

## Template Synthesis and Characterization of Transition Metal Complexes of 13, 15 and 17-Membered Tetraamide Macrocyclic Disubstituted Dimethyl Tetrasubstituted Tetraazacycloalka Tetrasubstituted Tetraene Disubstituted Diol

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A series of new transition metal complexes  $[ML(Ln)Cl_2]$  where  $L_n = L13, L15$  and  $L17$  ( $L(13) = 11,13$ -dimethyl-1,4,7,10-tetraazacyclotrideca-4,6,10,13-tetraene-5,6-diol,  $L(15) = 9,11$ -dimethyl-1,4,8,12-tetraazacyclopentadeca-1,3,8,11-tetraene-2,3-diol and  $L(17) = 10,12$ -dimethyl-1,4,9,13-tetraazacycloheptadeca-1,3,9,12-tetraene-2,3-diol) and  $M = Cu(II), Co(II), Ni(II), Mn(II)$  and  $Zn(II)$  have been synthesized by template method. All the synthesized complexes were characterized by IR, UV, ESR, X-ray microanalysis, elemental analysis, thermal studies and magnetic susceptibilities and the geometry of the complexes found to be octahedral.

**Keywords:** Coordination complexes, Macrocyclic ligand, Schiff base, Polyazamacrocycles.

### INTRODUCTION

A large number of synthetic polyaza macrocycle ligands [1-4] has undergone a rapid growth since the early 1960s due to the instigating contribution of Curtis [5-7] and Busch [8,9] by their synthesis of large number of synthetic polyaza macrocyclic ligands. The utilization of metal template method for the synthesis of multidendate macrocyclic ligands has been confessed as offering high yielding and selective routes to new ligands and their complexes [1,3,8,10-15]. The ability to interact with both metal cations [16-18] and anionic species [19-34] has attracted the inorganic chemist in several ways and macrocyclic ligands has been a fascinating area of current research in this growing world. Polyamine macrocycle can protonate in aqueous solution which in turn furnishing polyammonium receptors that can be applied for anion coordination. Two or more polyamine groups such as aliphatic chains or aromatic units has been acts as one of the most explored classes of aza macrocycles while the polyamine moieties act as binding sites for metal cations or anionic groups and the spacers can rearrange the distance between the binding moieties. An exact tuning of both the binding feature of polyamine units and structural

characteristics of spacers has led to the achievement of receptors with specific function, able not only to bind but also to find applications as models for catalytic metalloproteins [35-42] or as optical chemosensors [43-45] for metals or anions. This has been characterized as an achievement in terms of its flexibility, hydrophobicity or presence of additional functional group. These models figure out the application for protein metal binding sites in a substantial array of metallo proteins in various biological systems, which has resulted in growing interest and guest in designing innovative macrocyclic ligands, and also these models are very important to study the magnetic exchange phenomena, chemotherapy, specific metal intoxication and catalysis. From the knowledge of the importance of complex containing macrocyclic ligands has led to a great effort being supported in developing reliable inexpensive synthetic routes for these compounds [46-48]. Preparation of metallic complexes are of great importance in dealing with the functional role of metalloenzymes [49], magnetic interaction between, paramagnetic centers [50-52] and for the fabrication of metallo supramolecular architectures [53]. In addition to that cyclic polyamides have been extensively studied as anion receptors [54] and previously it has been shown [55,56] to bind DNA and

inhibit HIV replication. Enormous progress have been made in interpreting the structural aspects of anion coordination in recent years [57,58]. Many of the findings designate that these will be prominent structural parallels with transition metal coordination chemistry. For example, ditopic binding of nitrate [59,60], cascade complexes with fluoride [61] sandwich formation with sulfate [62], as well as the chelate and macrocyclic effects [59-63] in the stabilization of anion complexes. These similarities can be found out to resemblance between the coordinate covalent bonds in transition metal complexes and the hydrogen bonds formed in anion complexes. Further presumption of the topological relationship between transition metal and anion co-ordination chemistry the segregation of persistent structural motifs for given anion under a variety of conditions.

The present investigation achieves the template synthesis and characterization of series of transition metal complexes of 13, 15 and 17-membered tetraamide macrocycle disubstituted-dimethyl-tetraazacycloalka-tetraene-disubstituted-tetraene-disubstituted-diol with metals of Cu, Co, Ni, Mn and Zn and all the newly synthesized complexes were subjected to the experimental analysis by governing their characteristic features and structural elucidation.

