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Preparation and Spectroscopic Characterization of Iron(III) Complexes of a Functionalized Crown Ether

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ABSTRACT

This research includes the synthesis and characterization of Shiff's bases crown ethers prepared from condensation between cis-diaminodibenzo-18-crown-6 and benzaldehyde substituted with some groups such as;
4-H , 4-$CH_2(CH_2)_6CH_3$, 4-Cl , 4-Br and 4-NO_2 and their complexes with $Fe(NO_3)_3.9H_2O$ .The study involved solubility, melting points and thermal stability, elemental analysis have been detected with spectral studies using ^{1}H-NMR, UV-Visible and IR-spectroscopy .They found to be solid crystalline and appear to be salt Shiff's bases crown ethers formed by Ion-dipole interaction between the cation and the negatively charged oxygen atoms symmetrically placed in the crown ether ring .The complexes were prepared with molar ratio 1:1(ligand:metal salt) .they were found to have the general formula :-
$[Fe (L) (NO_3)_3.9H_2O]$.

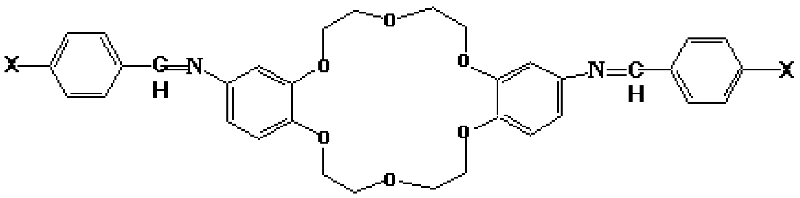
Keywords: Crown ethers, Schiff's bases, Crown ethers complexes.

INTRODUCTION

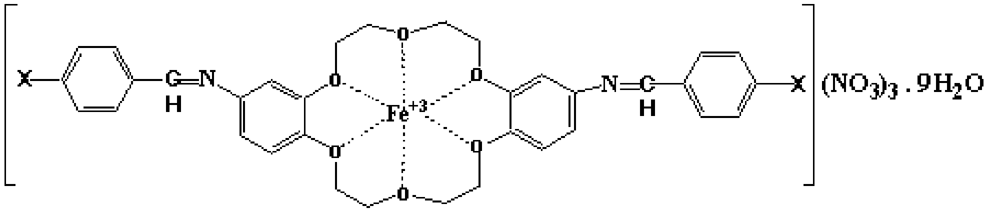
The study of macrocyclic ethers has attracted great interest in the last decades, not only from synthetic and a virtual explosion of solution and solid-state investigation of crown ethers and metal ions which include alkali metal, alkali earth metal, other main-group and transition-metal ions complexation properties point of view, but also with respect to their unusual characteristic(1-5) and include such applications as cation extraction, membrane transport,ion-selective electrodes, calorimetric measurements, and, guite recently, functionality of molecular structer using NMR spectroscopy(6-8). For the linkage of two crown ether units by means of aliphatic or aromatic chains, ester(9), amide(10), calixarene(11) and Schiff's bases(3,12-15) tybe precursors are commonly used .The formation of complexes by binding of cations, which is the most important characteristic of crown ethers, is caused by electrostatic ion-dipole interaction between cations and oxygen donor atoms arranged regularly in the polyether ring . The stability of the crown ethers with metals are affected by the relative size of the cation, the cavity of the crown ether, the number, arrangement and basicity of oxygen donor atoms, steric hindrance of the polyether ring, solvation of the cation, and electric charge on the cation(1).Uncommon complex stoichiometries, substitution effects, ring size effects, and sandwiching complexation of a series crown ethers by solvent extraction experiments have also been reported(13).

Many studies of ion complexation macrocyclic organic molecules, containing heteroatoms, are most often carried out using spectroscopic methods, among the latter electronic spectroscopy(16-18) .

In this study, we describe the synthesis of a new crown ether Schiff's bases . We have prepared an iron(III) complex of this Schiff's bases [Fe(L)$(NO_3)_3.9H_2O$].



CES_X



CES_XFe

where x is given below

SHIFF'S BASES	CES_1	CES_2	CES_3	CES_4	CES_5
Complexes	CES_1Fe	CES_2Fe	CES_3Fe	CES_4Fe	CES_5Fe
X	H	$CH_2(CH_2)_6CH_3$	Cl	Br	NO_2

EXPERIMENTAL

(i) Synthesis and materials

All the substituted aldehydes and dibenzo-18-crown-6 were commercial products of Anlar grade and were used without further purification. The preparation of Schiff's bases was carried out according to Schem 1.

