)\cdot LH\cdot 2H_2O$	Bright yellow	30.82	30.93	2.80	2.80	5.99	6.15	11.75	11.97	7.58	7.38	7.71	8.00
$FeL(ClO_4)\cdot (LH)_2\cdot 4H_2O$	Brown-yellow	33.59	33.44	3.44	3.66	6.53	6.87	8.68	9.04	5.51	5.43	11.20	11.50
$FeL_2(ClO_4)\cdot 4H_2O$	Orange yellow	28.62	28.27	3.20	3.31	5.56	5.32	11.09	10.91	7.04	7.42	14.31	14.10
$CoL(ClO_4)\cdot LH\cdot 3H_2O$	Brown-red	29.44	29.67	3.09	3.37	5.72	5.36	12.04	12.49	7.24	7.28	11.04	10.70
$NiL(ClO_4)\cdot LH\cdot 5H_2O$	Bright light green	27.43	27.81	3.65	4.02	5.33	5.12	11.17	11.44	6.75	7.15	17.28	17.50
CuL_2	Deep sky blue	42.42	42.29	2.37	2.64	8.25	8.46	18.70	18.39	0.00	0.15		
$ZnL(ClO_4)\cdot LH\cdot 2H_2O$	White	30.21	30.03	2.75	2.75	5.87	6.06	13.70	14.13	7.43	7.07	7.55	7.10

Water was determined by Karl Fischer titration.

Experimental

Chemicals

N-picOH(Aldrich) was utilized as received. Reagent grade hydrated metal perchlorates and organic solvents were used throughout this work.

Preparation of Metal Complexes

3.2 mmol N-picOH were mixed with 30 ml of a 3:2 (v/v) mixture of ethanol and teof, and heated to 60 °C for 2–3 hr, under stirring. 1 mmol hydrated metal perchlorate was separately treated in the same manner with 10 ml of the ethanol–teof mixture. Subsequently, the warm mixture of the ligand with ethanol-teof (still containing a small amount of undissolved N-picOH) was filtered through a sintered glass funnel, and the filtrate was immediately combined with the warm metal perchlorate solution. The resulting mixture was then refluxed for 1½ hr. Solid precipitates were obtained at the end of this treatment, in most cases ($M^{n+} = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$). These precipitates were separated by filtration, washed with warm ethanol–teof, and stored in an evacuated desiccator over anhydrous $CaSO_4$. With Cr^{3+} and Fe^{2+} perchlorates, semi-solid precipitates were initially obtained; these were separated from the supernatant, washed with 10 ml of warm ethanol–teof, and allowed to remain in an evacuated desiccator over $CaSO_4$. After a few days, these semi-solids were converted to glassy solids, which were ground into powders, washed with ethanol–teof and desiccated as described above. The new metal complexes are generally stable in the atmosphere; the Mn^{2+} complex, which is, as usual, photosensitive [20], was protected from any exposure to light [21]. Analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) are given in Table I. Some of the complexes ($M^{n+} = Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$) are either insoluble or very sparingly soluble in polar organic solvents, while the rest of the new metal complexes ($M^{n+} = Cr^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}$) dissolve in various organic solvents, including nitromethane.

Spectral, Magnetic and Conductance Studies

Infrared spectra (Table II) of the new metal complexes were obtained on Nujol mulls between IRTRAN 2 (4000–700 cm^{-1}) and high-density polyethylene (800–200 cm^{-1}) windows, in conjunction with a Perkin-Elmer 621 spectro-photometer. Solid-state (Nujol mull) electronic spectra (Table III), magnetic susceptibility (Table III) and molar conductivity measurements were obtained by methods previously described [22, 23]. Conductance data for the four new complexes that are sufficiently soluble in polar organic solvents (*vide supra*) are as follows (Λ_M, Ω^{-1} cm^2 mol^{-1} for 10^{-3} *M* solutions in CH_3NO_2 at 25 °C): $M^{n+} = Cr^{3+}$ 112; Fe^{2+} 99; Fe^{3+} 121; Ni^{2+} 124.