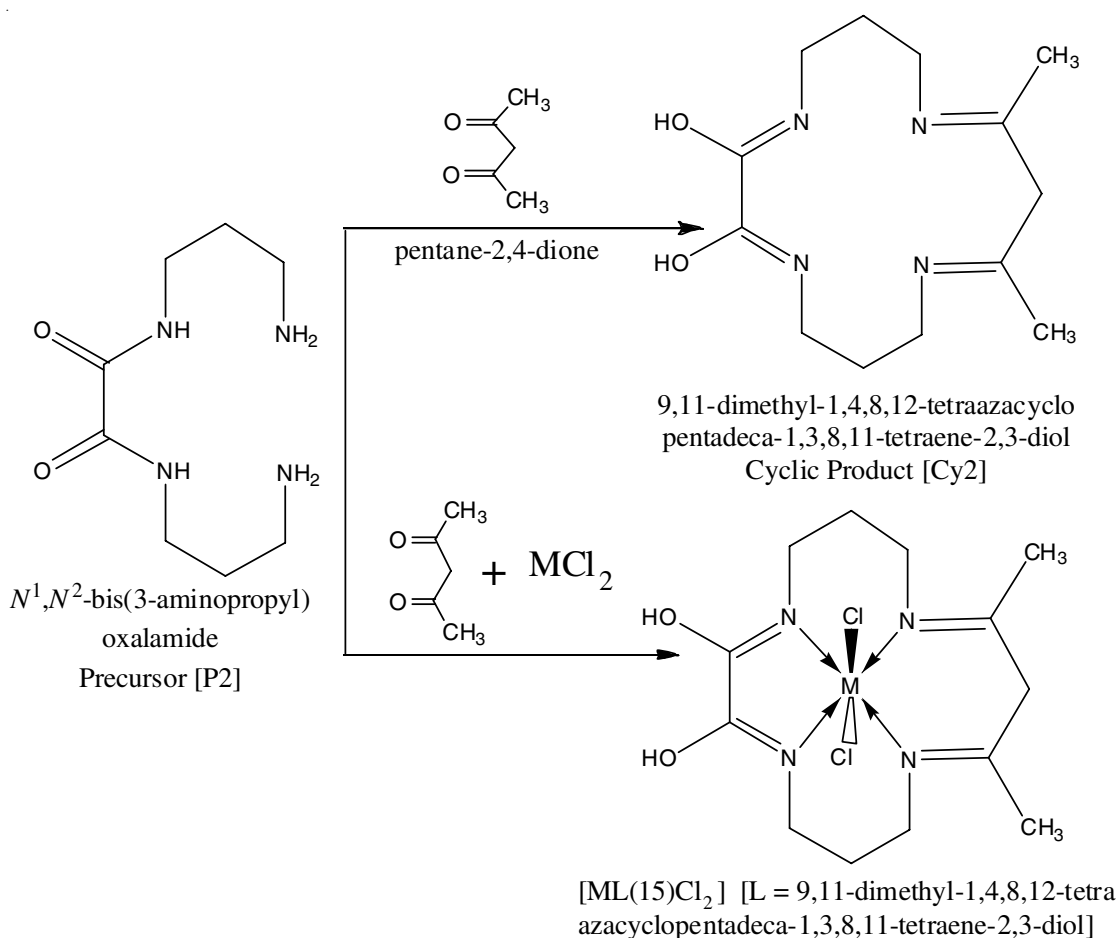
## EXPERIMENTAL

**Synthesis of precursor [P1], [P2] and [P3]:** Propane-1,3-diamine (47.8 mmol) was dissolved in minimum amount of ethanol in a beaker. When 7.4 mmol of diethyl oxalate was

added dropwise to propane-1,3-diamine solution, the precursor  $N^1,N^2$ -bis(3-aminopropyl)oxalamide [P2] (white precipitate) was formed and identified by TLC technique. The solution was stirred for about 0.5 h to ensure the completion of the reaction. Then the formed precursor was filtered, washed with  $\text{CHCl}_3$  and then subsequently dried in vacuum over anhydrous  $\text{CaCl}_2$ . Similarly [P1]  $N^1,N^2$ -bis(2-aminoethyl)oxalamide and [P3]  $N^1,N^2$ -bis(4-aminobutyl)oxalamide were synthesized using the corresponding ethane-1,2-diamine and butane-1,4-diamine, respectively. In order to avoid the cyclization, excess of corresponding alkane disubstituted diamine was added and compared to diethyl oxalate while in the preparation of all the three precursors [P1], [P2] and [P3].

**Synthesis of cyclic product [Cy1], [Cy2] and [Cy3]:** Precursor [P2, 2.47 mmol] was added to a hot ethanolic solution in a beaker. Then 2.47 mmol of acetyl acetone was added to the solution and stirred for 45 min to get a cyclic product [Cy2] and identified by TLC technique. It was filtered and dried in vacuum over anhydrous  $\text{CaCl}_2$ . Similarly, [Cy1] and [Cy3] are prepared using the corresponding precursors [P1] and [P3], respectively.

**Synthesis of metal complexes:** Precursor [P2, 2.93 mmol] was dispersed in hot ethanol. To this, about 2.93 mmol of copper(II) chloride dihydrate in hot ethanol was added. To the above mixture, 2.92 mmol of acetyl acetone was added and stirred for 1 h. Then solution was allowed to evaporate completely over water bath to obtain a green coloured precipitate (Scheme-I).



Scheme-I

The precipitate formed was washed with ether, filtered and dried in vacuum over anhydrous  $\text{CaCl}_2$  and the precipitate identified as  $[\text{CuL}(15)\text{Cl}_2]$ . Similarly, cobalt(II)  $[\text{CoL}(15)\text{Cl}_2]$ , nickel(II)  $[\text{NiL}(15)\text{Cl}_2]$ , manganese(II)  $[\text{Mn}(15)\text{Cl}_2]$  and zinc (II)  $[\text{ZnL}(15)\text{Cl}_2]$  complexes (**Scheme-I**) were synthesized using corresponding metal salts, respectively and also  $[\text{ML}(13)\text{Cl}_2]$  and  $[\text{ML}(17)\text{Cl}_2]$ , where  $\text{M} = \text{Cu(II), Co(II), Ni(II), Mn(II)}$  and  $\text{Zn(II)}$  were prepared using the corresponding precursors **[P1]** and **[P3]**, respectively as described above.

## RESULTS AND DISCUSSION

Table-1 shows that results of various physico-chemical analyses of the synthesized 13, 15 and 17-membered tetraamide macrocycle disubstituted-dimethyl-tetrasubstituted-tetraazacycloalka-tetrasubstituted-tetraene-disubstituted-diol with  $\text{Cu(II), Co(II), Ni(II), Mn(II)}$  and  $\text{Zn(II)}$  ions. Based on the experimental and analytical results, the various steps involved in the synthesis of the complexes  $[\text{ML}(15)\text{Cl}_2]$  can be seen in **Scheme-I**.

**[ML(15)Cl<sub>2</sub>]:** The elemental analysis data (Table-1) confirmed the formula  $[\text{ML}(15)\text{Cl}_2]$  where  $\text{L}(15) = 9,11$ -dimethyl-1,4,8,12-tetraazacyclopentadeca-1,3,8,11-tetraene-2,3-diol proposed for the complexes. Through the X-ray microanalysis data, the elements identified in the nickel(II) complex (Fig. 1)

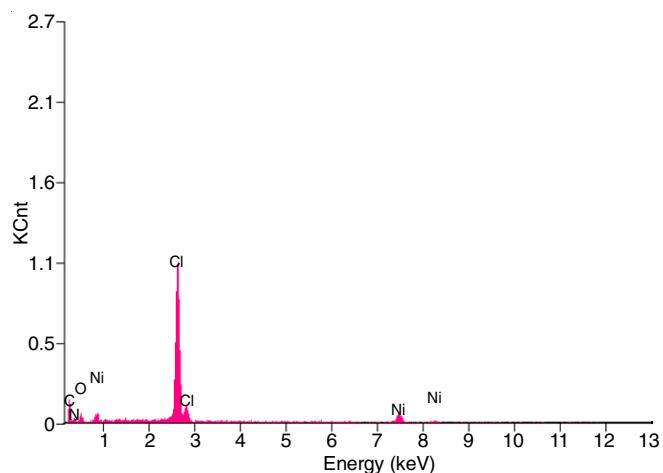


Fig. 1. X-ray microanalysis of 15-membered tetraamide Ni(II) complex

were carbon, nitrogen, oxygen, chlorine and nickel and the same elements were identified in zinc(II) complex. The weight % obtained for individual atoms support the proposed formula of the complexes.

In thermogravimetric analysis (Fig. 2), there was no change of mass, upto  $241.8^\circ\text{C}$  which revealed that there was no water molecule presents in the copper(II) complex. By weight loss method, thermal studies of other cobalt, nickel, manganese and zinc complexes were also analyzed for heating at  $120^\circ\text{C}$  for 2 h, which shows the absence of water molecules present in any of the above complexes.

