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Synthesis and Characterization of the New Fac-and Mer-[M (Caf)$_3$(SCN)$_3$],OH$_2$

El Amane M*, El Hamdani M, Bouhdada M and Kennouche Y

Université Moulay Ismail, Morocco

***Corresponding author:** Amane MEL, Université Moulay Ismail, Faculté des sciences, BP11201 Zitoune, Meknes Morocco

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Abstract

New fac-and mer-[M(caf)$_3$(SCN)$_3$]OH$_2$ caffeine complexes where caf = caffeine, SCN= thiocyanato and M= Cr(III), Fe(III) and Ru(III) were synthesized in simple reactions of chloride MCl$_3$, H$_2$O ; M= Cr(III), Fe(III) and Ru(III) with potassium thiocyanate in ethanol solution. The infrared and electronic spectral data of the complexes [M(caf)$_3$(SCN)$_3$]OH$_2$ suggest that the caffeine is coordinate through the nitrogen N9 and the thiocyanato behave a monodentate legend with sulphur atom donor towards metal ions. On the basis of the spectral data, the FT-IR, UV-Visible and EPR suggested the mer-and fac-octahedral complexes.

Keywords: Caffeine; Mer; Fac; Complexes; Thiocyanato; Infrared; UV-Visible; EPR; Molar conductance

Introduction

Transition metal Complexes have received great attention for many years, because of their catalytic, biological activity, essentially due to interaction with their heavy metal ions, bonding through nitrogen and oxygen. The interest in metal complexes of Purina and development of the field of bioinorganic chemistry have increased substantially, since it has been reorganized that many of the complexes may serve as models for biologically important species, i.e. the caffeine is a strong antioxidant that prevent DNA damage. The interaction between nucleic acid and metal ions constitutes a field with multidisciplinary characters such as the bioinorganic chemistry or inorganic biochemistry. N-heterocyclic carbines (NHCs) have been isolated in 1991 [1], and have become ubiquitous in coordination chemistry particularly in the field of catalysis [2-7]. In more recent years, metal NHCs, have shown promise as antimicrobial (AgI-NHCs) and as antitumor (Pd (II), Cu (II), Au (I) and Rh (II) NHCs) agents [8-12]. Caffeine (Figure 1) is the more thoroughly studied methylxanthines to date. Caffeine was first isolated from sea and coffee in the early 1820 [13-15]. Caffeine is widely perceived as a central nervous system (CNS) stimulant. It acts like a brain cortex stimulant and is usually sought for by those looking for a general sense of mental energy with increased awareness and wakefulness improved clear thinking and attenuated fatigue. It was reported as enhancing a wide range of exercise activities from those relying on explosive strength to short term [16]. Caffeine has a centrosymmetric Cs point group. Its number of normal modes of vibration can be distributed as Γ_{vib} = 27 A' + 12 A''. It's known from the literature that the coordination of the caffeine with nitrogen and oxygen atoms which is accompanied by elimination of the mirror plane σ_h and by a whole series of changes in the infrared spectrum [17]. We report here the synthesis and characterization of some new fac- and mer- [M(caf)$_3$X$_3$]; M= Cr(III), Fe(III) and Ru(III) containing caffeine and thiocyanato as legends. The synthesized complexes are characterized by molar conductance, infrared, EPR and electronic spectroscopic analysis.

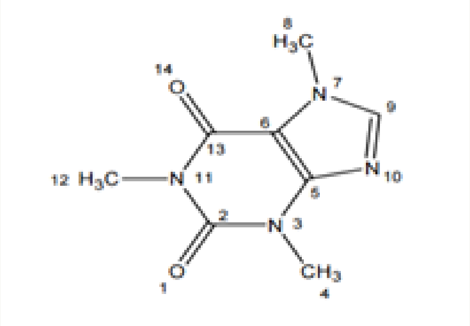

Figure 1: Structure of caffeine (1,3,7-trimethyl-3,7-dihydro-purine-2,6-dione).

Materials and Methods

All chemicals were obtained from commercial sources and were used without purifications: (FeCl$_3$, 6H$_2$O BDH; CrCl$_3$• 6H$_2$O BDH; RuCl$_3$(H$_2$O)$_3$ Sigma Aldrich), caffeine Sigma Aldrich, potassium thiocyanate Sigma Aldrich, Ethanol and DMSO Sigma Aldrich. Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 660 plus spectrophotometer in the range of 4000-400cm^{-1} at

298K while the UV–Visible spectra were obtained on a Shimadzu UV-1800 Spectrophotometer. The EPR spectrum was recorded on a conventional X band Burke ER 200D spectrometer operating at 9.5GHz. Conductivity measurements were performed at 25 °C in DMSO using Hatch HQ430d flexi.

