Template Synthesis, Structures and Spectral Behaviours of Binuclear Bimacrocyclic Pentaaza Complexes of Some Divalent Ions

Ahlam J. Abdul-Ghani & Nada A. Al-Najar*
Department of Chemistry, College of Science, University of Baghdad, Baghdad-Iraq.
**Department of Chemistry, College of Science for Women, University of Baghdad, Baghdad-Iraq.*
Received: 25/10/2005 Accepted: 17/4/2006

Abstract

Eight new binuclear metal complexes of pentaaza bimacrocyclic rings were prepared by condensation reactions of benzidine, formaldehyde, and o- phenylene diamine (o-p D) with one of the diketones: acetyl acetone (acac), dibenzoyl (DB), or dibenzoyl methane (DBM) in presence of Mn(II), Co(II), Cu(II), and Zn(II) chlorides, or with 1,2- dicyanobenzene (DCB) in presence of Zn(II) chloride in molar ratios of 1:4:4:2:2 respectively. Structures and bonding behaviour of complexes were characterized by elemental and thermal analyses, I.R and U.V-Visible spectra together with conductivity measurements and magnetic susceptibility. Octahedral geometries, were suggested for all prepared complexes. Five of the studied complexes exhibited fluorescence behaviour. Transitions and assignments were characterized from positions of excitation and emission bands in comparison with absorption spectra.

الخلاصة

حضرت ثمانية معقدات جديدة ثنائية الفلز ثنائية الحلقة الكبيرة بنتا ازا من تكاثف البزيدين والبنزالديهايد واورثوفنيلين ثنائي الامين مع احد المركبات ثنائية الكيتون: اسيتيل اسيتون (acac) ، ثنائي بنزويل(DB) او ثنائي بنزويل الميثان(DBM) بوجود كلوريد احد الفلزات: المنغنيز(II) ،الكوبلت(II)، النحاس(II) والخارصين او مع 2,1-ثنائي سيانوبنزين(DCB) بوجود كلوريد الزنك وبالنسب المولية 1:4:4 :2:2على التوالي. شخصت التراكيب الكيميائية وطبيعة التآصر في المعقدات المدروسة باعتماد التحليل الدقيق للعناصر والتحاليل الحرارية واطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية–المرئية فضلا عن قياسات توصيلية الكهربائية والحساسية المغناطيسية ووفقا للنتائج المستحصلة فقد اقترح الشكل ثماني السطوح لجميع المعقدات المحضرة. كما اظهرت خمسة من المعقدات المدروسة اطياف انبعاث من نوع الفلورة وشخصت الانتقالات من خلال مواقع قمم الاثارة وقمم الانبعاث بالمقارنة مع اطياف الامتصاص.

Introduction

The importance of macrocyclic complexes has been reported in a wide range of applications. In biological trend, they have been used as synthetic models for oxygen carriers(1), redox catalysts(2), and in enzymology(3).

In industry some macrocyclic complexes have been used as semiconductors(4), gas sensors(5), photosensitizers(6) and reaction catalysts(7). In medicine some macrocyclic complexes have been introduced into photodynamic therapy(8a,b). Some macrocyclic complexes have been evaluated for their antimicrobial effects on different species of pathogenic fungi and bacteria(8c) . The stability of these complexes is mainly controlled by ionic potential as well as electron configuration of metal ion, hole size of the ligand and by metal-ligand affinity(9). The synthesis of these complexes are mainly focused on template condensation reactions between diamines and dicarbonyls with formaldehyde in presence of metal ions(10). In this work we are studying the synthesis and characterization of a new series of binuclear 13- and 14- membered pentaaza bimacrocyclic complexes by template condensation of benzidine, formaldehyde and o-phenylenediamine (o-PD), with acetylacetone (acac), dibenzoyl methane (DBM), dibenzoyl (DB), and 1,2- dicyanobenzene (DCB) as cyclisation agents in presence of some divalent metal ions. The spectral behaviours of these complexes were also studied.

Experimental

a. Instrumentation

Melting points were recorded on a Gallenkamp MF B600 010F melting point apparatus. Elemental microanalyses were carried out by using EA- 1108 Carlo Erba elemental analyzer. Metal contents of complexes were determined by atomic absorption using Schimadzu-680G AAFE spectrophotometer. Infrared spectra were recorded on a Pye-Unicam SP-300 i.r spectrophotometer and Jasco IR- 810. Electronic spectra were recorded on Schimadzu UV-Visible 160A spectrophotometer.
Luminescence spectra were recorded on a Perkin Elmer MP-F44B spectrophotometer. Magnetic susceptibilities of samples in the solid state were measured by using a Bruker BM6 magnetic balance. Conductivity measurements of complexes in dimethyl formamide (DMF, 10^{-3}M) were recorded on Elektrleite A Higkeit conductivity meter. Thermal analysis were performed on a Stanton Redcorft TG 760 analyser.

b. Materials and Methods

The following chemicals were purified prior to use : dimethyl formamide (DMF) 99.5%, benzidine 95% (Fluka), and o-phenylene diamine (o-PD) 98% (BDH)(11,12). The other chemicals were of analar grade and were used as received from suppliers. The preparation and purification of 1,2- dicyanobenzene (1,2- DCB), (m.p. 138-140 °C) were carried out according to a published method(11). The purity of all studied compounds were detected by T.L.C using silica gel as a coating material and diethylether: chloroform (1:1) and ethyl acetate as eluents.

Synthesis of tetrachloro [1,1`-phenyl bis(4:5,10:11-BzO$_2$*-7,8-diphenyl–1,3, 6,9,12-pentaazacyclotridec-6,8-diene)] dimetal(II),*$[M_2(Ph_2BzO_2[13]diene\text{-}\ N_5)_2Cl_4]$ $M_2L_1Cl_4$*, M=Co(II) (*C_1*), and Zn(II), (*C_2*):*

To a solution of benzidine (0.01 mole) dissolved in a minimum amount of methanol were added, simultenously, formaldehyde and o-PD (0.04 mole each), with continuous stirring. A methanolic solution of metal chloride (0.02 mole) was added.Reflux was continued for 2h. Then a hot solution of DB (0.02 mole) in methanol: ethanol (2:1 v/v) was added. A change in colour was observed. The mixture was heated under reflux with continuous stirring for 7h, to achieve complete precipitation. The mixture was cooled to room temperature and the product was filtered off, washed several times with hot ethanol and vacuum dried.

Synthesis of tetrachloro [1,1`-phenyl bis(4:5,11:12-BzO$_2$*-7,8-diphenyl-1,3, 6,10,13-pentaaza cyclotetradec -6,9-diene)] dimetal(II),* $[M_2(Ph_2BzO_2\ [14]\ diene\ N_5)_2Cl_4]$,$M_2L_2Cl_4$*, M=Mn(II) (*$C_3$*) and Co(II) (*$C_4$*):*

The two complexes were prepared by adopting the same above mentioned method except that DBM (0.02 mole) was added instead of DB. Precipitation of Mn(II) complex (C_3) required the addition of ether to the cooled mixture. The solid mass was filtered off, washed several times with a cold mixture of methanol and ether (1:2 v/v) and vacuum dried.

Synthesis of tetrachloro [1,1`-phenyl bis(4:5,11:12-BzO$_2$*-7,9-dimethyl-1,3, 6,10,13-pentaazacyclotetradec-6,9-diene)]dimetal(II),* $[Me_2(BzO.[14]\ diene\ N_5)Cl_4]$, $M_2L_3Cl_4$*, M=Mn(II) (*C_5*), Cu(II) (*C_6*) and Zn(II) (*C_7*).*

The three complexes were prepared in methanol following the same previously mentioned procedure except that (acac) (0.02 mole) was added in the final step. The products were filtered off, washed thoroughly with hot methanol and vacuum dried.

