



Preparation, Characterization, Theoretical Treatment and Adsorption on Surfaces N₅ Acyclic Immobilizes on Silica Gel for Removal of Some Toxic Metals

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Authors' contributions

This work was carried out in collaboration between all authors. Author OHSAO designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author MNAJ managed the analyses of the study. These two authors read and approved the final manuscript.

Research Article

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ABSTRACT

A series of transition elements complexes with [2,6-diacetimidino-pheylenediamine – [2,2'diy] pyridine] of the general formula [MLCl]_xCl_x, (where M= Cr(III), Pb(II), Zn(II) and Cd(II), x= 2 for Cr(III)) respectively have been synthesized and fully characterized on the bases of C.H.N.M, elemental analysis, ¹³C NMR, UV- Visible and FTIR spectra , in addition the structure of complexes was characterized by magnetic moments and molar conductance in DMF solution ,and molar ratio of complexes were also determined. On the basis of electronic spectral studies .All complexes have an octahedral geometry around the metal center in (1:1) (L:M).

A theoretical treatment of the formation of complexes in the gas phase was studied, this was done using the HYPERCHEM-6 program for the Molecular mechanics and Semi-empirical calculations. The batch adsorption method has applied on N₅ polydentate ligand to remove the selected toxic metal ions from waste water after immobilization the newly n₅-ligand on silica gel by physic-chemical method.

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1. INTRODUCTION

Contamination of water resources by heavy metals has been serious environmental worldwide problem. Heavy metal pollution exists in waster effluents of many industries such as metal plating facilities .fertilizer industry, mining operations tanners, paints and pigments. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [1]. It is also known that heavy metals are carcinogenic. Therefore it is necessary to treat such toxic metals containing wastewater before discharging [2,3].

Among the conventional methods to remove heavy metals from wastewater include chemical precipitation, ion-exchange, membrane filtration, the adsorption has attracts attention as the results of new material type, available for the application of heavy metal removals. Complexation adsorption is a very efficient way to in activate and remove metal ions and chelating resins characterization by functional groups containing O,N and / or S and P donor atoms coordinate to different metal ions[4-6].

and modified pvc with ethylene[7] have been widely studied mostly by experimental methods modification of polymers such as polymethyl methacrylate polystyrene, poly(vinyl chloride)functionalized with heterocyclic ring possessing electron donating groups like isomethine C=N, hydroxyl groups -OH -anC=O groups may be helpful to act as chelating resin for toxic metals[8,9].

However, no work present has been initiated on the metal chelates of macrocyclic compounds behaved as adsorbents on the surface of natural resins in selected chromatographic columns to remove and chelate the toxic metals.

In the present paper the Cr(III) , Zn(II) ,Cd(II) and pb(II) chelate with N5-macrocyclic ligand derived from 2,6-acetylpyridine and O-phenylenediamine have prepared, fully characterized by common spectral and analytical techniques(¹H, ¹³C- NMR, F.T.I.R and UV-Visible spectra) , as well as application of remove swell metal ions from their solutions by passing on column.

2. EXPERIMENTALS

2.1 Physical Measurements

IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400) cm⁻¹. Electronic spectra of the prepared compounds were measured in the region 200-800nm in 1cm⁻¹ cell length for 10⁻³ M solution in DMF at 25°C using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001cm matched quartz cell. ¹H, ¹³C- NMR were acquired with BRUKER-400 spectrometer in DMSO-d₆ solvent. The NMR spectra were recorded at Queen Mary, University of London/ United Kingdom. Elemental microanalysis were performed on a (C.H.N) were performed by using Elemental analyzers Perkin -Elmer-240B, while metal contents of the complexes were determined by atomic absorption type Shimadzu A.A-670 model spectrometer. The chloride contents for metal complexes were determined by using potentiometer titration method on (686-Swiss). Electrical conductivity

measurements of the complexes were recorded at 25°C for 10⁻³ M solution of the sample in DMSO using a PW9527 digital conductivity meter. Magnetic susceptibility measurements were obtained at 298 K on the solid state applying Faraday's method using Bruker BM6 instrument.

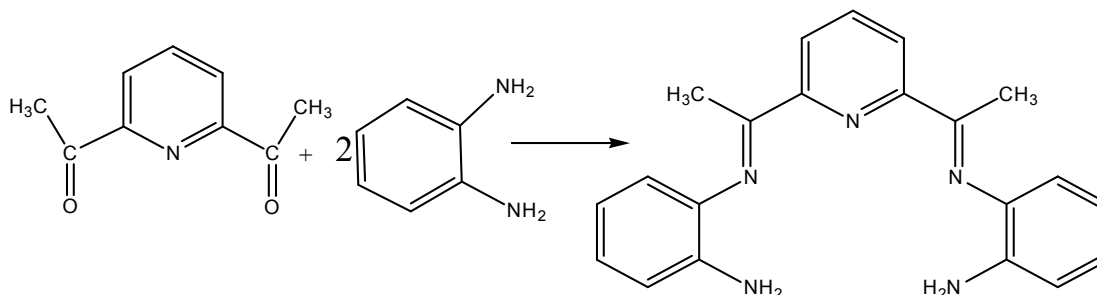
2.2 Materials

Reagents were purchased from Fluka and BDH and Redial-Dehenge Chemical Company. The N5 poly dentate ligand was prepared according to method published in literature[13].