TABLE II. Pertinent Infrared Data (cm^{-1}) for the Products of Reaction of N-picOH with $M(ClO_4)_n$.

N-picOH	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Cu^{2+}	M = Zn^{2+}	Band Assignment
3490–3450w	3500vw,sh	3470vw,sh	3490vw,sh		3505vw,sh	3510vw,sh		3480vw,sh	ν_{OH}(hydroxyl)
	3300m,b^a	3310m,w	3340mw,b^a	3330mw,b^a	3360m,b	3390m,b^a		3320mw	ν_{OH}(water)
3140s, 3070s	3120m,sh, 3070s,b	3145m,sh, 3080s	3110m,sh, 3075ms	3110m,sh, 3070m	3118m, 3075m	3119m, 3078m	3121m, 3085m	3105m, 3065m	ν_{CH}
1717vs, 1667vs	1747m, 1638vs,b	1630s,vb	1740m, 1645s,b	1740w, 1650ms,vb	1735ms,sh, 1625s	1751ms, 1627vs	1672s, 1650ms	1640svs, 1620svs	$\nu_{C=O} + \nu_{CO_2}$(asym)^b
1610s, 1555m, 1480m, 1440s	1588s, 1560s,sh, 1488m, 1438s	1591s, 1560m, 1486m, 1435s	1592s, 1561m, 1489m, 1437s	1588ms, 1565m, 1482m, 1433s	1592s, 1567m, 1490m, 1440s	1598svs, 1566m,sh, 1486m,sh, 1437s	1600ms, 1561m, 1478m, 1428ms	1590svs, 1558m, 1485m, 1437s	$A_1 + B_1(\nu_{CC} + \nu_{CN})$
1408s	1403m, 1360s	1363s,b	1397m,sh, 1364s	1400mw, 1377s	1399m,sh, 1368s	1398ms, 1369vs	1350ms,b	1361s,b	$\nu_{C–O} + \nu_{CO_2}$ (sym)^b
1285s, 1255s	1270m, 1230m, 1196m	1270m, 1213m	1270m,b, 1242m,sh, 1202m	1275m,b, 1250w,b, 1214ms	1280m,b, 1240w, 1204m	1276m, 1247m,sh, 1209m	1261m, 1188ms	1270m, 1218ms	$\nu_{N–O}$
	1075vs,vb	1078vs,b	1083vs,b	1088s,b	1083s,b	1082vs,b		1078vs,b	$\nu_3(ClO_4^-)$
921w	925w	920wvw	920wvw	918wvw	920wvw	920wvw	920vvw	921wvw	$\nu_1(ClO_4^-) + \nu_{Ligand}$
846s	871ms	866ms	869ms	861s	870ms	869ms	868s	871s, 861s	$\delta_{N–O}$
	617s	620s	620s	622s	621s	622s		619s	$\nu_4(ClO_4^-)$
466m, 436m, 400mw,b, 290m, 265m	460s, 438ms,sh 390w,b, 285w, 260w	470m,b, 438m, 400w, 290w,b, 263w,sh	477m,b, 432m,b, 400w,sh, 300w,sh, 261w,sh	482m,b, 436m,sh, 400w,b, 288w,sh, 267w	485m,b, 438m, 395w,b, 285w,sh	490m,b, 440m,sh, 400w,b, 303w,b, 261w,b	481m, 432ms,sh, 398w, 291m, 270m, 254m	479m, 437m, 393mw,sh, 360w,sh, 285w,sh, 255w,b	ν_{Ligand} (500–250 cm^{-1})
	490ms,b	391w	409m,sh	503m,sh	416mw,sh	422mw,sh		396m	$\nu_{M–O}$(aqua)
	447ms,sh	320w	326mw,b	444m,b	350mw,b	361mw	440ms^c	328w	$\nu_{M–O}$(N–O)
	333w,b	269w	278w	322m,b	281w	286w	369ms^c	274w	$\nu_{M–O}$(C–O and/or C=O)

