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Template Synthesis of Fe(III) and Cr(III) Acyclic Complexes Derived from Diacetyl or Benzil and 1-Amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one

Mehmet Sönmez [a]
[a] Department of Chemistry, Faculty of Science and Arts , Yüzüncü Yil University , 65080, Van, Turkey

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Template Synthesis of Fe(III) and Cr(III) Acyclic Complexes Derived from Diacetyl or Benzil and 1-Amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one

Mehmet Sönmez*

Department of Chemistry, Faculty of Science and Arts,
Yüzüncü Yil University, Van, Turkey

ABSTRACT

The template synthesis of diacetyl or benzil and 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one in the presence of Fe(III) and Cr(III) results in the formation of acyclic complexes of the types $[ML^1X_2]X$, $[ML^2X_2]X$, and $[Fe_2(L^1)_2Cl_4]Cl_2 \cdot H_2O$, where M = Fe(III), Cr(III), L^1 (benzyl derivative), or L^2 (diacetyl derivative) are N_2O_2/ONO acyclic ligands and X = Cl, NO_3). The complexes have been characterized by elemental analyses, molar conductance, magnetic measurements, IR, and UV/VIS spectral studies.

Key Words: Acyclic complexes; Template synthesis; Ligands; Schiff base complexes.

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[*] Correspondence: Mehmet Sönmez, Department of Chemistry, Faculty of Science and Arts, Yüzüncü Yil University, 65080, Van, Turkey; E-mail: vansonmez@hotmail.com.

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INTRODUCTION

There has been considerable interest among coordination chemists in studying the synthesis, structures, magnetic, and biological properties of acyclic and macrocyclic metal complexes.[1−3] Template reactions lie at the heart of macrocyclic or acyclic chemistry. Condensation reactions between dicarbonyls and primary diamines have played an important role in the development of synthetic acyclic and macrocyclic ligands and their metal complexes.[4,5] Furthermore, ligands containing heterocyclic rings are known to be biologically active.[6−8] Some study groups have reported the synthesis and characterization of acyclic and macrocyclic metal complexes derived from α- or β-diketones and various diamine compounds.[4,9,10] However, acyclic complexes derived from more rigid molecules such as α- or β-diketones and *N*-aminopyrimidine have not been reported so far. Several Schiff base complexes of *N*-amino pyrimidine-2-one have been synthesized in our laboratory.[11,12]

In this paper, we report the preparation and characterization of mononuclear and binuclear acyclic complexes with Fe(III) and Cr(III).

EXPERIMENTAL

Materials and Methods

MeOH, EtOH, BuOH, $CHCl_3$, DMF, toluene, diethyl ether, *n*-heptane benzil, and diacetyl were obtained from Fluka or Aldrich. The metal salts, $FeCl_3 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$, were obtained from E. Merck. All solvents were dried and purified before use. 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one were prepared as described previously.[13]

Elemental analyses (C, H, N) were performed by using a Carlo Erba 1106 elemental analyzer. The IR spectra were obtained using KBr discs (4000–400) cm^{-1} on a Bio-Rad-Win-IR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained in DMF on a Unicam UV2-100 UV/Visible spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the acyclic Schiff base metal complexes were determined in DMF at room temperature using a Jenway model 4070 conductivity meter.

Preparation of the Schiff Base Complexes

1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one (0.582 g, 2 mmol) was dissolved in 30 mL of *n*-butanol, and a solution of 0.1 mL (1 mmol) of

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diacetyl or 0.210 g (1 mmol) benzil in 20 mL *n*-butanol was added drop-wise with continuous stirring. To this was added drop-wise a solution of 1 mmol of the metal salt [$FeCl_3 \cdot 6H_2O$ (0.270 g) and $Cr(NO_3)_3 \cdot 9H_2O$ (0.400 g)] in 20 mL *n*-butanol with constant stirring and the mixture was boiled under reflux for 3–6 hr. At the end of the reaction, the volume was then reduced to 10 mL by rotary evaporation. The precipitated complexes were filtered, washed with dry diethyl ether, followed by cold chloroform or ethanol, and dried in a vacuum desiccator.