Synthesis of tetraaqua [1,1`-phenyl bis(7,10-diimino-4:5,8:9,12:13 BzO$_3$*-1, 3,6,11,14pentaazacyclopentadecdiene) dizinc]*$[Zn_2(BzO_3[14]diene$ *N5)2(H2O)4],* $Zn_2L_4(H_2O)_4$*, (*C_8*):*

To a hot solution of benzidine (0.01 mole) in isopentyl alcohol was added, formaldehyde and o-PD (0.04 mole each) followed by the addition of a hot solution containing 1,2-DCB, zinc chloride (0.02 mole each) and triethyl amine (0.04 mole) in the same solvent with continuous stirring. The mixture was heated under reflux at

120°C for 3h, then at 150°C for 9h using an oil bath. Colour of solution was changed from yellow, orange, green to dark brown. After cooling to room temperature a brown precipitate was formed. The product was purified by soxhlet extraction with ethanol and dried under vacuum, giving pale brown crystals.

Synthesis of diopen chain tetrachloro [5,5`-phenyl bis(1,9-diamino-1:2,8:9-diphenyl-3,5, 7-triaazanonane) dizinc] Zn_2QCl_4 *(C_9):*

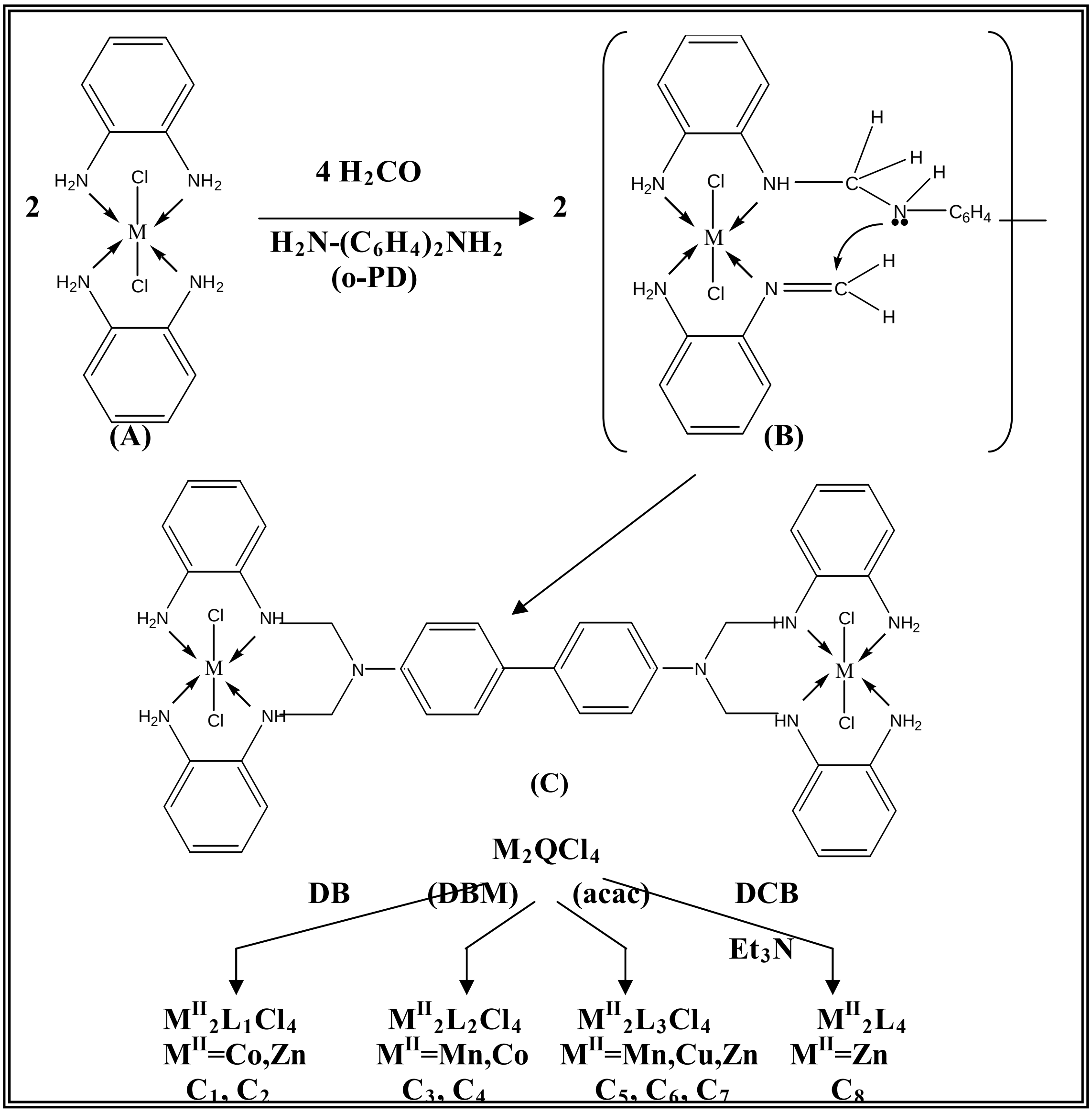
To a stirred methanolic solution of benzidine (0.01 mole) was added o-PD and formaldehyde (0.04 mole each) followed by a methanolic solution of zinc chloride (0.02 mole). The mixture was heated under reflux for 2h with continuous stirring. A white precipitate was formed.

The product was filtered off, washed several times with hot methanol and vacuum dried.

Results & Discussions

a. Mechanism of Reactions

The proposed mechanism for the synthesis of macrocyclic complexes is shown in scheme (1). The reaction involves the initial formation of the two tetramine octahedral complexes between each two o-PD molecules and metal salts (A). Condensation of two coordinated amines with two formaldehyde molecules lead to the formation of coordinated diimines nucleophilic attack of each primary amino group of the two imines gives a gem diamine (B) followed by cyclisation to a six membered chelate ring as is demonstrated by the binuclear di-open chain tetramine dimetal complex (C)^(13)^ (M_2QCl_4). Condensation with dicarbonyls such as DB, DBM, acac or with 1, 2-DCB gives rise to the binuclear bimacrocyclic dimetal complexes:



Scheme (1) : **Synthetic route of binuclear bimacrocyclic complexes**

This mechanism was confirmed by the isolation of diopen chain dizinc complex (Zn_2QCl_4) prior to reactions with cyclisation agents. Attempts to prepare the macrocycles in absence of metal ions were unsuccessful which refers to the importance of metal ion to direct the reaction towards cyclisation.

b. Physical Properties and Elemental Analyses

The colours, melting points and elemental analyses of the studied complexes are described in Table (1). All complexes were soluble in DMF and sparingly soluble in ethanol and methanol except C_3 which was soluble in ether. Some microanalytical results showed some deviation from calculated values which may be attributed to incomplete combustion. All complexes exhibited high melting points (>300°C).

The suggested molecular formula from C.H.N analyses were further supported by thermal and spectral analyses.

c. Infrared Spectra

The characteristic i.r bands of macrocyclic complexes and their assignment are described in Table (2). All spectra exhibited the absence of absorption bands related to free or coordinated carbonyl and primary amino groups. Instead a new single medium intensity band appeared in the frequency region (3330-3240 cm^{-1}) which was assigned to N–H stretching mode of the coordinated secondary amine(14), whereas the diopen chain dizinc complex (C_9) exhibited a single sharp band at 3270 cm^{-1} and a doublet at 3250 and 3192 cm^{-1} related to NH stretching modes for both secondary and primary coordinated amines respectively with NH bending vibrations at 1550 and 1660 cm^{-1} respectively(14-16).