Synthesis of the fac- and mer- caffeine complexes [M(caf)$_3$(SCN)$_3$OH$_2$, where caf = caffeine and M= Cr(III), Fe(III) and Ru(III)

To a solution of caffeine (3mmol) and potassium thiocyanate KSCN (3mmol) in ethanol, was added a solution of metal salts (Fe(III) and Cr(III)) (1mmol) in ethanol. The obtained solution was refluxed for 4h, after which the solution is concentrated, filtered and dried.

Results and Discussion

Characterization of fac- and mer- caffeine complexes [M(caf)$_3$(SCN)$_3$]OH$_2$ Where caf = caffeine and M= Cr(III), Fe(III) and Ru(III)

The analytical data and some physical properties of the fac- and mer- caffeine complexes [M(caf)$_3$(SCN)$_3$] OH$_2$; M= Cr^{3+}, Fe^{3+} and Ru^{3+} are collected in Table 1. The complexes are stable in air, soluble in DMSO and DMF. Molar conductance values of the fac- and mer- caffeine complexes in DMSO (10-3M solution at 25 °C) were (7.3-18.6)Ω^{-1}cm^2 mol^{-1} indicating, their non-electrolytic nature [18] (Table 1).

Table 1: Physico-chemical data of the fac-and mer-caffeine complexes.

Complexes	Color	M.P. (°C)	Yield (%)	Λ (Ohm^{-1} Cm^2 Mol^{-1})
[Cr(caf)$_3$(SCN)$_3$],OH$_2$	purple	>260	68	12.8
[Fe(caf)$_3$(SCN)$_3$],OH$_2$	white	>260	73	18.6
[Ru(caf)$_3$(SCN)$_3$],OH$_2$	Blue	>260	60	7.3

Infrared spectra

In order to study binding mode of the caffeine and thiocyanato ion to Chromium(III), Ruthenium(III) and Iron (III) in the new complexes. The infrared spectra of the free caffeine [19] and thiocyanato [20,21] were compared with their fac- and mer-caffeine complexes (Figure 2 & Table 2).

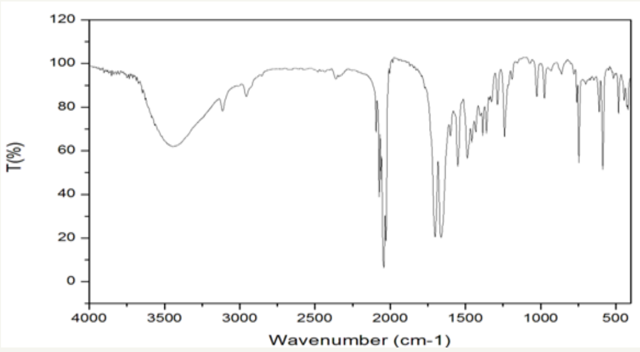

Figure 2: Infrared spectrum of [Fe(caf)$_3$(SCN)$_3$],OH$_2$ in KBr.

Table 2: Spectral data of the fac and mer-caffeine complexes [M(caf)$_3$(SCN)$_3$],OH$_2$; M=Cr^{3+}, Fe^{3+} and Ru^{3+}.

Kscn	Caffeine	Ru(Caf)$_3$(Scn)$_3$	Cr(Caf)$_3$(Scn$_3$)	Fe(Caf)$_3$(Scn)$_3$	Assignments
		3450m	3515m	3450m	υOH(OH$_2$)
	3110m	3110m	3120m	3109w	υ(CH=)
	2954m	2941m	2957m	2953w	υ(CH$_3$)
2052s		2112w, 2071w, 2048w	2086s, 2059s	2090s, 2085s 2071s, 2066s 2034s	υ(SCN)
	1700vs	1696m	1694s	1699s	υs(CO)
	1660vs	1648s	1641s	1653s	υa(CO)
	1600m	1600w	1553m	1593m	υ(C=N)
	1548s	1540s	1543m	1540m	δ(HCN)+υ(imid) +υ(pyri)
	1470m	1477m	1496s	1500 m	δ(HCN)+δ(CH$_3$)
	1466m	1450m	1443m	1455w	
	1432m	1423m	1415s		ɤ(CH$_3$)+δ(CH$_3$)
	1405m	1390w	1382m	1400w	
	1360s	1350m	1360s	1340w	δ(HCN)+υ(imid) +δ(CH$_3$)
	1326w	1320w	1331m	1310w	υ(imid) + υ(pyri)
	1285s	1283m	1291s	1288w	υ(pyri)
	1237vs	1238m	1236s	1242w	υ(CN) +ρr(CH$_3$)