Nitration of dibenzo-18-crown-6 :- (19)

6.41 g. (17 mmole) DB18C6 and 130 ml chloroform were placed in 500 ml two-neck round bottom flask equipped with reflux condencer and dropping funnel. After dissolution of the polyether by stirring 96.5 ml glacial acetic acid was added, followed by nitration solution which consist of 5 ml (78.9 mmole) concentrated nitric acid in 13 ml acetic acid. The latter was added dropwise over 30 minutes. The reaction mixture was stirred without heating for an hour, by which the solution turned green and then yellow. After refluxing for 4 hours, the reaction mixture was filtered of giving a 4.38 g. of trans-dinitrodibenzo-18- crown-6 m.p (245-248^{0}C). On sitting the mother ligour for more than 5 days, 3.04 g. of the cis isomer was collected m.p (209-213 ^{0}C). The products were recrystallized from DMF.

Reduction of dinitrodibenzo-18-crown-6 :- (20)

To a suspension of 2.5 g. (5.6 mmole) of cis-DNDB18C6 in 38 ml of 38% hydrochloric acid and 60 ml butanol; 7.5 g. of tin metal powder was added and refluxed for 4 hours. Two additional portion 38 ml of hydrochloric acid and 7.5 g.of tin metal powders were added and the mixture was refluxed for 6 hours and over night respectively.At the end of the reaction the mixture was colorless, then transferred to a refrigerator and kept for second day, a white waxy precipitate was formed. Fifty ml of 6.4 M sodium hydroxide solutions was added, heated on steam bath, a white to gray precipitate formed which recrystalized from ethanol giving about 0.5 g. white powder (cis-DADB18C6) m.p (180-182 ^{0}C) .

Synthesis of the Schiff's bases, CES$_X$:- (15)

A reaction mixture of cis-diaminodibenzo-18-crown-6 0.59 g. (1.5 mmole) in an absolute ethanol, (3 mmole) of the appropriate aldehyde, A red-brown compound was formed, recrystalized from ethanol yielded the pure Schiff's bases, CES$_X$.

Synthesis of the complexes, CES$_X$Fe :- (21)

A solution of the ligand (CES$_X$) (0.14 mmole) in methanol was added to the solution of the $Fe(NO_{3)}.9(H_2O)$ (0.41 mmole) in methanol (minimum quantity) (1:1,ligand:metal salt) with constant stirring for 30 minutes on water bath, after Cooling to 0^{0}C crystals of the black complexes was separated, which filtered off, washed with methanol and dried at room temperature (25^{0}C) .

The Schiff's bases, CES$_X$, and their complexes, CES$_X$Fe, were characterized by spectroscopic techniques.

(ii) Techniques

Elemental analysis was performed with a Themo Finniganl Eger 300F.^{1}H-NMR spectra were recorded on a GEMINI-200. IR spectra were obtained using a Buck Scientific model 500 spectrophotometer. U.V spectra were recorded on a U.V Spectronic – Helios Alpha.

RESULT AND DISCUSSION

Thermal stability

All complexes prepared in this work are solid and fairly thermally stable since they decompose (Table 2).

Solubility

The ligand is soluble in DMSO, EtOH, MeOH, $CHCl_3$.The complexes are stable, soluble in DMSO and insoluble in EtOH, MeOH, $CHCl_3$.

Spectroscopic study

The Schiff's bases was characterized by ^{1}H-NMR, IR, UV-Visible and
Elemental analysise.

The ^{1}H-NMR spectral data for these Schiff's bases show brodly similar
Spectral characteristics and the data for (CES_5) ligand (Figure 2) representive of the Schiff's bases (ppm, DMSO), δ 8.878(s, 2H, 2Ar-N=CH), 8.385-8.141(m, 8H, $2ArH_4$), 7.114-7.017(d, 6H, $2ArH_3$), 4.165(m, 8H, $4ArOCH_2$),3.887(m, 8H, $2CH_2$-O-CH_2), 2.508-2.5(DMSO, solvent) (13,22).

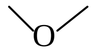
IR spectral (cm^{-1}, KBr disk), 3018-3076(=C-H aromatic), 2856-2934 (C-H aliphatic), 1620-1626(CH=N), 1231-1267(Ar-O-CH_2 aromatic), 1061-1135 (C-O-C aliphatic) (15) (Table 1, Figure 3).

The UV-Visible spectral [nm, (DMSO: EtOH) (1:4)$1x10^{-5}$M] of the ligands have two absorption bands were observed for it at (209-240) and (270-285) due to π-π^* and (335-371) n-π^* trasitions (15) (Table 2, figure 4).

The Fe(III) complexes was characterized by IR, UV-Visible and Elemental analysise.

The IR spectra (cm^{-1}, KBr disk) 3100-3500(OH, H2O groups), 2856-2950(C-H aliphatic), 1635-1654(CH=N), 1192-1262(Ar-O-CH_2 aromatic), 1028-1129(C-O-Cliphatic)(15) (Table 1, Figure 3).

