



# Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) MIXED LIGAND COMPLEXES OF 6-AMINOPURINE, THEOPHYLLINE AND THIOCYANATE ION, PREPARATION AND SPECTROSCOPIC CHARACTERIZATION

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## ABSTRACT

New mixed ligand complexes were prepared by adding an ethanolic solution of 6-aminopurine to an aqueous solution of metal salts. This is followed by adding an ethanolic solution of theophylline and thiocyanate ion to give complexes with general formula  $[M(Tp)_2(Ad)X_2]$  where Ad = 6-aminopurine, Tp = theophylline, X = thiocyanate ion and M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The resulting products were found to be crystalline which have characterized using UV-Visible spectroscopic properties and Infrared spectra. Elemental analyses were performed using (C, H, N) and atomic absorption technique. The magnetic susceptibility and the conductivity were also measured. The present results suggested that the adenine as bidentate is coordinated with metal ions through the two nitrogen atoms N3 and N9. The theophylline as monodentate is coordinated with metal ions through the nitrogen atom N9. Thiocyanate ions are coordinated through the sulfur atom.

**Keywords:** theophylline complexes, adenine complexes, 6-aminopurine complexes, thiocyanate complexes, mixed ligand complexes.

## INTRODUCTION

The metal complexes of adenine have considerable interest in the design of model complexes involving purines which could mimic three interactions of metal ions with DNA. In addition, a few purine like adenine have shown significant anti-inflammatory activity, antitumor activity and different animal cancer [1, 2]. Furthermore, theophylline has biological importance which can be used in anticancer drugs [3-6]. Einar and Sletten [7] have carried out extensive synthetic work on transition metal complexes of purine derivatives. They concluded that the chelating sites of copper (II) adenine complexes are probably formed due to the nitrogen atoms N(3) and N(9). Moreover, the anion derived from theophylline has often been used as model ligand in studying the interaction with metal ions [8]. In this work the synthesis and identification of some metal element complexes containing theophylline and 6-aminopurine as mixed ligand complexes are presented. The prepared complexes containing from three different ligands were found to be quite stable.

## MATERIALS AND METHODS

### Materials and measurements

All chemicals were obtained from commercial sources and were used without further purifications (CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, ZnCl<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O and KSCN) from Riedel-Dehaene. Theophylline and 6-aminopurine were obtained from BDH, methanol, ethanol and dimethylsulfoxide from Fluka.

The I.R spectra in the range of 4000-400 cm<sup>-1</sup> were recorded as potassium bromide disc on Shimadzu FTIR-8300 Fourier transform infrared spectrophotometer.

UV-Visible spectra were measured in DMSO using Shimadzu UV-Visible recorder spectrophotometer UV-160. Elemental analysis (C, H, N) was performed by the micro analytical unit on Berkin Elemer B-240 Elemental Analyzer. Determinations of metals were carried out using laboratory methods. Conductivity measurements were carried out at 25°C in DMSO using Philips Pw-9526 digital conductivity meter. Melting point was determined using Stuart-Melting Point Apparatus. The magnetic susceptibility measurements were obtained using Balance Magnetic Susceptibility Model MsB-MK1.

### General procedure for synthesis

An ethanolic solution 15ml of 6-aminopurine (Ad) with 1.78-2.99 g was added to an aqueous solution of the metal salts. This is followed by the addition of an ethanolic solution 12 ml of theophylline (Tp) with 1.25-2.78 g and an aqueous solution 10 ml of KSCN with 0.65-0.33 g. After constant stirring using appropriate amounts of materials needed as decided by the molar ratio 1:2:1:2 (M:Tp:Ad:X). Successively, the resulting precipitates were filtered off, washed several times and recrystallized with 1:3 ethanol:water. Then, it was dried in an oven at 65°C.

## RESULTS AND DISCUSSIONS

The prepared complexes were found to be solids, insoluble in most common organic solvents such as chloroform, acetone and acetonitrile but completely soluble in dimethylsulfoxide. The lower value observed of molar conductivities in DMSO indicates the non electrolyte behavior of the complexes [9, 10]. Elemental analysis (C, H, N) and metal determination were in good agreement with general formula given for the complexes. Table-1 gives the physical properties of the complexes.

