

Isonicotinic Acid Hydrazide의 Hydrazone으로부터 유도된 코발트(II) 착물의 합성, 물리-화학 및 생물학적 성질

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(2008. 7. 15 접수)

Synthesis, Physico-Chemical and Biological Properties of Complexes of Cobalt(II) Derived from Hydrazones of Isonicotinic Acid Hydrazide

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(Received July 15, 2008)

요 약. Isonicotinic acid hydrazide의 Hydrazones, 즉, N-isonicotinamido-furfuralaldimine (INH-FFL), N-isonicotinamido-cinnamalidine (INH-CIN) 및 N-isonicotinamido-3',4',5'-trimethoxybenzalimine (INH-TMB)를 isonicotinic acid hydrazide와 예를 들면 furfural, cinnamaldehyde 또는 3,4,5-trimethoxy-benzaldehyde 등과 같은 각각의 방향족 알데히드와의 반응으로부터 제조하였다. INH-FFL, INH-CIN and INH-TMB와 같은 새로운 hydrazones을 코발트(II) 염과 반응시켜 새로운 일련의 15개 코발트(II) 착물을 제조하였다. 적외선 분광 데이터를 통해 hydrazone 리간드들이 Co^{2+} 이온에 대해 N, O 주개원자의 배열을 갖는 두자리 리간드임을 규명하였다. 착물의 특성은 원소분석, 수자율, 전도도, 적외선 및 전자 스펙트럼 측정을 통해 조사하였다. 분석 데이터로부터 착물은 $[\text{Co}(\text{L})_2\text{X}_2]$ 및 $[\text{Co}(\text{L})_3](\text{ClO}_4)_2$ ($\text{L} = \text{INH-FFL}, \text{INH-CIN}$ 또는 INH-TMB , 그리고 $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{NCS}^-$ 또는 CH_3COO^-)의 일반적 조성을 가짐을 알 수 있었다. 열무게법으로부터 착물의 열적 행동을 조사하였다. 전자 스펙트럼 결과와 자화율 측정으로부터 코발트(II) 킬레이트가 6배위의 기하구조를 이루고 있다는 것을 확인할 수 있었다. 코발트(II) 착물과 약간의 표준약물에 대한 항균성으로부터 이들 착물이 매우 적합한 항균성질을 가짐을 알 수 있다.

주제어: 코발트(II), 착물, Hydrazones, 특성규명, 생물활성

ABSTRACT. Hydrazones of isonicotinic acid hydrazide, viz., N-isonicotinamido-furfuralaldimine (INH-FFL), N-isonicotinamido-cinnamalidine (INH-CIN) and N-isonicotinamido-3',4',5'-trimethoxybenzalimine (INH-TMB) were prepared by reacting isonicotinic acid hydrazide with respective aromatic aldehydes, i.e., furfural, cinnamaldehyde or 3,4,5-trimethoxy-benzaldehyde. A new series of fifteen complexes of cobalt(II) with these new hydrazones, INH-FFL, INH-CIN and INH-TMB, were synthesized by their reaction with cobalt(II) salts. The infrared spectral data reveal that hydrazone ligands behave as a bidentate ligand with N, O donor sequence towards the Co^{2+} ion. The complexes were characterized on the basis of elemental analysis, magnetic susceptibility, conductivity, infrared and electronic spectral measurements. Analytical data reveal that the complexes have general composition $[\text{Co}(\text{L})_2\text{X}_2]$ and $[\text{Co}(\text{L})_3](\text{ClO}_4)_2$ where $\text{L} = \text{INH-FFL}, \text{INH-CIN}$ or INH-TMB and $\text{X} = \text{Cl}^-$,

NO_3^- , NCS^- or CH_3COO^- . The thermal behaviour of the complexes were studied using thermogravimetric technique. Electronic spectral results and magnetic susceptibility measurements are consistent with the adoption of a six-coordinate geometry for the cobalt(II) chelates. The antimicrobial properties of cobalt(II) complexes and few standard drugs have revealed that the complexes have very moderate antibacterial activities.

Keywords: Cobalt(II), Complexes, Hydrazones, Characterization, Biological activity

INTRODUCTION

The metal chelates with ligands of biological importance have been playing an important role in the development of new coordination chemistry. Complexes containing chelating ligands, which show promising biological activity, have been recently studied by ourselves¹⁻⁹ and others.¹⁰⁻²⁰ We have been investigating the synthesis and characterization of cobalt(II),^{1,2} nickel(II),^{2,3} oxovanadium(IV)^{4,5} and platinum(II)⁶ and some lanthanide (III)⁷ complexes that contain a range of ancillary ligands such as semicarbazones[7], thiosemicarbazones^{1,2,4-6} derived from 4-aminoantipyrine and hydrazones³ derived from isonicotinic acid hydrazide. The antibacterial and antifungal properties of the thiosemicarbazone ligands and their cobalt(II),^{1,2} nickel(II)² and oxovanadium(IV)⁴ complexes and nickel(II) complexes with hydrazones³ have also been examined by us.

