Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4433-4437

Synthesis and Characterization of Urea Schiff Base Chelates of Cr(III), Cr(VI), TiO(IV) and Pb(II)

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New four Schiff base complexes derived from salicylaldehyde and urea have been prepared and characterized. The elemental analysis data show the formation of 1:1 [M:L] chelates. The molar conductance values of the prepared chelates reveal a non-electrolytic nature. The magnetic moment values exhibit the existence of three unpaired electrons in the Cr(III) chelate and diamagnetic phenomena for the other chelates. The infrared spectral data display the coordination sites of bonding of the Schiff base towards the metal ions under investigation. The electronic spectral data of the Schiff base and its chelates show $\pi \rightarrow \pi^*$ (phenyl ring), $n \rightarrow \pi^*$ (HC=N) and the expected geometrical structures. The electron paramagnetic resonance spectral data satisfy the presence of a paramagnetic phenomena and support the expected geometrical structure of Cr(III) chelate.

Key Words: Urea Schiff base, Chelates, Cr(VI), Cr(III), TiO(IV) and Pb(II).

INTRODUCTION

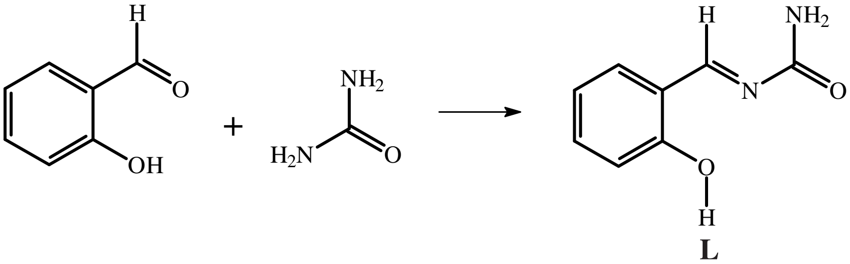
The synthesis and characterization of Schiff base complexes[1-6] have been prompted that the systematic characterization of these complexes may throw light on the nature of the free ligand environment. Boghaei *et al.*[7] prepared and characterized novel non-symmetrical Ni(II) and Cu(II) ions tetradentate Schiff base complexes with N_2O_2 and N_2O donor sites.

The present investigation aims to prepare a Schiff base (derived from the reaction of salicylaldehyde and urea), chelates of Cr(VI), Cr(III), TiO(IV) and Pb(II) ions and characterization the geometrical structures of the prepared chelates by using different techniques.

EXPERIMENTAL

All chemicals used in this investigation were reagent grade of BDH or Aldrich including CrO_3, $CrCl_3\cdot 6H_2O$, $TiOSO_4$, $Pb(NO_3)_2$, NH_4OH, C_2H_5OH, $CHCl_3$, DMSO, salicylaldehyde, urea and double distilled water.

Preparation of Schiff base: The Schiff base used was prepared by mixing an ethanolic solution (30 mL of 1.22 g; 0.01 mol) of salicylaldehyde (0.60 g; 0.01 mol) of urea in the same volume of ethanol. Few drops of dil. HCl were added to adjust pH = 4 and the obtained mixture then refluxes with stirring for 2 h. The precipitate was collected by filtration through Buchnner funnel, recrystallized from ethyl alcohol and dried at ambient temperature with 70 % yield.



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Preparation of chelates: The chelates under investigation were prepared by mixing 30 cm^3 ethanolic solution of the Schiff base (2.64 g; 0.01 mol) with the same amount of ethanolic solution of the metal salts (0.01 mol); CrO_3 (1.00 g), $CrCl_3{\cdot}6H_2O$ (1.66 g), $TiOSO_4$ (1.62 g) and $Pb(NO_3)_2$ (3.42 g). If the chelates did not isolate, few drops of ammonium hydroxide were added to adjust the pH = 8. The reaction mixture was refluxed with stirring for 3 h and then filtered, collected and then washed several times with hot ethanol until the filtrate becomes colourless. The chelates were dried in desiccators over anhydrous $CaCl_2$ under vacuum.

