SYNTHESIS AND CHARACTERIZATION OF NEW COMPLEXES OF ANTICIPATED ANALGESIC ACTIVITY FORMED BY TRANSITION METALS CO (II), NI (II) AND CU (II) WITH 4-AMINOANTIPYRINE [4-AAP] +

تحضير و تشخيص معقدات جديدة يتوقع ان تكون ذات فعالية مسكنة بوساطة الفلزات الانتقالية الكوبلت ،النيكل والنحاس مع٤- امين انتى بايرين (4-AAP)

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Abstract:

New transition metals complexes of anticipated analgesic activity were prepared by coordination of Co (II), Ni (II) and Cu (II) metals with the ligand L = 4-aminoantipyrine (4-AAP) in 1:2 and 1:3 molar ratio. The metal ions were bidentately bonded to the ligand in the complexes. Complexes have been synthesized by direct reaction in neutral medium to give complexes of the general formula $[(ML_2)Cl_2.2H_2O]$ and $[(ML_3)Cl_2]$. The molecular formula of these complexes were proved by CHN analysis in addition to the IR and UV spectra. The molar conductivity measurements showed the octahedral geometry around the metal ion. The geometry (three dimensional structures) of complex (IV) at minimized energy was established by chem.3D Ultra; molecular modeling and analysis confirmed the suggested structure.

المستخلص:

تم تحضيرمعقدات فلزات العناصر الانتقالية الأولى والمتوقع أن يكون لها فعالية كمسكنات بوساطة تناسق فلزات الكوبالت والنيكل والنحاس مع ٤-أمين انتى بايرين بنسبة مولارية١:٢و ١:٣.وقد اعطت هذه الفلزات معقدات ثنائية السن مع هذا الامين.حضرت هذه المعقدات بوساطة التفاعل المباشر وبوسط متعادل لإعطاء معقدات ذات الصيغة $[(ML_3)]Cl_2$ و$[(ML_2).2H_2O]Cl_2$.اثبتت الصيغة الجزيئية لهذه المعقدات بوساطة التحليل الدقيق لعناصر الكربون والهيدروجين والنتروجين ، اضافة الى اطياف الاشعة تحت الحمراء وفوق البنفسجية.

ان حساب التوصيلية الكهربائية المولارية اظهرت ان هذه المعقدات ثمانية التناسق. درست كذلك هيئة المعقد (IV) بأبعاد ثلاثية وبالطاقة الدنيا والتي اثبت الأشكال المتوقعة.

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Introduction:

The important of analgesic activity of complexes formed by transition metals and 4-aminoantipyrine (4-AAP) was due to increased a paralytic activity on the sensory and motor nerves, resulting in some anesthesia and vasoconstriction, and it was also exerted a feeble antiseptic effect [1-2].This was encourage us to undertake a systematic search in this field. Also our continuous interest in the field of coordination chemistry of metals with amines or Schiff bases enhances us to carry out this work[3-5] .Therefore, we were presented here the synthesis and characterization of new complexes of anticipated analgesic activity form by transition metals Co(II), Ni(II) and Cu(II) with 4-aminoantipyrine (4-AAP).

Experimental:

IR Spectra were recorded on Unicam SP 2000 Spectrometer at a range (200-4000) cm^{-1} using Nujol mull and KBr discs. Electronic spectra were recorded on a Shimadzu UV/Vis Spectrophotometer UV- 160 for 10^{-3}M solution of the complexes in ethanol at ambient temperature (25 ^{O}C), while DMF was the solvent used for molar conductivity measurements .Heat of formations and steric energies of products in addition to the geometry (three dimensional structure) of complexe (II) at minimized energy (MM2) were established by Chem3D Ultra; Molecular Modeling and Analysis.

Preparation of Complexes:[3]:

A mixture of the ligand (4-AAP)(0.378 gm,20m.mole) for the 1:2 molar ratio (0.567 gm, 30m.mole) for the 1:3 molar ratio and the Co (II), Ni (II) and Cu (II) salt (10m.mole) was refluxed in absolute ethanol (100ml.) with continuous stirring for two hours.