Isoniazid (isonicotinic acid hydrazide; INH) is a drug of proven therapeutical importance, used against wide spectrum bacterial ailments, viz., tuberculosis. Hydrazones derived from condensation of isoniazid with pyridine aldehydes have been found to show better antitubercular activity than isoniazid.²¹ We have recently turned our attention to the investigation on transition metal complexes of N and O donor ligands.^{3,8,9} In this paper we report the synthesis, characterization and biological activities of cobalt(II) complexes of hydrazones derived

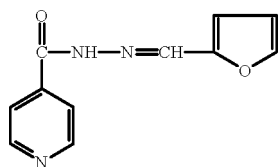


Fig. 1. N-Isonicotinamido-furfuraldimine (INH-FFL)

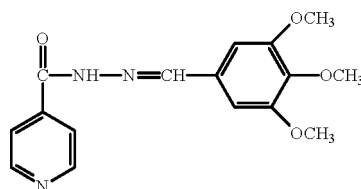


Fig. 2. N-Isonicotinamido-3',4',5'-trimethoxybenzalimine (INH-TMB)

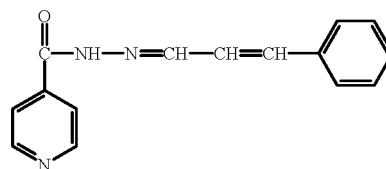


Fig. 3. N-Isonicotinamido-cinnamalidene (INH-CIN)

from isonicotinic acid hydrazide viz., N-isonicotinamido-furfural-2'-aldimine (INH-FFL), N-isonicotinamido cinnamalidine (INH-CIN) and N-isonicotinamido-3',4',5'-trimethoxybenzalaldimine (INH-TMB) (Fig. 1-3).

EXPERIMENTAL SECTION

Materials

The general experimental techniques have been previously described^{3,8}. $\text{CoX}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}^-$, NO_3^- or CH_3COO^-) were obtained from BDH and were used without further purification. Co(NCS)_2 was prepared by the reaction of CoCl_2 (in ethanol) and ethanolic solution of KNCS in 1:2 molar ratio. The precipitated KCl was filtered off and the filtrate having Co(NCS)_2 was used immediately for complex formation with hydrazones viz., INH-FFL, INH-CIN and INH-TMB. $\text{Co(ClO}_4)_2$ was prepared by the reaction of an ethanolic solution of CoCl_2 and NaClO_4 in 1:2 molar ratio. The white precipitate of NaCl was filtered off and the filtrate containing

$\text{Co}(\text{ClO}_4)_2$ was used as such for complex formation with hydrazones. During the preparation of $\text{Co}(\text{NCS})_2$ and $\text{Co}(\text{ClO}_4)_2$, KNCS and NaClO_4 were taken 10% excess.

Synthesis of hydrazones: INH-FFL, INH-TMB and INH-CIN

All the three hydrazones of INH *viz.*, INH-FFL, INH-CIN and INH-TMB were synthesized by method reported by us.^{3,8,9} INH (0.01 mol) was dissolved in 10 mL of 95% ethanol. To this solution respective aromatic aldehyde *i.e.* furfural, cinnamaldehyde or 3,4,5-trimethoxybenzaldehyde (0.01 mol) in 95% alcohol (10 mL) was added. The reaction mixture was refluxed on a water bath for ~ 2 hr. The partial removal of solvent on a water bath followed by cooling produced crystalline product of the complexes, which was suction filtered, washed with cold ethanol and dried under vacuum (yld. ~ 80%).

Synthesis of cobalt(II) complexes: $[\text{CoX}_2(\text{L})_2]$ and $[\text{Co}(\text{L})_3](\text{ClO}_4)_2$

Depending on nature of anionic ligands (Cl^- , NO_3^- , NCS^- , CH_3COO^- or ClO_4^-), the cobalt(II) complexes were synthesized by the reaction of warm ethanolic solution of ligand (INH-FFL, INH-TMB or INH-CIN) and metal salts in 1:2 or 1:3 molar ratio. The reaction mixture was refluxed on a water bath for 2-3 hr. It was then concentrated to a small volume on a hot plate at 50 °C. On cooling the solutions crystals of complexes appeared which were filtered, washed with ethanol and dried in vacuum over P_2O_{10} (yld. 60-75%).