**Table-1.** The physical properties of the prepared complexes.

Compound	Color	Yield %	M. P. (°C)	Elemental Analysis Calc. (found %)				Molar conductivity $\text{ohm}^{-1} \text{cm}^2 \cdot \text{mol}^{-1}$
				C	H	N	M	
$[\text{Co}(\text{TP})_2(\text{Ad})\text{X}_2]$	Pink	60	220	37.614 (38.45)	3.153 (2.23)	31.330 (31.42)	8.66 (9.66)	15.30
$[\text{Ni}(\text{TP})_2(\text{Ad})\text{X}_2]$	Light green	65	254	37.627 (37.50)	3.154 (3.21)	31.340 (31.24)	8.73 (9.46)	16.12
$[\text{Cu}(\text{TP})_2(\text{Ad})\text{X}_2]$	Gray	70	>300	37.358 (37.46)	3.132 (3.53)	31.116 (31.17)	9.4 (9.73)	24.19
$[\text{Zn}(\text{TP})_2(\text{Ad})\text{X}_2]$	White	72	254-255	37.256 (38.39)	3.123 (3.19)	31.031 (31.49)	9.33 (10.66)	21.42
$[\text{Cd}(\text{TP})_2(\text{Ad})\text{X}_2]$	White	66	256-258	34.836 (34.97)	2.920 (2.76)	29.016 (30.69)	15.5 (16.9)	24.59

**Magnetic susceptibility**

The magnetic moment for the prepared complex of cobalt ion should be around 3.872 B.M while the measured value of  $\mu_{\text{eff}}$  was shown to be higher than the expected value. This could be related to orbital-spin

coupling [11, 12]. However, the values of  $\mu_{\text{eff}}$  of all  $\text{Ni}^{+2}$  and  $\text{Cu}^{+2}$  complexes were found to be closer to that of spinning only [11, 13]. The complexes of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  were diamagnetic as expected from their electron configuration. All data are also included in Table-2.

**Table-2.** The magnetic properties of the complexes at 25°C.

Complexes	$d^n$	Electron configuration	Term symbol	Ground state	$\mu_{\text{eff}}$ (B.M)		Orbital contribution in octahedral
					Found	Calc.	
$[\text{Co}(\text{TP})_2(\text{Ad})\text{X}_2]$	$d^7$	$t_2g^5 eg^2$	$^4F$	$^4T_{1g}$	4.188	3.872	Yes
$[\text{Ni}(\text{TP})_2(\text{Ad})\text{X}_2]$	$d^8$	$t_2g^6 eg^2$	$^3F$	$^3A_{2g}$	2.864	2.828	No
$[\text{Cu}(\text{TP})_2(\text{Ad})\text{X}_2]$	$d^9$	$t_2g^6 eg^3$	$^2D$	$^2E_g$	1.723	1.732	No
$[\text{Zn}(\text{TP})_2(\text{Ad})\text{X}_2]$	$d^{10}$	$t_2g^6 eg^4$	$^1S$	-	diamagnetic	zero	-
$[\text{Cd}(\text{TP})_2(\text{Ad})\text{X}_2]$	$d^{10}$	$t_2g^6 eg^4$	$^1S$	-	diamagnetic	zero	-

**Electronic spectral studies**

The electronic spectra for free ligands Tp, Ad and  $\text{SCN}^-$  ion shows that the absorption bands in the UV region can be expressed as  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The Co(II) complex shows band at 275 nm which is attributed to the electronic transition  $^4T_{1g(F)} \rightarrow ^4A_{2g(F)}$ . Its band exhibited at 526 nm which belongs to  $^4T_{1g(F)} \rightarrow ^4T_{1g(P)}$ . Finally, the electronic transition of  $^4T_{1g(F)} \rightarrow ^4T_{2g(F)}$  appeared at 970 nm. The ligand field splitting energy  $10Dq$  was found to be  $12886.597 \text{ cm}^{-1}$  and the inter electronic repulsion parameter  $B$  was found to be  $658.338 \text{ cm}^{-1}$ , while  $\beta$  was found to be equal to 0.678.