2.2.1 Synthesis of N5 acyclic macrocyclic ligand (L)

A 20 cm² methanolic solution of 2,6-diacetyl pyridine 0.01 mole was refluxed with 100 ml methanolic solution of re crystallized O-phenylene diamine (0.02 mole) for about 4 hrs. A few drops of glacial acetic acid were added to the mixture and refluxed continued for (12-24) hrs. The mixture was concentrated to half of its volume and kept in desiccators for days. The ligand was filtered off, washed with methanol, acetone and ether, dried in vacuum, over CaCl₂ pellets, in yield 80%. The physical properties and analytical data, are shown in Table 1.

The general structure of ligand obtained from chemical analysis and spectral methods, are given in Scheme 1. The full name of the ligand will be replaced by (L) for the rest of this paper.



Scheme 1. Synthesis of acyclic ligand N5

2.2.2 General procedure for preparation of complexes

The preparation of complexes were carried out according to the method published in literature [10]. (0.344gm, 1 mmole) of N5 ligand in (10 ml) absolute ethanol was added drop wise with stirring to a solution of 1 mmole of ((Hg(NO₃)₂, 0.274gm), (Cd(NO₃)₂, 0.203gm)) or anhydrous (ZnCl₂, 0.131gm, in 5ml methanol) or Pb(NO₃)₂. The reaction were carried out for 24-36 hrs then coloring the mixture afforded colored precipitates. These complexes were filtered off, washed with ethanol, petroleum ether and dried in air. Yields: 65% [Zn(L)Cl]Cl and 60% [Cd(L)NO₃]NO₃ and 65%, [Hg(L)NO₃]NO₃. The preparation of metal complexes are shown in Scheme 2.

2.2.3 Preparation of [CrL(Cl)]Cl complex

(0.26 g, 0.001 mol) of $(CrCl_3 \cdot 6H_2O)$ in (20 mL) methanol was added to (2g, 0.001mol) of ligand dissolved in methanolic potassium hydroxide to keep the pH of the solution for ≈ 8 . The resulting mixture was refluxed under nitrogen atmosphere for 3 hrs until the color of solution became green, then after cooling to room temperature, green precipitate formed, filtered off, washed several times with 15ml of diethyl ether, and dried under vacuum to afford (1.31 g, 65%) yield, Scheme 2.

2.2.4 Adsorption study

The Ion exchange properties of the N5 have determined by the batch equilibrium method [11] after immobilization on silica gel *via* new moderate size to get high surface areas of beads with multi functional N5 groups [12].

2.2.4.1 Adsorption experiments

Batch adsorption experiments were conducted in 100ml flasks, each of which contained 50ml of metal solution prepared with $Pb(NO_3)_2$, $Hg(NO_3)_2$, $Cd(NO_3)_2$, $ZnCl_2$ and $CrCl_3 \cdot 6H_2O$. 0.25gm amount of N5-silica gel was added in to a flask, containing all contents shaken in a thermostatic water-bath shaker operated at $25^\circ C$ and 120rpm. Samples were taken from the flask at appropriate time intervals as necessary and the concentration of metal ions in the sample were analyzed with UV-visible spectroscopy, at maximum absorption (λ_{max} nm). After an experiment, the resin was separated from solution by filtration, rinsed with water de ionization and then prepared for other analyses with FTIR, 1H nmr, magnetic susceptibility.

For the Kinetic experiments, the initial concentration of metal ions were 35-90 mg/lit or 125mg/lit, and initial solution PH value was 2.0 (the solution PH was not controlled during the experiments). In investigation of the effect of solution PH values were changed from 2 to 8.

3. RESULT AND DISCUSSION

Although a few among the investigated complexes have previously been spectrally characterized to their structure [13], this study has provided an opportunity to compare the spectroscopic and other physical properties of all complexes by using data obtained under the similar set of experimental conditions. In addition, during the course of this study it was found necessary to compile and compare the physico-chemical characteristics of each investigated complexes. In order to choose the appropriate technique for probing the adsorption interaction. Thus, we compare the physical and spectroscopic characteristics of the investigated $Cr(II)$, $Zn(II)$, $Cd(II)$, $Hg(II)$ and $Pb(II)$ complexes before we discuss their adsorption study.

3.1 Spectroscopic Characterization

The metal salts of the complexes employed in this work have been fully characterized by UV/Visible, IR spectroscopic. These data summarized in Table 1 agree well with the reported values, in cases where applicable [13].