**[ML(13)Cl<sub>2</sub>]:** The elemental analysis data (Table-1) confirmed the formula  $[\text{ML}(13)\text{Cl}_2]$  where  $\text{L}(13) = 11,13$ -dimethyl-1,4,7,10-tetraazacyclotrideca-4,6,10,13-tetraene-5,6-diol proposed for the complexes. In addition to copper(II) (Fig. 3), nickel(II) and zinc(II) complexes were analyzed through X-ray microanalysis and cobalt(II) complex was analyzed by thermogravimetric analysis (Fig. 4).

**[ML(17)Cl<sub>2</sub>]:** The elemental analysis data (Table-1) corroborates the formula  $[\text{ML}(17)\text{Cl}_2]$  where  $\text{L}(17) = 10,12$ -dimethyl-1,4,9,13-tetraazacycloheptadeca-1,3,9,12-tetraene-2,3-diol proposed for the complexes. In addition to copper(II), nickel(II) and zinc(II) complexes were analyzed through X-ray microanalysis and cobalt(II) complex was analyzed by thermogravimetric analysis (Fig. 5).

**IR analysis:** The presence of amide moiety in all the precursor **[P1]**, **[P2]** and **[P3]** were confirmed and authenticated by the appearance of the bands in the region  $1654\text{ cm}^{-1}$  (for **[P2]** (amide I ( $\text{C}=\text{O}$  str.) and  $1524\text{ cm}^{-1}$  (amide II (NH deformation) (Fig. 6). Consequently, the absence of band at  $1751\text{ cm}^{-1}$  in the IR spectra shows that there was no unreacted carbonyl group of the starting material ester during the formation of precursor from condensation reaction of ester with amine.

By the reaction between precursor **[P2]** and pentane-2,4-dione yields the cyclic product **[Cy2]**. The IR spectrum of the cyclic product **[Cy2]** (Fig. 7), indicates that amide I band at  $1652\text{ cm}^{-1}$  and amide II band at  $1556\text{ cm}^{-1}$ . Further, a cyclic polyamide **[Cy2]** was synthesized to ascertain the mode of coordination of amide in complexes by the reaction between the precursor **[P2]** with ethane-1,2-diamine in the absence of

TABLE-1  
ANALYTICAL DATA OF TRANSITION METAL COMPLEXES OF 13, 15 AND 17-MEMBERED MACROCYCLIC COMPLEXES

Complexes	Elemental analysis (%): Obsd. (calcd.)				
	M	Cl	C	H	N
$[\text{CuL}(15)\text{Cl}_2]$	15.43 (15.86)	17.57 (17.73)	38.79 (38.95)	5.37 (5.49)	13.83 (13.98)
$[\text{CoL}(15)\text{Cl}_2]$	14.57 (14.89)	17.76 (17.93)	39.24 (39.40)	5.44 (5.56)	13.05 (14.14)
$[\text{NiL}(15)\text{Cl}_2]$	14.54 (14.81)	17.73 (17.95)	39.18 (39.43)	5.39 (5.56)	13.08 (14.16)
$[\text{MnL}(15)\text{Cl}_2]$	13.89 (14.01)	18.04 (18.12)	39.60 (39.81)	5.46 (5.61)	14.07 (14.29)
$[\text{ZnL}(15)\text{Cl}_2]$	14.02 (14.21)	17.91 (18.08)	39.55 (39.71)	5.48 (5.60)	14.04 (14.26)
$[\text{CuL}(13)\text{Cl}_2]$	17.37 (17.04)	18.96 (19.06)	35.89 (35.44)	4.78 (4.83)	15.30 (15.03)
$[\text{CoL}(13)\text{Cl}_2]$	16.29 (16.01)	19.17 (19.29)	35.97 (35.88)	4.81 (4.89)	15.27 (15.22)
$[\text{NiL}(13)\text{Cl}_2]$	16.21 (15.94)	19.05 (19.31)	35.98 (35.91)	4.79 (4.89)	15.24 (15.23)
$[\text{MnL}(13)\text{Cl}_2]$	15.33 (15.09)	19.26 (19.51)	36.55 (36.27)	4.88 (4.95)	15.43 (15.39)
$[\text{ZnL}(13)\text{Cl}_2]$	15.64 (15.29)	19.31 (19.46)	36.36 (36.18)	4.86 (4.93)	15.39 (15.35)
$[\text{CuL}(17)\text{Cl}_2]$	14.74 (14.82)	16.48 (16.57)	41.94 (42.01)	6.00 (6.07)	12.97 (13.07)
$[\text{CoL}(17)\text{Cl}_2]$	13.81 (13.89)	16.66 (16.75)	42.38 (42.46)	6.08 (6.13)	13.13 (13.21)
$[\text{NiL}(17)\text{Cl}_2]$	13.72 (13.83)	16.70 (16.76)	42.39 (42.49)	6.07 (6.14)	13.16 (13.22)
$[\text{MnL}(17)\text{Cl}_2]$	12.99 (13.07)	16.82 (16.91)	42.76 (42.87)	6.10 (6.19)	13.27 (13.34)
$[\text{ZnL}(17)\text{Cl}_2]$	13.18 (13.26)	16.79 (16.87)	42.94 (42.85)	6.09 (6.18)	13.25 (13.31)

