

# 4-Aminoantipyrine Thiosemicarbazone Complexes with cobalt(II): Synthesis, Spectroscopic, Thermal, and Antibacterial Research

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## ABSTRACT

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## Article History

Accepted: 01 Jan 2023 Published: 05 Jan 2023 An interesting series of cobalt(II) complexes of the new ligands: The antipyrinethiosemicarbazones 4[N-(benzalidene) amino]antipyrinethiosemicarbazone (BAAPTS), 4[N-(2-hydroxybenzalidene)amino]antipyrinethiosemicarbazone (2b), and 4[N-(2-hydroxy-1naphthalidene)amino]antipyrinethiosemicarbazone (2c) The complexes were discovered to have the typical stoichiometry [CoX2(H2O)(L)] and [Co(L)2](ClO4)2, where X = Cl, NO3, NCS, or CH3COO, and L =2a, 2b, or 2c. Elemental analyses, molar conductivity measurements, molecular weight estimations, magnetic moments at room temperature, infrared, and electronic spectra were used to describe the complexes. The behaviour of each and every thiosemicarbazone is that of neutral tridentate (N, N, S) donor ligands. The perchlorate complexes are 1:2 electrolytes, but the chloro, nitrato, thiocyanato, and acetate complexes are essentially non-electrolytes, according to the conductivity measurements in PhNO2 solution. Studies on thermodynamic behavior were conducted for a few typical complexes, and a decomposition process was suggested. The cobalt(II) complexes of the ligands and their antibacterial and antifungal activities have also been studied, and it has been found that the complexes are more effective bactericides than the ligands. Keywords: Metal complex, cobalt, PhNO2

## I. INTRODUCTION

Thiosemicarbazones have become a significant family of sulphur donor ligands for transition metal ions over the past 20 years. Thiosemicarbazones' biological and therapeutic qualities have piqued researchers' interest in developing the coordination chemistry of these compounds. They demonstrate a range of biological activity, including anti-tumor, fungicide, bactericide, anti-inflammatory, and anti-viral ones [1-4]. Recent publications from this lab include thiosemicarbazone complexes of lanthanide (III), platinum (II), cobalt (II), and nickel (II) generated from 4-aminoantipyrine, as well as semicarbazone complexes of lanthanide (III), oxovanadium (IV), platinum (II), and nickel (II). The thiosemicarbazone ligands and their cobalt(II) and nickel(II) complexes were also investigated for their antibacterial and antifungal activities [8]. The present

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research covers the synthesis, spectroscopic, thermal, and biological analyses of 4-aminoantipyrine-derived thiosemicarbazones complexes of metal ions, continuing our work on some of thermal and biological studies of a series of cobalt (II) complexes of2a, 2b and 2c (Figure 1).

EXPERIMENTAL

BDH (AR grade) of CoX2nH2O (X = Cl, NO3 or CH3COO) were used exactly as given. Cobalt (II) chloride (in ethanol) and a potassium thiocyanate ethanolic solution were combined in a 1:2 molar ratio to create Co(SCN)2. The precipitate containing cobalt (II) thiocyanate was employed right away after precipitated KCl was



removed using filtering. An ethanolic solution of sodium perchlorate was added to a solution of CoCl2 to create Co (ClO4)2. The white NaCl precipitate was removed by filtering, and the filtrate, Co(ClO4)2, was then employed to create the complex. The approach previously described elsewhere [9] was used to synthesis the Complexes were created by combining a metal salt solution in ethanolic solution with the matching ligands in either a 1:1 or 1:2 molar ratio. The reaction mixture was heated to 50 C and concentrated to a tiny volume on a hot plate after being refluxed on a water bath for two to three hours.

After cooling, the complexes' crystals were filtered, cleaned with ethanol, and vacuum-dried over P4O10.thiosemicarbazones2a, 2b, and 2c. After the complexes were broken down with concentrated H2SO4 and H2O2, cobalt was calculated complex metrically with EDTA [10]. The Volhards method was used to estimate halogens [11]. By titrating the complex's mildly acidic solutions with common silver nitrate solution, the amount of thiocyanate was calculated. BaSO4 was used as a gravimetric estimation of sulphur. The technique recommended by Kurtz et al. [12] was used to estimate perchlorate. The Kjeldahl method was used in the lab to calculate the nitrogen proportion. Molecular weights were calculated using a Beckmann thermometer with an accuracy of 0.01 C while freezing nitrobenzene. Using a conductivity bridge and dip type cell operating at 220 volts, at room temperature, in PhNO2, conductivity measurements were performed. At room temperature, an Evans balance was used to measure the magnetic properties of powders. On a Perkin Elmer FT-IR Spectrophotometer type Spectrum 1000 in KBr, infrared spectra were captured On UV-visible spectrophotometer, The paper-disc plate method was used to measure antibacterial activity. The What man No. 1 paper discs with a diameter of 5 mm and the nutrient agar medium (peptone, beef extract, NaCl, and agar-agar) were employed. At 500 and 1000 ppm, the chemicals were dissolved in DMF. The filter paper discs were submerged in various compound solutions, dried, and then seeded with the test organisms in petri plates. The inhibition zone around each disc was measured after the plates were incubated for 24-30 hours at 28°C Standard food poisoning techniques were used to assess the antifungal activity against Macrophomina phaseolina and Fusarium oxysporum at doses of 50, 100, and 200 ppm, with triplicate determinations in each case [13]. After 96 hours, the diameter of the fungal colony was measured to determine the fungus' linear growth. Inhibition (%) = 100 (C) T)/C, where C and T are the diameters of the fungal colonies in the control and test plates,

