

Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Mixed Ligand Complexes of Theophylline and Cyanate: Synthesis and Spectroscopic Characterization

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Abstract

New mixed ligand complexes were synthesized between theophylline and cyanate to give complexes with general formula $[M(Tp)_4Y_2]$ where Tp= theophylline, Y= cyanate ion and M=Co(II), Ni(II),Cu(II), Zn(II) and Cd(II). The resulting products were found to be crystallined which have been 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 for the complexes were also measured. The present results suggested the octahedral configuration for the metal complexes.

Keywords: Theophylline complexes, Cyanate complexes, Mixed ligand complexes

1. Introduction

The purines includes theophylline, theobromine and caffeine constitute an important class of anti-inflammatory agents (Satwinder, et al., 1995). Theophylline has biological importance as it is structurally related to nucleic acids components (Shohreh, et al., 2003). Thus it can be used as a drug in therapy for respiratory such as COPD or asthma under a variety of brand names and anticancer drugs. These drugs were extensively studied in terms of their inhibition and structural mode of binding against a family 18 chitinase from the opportunistic fungal pathogen *Aspergillus fumigates* (Francesco, et al., 2005; Jacek, et al., 2005; Kiriaki, et al, 2007). as, it can cause nausea, diarrhea, increasing of heart rate, arrhythmias and CNS excitation (Kiriaki, et al., 2007).

A few metal-theophylline complexes have shown significant antitumor activity (David, et al., 1999; Satwinder, et al., 1995). The anion derived from theophylline has often been used as a model ligand in studying the interaction with metal ions (Neville, et al., 1979). Therefore, it was of our interest to synthesis the complexation of metal ions like Co(II), Ni(II),Cu(II), Zn(II) and Cd(II) with theophylline and cyanate ion. The FTIR and UV-visible spectroscopic methods were used to examine the coordination site of these ligands with the metal ions.

2. Experimental

2.1 Material and Measurements

All chemicals were obtained from commercial sources and were used without further purifications (CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, ZnCl₂, Cd(NO₃)₂.4H₂O and KOCN) from Riedeal–Dehaenage. Theophylline was used from BDH, methanol, ethanol and dimethylsulfoxide from Fluka.

The I.R spectra in the range of 4000-400 cm⁻¹ were recorded as potassium bromid 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 analyses (C, H, N) were 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 performed at 25°C in DMSO using Philips Pw-9526 digital conductivity meter. Melting points were determined using Stuart-Melting Point Apparatus, the magnetic susceptibility measurements were obtained using Balance Magnetic Susceptibility Model MsB-MK1.

2.2 General Procedure for Synthesis

An ethanolic solution 10 ml of theophylline (Tp) 1.06-2.96 g and 8 ml an aqueous solution of KOCN 0.24-0.48 g were respectively added to an aqueous solution of the metal salts. After constant stirring using appropriate amounts of materials needed as decided by the molar ratio (1:4:2) (M:Tp:Y), the resulting precipitates were filtered off, washed several times and recrystallized with 1:3 ethanol:water. Then, it dried in an oven at 65°C.

3. Results and Discussion

The prepared complexes were found to be solids, insoluble in water but they were soluble in some organic solvents like dimethylformamide and dimethylsulfoxide. The lower value observed of molar conductivities in DMSO indicates the non electrolyte behavior of the complexes (Kettle, 1975; Quaglian, et al., 1961). Elemental analysis (C, H, N) and metal determination were in good agreement with general formula given for the complexes. Table 1 gives in details the physical properties of the complexes.

3.1 Magnetic Susceptibility

The magnetic moment for the complex of cobalt ions should be around 3.872 B.M while the measured value of μ_{eff} was found to be higher than the expected value; this could be related to orbital-spin coupling (David, 1984; Ehssan, 1988). However the values of μ_{eff} of all Ni⁺² and Cu⁺² complexes were found to be closer to that of spinning only (Clyde, 1983; David, 1984). The complexes of Zn²⁺, Cd²⁺ were diamagnetic as expected from their electron configuration. All these data are also included in Table1.

3.2 Electronic Spectral Studies

The electronic spectra for free ligands Tp and OCN⁻ ion shows absorption bands in the UV- region expressed as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (Satwinder, 1995). The Co(II) complex exhibited bands at 282 and 585 nm which is attributed to the electronic transition of ${}^{4}T_{1}g_{(F)} \rightarrow {}^{4}A_{2}g_{(F)}$ corresponding with charge transfer and the electronic transition of ${}^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{1}g_{(F)}$ respectively.

