

Synthesis, spectral and kinetic studies of N₂O₂ macrocycle ligand with divalent metal ions (Co, Ni and Cu) complexes

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الخلاصة

تضمن البحث تحضير ليكاند حلقة كبيرة يحوي على الاوكسجين والنيتروجين كذرات واهبة من خلال تحضير المشتق الاولي الذي نتج من تفاعل مكافئين من السلسلدهايد مع مكافئ واحد من الفلنلن ثنائي الامين وباستخدام الايثانول كوسط للتفاعل . اما الليكاند ومعداته مع ايونات الفلزات الثنائية للكوبلت والنيكل والنحاس فقد تم من خلال تفاعل القالب حيث اضيف الى محلول المشتق الاولي رباعي بروموايثان ومن ثم تمت اضافة ملح الفلز الذي سيقوم اضافة قاعدة لازالة بروتونات مجموعة الهيدروكسيل الفينولية للسلسلدهايد وباستخدام طريقة التصعيد العكسي وبوجود الميثانول كوسط للتفاعل. تم تشخيص المركبات المحضرة بواسطة مطيافية الاشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية ووطيف الرنين النووي المغناطيسي للبروتونات وطيف الكتلة – كروماتوغرافيا الغاز لمعرفة الوزن الجزيئي وعدد الايزومرات المتكونة اضافة الى قياس الحساسية المغناطيسية للمعقدات. كما وتمت دراسة حركات التفاعل بواسطة طريقة التوقف-جريان لمعرفة ميكانيكية التفاعل. وبينت الدراسات ان المعقدات رباعية التنسيق مع ايونات الفلزات ورباعية السطوح لمعقدي الكوبلت والنحاس ومربع مستوي لمعقد النيكل.

Abstract

The synthesis of macrocyclic ligand contain N and O as donor atoms have been carried out through the reaction of one equivalent of phenylenediamine with two equivalent of salicylaldehyde to obtained the precursor which that undergoes the template reaction with tetrabromoethane and the divalent metal ion (Cobalt, Nickel and Copper). The prepared compounds has characterized by [FTIR, UV-Vis, HNMR and GC- Mass spectroscopies], the kinetic study of complexes have been determined by stopped-flow spectrophotometry. The studies shows the geometry around the metal ions are four coordinate with unique isomer of the complexes since displayed a single signal in chromatograph of each one.

Introduction

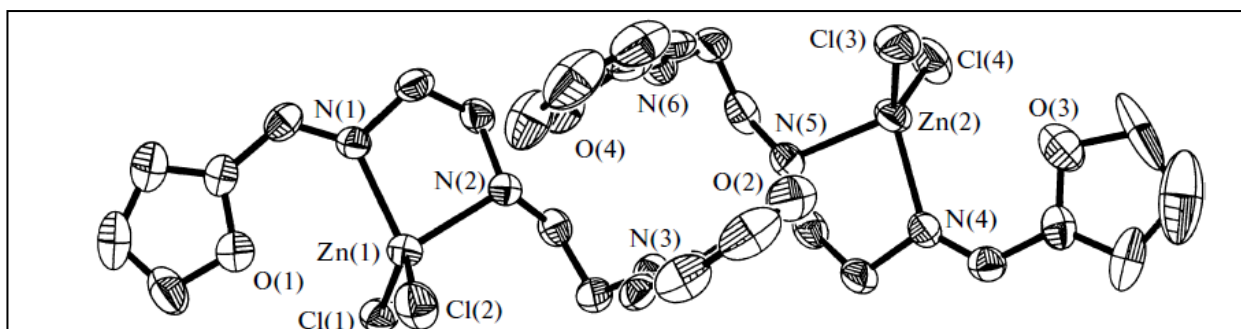
Recent studies of polydentate Schiff base macrocycles ligands showed larger importance applications in various fields as nuclear medicine, pharmacology, industry and analytical chemistry⁽¹⁻⁴⁾. In the case of N, O donor atoms Schiff base complexes have been investigated as antitumor chemotherapeutic agents and as adsorbed agents of sea pollution⁽⁵⁾. The radioactive isotopes of copper and cobalt

was based in radiopharmaceutical field.⁽⁶⁻⁸⁾, The finding that metal complexes of these ligands are ubiquitous is a reflection of their facile synthesis, wide application, and accessibility of diverse structural modifications. Schiff base complexes are of great interest especially for inorganic and bioinorganic chemistry⁽⁹⁾. To the best of our knowledge, in the past two decades, Schiff base complexes derived from furaldehyde have been less reported. In a recent papers⁽¹⁰⁾. This study covered the type macrocyclic ligands contain the nitrogen and oxygen as a donor atoms.

