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o-hydroxyaroyl-isonicotinoyl hydrazones as chelating agents with divalent transition metal ions

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Summary

Two series of bivalent metal complexes of the type M(Sal)·xH$_2$O and M(Naph) have been synthesized; where M = Co, Ni, Cu, Zn, Pd and Cd, and H$_2$-Sal and H$_2$-Naph are salicylaldehyde and *o*-hydroxynaphthaldehyde isonicotinoyl hydrazones which acted as dibasic terdentate ligands. The polymeric nature and coordination sites of the complexes have been characterized by elemental, d.t.a. and t.g.a analyses, molar conductance, pH, room temperature magnetic susceptibility and spectral (i.r., ^{1}H n.m.r, u.v.) measurements. The protonation constants of the ligands have been determined potentiometrically at different temperatures, ionic strengths and at different EtOH–H$_2$O compositions.

Introduction

Schiff bases derived from isonicotinic acid hydrazide (INH) and salicylaldehyde, acetylacetone, thenoylacetone and trifluoroacetylacetone have been prepared$^{(1)}$ and their titanium(IV) and organotin(IV) chelates investigated. Salicylaldehyde isonicotinoyl hydrazone H$_2$-Sal was used for the spectrophotometric determination of gallium(III) and indium(III)$^{(2)}$. The synthesis of nickel(II) complexes of H$_2$-Sal has been reported$^{(3)}$. 2-Hydroxyacetophenone isonicotinoyl hydrazone (2–OH–AIH) forms complexes with trivalent chromium, manganese and cobalt$^{(4)}$, vanadyl$^{(5)}$ and divalent palladium and copper$^{(6)}$ and trivalent lanthanides$^{(7)}$. Other hydrazones of INH have been reported. In this paper we report the synthesis and characterization of H$_2$-Sal and H$_2$-Naph and their complexes with some divalent metal ions.

Experimental

The ligands were prepared according to Sacconi$^{(8)}$ and solid complexes from metal acetates or Na$_2$PdCl$_4$ as previously described$^{(9)}$. The analysis of metals was carried out by established methods$^{(10)}$.

T.g.a. and d.t.a. curves were recorded on a Shimadzu XD-30 thermal analyzer. Molar conductance was measured in pyridine using a Bibby conductimeter type MC1. N.m.r. spectra were obtained with a Varian EM-390 90 MHz n.m.r. spectrometer using TMS as internal standard and DMSO as solvent. I.r. spectra were recorded on a Perkin-Elmer 598 Infrared spectrophotometer. Electronic spectra of the compounds in pyridine were recorded in the 700–200 nm range using a Perkin-Elmer u.v.–vis.550 S spectrophotometer and magnetic susceptibilities were measured using Faraday's method$^{(11)}$.

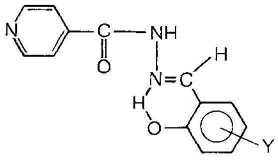
Stock 0.01 M ligand solutions were prepared in EtOH. Metal salt solutions (0.01 M) were prepared in deionized H$_2$O and standardized by recommended methods$^{(12)}$. Solutions of 0.1 M HCl, 0.09 M NaOH and 1 M KCl were also prepared. Potentiometric titrations were carried out using Chemtrix 62 digital pH meter at 25 ± 0.1° C and the pH-meter readings B were converted to hydrogen ion concentrations using the Le Grand method$^{(13)}$. The average numbers of protons $\bar{n}_H$ bound to the ligand at pH values were calculated using the various methods described previously$^{(9)}$.

Results and discussion

The elemental analysis and melting points of the ligands and their complexes are summarized in Table 1. All the complexes are stable and insoluble in common organic solvents but soluble in pyridine, DMF and DMSO.

