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Physico-Chemical Studies of Co(II) and Ni(II) Complexes with 2-Thiophene Hydroxamic Acid and N-Phenyl 2-Thiophene Hydroxamic Acid

SANJAY KUMAR SINGH†, SHIKHA SINGH†, S.C. SINGH† and RAJESH DHAKAREY*
Department of Chemistry, R.B.S. College, Agra-282 002, India

Some cobalt(II) and nickel(II) complexes of 2-thiophene hydroxamic acid and N-phenyl 2-thiophene hydroxamic acid have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, IR and electronic spectral data. An octahedral geometry has been assigned to all the isolated complexes.

Key Words: Co(II), Ni(II), Complex, 2-Thiophene hydroxamic acid, N-Phenyl-2-thiophene hydroxamic acid

INTRODUCTION

Hydroxamic acids (RCONHOH) are chemical compounds first reported by Lossen in 1869[1]. Extensive work has been carried out on their formations, reactions and structure in the ground state[2, 3]. The main reason for this interest is that this type of molecule contains the fragment of the simplest protein structure: HNC=O. The progress in hydroxamic acids chemistry has been stimulated by the isolation of naturally occurring acids, which are active as antibiotics, antitumour and antifungal agents and specific enzyme inhibitors[4]. They also play an important role in iron uptake and metabolism[5].

In the present paper, we report the synthesis and characterization of 2-thiophene hydroxamic acid (THA) and N-phenyl-2-thiophene hydroxamic acid (NPTHA) and their Co(II) and Ni(II) complexes.

EXPERIMENTAL

All the chemicals used were of AR grade.

Synthesis of Ligands

(I) Preparation of 2-Thiophene Hydroxamic Acid (THA)

An aqueous solution of 5.30 g (0.05 M) of sodium carbonate in 25 mL of water was added to 25 mL ethereal solution of 3.47 g (0.05 M) of finely powdered hydroxylamine hydrochloride. This mixture was stirred well using a mechanical stirrer and the temperature of the mixture was maintained about 0°C by external

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†Department of Chemistry, C.L. Jain College, Firozabad-283 203, India.

cooling using freezing mixture. 7.30 mL (0.05 M) thiophene 2-carbonyl chloride in 25 mL diethyl ether was added to this mixture very slowely (in *ca.* 1 h) with constant stirring. After the complete addition of carbonyl chloride solution, the stirring was continued for another 30 min. Almost 80% of the product was precipitated during the process of reaction. Some of the product, which was dissolved in ether layer during the process of coupling reaction was recovered from the ether layer by distillation under reduced pressure. The total product was triturated with sodium hydrogen carbonate and then repeatedly washed with cold water to remove the acidic impurities.

The crude thiophene hydroxamic acid thus obtained was dissolved in ethyl acetate and the recrystallized thiophene hydroxamic acid was obtained by keeping the filtered product at room temperature and dried over P_2O_5 in a vacuum desiccator. Yield = 8.50 g (crude); 4.00 g (recrystallized).

(II) Synthesis of N-phenyl 2-Thiophene Hydroxamic Acid (NPTHA)

25 mL of ethereal solution of 5.45 g (0.05 M) of finely powdered phenyl hydroxylamine was added to an aqueous solution of 5.30 g (0.05 M) sodium carbonate in 25 mL of water. This mixture was stirred well using a mechanical stirrer and the temperature of the mixture was maintained to about 0°C by external cooling using freezing mixture. 7.30 mL (0.05 M) thiophene 2-carbonyl chloride in 25 mL diethyl ether was added to this mixture very slowly (in *ca.* 1 h) with constant stirring. After the complete addition of carbonyl chloride solution, the stirring was continued for 30 min. Almost 80% of the product was precipitated during the process of the reaction. Some of the product, which was dissolved in ether layer during the process of coupling reaction, was recovered from the ether layer by distillation under reduced pressure. The total product was triturated with sodium hydrogen carbonate and then repeatedly washed with cold water to remove the acidic impurities.

The crude N-phenyl 2-thiophene hydroxamic acid, thus obtained, was dissolved in ethyl acetate and the recrystallized N-phenyl 2-thiophene hydroxamic acid was obtained by keeping the filtered product at room temperature and dried over P_2O_5 in a vacuum desiccator. Yield = 9.10 g (crude); 6.00 g (recrystallized).