The electronic spectra of Ni(II) complex shows electronic transition ${}^{3}A_{2}g_{(F)} \rightarrow {}^{3}T_{1}g_{(P)}$ and ${}^{3}A_{2}g_{(F)} \rightarrow {}^{3}T_{2}g_{(F)}$ at 284 and 993 nm respectively. These assignments correspond to Ni(II) octahedral complex.

The spectrum of Cu(II) complex shows bands in the visible region which are attributed to the electronic transition of ${}^{2}b_{2}g_{(D)} \rightarrow {}^{2}b_{1}g_{(D)}$ and ${}^{2}e_{2}g_{(D)} \rightarrow {}^{2}b_{1}g_{(D)}$ at 540 and 745 nm respectively.

Finally, the electronic configuration of Zn(II) and Cd(II) complexes were (d¹⁰) which confirms the absence of any (d-d) transitions (Lever, 1968; Monther, 1983). All the absorption bands were fully assigned in Table 2.

3.3 Infrared Spectra Studies:

3.3.1 Infrared Spectra of Free Ligands

The spectrum of theophylline shows weak band at 3350 cm⁻¹ which belongs to v(NH). While the strong band attributed to v(C=O) was found at 1720 cm⁻¹ and the other strong band exhibited at 1668 cm⁻¹ which is due to v(N=C).

Here we turn our attention to cyanato compounds. Cyanate, as a terminal ligand, is potentially ambidentate and it can coordinate to metal ions through the nitrogen or the oxygen atoms. Information on the coordination mode of the cyanate ion may be obtained from infrared spectroscopy (Jose, et al., 2006). Moreover, the spectra of potassium cyanate shows very strong bands at 2165cm^{-1} and 1207cm^{-1} which belongs to v(OCN) asymmetric and v(OCN) symmetric (Kazuo, 1997; Socrates, 1980).

3.3.2 Infrared Spectra of the Complexes

Further information about the coordination behavior of the free ligands with metal ions were carried out by the comparison of the infrared spectra of the free ligands and their complexes. The absorption band appeared at 1668 cm⁻¹ was caused by v (-N=C) bond in the structure of Tp (Cross & Alan, 1969; John, 1965; Socrates, 1980; William & Flemming, 1973). In the spectra of their complexes, this absorption band was around 1635-1655 cm⁻¹ which has shifted to lower frequencies by 33-13 cm⁻¹. Moreover, the spectra of the complexes exhibited weak bands between 460-490 cm⁻¹ due to v(M-N). This indicates the coordination of Tp with the metal ions through the nitrogen atom N9 in their structures (Elizabeth, & Elmer, 1979; Katsuyuki, & Hiroshi, 1980; Milan, 1981; Roger, et al., 1981).

Although the coordination chemistry of cyanate anion is well known, but surprisingly the adsorption of cyanate has been discussed only in a few papers (Jose, et al., 2006; Michael, & Rudolf, 1995). The asymmetrical stretching vibration was found to be in the region of 2200-2240 cm⁻¹ and it was shifted to higher frequencies by 65-75cm⁻¹. The absorption band in the case of symmetrical stretching vibration was shifted to higher frequencies by 3-13 cm⁻¹. The usual observed infrared band is due to the CN stretching vibration, which was shifted to higher wave numbers with more positive potential. It was no metal cyanate complexes observed yet with such a strong shift of the frequencies of the CN stretching vibration to lower frequencies (Michael, & Rudolf, 1995). Therefore, we suggested that the

coordination of cyanate ion with metal ions through its oxygen atom. Similar absorption was found in the I.R spectra of the complexes $[Re(OCN)_6]^2$, $[Re(OCN)_6]^-$ and $NBu_4[ReBr_4(OCN)(DMF)]$ where NBu_4 = tetrabutylammonium cation and DMF=N,N-dimethylformamide (Bailey, & Kozak, 1969; Jose, et al., 2006; Kazuo, 1997; Socrates, 1980).

Another significant point, that is the effect of cyanate on the trans position relative to the cis position depends on qualitative evidence. Even this highly specific trans effect still does not have any theoretical justification but some studies have performed arguments suggested that the trans effect must be greatest on highly electronegative and poor donor ligands (John, & Lorraine, 1978). Thus, the spectra of the complexes exhibited lower frequency absorptions bands in the range of 565-605cm⁻¹ have been assigned as δ (M-OCN). Table 3 gives the diagnostic absorptions and their assignments.

4. Conclusions

As part of our studies on the chemistry of transition metals, we have been able to synthesis and characterize a new mixed ligand complexes containing theophylline and cyanate ion coordinated with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The molar conductivity of the complexes in DMSO solution was non electrolyte. The configuration of the complexes were performed that the theophylline coordinated with metal ions through the nitrogen atom N9 and cyanate ion coordinated with metal ions through the oxygen atom, Therefore, from the results presented the metal complexes have octahedral configuration, see Fig 1.