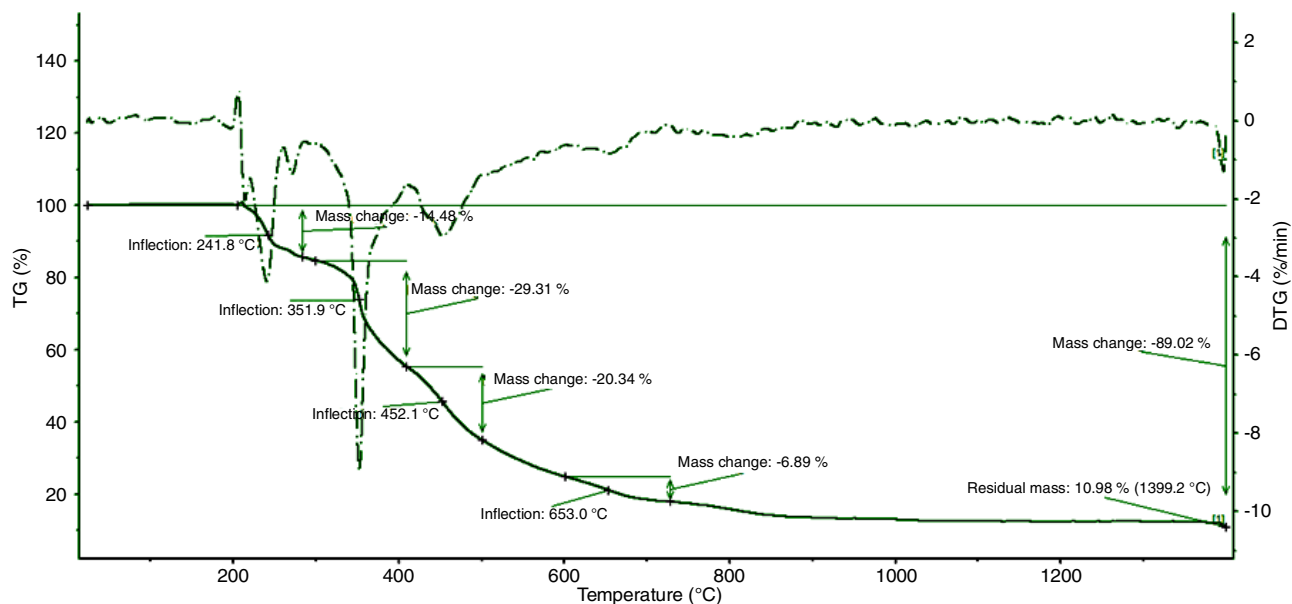


Fig. 2. Thermogram of 15-membered tetraamide macrocyclic copper(II) complex

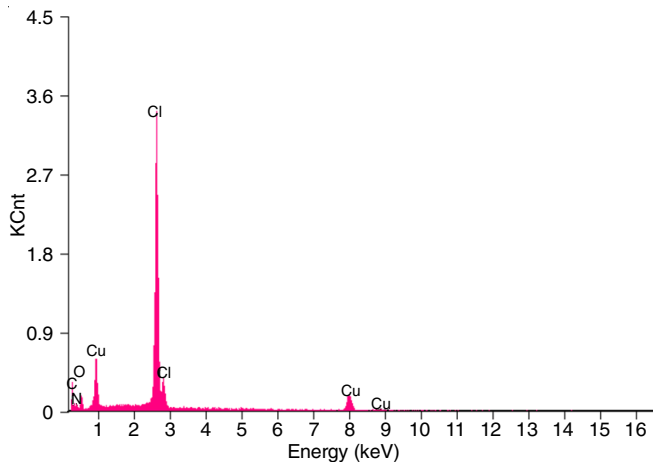


Fig. 3. X-ray microanalysis of 13-membered tetraamide Cu(II) complex

metal. Similar IR spectral data were also obtained for the cyclic products [Cy1] and [Cy3].

The IR spectrum of  $[\text{CuL}(15)\text{Cl}_2]$  (Fig. 8) implies that amide I peak at  $1664\text{ cm}^{-1}$  and amide II peak appears at  $1518\text{ cm}^{-1}$ . The IR spectra of metal complex  $[\text{ML}(15)\text{Cl}_2]$  showed that upon complexation, amide I band shifts by  $2\text{--}17\text{ cm}^{-1}$  towards higher frequency and amide II band shifts by  $5\text{--}13\text{ cm}^{-1}$  towards lower frequency. It has been known that amide I band shifts to higher side while amide II band shifts to lower frequency when in the situation of amide nitrogen was involved in the coordination. The observation of the present study clearly explained that amide nitrogen was involved in coordination with metal. The same observations had also been noticed for the complexes of  $[\text{ML}(13)\text{Cl}_2]$  and  $[\text{ML}(17)\text{Cl}_2]$ .