X-ray crystallography of Zn^{+2} complex.

Experimental part

All reagents were commercially available (Aldrich Chemical Company) and were used without further purification. The solvent used in the synthesis were distilled from the appropriate drying agent immediately prior to use all manipulations in the synthesis of precursor and template ligand complexes were performed under Nitrogen atmosphere. Electronic spectra were measured in the region 200-800 nm for solution methanol at room temperature using a Perkin Elmer precisely UV-Vis



spectrophotometer. Infrared spectra were recorded by using a Varian Resolutions – 300 FTIR spectrophotometer. HNMR spectra were recorded in DMSO-d_6 using a JEOL – JNM-ESC400; Mass spectra were obtained using GC-Mass ion-7879-US GC-mass spectrophotometer. (All measurements were done in New Castle University, School of Chemistry).

Preparation of precursor

To phenylenediamine (4.517g, 41.7 mmol) dissolved in ethanol (40 mL) was added two equivalent of salicylaldehyde (10.18g, 83.4 mmol) the mixture heated gently about 50 °C under nitrogen blanket for 0.5 hour, the color of solution became pale yellow stopped the heating and let the mixture to stirring only about 1.5 hours. The deep yellow precipitate was obtained , filtered washed with ethanol and ether twice times, recrystallized , dried gave orange crystals in color Yield = 88% .

Preparation of complexes

The complexes were performed with template reaction method, to solution of precursor (1.00g, 3.16 mmol) dissolved in (30 mL) absolute methanol added alcoholic KOH solution (0.354 g in 10 mL methanol), then a (1.092 g , 3.16 mmol) of tetrabromoethane was added slowly to the solution, to the resulted mixture a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.919 g, 3.16 mmol) were added as drop wise. The mixture heated under nitrogen atmosphere and reflux for three hours. The clear solution change to deep yellow in colour. Cooled to room temperature the solvent removed with vacuum, the result precipitate collected, washed with dry ether and dried. Yield = 65%. The cobalt and cupper complexes were carried out in the similar method which that showed in the preparation of nickel complex accept the metal cobalt and cupper salts instead with nickel ion salt.

Kinetic Studies

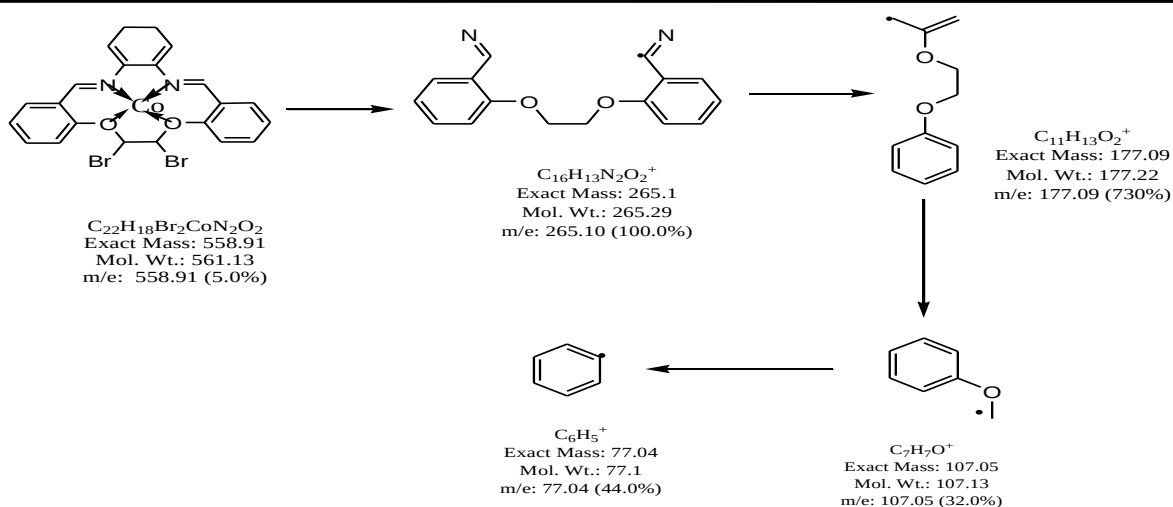
In the kinetic studies, the hydrated nitrate salts of Co, Ni and Cu were used. Acetonitrile (the solvent) was dried over CaH_2 and distilled under an atmosphere of dinitrogen immediately prior to use.