The strong absorption bands assigned to the stretching vibration of (C-O-C)
In the group (CH_2-CH_2) in the spectra of

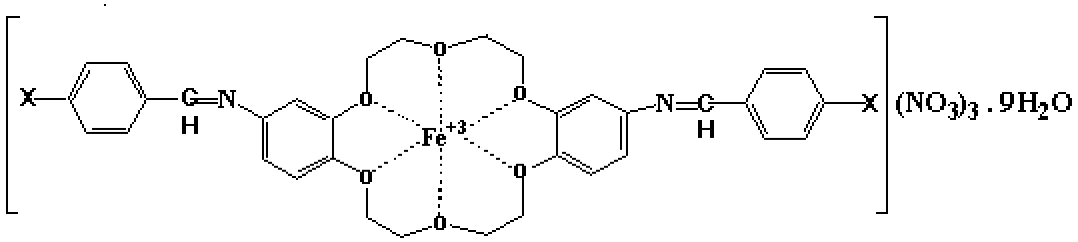


the free ligands were shifted to a lower
frequencies upon complexing of the ligand with the metal salt which give positive indication of complex rormation(15,23-25).As well as the strong absorption bands assigned to the stretching vibration of (CH=N) in the azomethine group were shifted to higer freguences in the complexes(15).This indicates that the oxygen atoms in the crown ether cavity involved in metal-oxygen bond formation.

Nature and structure of the complexes

The above studies give evidence about complex formation between the cavity of the crown ether and the Fe(III) used in this work .The formation of complexes by binding the cation is caused by electrostatic ion-dipole interaction between cation and negatively charged six oxygen atoms in the crown ether ring(26).

The following structural formula can be made for the complexes of 1:1 (ligand:metal) (Figuer 1) .The stable 1:1 complexes are obtained as the cation has an ionic diameter (Fe^{+3}=1.28A^0) fitted to the cavity size of crown ether size at DB18C6 (2.6-3.2A^0)(27) .



