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Preparation and spectroscopic investigation of a Schiff base metal complexes

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Abstract: Three new metal complexes of Cr(III), Pb(II)) and TiO(IV) ions with a Schiff base derived from salicylaldehyde and urea have been investigated. The obtained C, H and N elemental analysis data showed the formation of 1:1 [M:L] ratio. The prepared complexes revealed a non-electrolytic nature. The magnetic moment values of the complexes exhibited the existence of paramagnetic phenomena for a chromium (III) complex and diamagnetic phenomena for the other rest complexes. The coordination behavior of the metal ions towards to the investigated Schiff base takes place through –C=N and –OH groups. The electronic spectral data of the complexes displayed the proper transitions and the expected geometrical structures. The electron paramagnetic resonance spectral data for Cr(III) complex showed the presence of an octahedral structure and supported the data which obtained from the electronic transitions.

Key words: Schiff base, Salicylaldehyde, urea, Complexes

Introduction

Complexes of some metal ions with Schiff base derived from salicylaldehyde and tyrosine have been synthesized and characterized by using different physical tools and an octahedral structure was proposed for all complexes. (1) Maihub et al. (2) Prepared and investigated some Schiff base complexes of Co(II), Ni(II) and Cu(II) ions. It is found that the prepared complexes have square planar structures.

Boghaei (3) synthesized and investigated non-symmetrical tetradentate Schiff base complexes of Ni(II) and Cu(II) ions. .

The main aim of the present paper is to prepare a Schiff base (derived from the reaction of salicylaldehyde and urea) and its complexes with Cr(III), Pb(II) and TiO(IV) ions and illustrate their geometrical structures by using different physical techniques.

Experimental

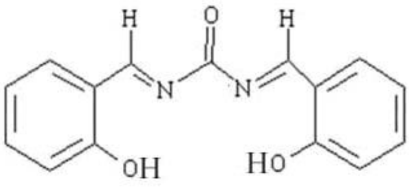
Material

All material used in this investigation were purchased from sigma / Aldrich and used as received. They include; salicylaldehyde, urea, Chromium(III) chloride hexahydrate ($CrCl_3.6H_2O$), lead nitrate ($Pb(NO_3)_2$), titanylsulphate ($TiOSO_4.H_2O$), ammonium hydroxide (NH_4OH), ethanol (C_2H_5OH), chloroform ($CHCl_3$), methanol, sodium hydroxide (NaOH), dimethylformamide (DMF), and double distilled water was used during the experimental procedures.

Preparation of Schiff base

The ligand under investigation was prepared by the condensation of 0.02 moles of salicylaldehyde and 0.01 mole of urea according to this method:

25 cm^3 of urea ethanolic solution (0.01 mole, 0.60 g) was added to the same volume of the same solvent of (0.02 mole, 2.44 g) of salicylaldehyde. Few drops of 10 % NaOH were added to adjust pH and the obtained mixture then refluxed with stirring for two hours and the obtained precipitate was collected by filtration through Buchnner funnel, recrystallized from ethanol, and dried at room temperature with 70-80 % yield and its melting point is in the range of 100-102 ^0C .



Preparation of complexes

The complexes of Cr(III), Pb(II) and TiO(IV)) ions derived from salicylaldehyde and urea were synthesized by refluxing 25 cm^3 of 0.01 mole; 2.66, 3.31 and 1.78 g of the mentioned metal salts, respectively, to 25 cm^3 of (0.02 moles; 2.44 g) of salicylaldehyde. Few drops of ammonium solution were added until pH 6-8 was obtained and then the mixtures were refluxed for 1.5 hrs, then 25 cm^3 of the urea ethanolic solution (0.01 mole; 0.60 g) was added and the mixtures were refluxed for extra 4-5 hrs. The obtained products were filtered, washed several times with hot ethanol unlit the filtrate becomes colorless and dried in a desiccator over anhydrous $CaCl_2$ under vacuum. The yield ranged from 60-75% and the melting points of all complexes are above 350 ^{0}C.

Measurements

The prepared Schiff base and its complexes were subjected to (C, H, and N) elemental analyses using 2400 elemental analyzer technique. The molar conductivity measurements were carried out in DMF solvent using conductivity meter model CMD650 digital. The magnetic moment measurements of the complexes 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 4000-400 cm^{-1}. The electronic absorption spectra of the complexes were measured in chloroform solvent using a perkin– Elmer lambda 4β spectrophotometer. The electron paramagnetic resonance spectrum of the Cr(III) complex was recorded by using EMX EPR spectrometer (Bruker) 1998Y at Al-Fateh University, Tripoli-Libya. The rest analyses were done at the Micro analytical center, Cairo- University.