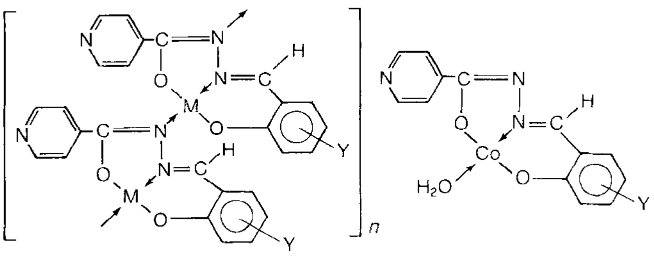
Thermal analysis

D.t.a. and t.g.a. data showed that H$_2$-Sal and H$_2$-Naph ligands as well as their nickel, copper, zinc and palladium complexes are anhydrous, whereas [CoSal]·H$_2$O loses its H$_2$O molecule at 50–160° C.



H$_2$-Sal, Y = ---
H$_2$-Haph, Y = C$_4$H$_4$

(1)



M = Ni, Cu, Zn, Pd

(2)

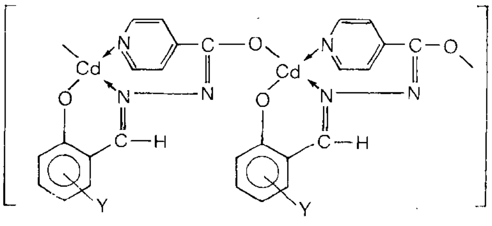


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Table 1. Colour, m.p., Λ_m analytical, spectral and magnetic moment data of salicylaldehyde and 2-hydroxy-naphthaldehyde isonicotinoyl hydrazone and their chelates.

Compound	Colour	M.p. or d.p. (°C)	Found (Calcd.)(%) C	H	N	M	Λ_m	Electronic spectral bands (nm) π–π^*(aryl)	π–π^*(C=N)	C.T.	μ_{eff} (B.M.)
H_2-Sal	White	243–245[a]	63.8 (64.7)	4.6 (4.6)	17.7 (17.4)	–	0.54	300	330, 365	418	–
[Co(Sal)·H_2O]	Brown	(235)	49.1 (49.4)	3.4 (3.5)	12.8 (12.3)	19.1 (18.6)	7.66	300–320	–	407	3.297
[Ni(Sal)]	Orange red	>275	51.8 (52.4)	3.4 (3.0)	13.2 (14.1)	19.0 (19.7)	0.61	302, 318	330, 343(sh)	415, 430	diamag.
[Cu(Sal)]	Green	(270)	51.2 (51.6)	3.0 (3.0)	13.4 (13.9)	21.0 (21.0)	0.53	303–308	322, 335	405, 420	1.63
[Zn(Sal)]	Yellow	>275	51.2 (51.3)	3.7 (3.0)	14.0 (13.8)	21.3 (21.5)	0.41	303(sh)	325, 337(sh)	408, 430(sh)	diamag.
[Pd(Sal)]	Green	(250)	45.1 (45.2)	2.5 (2.6)	12.1 (12.2)	29.9 (30.8)	0.47	300, 310, 318	345(sh)	400(sh), 414	diamag.
[Cd(Sal)]	Yellow	>250	44.3 (44.4)	3.3 (2.6)	12.3 (12.0)	31.3 (31.0)	0.21	295, 320(sh)	321, 330(sh)	410	diamag.
H_2-Naph	Yellow	254–255[a]	69.3 (70.1)	4.6 (4.5)	14.5 (14.4)	–	0.16	315(sh)	327, 367, 380	435	diamag.
[Ni(Naph)]	Dark red	>270	58.5 (58.7)	4.0 (3.2)	12.0 (12.1)	16.4 (16.9)	0.91	302	335, 347, 360(sh)	420(sh), 440	diamag.
[Cu(Naph)]	Yellow brown	(270)	58.2 (57.9)	3.9 (3.1)	12.0 (11.9)	18.2 (18.0)	0.71	302	330, 345	430, 453	1.27
[Zn(Naph)]	Orange yellow	>270	56.9 (57.6)	3.6 (3.1)	11.0 (11.9)	18.3 (18.4)	0.33	300	330, 345(sh), 388	420, 433, 458, 447(sh), 763	diamag.
[Pd(Naph)]	Orange	>270	51.0 (51.6)	3.7 (2.8)	10.5 (10.6)	26.0 (26.9)	3.28		322, 327, 333, 350	420, 442	diamag.
[Cd(Naph)]	Yellowish orange	>270	50.9 (50.8)	3.5 (2.8)	9.7 (10.5)	27.3 (28.0)	0.66	315	320(sh), 325, 345, 367(sh) 374(sh), 385	410, 436, 460, 495	diamag.