The Ni(II) complex exhibited absorption bands at 275, 415, 498 and 995 nm which are attributed to the electronic transition  $^3A_{2g(F)} \rightarrow ^3T_{1g(P)}$ ,  $^3A_{2g(F)} \rightarrow ^3T_{1g(F)}$  and  $^3A_{2g(F)} \rightarrow ^3T_{2g(F)}$ . The  $10Dq$  value for the complex was found to be  $10050.251 \text{ cm}^{-1}$  and  $B$  value was found to be

$855.93 \text{ cm}^{-1}$  while  $\beta$  was equal to 0.831. The assignment corresponds for Ni(II) was octahedral complex.

The spectrum of Cu(II) complex shows that its bands in the visible region is attributed to the electronic transitions of  $^2a_{1g(D)} \rightarrow ^2b_{1g(D)}$  and  $^2eg(D) \rightarrow ^2b_{1g(D)}$  at 480 and 740 nm, respectively.

Finally, the electronic configuration of Zn(II) and Cd(II) complexes were  $d^{10}$  which confirm the absence of any (d-d) transitions, but the absorption bands in their spectra suffered red shift with hypochromic effect [14,15]. These absorptions were fully assigned in Table-3.

**Table-3.** U.V-visible spectra of free ligands and their complexes  $10^{-3}$ M in DMSO.

Compound	$\lambda_{\max}$ n.m	ABS	Wave number $\text{cm}^{-1}$	$\epsilon_{\max}$ $\text{Lmol}^{-1}\text{cm}^{-1}$	Assignment
Tp	274	1.728	36496.35	1728	$\pi \rightarrow \pi^*$
	340	0.554	29411.764	544	$n \rightarrow \pi^*$
Ad	273	1.599	36630.036	1599	$\pi \rightarrow \pi^*$
	320	0.153	31250	153	$n \rightarrow \pi^*$
KSCN	276	0.529	36231.884	529	$\pi \rightarrow \pi^*$
	360	0.329	27777.777	329	$n \rightarrow \pi^*$
[Co(Tp) <sub>2</sub> (Ad)X <sub>2</sub> ]	275	1.720	36363.636	1720	${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}(v_2)$
	526	0.013	19011.406	13	${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}(v_3)$
	970	0.007	10309.278	7	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}(v_1)$
[Ni(Tp) <sub>2</sub> (Ad)X <sub>2</sub> ]	275	1.717	36363.636	1717	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}(v_3)$
	415	0.025	24096.385	25	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}(v_2)$
	498	0.036	20080.321	36	
	995	0.072	10050.251	72	${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}(v_1)$
[Cu(Tp) <sub>2</sub> (Ad)X <sub>2</sub> ]	275	1.798	36363.636	1798	(C-T)
	480	0.040	20833.333	40	${}^2a_{1g(D)} \rightarrow {}^2b_{1g(D)}$
	740	0.086	13513.513	86	${}^2e_{g(D)} \rightarrow {}^2b_{1g(D)}$
[Zn(Tp) <sub>2</sub> (Ad)X <sub>2</sub> ]	275	1.718	36363.636	1718	charge transfer M $\rightarrow$ L
[Cd(Tp) <sub>2</sub> (Ad)X <sub>2</sub> ]	275	1.723	36363.636	1723	charge transfer M $\rightarrow$ L
	347	0.018	28818.443	18	Red shift with hypo chromic effect

## INFRARED SPECTRA STUDIES

### Infrared spectra of free ligands

The spectrum of 6-aminopurine have bands at 3350, 1672 and 1356  $\text{cm}^{-1}$  were assigned as  $\nu(\text{NH})$ ,  $\nu(\text{N}=\text{C})$  and  $\nu(\text{C}-\text{N})$  respectively. The spectrum of theophylline shows strong band at 3350  $\text{cm}^{-1}$  which belongs to  $\nu(\text{NH})$ , another strong bands were found at 1720 and 1668  $\text{cm}^{-1}$  which are attributed to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{N}=\text{C})$ , respectively [16-21].

The potassium thiocyanate spectrum appeared in very strong bands at 2048  $\text{cm}^{-1}$  which are caused by the  $\nu(\text{CN})$  and the band at 740  $\text{cm}^{-1}$  which was assigned as  $\nu(\text{CS})$  [19, 22].