respectively, was used to compute the average percentage inhibition.

## II. RESULTS AND ANALYSIS

In the presence of 2a, 2b, and 2c, Co2+ salts reacted to produce [CoX2 (H2O)L] and [Co(L)2](ClO4)2. Table 1 lists the analytical information for these complexes. The complexes are all stable and could be kept for months without experiencing any significant changes. The electrical conductance of the complexes in PhNO2 is reported in Table 1, and the values demonstrate that the perchlorate complexes dissociate in PhNO2 and behave as 1:2 electrolytes, but the chloro, nitrato, thiocyanato, and acetate complexes are virtually non-electrolytes in PhNO2. Table 1 provides the molecular weights calculated using the cryoscopic approach in PhNO2, and the findings are largely consistent with the conductance data. Table 1 lists the complexes' observed magnetic moments. The coordination geometry may typically be determined from the magnetic moments of cobalt(II) complexes. Values of leff in the range of 2.1-2.9 BM, resulting from one unpaired electron plus an apparent

significant orbital contribution, can be used to quickly identify the low-spin square planar cobalt (II) complexes [14]. Despite having three unpaired electrons in common, tetrahedral and high-spin octahedral cobalt(II) complexes can be identified by the degree to which leff deviates from the spin alone value. Higher orbitally degenerate terms contribute to the magnetic moment of tetrahedral cobalt (II) complexes with an orbitally non-generate ground term, which is raised above the spin alone value and occurs in the range of 4.2-4.7 BM [15].Octahedral cobalt(II) complexes however maintain a large contribution due to 4Tg ground term and exhibit magnetic moment in the range 4.8–5.2 BM [16]. Very few data are available for high spin five-coordinate complexes; however the range has been given as 4.5-4.8 BM. The magnetic measurements on the complexes reported here in show that all the complexes are paramagnetic and have three unpaired electron indicating a high spin octahedral configuration. For the present complexes these values lie in the range 4.7–5.4 BM (Table1).

Complex	Analysi	Со	N	S	Anion	Mol.w	Ω Μ	μeff
	s found					t.	(ohm)-1	(BM)
	(cal)%Y					Cal.	cm2mol <sup>-</sup>	
	ield						1)	
CoCl <sub>2</sub> (H <sub>2</sub> O)(BAAPTS)	75	11.4	16.3	6.2	13.7	506	4.3	4.9
		(11.5)	(16.4)	(6.2)	(13.9)	(512)		
Co(NO3)2(H2O)(BAAPTS)	70	10.4	19.7	5.6	-	506	4.9	5.1
		(10.4	(19.8)	(5.7)		(512)		
Co(NCS)2(H2O)(BAAPTS)	68	10.5	20.0	17.2	20.7	552	3.2	5.2
		(10.6)	(20.1)	(17.2)	(20.8)	(557)		
Co(CH3COO)2(H2O)(BAAPT	65	10.5	14.9	5.7	-	553	3.7	4.8
S)		(10.6)	(15.0)	(5.7)		(559)		
Co(ClO4)2 . 2(BAAPTS)	63	5.9	16.9	6.4	20.0	324	52.7	5.0
		(6.0)	(17.0)	(6.5)	(20.2)	(986)		

#### **III.INFRARED SPECTRA**

The se ligands act as neutral tridentate (N,N,S) and essentially the metal is coordinated through N s of two would rule azomethine groups and of S of thioketo group, to previou according to an analysis and comparison of the vibrations infrared spectra of free ligands (BAAPTS, HBAAPT, absorption and 2c) and their Co2+complexes (Tables 2-4). The frequencies m(NH) vibrations have been identified as the source during cor Infrared absorption frequencies (cm)<sup>-1</sup> of cobalt (II) complexes of 2a

of the strong bands seen in the 3440-3200cm)-1 range in the free ligands. After complexation, there is essentially little impact on these frequencies that would rule out complexation of this group. According to previous researchers' observations [17], the m(C=N) vibrations of iminenitrogen are responsible for the absorptions at 1600 cm-1 in the free ligands. These frequencies were seen to shift to lower wavenumbers during complexation (Tables2).

