

The template synthesis, spectral characterization and thermal behaviour of new binuclear Schiff base complexes derived from *N*-aminopyrimidine with 2,3-butandion

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Abstract: A new series of two types of acyclic binuclear Schiff base complexes, prepared by the template condensation of *N*-aminopyrimidine and 2,3-butandion in the presence of Cu(II), Ni(II), Co(II) and Zn(II) in *n*-BuOH solution, were analyzed and characterized by elemental analyses, IR and electronic spectroscopy, conductivity and magnetic measurements. From the conductivity measurements, it is concluded that the complex of Ni^{II} is a 1:1 type of electrolyte. All the complexes have sub-normal magnetic moments in accordance with their binuclear nature. The thermal behaviour of the complexes was studied by thermogravimetry.

Keywords: acyclic Schiff base complexes, Cu(II), Co(II), Ni(II), Zn(II) template synthesis.

INTRODUCTION

The synthesis of cyclic and acyclic organic substrates which preferentially interact with particular metal ions is of fundamental importance in many areas of chemistry.^{1,2} The majority of the ligand systems employed in model studies are derived from Schiff bases.³ Amino heterocycles containing two or more potential donor centers play an important role in the study of competitive reactivity of ambidentate ligand systems.⁴ Moreover, transition complexes containing an imidazole or pyrimidine ligand are commonly found in biological studies and play important roles in processes, such as catalysis of drug interaction with biomolecules.^{5–7} Recently, the synthesis and characterization of heterocyclic Schiff base complexes obtained from *N*-aminopyrimidine was reported.^{8–11}

In this paper, recent research on the template reactions of *N*-amino pyrimidine-2-one with 2,3-butandion in the presence of copper(II), nickel(II), cobalt(II) and zinc(II) ions a result of (2+1+2) Schiff base condensation complexes is re-

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ported. New binucleating complexes were obtained and characterized by elemental analyses, UV-VIS and IR spectroscopy, magnetic measurements, and thermogravimetry.

EXPERIMENTAL

Materials

All solvents and 2,3-butandion were obtained from Fluka and Aldrich. The metal salts $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were obtained from Merck. All solvents were dried and purified before use. *N*-Aminopyrimidine (1-amino-5-benzoyl-4-phenyl-1*H* pyrimidine-2-one) was prepared as described in the literature.¹²

Physical measurements

Elemental analyses (C, H, N) were performed using a Carlo Erba 1106 elemental analyser. Chlorine was determined gravimetrically as AgCl . The IR spectra were recorded using the KBr disc technique ($4000\text{--}400$) cm^{-1} on a Bio-Rad-Win-I.R. spectrophotometer. The electronic spectra in the range $200\text{--}900$ nm range were obtained in DMF on a Unicam UV2-100 UV/VIS spectrophotometer. Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. Molar conductances of the Schiff base metal complexes were in DMF at room temperature using a Jenway model 4070 conductimeter. Non-isothermal TG curves of the complexes (5 ± 8 mg) were recorded on a Shimadzu-50 thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ between 25°C and 800°C under a N_2 atmosphere.

Preparation of the Schiff base complexes

1-Amino-5-benzoyl-4-phenyl-1*H* pyrimidine-2-on (AP) (0.582 g (2 mmol)), was dissolved in 30 cm^3 of CHCl_3 , and a solution of 0.1 cm^3 (1 mmol) of 2,3-butandion in 20 cm^3 *n*-BuOH was added dropwise with continuous stirring. To this a solution of the metal salt (1 mmol) [$\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (0.20 g), $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.25 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g) and $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g)] in 20 cm^3 *n*-BuOH in the presence of sodium acetate was added dropwise with constant stirring and the mixture was boiled under reflux for 3–6 h. Then, the volume of the reaction mixture was reduced to 15 cm^3 by rotary evaporation. The precipitated complexes were filtered off, washed with Et_2O , followed by a cold 1:1 CHCl_3 / EtOH mixture and then dried *in vacuo*.