[a] Literature m.p.s. or H_2-Sal and H_2-Naph are 244–245 and 155–157° C, respectively; the latter value from reference 8 may be the result of a typographical error.

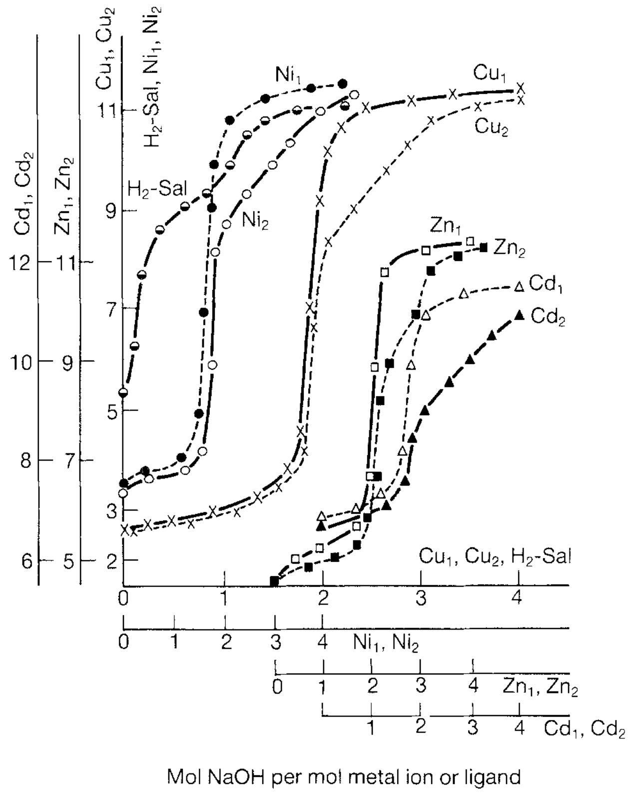

Figure 1. pH-Titration curves of H_2-Sal in the absence and presence of metal ions (nickel, copper, cadmium and zinc). Subscripts 1 and 2 refer to 1:1 and 1:2 M:L, respectively.

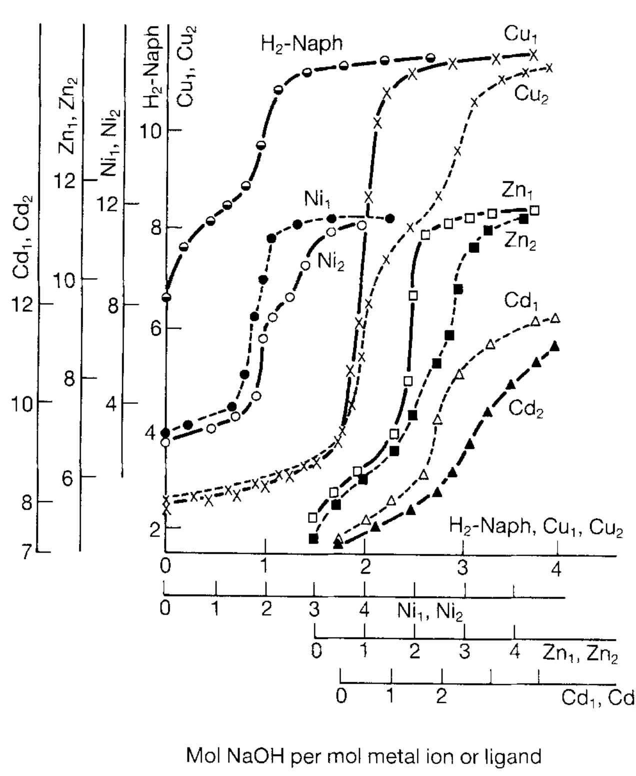

Figure 2. pH-Titration curves of H_2-Naph in the absence and presence of metal ions (nickel, copper, cadmium and zinc). Subscipts 1 and 2 refer to 1:1 and 1:2 M:L, respectively.