Stretching vibrations of coordinated imines (C_1-C_7) and imidate group (C_8) appeared as a single strong band at frequency region 1625-1600 cm^{-1} (C_1, C_3-C_5, C_7 and C_8) or with a shoulder at 1600-1580 cm^{-1} (C_2 and C_4)(14, 15). Bands observed at frequency regions 2950-2900 cm^{-1} and 1480-1400 cm^{-1} (C_5-C_7) were attributed to C–H stretching and bending vibrations respectively of methyl groups(16), while those appeared at 2900-2800 cm^{-1} and 1460-1400 cm^{-1} were related to stretching vibrations of methylene linkage of the chelate rings(16,17). Vibrational modes for C–N stretching vibrations of secondary aromatic amines were observed at (1320-1270) cm^{-1} and those of tertiary aromatic amines were observed at (1360-1350) cm^{-1} (16,17). A sharp medium intensity band was observed in the spectra of C_1 and C_2 at ~ 1200 cm^{-1} and was assigned to α-diimine fragments (18).

Vibrational modes related to aromatic C–H stretching and bending appeared at 3040-3000 and 1060-1000 cm^{-1} respectively (16). Ring substitutions at ortho and para positions as well as ring deformation vibrations were observed at 840, 750 and 680-500 cm^{-1} respectively(16). The spectrum of C_8 exhibited vibrational modes of coordinated water (14), while those of C_1, C_2, and C_5 exhibited vibrations of lattice water (14,16). Bands attributed to M–N=C, M–NH, M–Cl, and M–OH_2 stretching modes were observed at lower frequencies, Table (2).

d. Thermal Analyses

Steps of thermal decomposition by TG and DTG for some selected macrocyclic complexes with weight losses are described in Table (3).

The results reflected the nature of bonding between metal ions and macrocyclic ligands, as well as the stability of complexes. Lattice water as well as organic fragments that are not involved in coordination with metal ions were found to leave the compound at lower temperatures compared with those directly coordinated. The horizontal stretching exhibited by C_1 and C_3 which started at 632 and 615°C respectively indicated the formation of $CoCl_2$ and $MnCl_2$ respectively(19) while those exhibited by C_6 and C_7 at 574 and 759°C respectively referred to the formation of CuO and ZnO respectively(19, 20).

Other complexes were not completely decomposed within the heating range (20-1000). Decomposition fragments of C_5 and C_8 were sublimed before the end of heating process. Thermal decomposition of the diopen chain Zinc complex C_9 ended with the formation of ZnO(19, 20).

Thermographs of C_1, C_3, C_6, and C_7 are shown in Figure (1).

e. Electronic Spectra

i. Absorption Spectra and Magnetic Properties:

The spectral behaviours of all metal complexes in the U.V-visible and near I.R regions using DMF as a solvent as well as magnetic susceptibilities of solid products are described in Table (4). All complexes exhibited a high intensity band in the u.v. region at wave number ranges 36000-27000 cm^{-1}. This band was attributed to intraligand (IL) $\pi\rightarrow\pi^*$ transitions(16). Another band of lower intensity appeared at 25000-23200 cm^{-1} was assigned to the $\pi\rightarrow\pi^*$ transitions of the cyclisation product(16). Bands related to $n\rightarrow\pi^*$ transitions were masked by $\pi\rightarrow\pi^*$ transitions(16). Bands observed in the visible and near i.r regions were referred to charge transfer and in the case of transition metal complexes, ligand field transition(21, 22). The spectral parameters B`, 10Dq and β were obtained by applying the observed band energies on Tanaba Saugano diagram of the specific transition metal ion(21, 22), Table (4). The Mn(II) complexes exhibited bands related to the forbidden state transition $^6S\rightarrow{}^6G$ (21) while the Co(II) and Cu(II) complexes showed spin-allowed transitions of ^4F and ^2D states respectively, with the latter showing octahedral Jahn- Teller distortions(21). Since the chemistry of d^{10} configuration affords no crystal field stabilization energy, bands observed in the visible region of Zn(II) complex spectra were attributed to ligand to metal charge transfer transitions(21, 22). Magnetic moments ($\mu_{eff.}$ BM) of Mn(II), Co(II) and Cu(II) complexes refer to high spin paramagnetic octahedral geometries(22, 23). The high values in the Cu(II) complexes are attributed to spin- orbital coupling resulted from mixing of ground term with higher energy terms(21). Molar conductance in DMF at room temperature showed that all complexes were of nonionic nature(24).

According to the above mentioned analytical and spectral results, the stereochemical structures of the binuclear pentaaza bimacrocyclic complexes of this work may be suggested as illustrated in Scheme (2).

ii. Fluorescence Spectra:

Luminescence investigations of coordination compounds, especially of transition elements are still limited. The presence of spin-orbital coupling, unfilled orbitals, inter-electronic repulsions, and ligand field effects may result in excited states of different behaviours from those originating from excitation of organic molecules(25,26). Emission in coordination compounds can originate from different types of one electron excited intraligand (IL), CT, IL+CT, LF or metal – metal (M – M) transitions(25).

Table (5) describes the important absorption bands together with excitation and emission bands exhibited by five of the eight studied macrocyclic complexes (C_1–C_3, C_6 and C_7) which exhibited fluorescence using DMF as a solvent (10^{-5} M). No fluorescence was reported by the original reactants or by macrocyclic complexes derived from non aromatic diamines(10, 17, 18), showing the role of o-PD in increasing degree of configuration and coplanarity of the macrocycles which promotes fluorescence(25). As far as diketones are concerned, macrocyclic complexes containing phenyl substituents (C_1-C_3) exhibited both absorption and excitation spectra at lower energies compared with those of methyl substituents, (Figures 2), because of higher aromatic character in the formers(25). Excitation energies observed in C_1, C_2 and C_7 are closely related to absorption bands assigned to IL $\pi\rightarrow\pi^*$ transition(27), while those of C_3 and C_6 are more related to CT transitions(28). None of the complexes exhibited fluorescence related to LF transition since emissions of such transitions appear at much lower energies(26). Geometric effect on fluorescence spectra of complexes is illustrated by comparison of intensity and profiles between excitation and emission bands and by energy separation ($\Delta\bar{\upsilon}$) between absorption and excitation energies. The spectrum of C_7 ($\Delta\bar{\upsilon}$=764 cm^{-1}) exhibited equal intensity and profile for both emission and excitation bands, Figure (3) which indicates that both ground and excited states are structurally similar(28). Bands of C_1 ($\Delta\bar{\upsilon}$=994 cm^{-1}) were of different intensities which means that excited and ground states have dissimilar structures(28).

The copper complex C_6 ($\Delta\bar{\upsilon}$=343 cm^{-1}) exhibited different profiles , Figure (3), while the spectra of C_2 and C_3 ($\Delta\bar{\upsilon}$=1207 and –90 cm^{-1}) respectively, exhibited differences in both profiles and intensities of excitation and emission spectra which reflects higher degree of structural changes upon excitation(28). This is confirmed by $\Delta\bar{\upsilon}$ values which refer to the degree of distortion between ground and excited states(28).

Although more investigations are required to cover this area, the fluorescence behaviours of these complexes give recommendation for using such complexes in fluorescence applications(8) especially photodynamic therapy.

Table (1): Physical properties and analytical data for the binuclear bimacrocyclic complexes.