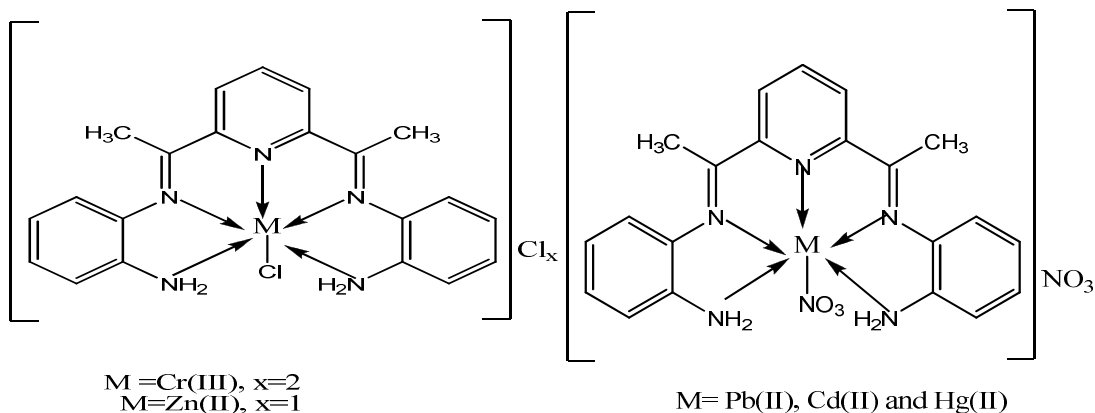
3.2 Conductivity Measurement

The conductivity for 10^{-3} M solutions of metal complexes Table 1 in(DMSO) at 25°C , show that Zn(II), Cd(II), Hg(II) and pb(II)to be 1:1 electrolyte. While Cr(III) complex shows electrolyte behavior in 1: 2 ratio, this agrees well with the proposed formula of the complexes[14].

3.3 The proposed Structure

It is obviously, observed that free ligand of N_5 system differs from N_6 -system, percent in literature [13]. Where the reaction conditions of metal salts sported coordination with N_4 system proceeds rapidly, rather than template system, this facts has investigation the basis of data obtained from, FT-IR., UV-Vis., and others measurements.

A according to the elemental analysis, IR, UV-Vis. spectra and magnetic moment of complexes , all the complexes could have the proposed structure in Scheme 2 Where The ligand behavior pentadante of N_5 system .



Scheme 2. The proposed structure of metal complexes

3.4 Theoretical Study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Table 2, Fig. 1. As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

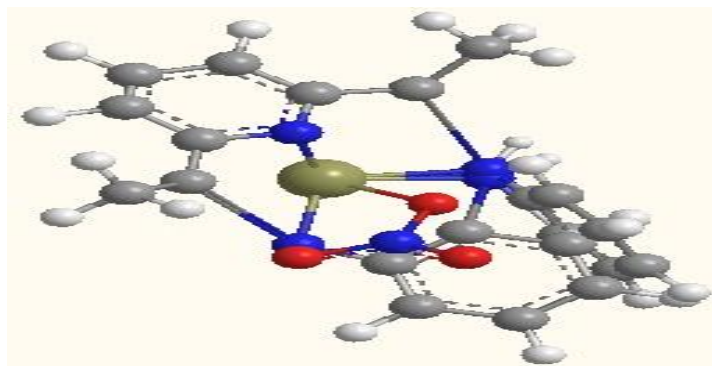


Fig. 1. The optimized structural geometry of Pb(II) complex

3.5 Application Adsorption on Surfaces Column

3.5.1 Adsorption isotherms

For studying the adsorption behavior of high concentrations of metal ions, isotherms for the adsorption of Cr(III), Pb(II), Cd(II) and Zn(II) were obtained by batch method. The isotherms of metal ions can be described by Freundlichequation [15]:

$$\text{Log}Q = 1/n \text{Log}c + \text{log}K \quad (1)$$

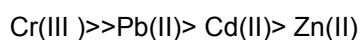
[Q is the amount of metal ion adsorbed per gram of adsorbent (mg.g^{-1}), C is the concentration of the metal ion solution (mg.lit^{-1}) and the value 1/n and LogK were 0.99, 0.90, 0.95 and 0.63 for Cr(III), Pb(II), Zn(II) and Cd(II) respectively. This also indicates that the adsorption capacity of PVC-L was high. The adsorption efficiency of batch method calculation by the equation:-

$$(\% \text{Adsorption}) = [(C_0 - C_w) / C_0] \cdot 100 \quad (2)$$

Where C_0 is the initial concentration of metal ion in solution (mg. Lit^{-1}), and C_w is the concentration of metal ion in the filtrate (mg.lit^{-1}). Table 3.

The effect of PH on the amount of metal ions distributed between two phases can be explained by the results given in Fig. 2, Table 4. The data obtained from effect of PH on the removal of metal ions from aqueous solutions indicate that the relative amount of metal taken up by N5 ligand increases with increasing PH of the medium [16].

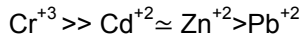
The study was carried out to a definite PH value for the particular metal ion to prevent hydroxide formation of the metal ions at higher PH. In the case of Cu(II) and Ni(II) ions, the highest distribution ratio (D) (390 - 400) of $\text{PH} \approx 7.0$ whereas the highest value for (D) for Hg(II) and Cd(II) at $\text{PH} = 6.0$. The results of this study help in selecting the optimum PH for selective uptake of a metal ion from a mixture of different ions [17]. Exchange Anal. Fig. 3. The order of distribution ratio of metal ions measured in PH range 2 to 8 is found to be:



The N5 ligand is considered as cationic exchange resin, therefore, the exchange.