RESULTS AND DISCUSSION

The template condensation of 1-amino-5-benzoyl-4-phenyl-1*H*-pyrimidine-2-one ($\text{L}'\text{H}_2$) and 2,3-butandion ($\text{L}''\text{O}_2$) in the presence of $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ produced 4 new binuclear metal complexes of the type $[(\text{M})_2(\text{APB})_2(\text{X})_4] \cdot n\text{H}_2\text{O}$ as shown in Fig. 1. The newly synthesized binuclear Schiff base complexes are very stable at room temperature in the solid state. The metal complexes are generally soluble in DMF and DMSO. The elemental analytical data of the complexes revealed that the compounds have a metal:ligand stoichiometry of 1:1, corresponding to the general formulae $[(\text{M})_2(\text{APB})_2(\text{X})_4] \cdot n\text{H}_2\text{O}$. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The colours, yields, melting points, IR and electronic absorption spectral data of all the compounds are presented in Table I and Table II. All the complexes were of a non-electrolyte type, as the measured conductivities were in the range $5.1\text{--}9.5\text{ S cm}^2\text{ mol}^{-1}$, except for the Ni(II) complex ($74.1\text{ S cm}^2\text{ mol}^{-1}$). The molar conductance value of the Ni(II) com-

plex in DMF was in good agreement with a 1:1 electrolyte. The conductance value indicates that the coordinated chloro group is replaced by solvent molecules.¹³

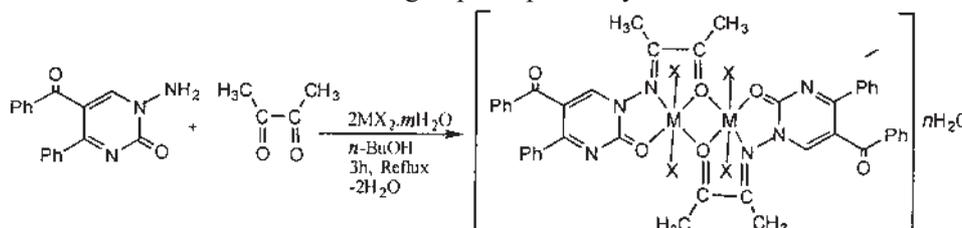


Fig. 1. Suggested structures of the binuclear complexes.

TABLE I. Analytical and physical data of the complexes

Compounds	Color	M.p. °C	Yield %	μ_{eff} μ_{B}	Found (Calcd.)/%			λ_{M} S cm ² mol ⁻¹
					C	H	N	
(1) [Cu ₂ (APB) ₂ (AcO) ₄]·5.5H ₂ O	Light brown	220	82	1.59	51.2	4.1	7.8	9.5
C ₅₀ H ₅₇ N ₆ O ₁₉ Cu ₂ (1180.08 g/mol)				(50.8)	(4.8)	(7.5)		
(2) [Co ₂ (APB) ₂ (AcO) ₄]·H ₂ O	Milk brown	244	70	2.82	55.3	4.3	7.9	5.6
C ₅₀ H ₄₈ N ₆ O ₁₅ Co ₂ (1089.86 g/mol)				(55.0)	(4.4)	(7.7)		
(3) [Ni ₂ (APB) ₂ Cl ₄]·4H ₂ O	Yellow	213	63	1.83	48.3	4.3	8.4	74.1
C ₄₂ H ₄₂ N ₆ O ₁₀ Cl ₄ Ni ₂ (1049.22 g/mol)				(48.0)	(4.0)	(8.0)		
(4) [Zn ₂ (APB) ₂ (AcO) ₄]·4H ₂ O	Dark brown	237	85	D	51.7	4.7	7.0	5.1
C ₅₀ H ₅₄ N ₆ O ₁₈ Zn ₂ (1156.00 g/mol)				(51.9)	(4.6)	(7.2)		