All kinetic studies were performed using an Applied Photo-physics SX.18MV stopped-flow spectrophotometer modified to handle air-sensitive and non-aqueous solutions. The spectrophotometer was controlled *via* a RISC pc. The temperature was maintained at $25.0 \pm 0.1^\circ \text{C}$ using a Grant LTD 6G thermostat tank with combined recirculating pump. The reactant solutions of metal salt and ligand were prepared in CH_3CN under an atmosphere of dinitrogen and transferred to the spectrophotometer *via* gas-tight, all-glass syringes. The solutions of all reagents were prepared by dilution from freshly made stock solutions and used within 1 hour of preparation.

The absorbance-time traces were fitted to exponential curves using the Applied Photophysics software. The observed rate constants (K_{obs}) presented in Figs. are the average of at least three experiments. The error bars presented in the figures show a 10% reproducibility. All experiments were performed under pseudo-first-order conditions with the concentration of the ligand in an excess over the concentration of the metal ion." The dependence on the concentration of ligand was determined from plots of k_{obs} *versus* ligand, as illustrated in Fig. 17 . The straight line plots were analysed by least-square fits, constrained to go through the origin.

Results and Discussion

The precursor synthesized contain N and O donor atoms from reaction of two eq. salicylaldehyde with one eq. phenylinediammine, the ligand and their complexes were obtained by template reaction deprotonation the OH protons, added the tetrabromoethane, and the metal salts **Scheme 1**. The compounds was characterised by FT-IR, UV-Vis, HNMR and GC-Mass spectroscopies



Scheme 1: Synthetic route of precursor and complexes

FT-IR spectroscopy

The IR spectrum of the precursor **Fig.1** displays a broad band at (3326 cm^{-1}) due to the $\nu(\text{O-H})$ stretching with hydrogen bonding between two hydroxyl groups, the $\nu(\text{C-H})$ stretching of rings and aliphatic appeared at (3055 cm^{-1}) and (2974 cm^{-1}) respectively. The characteristic band at (1609 cm^{-1}) assigned to $\nu(\text{C=N})$ stretching indicating the disappear the aldehyde carbonyl which that appear at (1720 cm^{-1})⁽¹¹⁾. While the IR spectra of complexes Co^{+2} , Ni^{+2} , Cu^{+2} , **Fig.2**, **Fig.3**, **Fig.4** respectively showed disappear the band at (3326 cm^{-1}) due to $\nu(\text{O-H})$ stretching in precursor as well as the shifting to lower frequency between ($6\text{--}9\text{ cm}^{-1}$) This shifting can be attributed to the delocalisation of the electron density of the metal ion into the π -system of the ligand ($\text{HOMO} \rightarrow \text{LUMO}$) [where HOMO= Highest Occupied Molecular Orbital; LUMO= Lowest Unoccupied Molecular Orbital], the weak band at ($1531, 1527, 1526\text{ cm}^{-1}$) assigned to $\nu(\text{C=C})$ aromatic stretching of the complexes⁽¹²⁾. **Table 1**.

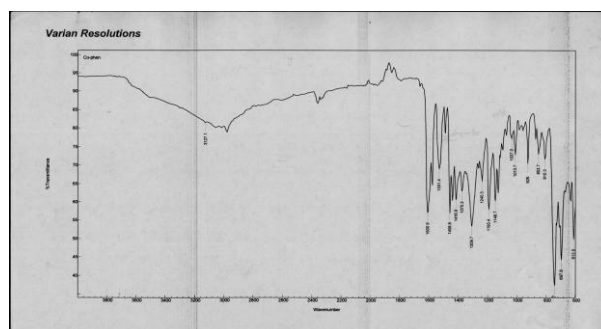
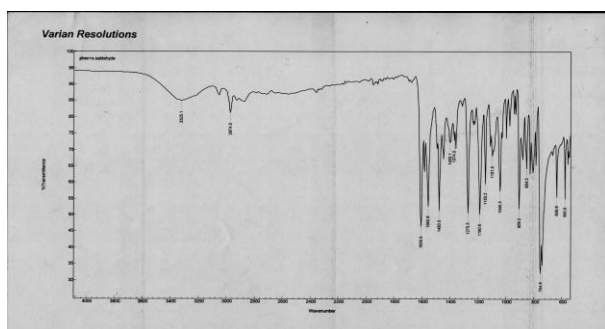