Assignments	BAAPTS	CoCl2-	Co(NO3)2-	Co(NCS)2-	Co(CH3COO)2-	Co(ClO4)2-
		2a.H2O	2a.H2O	2a.H2O	2a.H2O	2(BAAPTS)
v(NH)	3442s	3430s	3442s	3430s	3440s	3430s
	3272s	3265s	3271s	3270s	3272m	3270m
υ (C=N)	1600vs	1572s	1560s	1560s	1570m	1572m
υ	1332s	1382s	1375s	1375s	1375m	1370m
(C=S)+m(C=N)	1305s	1330m	1330m	1330m	1335m	1325m
+ m(C–N)						
δ(NCS) + CS	1120m	1160m	1160m	1160m	1155m	1162m
bending	1095m	1133m	1130m	1135m	1130m	1140m
υ (N–N)	1055m	1065ms	11 <b>62</b> m	1060m	1155m	1065m
v (C=S)	825s	796s	790m	782m	780m	780m
	760vs	712m	710m	720m	725m	722m
υ (Co–		455m	460m	440m	445m	450m
N)/m(Co–S)		350	340m	330m	325	335m

#### **IV.CONCLUSION**

indicating that the two azomethine groups' unsaturated nitrogen n atoms were involved in their interacting with the metal ions. The (C=S) stretching vibrations in substituted thiourea mix with several other vibrations to form the (CN) stretching and bending as well as (N-C-S) bending modes [18]. Bands in the spectra of the current ligands were attributed to [m(C=S) +m(C=N) +m(C-N)], [d (N-CS) +d(C=S)] bending, and [m(C=S)] stretching, respectively, based on the observations of some other researchers [19]. The (C=S) bond would become weaker as a result of the displacement of electrons caused by the

coordination of sulphur with the metal ion. Stretching vibrations should therefore diminish and (CN) vibrations should increase upon complexation (C=S) [19]. All of the Co2+ complexes with2a, 2b, and 2c that are currently known have frequencies in the rangeNearly 50-60 cm-1 are added to 1300-1125 cm-1. Similarly, albeit to a lesser extent, the bending modes of (N-C-S) and (C=S) also increase. On the other hand, the strength of the bands is decreased and the frequencies in the range of 840 to 760 cm-1 are shifted to lower wavenumbers upon complexation. These complexional modifications categorically support Co-S coordination.

## MICROBIAL RESISTANCE

By using the Agarplate procedures, the antifungal activity of the ligand,2a, and several representative cobalt (II) complexes of2a was assessed against Fusarium oxysporum and Macrophomina phaseolina (videinfra). The medium was then combined with various concentrations of the metal-complex solutions in DMF. By measuring the colony's diameter after 96 hours, the fungus' linear growth was determined, and the percentage inhibition was computed using the formula 100(C)T)/C, where C and T It is concluded that at a concentration of 200 ppm, the ligand and the

complexes exhibit significant toxicity for all fungus. Additionally, activity declines as concentration does. The complexes, however, are stronger fungicides than the parent ligand. The chelation and sulphur atom's existence may be to blame for this. In the fight against Macrophominaphaseolina, the ligands and complexes are more effective. Table 9 displays the complexes' and the parent ligands' antimicrobial screening results against the E. coli and K. aer-ogenous species. It demonstrates that the cobalt (II) complexes have antibacterial properties.

Fungicidal screening data of cobalt (II) complexes of 2a

C 1								
Compound	Average % inhibition after 90 h. (conc. in ppm)							
	Fusariumox	ysporum		Macrophominaphaseolina				
	50	100	200	50	100	200		
BAAPTS (2a)	41	50	55	40	50	55		
[CoCl <sub>2</sub> (2a)H <sub>2</sub> O]	44	51	57	42	53	57		
$[Co(OAc)_2(2a)H_2O]$	44	50	57	42	54	58		
[Co(NO3)2(2a)H2O]	43	51	56	43	55	58		
$[Co(NCS)_2(2a)H_2O]$	46	52	57	47	56	59		

## CONCLUSION

The current investigation verified that Co (II) complexes with neutral tridentate thiosemicarbazones have octahedral geometry. Collaborating with N, N, and S-donors. The results of the antimicrobial activity demonstrate the antibacterial capabilities of the metal-complexes, and it is significant to note that they demonstrate improved inhibitory action in comparison to the parent ligand

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