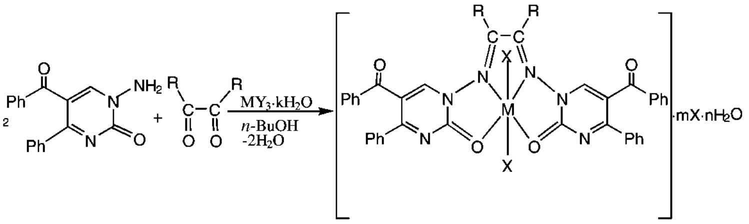
RESULTS AND DISCUSSION

The template condensation of 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one[13] and benzyl or diacetyl in the presence of $FeCl_3 \cdot H_2O$ and $CrCl_3 \cdot 4H_2O$ produced new tetradentate acyclic mononuclear or tridentate binuclear metal complexes of the types $[MLX_2]X \cdot nH_2O$ and $[Fe_2(L_1)_2Cl_4]$-$Cl_2 \cdot H_2O$ as shown in Figs. 1 and 2.

The newly synthesized Schiff base complexes are very stable at room temperature in the solid state. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The colors, yields, melting points, electronic, and IR absorption spectral data of all the compounds are presented in Tables 1–3.

Infrared Spectra

Important IR bands of the acyclic complexes are given in Table 2. All the acyclic complexes show a strong band in the region 1600–1625 cm^{-1}



	M	R	Y	X	k	m	n
(2)	Fe	Me	Cl	Cl	6	1	2
(3)	Cr	Ph	NO_3	NO_3	9	1	3
(4)	Cr	Me	NO_3	NO_3	9	1	1

Figure 1. Scheme for the preparation of the acyclic Schiff base complexes (**2**)–(**4**).

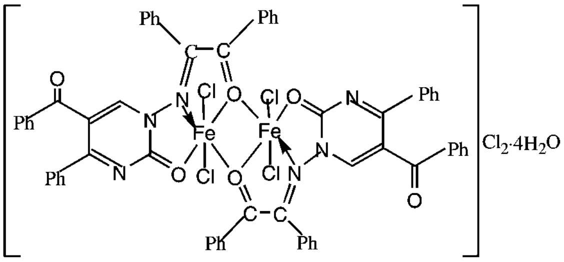


Figure 2. Suggested structure of the Fe(III) complex (**1**) of the ligand derived from benzil.

attributable to the coordinated (C=N) azomethine group and indicating the condensation of the carbonyls of benzil or diacetyl and the amino groups of 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one. The spectrum shows other bands at ~1660, ~3060, and 1580 cm^{-1} assigned to ν(C=O), the pyrimidine ring, and ν(Ar-C=O–M), respectively.[12,14] The nitrate complexes exhibit intense absorption bands at ~1515, ~1270, and 950–1020 cm^{-1} assigned to unidentate coordinated nitrate while free nitrate absorptions appear[14] at 1380–1400, 810–820, and 720–730 cm^{-1}. In the chloro complexes a band at ~400 cm^{-1} is observed which may be assigned to the coordinated chloro group. The IR spectra of all the complexes show absorption bands in the region 3200–3400 cm^{-1}, indicating the presence of water molecules. The spectra of all the complexes show two absorptions in the far-infrared region at 427–460 cm^{-1} and 500–524 cm^{-1}, which are assignable to ν(M–N) and ν(M–O), respectively.[14]

Electronic Spectra and Magnetic Measurements

The electronic spectral data for the compounds are shown in Table 3. The spectra were recorded in DMF as solvent. In the spectrum of the N_2O_2 tetradentate and ONO tridentate acyclic Schiff base complexes, the band of 390 nm is attributed to the azomethine group of the free ligand $\pi \rightarrow \pi^*$ transition. The bands at 300–235 nm are associated with the pyrimidine ring $\pi \rightarrow \pi^*$ transition.[11,12,16] In the spectra of the complexes, the band of the azomethine chromophore $\pi \rightarrow \pi^*$ transition is shifted to about 330–370 nm indicating that the imino nitrogen is involved in coordination to the metal ion.

The magnetic moment values of the Cr(III) complexes are 3.90 and 3.68 B.M. which is in good agreement with the presence of three unpaired

Table 1. Analytical and physical data of the complexes.