Fig.1: FT-IR spectrum of precursor

Fig.2: FT-IR spectrum of Co^{+2} complex

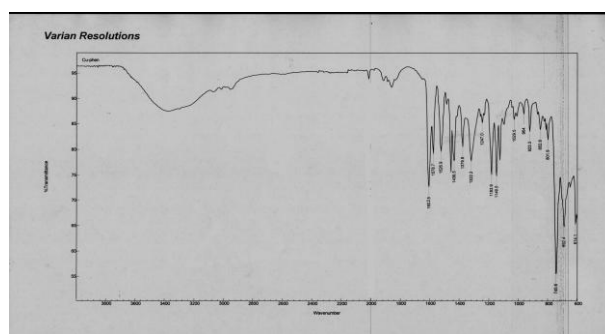
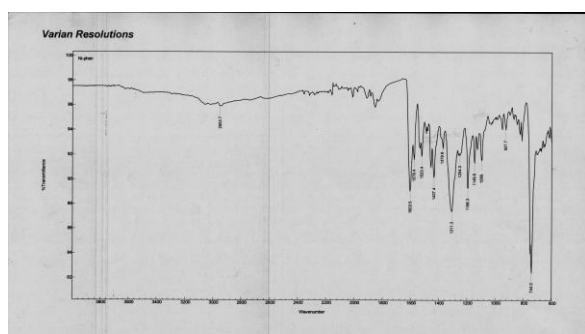


Fig.3: FT-IR spectrum of Ni²⁺ complex Fig.4: FT-IR spectrum of Cu²⁺ complex

Table 1: Infra red spectral data of the compounds in cm⁻¹

Comp.	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{H})$ aliphatic	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}=\text{C})$
precursor	1609	3326	2979	3055	1578
[Co L]	1600	-	2934	3069	1531
[Ni L]	1603	-	2953	3080	1526
[Cu L]	1602	-	2950	3080	1527

Uv-Vis spectra

The UV-Vis spectra of complexes **Figs. 5,6,7,8** for Co²⁺, Ni²⁺, Cu²⁺ and mixed complexes respectively appears the absorption peaks for Co²⁺ complex at (372 nm, $\epsilon_{\text{max}} = 1090 \text{ molar}^1 \text{ cm}^1$) due to charge transfer and (522 nm, $\epsilon_{\text{max}} = 35 \text{ molar}^1 \text{ cm}^1$) due to d-d transition type $^4\text{T}_2 \rightarrow ^4\text{E}$ corresponding with tetrahedral geometry, the Ni²⁺ complex showed the peaks at (365 nm, $\epsilon_{\text{max}} = 1100 \text{ molar}^1 \text{ cm}^1$) due to charge transfer and (475 nm, $\epsilon_{\text{max}} = 30 \text{ molar}^1 \text{ cm}^1$) due to d-d transition type $^1\text{B}_{2g} \rightarrow ^1\text{B}_{1g}$ which that proper with square planar geometry. While the Cu²⁺ complex displays the twin head peak at 370,382 nm, $\epsilon_{\text{max}} = 1050 \text{ molar}^1 \text{ cm}^1$) due to charge transfer and (630 nm, $\epsilon_{\text{max}} = 06 \text{ molar}^1 \text{ cm}^1$) due to d-d transition type $^2\text{E} \rightarrow ^2\text{T}_2$ corresponding with tetrahedral geometry⁽¹³⁾, **Table 2**.

