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Isonicotinic Acid N-Oxide Salts of some Bivalent Metal Ions

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Introduction

Since 1961, several studies have been made on the complex forming ability of pyridine monocarboxylic acids and their N-oxides. The picolinate ligand has the tendency to function as a bidentate N,O-chelating agent [1–3]. Nicotinate N-oxide complexes with dipositive 3 d metal ions were studied by Speca *et al.* [4]. These compounds seemed to be hexacoordinated polynuclear complexes with coordination through N–O oxygen and one of the COO oxygens, while the other carboxylate oxygen is hydrogen bonded to water.

As part of a program on the preparation and characterization of bivalent metal complexes of heterocyclic acid N-oxides, a series of bivalent metal isonicotinate N-oxide complexes were prepared and studied. While the work was in progress at our labs, Gelfand *et al.* [5] published the results of the preparation and characterization of isonicotinate N-oxide complexes of Fe, Co, Ni, Zn, Mn and Cu. Our results agree with the published results of Gelfand *et al.* and in the present communication we wish to present the results of some bivalent metal complexes of isonicotinic acid N-oxide that were not studied by Gelfand *et al.* [5].

Experimental

Isonicotinic acid N-oxide (Reilly Tar and Chemical Corp.) was used as received. Reagent grade metal salts and ammonium carbonate were used in the preparation of complexes. Isonicotinic acid N-oxide was dissolved in water by adding ammonium carbonate until the effervescence diminished. The solution was then allowed to stand on a water bath until precipitation of the ammonium salt occurred. Aqueous solutions of metal salt and ammonium isonicotinate N-oxide were combined using an excess of the latter. The resulting solutions were heated on a water bath to promote precipitation. The new complexes were filtered, washed, allowed to dry in the atmosphere and then stored in a dessicator over Drierite. The complexes were insoluble in water and in most organic solvents, but were soluble in aqueous mineral acid solutions. Metal analysis was made by standard procedures [6–7]. C, H, N analysis was obtained using a Perkin-Elmer C, H, N analyser (Table I).

Percentage of water in the complexes was determined by Thermogravimetric analysis (Table III). Infrared spectra (Table II) were obtained with KBr disks (4000–250 cm^{-1}) by using a P.E. 180 spectrophotometer. Thermal analysis and D.S.C. studies were carried out on a Dupont 990 Thermal analyser (Tables III and IV) and X-ray powder diffraction studies were obtained by the tape method on a Philips-Norelco diffractometer (Table V).

Discussion

Infrared Spectra

In the region 3600–3200 cm^{-1} in most complexes broad medium bands were observed attributable to the simultaneous presence of aqua ligands and lattice water [8]. In the 1800–800 cm^{-1} region isonicotinic acid N-oxide exhibits the characteristic $\nu_{C=O}$ (1720, 1708 cm^{-1}), ν_{C-O} (1439 cm^{-1}), ν_{N-O} (1290 cm^{-1}) and δ_{N-O} (867–852 cm^{-1}) absorptions [9]. In the new complexes the ν_{CO_2} (assym) lowered to 1675–1640 cm^{-1} and ν_{CO_2} (sym) to 1375 cm^{-1}. These features are in favour of the participation of the carboxylate oxygens in coordination [8]. Coordination through N–O oxygen is demonstrated by shifts of ν_{N-O} mode to lower frequency and small δ_{N-O} shifts [10–11]. Other ligand bands at 1800–800 cm^{-1} such as ν_{CC} and ν_{CN} modes [12] are not affected by coordination as much as the ν_{CO_2} and ν_{N-O} modes (Table II). No attempt was made to assign the bands in the 450–250 cm^{-1} region to ν_{M-O}, as these bands are weak and present in the free acid. The water δ H–O–H mode in the complexes could not be assigned because of the overlapping with the strong absorption due ν_{CO_2} (assym) and (ν_{CC} + ν_{CN}). These bands become sharper in the infrared spectrum of dehydrated compounds, further substantiating the above assumption. From the infrared spectral data it is concluded that the carboxylate groups in the present study function in the same manner as in the case of other bivalent metal complexes reported by Gelfand *et al.* [5].

Thermal Analysis

T.G.A. was used to determine the percentage of water in the complexes (Table III). The results agree well with the proposed formulae. In the case of the Barium salt, the water is given off in two steps. This is

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TABLE I. Analytical Data for Isonicotinate N-oxide (L)–Bivalent Metal Complexes.