IR Spectra

In all the complexes, no peaks corresponding to unreacted primary amines or carbonyl groups were present. The most relevant IR absorption bands from the spectra of the complexes, along with their assignments, are given in Table II. All the complexes show a strong absorption band in the region 1600–1610 cm⁻¹, attributable to the azomethine groups. This observation indicates the condensation of carbonyl and amino groups with the involvement of the nitrogen atom of the azomethine $\nu(\text{C}=\text{N})$ group in the complexes.^{8–11} As a general remark, a broad band in the range 3290–3500 cm⁻¹ was observed in the spectra of all the complexes. This band may be assigned to water molecule –OH stretching vibrations. The spectrum of all the complexes displays $\nu(\text{C}-\text{O})$ at 1485–1580 cm⁻¹ indicating the presence

of bridging ketonic oxygen atoms. The bands in the range 417–444 and 520–530 cm^{-1} range are assigned to the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibration modes, respectively.^{8–11,14}

TABLE II. Characteristic IR and electronic absorption spectral data of all the metal complexes

Compounds	OH/H ₂ O	C=N	C=O-M	M-N	M-O	M-AcO	$\lambda_{\text{max}}(\epsilon_{\text{max}}/\text{M}^{-1} \text{cm}^{-1})$
(1)	3421 <i>m,br</i>	1600 <i>s</i>	1581 <i>m</i>	502 <i>w</i>	430 <i>w</i>	1548 <i>m</i>	763 (30), 490 (902), 380 (1140), 325 (1570)
(2)	328 <i>w,br</i>	1610 <i>s</i>	1580 <i>m</i>	529 <i>w</i>	425 <i>w</i>	1540 <i>m</i>	503 (54), 460 (254), 429 (1816)
(3)	3410 <i>m,br</i>	1610 <i>m</i>	1581 <i>m</i>	520 <i>w</i>	431 <i>w</i>	-	571 (42), 483 (660), 440 (690), 329 (3828)
(4)	3430 <i>m,br</i>	1606 <i>s</i>	1581 <i>m</i>	528 <i>w</i>	417 <i>w</i>	1554 <i>m</i>	359 (2680), 322 (3200)

s = Strong, *m* = medium, *w* = weak, *br* = broad

Magnetic moments and electronic spectra

The electronic spectra of all the complexes were recorded in DMF. The electronic spectrum of the copper(II) complex shows only two weak d-d. transitions at 490 and 765 nm. The room temperature magnetic moment of $1.59 \mu_{\text{B}}$ Cu atom for $[\text{Cu}_2(\text{APB})_2(\text{AcO})_4] \cdot 5.5\text{H}_2\text{O}$, indicates that, as expected, magnetic exchange occurs between the two copper sites. On the basis of the magnetic data, the copper(II) complex probably has a binuclear structure with ketonic oxygen bridges. The copper(II) complex with L'H₂ and L'O₂, a tridentate, has been found to have two acetate groups in the coordination sphere.¹¹

The electronic spectra of the cobalt(II) showed rather *d-d* transition in the visible region of the spectrum. The bands at 460 and 503 nm may be assigned to ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ and ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}$ transitions as expected for a cobalt(II) octahedral complex.¹⁵ The magnetic moment value, $2.82 \mu_{\text{B}}$ (300 K) per Co atom obtained for the milk-brown complex was in the range expected for an octahedral complex.

The $[\text{Ni}_2(\text{APB})_2\text{Cl}_4] \cdot 4\text{H}_2\text{O}$ complex shows two absorption bands at 571 and 483 nm which are attributed to ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$ and ${}^3\text{T}_{1\text{g}}(\text{P})$ transitions, respectively, on the basis of an octahedral geometry. The complex is also paramagnetic with a low μ_{eff} value ($1.83 \mu_{\text{B}}$ per nickel) at room temperature. This may be caused by a strong nickel-nickel interaction. The magnetic moment value for the nickel(II) complex fall in the range usually observed for octahedral nickel(II) complexes.

Thermal analysis

The thermal decomposition of all complexes was investigated (Table III). The TG curves indicate that the decomposition is a multiple step process and that the final residual weight corresponds to the metal oxide. The copper(II) complex was stable up to 38 °C after which its decomposition started and was complete at 578 °C. The copper(II) complex decomposed and produced 2CuO as the residue in five