Results and discussion

Microanalysis

Table-1 comprises that the found data are in a good agreement with those theoretical ones, and the obtained analytical data indicate the formation of 1:1[M: L] complexes.

Molar conductivity

The conductance measurements of the complexes were carried out in DMF solvent and the obtained values (Table-1) were taken as a good evidence for the existence of a non-electrolyte nature. (4)

Table 1: Some physical properties of the Schiff base and its complexes

Ligand/ complexes	M.Wt	C%	H%	N%	Λm*	M.P ^{0}C
$C_{15}H_{12}N_2O_3$(L)	268	67.50 (67.16)	4.40 (4.47)	10.18 (10.44)	-	100-102
[CrL (OH)(H_2O)]2H_2O	389	46.36 (46.27)	4.73 (4.31)	6.90 (7.19)	4.98	>350
[PbL (H_2O)$_2$]H_2O	427	41.98 (42.15)	4.01 (3.74)	6.67 (6.55)	13.95	>350
[TiOL (H_2O)] H_2O	366	48.85 (49.18)	3.35 (3.82)	7.00 (7. 65)	12.77	>350

( ) Calculated values.
M.Wt = Molecular weight.
* Ohm^{-1} cm^2 mol^{-1}

Infrared spectra

The spectra of the complexes illustrate broad bands in the range of 3190-3422 cm^{-1} assigned to the presence of water molecules.(5) Whereas, the same spectra display a band in the range of 1605-1616 cm^{-1} assigned to –CH=N vibration, this range is shifted to lower frequency compared to its position in the original ligand (1620 cm^{-1}) indicating its involvement in coordination with the metal ions.(6) Whereas, the disappearance of υ NH_2 group in the spectra of all complexes suggests its participation as imine group in complexation.(7) There is no change in υ C=O group, this mean that this group is not entered in chelation. New bands observed at 575-671 cm^{-1} and 444-540 cm^{-1} which are not seen in the spectrum of the free ligand can be attributed to υ (M-O) and υ (M-N) vibrations, respectively.(8) Also the absorption band at 1262 cm^{-1} due to υ C-O vibration of the ligand is shifted to higher frequency indicating its involvement in coordination with the metal ions through the oxygen atoms.(9,10) The spectrum of [TiOL(H_2O)]H_2O complex displays a bands at 1030 cm^{-1} assigned to υ (M=O) vibration suggesting the involvement of this group as a coordinate band with TiO(IV) ion.(11)