Compound	% C		% H		% N		% Metal	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$MgL_2 \cdot 6H_2O$	35.27	35.25	4.92	4.89	6.92	6.85	6.00	5.95
$CaL_2 \cdot 2H_2O$	40.25	40.87	3.52	3.43	7.58	7.95	11.11	11.38
$BaL_2 \cdot 3H_2O$	31.09	30.80	3.10	2.99	6.09	5.99	28.95	29.38
$CdL_2 \cdot 2H_2O$	33.85	33.94	2.83	2.85	6.80	6.59	26.32	26.47
$PbL_2 \cdot 1.5H_2O$	28.47	28.21	2.31	2.35	5.39	5.49	40.10	40.59

TABLE II. Infrared Spectra.[a]

Compound	Absorptions (cm^{-1})
$CdL_2 \cdot 2H_2O$	3230 (s, b), 3100 (w), 2940 (m, b), 1640 (s), 1610 (m, sh), 1590 (s), 1550 (s), 1485(m), 1440 (m), 1375 (s), 1210 (s), 870 (m), 852 (s), 685 (m), 665 (w), 639 (s), 555 (w), 505 (w), 470 (w), 400 (w), 330 (w), 260 (m)
$PbL_2 \cdot 1.5H_2O$	3400 (m, b), 3100 (w), 1675 (s), 1615 (m), 1585 (s), 1550 (m), 1480 (m), 1435 (m), 1380 (s, b), 1210 (s), 860 (m), 808 (w), 680 (m), 665 (w), 635 (s), 505 (w), 455 (w), 365 (w) 320 (w)
$BaL_2 \cdot 3H_2O$	3380 (s, b), 3200 (b), 3100 (w), 1640 (s), 1610 (m, sh), 1585 (s), 1540 (m), 1475 (m), 1430 (m), 1384 (s, b), 1220 (s), 860 (m), 825 (w), 680 (m), 662 (w), 634 (s), 535 (w), 515 (w), 450 (m), 365 (m), 310 (w)
$CaL_2 \cdot 2H_2O$	3330 (s, b), 3180 (w), 3040 (w), 1630 (s), 1605 (s, sh), 1580 (s), 1550 (s), 1475 (m), 1430 (m), 1395 (s), 1212 (s), 865 (s), 815 (w), 685 (m), 664 (w), 630 (m), 554 (w), 502 (w), 465 (w), 354 (w), 295 (m), 275 (w)
$MgL_2 \cdot 6H_2O$	3380 (s, br), 3120 (w), 3090 (w), 2940 (w), 1660 (m), 1625 (m), 1592 (s), 1544 (m), 1484 (m), 1430 (m), 1385 (s, br), 1225 (s), 865 (m), 830 (w), 670 (m), 635 (m), 545 (w), 510 (w), 375 (w), 315 (w), 275 (w).

[a] L = isonicotinate N-oxide.

TABLE III. Thermogravimetric Analysis.

Compound	Dehydration Temp. (°C)	% of Wt. Loss		Explanation
		Found	Cal.	
$MgL_2 \cdot 6H_2O$	50–210	26.00	26.40	Loss of $6H_2O$
$CaL_2 \cdot 2H_2O$	120–260	10.50	10.20	Loss of $2H_2O$
$BaL_2 \cdot 3H_2O$	30–97	7.0	7.7	Loss of $2H_2O$
	97–150	4.1	3.9	Loss of H_2O
$CdL_2 \cdot 2H_2O$	90–200	8.4	8.5	Loss of $2H_2O$
$PbL_2 \cdot 1.5H_2O$	40–110	5.4	5.5	Loss of $1.5H_2O$

TABLE IV. D.S.C. Studies.