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

[a] The ν_{OH}(water) regions of these complexes are also characterized by a weaker continuous absorption at 3500–3150 cm^{-1}. [b] $\nu_{C=O}$ and $\nu_{C–O}$ for N-picOH; ν_{CO_2}(asym) and (sym) for N-picO. The $\delta_{H–O–H}$(water) band in the spectra of the hydrated new complexes is masked by the stronger $\nu_{C=O} + \nu_{CO_2}$(asym) absorption. [c] Literature data for $Cu(N\text{-}picO)_2$: $\nu_{Cu–O}$(N–O) 441s; $\nu_{Cu–O}$(C–O) 370s (cm^{-1}) [12].

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Moments (295 °K) of 3d Metal Perchlorate Complexes with N-picOH(LH) and N-picO(L).

Compound	λ_{max}, nm	Dq, cm^{-1} (β)[b]	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μ_B
LH[a]	201vvs,b, 219vvs,sh, 262vs,b, 309svs,sh, 348w,sh			
$CrL_2(ClO_4) \cdot LH \cdot 5H_2O$	207vvs, 217vvs,sh, 264vs, 276vs,b, 310vs,vb, 412s,vb, 576s,vb	1736	5524	3.63
$MnL(ClO_4) \cdot LH \cdot 2H_2O$	208vvs, 219vvs,sh, 263s,sh, 275s, 283s, 312ms,b, 395m,b		15,743	6.12
$FeL(ClO_4) \cdot (LH)_2 \cdot 4H_2O$	204vvs, 220vvs,sh, 264vs, 277s,b, 310ms,vb, 464m, 790mw,b 951w,sh, 1000w,vb, 1095w,b,sh	1043	12,542	5.46
$FeL_2(ClO_4) \cdot 4H_2O$	207vvs, 215vvs,sh, 255vs,sh, 276s,b, 307s,sh, 410m,vb		14,601	5.89
$CoL(ClO_4) \cdot LH \cdot 3H_2O$	203vvs, 221vvs,sh, 262vs, 279vs, 303ms,sh, 420m,sh, 496mw,b, 519mw,vb, 1140w,vb	1020(0.76)	10,123	4.91
$NiL(ClO_4) \cdot LH \cdot 5H_2O$	203vvs, 220vvs,sh, 263vs,sh, 274vs, 279vs, 308ms,b, 394m,sh, 407m,sh, 673mw,sh, 734mw,sh, 870w,sh, 1070w,vb	935	4635	3.32
CuL_2	206vvs, 217vvs,sh, 262vs, 274vs,b, 305s,sh, 364ms, 680m, 702m, 724m,sh		1482	1.88
$ZnL(ClO_4) \cdot LH \cdot 2H_2O$	203vvs, 222vvs,sh, 253s,sh, 269s,b, 274s,sh, 295ms,vb		Diamagnetic	

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

[a] Solution spectra of N-picOH, nm: Aqueous solution: 204, 258.5–259, 313sh [45, 46]; in methanol: 265, 314 [4]; in ethanol: 225, 261.5, 307.5–308, 330sh [45, 46]; in *p*-dioxane: 268, 313 [45]. [b] Approximate values.

Discussion

Stoichiometries of the New Metal Complexes

Under our synthetic conditions, reactions involving substitution of at least one anionic ClO_4^- group with the N-picO$^-$ anion occurred in all cases investigated. Similar behavior was reported by Boyd *et al.* for interactions between N-picOH and lanthanide(III) perchlorates [13]. These reactions led to the formation of mixed ligand (N-picOH-N-picO) complexes with Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. All these complexes contain one (in most cases) or two (Fe^{2+}) neutral N-picOH ligands, one (in most cases) or two (Cr^{3+}) N-picO$^-$ anionic groups, and a single perchlorate group (Table I). In addition, they contain between two and five molecules of water per metal ion, despite the use of teof, a usually effective dehydrating agent [24], during their preparation. With $Fe(ClO_4)_3$, two ClO_4^- groups were replaced by the anionic N-picO$^-$ ligands, and a complex of the $Fe(N\text{-}picO)_2(ClO_4) \cdot 4H_2O$ type, not comprising neutral N-picOH ligands, was isolated. Finally, the reaction between $Cu(ClO_4)_2$ and N-picOH led to the complete elimination of the perchlorate groups (only a trace of residual chlorine was found in the precipitate; *cf.* Table I), and the formation of the previously reported [4, 5, 12] square-planar $Cu(N\text{-}picO)_2$ chelate.