Instrumentation, physical, analytical and anti-microbial studies

The cobalt in the complexes was estimated, spectrophotometrically using 2-nitroso-1-naphthol, after decomposing the complex with conc. H_2SO_4 and H_2O_2 .²² The chloro content in the complexes was estimated by Volhard's method.²² The thiocyanate was estimated by titrating slightly acidic solution of the complex with standard AgNO_3 solution. The perchlorate was estimated by the

methods of Kurz *et al.*²³ The percentage of nitrogen was determined in the laboratory by Kjeldahl method. The molecular weight of the complexes was determined cryoscopically in freezing PhNO_2 using a Beckmann thermometer of accuracy ± 0.01 °C. The conductivity measurements were carried out using a Toshniwal conductivity bridge and dip type cell operated at 220 volts, AC mains. All the measurements were done at room temperature in PhNO_2 as solvent.

The magnetic measurements on powder form of the complexes were carried out at room temperature on Evans magnetic balance (Sherwood Scientific, Cambridge, England) using copper sulphate as calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model 521 in KBr in the range of 4000-200 cm^{-1} . Diffused reflectance spectra of the solid compounds were recorded on a Beckman DK-2A spectrophotometer. Thermogravimetric analyses of the complexes were carried out at IIT Roorkee, India, on a Perkin Elmer Pyris Diamond thermogravimetric analyzer, in static air with open small platinum boat sample holders using the heating rate of 6 °C min^{-1} . The antibacterial and antifungal activities of some of the representative cobalt(II) complexes and standard drugs (ampicillin and tetracycline) were screened by following the methods reported else where.^{1,2}

RESULTS AND DISCUSSION

The reaction of Co^{2+} salts with INH-FFL, INH-CIN or INH-TMB on refluxing afforded the complexes of the general composition $\text{Co}(\text{L})_n\text{X}_2$ where $\text{X} = \text{Cl}^-$, NO_3^- , NCS^- or CH_3COO^- , $n = 2$ while $\text{X} = \text{ClO}_4^-$, $n = 3$ and $\text{L} = \text{INH-FFL}$, INH-CIN or INH-TMB . The products were characterized by elemental analysis, magnetic susceptibility, and conductivity, infrared and electronic spectral measurements. The analytical data of these complexes are given in Table 1. All the complexes were quite stable and could be stored for months without any appreciable change. The complexes were soluble in common organic solvents such as dichloromethane, acetone,

Table 1. Analytical, conductivity, molecular weight and magnetic moment data of Co(II) complexes of hydrazones of isoniazid.

Complex	Yield (%)	Analysis: Found (Calcd.) (%)			Mol. wt. Found (Calcd.)	Ω_m (Ohm ⁻¹ cm ² mole ⁻¹)	μ_{eff} (BM)
		Co	N	Anion			
[Co(INH-FFL) ₂ Cl ₂]	75	10.11 (10.17)	14.36 (14.48)	12.14 (12.24)	575 (580)	2.3	4.8
[Co(INH-FFL) ₂ (NO ₃) ₂]	75	9.27 (9.32)	17.50 (17.69)	— —	628 (633)	3.7	5.0
[Co(INH-FFL) ₂ (NCS) ₂]	70	9.51 (9.56)	18.09 (18.15)	18.65 (18.80)	612 (617)	3.9	4.6
[Co(INH-FFL) ₂ (CH ₃ COO) ₂]	72	9.33 (9.40)	13.28 (13.39)	— —	622 (627)	2.9	4.7
Co(INH-FFL) ₃ (ClO ₄) ₂	70	6.27 (6.32)	13.39 (13.50)	21.11 (21.32)	310 (933)	51.2	5.1
[Co(INH-TMB) ₂ Cl ₂]	70	7.70 (7.76)	10.95 (11.05)	9.27 (9.34)	757 (760)	2.1	4.9
[Co(INH-TMB) ₂ (NO ₃) ₂]	72	7.19 (7.25)	13.63 (13.77)	— —	808 (813)	1.9	5.1
[Co(INH-TMB) ₂ (NCS) ₂]	65	7.26 (7.32)	13.77 (13.91)	14.30 (14.40)	800 (805)	2.2	5.2
[Co(INH-TMB) ₂ (CH ₃ COO) ₂]	65	7.25 (7.31)	10.36 (10.40)	— —	802 (807)	1.8	4.8
Co(INH-TMB) ₃ (ClO ₄) ₂	60	4.85 (4.90)	10.40 (10.47)	16.40 (16.54)	399 (1203)	52.7	5.0
Co(INH-CIN) ₂ Cl ₂]	70	9.28 (9.33)	13.19 (13.29)	11.11 (11.23)	627 (632)	2.7	5.7
[Co(INH-CIN) ₂ (NO ₃) ₂]	73	8.56 (8.61)	16.22 (16.35)	— —	680 (685)	3.1	4.9
[Co(INH-CIN) ₂ (NCS) ₂]	65	8.65 (8.71)	16.42 (16.54)	17.02 (17.13)	673 (677)	2.9	5.1
[Co(INH-CIN) ₂ (CH ₃ COO) ₂]	72	8.55 (8.60)	12.29 (12.37)	— —	675 (679)	2.6	4.7
[Co(INH-CIN) ₃ (ClO ₄) ₂]	65	9.79 (5.83)	12.38 (12.46)	19.49 (19.68)	340 (1011)	52.9	5.4