The solid product formed was filtered off and crystallized from ethanol and dried under vacuum for four hours. These complexes were kept in desiccator containing silica gel. Physical properties and spectral data of the complexes were listed in Table (1).Note that complexes I-VI were soluble in organic solvents: ethanol, methanol, DMF and THF and CHCl3.

Table (1) Physical properties and spectra data of the complexes (I-IV)

Complex No.	Complex formula	M.P. °C	Color	Molecular weight	Selected IR bands (cm^{-1})					UV/Vis λmax (nm)	Conductivity Ohm$^{-1}cm^2mol^{-1}$ DMF solvent	CHN % Theoretical (Calculated)		
												C	H	N
1	$[Co(4\text{-}AAP)_2 H_2O]2Cl_2$	153-4	Pink	570	Pr H_2O 875	Pw H_2O 520	Co-OH_2 400	Co-N 420	Co-O 450	298 401 520	130	46.31 (46.28)	5.26 (5.24)	14.73 (14.70)
II	$[Ni(4\text{-}AAP)_2H_2O]2Cl_2$	147-8	Brown	569.7	Pr H_2O 770	Pw H_2O 680	Ni-OH_2 380	Ni-N 380	Ni-O 410	297 401 487	170	46.34 (46.30)	5.26 (5.25)	14.74 (14.72)
III	$[Cu(4\text{-}AAP)_2 H_2O]2Cl_2$	152-3	Pale brown	574.5	Pr H_2O 950	Pw H_2O 590	Cu-OH_2 430	Cu-N 330	Cu-O 380	401	140	45.95 (45.91)	5.22 (5.20)	14.62 (14.58)
IV	$[Co(4\text{-}AAP)_3]Cl_2$	173-4	Pink	736	Co-O 420			CO-N 360		296 382 468	150	53.80 (53.77)	5.29 (5.21)	17.11 (17.09)
V	$[Ni(4\text{-}AAP)_3]Cl_2$	152-3	Brown	735.7	Ni-O 400			Ni-N 370		291 382 466	180	53.82 (53.80)	5.30 (5.27)	17.12 (17.10)
VI	$[Cu(4\text{-}AAP)_3]Cl_2$	182-3	Pale brown	740.5	Cu-O 400			Cu-N 350		464	150	53.47 (53.43)	5.26 (5.25)	17.01 (17.00)

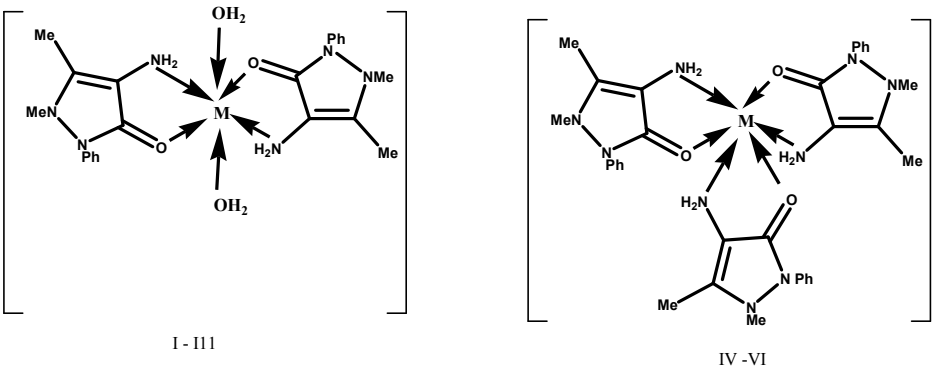
Results and Discussion:

The molecular formula of these complexes were proved by CHN analysis in addition to the IR and UV spectra.