Infrared and Conductance Evidence

Free N-picOH exhibits the following ir bands, in connection with its COO and N-O functions [4, 12, 25, 26]: $\nu_{C=O}$ 1715, 1667; ν_{C-O} 1408; ν_{N-O} 1285, 1255; δ_{N-O} 847 cm^{-1}. Regarding the ν_{N-O} mode, some research groups have considered both the 1285 and 1255 cm^{-1} bands as involving contributions of this vibration [26], whereas other groups have characterized either the 1285 cm^{-1} [25] or the 1255 cm^{-1} [4, 12] maximum as due to a single ν_{N-O} absorption band. Whichever is the correct assignment, the coordination of all the ligands present in the new metal complexes through the N-O oxygen is clearly manifested by the fact that both these bands undergo sizeable shifts to lower wavenumbers, upon coordination of N-picOH or N-picO to a metal ion [4, 12, 13, 27]. The δ_{N-O} mode of the ligand shows small positive shifts in the spectra of the complexes, as expected [12, 27]. The mixed ligand (N-picOH-N-picO) metal complexes exhibit generally broader $\nu_{C=O} + \nu_{CO_2}$(asym) and $\nu_{C-O} + \nu_{CO_2}$(sym) bands, relative to the corresponding absorptions in complexes involving either the neutral or the anionic ligand only [4, 12–14, 16–19].

There appears to be a good correlation between the features of the carboxylate and N–O ir bands, as far as the indications regarding the mode of coordination of the various ligands present are concerned. Thus, in the case of the Mn^{2+}, Cu^{2+} and Zn^{2+} complexes, both the $\nu_{C=O}$ + ν_{CO_2}(asym) and ν_{C-O} + ν_{CO_2}(sym) bands occur at lower wavenumbers than the $\nu_{C=O}$ and ν_{C-O} modes in free N-picOH. These complexes show only two maxima in the ν_{N-O} region (Table II). These features are in favor of exclusively chelating N-picO, coordinating through the N–O and C–O oxygens [2–6, 8–14], and N-picOH, coordinating through the N–O and C=O oxygens [19, 28–31]. On the other hand, the rest of the complexes under study (M^{n+} = Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}) seem to comprise both chelating N-picO and unidentate N-O oxygen-bonded N-picOH or N-picO ligands. In fact, these compounds exhibit one $\nu_{C=O}$ (N-picOH) or (for M^{n+} = Fe^{3+}) ν_{CO_2}(asym) (N-picO) maximum at 1751–1735 cm^{-1} and a second band (ν_{CO_2}(asym)) at 1650–1625 cm^{-1}; two bands also appear in the ν_{C-O} + ν_{CO_2}(sym) region, *i.e.*, one maximum near 1400 and a second one at 1377–1360 cm^{-1}. Furthermore, three maxima are observed in the ν_{N-O} region, indicating the presence of chemically non-equivalent N-oxide ligands [32]. These ir characteristics are in favor of some of the ligands functioning as bidentate chelating, and some as unidentate, exclusively N-O oxygen-bonded [4, 12–14, 16–19, 32, 33].