Electronic spectra and magnetic moments

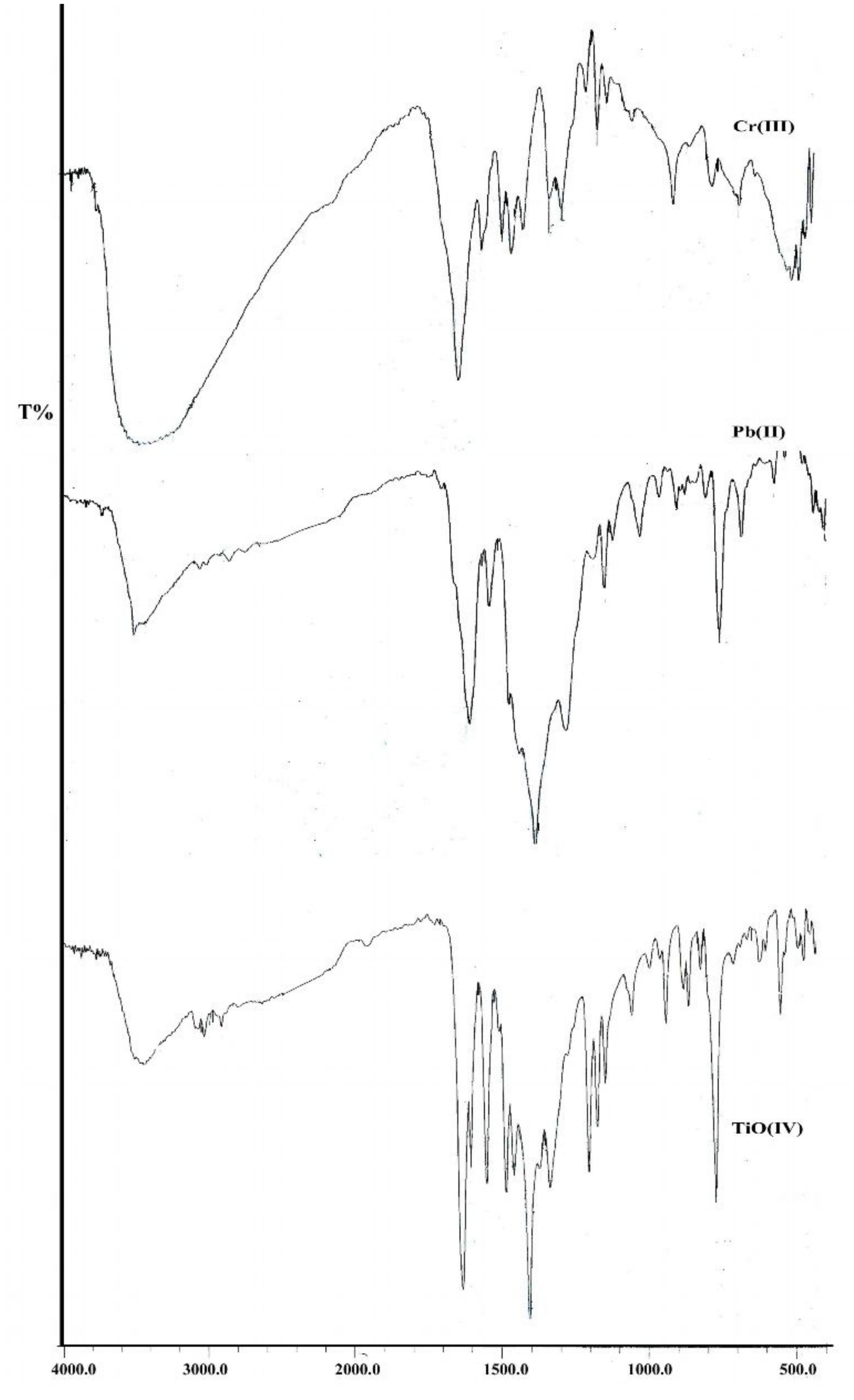
The electronic spectra data of the Schiff base and its chelates were recorded in chloroform and their assignments (table 2 and figure 2).The spectral data of the Schiff base show a band at 288 nm (34662 cm^{-1}) due to $\pi\rightarrow\pi^*$ *and* $n\rightarrow\pi^*$ transitions.(11) The electronic spectral data of the titanium (IV)-L complex of the formulae $[TiO(L)(H_2O)]H_2O$ reveal three bands at 386 (25940 cm^{-1}), 322 nm (31104 cm^{-1}) and 292 nm (34305 cm^{-1}) assigned to the presence of charge transfer transition and an octahedral geometry was proposed.(12) The Pb(II) complex spectrum shows two bands at 383 nm (26109 cm^{-1}) and 320 nm (31250 cm^{-1}) attributed to charge transfer transition and an octahedral structure was suggested for this complex.(13) The chromium(III) complex spectrum displays three bands at 400 nm (25000 cm^{-1}), 305 nm (32840 cm^{-1}) and 290 nm (34542 cm^{-1}) due to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, $^4A_2g\ (F) \rightarrow {}^4T_1g\ (F)$ and charge transfer transitions. The intensity of the bands indicate the presence of an octahedral geometry.(14) The magnetic moment value of chromium (III)-L complex (4.40 BM) supports the existence of three odd electrons, meanwhile, the magnetic moment values of the Pb(II) and TiO (IV)-L complexes are zero. These values indicate the presence of a diamagnetic phenomena.(15)

Table (2): Infrared and electronic spectral data of the Schiff base and its complexes

Ligand / Complexes	IR Bands (cm^{-1})									λ_{max} nm (cm^{-1})
	υOH	υNH_2	υC=N	υC-O	υC=O	υM=O	υM-O	υM-N	υOH (coord)	
$C_{15}H_{12}N_2O_3$(L)	3446	-	1620	1262	1625	-	-	-	-	**392** (25510), **329** (30395), **289** (34662)
$[CrL (OH)(H_2O)]2H_2O$	3190	-	1616	1273	1625	-	671	467	-	**290** (34542), **305** (32840), **400** (25000).
$[PbL (H_2O)_2]H_2O$	3421	-	1605	1280	1625	-	575	540	-	**320** (31250), **383** (26109).
$[TiOL (H_2O)]\ H_2O$	3422	-	1612	1280	1625	1030	594	444	-	**292** (34305), **322** (31104),**386** (25940).