UV Spectra data for these complexes Table (1) showed absorption bands attributed to 4-AAP in its complexes, these bands appeared in the region (560-564nm) which are attributed to $\pi \longrightarrow \pi^*$ electronic transition in the pyrazoline ring of the 4-AAP ring. $\pi \longrightarrow \pi^*$ electronic transition in both NH_2 and exocyclic carbonyl groups and $n \longrightarrow \pi^*$ electronic transition in the NH2 group respectively [6].

The only one brood band with the cupper complex was appeared due to the two electrons transfer which indication of irregular octahedral because of Jane Teler effect [6-7]. On the other hand, the decrease (25-60cm^{-1}) in the exocyclic C=O value on going from the free legend to its complexes IR spectrum was provided an additional support for this value which was strongly involved in the
coordination with metal salts[8-9].The molar conductance measurements in 10^{-3} M DMF and EtOH solutions showed 1:3 conductance indicating the electrolytic nature for all complexes [10-11].

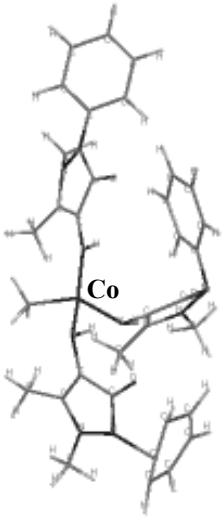
Ligand 4-AAP can coordinate with MCl_2[M = Co(II), Ni(II) and Cu(II)] in a bidentat fashion via N-amine and O-exocyclic carbonyl atoms(as the most reactive site of the legends) in 1:2 molar ratio forming with the water eight membered chelate rings and in 1:3 molar ratio forming eight membered chelate rings Scheme (1) .



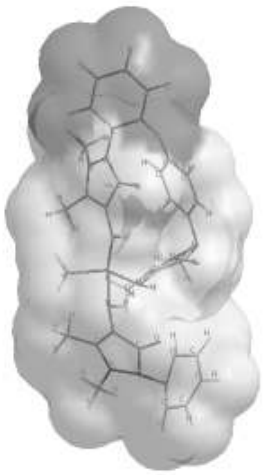
I - I11 IV -VI

Scheme (1)
The model of metal complexes

The characterization and inference of geometrical optiminization by computing the minimum steric energy and the heat of formations was accepted with literature's calculations[12Rappe et al-1997 and 13Allen et al-1991] .Computational configuration of complex(IV) ,which was chose as representative for these complexes was showed in Scheme(2), A computer - generated representation of the octahedral geometry (three dimensional structure) of complex (IV) has been minimized with the MM2 force field, and was drawn by Chem 3D Ultra, Molecular Modeling and Analysis Version 8.0.3



(a)



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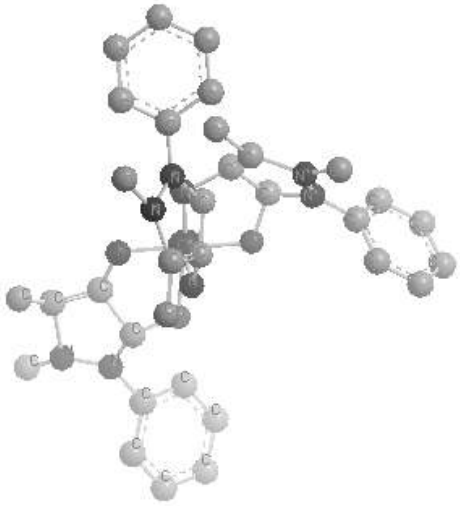

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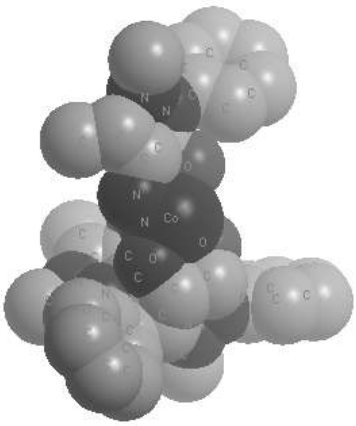

(d)

Scheme (2)

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