No	Compounds	Color	M.p. (°C) (dec.)	Yield (%)	Elemental analyses, found (calcd.)		
					C	H	N
(**1**)	$[Fe_2(L^1)_2Cl_4]Cl_2 \cdot 4H_2O$ $C_{62}H_{50}Cl_6Fe_2N_6O_{10}$ (1362.68 g/mol)	Brown	108	69	53.9 (54.5)	3.9 (3.6)	6.4 (6.1)
(**2**)	$[Fe(L^2)Cl_2]Cl \cdot 2H_2O$ $C_{38}H_{32}Cl_3FeN_6O_6$ (830.19 g/mol)	Red-brown	265	61	55.0 (54.5)	4.1 (3.8)	9.7 (10.1)
(**3**)	$[Cr(L^1)(NO_3)_2]NO_3 \cdot 3H_2O$ $C_{48}H_{38}CrN_9O_{16}$ (1048 g/mol)	Green	340	70	55.0 (54.9)	3.3 (3.6)	11.8 (12.0)
(**4**)	$[Cr(L^2)(NO_3)_2]NO_3 \cdot H_2O$ $C_{38}H_{30}CrN_9O_{14}$ (888 g/mol)	Dark green	<370	57	51.4 (51.3)	3.7 (3.3)	13.7 (14.1)

Table 2. Characteristic IR spectral data of the ligand and their metal complexes.

Compounds	H_2O	C=O	C=N	Ar–C=O–M	$M–NO_3$	M–Cl	M–N	M–O
(**1**)	3,280–3,410 br	1,663 s	1,620 s	1,266 m	—	405 w	427 w	520 w
(**2**)	3,217 w, br	1,658 m	1,600 s	1,260 m	978–1,273 1,477 m, w	—	442 w	524 w
(**3**)	3,248 w, br	1,659 m	1,623 s	1,272 m	—	410 w	448 w	505 w
(**4**)	3,229 w	1,660 s	1,598 s	1,270 m	950–1,270 1,510 m, w	—	460 w	522 w

Table 3. Molar conductance, magnetic and electronic absorption spectral data of all the compounds.

Compounds	μ_{eff} [B.M.]	Λ_M ($S\,cm^2\,mol^{-1}$)	λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$)
(**1**)	3.86	54.8	712 (21), 595 (38), 504 (89), 378 (3,540)
(**2**)	5.86	30.6	705 (13), 594 (57), 510 (112), 365 (3,602)
(**3**)	3.90	30.1	595 (40), 468 (1,630), 380 (4,900)
(**4**)	3.68	25.6	610 (21), 478 (1,700), 370 (5,200)

electrons. The electronic spectrum of these complexes exhibits two bands at 595–610 and 468–478 nm assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (F), respectively, suggesting an octahedral environment around chromium(III). The magnetic moment measurements of the Fe(III) complex (**1**) shows a magnetic moment of 3.86 B.M. which is abnormally small and consistent with a dimeric structure (Fig. 2), whereas the magnetic moment for the Fe(III) complex (**2**) is 5.86 B.M. which is monomeric and high-spin at room temperature. The electronic spectrum of these complexes displays three bands around 714, 594, and 505 nm, which may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4A_{1g}$, E_g, respectively. From the electronic and magnetic studies, it is evident that the Fe(III) complexes possess a high-spin octahedral configuration.[15,17]

Conductivity

Molar conductance values of 10^{-3} M solutions ($M = mol\,dm^{-3}$) of the complexes in DMF are in the range of 25.6–54.8 $\Omega^{-1}\,cm^2\,mol^{-1}$ indicating their slightly polar nature due to the electrolytic behavior of chlorine or nitrate in all of the complexes.[16] The molar conductance values indicate that complexes (**2**)–(**4**) have 1 : 1 stoichiometry whereas the $[Fe_2(L^1)_2Cl_4]$-$Cl_2 \cdot H_2O$ complex (**1**) is formed in 1 : 2 ratio. The complexes (**2**)–(**4**) include one additional chloride or nitrate anion. On the other hand, the complex (**1**) includes two additional chloride anions. All of these complexes are electrolytic in nature confirming the ionic nature of the chloride or nitrate anions.