**Electronic and magnetic moment analysis:** At room temperature, the magnetic moment of copper(II), cobalt(II),

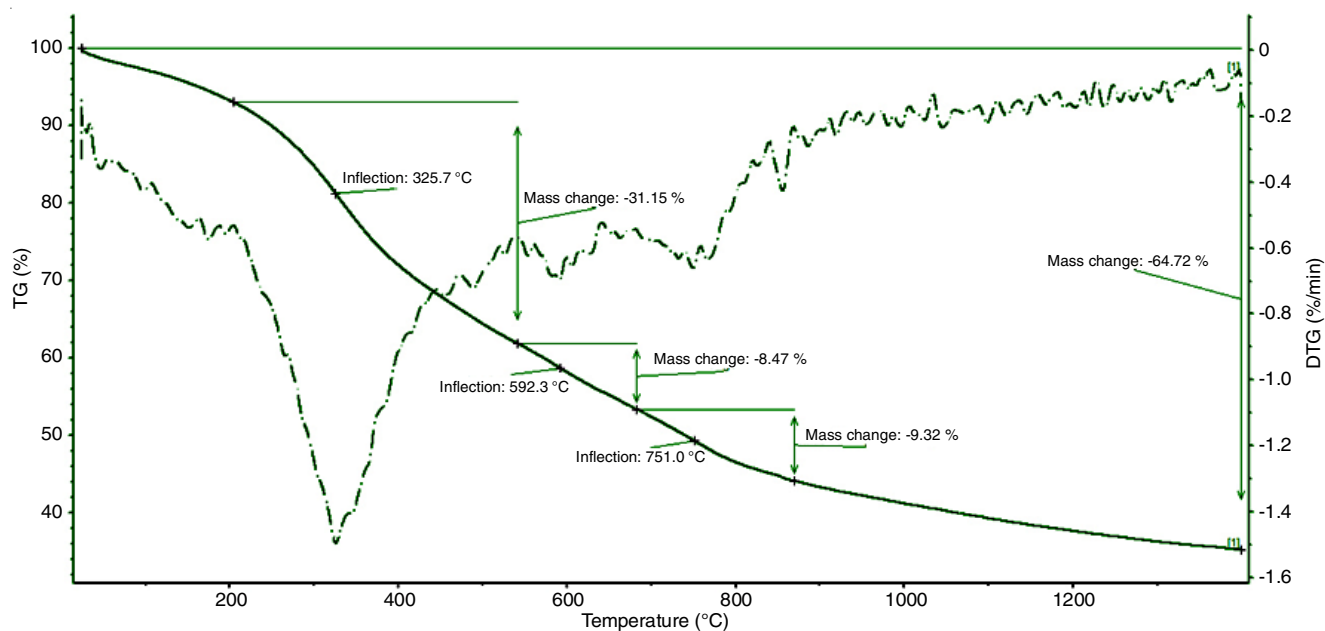


Fig. 4. Thermogram of 13-membered tetraamide macrocyclic cobalt(II) complex

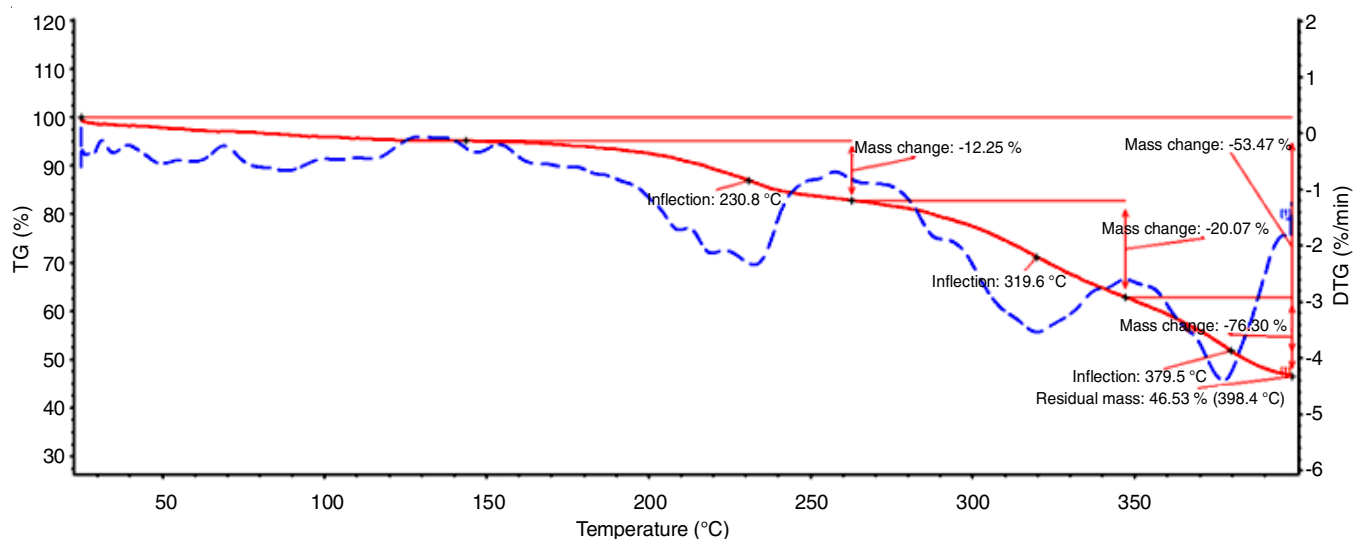


Fig. 5. Thermogram of 17-membered tetraamide macrocyclic copper(II) complex

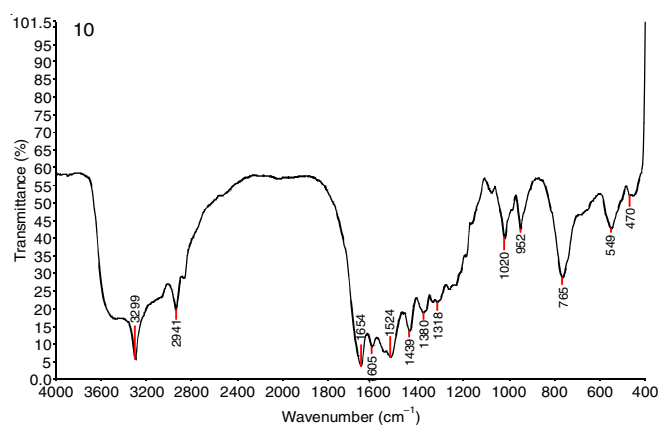


Fig. 6. IR spectrum of precursor

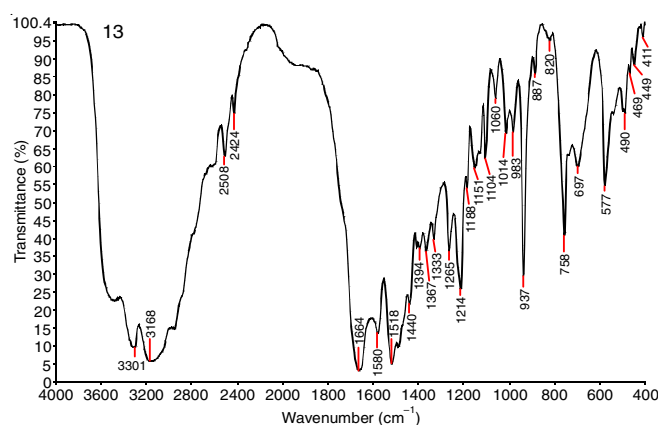


Fig. 8. IR spectrum of 13-membered tetraamide macrocyclic Cu(II) complex

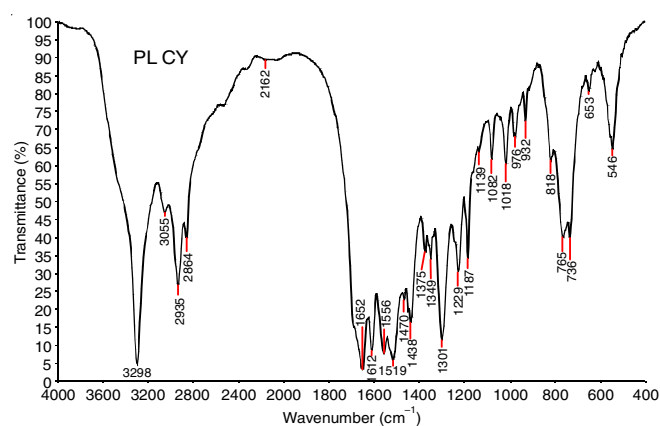


Fig. 7. IR spectrum of cyclic product

nickel(II) and manganese(II) complexes present in  $[\text{ML}(15)\text{Cl}_2]$  are shown in Table-2. The results showed the octahedral nature of all four synthesized complexes. The same observation had also been observed for  $[\text{ML}(13)\text{Cl}_2]$  and  $[\text{ML}(17)\text{Cl}_2]$  complexes.

With the evidence from the literature available, it was compared with the electronic spectrum of octahedral Cu(II) complex  $[\text{CuL}(15)\text{Cl}_2]$  (Fig. 9) in visible region the band observed at  $\lambda_{\text{max}} = 634 \text{ nm}$  ( $15773 \text{ cm}^{-1}$ ) was attributable to the transition  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ . Similarly, the same electronic spectral details has been observed for the complexes of  $[\text{CuL}(13)\text{Cl}_2]$  and  $[\text{CuL}(17)\text{Cl}_2]$ .