### Infrared spectra of complexes

The spectrum of the complexes have shown bands shifted to the lower frequencies by 20-5  $\text{cm}^{-1}$  which belongs to the  $\nu(\text{C}-\text{N})$  compared with 6-aminopurine. Moreover, the complexes have also shown  $\nu(\text{N}=\text{C})$  in the

range of 1630-1665  $\text{cm}^{-1}$  were shifted to lower frequencies by 42-7  $\text{cm}^{-1}$  compared with adenine and by 38-3  $\text{cm}^{-1}$  compared with theophylline. Furthermore, the infrared of the prepared complexes have shown weak bands at 545-590  $\text{cm}^{-1}$  which belong to  $\nu(\text{M}-\text{N})$ . Therefore, 6-aminopurine is coordinated with metal ions through N3 and N9, while the theophylline was coordinated with metal ions through N9 [23-25].

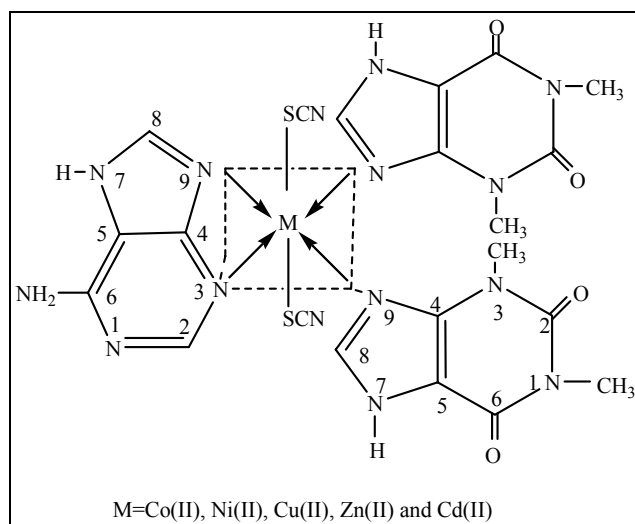
Strong band at 2048  $\text{cm}^{-1}$ , in the spectra of the potassium thiocyanate, may be attributed to the CN stretching frequencies. However, on complexes formation this band is shifted to higher frequencies by 12-82  $\text{cm}^{-1}$ . The coordination through the sulfur atom is further supported by the occurrence of new bands at 410-440  $\text{cm}^{-1}$  in the spectra of the complexes which may be assigned to  $\delta(\text{M}-\text{SCN})$  [26].

**Table-4.** The characteristic infrared absorptions of the prepared complexes.

Compound	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{C=O})$	$\nu(-\text{N}=\text{C})$	$\nu(\text{C-N})$	$\nu(\text{CS})$	$\nu(\text{M-N})$	$\delta(\text{M-SCN})$
$[\text{Co}(\text{TP})_2(\text{Ad})\text{X}_2]$	3320	2130	1715	1665	1360	690	580 500	410
$[\text{Ni}(\text{TP})_2(\text{Ad})\text{X}_2]$	3320	2080	1700	1645	1355	735	590 560	420
$[\text{Cu}(\text{TP})_2(\text{Ad})\text{X}_2]$	3340	2070	1700	1650	1355	730	585 560	430
$[\text{Zn}(\text{TP})_2(\text{Ad})\text{X}_2]$	3310	2060	1700	1630	1345	725	575 545	430

## CONCLUSIONS

The interaction of 6-aminopurine, theophylline and thiocyanate with metal transition ions to yield mixed ligand complexes of the type  $[\text{M}(\text{TP})_2(\text{Ad})\text{X}_2]$ , where Tp = theophylline, Ad = 6-aminopurine, X = thiocyanate ion and M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were studied. The paramagnetic properties for the Co(II), Ni(II) and Cu(II) complexes and the diamagnetic for the Zn(II) and Cd(II) complexes were investigated by magnetic susceptibility measurements. The molar conductivity of complexes in DMSO solution was non electrolyte. All the complexes are octahedral, the configuration being realized by coordination the 6-aminopurine with metal ions through the nitrogen atoms N3 and N9, while the theophylline is coordinated with metal ions through the nitrogen atom N9. The two of thiocyanate ion are coordinated through the sulfur atom (Figure-1).



**Figure-1.** Structure of the prepared complexes  $[\text{M}(\text{Tp})_2(\text{Ad})\text{X}_2]$ .

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