In view of the reported tendency of N-picOH to act as a unidentate ligand more often than N-picO does [4, 15], it seems quite reasonable to consider the mixed ligand (N-picOH-N-picO) Cr^{3+}, Fe^{2+}, Co^{2+} and Ni^{2+} complexes as involving unidentate N-O oxygen-bonded N-picOH, and bidentate chelating N-picO ligands. In the case of the Fe^{3+} new complex, it appears that one of the N-picO ligands is chelating, and the other unidentate N-O oxygen-bonded. Ir N-picOH bands, not associated with the COO or N–O functions, do not undergo any severe shift upon coordination. Thus, the ligand absorptions at 1610–1440 (A_1 + B_1 (ν_{CC} + ν_{CN}) (26)) and at 500–250 cm^{-1} do not show dramatic changes upon metal complex formation (Table II).

The ir evidence is generally in favor of the exclusive presence of ionic perchlorate in the new complexes. Thus, both the ν_3 and ν_4 fundamental vibrational modes of the ClO_4^- ion appear as single absorptions in the spectra of the metal complexes [34]. In addition, there is not any significant difference in intensity between the spectra of N-picOH and the perchlorate-free Cu^{2+} complex, on the one hand, and those of the new metal perchlorate complexes, on the other, in the $\nu_1(ClO_4)$ region (*ca.* 920 cm^{-1}; ν_1 is ir-inactive in compounds containing exclusively ionic perchlorate) [34]. The molar conductivities of the Cr^{3+}, Fe^{2+}, Fe^{3+} and Ni^{2+} complexes (see experimental section) are also in favor of the presence of ionic perchlorate. These complexes show Λ_M values intermediate between those corresponding to 1:1 and 1:2 electrolytes [35]. This establishes the ionic nature of the perchlorate group in solution. Normally, these complexes, which involve one ClO_4 group per metal ion, ought to behave as 1:1 electrolytes; the somewhat higher Λ_M values observed are presumably due to partial displacement of N-picO by nitromethane ligands in solution.

All the hydrated metal complexes show ir bands (ν_{OH} and ν_{M-O}(aqua)) attributable to the presence of coordinated aqua ligands [16, 36, 37] (Table II). The Cr^{3+}, Fe^{2+}, Fe^{3+} and Ni^{2+} complexes exhibit also a weaker continuous absorption, covering the whole 3500–3150 cm^{-1} region; the presence of this very broad band implies that, in addition to the aqua ligands, lattice water is also present in these compounds [38]. Tentative ν_{M-O} (aqua, N–O, C=O and C–O) band assignments in the lower frequency ir region were based on previously reported ir studies of aromatic amine N-oxide (including pyridinecarboxylate N-oxides) [12, 16–19, 39–41], carboxylato [42] and aqua [16, 36, 37] 3d metal complexes. On the basis of these assignments, $Cu(N\text{-}picO)_2$ appears to be tetracoordinated [16–19, 41], and the rest of the new metal complexes hexacoordinated [16–19, 39, 40, 42].

Electronic Spectra and Magnetic Moments

The ambient temperature magnetic moments of the new metal complexes (Table III) are generally normal for high-spin $3d^3$ and $3d^5$–$3d^8$ compounds or the $3d^9$ configuration [43]. The magnetic moment determined for the previously reported $Cu(N\text{-}picO)_2$ chelate (1.88 μB) is in agreement with the literature value (1.87 μB) [4]. The magnetic moment of the Co^{2+} complex (4.91 μB) is within the 'octahedral' region for Co^{2+}, while that of the new Ni^{2+} complex (3.32 μB) is slightly higher than the upper limit (3.30 μB) of the "octahedral" region for this metal ion [43]; several low symmetry hexacoordinated Ni^{2+} complexes with aromatic amine N-oxides reportedly exhibit μ_{eff} values slightly exceeding 3.30 μB [2, 32, 44].