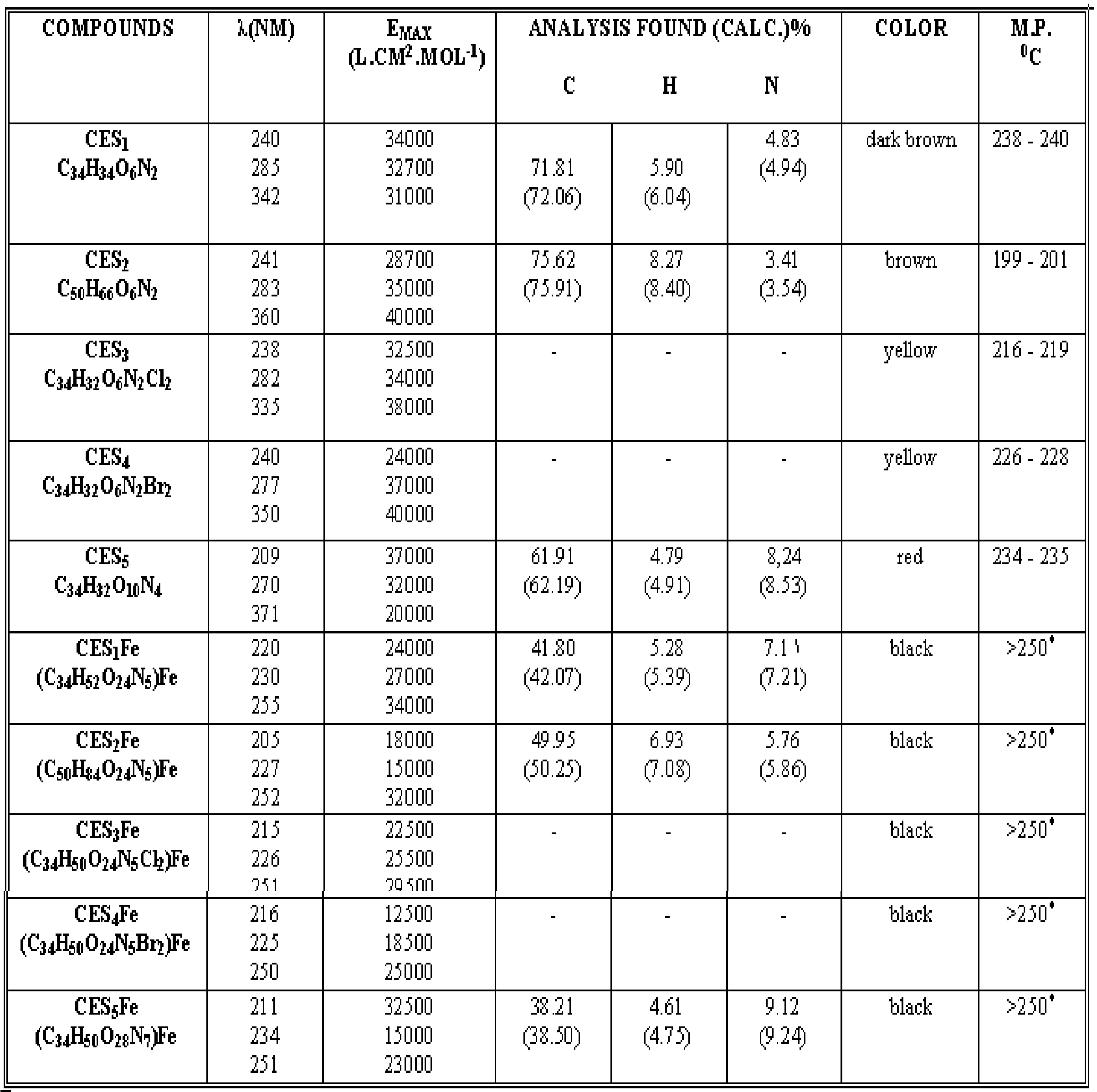
CES_XFe
Figure 1

The UV-Visible spectral[nm,(DMSO:EtOH) (1:4)1x10^{-5}M] of the complexes contained three bands were found to be shifted to lower wave length in the spectra of the complexes, complexation by a cation reduces the donor ability of the oxygen atoms of crown and results in ahypsochromic effect$^{(28)}$ (Table 2, Figure 4,5) .

Table 1: Major IR absorption band (cm^{-1}) of the Shiff's bases crown ethers and their complexes with Fe^{+3}

Compounds Vcm^{-1}	CES$_1$	CES$_2$	CES$_3$	CES$_4$	CES$_5$	CES$_1$Fe	CES$_2$Fe	CES$_3$Fe	CES$_4$Fe	CES$_5$Fe
ν(O-H)	-	-	-	-	-	3500-3200	3500-3200	3500-3100	3500-3200	3500-3100
ν(=C-H) aromatic	3050	3037-3018	3070	3076	3110-3075	-	-	-	-	-
ν(C-H) aliphatic	2934-2873	2923-2856	2929-2878	2917-2873	2922-2878	2885	2923-2856	2941-2867	2950	2941-2878
ν(C=N)	1620	1624	1621	1623	1626	1635	1654	1654	1654	1654
ν(Ar-O-CH$_2$) aromatic	1264 1231	1260 1235	1264 1236	1264 1236	1267 1240	1243	1192	1260	1258	1262
ν(C-O-C) aliphatic	1131 1062	1135 1061	1135 1089	1135 1067	1135 1061	1128 1060	1100 1028	1129 1050	1129 1061	1129 1050

Table 2: electronic data, physical properties and analysis of the Shiff's bases crown ethers and their complexes with Fe^{+3}



COMPOUNDS	λ(NM)	E_{MAX} ($L.CM^2.MOL^{-1}$)	ANALYSIS FOUND (CALC.)%			COLOR	M.P. ^0C
			C	H	N		
CES$_1$ $C_{34}H_{34}O_6N_2$	240 285 342	34000 32700 31000	71.81 (72.06)	5.90 (6.04)	4.83 (4.94)	dark brown	238 - 240
CES$_2$ $C_{50}H_{66}O_6N_2$	241 283 360	28700 35000 40000	75.62 (75.91)	8.27 (8.40)	3.41 (3.54)	brown	199 - 201
CES$_3$ $C_{34}H_{32}O_6N_2Cl_2$	238 282 335	32500 34000 38000	-	-	-	yellow	216 - 219
CES$_4$ $C_{34}H_{32}O_6N_2Br_2$	240 277 350	24000 37000 40000	-	-	-	yellow	226 - 228
CES$_5$ $C_{34}H_{32}O_{10}N_4$	209 270 371	37000 32000 20000	61.91 (62.19)	4.79 (4.91)	8,24 (8.53)	red	234 - 235
CES$_1$Fe $(C_{34}H_{52}O_{24}N_5)Fe$	220 230 255	24000 27000 34000	41.80 (42.07)	5.28 (5.39)	7.11 (7.21)	black	>250*
CES$_2$Fe $(C_{50}H_{84}O_{24}N_5)Fe$	205 227 252	18000 15000 32000	49.95 (50.25)	6.93 (7.08)	5.76 (5.86)	black	>250*
CES$_3$Fe $(C_{34}H_{50}O_{24}N_5Cl_2)Fe$	215 226 251	22500 25500 29500	-	-	-	black	>250*
CES$_4$Fe $(C_{34}H_{50}O_{24}N_5Br_2)Fe$	216 225 250	12500 18500 25000	-	-	-	black	>250*
CES$_5$Fe $(C_{34}H_{50}O_{28}N_7)Fe$	211 234 251	32500 15000 23000	38.21 (38.50)	4.61 (4.75)	9.12 (9.24)	black	>250*