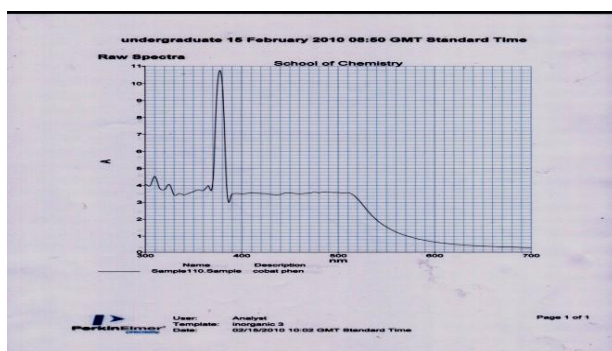


Fig.5: UV-Vis spectrum of Co²⁺

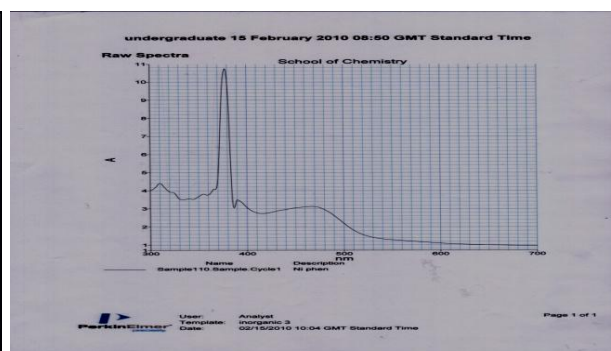


Fig.6: UV-Vis spectrum of Ni²⁺

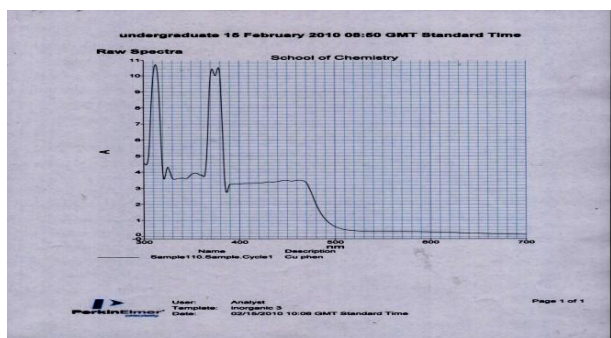
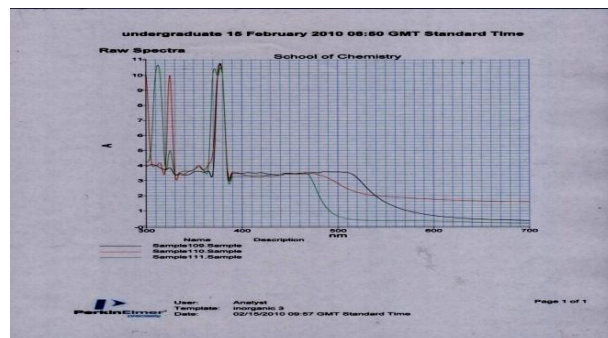
Fig.7: UV-Vis spectrum of Cu^{+2} 

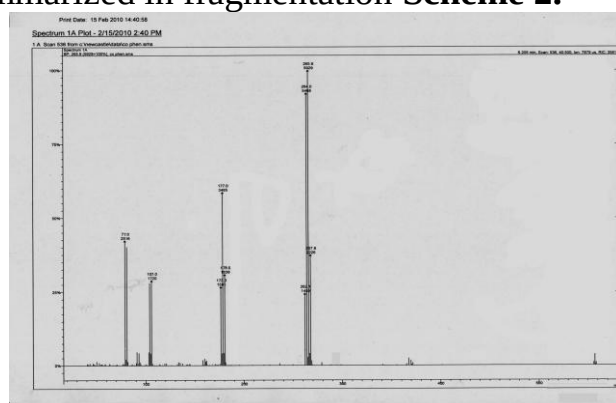
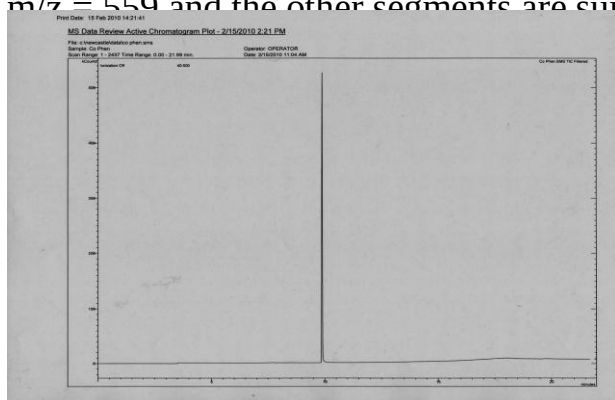
Fig.8: UV-Vis spectrum of mixed complexes

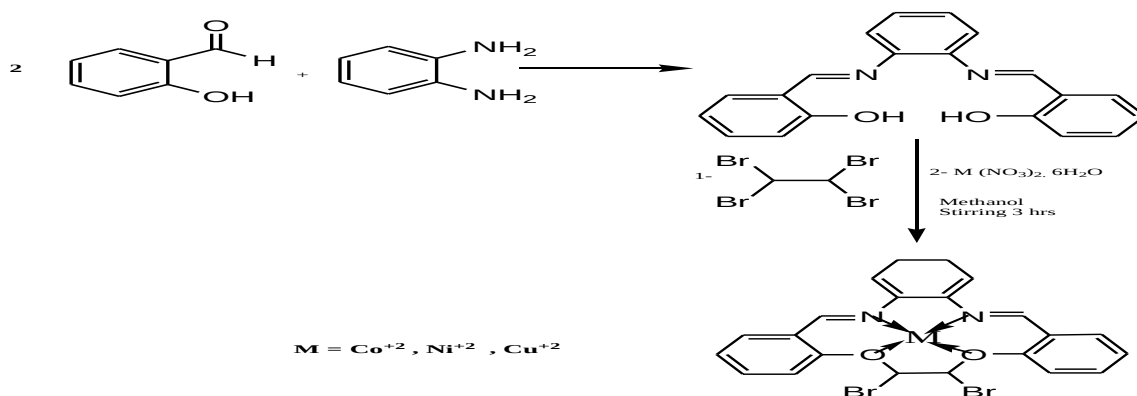
Table 1: physical properties and UV-Vis data of the compounds