3.5.2 Estimation rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time within which equilibrium could be achieved as while operating as close to equilibrium condition as possible. As shaking time increases the N5 gets more time for adsorption, hence uptake increases. Fig. 4, shows that rate of metal ion uptake follows the order:



The sequence of rate metal ion uptake indicates, that the rate is directly proportional to size of the metal ion. For example Cr^{+3} has more charge and small size, therefore equilibrium is attained within 90 minutes, while other ions Pb^{+2} , Cr^{+3} and Cd^{+2} have nearly equal cationic size, having same charge, therefore required 120 minute, to attain equilibrium while, Cd^{+2} , and Hg^{+2} and Pb^{+2} have large atomic size, therefore requiring 125 minute to attain equilibrium. The trend is in good agreement with earlier workers [18] comparing to soft acids Pb^{+2} , Cd^{+2} and Hg^{+2} [19].

A typical adsorption isotherms at given temperature was obtained by plotting q_e vs C_e for again N5-silica gel, equation [20], Fig. 6.

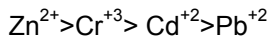
$$q_e = \left(\frac{C_0 - C_e}{d} \right) V \quad \text{----- 3}$$

Where q_e = the equilibrium metal ion concentration resin in mole /g
 C_0 , C_e = initial and equilibrium concentrations of metal ions under study in mole/lit.
 V = volume of solution in liter, and d = weight of (N5) in g.

The Fig. 5 clearly indicate that these isotherms are all of the favorable type referred to in literature [21]. With increasing values of C_e the values of q_e reaches the saturation level of the adsorbent on the adsorbent lie, formation of monolayer of the N5 – bonded.

With metal ions under study. This value actually represents the maximum amount of metal ions that the (N5) could hold under a given set of experimental conditions. In order to verify to what extent the isotherms adhere to Langmuir and Freundlich adsorption isotherm representative plots of $\ln q_e$ vs $\ln C_e$ for Freundlich (equation 1) and $1/q_e$ vs $1/C_e$ for Langmuir (equation 3) are accordingly shown in Fig. 6. These plots indicate satisfactory adherence to isotherms within the range of concentrations employed in this work.

The high efficiency of (N5) to remove the metal ions especially Cr(III), Pb(II) and Cd(II), may be attributed to homogeneous distribution of active sites on the N5 surface, since the displacement of NH with metal ions under study and nitrogen (N_1) of pyridine ring tend to form five membered ring which is kinetically stable [22] and agree with sequins stability of metal complexes Irving Williamson.



The maximum amount of metal ion adsorbed by 0.25 gm was calculated by Langmuir and Freundlich models [23,24] (equations 1, 3). The adsorption capacity [25] of modified N5 for metal ions is shown in Table 5. As can be seen, the plots of Langmuir and Freundlich models

effective describe the adsorption data with all R^2 values more than 0.98 for all ions. Furthermore the figures of Langmuir and Freundlich isotherms (Figs. 5 and 6) indicates that the adsorption process as heterogeneous type. The maximum adsorption of metal ions on adsorbent silica gel modified with N5 ligand has reached a plateau, Fig. 2, when the concentrations of $[H+]$ decreases, this is in agreement with literatures of adsorption of chromium, copper and lead ions(II) on silica gel surfaces [22].

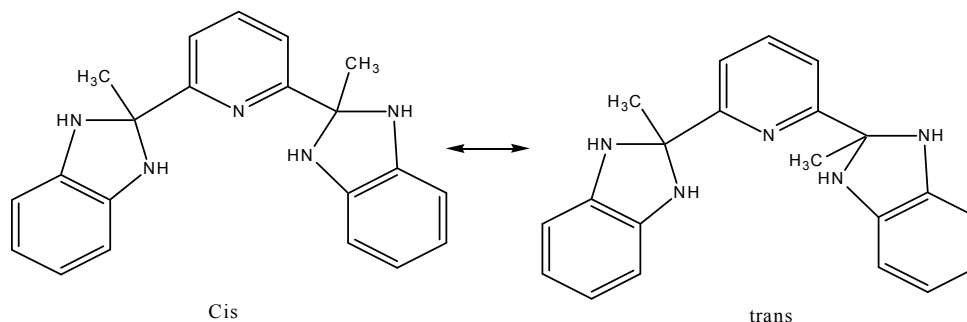


Table 1. UV/Visible and IR spectra data of prepared compound

Compound	M.p.	Colour	$\nu^{(M-N)}$	$\nu^{(NH_2)}$	$\nu^{(C-N)}$ $\nu^{(C=N)(py)}$	$\nu^{(C=N)}$	λ max (nm)	ΔM (Ω^{-1} $cm^2 mol^{-1}$) In DMSO
L	225- 227-	Brown sh- yellow	-	3389- 3365(m)	1589- 1600(s)	1637 (s)	266,320	-
[CrLCl] Cl_2	>29 0	Olive	651- 500	3340(br)	1489(m)	1620	287,625 576,455	183
[ZnLNO $_3$] NO_3	300d	Cream	455(m)	3400	1522(m)	1654	321, 360	78
[CdLNO $_3$] NO_3	385d	yellow	434(m)	3245(br)	1533(s)	1633	215, 370	77
[HgLNO $_3$] NO_3	290d	Cream	421(w)	3521(m)	1539(s)	1640 (s)	225, 348	83
[PbLNO $_3$] NO_3	366d	Grey	444(m)	3390(m)	1510(s)	1630 (s)	230, 365	88

W=weak, br=broad, s=strong, and m=medium.