Cpd. No.	*Colour*	*Decom. Temp. (m.p)°C*	*Yield %*	*Elemental Analysis % Found (Calculated) %*			*M% Found (Calculated)*
				C%	*H%*	*N%*	
C_1* Co(II)	Black	(>300)	32.70	-	-	-	8.42 (8.76)
C_2 Zn(II)	Cream Colour	215 brown 240 black (>300)	33.98	63.71 (62.64)	3.99 (4.48)	11.20 (10.74)	9.35 (9.76)
C_3 Mn(II)	Brown	230 black brown 240 black (>302)	55.82	65.92 (65.02)	4.53 (4.68)	10.43 (10.83)	8.29 (8.49)
Co(II)	Black	(>303)	50.34	63.89 (64.6)	5.01 (4.6)	9.88 (10.8)	9.57 (9.06)
C_5 Mn(II)	Black	(>300)	69.99	52.82 (53.78)	5.09 (5.42)	13.08 (12.54)	9.62 (9.84)
C_6 Cu(II)	Black	(>301)	74.54	56.91 (56.6)	5.37 (4.94)	13.86 (13.2)	11.90 (11.97)
C_7 Zn(II)	Brown	280 black (>300)	68.52	56.33 (56.31)	5.41 (4.92)	13.26 (13.14)	11.87 (12.27)
C_8* Zn(II)	Pale Brown	200 brown 250 black (>301)	67.02	-	-	-	11.38 (11.68)
C_9* Zn(II)	white	(>300)	33.26	-	-	-	13.51 (13.95)

*** Formula of complexes with no. C.H.N microanalyses were suggested according to atomic absorption and thermal analyses.**

Table (2): Main characteristic vibrational frequencies of binuclear bimacrocyclic complexes.

Symbol of complex	υ_{NH} *secondary*	$\upsilon_{C=N}$	υ_{H_2O} *lattice (coordinated)*	$\upsilon_{M\text{-}N=C}$	$\upsilon_{M\text{-}NH}$	$\upsilon_{M\text{-}Cl}$
C_1, Co(II)	3300	1600	3600-3400 1665	460	440	-
C_2, Zn(II)	3260	1625 asy. 1580 sym.	3540-3320 1640	465	345	309 291
C_3, Mn(II)	3320	1625	-	460-430	399	290
C_4, Co(II)	3333	1620	-	480	455	262
C_5, Mn(II)	3300	1620	3500-3400	475	379	-
C_6, Cu(II)	3330	1620 asy. 1600 sym.	-	480	435	332 310
C_7, Zn(II)	3260	1620	-	460	345	309 291
C_8, Zn(II)	3305	1614	3500 (550, 374)	520	466	-

binuclear di-open-chain Zn(II) complex.

Symbol of complex	υ_{NH}	υ_{NH_2}	σ_{NH} (σ_{NH})	$\upsilon_{M\text{-}NH}$	υ_{M-NH_2}	$\upsilon_{M\text{-}Cl}$
C_9, Zn(II)	3273	3250 3192	1640 (1550)	415	374	322 291

Table (3): Thermal degradation of some binuclear bimacrocyclic metal complexes by TG and DTG at temperature range 20-1000 °C.

C_1

Stable phase (M.wt) $[Co_2L_1Cl_4].4H_2O$ (1345.0)	*Temp-range of decomposition at TG (°C)*	*Peak temp. at DTG (°C)*	*Weight loss % found (calc.)*
$\downarrow$-$4H_2O$	83-157	103	5.5 (5.36)
$\downarrow$-C_6H_4NNH	157-263	246	7.84 (7.82)
$\downarrow$-$(CH_2)_2N(C_6H_4)_2N(CH_2)_2$	263-331	295	16.97 (17.57)
$\downarrow$-$3(C_6H_4NNH)$ $\downarrow$-$2(C_6H_5)_2C_2$	331-632	*	49.10 (49.95)
$2CoCl_2$	632-1000	*	20.29 (19.31)

C_3

Stable phase (M.wt) $Mn_2L_1Cl_4$ (1293.0)	*Temp-range of decomposition at TG (°C)*	*Peak temp. at DTG (°C)*	*Weight loss % found (calc.)*
$\downarrow$-$2[(C_6H_5)_2C_3H_2]$	323-339	390	29.65 (29.74)
$\downarrow$-$4(CH_2)$ $\downarrow$-$4(C_6H_4NNH)$	399-507	466	36.5 (36.9)
$\downarrow$-$(C_6H_4)_2N_2$	507-615	548	14.5 (13.94)
$2MnCl_2$	615-1000	*	19.01 (19.47)

C_5

Stable phase (M.wt) $[Mn_2L_5Cl_4].4H_2O$ (1116.78)	*Temp-range of decomposition at TG (°C)*	*Peak temp. at DTG (°C)*	*Weight loss % found (calc.)*
$\downarrow$-$4H_2O$	90-190	120	6.45 (6.45)
$\downarrow$-$4(CH_2)$	190-350	*	4.89 (5.02)
$\downarrow$-$2[(CH_3C_3H_2$-$C_6H_4NNH]$ $\downarrow$-$(C_6H_4)_2N_2$ $\downarrow$-C_6H_4NNH	350-686	505	56.18 (56.58)
C_6H_4NNH $2(MnCl_2)$	686-908	*	31.76 (31.95)

C_6

Stable phase (M.wt) $Cu_2L_3Cl_4$ (1061.94)	*Temp-range of decomposition at TG (°C)*	*Peak temp. at DTG (°C)*	*Weight loss % found (calc.)*
$\downarrow$-$2[(CH_2)_2$-$(NHC_6H_4N)_2$-$(CH_3)2C_3H_2]$	270-478	424	57.71 (57.71)
$\downarrow$-$(C_6H_4)_2N_2$ $\downarrow$-$4Cl$	478-597	563	29.52 (30.3)
$2CuO$	597-1000	*	

C_7

Stable phase (M.wt) $Zn_2L_3Cl_4$ (1065.6)	*Temp-range of decomposition at TG (°C)*	*Peak temp. at DTG (°C)*	*Weight loss % found (calc.)*
$\downarrow$-$2[(CH_2)_2C_3H_2]$ $\downarrow$-$2(CH_2)$	218-409	365	15.17 (15.40)
$\downarrow$-$2(CH_2)$	409-443	*	2.8 (2.60)
$\downarrow$-$(C_6H_4)_2N_2$ $\downarrow$-$2(C_6H_4NNH)$ $\downarrow$-$4Cl$	443-759	584	68.76 (69.6)
ZnO	759-1000	*	

Table (3): continued

C_8

Stable phase (M.wt) $Zn_2L_9(H_2O)_4$ (1119.9)	Temp-range of decomposition at TG (°C)	Peak temp. at DTG (°C)	Weight loss % found (calc.)
↓-$4H_2O$ ↓-$2(CH_2C_6H_4N_2H_2)$	107-248	133	13.52 (13.95)
↓-$(C_6H_4)_2N_2$ ↓-$3(CH_2)$	248-450	373	20.59 (19.85)
↓-$(C_6H_4N_2H_2\text{-}C_2)\text{-}C_6H_4$	450-566	525	22.32 (23.07)
$[(C_6H_4N_2H_2)_2\text{-}C_2]\text{-}C_6H_4\text{-}Zn_2N_4$	566-777	610	41.92 (42.07)