Comp.	Color	Yield	λ nm	E_{max} $\text{L.mol}^{-1}.\text{cm}^{-1}$	μ_{eff} BM	Type of transition	geometry
precursor	orange	88%	-	-	-	-	-
[Co L]	brown	67%	372 522	1090 35	4.1	C.T ${}^4\text{T}_2 \rightarrow {}^4\text{E}$	Td
[Ni L]	Deep yellow	65%	365 475	1100 30	-	C.T ${}^1\text{B}_{2g} \rightarrow {}^1\text{B}_{1g}$	D_{4h}
[Cu L]	green	58%	370,382 630	1050 06	1.72	C.T ${}^2\text{E} \rightarrow {}^2\text{T}_2$	Td

GC-Mass spectroscopy

The gas chromatography of Co^{+2} **Fig.9** the chromatograph showed a single peak at retention time ($R_t = 9.8$ mint.) indicated the complex found in solution as one isomer. Whereas the mass spectrum of the complex **Fig.10** show the parent ion at $m/z = 559$ and the other segments are summarized in fragmentation **Scheme 2**.

Fig.9: Chromatograph of Co^{+2} complex Fig.10 Mass spectrum of Co^{+2} complex



Scheme 2: mass fragmentation of Co^{+2} complex

The gas chromatograph of Cu^{+2} **Fig.11** showed two peaks at ($R_t = 9.7$ minut.) attributed to the complex isomer and ($R_t = 10.7$ minut.) can be attributed to a small amount of impurity that is supported by the intensity of peak compare with parent isomer 40: 350.

The mass spectrum of complex **Fig.12** showed the parent ion at $m/z = 563$. While the segment fragmentation similar to the fragmentation which that showed in Co^{+2} complex.

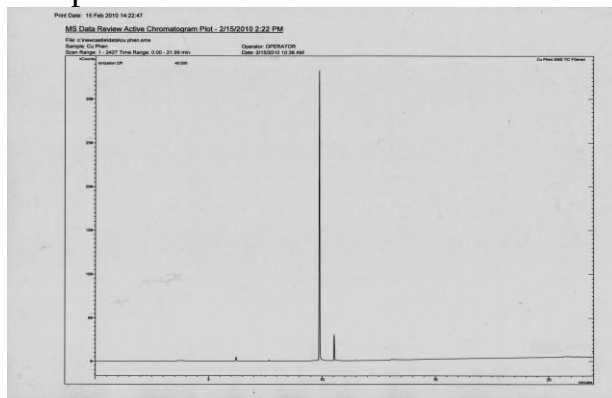


Fig.11: Chromatograph of Cu^{+2} complex

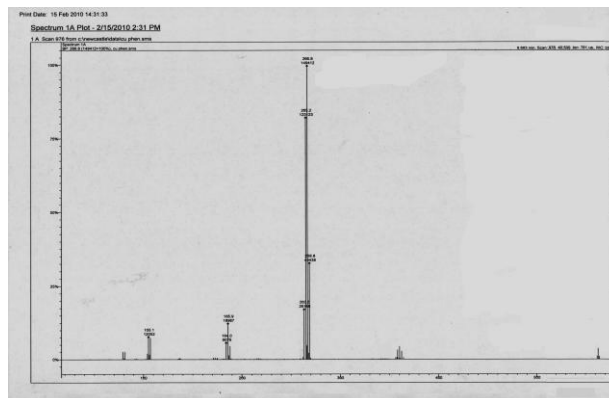


Fig.12: Mass spectrum of Cu^{+2} complex

HNMR spectra

HNMR spectra in $DMSO-d_6$ of precursor and complexes **Figs.13-16** displays the data. The precursor showed the chemical shift at ($\delta = 8.92$ ppm, 2H) assigned to imines proton ($H-C=N$), the signals at ($\delta = 7.44$ ppm, 2H, $\delta = 7.40$ ppm, 6H, $\delta = 6.95$ ppm, 4H) attributed to aromatic three rings in different environments, the signal at ($\delta = 3.32$ ppm, 2H) assigned to ($H-O$) protons attached directe to aromatic