Compound	Peak Temp. (°C)	Description
$MgL_2 \cdot 6H_2O$	140	Endotherm Dehydration
	295	Exotherm Crystallization
	400	Exotherm Decomposition
$CaL_2 \cdot 2H_2O$	200	Endotherm Dehydration
	387 418	Exotherm Decomposition
$BaL_2 \cdot 3H_2O$	63	Endotherm Dehydration
	112	Endotherm Dehydration
	276	Exotherm Crystallization
	392 480	Exotherm Decomposition
$CdL_2 \cdot 2H_2O$	150	Endotherm Dehydration
	253	Exotherm Crystallization
	360 480	Exotherm Decomposition
$PbL_2 \cdot 1.5H_2O$	80	Endotherm Dehydration
	203	Exotherm Crystallization
	320 440	Exotherm Decomposition

further supported by two dehydration endotherms in the DSC study. The loosely bound water comes off first followed by the strongly held water. Most of the compounds underwent violent decomposition disrupting the balance pan and therefore the complete weight loss studies could not be carried out. In the Differential Scanning calorimetric studies (Table IV) the first endotherm corresponds to dehydration followed by a small exotherm which is not reversible. X-ray diffraction studies before and after these exotherms indicate that the peak is due to recrystallization of the anhydrous complexes formed before decomposition. The final exotherms are due to violent decomposition of the complex. No attempts were made to identify the products.

TABLE V. X-Ray Powder Diffraction Patterns of $ML_2 \cdot XH_2O$ Complexes. L = Isonicotinate N-oxide (d spacings, Å; I in parentheses).

INO	M = Mg x = 6	M = Ca x = 2	M = Ba x = 3	M = Cd x = 2	M = Pb x = 1.5
7.25(4)	7.60(100)	8.00(100)	8.67(100)	7.13(15)	7.12(36)
6.22(18)	5.27(8)	6.17(12)	5.30(33)	5.74(35)	5.79(76)
5.92(9)	4.88(51)	4.90(24)	5.03(83)	5.45(25)	5.43(32)
5.61(4)	3.83(18)	4.29(6)	4.35(33)	5.09(18)	4.69(64)
5.51(5)	3.42(62)	4.03(13)	4.18(46)	4.15(100)	4.35(24)
5.06(100)	3.21(5)	3.99(17)	4.10(79)	3.93(15)	4.30(28)
4.91(13)	3.15(21)	3.86(6)	3.83(21)	3.80(15)	4.22(100)
3.76(24)	2.91(3)	3.70(8)	3.70(58)	3.33(93)	3.66(20)
3.69(23)	2.57(29)	2.56(59)	3.66(38)	3.20(20)	3.57(60)
3.66(8)	2.41(16)	3.47(5)	3.51(8)	3.09(63)	3.41(68)
3.63(4)	1.92(4)	3.27(6)	3.30(46)	2.94(28)	3.24(28)
3.51(10)	1.86(4)	3.12(41)	3.12(21)	2.85(30)	3.18(64)
3.39(8)		3.08(5)	3.09(29)	2.78(10)	3.12(96)
3.32(5)		3.03(8)	3.05(17)	2.60(10)	3.02(16)
3.24(8)		2.96(5)	2.93(25)	2.52(5)	2.87(48)
3.15(11)		2.85(4)	2.88(13)	2.41(8)	2.84(24)
3.11(7)		2.81(4)	2.76(17)	2.37(5)	2.72(16)
3.03(5)		2.65(12)	2.71(13)	2.34(23)	2.69(16)
3.01(5)		2.57(4)	2.67(13)	2.07(15)	2.59(28)
2.53(9)		2.45(3)	2.64(17)	2.01(18)	2.51(28)
2.44(6)		2.40(9)	2.58(17)	1.97(8)	2.45(36)
2.16(3)		2.19(3)	2.48(21)	1.85(8)	2.35(32)
2.06(3)		2.14(5)	2.41(29)		2.28(32)
1.90(6)		2.03(3)	2.36(13)		2.07(32)
		1.99(6)	2.28(8)		
		1.94(4)	2.17(13)		
		1.91(10)	2.12(8)		
		1.89(3)	2.09(17)		
			1.99(13)		
			1.89(8)		
			1.81(13)		

X-Ray Diffraction Studies

A comparison of the X-ray diffraction pattern of the complexes indicates that the structures are not isomorphous. The X-ray powder pattern of Mg complex which is hexahydrate is very similar to the hexahydrates of Zn, Co, Ni [5] indicating that they are about the same structure, but cannot be characterized as isostructural. Other complexes exhibited several strong, sharp lines indicating high crystallinity.

In conclusion, the solubility characteristics and the infrared spectral evidence of the new complexes are definitely in favour of polynuclear in nature as suggested by Gelfand *et al.* [5].

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