The electronic spectrum of Co(II) complex  $[\text{CoL}(15)\text{Cl}_2]$ , the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transitions in the UV regions appeared to overlap to produce only one band at  $\lambda_{\text{max}} = 239 \text{ nm}$ . Usually

TABLE-2  
SPECTRAL AND MAGNETIC MOMENT ( $\mu_{\text{eff}}$ ) DATA OF THE METAL COMPLEXES

Complex	Vibrational frequency ( $\text{cm}^{-1}$ )			Electronic spectral ( $\text{cm}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)
	$\nu(\text{NH})$	$\nu(\text{C=O})$ (amide I)	$\delta(\text{NH})$ (amide II)		
[Cy2]	3298	1652	1556	–	–
$[\text{CuL}(15)\text{Cl}_2]$	3301	1664	1518	15773	1.9
$[\text{CoL}(15)\text{Cl}_2]$	3301	1660	1523	15083 and 18797	4.6
$[\text{NiL}(15)\text{Cl}_2]$	3297	1652	1518	13966	3.3
$[\text{MnL}(15)\text{Cl}_2]$	3301	1656	1528	–	5.3
$[\text{ZnL}(15)\text{Cl}_2]$	3298	1655	1524	–	–

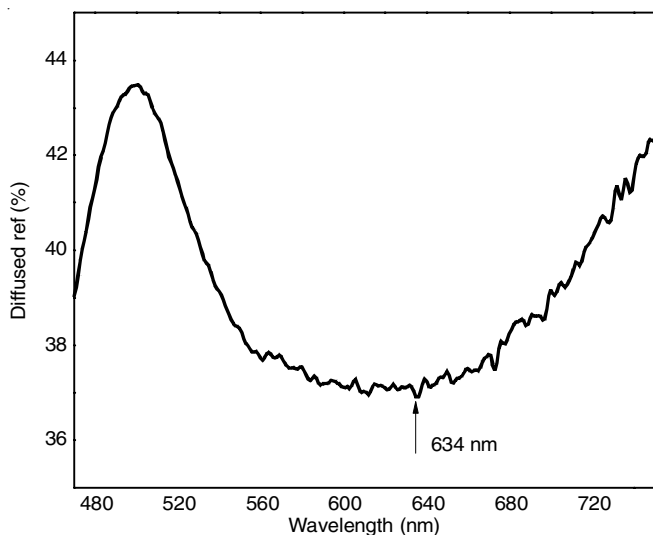


Fig. 9. Electronic spectrum of 15-membered tetraamide Cu(II) complex

for octahedral Co(II) complex (Fig. 10), the bands correspond to the transitions  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  can be expected. The observed band at  $15083\text{ cm}^{-1}$  and  $18797\text{ cm}^{-1}$  may be assigned for the transition  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ , respectively, by comparing the observed value with the reported in the literature value and it was found to be various transitions of octahedral cobalt(II) complexes. Similarly, same electronic spectral data had been observed for  $[\text{CoL}(13)\text{Cl}_2]$  and  $[\text{CoL}(17)\text{Cl}_2]$  complexes.

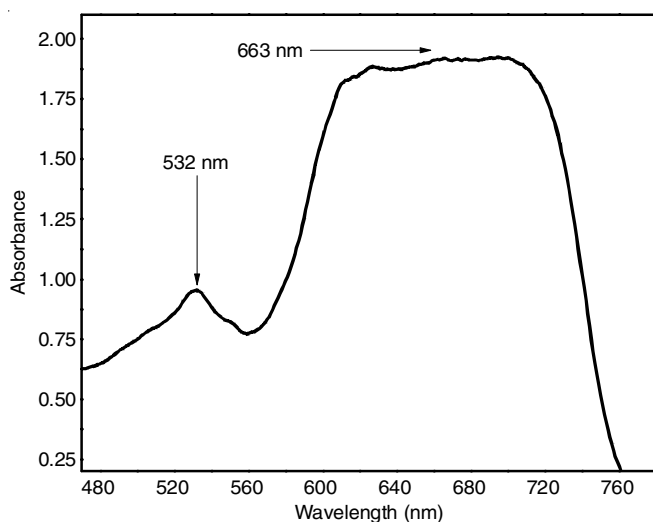


Fig. 10. Electronic spectrum of 15-membered tetraamide Co(II) complex

The electronic spectrum of Ni(II) complex in  $[\text{NiL}(15)\text{Cl}_2]$ , UV regions shows two bands due to  $\pi\text{-}\pi^*$  ( $\lambda_{\text{max}} = 236\text{ nm}$ ) and  $n\text{-}\pi^*$  ( $\lambda_{\text{max}} = 310\text{ nm}$ ) transitions. Electronic spectrum of the complex displays band at  $13966\text{ cm}^{-1}$  attributed to the transition and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) of an octahedral Ni(II) complex (Fig. 11). Similarly, same electronic spectral data had been observed for  $[\text{NiL}(13)\text{Cl}_2]$  and  $[\text{NiL}(17)\text{Cl}_2]$  complexes.

In solid state, EPR spectrum of  $[\text{CuL}(15)\text{Cl}_2]$  was recorded at room temperature (Fig. 12). This spectrum shows that  $\mu = 1.81\text{ B.M.}$  and it is in good concordance with the usual observed value for Cu(II) system corresponding to one unpaired electron. Similarly, same EPR spectral data has been observed for the

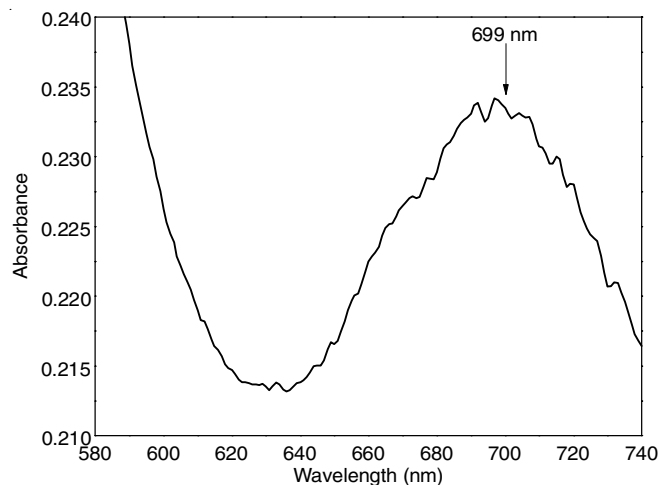


Fig. 11. Electronic spectrum of 15-membered tetraamide Ni(II) complex

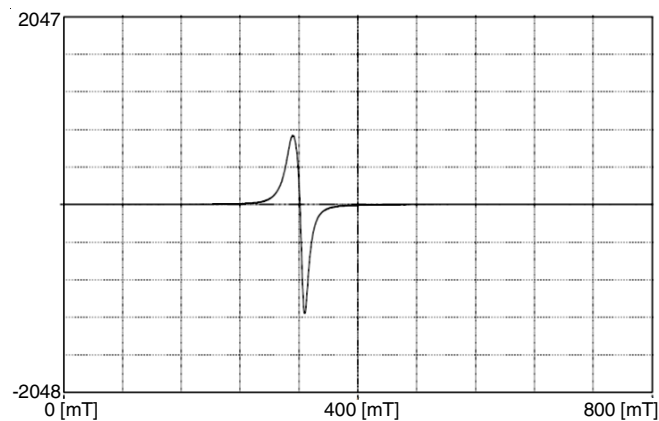


Fig. 12. ESR spectrum of 15-membered tetraamide Cu(II) complex

complexes of 13- and 17-membered macrocyclic copper(II) complexes.