(CH₃)₃SO etc. The complexes do not have sharp melting points but decomposed on heating beyond 250 °C. The molecular weights determined by cryoscopic method in nitrobenzene are given in Table 1. The results are in broad agreement with conductance data. The molar conductance data showed that the chloro, nitrate, isothiocyanato and acetato complexes were essentially non-electrolytes in PhNO₂, while the perchlorato complexes dissociated in PhNO₂ and behaved as 1:2 electrolytes. The magnetic moment data of the complexes reported in Table 1 show that all the cobalt(II) complexes are paramagnetic corresponding to three unpaired electrons indicating a high-spin octahedral configuration. For the present complexes the magnetic moment values lies in the range 4.6-5.7 BM.²⁴

Infrared spectra

A study and comparison of the infrared spectra of all the three ligands, viz., INH-FFL, INH-TMB and INH-CIN and their Co(II) complexes, imply that all the ligands are bidentate with azomethine nitrogen and carbonyl-oxygen as two (N, O) coordination sites. The infrared data of all the complexes are provided in Table 2. The infrared frequencies in the present ligands associated with amide group carbonyl-oxygen (C=O), azomethine-nitrogen(C=N) and heterocyclic nitrogen are expected to be influenced on complex formation with metal ion. Generally, all amides show two absorption bands: (i) the carbonyl absorption band near 1640 cm⁻¹ known as amide-I band and (ii) strong band in the 1600-1500 cm⁻¹ region, known as

Table 2. Key infrared bands (cm^{-1}) of Co(II) complexes of hydrazones of isoniazid.

Compounds	Assignments	$\nu(\text{NH})$ asym & sym	Amide-I	$\nu(\text{C}=\text{N})$ (azomethine)	Amide-II + $\delta(\text{NH})$	$\nu(\text{Co-N}) /$ $\nu(\text{Co-O})$
INH-FFL		3300 m 3220 m	1705 vs 1632 s	1585 s	1540 m 1532 m	— —
[Co(INH-FFL) ₂ Cl ₂]		3305 m 3220 w	1670 vs 1605 vs	1525 m	1510 s, br	490 w 405 w
[Co(INH-FFL) ₂ (NO ₃) ₂]		3302 m 3220 w	1670 s 1610 vs 1580 m	1530 s	1505 s, br	492 m 400 w
[Co(INH-FFL) ₂ (NCS) ₂]		3300 m 3220 w	1680 s 1620 s	1555 s	1525 m 1510 m	485 m 405 w
[Co(INH-FFL) ₂ (CH ₃ COO) ₂]		3302 m 3220 w	1670 vs 1600 vs	1525 m	1510 s, br	480 w 398 w
[Co(INH-FFL) ₃](ClO ₄) ₂		3300 m 3222 w	1672 s 1600 s	1535 sh	1530 s	482 w 395 w
INH-TMB		3300 m 3210 w	1655 vs	1588 vs	1540 sh 1520 s	— —
[Co(INH-TMB) ₂ Cl ₂]		3300 m 3222 m	1630 s 1610 m	1565 s	1540 s 1520 s	490 m 395 w
[Co(INH-TMB) ₂ (NO ₃) ₂]		3310 m 3200 m	1635 m 1610 sh	1560 s	1530 s 1515 m	510 m 430 w
[Co(INH-TMB) ₂ (NCS) ₂]		3300 m 3220 m	1635 m 1600 vs	1568 s	1528 m 1520 m	502 m 425 w
[Co(INH-TMB) ₂ (CH ₃ COO) ₂]		3320 m 3220 m	1650 m 1610 vs, br	1572 s	1522 m 1510 m	495 m 410 w
[Co(INH-TMB) ₃](ClO ₄) ₂		3305 m 3250 m	1635 s 1615 s	1575 s 1570 sh	1525 s	490 m 405 w
INH-CIN		3290 m 3200 sh 3185 m	1698 s 1640 s	1590 vs	1570 sh 1540 m	— —
[Co(INH-CIN) ₂ Cl ₂]		3292 m 3200 w 3180 m	1672 vs 1620 vs	1580 s 1530 s	1530 s 1470 vs, br	462 m 395 w
[Co(INH-CIN) ₂ (NO ₃) ₂]		3290 m 3202 sh 3180 m	1680 s 1610 s	1555 sh 1530 s, br	1525 s	490 m 405 w
[Co(INH-CIN) ₂ (NCS) ₂]		3300 w 3202 sh 3185 m	1670 s 1615 s	1560 s 1525 s	1505 m 1480 m, br	480 m 410 w
[Co(INH-CIN) ₂ (CH ₃ COO) ₂]		3302 m 3200 w	1610 s	1570 s 1530 w	1502 sh 1492 m	492 m 405 w
[Co(INH-CIN) ₃](ClO ₄) ₂		3300 m 3192 m	1670 m 1600 s, br	1530 m	1510 m	490 m 402 w