Acknowledgements

Thanks are due to the Ministry of Higher Education of Malaysia for grants (UKM-GUP-NBT-08-27-112, UKM-ST-01-FRGS0022-2006) and members of staff of faculty of science and Technology and the Chemistry Department at College of Ibn-Alhaitham of Education, Baghdad University, Iraq. Additional thanks are due to college of sciences of Al-Naherain and University of Mosul, Iraq for their kind technical assistance.

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Compound		M.P	Elemental analysis: Calc. (Found)%				Magnetic moment	Molar
	Color	°C						conductivity
		Ċ	С	Н	Ν	М	Calc. (Found)%	Ohm ⁻¹ cm ² mol ⁻¹
$[Co(Tp)_4Y_2]$	Pink	260-262	41.722	3.731	29.191	6.66	3.872	18.75
			(41.65)	(3.90)	(30.25)	(7)	(4.037)	
$[Ni(Tp)_4Y_2]$	Light	>300	41.732	3.732	29.198	6.66	2.828	19.23
	blue		(40.83)	(3.67)	(29.27)	(7.33)	(2.766)	
$[Cu(Tp)_4Y_2]$	Green	>300	41.500	3.711	29.036	7.3	1.732	15.78
	blue		(41.62)	(4.68)	(28.16)	(7.9)	(1.678)	
$[Zn(Tp)_4Y_2]$	white	262-264	41.412	3.703	28.974	7.5	zero	15
			(41.35)	(3.59)	(28.91)	(6.16)		
$[Cd(Tp)_4Y_2]$	white	260-261	39.289	3.513	27.489	12.23	zero	15.78
		-	(39.37)	(3.63)	(26.54)	(12.6)		

Table 1. The physical properties of the metal complexes $[M(Tp)_4Y_2]$

Compound	λ_{max} n.m	ABS	Wave number cm ⁻¹	ε _{max} Lmol ⁻¹ cm ⁻¹	Transitions
KOCN	272	0.614	36764.705	614	$\pi \rightarrow \pi^*$
	310	0.718	32258.064	718	$n \rightarrow \pi^*$
TP	274	1.728	36496.35	1728	$\pi \rightarrow \pi^*$
	340	0.554	29411.764	544	$n \rightarrow \pi^*$
$[Co(TP)_4Y_2]$	282	1.939	35460.992	1939	${}^{4}T_{1}g_{(F)} \rightarrow {}^{4}A_{2}g_{(F)}$
	585	0.132	17094.017	132	${}^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{1}g_{(P)}$
[Ni(TP) ₄ Y ₂]	284	1.935	35211.267	1935	${}^{3}A_{2}g_{(F)} \rightarrow {}^{3}T_{1}g_{(P)}$
	993	0.012	10070.493	12	${}^{3}A_{2}g_{(F)} \rightarrow {}^{3}T_{2}g_{(F)}$
$[Cu(TP)_4Y_2]$	287	2.090	34843.205	2090	Charge transfere
	540	0.024	18518.518	24	${}^{2}b_{2}g_{(D)} \rightarrow {}^{2}b_{1}g_{(D)}$
	745	0.060	13422.818	60	$^{2}e_{2}g_{(D)} \rightarrow ^{2}b_{1}g_{(D)}$
$[Zn(TP)_4Y_2]$	277	1.781	36101.083	1781	Charge transfere $M \rightarrow L$
[Cd(TP) ₄ Y ₂]	279	1.858	35842.293	1858	Charge transfere $M \rightarrow L$

Table 2. U.V-visible spectra of free ligands and their complexes 10⁻³M in DMSO

Table 3. The characteristic infrared absorptions of free ligands and their complexes

Compound	v(NH)	v(OCN) _{asy}	v(C=O)	v(-N=C)	$\nu(OCN)_{Sy}$	δ(M-OCN)	v(M-N)
KOCN	-	2165	-	-	1207	-	-
TP	3350	-	1720	1668	-	-	-
[Co(TP) ₄ Y ₂]	3360	2240	1725	1650	1210	605	460
						575	
[Ni(TP) ₄ Y ₂]	3360	2240	1730	1650	1215	605	480
						580 600	
$[Cu(TP)_4Y_2]$	3320	2200	1700	1635	1210	565	460
						505	490
$[Zn(TP)_4Y_2]$	3330	2220	1730	1655	1215	580	.50
$[Cd(TP)_4Y_2]$	3320	2200	1725	1650	1220	590	480



Figure 1.