ring⁰. While the signal at ($\delta = 2.48$ ppm) attributed to solvent DMSO- d_6 . The HNMR spectra of three complexes appeared the disappear of the signal at ($\delta = 3.32$ ppm, 2H) assigned to (H-O) protons in the precursor and appeared new chemical shift at ($\delta = 7.2$ -7.6 ppm, 2H) assigned to (H-C-Br) indicated the binding of tetrabromoethane with precursor, while the shifting of aromatic ring protons and the change of intensity indicated the coordination between the metal ions and ligand was take place⁽¹⁴⁾.

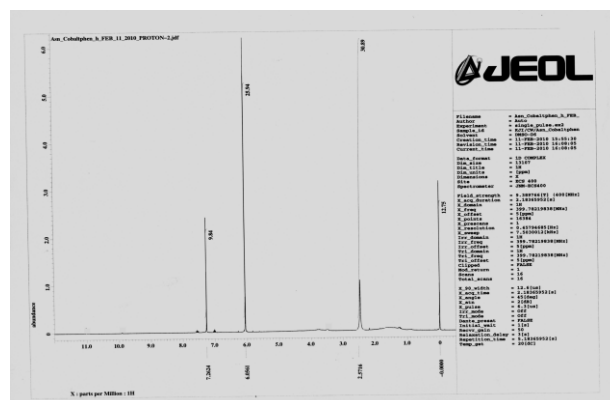
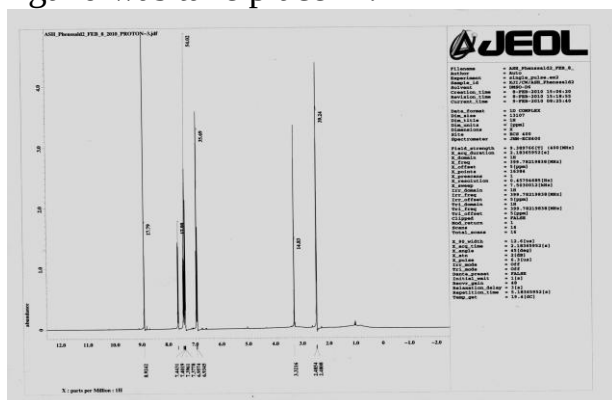


Fig.13: HNMR spectrum of precursor

Fig.14: HNMR spectrum of Co^{+2} complex

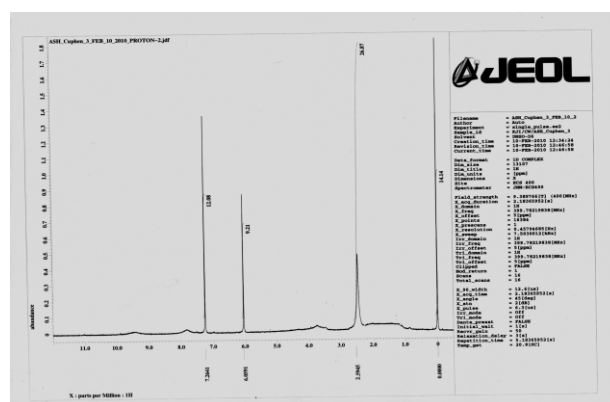
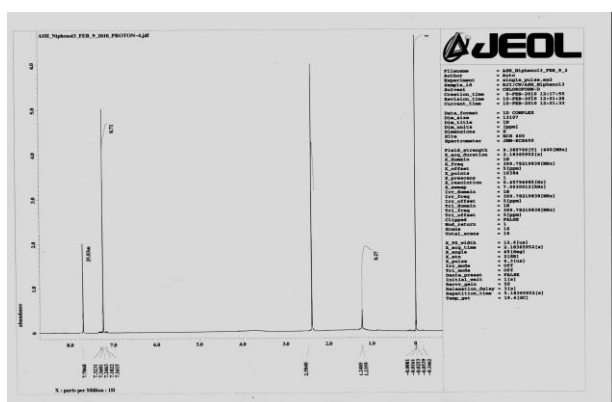