The UV spectrum of the free ligand is characterized by $\pi \rightarrow \pi^*$ transition maxima at 201–262 nm and an $n \rightarrow \pi^*$ transition band at 309 nm [4, 45, 46]. The higher energy doublet (201, 209 nm) of uncomplexed N-picOH is not too significantly shifted upon metal complex formation, whereas the $\pi \rightarrow \pi^*$ transition band at 262 nm appears as split into two or three components in the spectra of the new metal complexes. One of these components occurs at about the same or higher energy than 38,931 cm^{-1} (262 nm) [4], whilst the second and third components of this $\pi \rightarrow \pi^*$ transition appear at considerably lower energies. The overall effect of metal complex formation is a red shift of this $\pi \rightarrow \pi^*$ ligand band, as would be expected [16–19]. It is also noteworthy that the $\pi \rightarrow \pi^*$ transition bands in the spectra of the complexes appearing to involve exclusively bidentate chelating N-picOH or N-picO ligands (M^{n+} = Mn^{2+}, Cu^{2+}, Zn^{2+})

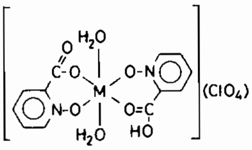
are considerably less intense than those of the rest of the new complexes, in which some ligands seem to be chelating and some unidentate, N-O oxygen-bonded [4]. The n → π* transition band of the ligand appears at 303–312 nm in the UV spectra of the metal complexes (Table III). The new M^{2+} complexes (M = Mn–Cu) show strong charge-transfer absorption bands, originating in the UV and trailing off into the visible region. These bands, which are due to metal-to-ligand charge-transfer [4, 5], occur at about the same energies, and follow the same order of decreasing energies, and follow the same order of increasing 420 nm < Ni^{2+} 407 nm < Mn^{2+} 395 nm < Cu^{2+} 364 nm), as in the corresponding spectra of the M(N-picO)$_2$·2H_2O (M = Mn–Cu) and Cu(N-picO)$_2$ chelates [4, 5]. In the case of the new Ni^{2+} complex, the 407 nm band was assigned as charge-transfer and that at 394 nm as the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ d–d transition, since hexacoordinated $NiL_2 \cdot xH_2O$ complexes with N-nicO or N-inicO reportedly show the latter d–d band at 388–395 nm [16, 18].

The d–d transition spectrum of the Cu^{2+} complex (maxima in Nujol mull solid-state spectrum at 680, 702, 724 nm) (Table III) is virtually similar to that reported for Cu(N-picO)$_2$ (reflectance spectrum: 705, 720 nm) [4]. This previously characterized complex is a square-planar chelate of type (I) (M = Cu; n = 2) [4]. The new metal complexes isolated during this work, appear to be generally hexacoordinated, on the basis of both the ν_{M-O} (*vide supra*) and d–d band assignments. The broad or split character of the various d–d transition bands (Table III) suggests that the new complexes involve low symmetry hexacoordinated configurations [32]. The d–d band assignments are as follows, nm: $M^{n+} = Cr^{3+}$: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 412; $\rightarrow {}^4T_{2g}(F)$ 576; Fe^{2+}: $^5T_{2g} \rightarrow {}^5E_g$ 790, 951, 1000, 1095; Co^{2+}: $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 496; $\rightarrow {}^4A_{2g}(F)$ 519; $\rightarrow {}^4T_{2g}(F)$ 1140; Ni^{2+}: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 394; $\rightarrow {}^3T_{1g}(F)$ 673, 734; $\rightarrow {}^1E_g(D)$ 870; $\rightarrow {}^3T_{2g}(F)$ 1070. Calculated approximate Dq values (Table III) are generally close to those reported for Cr(N-picO)$_3$·H_2O (Dq = 1755 cm^{-1}) and M(N-picO)$_2$·2H_2O (M = Fe, Dq = 1020 cm^{-1}; M = Co, Dq = 1030 cm^{-1}; M = Ni, Dq = 935 cm^{-1}) chelates [4, 5].