Preparation of the Metal Complexes

The metal acetate/chloride (0.005 M, 25 mL) in ethanol was added dropwise to a solution of the ligand THA (0.01 M, 25 mL) or ligand NPTHA (0.01 M, 25 mL) in the same solvent. The resulting mixture was stirred for 30 min. and refluxed for 1.5 h on a water both, 2 mL ammonia solution was slowly added to this solution and again refluxed for 1 h. After this the hot solution was filtered and the filtrate was kept at room temperature for crystallization. The crystals were obtained after 24 h, washed with water, alcohol followed by ether. Finally the crystals were dried over P_2O_5 in a vacuum desiccator.

The elemental analysis of carbon, hydrogen and nitrogen, infrared spectra of the ligands and their metal complexes were recorded in KBr on Perkin's Elmer 577 spectrophotometer in the region *ca.* 4000–200 cm^{-1}, mass spectra of the ligands were recorded in the region 50–350 MHz and NMR spectra of the ligands were recorded at RSIC, CDRI, Lucknow. Magnetic susceptibility measurements of the synthesised complexes were carried out at room temperature on EG & G Model 155 VSM (vibrating sample magnetometer) at RSIC, IIT, Chennai. The electronic spectra of complexes in solution (H_2O/DMF) were recorded on Systronics-106 at room temperature at the Department of Chemistry, R.B.S. College, Agra.

RESULTS AND DISCUSSION

Characterization of the Ligands

(a) 2-Thiophene hydroxamic acid (THA): m.f. = $C_5H_5NO_2S$, m.p. = 105°C. IR Spectra: bands at *ca.* 3211 ν(OH), *ca.* 1650 ν(C═O), *ca.* 1355 ν(C—N), *ca.* 944 ν(N—O) and *ca.* 858 ν(C—S—C). Mass spectra: m/e = 126 (M^+), 111 (M^+), 84 (M^+). Elemental analysis: % found (calculated): C = 47.25 (46.95), H = 2.75 (3.49), N = 5.75 (5.09). NMR spectra: Chemical shifts were (observed as singlet), aromatic proton 7.10–7.70, thiophene due to proton 7.10–7.30, hydroxy proton 7.99, N—H due to aromatic proton 3.90 singlet.

(b) N-Phenyl 2-thiophene hydroxamic acid (NPTHA): m.f. = $C_{11}H_9NO_2S$, m.p. = 80°C. IR spectra: bands at *ca.* 3285 ν(OH), *ca.* 1645 ν(C═O), *ca.* 1355 ν(C—N), *ca.* 976 ν(N—O) and *ca.* 849 ν(C—S—C). Mass spectra: m/e = 219 (M^+), 202 (M^+), 142 (M^+), 111 (M^+), 84 (M^+). Elemental analysis: % found (calculated): C = 59.30 (60.27), H = 3.35 (4.10), N = 4.57 (6.39). NMR spectra: Chemical shifts were (observed as singlet), aromatic proton 7.10–7.70, proton due to thiophene 7.07–7.25, hydroxy proton 7.98 singlet.

The analytical results, melting points, colour and magnetic moments of the complexes are presented in Table-1.

The magnetic moment data are presented in Table-1. The magnetic moment values of Co(II) complexes fall in the range 4.25–4.43 B.M. expected for octahedral geometry which are quite higher than the spin only values of 3.87 B.M., this can be explained on the basis of octahedral symmetry involving a high degree of orbital contribution due to the three fold degeneracy of the $^4T_{1g}$ ground state. The magnetic moment values of Ni(II) complexes lie between 2.76–2.95 B.M. These values are slightly higher than the spin only value of (2.83 B.M.) probably due to slight distortion from the pure octahedral to D_{4h} symmetry. This is not uncommon in d^8 configuration because of Jahn-Teller effect.

The electronic spectra of the Co(II) complexes showed the presence of three bands at around 11429–11905, 15152–17241, 20202–20978 cm^{-1} corresponding to the transitions $^4T_{1g} \rightarrow {}^4T_{2g}(\upsilon_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{1g}(\upsilon_2)$ and $^4T_{1g}(F) \rightarrow {}^4A_{1g}(\upsilon_3)$ respectively. The values of transition υ_1, υ_2 and υ_3 were obtained by using Konig's equation[6]. The ligand field parameters B and the ligand field splitting energy (10 Dq) in the Co(II) complexes were calculated.