amide-II band. The amide-I band in INH-derivatives, however, appears at 1655 cm^{-1} .^{25,26} In the infrared spectra of the complexes, a considerable negative shift in $\nu(\text{C}=\text{O})$ is observed indicating a decreased in the stretching force constant of $\text{C}=\text{O}$ as a

consequence of coordination through the carbonyl oxygen atom of the free base. The amide-II band appears at the normal position in the NH- deformation rather than C-N link. In all these ligands the absorptions at $1540\text{--}1530 \text{ cm}^{-1}$ have been assigned

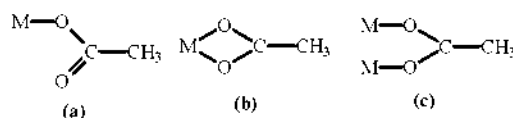
to amide-II absorptions. The NH stretching absorption in free ligands occurs at ~ 3300 and 3220 cm^{-1} which remain unaffected after complexation. This observation clearly discards any possibility of coordination through imine-nitrogen atom. Another important band occurs in $1590\text{--}1585\text{ cm}^{-1}$ range is attributed to $\nu(\text{C}=\text{N})$ (azomethine) mode.^{27–29} In spectra of all the complexes this band shifted to lower wave number and appeared at $1550\text{--}1525\text{ cm}^{-1}$ region, respectively indicating the involvement of N-atom of the azomethine group in coordination with Co^{2+} ion.^{27–29} The strong bands observed at $1575\text{--}1520\text{ cm}^{-1}$ and $1080\text{--}1000\text{ cm}^{-1}$ are tentatively assigned to asymmetric and symmetric $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ of pyridine ring^{30,31} while pyridine ring breathings and deformations remained practically unchanged in frequency and band intensities which clearly revealed non-involvement of pyridine-nitrogen in bonding with Co^{2+} ion. In far infrared spectral region, the bands in INH-FFL, INH-TMB and INH-CIN were practically unchanged in these complexes. Some new bands with medium to weak intensities appeared in the regions $450\text{--}380\text{ cm}^{-1}$ for the complexes under study, which are tentatively assigned to $\nu(\text{Co-N})/\nu(\text{Co-O})$ modes.^{8,30,31} The overall infrared spectral evidence suggests that the present ligands act as bidentate ligand and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five membered chelate ring.

Anions

The pseudo halide NCS^- ion is very interesting anion for it may coordinate through the sulfur (thio) or through the nitrogen (isothio) or through both these atoms (bridging). Infrared spectroscopy is very useful in elucidating which type of bonding exists. The various criteria proposed for determining the mode of bonding have been discussed in literature.³¹ In general the bonding depends on (a) the nature of central atom (b) the nature of other ligands in the coordination sphere and (c) environmental controls and kinetic (mechanistic) controls. The first transition metal series, *i.e.*, Class-A metals form M-N type bonds, whereas metals of

second and third transition series, *i.e.*, Class-B metals form the M-S bonds. The C-N stretching frequency (ν_1) is generally lower for M-NCS complexes than for M-SCN complexes. Bailey *et al.* suggested the region near or above 2100 cm^{-1} for S-bonding below 2100 cm^{-1} for N-bonding.³² The C-S stretching frequency (ν_2) is assigned in the $860\text{--}780\text{ cm}^{-1}$ region for M-NCS and $720\text{--}690\text{ cm}^{-1}$ for M-SCN bonding modes.^{33,34} The $\delta(\text{NCS})$ frequency (ν_3) is also different for the two isomers: $490\text{--}450\text{ cm}^{-1}$ for the M-NCS and $440\text{--}400\text{ cm}^{-1}$ for M-SCN bonding.^{33,34} Bridging thiocyanate usually give higher CN^- stretching frequencies than terminal NCS^- group.^{33,34} The three fundamental absorption (C-N) stretching (ν_1), (C-S) stretch (ν_2) and (N-C-S) bending (ν_3) in present complexes were identified at $2040\text{--}2035$, $845\text{--}830$ and $470\text{--}465\text{ cm}^{-1}$ region respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions.^{33,34}