Electron paramagnetic resonance spectrum

The electron paramagnetic resonance spectrum of Cr(III) complex shows a g_{eff} value of 1.991. The large deviation of g_{eff} value than the ideal value (2.0023) results from the partial ionic character of the covalent bond between the Cr(III) ion and the Schiff base under investigation. This value supports the existence of an octahedral geometry (16) and confirms the obtained data from the electronic spectra.



Wave number (cm^{-1})

Fig. (1): Infrared spectra of the Cr(III), Pb(II) and TiO(IV)-L complexes

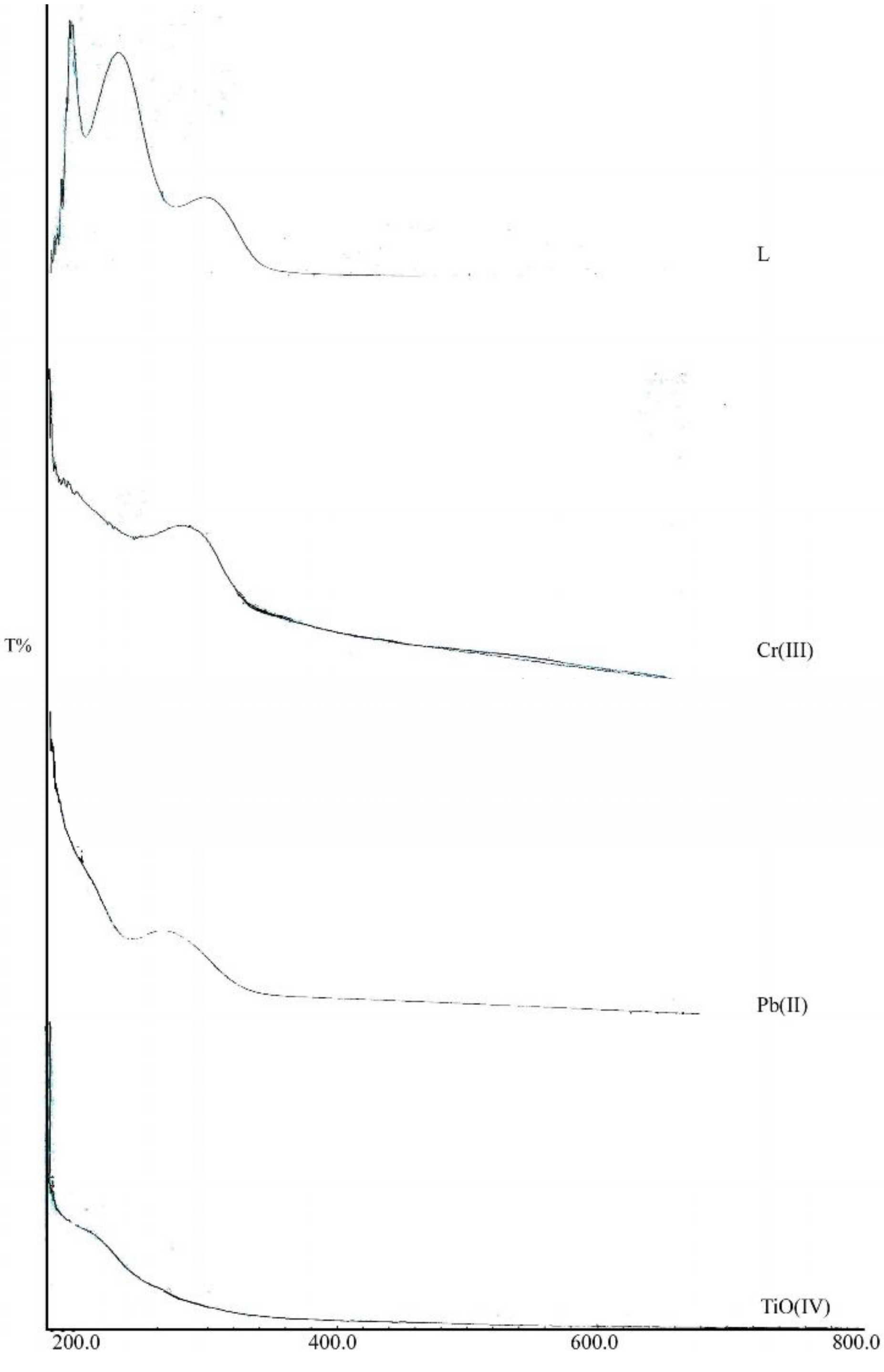


Fig. (2): Electronic spectra of the Cr(III), Pb(II) and TiO(IV)-L complexes

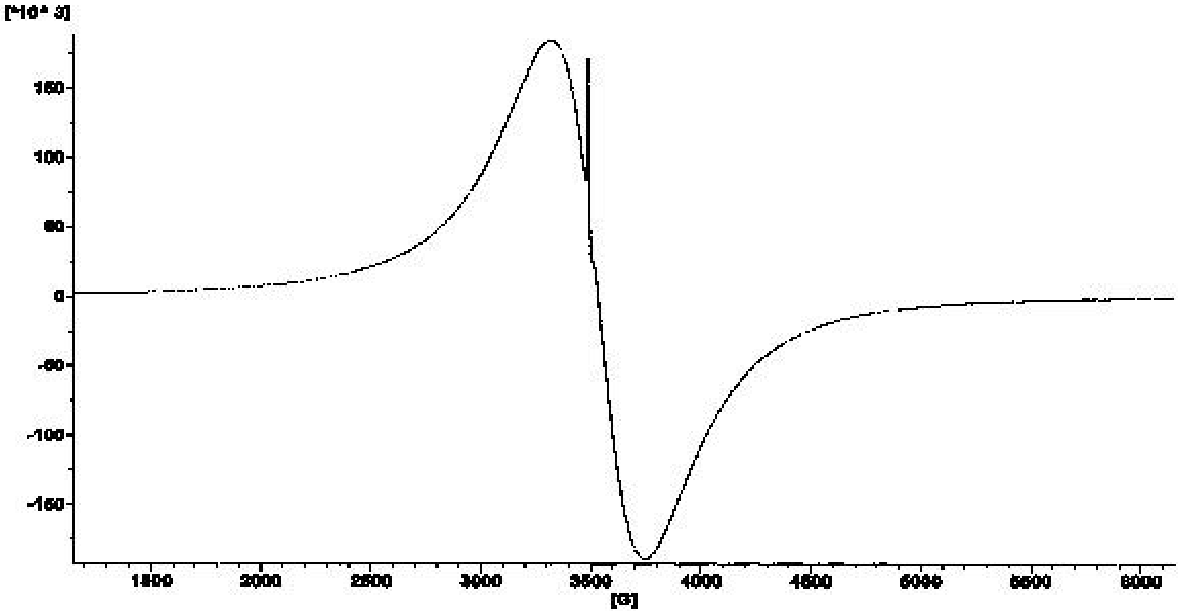
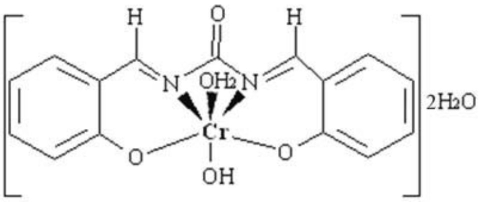


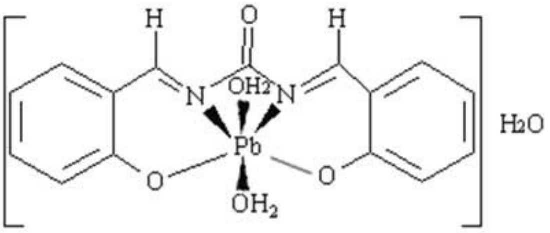
Fig. (3): Electron paramagnetic resonance spectrum of Cr(III)-L complex

Conclusion:

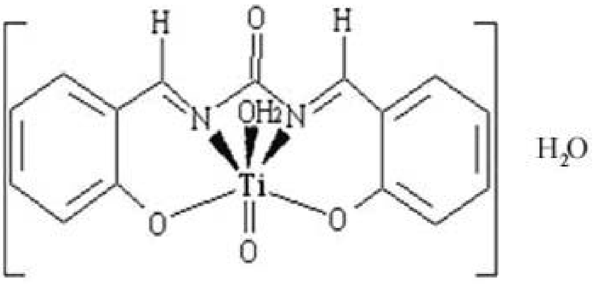
From the previous chemical analyses, the following geometrical structures were suggested.



[CrL (OH)(H_2O)] $2H_2O$



[PbL $(H_2O)_2$] H_2O



[TiOL (H_2O)] H_2O

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