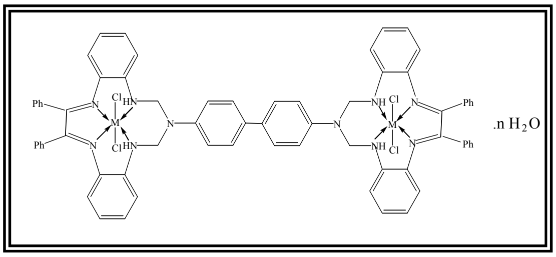
C_9

Stable phase (M.wt) Zn_2QCl_4 (937.43)	Temp-range of decomposition at TG (°C)	Peak temp. at DTG (°C)	Weight loss % found (calc.)
↓-$2(CH_2)$	152-248	201	2.55 (2.99)
↓-$C_6H_4NHNH_2$	248-422	385	11.22 (11.43)
↓-$(C_6H_4)_2N_2$ ↓-$C_6H_4NHNH_2$	422-630	539	30.61 (30.65)
↓-$2(C_6H_4NHNH_2CH_2)$ ↓-4Cl	630-892	788	39.29 (40.98)
ZnO	892-1000	*	16.58 (17.36)

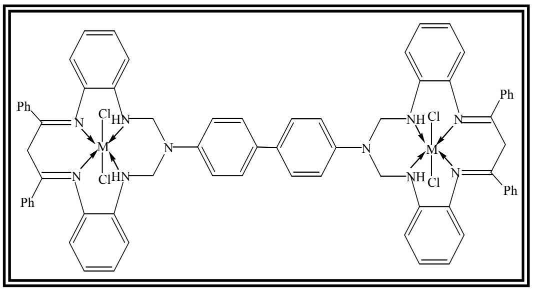
Table (4): Electronic spectra, racah parameters (B\`), 10Dq nephelauxetic parameter β, molar conductivity in DME (10^{-3}M) and magnetic moments $\mu_{eff.}$ BM of binuclear bimacrocyclic complexes C_1-C_8 and di-open-chain zinc complex C_9.

Comp. No.	Band position $\bar{\upsilon}$ (cm^{-1})	Assignment	Dq/B	B\` cm^{-1}	β	10Dq cm^{-1}	$\mu_{eff.}$ BM (suggested geometry)	Conductivity Ωm cm^2.ohm^{-1}. mol^{-1}
C_1 Co(II)	υ_1 5985(cal) υ_2 13123 υ_3 17182 υ_4 23529 υ_5 32895	$^4T_{1g}\to{}^4T_{2g}$ $^4T_{1g}\to{}^4A_{2g}$ $^4T_{1gF}\to{}^4T_{2g(F)}$ CT$^{(4)}$ $\pi\to\pi^*$ IL^b	0.84	792	0.707	6650	5.33 (octahedral)	22.8
C_2 Zn(II)	υ_1 17241 υ_2 23980 υ_3 29851	CT $\pi\to\pi^*$ IL $\pi\to\pi^*$	-	-	-	-	Diamagnetic (octahedral)	29.4
C_3 Mn(II)	υ_1 18622 υ_2 20877 υ_3 22422 υ_4 24096 υ_5 32362	$^6A_{1g}\to{}^4T_{2g}$ $^6A_{1g}\to{}^4T_{1g}$ CT $\pi\to\pi^*$ IL $\pi\to\pi^*$	-	-	-	-	5.88 (octahedral)	20.2
C_4 Co(II)	υ_1 6400(cal) υ_2 13812 υ_3 17733 υ_4 23419 υ_5 27248 υ_6 29762 υ_7 35714	$^4T_{1g}\to{}^4T_{2g}$ $^4T_{1g}\to{}^4A_{2g}$ $^4T_{1g(F)}\to{}^4T_{1g(P)}$ CT $\pi\to\pi^*$ $\pi\to\pi^*$ IL $\pi\to\pi^*$	0.91	823	0.74	7893	4.76 (octahedral)	59.1
C_5 Mn(II)	υ_1 18248 υ_2 28011 υ_3 33333	$^6A_{1g}\to{}^4T_{2g}$ $\pi\to\pi^*$ or CT $\pi\to\pi^*$ IL	-	-	-	-	6.76 (octahedral)	15.25
C_6 Cu(II)	υ_1 15909 υ_2 17699 υ_3 24097 υ_4 35842	$^2B_{1g}\to{}^2E_g$ CT $\pi\to\pi^*$ IL $\pi\to\pi^*$	-	-	-	-	2.9 (octahedral)	28.44
C_7 Zn(II)	υ_1 23810 υ_2 32051	CT $\pi\to\pi^*$	-	-	-	-	Diamagnetic (octahedral)	26.9
C_8 Zn(II)	υ_1 16556 υ_2 27624 υ_3 30030	CT $\pi\to\pi^*$ IL $\pi\to\pi^*$	-	-	-	-	Diamagnetic (octahedral)	6.78
C_9 Zn(II)	υ_1 25000 υ_2 32051	CT $\pi\to\pi^*$ IL	-	-	-	-	Diamagnetic (octahedral)	27.5

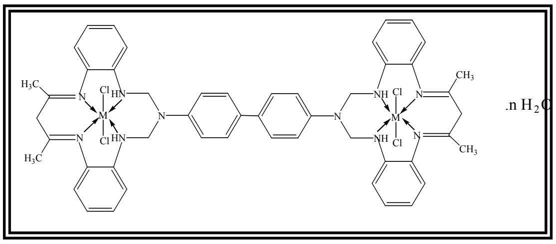
(a) CT= Charge Transfer
(b) IL= Intraligand



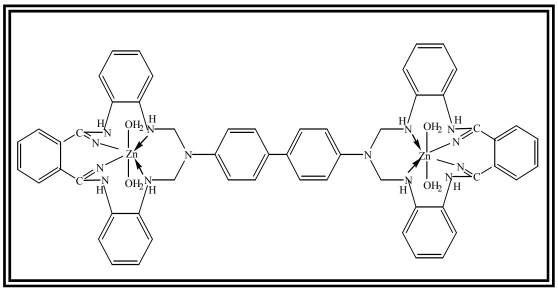
C_1, Co(II), n=0 ***C_2, Zn(II), n=4***



C_3, Mn(II) ***C_4, Co(II)***

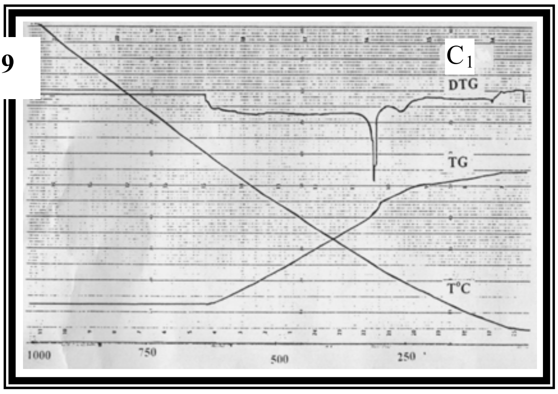


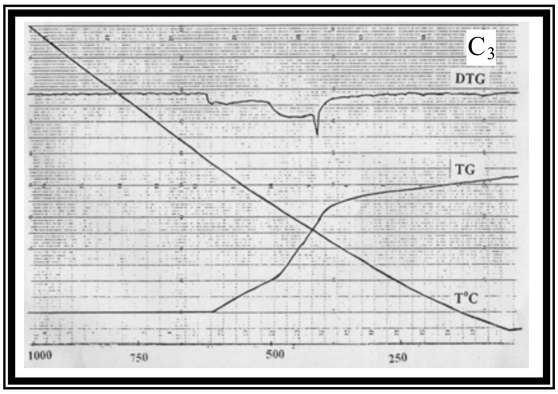
C_5, Mn(II), n=0 ***C_6, Cu(II), n=0*** ***C_7, Zn(II),***

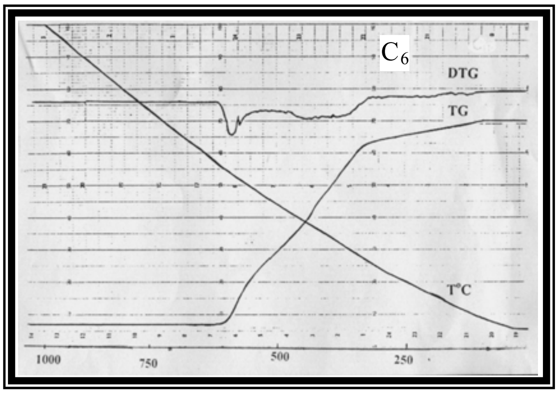


C_8, Zn(II)

Scheme (2): Suggested stereochemical structures for binuclear bimacrocyclic bimetal complexes.