	1210vw	1212vw	1220s		δ(CH) + ρr(CH$_3$)
	1188m	1183m	1185m	1182w	δ(CH) + ρr(CH$_3$)
	1130vw	1124w	1128m	1123m	ρr(CH$_3$) out of plan
	1071s	1070w	1077w	1071m	ρ(CH$_3$) + ρ(CH)
	1025s	1025m	1031m	1033s	ρ(CH$_3$) + ρ(CH)
	973s	970m	978m	974m	υ(N-CH$_3$)+ρr(CH$_3$) +δ(imid)
	923w	930w	929m	930w	γ(CH)
	862m	860vw	866m	882m	ρ(CH$_3$)+ υ(N-CH$_3$)+δ(C=O)
	800s	803vw	803w	800w	ρ(pyrim) + δ(C=O)
750		760m	762m	760m	υ(C-S)
	743vs	742m	748m,740m	744s	γ(pyr)+γ(imid)
	700m	700vw	693w	700w	γ(pyrim)+γ(imid)
	642s	666vw	651w	667w	δ(pyrim)+ρ(imid)
	611s	610m	608m	610m	γ(imid)
		540w	555 w	586w	υ(M-N)
	481vs	450m	486m	482m	Ţ(caf)
		452m	448m	444m	υ(M-SCN)
	420vs	418m	427m	420m	ρr(C=O)

The infrared spectrum of the free caffeine [19] (Table 2) is characterized by absorption peaks at 3110cm^{-1} and 2954cm^{-1} assigned to the ν(C-H) stretching vibrations in imidazole ring and ν(CH$_3$) stretching vibration in imidazole and pyrimidine rings respectively. A strong bands are observed at 1700cm^{-1} and 1660cm^{-1} which are characteristic of the asymmetric and symmetric ν(C=O) stretching vibration in pyrimidine ring respectively. The ν(C=C) and ν(C=N) vibrations of the free caffeine that occur at 1600cm^{-1} and 1548cm^{-1} for imidazole ring. The different modes of the methyl bending and rocking are observed in (1470-1025)cm^{-1} range. In the infrared spectra of all fac-and mer-caffeine complexes, the characteristic bands of the free caffeine are shifted to lower frequencies. The ν(C-H) stretching vibrations in imidazole ring and methyl groups in pyrimidine ring are shifted to higher frequencies with the higher intensity in the fac-and mer- caffeine complexes. The stretching frequencies of the symmetric and asymmetric νs(C=O), νas(C=O), ν(C=C), ν(C=N), δHCN which appeared in (1694-1699)cm^{-1}, (1641-1655)cm^{-1}, (1553-1598)cm^{-1} and (1540-1550) cm^{-1} ranges respectively [22,23] are shifted to lower frequencies in the fac-and mer-caffeine complexes. The methyl vibrations attached with nitrogen bending and rocking atom in the side chain N-CH$_3$ vibration which are found to be observed around (1340-1496) cm^{-1} and (978-1077)cm^{-1} respectively are shifted in the fac-and mer-caffeine complexes. Bands of variable intensity are observed in the region (1100-1000)cm^{-1} due to in plane deformation vibration in the imidazole and pyrimidine rings. The medium and strong vibrational bands in the regions (974-978)cm^{-1} and (800-803)cm^{-1} are assigned to the δ (imid) +ν (N-C) and ρ (pyrimid) +δ (C=O) respectively [24,25]. However, during the complexes formation of the caffeine, the imidazole ring gets more frequency changes with higher intensity (Table 2), suggesting that the caffeine coordinate through the imidazole vibration N9 atom, and acting as monodentate ligand [26]. The thiocyanato ligand in the fac- and mer- caffeine complexes absorbed at five frequencies [27]. Strong vibrations in the (2034-2122)cm^{-1} range for [Fe(caf)$_3$(SCN)$_3$] and [Ru(caf)$_3$(SCN)$_3$] are due to ν(SCN) stretching vibration and may attributed to the presence of the thiocyanato in the coordination sphere of these complexes. The multiplicity of the band indicated two isomers which are distinguishable by the infrared spectroscopy [27]. The five absorptions are characteristic for mer and fac isomers in the new complexes. The thiocyanato ligand can coordinate the metal through either the nitrogen or the sulphur. The free thiocyanate ion absorbs at about 2052cm^{-1} and 750cm^{-1} which are due to ν (SCN) and ν (C-S) stretching vibrations [28].These peaks are shifted to higher frequencies in the complexes suggesting the coordination through the sulphur atom (M-SCN). Therefore, the spectra show five bands in (2034-2090) cm^{-1} range attributed to two isomers mer [M(caf)$_3$(SCN)$_3$] (2A1+B1) with three actives bands in IR (2A1+B1) and the fac isomer has two actives bands in IR (A1+E) [27]. New bands in (555-586)cm^{-1} range are assigned to υ (M-N) vibration [22].