CONCLUSIONS

From the above spectral studies and elemental analyses, the following structures (Figs. 1 and 2) have been proposed showing the mode of chelation. The Cr(III) complexes and the Fe(III) complex (**2**) are of mononuclear octahedral configuration while the Fe(III) complex (**1**) exist in a binuclear octahedral form.

REFERENCES

1. Tenor, E.; Ludwig, R. Bioactivity of copper and zinc complexes of Schiff bases derived from salicylaldehyde or acetylacetone. Pharmazie **1971**, *26*, 534–539.
2. Kotočová, K.; Šima, J. Electrochemical behaviour of a series of Fe(III) complexes with tetradentate Schiff base ligands. Monatsh. Chem. **1994**, *125*, 491–495.
3. Vincent, J.B. The bioinorganic chemistry of chromium(III). Polyhedron **2001**, *20*, 1–26.
4. Rai, P.K.; Prasad, R.N. Cr(III), Fe(III), and Co(II) complexes of tetraazamacrocycles derived from 2,3-butanedione or benzyl and 1,8-diamino-3,6-diazaoctane. Monatsh. Chem. **1994**, *125*, 385–394.
5. Abu Ismaiel, A.A.; Baraka, R.M.; Nasman, O.S.M. Template synthesis and characterization of mono, and homobinucleating mixed dithiatetraazamacrocyclic complexes. Polyhedron **2001**, *20*, 455–459.
6. Hussain, M.; Al-Afaj, A.; Hossain, L. Recent studies of some pyridine, pyrimidine and imidazole complexes. Transition Met. Chem. **1990**, *13*, 264–270.
7. Mishra, L.; Tiwari, L.B.; Pandey, H.N.; Upadhyay, V.; Agarwala, U.C. Metal chelates as fungicides: Part IV. Metal(II) complexes of 4-chloro-5,6,7,8-tetrahydrobenzothieno(2,3-d)pyrimidine. Indian J. Chem. Sect. A **1988**, *27*, 742–744.
8. Salas, J.M.; Romero, M.A.; Sánchez, P.; Quirós, M. Metal complexes of [1,2,4]-triazolo-[1,5,a]-pyrimidine derivatives. Coord. Chem. Rev. **1999**, *193*, 1119–1142.
9. Chen, Y.W.D.; Bard, A.J. Electrochemical and spectrophotometric studies of iron complexes with a pentaaza macrocyclic ligand. Inorg. Chem. **1984**, *23*, 2175.
10. Gerli, A.; Sabat, M.; Marzilli, L.G. Lariat-type B12 model complexes. 1. New pendant methylpyridyl costa-type organocobalt complexes provide insight into the role of the axial ligand in butterfly bending and redox properties. J. Am. Chem. Soc. **1992**, *114*, 6711–6718.

11. Sönmez, M.; Şekerci, M. Synthesis and characterization of Cu(II), Co(II), Ni(II), and Zn(II) Schiff base complexes from 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one with salicylaldehyde. Polish J. Chem. **2002**, *76*, 907–914; Chem. Abstr. **2002**, *137*, 225,752.
12. Sönmez, M. Synthesis and spectroscopic studies of Cu(II), Co(II), Ni(II), and Zn(II) Schiff base complexes from 1-amino-5-benzoyl-4-phenyl-1H-pyrimidine-2-one with 2-hydroxynaphthaldehyde. Polish J. Chem. **2003**, *77*, 397–402; Chem. Abstr. (Accession no) 2003, 292,112.
13. Akçamur, Y.; Altural, B.; Saripinar, E.; Kollenz, G. A simple synthesis of functionalized 1H pyrimidines, reaction of cyclic oxalyl compound. Monatsh. Chem. **1989**, *120*, 1015–1020.
14. Bellamy, L.J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1978.
15. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.
16. Geary, W.J. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord. Chem. Rev. **1971**, *7*, 81.
17. Figgis, B.N.; Lewis, J. *Progres in Inorganic Chemistry*; Wiley Interscience: New York, 1964; Vol. 6.

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