The synthesized Schiff base and its chelates were subjected to elemental analyses. The molar conductivity measurements were carried out in DMF solvent using conductivity meter model CMD650 digital. The magnetic moment measurements of the chelates were measured by using magnetic susceptibility balance Sherwood Scientific England. Infrared spectra were obtained by using KBr disk technique on IFS-25 DPUS/Ir spectrometer (Bruker) in the range of 4000-500 cm^{-1}. The electronic absorption spectra of the chelates were measured in chloroform solvent using a Perkin-Elmer lambda 4β spectrophotometer. The electron paramagnetic resonance spectrum of the Cr(III) chelate was recorded by using EMX EPR spectrometer (Bruker) 1998Y at Al-Fateh University, Tripoli, Libya. The rest analysis were done at the Microanalytical Center, Cairo University.

RESULTS AND DISCUSSION

Table-1 suggests that the found data are in a good agreement with those theoretical one and the obtained analytical data indicate the formation of 1:1 [M:L] ratio. The conductance measurements of the prepared chelates were carried out in DMSO solvent. The obtained values of 1:1 [M:L] chelates, Table-1 were taken as a good evidence for the existence of a non-electrolyte nature for Cr(VI), Pb(II) and TiO(IV) chelates[8], except Cr(III) chelate, which is electrolyte. The obtained values show that no inorganic anions (OH^-) are present out side the coordination sphere in Cr(VI), Pb(II) and TiO(IV) chelates and presence of same anion out side the coordination sphere in Cr(III) chelate.

TABLE-1
PHYSICAL DATA OF SCHIFF BASE AND ITS METAL COMPLEXES

Ligand/complexes	m.w.	Calcd. (Found) %			M.C.*	μ_{eff} (BM)
		C	H	N		
$C_8H_8N_2O_2$	164	58.86 (58.05)	4.87 (4.52)	17.07 (17.07)	–	–
$[CrO_3L]\cdot 7H_2O$	390	24.66 (24.71)	5.38 (5.34)	7.18 (7.17)	2.67	Diamag
$[CrL(H_2O)_3]2OH\cdot H_2O$	321	29.90 (30.50)	5.30 (6.30)	8.72 (9.38)	62.63	4.12
$[PbL(OH)(H_2O)_2]\cdot H_2O$	441	21.77 (22.50)	3.17 (4.22)	6.35 (6.34)	9.38	Diamag
$[TiOL(OH)(H_2O)]\cdot H_2O$	279	34.41 (35.21)	4.66 (4.11)	10.04 (10.08)	1.07	Diamag

*Molar conductivity (Ohm^{-1} cm^2 mol^{-1}).

The infrared band assignments of the Schiff base chelates of Cr(VI) Cr(III), TiO(IV) and Pb(II) ions (Table-2) exhibit a broad band in the range of 3364-3200 cm^{-1} corresponding to the presence of water molecules[9]. Meanwhile, the same spectra of the chelates display a band at 1630 cm^{-1} which is due to –C=O group of the urea moiety. The disappearance of this group indicates its involvement in coordination with the metal ions under study[10]. New bands in the range of 532-420 and 683-594 cm^{-1} are assigned to the ν(M-N) and ν(M-O) vibrations[11], respectively. The appearance of these bonds support the involvement of azomethine and hydroxyl groups *via* nitrogen and oxygen atoms. The spectra of $[CrO_3L]\cdot 7H_2O$ and $[TiOL\cdot OH\cdot H_2O]\cdot H_2O$ chelates display two bands at 1030 and 990 cm^{-1}, attributable to (Cr=O) and (Ti=O) bonds[12]. The band in the range of 3221-3016 cm^{-1} indicates that the NH_2 group is not participating in coordination with the metal ions under study[13].