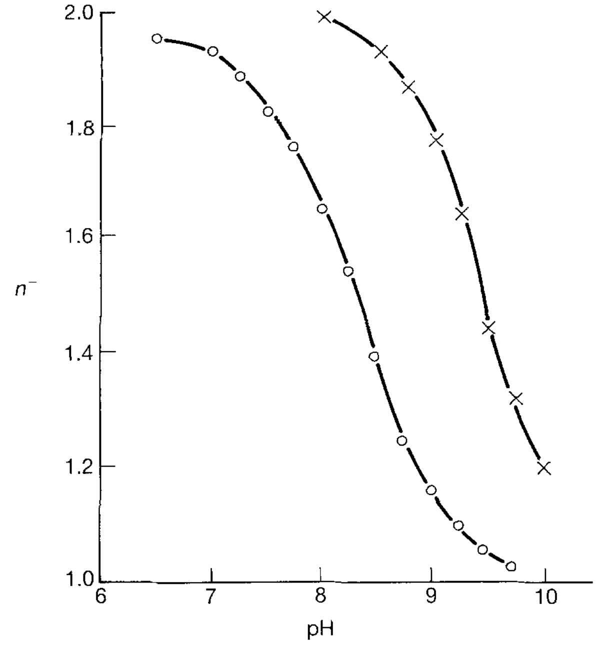

Figure 3. Formation curves of H_2-Sal (X) and H_2-Naph (O) in 70% EtOH–H_2O at 25° C ($\mu = 0.1$).

pH-titration

pH titrations of the H_2-Sal and H_2-Naph ligands in 70% EtOH–H_2O (ionic strength = 0.1 NaCl) at 25° C (Figures 1 and 2) showed that both ligands behave as dibasic acids.

Protonation constants

The first dissociation constant (second protonation constant) $\log K^H$ was determined from the formation curve ($\bar{n}_H$–pH) in which $\bar{n}_H$ extends between 2 and 1. The second dissociation constant was difficult to be determined with accuracy. Values of $\log K^H$ were obtained directly from Figure 3 and also calculated by the average value method(14).

The effect of solvent, composition, ionic strength (μ) and temperature were studied. It was found (Table 2, Figure 3) that the $\log K^H$ value was insensitive to μ in the 0.01–0.1 mol l^{-1} range and to temperature in the 25–55° C range. Also, $\log K^H$ increases to a small extent with increasing % EtOH. For 70% EtOH–H_2O solvent, $\log K^H$ is 8.05 and 9.21 for H_2-Sal and H_2-Naph ligands, respectively.

Magnetic moments

Table 1 shows that nickel, palladium, zinc and cadmium complexes are all diamagnetic. The effective magnetic moment of the copper complexes (1.27 and 1.63 B.M.) and of Co-Sal complex (3.29 B.M.) are fairly close to those observed for complexes with one unpaired electron [copper(II): $e_g^6\ t_{2g}^3$ and cobalt(II): $e_g^6\ t_{2g}^1$] in square planar environments(16). The low values for the copper complexes are indicative of some extended interaction in these complexes(17).

Electronic spectra

The spectra of pyridine solutions show two bands at 295–315 and 327–333 nm for H_2-Sal, H_2-Naph and their complexes. The first band is associated with a chelate enol ring of the imidol part(18) and the second band could be considered as the 325 nm band of the salicylaldehyde(19) shifted to longer wavelengths owing to the formation of the aroylhydrazone. This band can be assigned to the