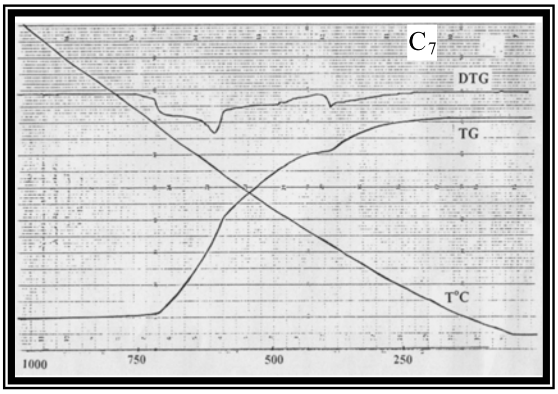


Figure (1): Thermal degradation of Co(II), Mn(II), Cu(II) and Zn(II) complexes (C_1, C_3, C_6 and C_7 respectively).

Table (5): Bands of absorption, excitation and emission exhibited by some binuclear bimacrocyclic complexes in DMF (10^{-5} M).

30

Comp. no.	*Important absorption maxima υ_{max} (cm^{-1})*	*Excitation υ_{max} (cm^{-1})*	*Emission υ_{max} (cm^{-1})*
C_1, Co(II)	(32895), (23029)	28901	25252
C_2, Zn(II)	(29851), (23980)	29940	24691
C_3, Mn(II)	(32362), (23641)	21834	20040
C_6, Cu(II)	(35842), (24096)	23 753	19569
C_7, Zn(II)	(32510), (23810)	31746	25252

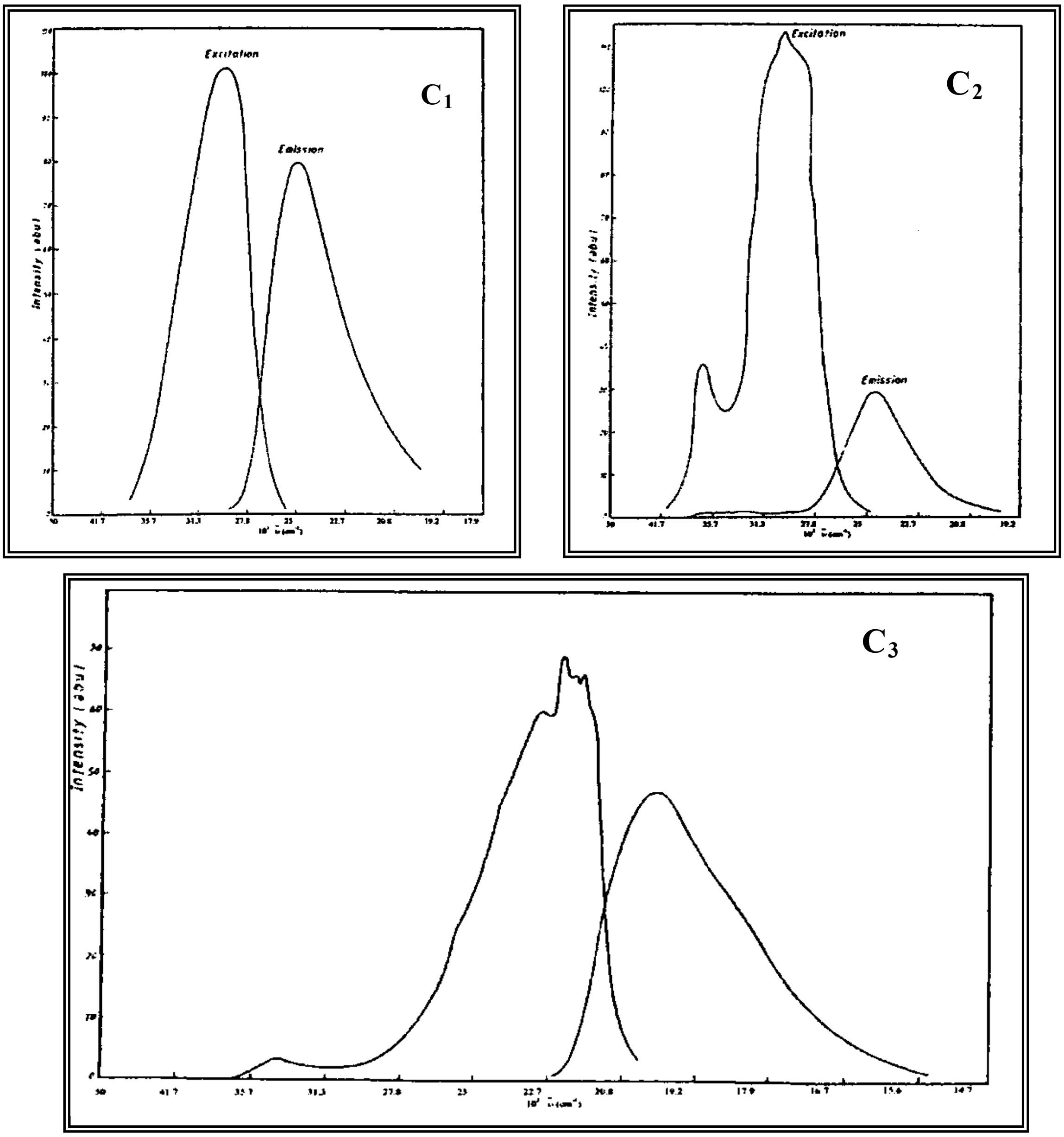


Figure (2): Fluorescence spectra of Co(II), Zn(II) and Mn(II) complexes (C_1, C_2 and C_3 respectively).