The electronic spectra of the chelates were recorded in chloroform and their assignments are presented in Table-2. The magnetic moment value of the Cr(III) Schiff base chelate (4.12 BM) exhibits the presence of three unpaired electrons in the chelate. The electronic spectral data of the

TABLE-2
INFRARED, ELECTRONIC AND ELECTRON PARAMAGNETIC RESONANCE SPECTRAL DATA OF THE SCHIFF BASE AND ITS COMPLEXES

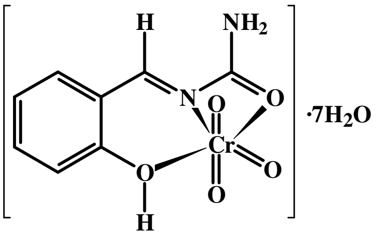
Ligand/complexes	Bands (cm^{-1})									Electronic spectra mm (cm^{-1})	g_{eff}
	ν(OH)H_2O	ν(NH_2)	ν(C=N)	ν(C-O)	ν(C=O)	ν(M=O)	ν(M-O)	ν(M-N)	ν(OH)*		
$C_8H_8N_2O$(L)	3350	3221	1612	1265	1630	–	–	–	–	298 (34602) 328 (30487) 393 (25477)	–
[CrO_3L]·$7H_2O$	3364	3182	1616	1319	–	1030	667	532	2311	291 (34364) 392 (25477)	1.991
[CrL(H_2O)$_3$]2OH·H_2O	3200	3110	1620	1311	–	–	625	498	–	269 (33783) 395 (25348)	–
[PbL(OH)(H_2O)$_2$]·H_2O	3506	3016	1605	1284	–	–	683	540	–	323 (31007) 382 (26178)	–
[TiOL(OH)(H_2O)]·H_2O	3287	3186	1612	1308	–	990	594	420	–	323 (30959	

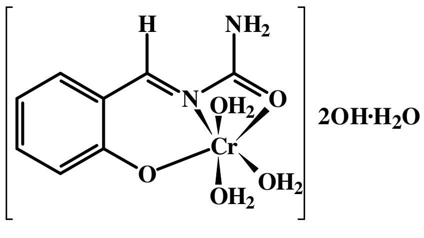
*For coordinate bond

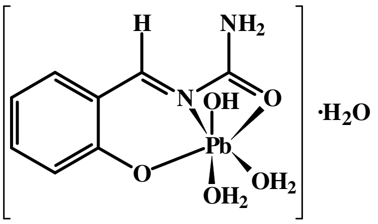
[CrO_3L]·$7H_2O$ chelate show three bands (Table-2) suggesting the existence of charge transfer transition and an octahedral geometry was proposed for this chelate[14]. The Cr(III) chelate spectrum exhibits two band at 269 nm (33783 cm^{-1}) and 395 nm (25348 cm^{-1}) which is due to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions. An octahedral structure was suggested[15]. The electronic spectral data of [TiOL·OH·H_2O]·H_2O chelate shows one band at 323 nm (30959 cm^{-1}) assigning the presence of a charge transfer and an octahedral geometry was suggested for the chelate[16]. Meanwhile the spectrum of [PbL·OH·$2H_2O$] chelate displays two bands at 323 nm (30959 cm^{-1}) and 382 nm (26178 cm^{-1}) assigning the charge transfer transition, a distorted octahedral geometry was suggested for the chelate and the lone pair on lead is stereochemically inactive and does not appear to influence the structure[17].

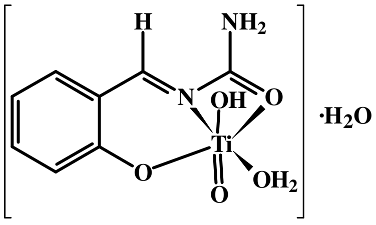
The electron paramagnetic resonance spectrum of the Cr(III) chelate shows g_{eff} value of 1.991. The small deviation of g_{eff} value than the ideal value (1.991) results from the partial ionic character of the covalent bond between the Cr(III) ion and the Schiff base under investigation. This value suggests an octahedral geometry[18] and supports the obtained data from the electronic spectra.

From the chemical analyses, the following geometrical structures of the synthesized complexes are suggested.









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(*Received*: 22 May 2006; *Accepted*: 16 April 2007) AJC-5575