Fig.15: HNMR spectrum of Ni^{+2} complex

Fig.16: HNMR spectrum of Cu^{+2} complex

Kinetic and mechanism of complex formation

We have investigated the kinetics of the reactions of the ligand with M^{2+} ($M = Co, Ni$) in CH_3CN , using stopped-flow spectrophotometry to see if there is a difference in the kinetics for the formation of the complexes where the ligand is coordinated ($M = Co, Ni$). The reactions were studied under pseudo-first-order conditions with $[Ligand] > 10[M^{2+}]$. In all cases, the stopped-flow absorbance-time traces can be fitted to a single exponential curve (Fig. 17), indicating that the reaction exhibits a first-order dependence on the concentration of M^{2+} . This conclusion is confirmed in

studies where the concentration of M^{2+} was varied in the range 0.2-1.0 mmol dm⁻³ with [Ligand] = 10 mmol dm⁻³, but the values of the observed rate constants (K_{obs}) for each reaction did not change. For each different metal ion, the dependence of K_{obs} on the concentration of ligand was the same⁽¹⁵⁻¹⁷⁾, with all reactions exhibiting a first-order dependence on the concentration of ligand, as typified by the plot shown in Fig. 17 and the corresponding rate law in eqn (1). In line with other studies on chelate formation," we propose that the rate-limiting step of the chelate formation is the initial binding of ligand to $[M(NCMe)_n]^{2+}$ by replacement of one of the coordinated CH₃CN molecules. The usual intimate mechanism for such a reaction is dissociative and involves initial dissociation of a coordinated solvent from $[M(NCMe)_n]^{2+}$, generating $[M(NCMe)_{(n-1)}]^{2+}$ containing a vacant site at which ligand can bind (we suggest initially through a nitrogen). The full rate law for this mechanism is shown in eqn (2) and indicates that, over a large concentration range of ligand, the kinetics would exhibit a non-linear dependence on concentration of ligand. However, when the concentration of ligand is small, $K_1^M[MeCN] > K_2^M[Ligand]$ the rate law would simplify to that shown in eqn (3), which is of the same form as observed experimentally in eqn (1). For each of the reactions studied,

$$\frac{-d[M]}{dt} = K_a^M [Ligand][M^{+2}] \quad \dots\dots\dots (1)$$

$$\frac{-d[M]}{dt} = \frac{K_1^M K_2^M [ligand][M^{+2}]}{K_1^M [CH_3CN] + K_2^M [ligand]} \quad \dots\dots\dots (2)$$

$$\frac{-d[M]}{dt} = K_1^M K_2^M [ligand][M^{+2}] / K_1^M [CH_3CN] \quad \dots\dots\dots (3)$$

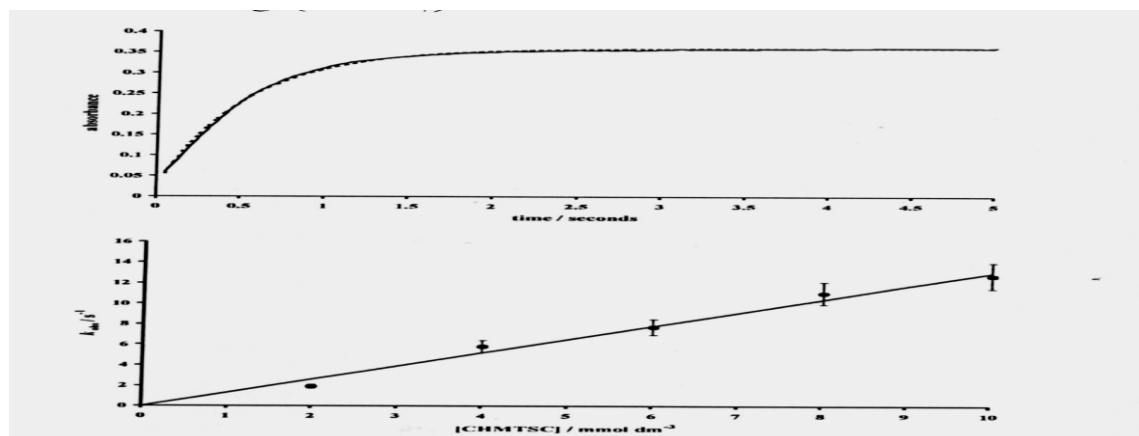


Fig. 17: Typical kinetic data for the reactions of M^{2+} with ligand in MeCN at 25 °C. The example shown is for the reaction with Co^{2+} . Top shows a typical stopped-flow absorbance-time curve when $[Co^{2+}] = 0.2$ mmol dm⁻³ and $[Ligand] = 2$ mmol dm⁻³. The fit is defined by the equation $A_1 = 0.359 - 0.335e^{-1.9t}$.

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