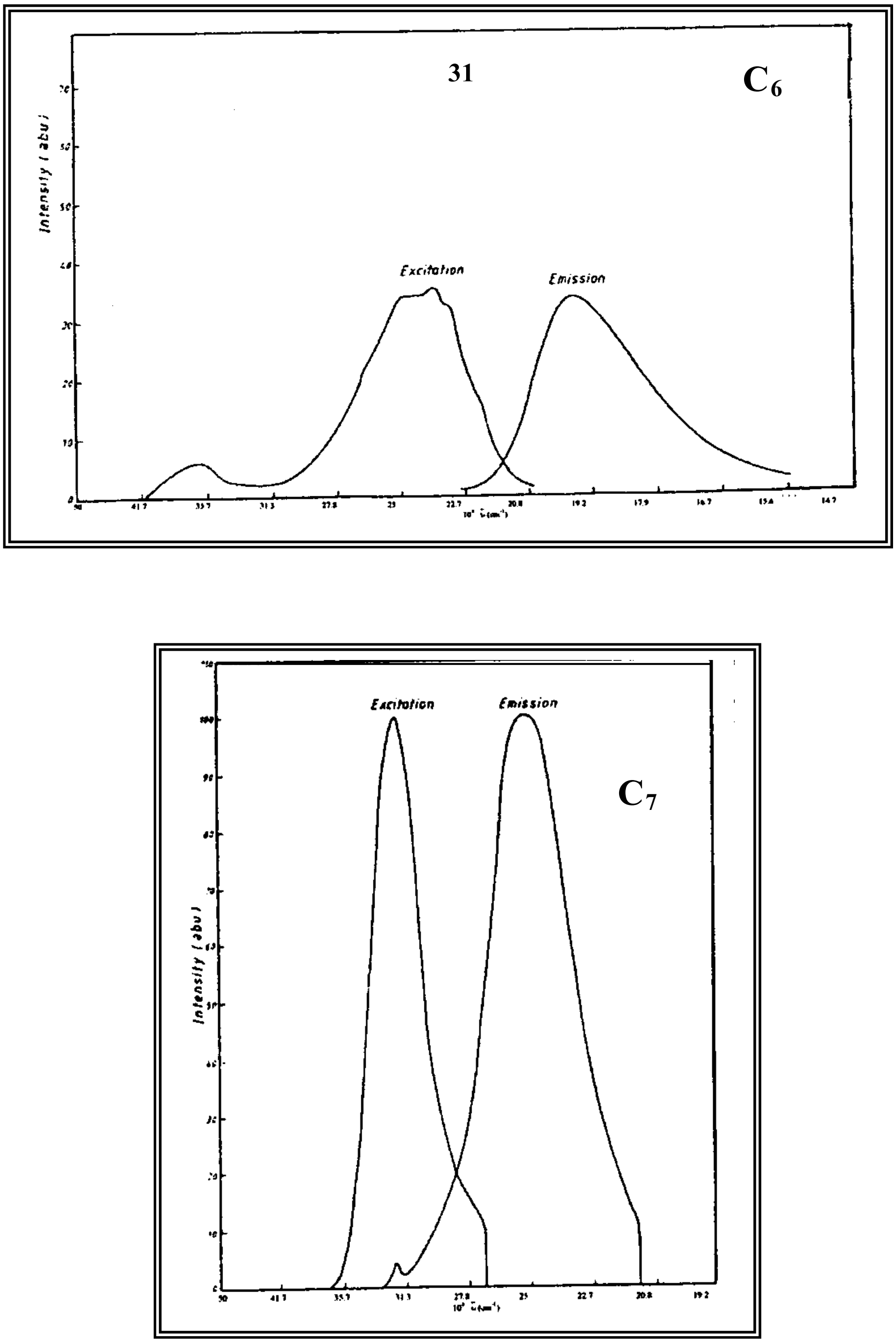


Figure (3) : Fluorescence spectra of Cu(II) and Zn(II) complexes (C_6 and C_7 respectively).

References

1. **a:** Collman, J. P.; Zhang, X.; Wong, K.; Brauman, J. I.; (**1994**) "*Dioxygen Binding in Iron and Cobalt Picnic Basket Porphyrins*" J. Am. Chem. Soc., **116(14)**, 6245; **b:** Fraser,C.; Ostrander, R.; Rheingold, A. L.; White, C.; Bonich, B.; (**1994**) "*Bimetallic Reactivity: Controlled Synthesis of Monometallic and Homo- and Hetro bimetallic Complexes of a Chiral Binucleating Macrocyclic Ligand Bearing 6- and 4- Coordinate Sites*". Inorg. Chem., **33(2)**, 324; **c:** Nelson, S. M.; Esho, F.; Lavery,A.; (**1983**) "*Dicopper Complexes of a Macrocyclic ligand as Models for Type 3 Copper Proteins*" J. Am. Chem. Soc., **105**, 5693.
2. Reddy, M.R.; Raju, K. M.; Reddy, H.; (**1996**) "*Synthesis Characterization and Electrochemistry of Unsymmetrical*

Macrocyclic Cobalt(II) Complexes Derived From bis(benzyl)-ethylenediamine" Indian J.Chem., **35(A)**,677.

3. **a:** Osterloh,F.; Saak,W.; Pohl,S.;(**1997**), "*Unidentate and Bidentate Binding of Nickel (II) Complexes to an Fe_4S_4 Cluster via Bridging Thiolates, Synthesis, Crystal Structures and Electrochemical Properties of Model Compounds for the active Sites of Nickel Containing CO Dehydrogenase/ Acetyl-CoA Synthatase*" J. Am. Chem. Soc., **119(24)**, 5648; **b:** Koike,T.; Takamura, M.; Kimura,E.; (**1994**) "*Role of Zinc (II) in β-Lactamase II: A Model Study with a Zinc (II) Macrocyclic Tetramine (1,4,7,10-tetraazacyclododecane, Cyclen) Complex*" J. Am. Chem. Soc., **116(19)**, 8443; **c:** Riley,D.P.; Lennon,P.J.; Neumann, W.L.; Weiss,R.H.; (**1997**) "*Towards the Rational Design of Superoxide Dismutase Mimics: Mechanistic Studies for the Elucidation of Substituent Effects on the Catalytic Activity of Macrocyclic Manganese (II) Complexes*" J. Am. Chem. Soc., **119(28)**, 6522; **d:** Landrum,J.T.; Grimmett,D.; Haller,K.J.; Scheidt, W.R.; Reed,C.A.; (**1981**) "*Imidazolate – and Oxo- dridged Metalloporphyrins*", J. Am. Chem. Soc., **103(10)**, 2640.
4. **a:**. Loutfy,R.O.;. Mcintyre, L.F.(**1982**) "*Photochemical Solar Energy Conversion by Polycrystalline Films of Phthalocyanines* " Solar Energy Materials, **6**, 467, **b:**.Loutfy, R.O.; Sharp, J,H. (**1979**) "*Photovoltaic Properties of metal-free Phthalocyanines I Al/H_2Pc Schottky Barrier Solar Cells*" J.Chem. Phys. **71(3),** 211.
5. Honeyboume,C. L.; Ewen, R. J.; Hill, C.(**1984**)" *use of Thin Films of Conjugated Organic macrocycles as the Active Elements in Toxic Gas Sensors Operating at Room Temperature*", J. Chem. Soc. Trans I, **80(4)**, 851.
6. **a:**. Bernhardt,P.V.;(**1997**),"*ON the Structure , Electrochemistry, and Spectroscopy of the* ($N,N^{\backslash}$ *-Bis(2-dimethylamino)ethyl)-*$N,N^{\backslash}$ *- dimethyl Propane-1,3-diamine)Copper(II) Ion*, J. Am. Chem. Soc., **119(4)**, 711; **b:** Balzani, V.(**1989**) "*Tailoring Luminscent Compounds and Sensitizers: Cage Type Metal Complexes*" Gazzetta Chimica Italiano, **119**, 311.
7. **a:** Collin, J. P.; Jouaiti, A.;and Sauvage, J. P.(**1988**) "*Electrolytic Properties of* $Ni(Cyclam)^{2+}$ *and* $Ni_2(bicyclam)^{4+}$ *with Respect to* CO_2 *and* H_2O *Reduction*", Inorg. Chem., **27(11)**, **1986**; **b:**. Abba, F.;.De Santis, G.; Fabbrizzi, L. F.; Lichelli,M.; Lanfredi , A.M.M.; Pallavicini,P.;Poggi, A.; Ugozzoli,F.(**1994**) "*Nickel(II) Complexes of Azacyclams; Oxidation and Reduction Behaviors and Catalytic Effects in the Electroreduction of Carbon Dioxide*", Inorg. Chem.,**33(7)**,1366 (**1994**);**c:** Goncharov, A.V.; Gridnev, A.A.; Lampeka, Ya. D.; Gavrish,S.P.(**1989**) Theor EKSP. Khim, **25(6)**, 698 (Russ). Cf. Chem. Abs., **113(2)**, 6864d (**1990**).
8. **a:** Valduga,G.; Nonell,S.; Reddi,E.; Jori,G.; Braslavsky,S.E.(**1988**) "*The Production of Singlet Molecular Oxygen by Zinc(II) Pthalocyanine Photochem. Photobiol.* **48(1)**, 1; **b:** Moan,J.; peng, O.; Evenson, J.F.; Berg, K.; Western,A.;Rimington,C .(**1987**) "*Photosensitizing Efficiencies , Tumer and Cellular Uptake of Different Photosensitizing Drugs Relevent for Photodynamic Therapy of Cancer*" Photochem. Photobiol, **46(5)**, 713.; **c:**Singh, R.V.; Joshi. S.C.; Kulshrestha, S.; Nagpal, P.; Bansal, A., (**2001**), "*Antiandrogen and Antimicrobial Aspects Coordination Compounds of Palladium(II), Platinum(II),and Lead(II)*", Metal Based Drugs,**8** ,149.
9. **a:** Lindoy, L.F.(**1989**) “*The Chemistry of Macrocyclic Ligand Complexes*” Cambridge University press, Cambridge, New York; **b:** Melson,G.A. (**1979**) “*Coordination Chemistry of Macrocyclic Compounds*” Plenum Press, New York and London ; **c:** Honghton ,R.P. (**1979**) “*Metal Complexes in Organic Chemistry*” Cambridge University Press, Cambridge, New York and London and references therein.
10. **a:** Sharkir, M.; Varkey,S. P.; Kumar,D. (**1994**), "*Binuclear Transition Metal Complexes of Schiff Base Macrocycles Containing the Furanyl Moiety*", Synth React Inorg. Met-Org. Chem., **24(6)**, 941.; **b:** Gagne , R.R.; Spiro, C.L. (**1980**), "*An Electrochemical Method for Measuring Elecronic Delocalisation in Mixed Valent Species*", J. Am. Chem. Soc., **102(4)**, 1442.; **c:** Mandal, S.K.; Nag, K. (**1983**), "*Dinuclear Metal Complexes Part 2: Synthesis, Characterisation, and Electrochemical Studies of Macrocyclic Dicopper(II) Complexes*" , J. Chem. Soc., Dalton Trans, 2429 .