*(decompose temperature)

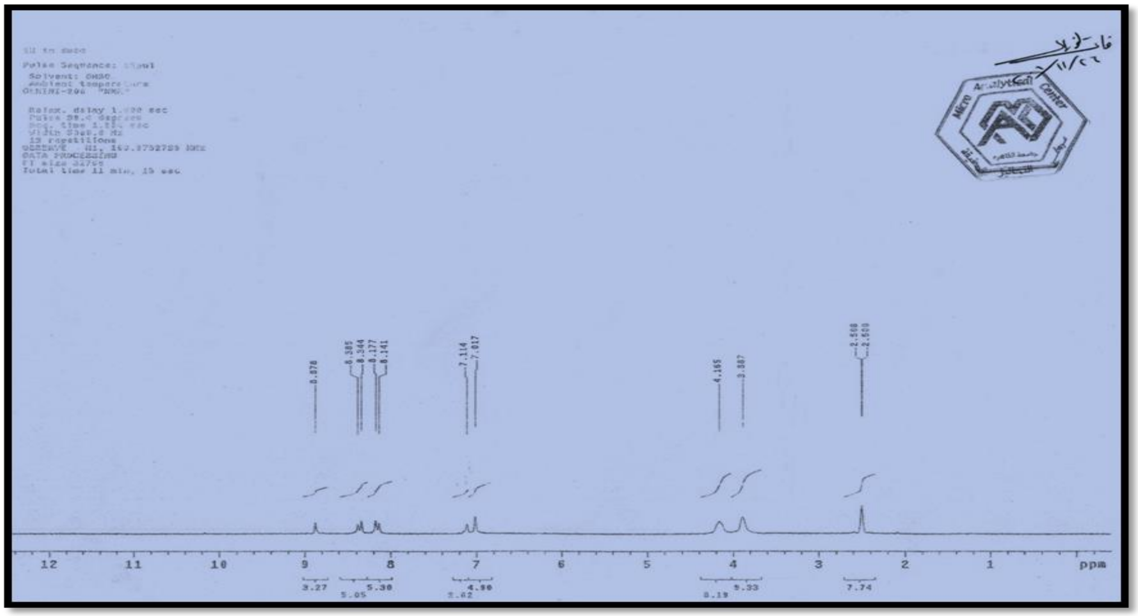
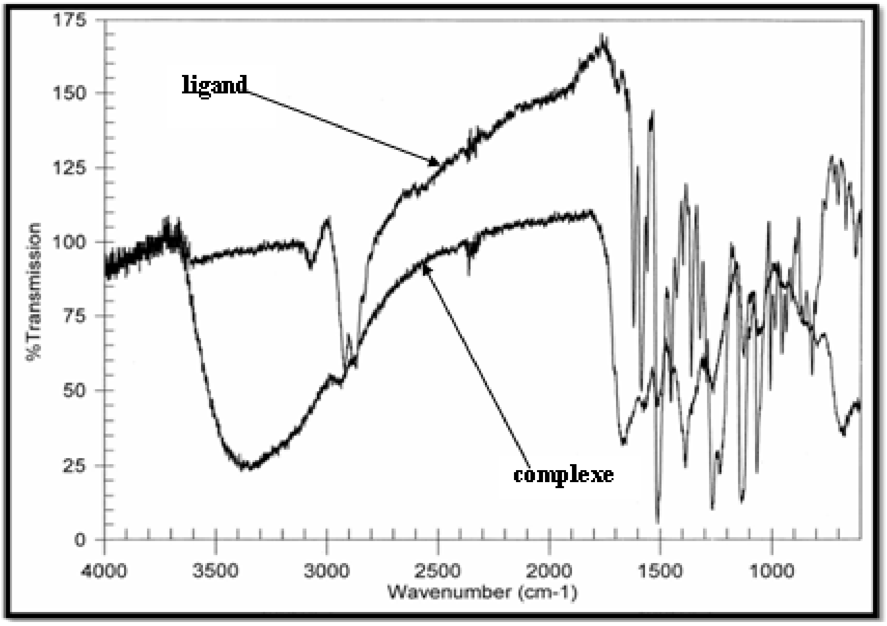