Table 2. Structural parameters, bond length (\AA) and angles ($^\circ$) of the [Pb(L) NO_3] NO_3 complex

Parameters	Parameters	Parameters
Bond angles ($^\circ$)	Bond lengths (\AA)	Bond angles ($^\circ$)
N(29)-O(31) 1.3100	N(29)-O(31) 1.3100	O(31)-N(29)-O(30) 119.9998
N(29)-O(30) 1.3100	N(29)-O(30) 1.3100	O(31)-N(29)-O(28) 119.9998
O(28)-N(29) 1.6100	O(28)-N(29) 1.6100	O(30)-N(29)-O(28) 120.0004
Pb(27)-O(28) 2.1100	Pb(27)-O(28) 2.1100	H(47)-C(21)-C(22) 120.3560
N(26)-H(50) 1.0500	N(26)-H(50) 1.0500	H(47)-C(21)-C(20) 120.3560
N(26)-Pb(27) 2.1460	N(26)-Pb(27) 2.1460	C(22)-C(21)-C(20) 119.2880
C(25)-H(49) 1.1000	C(25)-H(49) 1.1000	H(46)-C(20)-C(25) 120.3303
C(24)-C(25) 1.3370	C(24)-C(25) 1.3370	H(46)-C(20)-C(21) 120.3306

C(23)-N(26)	2.0244	C(23)-N(26)	2.0244	C(25)-C(20)-C(21)	119.3391
C(23)-C(24)	1.3370	C(23)-C(24)	1.3370	H(49)-C(25)-C(24)	119.9997
C(22)-H(48)	1.1000	C(22)-H(48)	1.1000	H(49)-C(25)-C(20)	120.0006
C(22)-C(23)	1.3370	C(22)-C(23)	1.3370	C(24)-C(25)-C(20)	119.9997
C(21)-H(47)	1.1000	C(21)-H(47)	1.1000	H(48)-C(22)-C(23)	120.0000
C(21)-C(22)	1.3370	C(21)-C(22)	1.3370	H(48)-C(22)-C(21)	119.9999
C(20)-H(46)	1.1000	C(20)-H(46)	1.1000	C(23)-C(22)-C(21)	120.0001
C(25)-C(20)	1.3370	C(25)-C(20)	1.3370	N(26)-C(23)-C(24)	28.7933
C(20)-C(21)	1.3516	C(20)-C(21)	1.3516	N(26)-C(23)-C(22)	148.7925
N(19)-H(45)	1.0500	N(19)-H(45)	1.0500	C(24)-C(23)-C(22)	119.9999
N(19)-Pb(27)	2.1460	N(19)-Pb(27)	2.1460	H(43)-C(17)-C(18)	120.0011
C(18)-H(44)	1.1000	C(18)-H(44)	1.1000	H(43)-C(17)-C(16)	120.0007
C(17)-H(43)	1.1000	C(17)-H(43)	1.1000	C(18)-C(17)-C(16)	119.9983
C(17)-C(18)	1.3370	C(17)-C(18)	1.3370	H(42)-C(16)-C(17)	120.0009
C(16)-H(42)	1.1000	C(16)-H(42)	1.1000	H(42)-C(16)-C(15)	120.0010
C(16)-C(17)	1.3371	C(16)-C(17)	1.3371	C(17)-C(16)-C(15)	119.9980
C(15)-H(41)	1.1000	C(15)-H(41)	1.1000	H(44)-C(18)-C(17)	120.0000
C(15)-C(16)	1.3370	C(15)-C(16)	1.3370	H(44)-C(18)-C(13)	119.9997
C(14)-N(19)	1.9343	C(14)-N(19)	1.9343	C(17)-C(18)-C(13)	120.0004
C(14)-C(15)	1.3370	C(14)-C(15)	1.3370	H(41)-C(15)-C(16)	120.0001
C(18)-C(13)	1.3370	C(18)-C(13)	1.3370	H(41)-C(15)-C(14)	120.0000
C(13)-C(14)	1.3370	C(13)-C(14)	1.3370	C(16)-C(15)-C(14)	119.9998
N(12)-Pb(27)	2.1460	N(12)-Pb(27)	2.1460	N(19)-C(14)-C(15)	93.0459
C(24)-N(12)	1.2600	C(24)-N(12)	1.2600	N(19)-C(14)-C(13)	142.2659
C(11)-H(40)	1.1130	C(11)-H(40)	1.1130	C(15)-C(14)-C(13)	120.0002
C(11)-H(39)	1.1130	C(11)-H(39)	1.1130	N(29)-O(28)-Pb(27)	120.0002
C(11)-H(38)	1.1130	C(11)-H(38)	1.1130	H(50)-N(26)-Pb(27)	132.9321
C(10)-H(37)	1.1130	C(10)-H(37)	1.1130	H(50)-N(26)-C(23)	132.9323
C(10)-H(36)	1.1130	C(10)-H(36)	1.1130	Pb(27)-N(26)-C(23)	94.1356
C(10)-H(35)	1.1130	C(10)-H(35)	1.1130	H(45)-N(19)-Pb(27)	143.0687
C(9)-N(12)	2.8552	C(9)-N(12)	2.8552	H(45)-N(19)-C(14)	143.0686
C(9)-C(11)	1.4970	C(9)-C(11)	1.4970	Pb(27)-N(19)-C(14)	73.8627
N(8)-Pb(27)	2.1460	N(8)-Pb(27)	2.1460	C(25)-C(24)-C(23)	119.9982
C(13)-N(8)	1.2600	C(13)-N(8)	1.2600	C(25)-C(24)-N(12)	128.9979
C(7)-C(10)	1.4970	C(7)-C(10)	1.4970	C(23)-C(24)-N(12)	111.0004
C(7)-N(8)	2.8206	C(7)-N(8)	2.8206	H(40)-C(11)-H(39)	109.5196
C(6)-H(34)	1.1000	C(6)-H(34)	1.1000	H(40)-C(11)-H(38)	109.4621
C(5)-H(33)	1.1000	C(5)-H(33)	1.1000	H(40)-C(11)-C(9)	109.4616
C(5)-C(6)	1.0286	C(5)-C(6)	1.0286	H(39)-C(11)-H(38)	109.4422
C(4)-C(7)	1.3370	C(4)-C(7)	1.3370	H(39)-C(11)-C(9)	109.4417
C(4)-C(5)	1.3370	C(4)-C(5)	1.3370	H(38)-C(11)-C(9)	109.5001
N(3)-Pb(27)	1.3370	N(3)-Pb(27)	2.1460	Pb(27)-N(12)-C(24)	104.0001
N(3)-C(4)	1.3370	N(3)-C(4)	1.2600	Pb(27)-N(12)-C(9)	72.1636
C(2)-C(9)	1.1000	C(2)-C(9)	1.3370	C(24)-N(12)-C(9)	114.9998
C(2)-N(3)	1.2600	C(2)-N(3)	1.2600	C(18)-C(13)-C(14)	119.9983
C(1)-H(32)	1.3370	C(1)-H(32)	1.1000	C(18)-C(13)-N(8)	128.9984
C(6)-C(1)	1.2600	C(6)-C(1)	1.3370	C(14)-C(13)-N(8)	110.9999
C(1)-C(2)	2.1460	C(1)-C(2)	1.3370	H(37)-C(10)-H(36)	109.4616
Bond lengths (°A)		Bond lengths (°A)		H(37)-C(10)-H(35)	109.5205
O(28)-Pb(27)-N(26)	67.3131	N(8)-Pb(27)-N(3)	104.0000	H(37)-C(10)-C(7)	109.4617
O(28)-Pb(27)-N(19)	61.8588	C(7)-C(4)-C(5)	128.9979	H(36)-C(10)-H(35)	109.4424
O(28)-Pb(27)-N(12)	63.2663	C(7)-C(4)-N(3)	110.9996	H(36)-C(10)-C(7)	109.4414
O(28)-Pb(27)-N(8)	60.9232	C(5)-C(4)-N(3)	119.9999	H(35)-C(10)-C(7)	109.4998
O(28)-Pb(27)-N(3)	78.9723	N(12)-C(9)-C(11)	125.6523	Pb(27)-N(8)-C(13)	104.0001
N(26)-Pb(27)-N(19)	5.9330	N(12)-C(9)-C(2)	108.6954	Pb(27)-N(8)-C(7)	72.9112
N(26)-Pb(27)-N(12)	5.9330	C(11)-C(9)-C(2)	125.6523	C(13)-N(8)-C(7)	146.7731
N(26)-Pb(27)-N(8)	109.5000	C(9)-C(2)-N(3)	110.9996	H(34)-C(6)-C(5)	122.1913