In nitrate (NO_3^-) complexes, the infrared spectral data indicate the occurrence of two strong absorption bands in the regions $1555\text{--}1500\text{ cm}^{-1}$ and $1310\text{--}1295\text{ cm}^{-1}$ which are attributed to ν_4 and ν_1 modes of vibrations, of the covalently bonded nitrate groups, respectively. This suggests that nitrate groups are present inside the coordination sphere.³⁵ Distinction between monodentate and bidentate nitrate is usually different. However, by applying Lever's separation method,³⁶ a separation of $15\text{--}25\text{ cm}^{-1}$ in the combination bands ($\nu_1 + \nu_4$) in the $1800\text{--}1700\text{ cm}^{-1}$ region concluded the monodentate nitrate coordination. Other bands appeared at ~ 1040 (ν_2), 810 (ν_6) and 7335 cm^{-1} (ν_3/ν_5) due to nitrate groups.



The acetate ion (CH_3COO^-) may coordinate to a metal ion in one of the following modes (a–c):

The $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ of free acetate ion are at $\sim 1560\text{ cm}^{-1}$ and 1416 cm^{-1} respectively. In the unidentate complex (structure a) $\nu(\text{C}=\text{O})$ is higher than $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu(\text{C-O})$ is lower than

$\nu_{\text{asym}}(\text{COO}^-)$. As a result the separation between the two $\nu(\text{CO})$ is much larger in unidentate complexes than free CH_3COO^- ion. The opposite trend is observed in the bidentate complexes (structure b) i.e. the separation between two $\nu(\text{CO})$ is smaller than that of free CH_3COO^- ion in this case. In the bridging complexes (structure c), however, two $\nu(\text{CO})$ are close to the free ion $\nu(\text{CO})$ values. The present complexes show infrared absorption frequency bands corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ at ~ 1610 and 1370 cm^{-1} respectively. These observations indicate that both the acetate groups in present complexes are unidentate.^{2,37}

In all the perchlorato complexes, the presence of the $\nu_3(1100\text{-}1090 \text{ cm}^{-1})$ and $\nu_4(625\text{-}620 \text{ cm}^{-1})$ bands indicates that the tetrahedral symmetry of ClO_4^- is maintained in all these complexes. Thus it suggested the presence of ClO_4^- outside the coordination sphere in these complexes.^{17,38}

Electronic spectra

The electronic spectra of all the complexes recorded herein consist of three bands: one in the $7800\text{-}7772 \text{ cm}^{-1}$ (ν_1), other in the $15400\text{-}15500$ (ν_2), or $18000\text{-}18520 \text{ cm}^{-1}$ (ν_3), and the third in the $20000\text{-}20800 \text{ cm}^{-1}$ (ν_4), regions, which clearly indi-

cate the octahedral stereochemistry of the complexes. The energy of ν_1 corresponds to $10D_q$ for weak field and the value of D_q is obtained from it. All the bands, ν_1, ν_2 and ν_3 observed are free from shoulders. So the ligand field parameters, D_q , B and nephelauxetic effect (β) have been calculated using first order perturbation theory from the ligand field spectra of octahedral Co(II) complexes as discussed by Lever³⁹ and Reedijk *et al.*⁴⁰ The band maxima, their assignments, the calculated nephelauxetic effect (β) and the ligand field parameters B and D_q for some representative chelate complexes are listed in Tables 3. The appreciable intensity enhancement in all the bands of the Co(II) complexes studied herein clearly shows the existence of distortion from a regular octahedral structure of the present Co(II) complexes. Apart from this, there is no difference in the spectra of regular and pseudo octahedral Co(II) complexes.

Thermo gravimetric studies Co(II) complexes of INH-TMB and INH-CIN

The results of the thermo gravimetric studies of $[\text{Co}(\text{INH-TMB})_2\text{X}_2]$ ($\text{X} = \text{Cl}^-, \text{NO}_3^-$ or NCS^-) complexes are presented in Table 4. The thermo gravimetric data indicate that the complexes are

Table 3. Electronic spectral bands (cm^{-1}) and ligand field parameters of Co(II) complex of hydrazones.