Figure 2 : The ^{1}H-NMR spectrum of compound CES 5



Figuer 3: The IR spectrum of compound CES_4 and CES_4Fe

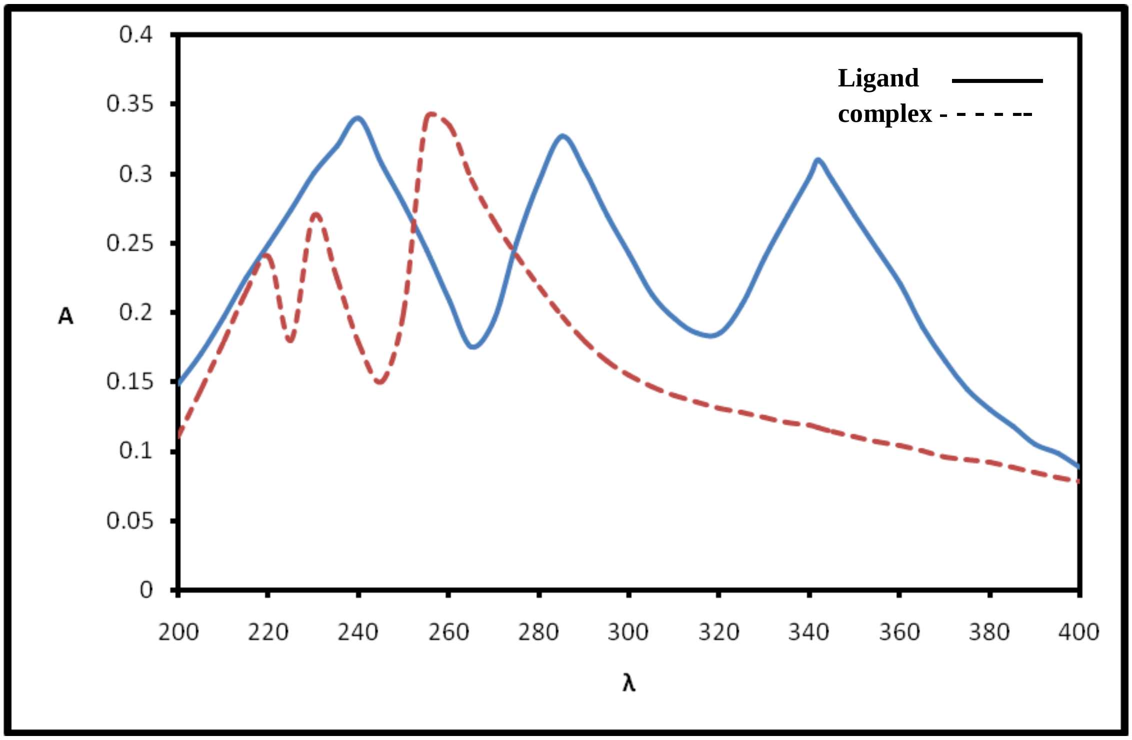


Figure 4: The U.V-Visible spectrum of compound CES_1 and CES_1Fe

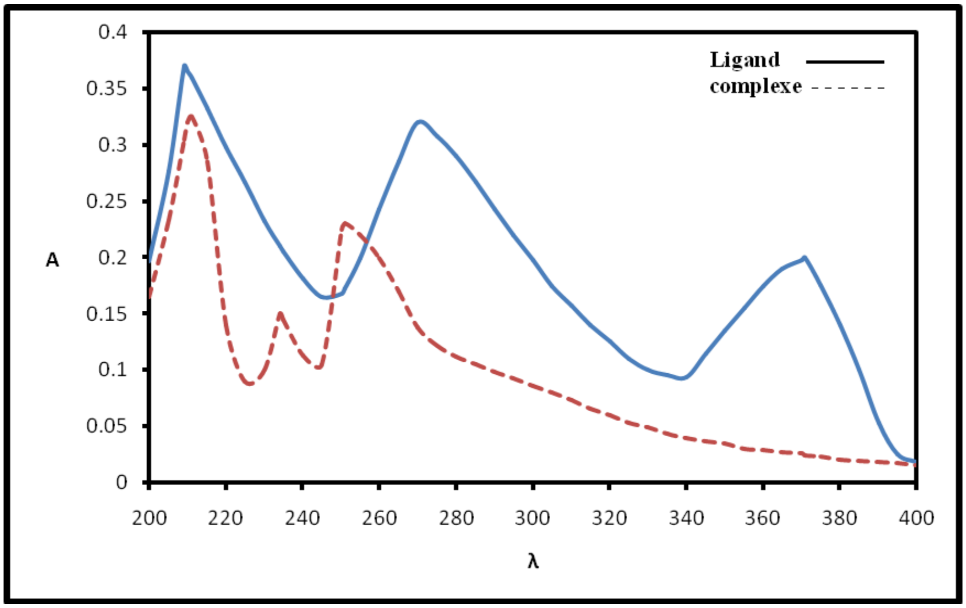
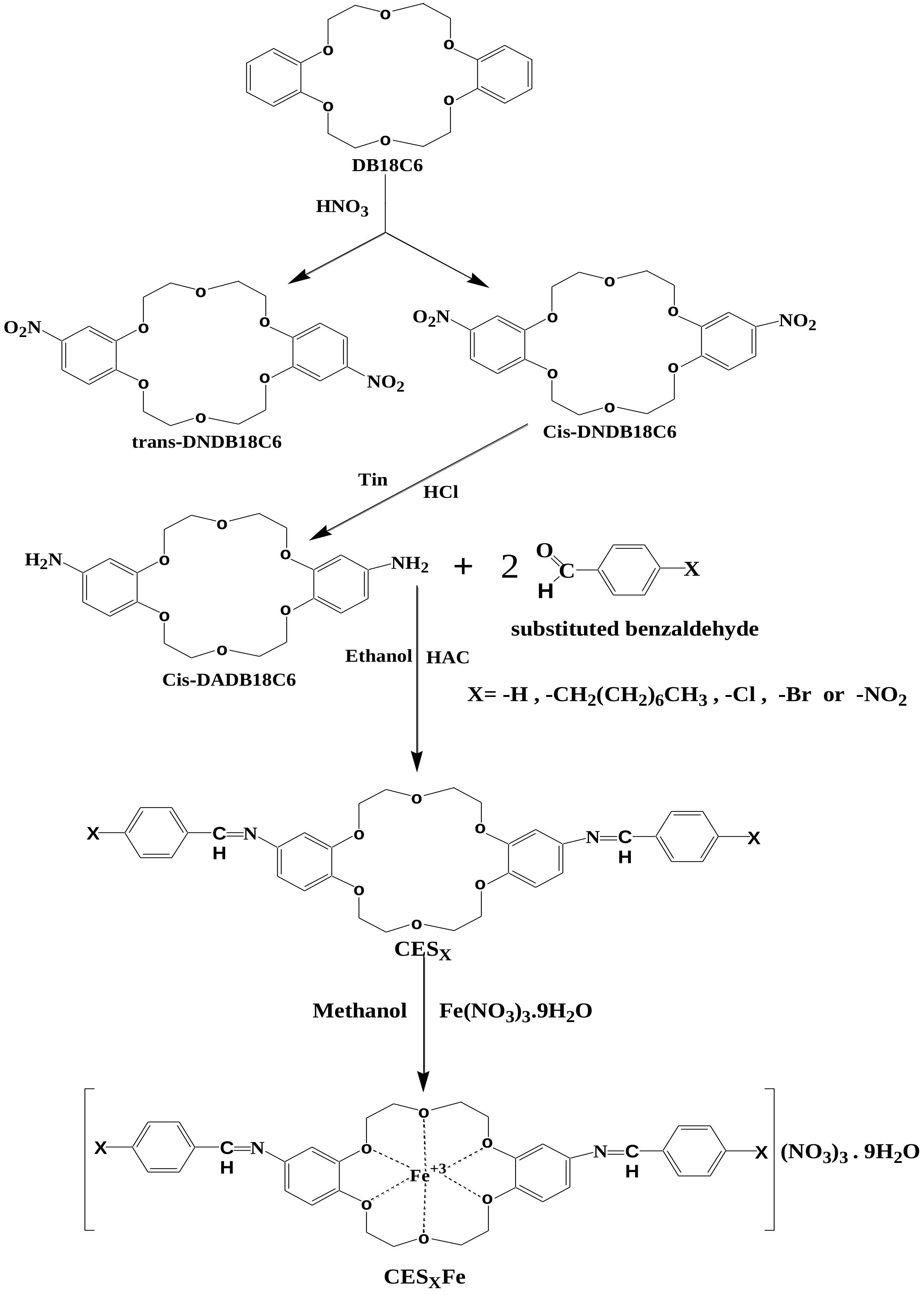


Figure 5: The U.V-Visible spectrum of compound CES_5 and CES_5Fe


DB18C6
HNO3
trans-DNDB18C6
Cis-DNDB18C6
O2N
NO2
Tin
HCl
H2N
NH2
+ 2
Cis-DADB18C6
substituted benzaldehyde
Ethanol
HAC
X= -H , -CH2(CH2)6CH3 , -Cl , -Br or -NO2
CESX
Methanol
Fe(NO3)3.9H2O
Fe+3
(NO3)3 . 9H2O
CESXFe

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REFERENCES

1-C.J. Pedersen, 1967, J.Am.Chem.Soc., 89, 2495.

2L.Y.Zhu,J.M.Dou,Y.Liu,P.J.Zheng,C.X.Du and Y.Zhu, 2000,Chinese Chemical Letters, 11(9), 835.