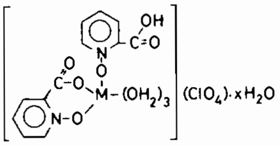
Conclusion

On the basis of the overall evidence presented, the new Mn^{2+} and Zn^{2+} complexes appear to be of type (III), with both the organic ligands functioning as chelating, and with exclusively coordinated water. In contrast, the Co^{2+} and Ni^{2+} complexes involve one chelating N-picO and one unidentate N-picOH ligand, with coordination number six being attained by the presence of three aqua ligands, as shown in (IV); the Ni^{2+} complex contains also lattice water. Very similar to these compounds is the Fe^{3+} complex (V), which involves one chelating and one unidentate anionic N-picO ligand. The Cr^{3+} and Fe^{2+} complexes contain a total of three N-picOH or N-picO ligands per metal ion, as compared to two for the rest of the new metal complexes. Structures (VI) and (VII), respectively, with chelating N-picO and unidentate N-picOH ligands, as well as both coordinated and lattice water, seem most likely for these two compounds.

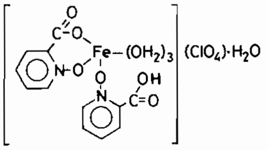
The fact that none of the latter two complexes is a tris-chelate is not surprising. Actually, the N-picO, N-picOH and aqua ligands are of comparable strengths [4], and their competition for the inner coordination sphere of the central metal ion presumably prevents the chelation of the N-picOH ligands. $CrL_3 \cdot H_2O$ complexes with two chelating and one unidentate L groups and one aqua ligand are reportedly formed not only with L = N-picO [4], but also with L = picolinate (the parent amine) [47]. The chelation of all three N-picO ligands does not seem to be favored even in anhydrous M(N-picO)$_3$ complexes (M = Cr [12], Mn, Fe [4]); in fact, these compounds appear to be polymeric, with two chelating and one bridging N-picO ligand per M^{3+} ion [4].



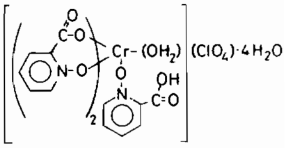
(M = Mn, Zn)
(III)



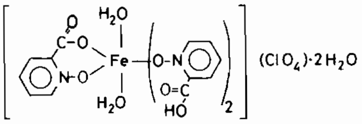
(x = 0 for M = Co; x = 2 for M = Ni)
(IV)



(V)



(VI)



(VII)

Regarding the whole series of new complexes reported, it should be mentioned that the insolubility of some of these compounds in organic media might be considered, *prima facie*, as suggestive of polymeric configurations. Nevertheless, some monomeric M(N-picO)$_2$·xH_2O chelates, including Cu(N-picO)$_2$, are reportedly insoluble in most organic solvents [4]. Hence, there is no particular reason for considering the new Mn^{2+}, Co^{2+} and Zn^{2+} complexes as polymeric, especially in view of the ir-spectral similarities between the Co^{2+} and Ni^{2+} complexes, on the one hand, and the Mn^{2+}, Cu^{2+} and Zn^{2+} complexes, on the other. Another point of interest is that interactions of Fe(II) salts with pyridine-carboxylic acids may lead to partial or complete oxidation of Fe^{2+} to Fe^{3+} [48]. Since the sum of the N-picOH and N-picO ligands in the new ferrous complex is three, the possibility that this compound contains substantial amounts of Fe^{3+} was examined, but ruled out, in view of the normal magnetic moment and the ν_{Fe-O}, charge-transfer and d-d spectral bands, all of which point to the presence of Fe^{2+}; in addition, no ν_{Fe-O} absorptions attributable to any significant amount of Fe^{3+} are observed in the ir spectrum of this complex. Finally, it should be briefly mentioned that all the hydrated new metal complexes show several weak ν_{OH} absorptions at 3000–1800 cm^{-1} (most prominent bands at *ca.* 2750, 2400, 2200 and 2000 cm^{-1}); these are presumably due to hydrogen-bonding between hydrogen atoms of the coordinated or lattice water and carboxylate oxygen atoms, not involved in coordination [13, 14, 18, 19, 49, 50]. Free N-picOH, which involves intramolecular H-bonding between the COOH hydrogen and the N-O oxygen [45], also shows weak ν_{OH} absorption in the same region (2780m, 2390w, vb, 2190w, 1990w, 1970vw, 1860vw).

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