Electronic spectra

Table 3: UV-Visible data of the fac-and mer-caffeine complexes [M(caf)$_3$(SCN)$_3$]OH$_2$; M= Cr^{3+}, Fe^{3+} and Ru^{3+}.

Complexes	Λ Max (Nm)	Assignment
Caff	275	π→π*
	316	n→π*
	365	n→π*
	493	d→d
KSCN	276	n→π*
	360	n→π*
[Cr(caf)$_3$(SCN)$_3$],OH$_2$	210	n→π*
	243	n→π*
	275	n→π*
	434	d→d
	562	d→d
	756	d→d
[Fe(caf)$_3$(SCN)$_3$],OH$_2$	210	n→π*
	245	n→π*
	277	n→π*
	468	d→d
[Ru(caf)$_3$(SCN)$_3$],OH$_2$	210	π→π*
	244	π→π*
	274	n→π*
	425	d→d
	550	d→d

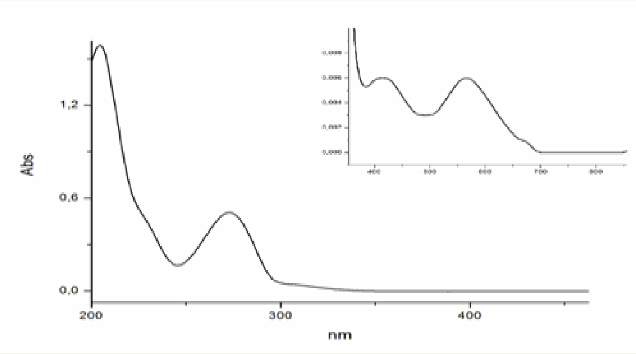

Figure 3: Electronic spectrum of [Cr(caf)$_3$(SCN)$_3$],OH$_2$, in DMSO.

All absorptions were fully assigned in Table 3 and the electronic spectrum of [Cr(caf)$_3$(SCN)$_3$] is shown in Figure 3. The UV-Visible data of the thiocyanato and caffeine ligands [29] were compared with those of the fac- and mer-caffeine complexes [M(caf)$_3$(SCN)$_3$],OH$_2$; M= Cr^{3+}, Fe^{3+} and Ru^{3+}. The electronic spectra of the thiocyanato and caffeine ligands [29] show the absorption bands in the UV region can be attributed to π→π* and n→π* transitions which were shifted to higher wavelength upon coordination. Therefore, new bands at longer wavelength observed in (366-756)nm range may be assigned to d-d transitions.

EPR spectra

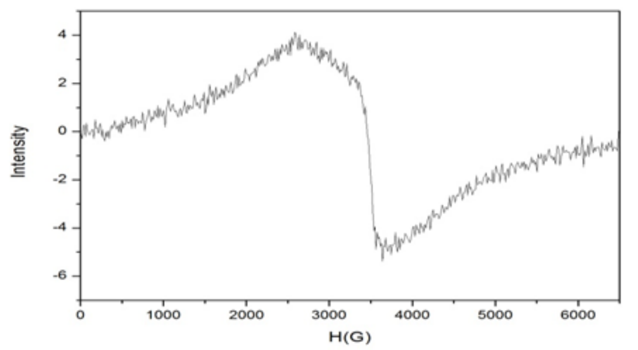

Figure 4: EPR spectrum of [Fe(caf)$_3$(SCN)$_3$]OH$_2$ at room temperature on X band in solid state.

The X-band EPR spectrum of the complex [Fe(caf)$_3$(SCN)$_3$]OH$_2$, in the solid state recorded at room temperature are shown in Figure 4. ESR spectrum of the complex shows only an intense and broad signal without hyperfine splitting (giso=2.151). The shape of the spectrum is consistent with octahedral environment around Fe (II) ion and the higher g value for the investigated complex, when compared to that of free electron (g = 2.0023) revealing an appreciable covalence of metal-ligands (M-N9 and M-SCN) bonding characteristic of octahedral stereochemistry [30-32] (Table 3).

Conclusion

New fac- and mer- caffeine complexes [M(caf)$_3$(SCN)$_3$],OH$_2$; where caf=caffeine, M= Cr^{3+}, Fe^{3+}, Ru^{3+} were synthesized and characterized on the basis of molar conductance, infrared, UV-Visible EPR. The spectroscopic data suggest that the M (III) caption lies on a fac-and mer-arranged octahedral coordination geometry provided by sulfur atoms of three thiocyanato ligands and nitrogen atoms of three coordinated caffeine molecules and hydration water molecule.

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