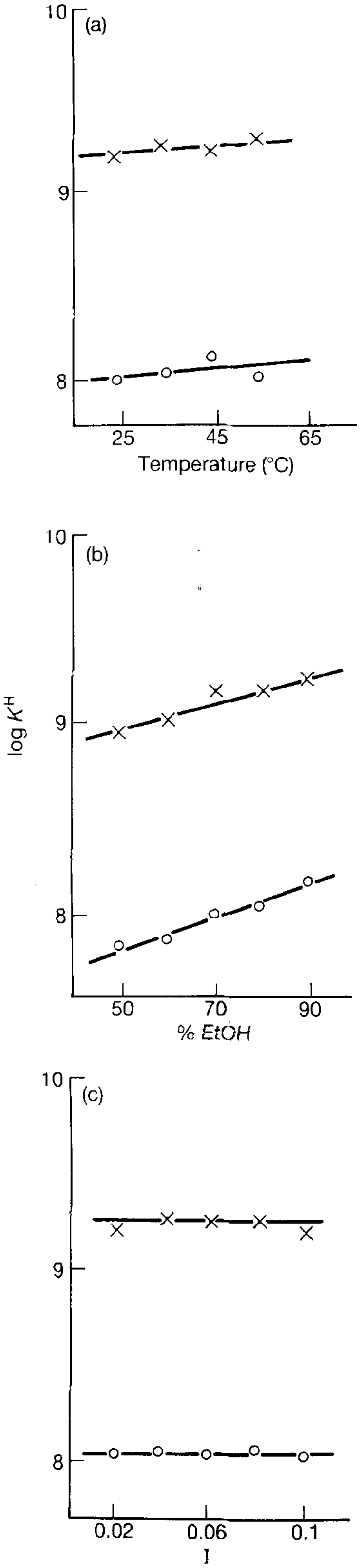

Figure 4. Effect of (a) temperature, (b) solvent composition and (c) ionic strength (μ) on $\log K^H$ of H_2-Sal and H_2-Naph ligands ($\mu = 0.1$, temperature = 25° C, 70% EtOH–H_2O).

Table 2. Effect of % EtOH, ionic strength and temperature on $\log K^{H}$ of H_2-Sal and H_2-Naph ligands.

EtOH effect ($\mu = 0.1$, $t = 25°$ C) % EtOH	H_2-Sal	H_2-Naph	Ionic strength effect (70% EtOH, $t = 25°$ C) μ	H_2-Sal	H_2-Naph	Temperature effect ($\mu = 0.1$, 70% EtOH) t(°C)	H_2-Sal	H_2-Naph
50	8.95	7.80	0.02	9.17	8.04	25	9.16	8.00
60	9.00	7.86	0.04	9.24	8.05	35	9.23	8.03
70	9.16	8.00	0.06	9.23	8.02	45	9.19	8.12
80	9.16	8.02	0.08	9.22	8.05	55	9.28	7.98
90	9.21	8.17	0.10	9.16	8.00			

existence of a chelate enol ring stabilized through metal ion or H-bond formation and enol resonance(18).

The spectra of the complexes show another band at 400–440 nm which may be due to the presence of chelate ring of which the metal is a member(20). The intensity of this band of ($\varepsilon \approx 10^4$) is that of an allowed transition(21).

^{1}H n.m.r. spectra

The spectra of H_2-Sal and H_2-Naph ligands (in DMSO and D_2O, chemical shift in p.p.m.) are recorded in Table 3. The spectra reveal signals at 12.25 and 12.55 p.p.m. for H_2-Sal and H_2-Naph respectively, assigned to imino free proton (H, NHCO-)(1). The signal appears in the spectra of H_2-Sal at 11.15 and H_2-Naph at 12.25 p.p.m. may be assigned to the aromatic (H, OH$\cdots$N)(22).

The singlets at 8.8 and 9.4 p.p.m. in the spectra of H_2-Sal and H_2-Naph respectively may be assigned to the azomethine hydrogen(23). This assignment suggests that the two ligands are in the keto form (1).

Table 3. ^{1}H n.m.r. bands and their assignments for H_2-Sal, H_2-Naph and Cd-Naph complex.