## Conclusion

Transition metal complexes of 13-, 15- and 17-membered tetraamide macrocycle disubstituted-dimethyl-tetraazacycloalka-tetra-substituted-tetraene-disubstituted-diol have been synthesized by template fashion. The synthesized complexes are characterized by X-ray microanalyses, TGA, elemental analyses and magnetic susceptibilities as well as by IR, UV, ESR spectral studies and the geometry of all the synthesized complexes were found to be octahedral.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

- G.A. Melson, ed., Coordination Chemistry of Macrocyclic Compounds; Plenum: New York (1979).
- R.M. Izatt and J.J. Christensen, eds., Synthesis of Macrocycles: The Design of Selective Complexing Agents, In: Progress in Macrocyclic Chemistry; Wiley-Interscience: New York, vol. 3 (1987).
- R. Chaudhary and R.V. Singh, **28**, 35 (2008); <https://doi.org/10.1515/REVVIC.2008.28.1.35>
- N.K. Dalley, In Synthetic Multidentate Macrocyclic Compounds; R.M. Izatt and J. J. Christensen, Eds.; Academic Press: New York, (1978).
- D.A. House and N.F. Curtis, *Chem. Ind.*, 1708 (1961).

6. N.F. Curtis, *J. Chem. Soc.*, 4409 (1960); <https://doi.org/10.1039/jr9600004409>
7. N.F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968); [https://doi.org/10.1016/S0010-8545\(00\)80104-6](https://doi.org/10.1016/S0010-8545(00)80104-6)
8. L.F. Lindoy and D.H. Busch, ed.: W.L. Jolly, In *Preparative Inorganic Reactions*, Wiley-Interscience: New York, vol. 6 (1971).
9. M.C. Thompson and D.H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964); <https://doi.org/10.1021/ja01072a012>
10. D.E. Fenton and P.A. Vigato, *Chem. Soc. Rev.*, **17**, 69 (1988); <https://doi.org/10.1039/cs9881700069>
11. P. Comba, N.F. Curtis, G.A. Lawrance, A.M. Sargeson, B.W. Skelton and A.H. White, *Inorg. Chem.*, **25**, 4260 (1986); <https://doi.org/10.1021/ic00243a040>
12. H. Stetter and W. Frank, *Angew. Chem.*, **88**, 760 (1976); <https://doi.org/10.1002/ange.19760882208>
13. H. Hafliger and Th.A. Kaden, *Helv. Chim. Acta*, **62**, 683 (1979); <https://doi.org/10.1002/hlca.19790620306>
14. Th.A. Kaden, eds.: F. Vögtle and E. Weber, *Synthesis and Metal Complexes of Aza-Macrocycles with Pendant Arms having Additional Ligating Groups*, In: *Host Guest Complex Chemistry III, Topics in Current Chemistry*, Springer, Berlin, Heidelberg, vol 121, pp. 157-179 (1984).
15. J. Xu, S. Ni and Y. Lin, *Inorg. Chim. Acta*, **111**, 61 (1986); [https://doi.org/10.1016/S0020-1693\(00\)82218-5](https://doi.org/10.1016/S0020-1693(00)82218-5)
16. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **95**, 2529 (1995); <https://doi.org/10.1021/cr00039a010>
17. J.M. Lehn, *Supramolecular Chemistry*, VCH: New York (1995).
18. L.F. Lindoy, *Pure Appl. Chem.*, **69**, 2179 (1997); <https://doi.org/10.1351/pac199769102179>
19. P.A. Gale and R. Quesada, *Coord. Chem. Rev.*, **250**, 3219 (2006); <https://doi.org/10.1016/j.ccr.2006.05.020>
20. N. Gimeno, R. Vilar, P.A. Gale and R. Quesada, *Coord. Chem. Rev.*, **250**, 3161 (2006); <https://doi.org/10.1016/j.ccr.2006.05.016>
21. E. Garcia-Espana, P. Diaz, J.M. Llinares and A. Bianchi, *Coord. Chem. Rev.*, **250**, 2952 (2006); <https://doi.org/10.1016/j.ccr.2006.05.018>
22. V. Amendola, M. Bonizzoni, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, F. Sancenon and A. Taglietti, *Coord. Chem. Rev.*, **250**, 1451 (2006); <https://doi.org/10.1016/j.ccr.2006.01.006>
23. K. Bowman-James, *Acc. Chem. Res.*, **38**, 671 (2005); <https://doi.org/10.1021/ar040071t>
24. L. Fabbrizzi, M. Licchelli, G. Rabaioli and A. Taglietti, *Coord. Chem. Rev.*, **205**, 85 (2000); [https://doi.org/10.1016/S0010-8545\(00\)00239-3](https://doi.org/10.1016/S0010-8545(00)00239-3)
25. R. Martinez-Manez and F. Sancenon, *Chem. Rev.*, **103**, 4419 (2003); <https://doi.org/10.1021/cr010421e>
26. V. McKee, J. Nelson and R.M. Town, *Chem. Soc. Rev.*, **32**, 309 (2003); <https://doi.org/10.1039/b200672n>
27. D.R. Turner, A. Pastor, M. Alajarin and J.W. Steed, *Struct. Bonding*, **108**, 97 (2003); <https://doi.org/10.1007/b14138>
28. M.D. Best, S.L. Tobey and E.V. Anslyn, *Coord. Chem. Rev.*, **240**, 3 (2003); [https://doi.org/10.1016/S0010-8545\(02\)00256-4](https://doi.org/10.1016/S0010-8545(02)00256-4)
29. P.A. Gale, *Coord. Chem. Rev.*, **240**, 191 (2003); [https://doi.org/10.1016/S0010-8545\(02\)00258-8](https://doi.org/10.1016/S0010-8545(02)00258-8)
30. J.L. Sessler, S. Camiolo and P.A. Gale, *Coord. Chem. Rev.*, **240**, 17 (2003); [https://doi.org/10.1016/S0010-8545\(03\)00023-7](https://doi.org/10.1016/S0010-8545(03)00023-7)