11. Vogel, A. (**1972**), "*Text Book of Practical Organic Chemistry*" 3rd Edn, Longman, New York 167.

12. Perrin, D.D.; Armarego, W.L.F.(**1980**) "*Purification of Laboratory Chemicals*" 2nd Ed. Pergamon Press.

13. Suh, M.P.; Kang, S.G.(**1988**) "*Synthesis and Properties of Nickel(II) and Copper(II) Complexes of 14-Membered Hexaazacyclootetradecane*", Inorg. Chem., **27**, 2544**.**

14. **a:** Shakir, M.; Mohamed, A.K.; Varkey , S.P.; Nasman, O.S.M. (**1996**), "*Synthesis and Structural Studies of Bis(macrocyclic) Dimetal (II) Complexes Based on14-18 Membered Pentaaza Unit*", Indian J. Chem., **35A**, 935.; **b:** Ferraro, J.R. (**1972**), "*Low Frequency Vibrations of Inorganic and Coordination Compounds*" Plenum Press, New York; **c:**. Nakamato, K. (**1997**) "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*" 5th Ed., John Wiley and Sons Inc., New York.

15. Shakir,M. ;Varkey, S.P.;Hameed (**1993**), "*Synthesis and Characterisation of Cobalt(II), Nickel(II), and Copper(II) Compleexes of Dithiadiazamacrocycles*", J. Chem. Research, 442.

16. **a:** Silverstein, R.M.; Basseler, C.G.; Morrill, T.C. (**1974**) "*Spectrometric Identification of Organic Compounds*" 3rd Ed. John Wiley and Sons, Inc., New York.; **b:** Williams, D. H.; Fleming, I. (**1973**) "*Spectroscopic Methods in Organic Chemistry*" 2nd Ed., McGraw Hill, Book Company U. K. LTD.

17. **a:** Shakir, M.; Mohamed, A.K.; Varkey, S.P.; Nasman, O.S..M.; Siddiqi, Z.A. (**1995**), "*Preparation and Structural Characterization of 14-16 Membered Pendent Arm Macrocyclic Complexes of Transition Metal Ions*" , Polyhedron, **14(10)**, 1277; **b:** Shakir, M.; Varkey, S.P.; Hameed,P.S. (**1994**),"*Synthesis and Spectral Studies of Binuclear Transition Metal Complexes of Diamidediimine Hexaazamacrocycles*", Polyhedron, **13(9)**, 1355. ; **c:** Pouchert, C.J.,(**1981**) , "*The Aldrich Library of I.R. Spectra*" 3rd Ed., Aldrich Chemical Company Inc., Milwaukee, WI 53201, USA.

18. **a:** Farmery, K.;Kildahl, N.K.; Busch, D.H.,(**1980**),"*Axiial Coordination in Cobalt(II) Complexes of Two Synthetic Macrocyclic Ligands Containing the Bidentate α-Diimine Group*" J. Coord. Chem., **10**, 85.; **b:** Baldwin, D.A.; Pfeffer, R.M.; Reichgott, D.W.; Rose, N.J., (**1973**), "*Synthesis and Reversible Ligation Studies of Low-spin Iron(II) Complexes Containing a Planar Cyclic Tetradentate Ligands and Other Molecules Including Carbon Monoxide*", J. Am. Chem. Soc., **95(16)**, 5152.

19. Duval, C. (**1963**), "*Inorganic Thermogravimetric Analysis*" 2nd Ed., Elsevier Publishing Company, New York, London.

20. Buzus, I. (**1975**), "*Thermal Analysis" Organic and Macromolecular* Chem. Earth Science Akademiaikiado., Budapest vols 1, and 2.

21. **a:** Figgis, B.N., (**1966**), "*Introduction to Ligand Fields*", Interscience Publishers, A division of John Wiley and Sons, New York, Sydney.; **b:** Sutton, D. (**1968**), "*Electronic Spectra of Transition Metal Complexes*" 1st Ed.,McGraw-Hill Publishing Company LTD., New York. **c:** Lever, A..B.P.(**1968**), "*Inorganic Electronic Spectroscopy*" Elsevier publishing Company, Amsterdam-London-New York .

22. Greenwood, N.N.; Earnshaw, A., (**1986**), "*Chemistry of Elements*" Pergamon Press, London.

23. Aggarwal, R.C.; Narayana, D.S., (**1984**), "*Complexes of Some First Transiition Metal Ions with Schiff Bases Derived from Acetylacetone and Aromatic Diamines*", Indian J. Chem., **23(A)**, 920.

24. Geary, W.J., (**1971**),"*The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds*" Coord. Chem. Rev., **7(1)**, 81.

25. Khopkar, S.M.,(**1970**), "*Concepts in Analytical Chemistry*" Holsted Press, John Wiley and Sons, New York.

26. **a:** Balzani, V.; Carassiti,V.,(**1970**), "*Photochemistry of Coordination Compounds*", Academic Press, London and New York .; **b:** Adamson, A.W.; Fleischauer, P.D.,(**1975**), "*Concept of Inorganic Photochemistry*", Wiley Interscience Publications John Wiley and Sons, New York.

27. Allen, N. S. and Mckeller, J. F. (**1980**), "*Photochemistry of Dyed and Pigmented Polymers*" , Applied Science Publishers Ltd. New York, Chapter 1.

28. Geoffery, G.L.; Wrighton, M.S.(**1979**), "*Organometallic Photochemistry*" Academic Press, New York and London.