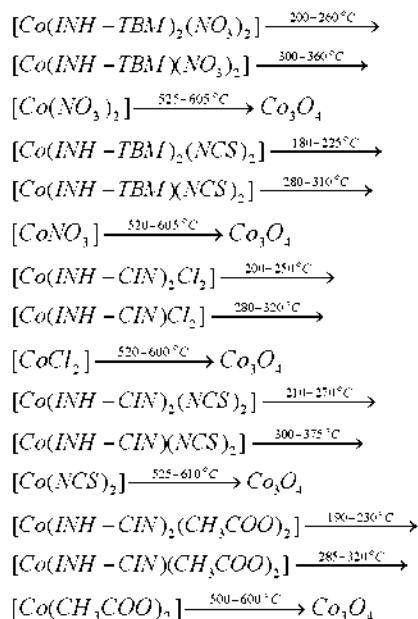
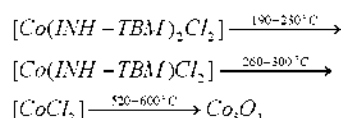
Complex	ν_2 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$	ν_3 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	D_q (cm^{-1})	B (cm^{-1})	β	D_q/B	ν_1 (cm^{-1})
$[\text{Co}(\text{INH-FFL})_2\text{Cl}_2]$	15450	20670	858	953	0.850	0.90	7806
$[\text{Co}(\text{INH-FFL})_2(\text{NO}_3)_2]$	15400	20500	855	950	0.848	0.90	7830
$[\text{Co}(\text{INH-FFL})_2(\text{NCS})_2]$	15450	20670	858	953	0.850	0.90	7806
$[\text{Co}(\text{INH-FFL})_2(\text{CH}_3\text{COO})_2]$	15500	20830	861	956	0.853	0.90	7955
$[\text{Co}(\text{INH-FFL})_3](\text{ClO}_4)_2$	15400	20500	855	950	0.848	0.90	7830
$[\text{Co}(\text{INH-TMB})_2\text{Cl}_2]$	18100	20835	1105	1061	0.95	1.04	8700
$[\text{Co}(\text{INH-TMB})_2(\text{NO}_3)_2]$	18520	20000	1115	1070	0.96	1.04	8770
$[\text{Co}(\text{INH-TMB})_2(\text{NCS})_2]$	18180	20000	1104	1060	0.95	1.04	8700
$[\text{Co}(\text{INH-TMB})_2(\text{CH}_3\text{COO})_2]$	18000	20835	1104	1060	0.95	1.04	8690
$[\text{Co}(\text{INH-TMB})_3](\text{ClO}_4)_2$	18520	20000	1115	1070	0.96	1.04	8772
$[\text{Co}(\text{INH-CIN})_2\text{Cl}_2]$	18000	20833	1104	1060	0.95	1.04	8690
$[\text{Co}(\text{INH-CIN})_2(\text{NO}_3)_2]$	18180	20000	1104	1060	0.95	1.04	8700
$[\text{Co}(\text{INH-CIN})_2(\text{NCS})_2]$	18520	20835	1104	1060	0.95	1.04	8770
$[\text{Co}(\text{INH-CIN})_2(\text{CH}_3\text{COO})_2]$	18180	20000	1115	1070	0.96	1.04	8700
$[\text{Co}(\text{INH-CIN})_3](\text{ClO}_4)_2$	18100	20835	1105	1061	0.95	1.04	8700

Table 4. Thermoanalytical results obtained for Co(II) complexes of INH-TMB and INH-CIN.

Complexes	Decomposition temp. (°C)		Decomposition products	Weight loss (%)	
	Initial	Final		Found	Calcd.
[Co(INH-TMB) ₂ Cl ₂]	190	230	Co(INH-TMB)Cl ₂	42.32	41.44
	260	300	CoCl ₂	83.95	82.89
	520	600	Co ₃ O ₄	90.32	89.42
[Co(INH-TMB) ₂ (NO ₃) ₂]	200	260	Co(INH-TMB)(NO ₃) ₂	39.36	38.74
	300	360	Co(NO ₃) ₂	78.42	77.49
	525	605	Co ₃ O ₄	91.66	90.11
[Co(INH-TMB) ₂ (NCS) ₂]	180	225	Co(INH-TMB)(NCS) ₂	39.86	39.13
	280	310	Co(NCS) ₂	79.16	78.26
	520	605	Co ₃ O ₄	91.38	90.02
[Co(INH-CIN) ₂ Cl ₂]	200	250	Co(INH-CIN)Cl ₂	40.26	39.71
	280	320	CoCl ₂	80.39	79.43
	520	600	Co ₃ O ₄	88.56	87.28
[Co(INH-CIN) ₂ (NCS) ₂]	210	270	Co(INH-CIN)(NCS) ₂	37.11	36.64
	300	375	Co(NCS) ₂	74.06	73.28
	525	610	Co ₃ O ₄	89.19	88.27
[Co(INH-CIN) ₂ (CH ₃ COO) ₂]	190	230	Co(INH-CIN)(CH ₃ COO) ₂	37.46	36.96
	285	320	Co(CH ₃ COO) ₂	75.00	73.93
	500	600	Co ₃ O ₄	89.32	88.16

stable upto 150 °C, which indicates that the complexes are non-hygroscopic in nature and does not have any water molecule. The decomposition and deligation process started above 150 °C. During 180-360 °C both the INH-TMB molecules are lost. Finally at ~605 °C, the cobalt oxide, Co₃O₄ formation takes place.