3-M.Yildiz,A.Kiraz and B.Dulger, 2007, J.Serb.Chem. Soc., 72(3), 215.

4-P.D.Beer,C.G.Graneand M.G.M.Drew,1991, J. Chem.SOC., Dalton Trans., 3235.

5-D.Wand, 1989, X.Sun and H.Hu, Polyhedron, 8, 5051.

6-C.Erk, M.Heydenreich and E.Kleinpete, 2006r, Turk J.Chem., 30, 261.

7-E.Makrlik, P.Vanura, and P.Selucky, 2009, Acta.Chim.Solv., 56, 475.

8-O.Sendil, E.Pecenek, G.Ekmekci and G.Somer, 2009, Current Analytical Chemistry, 5, 53.

9-E.Luboch, A.Cgon and J.F.Biernat, 1991, Tetrahydron, 47, 4101.

10-H.Dugas and J.Vaugeois, 1991, Synthesis, 5, 420.

11-B.Guan, M.Jiang, X.Yang, Q.Liang and Y.Chen, J.Royal Society of Chemistry, 4, 1393, 2008.

12-Z.Hayvali, M.Hayvali and H.Dai, 2004, J.of Molecules, 9, 860.

13-Y.Y.Wei, L.C.Ju, Z.H.Yi and L.Yu, 2004, Chinese Journal of Science Engineering and Technology, 22, 616.

14-T.P.Dhakal, T.Oshima and Y.Baba, 2009, World Academy of Sciencs Engineering and Technology, 56, 204.

15-Z.Hayvali, 2009, Transition Met.Chem., 34, 97.

16-S.M.Bakalova,M.P.Vladimirova, E.Stanoeva,M.Mitewaand J.Kaneti, 2003, Bulgarian Chemical Communications, 35(4), 245.

17-S.Ilhan, H.Temel, M.Sunkur and I.Tegin, 2008, Indian Journak of Chemistry, 47 A, 560.

18-M.Barboiu,C.T.Supuran, 1999,.Scozzafava and C.Guran, Metal-Based Drugs,6(2), 101.

19-W.H.Feigenbaum and R.H.Mickel, 1971, J.Polymer Sci., 9 A1, 817.

20-J.R.Johnson and R.Ketcham, J.Amer, 1960.Chem. Soc., 82, 2719.

21-I.M.Kolth), 1979, Analytical Chemistry, 51(5.

22-Shu-Yuan Zhang, Ke-Ke He and Shi-Jun Zheng, 2004, Chinese J. of Chem., 22, 395.

23-J.Cloud, G.Bunzil, D. Wessner, 1979, Inorganic Chimica Acta., 32.

24-M.Hiraok, 1982,"Crown Compounds their Chracteristics and Applications" Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York.

25-Nakamoto, 1985, "Infrared Spectra of Inorganig and Corrdination Compounds",Wiely, New York,.

26-M.Campelini and N.Nardi. , 1972,Inorganic Chimica Acta., 32.

27-R.MIzatt, D.J.Eatouh and J.J.Christenesen, Structture and Bonding, 16, 162, 1974.

28- Z.Guo, Y.Li, J.Yan, F.Bai, F.Li,D.Zhu, J.Si and P.Ye, 2000, Appl.Phys, B 70, 257.

تحظير ودراسة الخصائص الطيفية لمعقدات الحديد الثلاثي مع مركبات تحتوي الايثر التاجي كمجموعة فعالة

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الخلاصـــــة

لقد تضمن موضوع البحث تحضير وتشخيص صنف جديد من قواعد شف الايثرية التاجية الناتجة من تكثيف الايزومر سز- ثنائي أمينو ثنائي بنزو–١٨–كراون–٦ مع مشتقات البنزلديهايد المعوضة ببعض المجاميع في الموقع بارا وهي :– 4-H ، $4-CH_2(CH_2)_6CH_3$ ، 4-Cl ، 4-Br ، $4-NO_2$. ومعقداتها مع ملح الحديد الثلاثي $Fe(NO_3)_3.9H_2O$. وقد تمت دراسة قواعد شف ومعقداتها من حيث قابلية الذوبان، درجات الانصهار والتفكك الحراري، كما تم اجراء التحليل الدقيق للعناصر (C, H, N) بالاضافة الى دراستها طيفيا" باستخدام مطيافية الرنين النووي المغناطيسي للبروتون، مطيافية الاشعة فوق البنفسجية- المرئية ومطيافية الاشعة تحت الحمراء . وقد تبين من خلال الدراسة ان المعقدات المحضرة هي صلبة بلورية وان طبيعة هذه المعقدات عبارة عن ترابط الكتروستاتيكي ما بين الايون الموجب لملح الفلز وذرات الاكسجين الستة في حلقة الايثر التاجي ثنائي بنزو–١٨–كراون–٦ .