Chemical shifts, δ(ppm)	N—H	aryl O—H	N=C—H	aryl, py. ring protons
H_2-Sal	12.25	11.15	8.80	6.7–7.9
H_2-Naph	12.55	12.25	9.40	7.1–8.9
Cd-Naph	–	–	9.65	7.1–8.9

I.r. spectra of cobalt, nickel, copper, zinc and palladium

Comparison of complexes with those of the free ligands (Table 4), shows that the spectra do not differ as regards the pyridine ring vibrations, showing that the pyridine nitrogen does not take part in coordination(24). However, all the amide bands disappear in the complexes and new bands characteristic of ν(NCO) appear at 1550–1510 and 1375–1350 cm^{-1} due presumably to coordination through the imidol oxygen(25). With the exception of cobalt the

Table 4. Important i.r. spectral bands (cm^{-1}) and their assignments for salicylaldehyde and 2-hydroxy naphthaldehyde isonicotinoyl hydrazones and their chelates.

Compound	Pyridine ring.vibrations	Pyridine ring breathing mode	ν(C=N)	ν(NCO)	ν(N—N)
H_2-Sal	1610m, 1565s, 1490m, 1405m	1030m	1620m	–	890m
[Co(Sal)·H_2O]	1600, 1560, 1470, 1420	1032	1610	1510 1350	960
[Ni(Sal)	1595, 1570, 1495, 1418	1025	1610	1530 1360	940
[Cu(Sal)]	1600, 1570, 1500, 1420	1030	1610	1530 1360	960
[Zn(Sal)]	1600, 1570, 1500, 1418	1025	1610	1550 1300	965
[Pd(Sal)]	1600, 1570, 1500, 1420	1025	1610	1530 1350	942
[Cd(Sal)]	1602, 1565, 1470, 1435	1060	1602	1550 1350	1025
H_2-Naph	1595m, 1575s, 1475m, 1415s	1030m	1625m	–	912m
[Ni(Naph)]	1600, 1580, 1495, 1430	1025	1615	1525 1360	972
[Cu(Naph)	1602, 1588, 1500, 1430	1030	1620	1540 1300	970
[Zn(Naph)]	1603, 1570, 1495, 1430	1030	1618	1510 1360	962
[Pd(Naph)]	1600, 1580, 1490, 1420	1030	1612	1530 1350	965
[Cd(Naph)]	1600, 1565, 1455, 1438	1060	1615	1350 1370	1013

complexes, show a downward shift (5–20 cm^{-1}) in ν(C=N) and a large positive shift (50–100 cm^{-1}) in ν(N—N), indicating that both nitrogens are involved in coordination, one of them possible as a bridge between two molecules(26). The broad bands observed in ligands at 3220–3160 cm^{-1}, assigned to NH and phenolic OH strongly H-bonded with azomethine nitrogen(26), are absent in the spectra of the complexes. The shift of the phenolic ν(C—O) band to lower frequency on chelation indicates coordination through the C—O group.

The cobalt–Sal complex shows a smaller frequency increase for ν(N—N) indicating that only one nitrogen atom is involved in coordination(26). The presence of two extra bands, one broad at 3650–3000 cm^{-1} assignable to ν(O—H) and the other medium at 750 cm^{-1} assignable to $\delta(H_2O)$(27) indicate the presence of the coordinated H_2O molecule.

As the complexes do not melt and are insoluble in common organic solvents, it is suggested that they are polymers (except for Co), in which one nitrogen of the —N—N—group is involved in bridging to the metal atom (28). So the complexes may be represented as *(2)*.

I.r. and ^1H n.m.r. spectra of cadmium complexes

NH and OH signals are absent in the ^1H n.m.r. spectrum of Cd-Naph complex. The disappearance of ν(O—H) (phenolic) vibration at 3470–3420 cm^{-1} in the complexes and the shift in ν(C—O) (phenolic) to higher frequency indicate coordination through phenolic oxygen(29).

The absense of amide bands and the presence of new bands characteristic of ν(NCO) at 1550 and 1350–1370 cm^{-1} regions are commensurate with the destruction of the amide group by enolization. Furthermore, the appearance of a band at 1600 cm^{-1} diagnostic of the azine (C=N—N=C) group(30), with negative ν(C=N) shift and the positive ν(N—N) shift, suggests that the azomethine group nitrogen is coordinated to cadmium.

Changes in the pyridine bands shows that the pyridine nitrogen takes part in coordination(30). As the complexes have low Λ_m, high decomposition temperatures and insolubility in common organic solvents, the polymeric formula (*3*) may be suggested.

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