31. H.J. Schneider, *Angew. Chem.*, **30**, 1417 (1991); <https://doi.org/10.1002/anie.199114171>
32. A.V. Eliseev and H.J. Schneider, *J. Am. Chem. Soc.*, **116**, 6081 (1994); <https://doi.org/10.1021/ja00093a004>
33. A.C. Warden, M. Warren, M.T.W. Hearn and L. Spiccia, *Inorg. Chem.*, **43**, 6936 (2004); <https://doi.org/10.1021/ic049633v>
34. A.C. Warden, M. Warren, M.T.W. Hearn and L. Spiccia, *New J. Chem.*, **28**, 1301 (2004); <https://doi.org/10.1039/b409088h>
35. L.J.K. Boerner and J.M. Zaleski, *Curr. Opin. Chem. Biol.*, **9**, 135 (2005); <https://doi.org/10.1016/j.cbpa.2005.02.010>
36. H.-J. Schneider and A. Yatsimirsky, eds.: H. Sigel and A. Sigel, *Metal Ion in Biological Systems*; Marcel Dekker: New York, vol. 40, pp 369-462 (2003).
37. M. Komiyama, eds.: H. Sigel and A. Sigel, *Metal Ion in Biological Systems*; Marcel Dekker: New York, vol. 40, pp 463-475 (2003).
38. A. Blasko and T.C. Bruice, *Acc. Chem. Res.*, **32**, 475 (1999); <https://doi.org/10.1021/ar980060y>
39. E.L. Hegg and J.N. Burstyn, *Coord. Chem. Rev.*, **173**, 133 (1998); [https://doi.org/10.1016/S0010-8545\(98\)00157-X](https://doi.org/10.1016/S0010-8545(98)00157-X)
40. R. Krämer, *Coord. Chem. Rev.*, **182**, 243 (1999); [https://doi.org/10.1016/S0010-8545\(98\)00235-5](https://doi.org/10.1016/S0010-8545(98)00235-5)
41. E. Kimura, *Curr. Op. Chem. Biol.*, **4**, 207 (2000); [https://doi.org/10.1016/S1367-5931\(99\)00076-9](https://doi.org/10.1016/S1367-5931(99)00076-9)
42. S. Aoki and E. Kimura, *Rev. Mol. Biotechnol.*, **90**, 129 (2002); [https://doi.org/10.1016/S1389-0352\(01\)00070-8](https://doi.org/10.1016/S1389-0352(01)00070-8)
43. L. Fabbrizzi, M. Licchelli and A. Taglietti, *Dalton Trans.*, 3471 (2003); <https://doi.org/10.1039/B304172G>
44. V. Amendola, L. Fabbrizzi, F. Foti, M. Licchelli, C. Mangano, P. Pallavicini, A. Poggi, D. Sacchi and A. Taglietti, *Coord. Chem. Rev.*, **250**, 273 (2006); <https://doi.org/10.1016/j.ccr.2005.04.022>
45. A.W. Czarnik and J.-P. Desvergne, *Chemodosensors of Ions and Molecular Recognition*, Kluwer Academic Publishers: Dordrecht, NATO ASI Ser., Ser. C, vol. 492 (1997).
46. E. Kimura and T. Koike, *Chem. Soc. Rev.*, **27**, 179 (1998); <https://doi.org/10.1039/a827179z>
47. G.A. Melson, Ed. *Coordination Chemistry of Macrocyclic Compounds*, Plenum: New York (1979).
48. L.F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge (1989).
49. S. Torelli, C. Belle, I. Gautier-Luneau, J.L. Pierre, E. Saint-Aman, J.M. Latour, L. Le Pape and D. Luneau, *Inorg. Chem.*, **39**, 3526 (2000); <https://doi.org/10.1021/ic991450z>
50. O. Kahn, *Molecular Magnetism*, VCH Publishers Inc.: Weinheim Germany (1993).
51. N. Kuhn, *Adv. Inorg. Chem.*, **43**, 179 (1995).
52. O. Kahn, *Acc. Chem. Res.*, **33**, 647 (2000); <https://doi.org/10.1021/ar9703138>
53. C.R. Bondy and S.R. Loeb, *Coord. Chem. Rev.*, **240**, 77 (2003); [https://doi.org/10.1016/S0010-8545\(02\)00304-1](https://doi.org/10.1016/S0010-8545(02)00304-1)
54. L. Cronin, A.R. Mount, S. Parsons and N. Robertson, *J. Chem. Soc., Dalton Trans.*, 1925 (1999); <https://doi.org/10.1039/a902792k>
55. H.-Z. Kou, B.C. Zhou, S. Gao and R.-J. Wang, *Angew. Chem. Int. Ed.*, **42**, 3288 (2003); <https://doi.org/10.1002/anie.200351248>
56. J.-K. Tang, S.-F. Si, L.-Y. Wang, D.-Z. Liao, Z.-H. Jiang, S.P. Yan, P. Cheng and X. Liu, *Inorg. Chim. Acta*, **343**, 288 (2003); [https://doi.org/10.1016/S0020-1693\(02\)01241-0](https://doi.org/10.1016/S0020-1693(02)01241-0)
57. A. Bianchi, K. Bowman-James and E. Garcia-Espan, *Supramolecular Chemistry of Anions*, Wiley-VCH: New York (1997).
58. J. Zhao, D. Yang, X.-J. Yang and B. Wu, *Coord. Chem. Rev.*, **378**, 415 (2019); <https://doi.org/10.1016/j.ccr.2018.01.002>
59. S. Mason, T. Clifford, L. Seib, K. Kuczera and K. Bowman-James, *J. Am. Chem. Soc.*, **120**, 8899 (1998); <https://doi.org/10.1021/ja9811593>
60. T. Clifford, A. Danby, J.M. Llinares, S. Mason, N.W. Alcock, D. Powell, J.A. Aguilar, E. Garcia-Espan and K. Bowman-James, *Inorg. Chem.*, **40**, 4710 (2001); <https://doi.org/10.1021/ic0101351>
61. A. Hossain, J.M. Llinares, S. Mason, P. Morehouse, D. Powell and K. Bowman-James, *Angew. Chem., Int. Ed.*, **41**, 2335 (2002); [https://doi.org/10.1002/1521-3773\(20020703\)41:13<2335::AID-ANIE2335>3.0.CO;2-3](https://doi.org/10.1002/1521-3773(20020703)41:13<2335::AID-ANIE2335>3.0.CO;2-3)
62. M.A. Hossain, S.O. Kang, D. Powell and K. Bowman-James, *Inorg. Chem.*, **42**, 1397 (2003); <https://doi.org/10.1021/ic0263140>
63. M.A. Hossain, J.M. Llinares, D. Powell and K. Bowman-James, *Inorg. Chem.*, **40**, 2936 (2001); <https://doi.org/10.1021/ic015508x>