Following the Konig's equations υ_1 was used along with observed υ_1 and υ_3 to calculate various parameters such as 10Dq, B, C, F_2, F_4, β_{35} and f etc. for the Co(II) complexes, (Tables 2 and 3).

TABLE-1

PHYSICAL PROPERTIES, ANALYTICAL DATA AND MAGNETIC MOMENT VALUES OF Co(II) and Ni(II) COMPLEXES

Complexes	Physical Properties				Analytical data, Found (Calcd.)					$\mu_{(eff.)}$ (B.M.)
	m.p. (°C)	Colour	m.w.	State	C	H	N	Cl	M	
$Co(C_5H_5NO_2S)_2Cl_2$	155	Light green	416.16	Solid (crystalline)	28.94 (28.86)	2.48 (2.42)	6.81 (6.73)	17.08 (17.03)	14.24 (14.16)	4.25
$Co(C_{11}H_9NO_2S)_2Cl_2$	162	Green	568.35	Solid (powder)	46.52 (46.49)	3.28 (3.19)	4.98 (4.92)	12.58 (12.47)	10.42 (10.36)	4.43
$Co(C_5H_5NO_2S)_2(CH_3COO)_2$	80	Brown	463.35	Solid (powder)	36.34 (36.28)	3.52 (3.48)	6.11 (6.04)	—	12.81 (12.71)	4.29
$Co(C_{11}H_9NO_2S)_2(CH_3COO)_2$	170	Brown	615.54	Solid (powder)	50.84 (50.73)	3.94 (3.92)	4.62 (4.55)	—	9.65 (9.57)	4.40
$Ni(C_5H_5NO_2S)_2Cl_2$	185	Light brown	415.92	Solid (powder)	28.92 (28.87)	2.48 (2.42)	6.81 (6.73)	17.11 (17.04)	14.18 (14.11)	2.76
$Ni(C_{11}H_9NO_2S)_2Cl_2$	155	Brown	568.12	Solid (powder)	46.58 (46.51)	3.23 (3.19)	4.98 (4.93)	12.52 (12.48)	10.38 (10.33)	2.95
$Ni(C_5H_5NO_2S)_2(CH_3COO)_2$	165	Brown	463.11	Solid (powder)	36.36 (36.30)	3.52 (3.48)	6.09 (6.04)	—	12.72 (12.67)	2.75
$Ni(C_{11}H_9NO_2S)_2(CH_3COO)_2$	182	Brown	615.30	Solid (powder)	50.83 (50.75)	3.98 (3.95)	4.59 (4.55)	—	9.59 (9.53)	2.80

TABLE-2: ELECTRONIC SPECTRAL DATA (cm^{-1}) AND VARIOUS LIGAND FIELD PARAMETERS FOR Co(II) COMPLEXES

Methods of calculation	$^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_2)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3)	B	10Dq	β_{35}	$\delta\nu$	$\delta\nu$ %	ν_2/ν_1	π	π/B
				$Co(C_5H_5NO_2S)_2Cl_2$							
Exptl.	11627	17241	23809	—	—	—	—	—	—		
(a)	Fitted	Fitted	13809	–653	5614	—	–9901	—	—		
(b)	Fitted	29070	Fitted	1061	15360	1.09	11829	40.2	—		
(c)	7988	Fitted	Fitted	1138	9248	1.17	–3639	49.9	2.43		
(d)	7988	17241	23809	1139	9253	1.17	—	—	—	3189.90	1.94
				$Co(C_{11}H_9NO_2S)_2Cl_2$							
Exptl.	11905	15152	20833	—	—	—	—	—	—		
(a)	Fitted	Fitted	13275	–738	3247	—	–7558	—	—		
(b)	Fitted	30195	Fitted	858	15847	.88	15043	49.8	—		
(c)	7022	Fitted	Fitted	994	8127	1.02	–4883	70.0	2.43		
(d)	7022	15152	20833	995	8130	1.09	—	—	—	28322.50	1.94
				$Co(C_5H_5NO_2S)_2(CH_3COO)_2$							
Exptl.	11695	15748	20202	—	—	—	—	—	—		
(a)	Fitted	Fitted	25029	–705	4053	—	4827	—	—		
(b)	Fitted	29672	Fitted	825	15563	0.85	13924	47.0	—		
(c)	7324	Fitted	Fitted	933	8430	0.96	–4371	59.6	2.15		
(d)	7324	15748	20202	932	8424	0.96	—	—	—	27461.74	1.94
				$Co(C_{11}H_9NO_2S)_2(CH_3COO)_2$							
Exptl.	11429	16260	21978	—	—	—	—	—	—		
(a)	Fitted	Fitted	26308	–665	4831	—	4330	—	—		
(b)	Fitted	28739	Fitted	951	15145	0.98	12479	43.4	—		
(c)	7542	Fitted	Fitted	1041	8718	1.07	–3887	51.5	2.15		
(d)	7542	16260	21978	1041	8718	1.07	—	—	—	24676.73	1.94