N(26)-Pb(27)-N(3)	109.5001	C(9)-C(2)-C(1)	128.9979	H(34)-C(6)-C(1)	122.1913
N(19)-Pb(27)-N(12)	6.6846	N(3)-C(2)-C(1)	119.9999	C(5)-C(6)-C(1)	115.6174
N(19)-Pb(27)-N(8)	104.0000	H(32)-C(1)-C(6)	119.9997	C(10)-C(7)-N(8)	125.5494
N(19)-Pb(27)-N(3)	109.5001	H(32)-C(1)-C(2)	120.0001	C(10)-C(7)-C(4)	125.5496
N(12)-Pb(27)-N(8)	109.5000	C(6)-C(1)-C(2)	120.0002	N(8)-C(7)-C(4)	108.9010
N(12)-Pb(27)-N(3)	104.0001	Pb(27)-N(3)-C(4)	104.0000	H(33)-C(5)-C(6)	115.3085
Pb(27)-N(3)-C(2)	103.9999			H(33)-C(5)-C(4)	115.3092
				C(6)-C(5)-C(4)	129.3823

Table 3. %Uptake metal ions on N₅-immobilized with silica gel

mg.lit ⁻¹	mg.lit ⁻¹			
Q	Cr ⁺³	Pb ⁺²	Cd ⁺²	Zn ⁺²
0	0	0	0	0
12	35	28	18	25
15	55	50	22	45
18	65	70	35	62

Table 4. Distribution ratio (D) of different metal ions as function of the PH of N₅-silica gel

PH	D-Cr(III)	D-Ni(II)	D-Cd(II)	D-Hg(II)	D-Pb(II)
2	95	20	10	55	4
3	130	95	70	96	65
4	180	135	200	195	110
5	275	195	350	310	175
6	350	450	450	495	285
7	390	410	370	485	395
8	60	38	310	209	380