steps in the temperature ranges 38–205, 205–260, 260–335, 335–362, 362–578 °C, corresponding to the loss of 5.5H₂O, 2CH₃COO, 2CH₃COO, 2L''O and 2L', respectively. The nickel(II) complex was stable up to 35 °C after which its decomposition started and was completed at 575 °C. The nickel(II) complex decomposed and produced 2NiO as the residue in three steps in the temperature ranges 35–90, 90–414, 414–576 °C, corresponding to the loss of 4H₂O, 4Cl and 2L''O and 2L', respectively. The cobalt(II) complex was stable up to 34 °C after which its decomposition started and was completed at 496 °C. The cobalt(II) complex decomposed and produced Co₂O₃ as the residue in three steps in the temperature ranges 34–117, 117–262 and 262–496 °C, corresponding to the loss of H₂O, 2CH₃COO and 2CH₃COO, 2L''O and 2L', respectively. The zinc(II) complex was stable up to 32 °C after which its decomposition commenced and was completed at 612 °C. The zinc(II) complex decomposed and produced 2ZnO as the residue in four steps in the temperature ranges 33–192, 192–301, 301–455 and 455–612 °C, corresponding to the loss of 4H₂O, 2CH₃COO, 2CH₃COO and 2L''O and 2L', respectively.

TABLE III. Thermogravimetric data of the complexes [Weight loss, %; Found (Calculated)]

Compounds	First. step	Second step	Third step	Fourth step	Fifth step	Residue
	°C	°C	°C	°C	°C	Found (Calcd.)/%
(1)	38–205 8.30 (8.38)	205–260 9.80 (10.00)	260–335 10.10 (10.00)	335–362 13.02 (14.57)	362–578 45.87 (43.57)	13.01 (13.48) CuO 86.99 (86.52)*
(2)	34–117 1.60 (1.65)	117–262 13.33 (12.83)	262–496 68.57 (70.22)	–	–	16.50 (15.30) Co ₂ O ₃ 83.50 (84.70)*
(3)	35–90 6.20 (6.86)	90–414 30.25 (29.54)	414–575 49.83 (49.36)	–	–	13.72 (14.24) NiO 86.28 (85.76)*
(4)	33–192 6.20 (6.23)	192–301 11.00 (10.21)	301–455 23.80 (24.74)	455–612 45.61 (44.74)	–	13.39 (14.08) XnO 86.61 (95.92)*

* Total values

Single crystals of the complexes could not be isolated from any common solvent, thus no definitive structure can be described. However, the analytical, spectroscopic, magnetic and TG data enabled the production of the possible structures, as shown in Fig. 1. On the basis of the type [(M)₂(APB)₂(X)₄].nH₂O, the ligand is attached to the metal ions at two coordination sites involving azomethine nitrogen and carbonyl oxygens. The binuclear M(II) complexes with AP as a tridentate ligand contained two acetate or chloro groups in the coordination sphere per metal atom. All the metal complexes have a binuclear octahedral configuration.

ИЗВОД

ТЕМПЛАТНА СИНТЕЗА, СПЕКТРАЛНА КАРАКТЕРИЗАЦИЈА И ТЕРМИЧКО ПОНАШАЊЕ НОВИХ БИНУКЛЕАРНИХ КОМПЛЕКСА ШИФОВИХ БАЗА ИЗВЕДЕНИХ ИЗ *N*-АМИНОПИРИМИДИНА СА 2,3-БУТАНДИОНОММЕHMET SÖNMEZ^a и MEMET ŞEKERCI^b^aDepartment of Chemistry, Faculty of Science and Arts, Yüzüncü Yıl, University, 65080, Van, Turkey u ^bDepartment of Chemistry, Faculty of Science and Arts, Firat University, 23169, Elazığ, Turkey

Темплатном кондензацијом *N*-аминопириимидина и 2,3-бутандиона у присуству Cu^{II}, Ni^{II}, Co^{II} и Zn^{II} у *n*-BuOH припремљена је нова серија два типа динуклеарних комплекса ацикличних Шифових база, анализираних и окарактерисаних елементалном анализом, IR, електронским спектралним подацима, магнетним мерењима и мерењима проводљивости. Мерењем проводљивости закључено је да комплекс Ni(II) припада 1:1 типу електролита. Сви комплекси имали су ниже вредности магнетних момената у складу са њиховом динуклеарном природом. Термичко понашање комплекса је проучавано TG техником.

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