TABLE-3
SPECTRAL DATA AND COMPUTED VALUES OF SPECTRAL PARAMETERS OF Co(II) COMPLEXES

Parameters		Complexes			
		$Co(C_5H_5NO_2S)_2$ Cl_2	$Co(C_{11}H_9NO_2S)_2$ Cl_2	$Co(C_5H_5NO_2S)_2$ $(CH_3COO)_2$	$Co(C_{11}H_9NO_2S)_2$ $(CH_3COO)_2$
Experimental band transitions (cm^{-1})	ν_1	16627	11905	11695	11429
	ν_2	17241	15152	15748	11260
	ν_3	23809	20833	20202	21978
Racah parameters from numerical fitting (cm^{-1})	B	1061	858	825	951
	C	4912	3973	3819	4403
Crystal field parameter from numerical fitting (cm^{-1})	10Dq	15360	15847	15563	15145
Slator-Condon shortly parameters (cm^{-1})	F^2	1762.5	1425.5	1284.6	1480.8
	F^4	140.3	113.54	91.92	105.96
Crystal field parameter	f	1652	1703	1729.2	1682.8
Nephelauxetic ratio	$\beta_{(35)}$	1.09	0.88	0.85	0.98
Nephelauxetic ratio between υ_1, ν_2 and ν_3	ν_3/ν_1	2.05	1.75	1.73	1.92
	ν_3/ν_2	1.38	1.37	1.28	1.35
Mean pairing energy	π	3189.90	28322.50	27461.74	24676.73
Exact spin paring energy	π/B	1.94	1.94	1.94	1.94

The electronic spectra of the Ni(II) complexes are consistent with octahedral geometry showing bands at *ca.* 8100–8415, *ca.* 10790–10920, *ca.* 14100–14600, *ca.* 16500–17150 and *ca.* 25500–26140 assignable to $^3B_{1g} \rightarrow {}^3B_{2g}(\upsilon_B)$, $^3B_{1g} \rightarrow {}^3E_g(\upsilon_E)$, $^3B_{1g} \rightarrow {}^1B_g(sh)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\upsilon_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\upsilon_3)$ transitions respectively. The various octahedral parameters such as Dt, Dq^E, Dq^z and Dq^{xy} have been calculated and the ratio of NSH (Normalized Spherical Harmonic Hamiltonian Parameters) DT/DQ have been calculated[7]. These data suggest the octahedral geometry around the Ni(II) ion (Tables 4 and 5).

A broad band appeared at *ca.* 3285–3211 cm^{-1} in the infrared spectra of both the ligands, which may be assugned to ν(OH)[8]. This band disappears in Co(II) complexes, indicating that the proton of the OH group is replaced by the metal ion upon chelation. The ν(C=O) mode is shifted from 1650 cm^{-1} in hydroxamic acid to 1580–1560 cm^{-1} in all the complexes, indicating coordination through carbonyl oxygen[9]. The ν(C—N) mode[10] is shifted 1355 cm^{-1} in hydroxamic acid to *ca.* 1450–1425 cm^{-1} indicating that coordination of hydroxamic acid occurs through oxygen of carbonyl group. The band due to N—O stretching vibration in free ligand *ca.* 970–940 cm^{-1} gets shifted to higher frequency side *ca.* 1070–1040 cm^{-1} on complexation. At *ca.* 500–430, *ca.* 300–270 and *ca.* 1360–1325 cm^{-1} the bands indicate the formation of ν(M—O), ν(M—Cl) and ν(M—CH_3COO)[11, 12] bonds respectively (Table-6).