Table 5. Langmiur isotherms of Metal ions on N5-silica gel surface of Cr⁺³, Pb⁺², Cd⁺², Zn⁺², at 30°C

Comp.	C _e (mg/l)	Q _e (mg/g)	C _e /Q _e (g/l)
[CrLCI]Cl ₂	0.536	0.3446	1.5554
[ZnLNO ₃]NO ₃	1030.96	24.690	41.756
[CdLNO ₃]NO ₃	0.965	3.4903	0.2764
[PbLNO ₃]NO ₃	0.911	5.230	0.1741

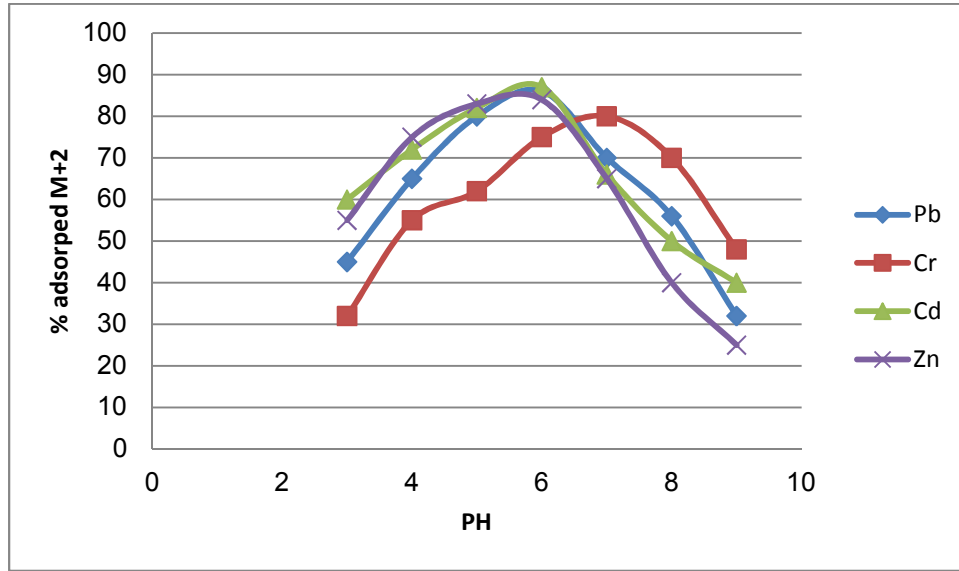


Fig. 2. Variation of %adsorption of Metal ions with PH values,3gm in 50ml, Conc. M^{+2} ,50 mg/lit, Contact Time =90min.,Temp.=30 C, Shaking Rate =50rpm

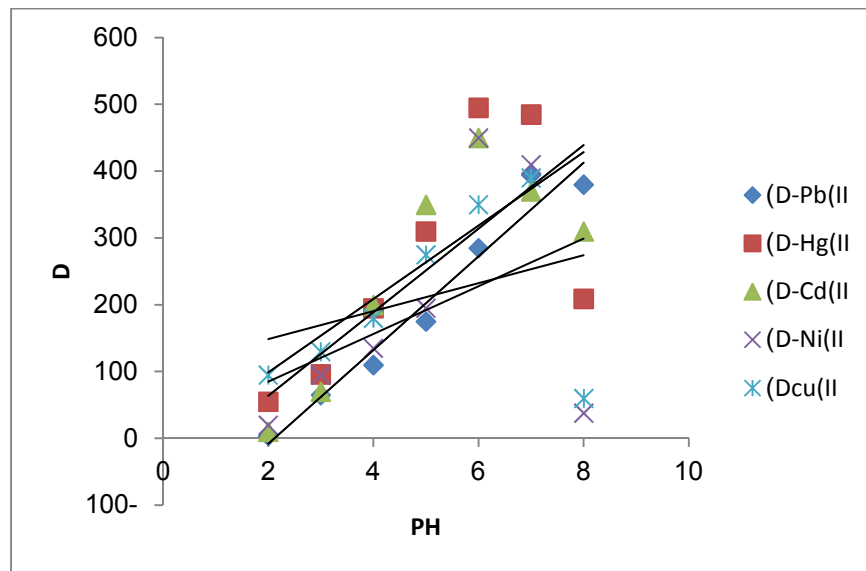


Fig. 3. Effect of PH on Distribution ratios of metal ions adsorbed on N5 immobilized on silica gel

$$D = \frac{\text{Amount of metal ion absorbed. } 100}{\text{amount of metal ion in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin gm}}$$

Whereas, $[MCl_2 = Cr(III), Ni, Hg, Cd(II), \text{ and } Pb(NO_3)_2]$, Volume =2ml, $NaNO_3$ 0.35mol/L, V=15ml, Room Temp, Time =90 equilibrium.