In case of [Co(INH-CIN)₂X₂] (X = Cl⁻, NCS⁻ or CH₃COO⁻) complexes the thermo gravimetric curves suggest that in temperature region 190-270 °C, the weight loss 37.11-40.26% corresponds to the loss of one molecule of INH-CIN (Table 4). Further heating the [Co(INH-CIN)X₂] complexes at temperature range 280-375 °C, the weight loss (74.06-80.39%) suggests that second molecule of INH-CIN is also evaporated off. Finally at ~666-610 °C, Co₃O₄ is formed. The thermal decomposition of Co(II) complexes studied may be represented by the following equations (cf. Table 4):



Biological studies

The antibacterial activities of the cobalt(II) complexes and standard drugs (ampicillin and tetracycline) were screened by agar-disc method

Table 5. Antifungal and antibacterial activities of cobalt(II) complexes of INH-FFL and INH-CIN

Complex	Antibacterial activity				Antifungal action	
	Zone of inhibition (mm)					
	<i>B.s.</i>	<i>S.a.</i>	<i>E.c.</i>	<i>S.t.</i>	<i>A. niger</i>	<i>C. albicans</i>
[Co(INH-FFL) ₂ Cl ₂]	11	10	10	9	++	++
[Co(INH-FFL) ₂ (NO ₃) ₂]	10	10	9	10	++	++
[Co(INH-FFL) ₂ (NCS) ₂]	15	14	14	13	+++	+++
[Co(INH-FFL) ₂ (CH ₃ COO) ₂]	13	12	12	11	++	++
[Co(INH-FFL) ₃](ClO ₄) ₂	12	10	11	11	++	++
[Co(INH-CIN) ₂ Cl ₂]	10	10	10	9	+	+
[Co(INH-CIN) ₂ (NO ₃) ₂]	11	11	10	11	+	+
[Co(INH-CIN) ₂ (NCS) ₂]	15	15	14	14	++	++
[Co(INH-CIN) ₂ (CH ₃ COO) ₂]	12	11	10	11	+	+
[Co(INH-CIN) ₃](ClO ₄) ₂	13	12	11	10	+	+
Ampicillin	24	22	17	16	-	-
Tetracycline	18	17	21	22	-	-
Salicylic acid	-	-	-	-	++++	++++

in DMF solvent at a concentration of 50 $\mu\text{g mL}^{-1}$. The organisms used in the present investigations included *Bacillus subtilis* (*B.s.*) and *Staphylococcus aureus* (*S.a.*) as gram positive bacteria and *Escherichia coli* (*E.c.*) and *Salmonella typhi* (*S.t.*) as gram negative bacteria. The zone of inhibition around each disc containing the test compound was measured accurately. The diameters of zone of inhibition (mm) of the standard drug ampicillin against gram positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* and gram negative bacteria *Escherichia coli* and *Salmonella typhi* were found to be 24, 22, 17 and 16 respectively, while tetracycline gave 18, 17, 21 and 22 respectively. The results of the antibacterial activities are summarised in Table 5. Under the same conditions, Table 5 shows that all the cobalt(II) complexes of hydrazones studied have moderate antibacterial activities against these bacteria. The cobalt(II) complexes of hydrazones also screened for their antifungal activities against two fungi, *Aspergillus niger* (*A. niger*) and *Candida albicans* (*C. albicans*). The results are presented in Table 5, which show that almost all the complexes studied showed nearly the same extent of activity but they are less active compared to salicylic acid. These complexes appear to be good antifungal agents.

CONCLUSION

The present study reveals that the hydrazone ligands, INH-FFL, INH-CIN or INH-TMB act as a neutral bidentate ligand coordinating Co^{2+} ion through N, O-donor sites. The overall experimental evidences reveal that the studied Co(II) complexes display a coordination number six and have distorted octahedral structures. The experimental analyses of the chloro, nitrate, thiocyanato and acetato cobalt(II) complexes of INH-FFL, INH-TMB and INH-CIN suggest that the complexes are non-ionic in nature while the perchlorato complexes are 1:2 electrolyte and have general composition as $[\text{Co}(\text{L})_2\text{X}_2]$ and $[\text{Co}(\text{L})_3](\text{ClO}_4)_2$ ($\text{X} = \text{Cl}^-$, NO_3^- , NCS^- or CH_3COO^- ; $\text{L} = \text{INH-FFL}$, INH-TMB and INH-CIN) respectively.

ACKNOWLEDGMENTS

The authors are thankful to URC of the University of the South Pacific for supporting finance for this research through Project Nos. 6395-1321 and 6394-1321 (6C127-1321 and 6C126-1321) and Dr. Abdul Mohammed Hatha, Lecturer, Department of Biology, FST, USP for assisting in studying the

biological properties of the compounds.

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