TABLE-4

LIGAND FIELD SPECTRAL DATA (cm^{-1}) OF Ni(II) COMPLEXES

Complexes	Electronic Transitions				
	$^3B_{1g}\rightarrow{}^3B_{2g}(\nu B)$	$^3B_{1g}\rightarrow{}^3Eg(\nu E)$	$^3B_{1g}\rightarrow{}^1Eg(sh)$	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)\nu_2$	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(P)\nu_3$
$Ni(C_5H_5NO_2S)_2Cl_2$	8400	10920	14400	17000	26000
$Ni(C_{11}H_9NO_2S)_2Cl_2$	8200	10850	14100	16500	25500
$Ni(C_5H_5NO_2S)_2$ $(CH_3COO)_2$	8100	10790	14380	16920	25810
$Ni(C_{11}H_9NO_2S)_2$ $(CH_3COO)_2$	8415	10935	14600	17150	26140

TABLE-5

ELECTRONIC SPECTRAL PARAMETERS (cm^{-1}) OF Ni(II) COMPLEXES

Parameters	Complexes			
	$Ni(C_5H_5NO_2S)_2$ Cl_2	$Ni(C_{11}H_9NO_2S)_2$ Cl_2	$Ni(C_5H_5NO_2S)_2$ $(CH_3COO)_2$	$Ni(C_{11}H_9NO_2S)_2$ $(CH_3COO)_2$
Dq^{XY}	1092	1085	1079	1100
Dq^Z	588	555	541	552
Dt	288	303	307.5	313
Ds	493	463	487	496.8
–DT	3904	4107	3409	3477.6
DQ	23096	22546	22271.31	32711.24
–DS	3451	3241	4168.29	4242.85
DQ^L	18477	17687	17339.31	17691.03
DQ^Z	32335	32264	32135.30	32751.66
DQ_A	13857	12827	12407.31	12670.82
DQ_E	27715	27405	27203.30	27731.46
–DT/DQ	0.169	0.182	0.18	0.18
$d\sigma$	–1280	–1263	–1307.06	–1332.07
$d\pi$	–19	63	38.24	37.29
Δ_1	39	–126	–76.49	–74.59
Δ_2	10079	9967	9893.76	10085.85
Δ_3	3412	3367	3485.49	3552.19
Dq^E	1008	997	989.37	1008.5
Dt/Ds	0.584	0.654	0.631	0.630

TABLE-6

KEY INFRARED BANDS (cm^{-1}) OF Co(II) AND Ni(II) COMPLEXES

Complexes	Assignments						
	ν(OH)	ν(C=O)	ν(C–N)	ν(N–O)	ν(M–O)	ν(M–Cl)	$\nu(M–CH_3COO^-)$
$Co(C_5H_5NO_2S)_2Cl_2$	—	1588s	1425s	1120m	430s	270w	—
$Co(C_{11}H_9NO_2S)_2Cl_2$	—	1569s	1438s	1037m	510s	280w	—
$Co(C_5H_5NO_2S)_2$ $(CH_3COO)_2$	—	1586s	1425s	1057m	415s	—	1384s
$Co(C_{11}H_9NO_2S)_2$ $(CH_3COO)_2$	—	1598s	1436m	1124m	425s	—	1357s
$Ni(C_5H_5NO_2S)_2Cl_2$	—	1581b	1428s	1122m	600s	425w	—
$Ni(C_{11}H_9NO_2S)_2Cl_2$	—	1567s	1439s	1039m	521s	483w	—
$Ni(C_5H_5NO_2S)_2$ $(CH_3COO)_2$	—	1572b	1425s	1056b	610s	—	1385s
$Ni(C_{11}H_9NO_2S)_2$ $(CH_3COO)_2$	—	1572b	1453s	1049m	525m	—	1380w

S = Sharp; b = Broad; m = Medium; w = weak

Thus from the infrared spectra of ligand and complexes, the conclusion may be drawn that the ligand is bidentate in nature and that both Co(II) and Ni(II) complexes are octahedral in nature.

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