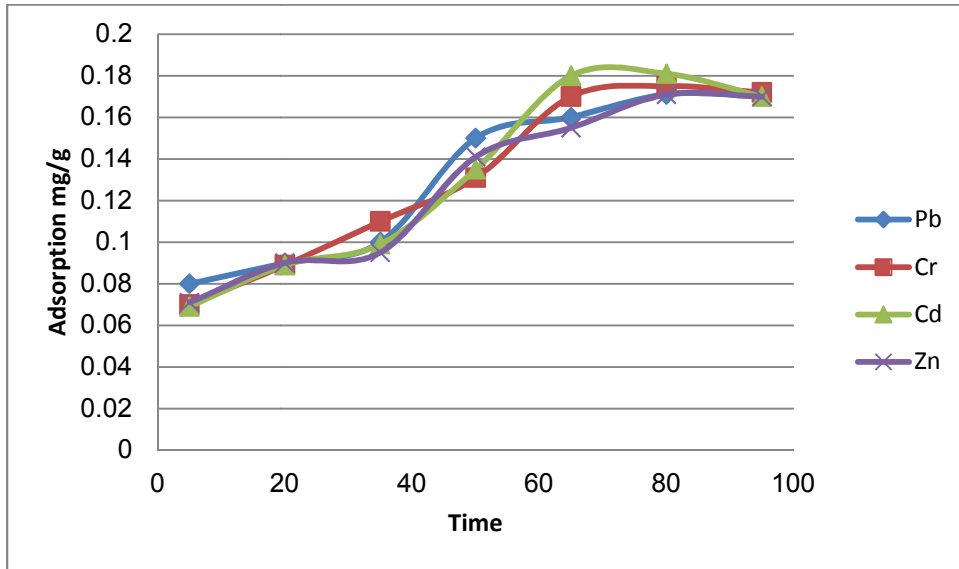


Fig. 4. Effect of Time on %adsorption of Metal ion on N5-silica gel surface

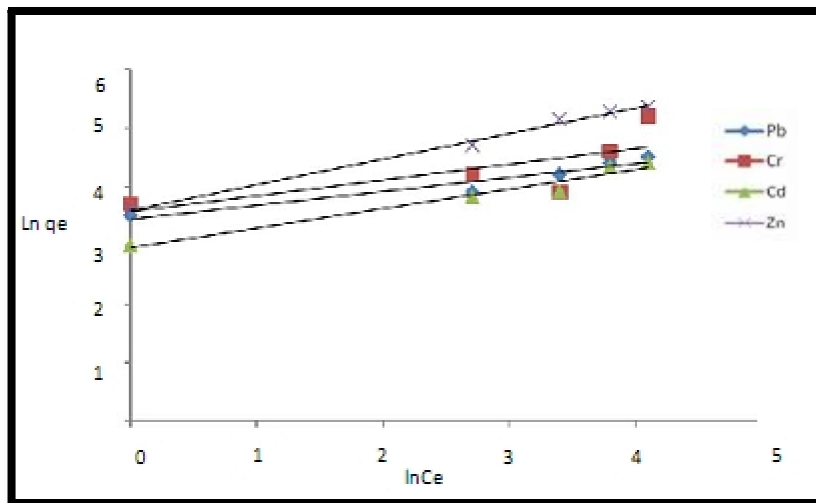


Fig. 5. Freundlich isotherms of metal ions on N5-silica gel surface

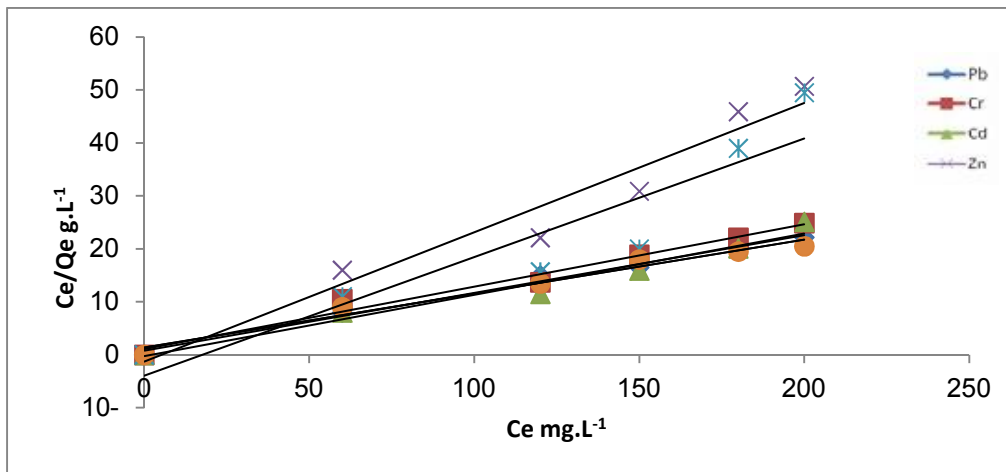


Fig. 6. Langmuir isotherms of metal ions on N5-silica gel surface of Cr^{+3} , Pb^{+2} , Cd^{+2} , Zn^{+2} , at different Time of Contact, Temp 30°C

4. CONCLUSION

The complexes have been synthesized and fully characterized on the bases of C.H.N.M, elemental analysis, ^{13}C NMR, UV- Visible and FTIR spectra as well as, the structures of complexes was characterized by magnetic moments and molar conductance in DMSO solution and molar ratio of metal were also determined. All complexes have an octahedral geometry around the metal center in (1:1) (L:M). The adsorption study on N5-ligand immobilized on silica gel showed high efficiency toward Cr(III), ion rather other ones depending on the parameters of K_d constant calculated from batch adsorption method.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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