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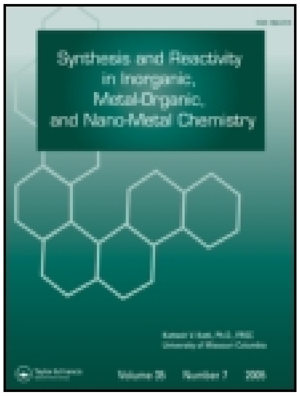

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SYNTHESIS AND SPECTRAL STUDIES OF TRANSITION METAL COMPLEXES WITH 5,7,12,14-TETRAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-4,7,11,14-TETRAENE, A FOURTEEN-MEMBERED TETRADENTATE MACROCYCLIC LIGAND

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SYNTHESIS AND SPECTRAL STUDIES OF TRANSITION METAL COMPLEXES WITH 5,7,12,14-TETRAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-4,7,11,14-TETRAENE, A FOURTEEN-MEMBERED TETRADENTATE MACROCYCLIC LIGAND

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ABSTRACT

Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Pd(II) and Cu(II) with a fourteen-membered macrocyclic ligand have been prepared and characterized by magnetic moment, infrared, electronic and EPR spectral studies. All of complexes were found to have six-coordinate geometry and are of the high-spin type except the Pd(II) complex which is four-coordinate, square-planar and diamagnetic.

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INTRODUCTION

Transition metal complexes of synthetic macrocyclic ligands are of significance because porphyrins and cobalamines play vital roles in biological systems. Such chelating molecules are important since they are capable of furnishing an environment of controlled geometry and ligand field strength. Curtis and coworkers[1] were first to report the synthesis of some macrocyclic ligands, especially of hexamethyltetraazacyclotetradecatetraene. Since then, several other macrocyclic ligands such as cyclam[2], cyclen[3], aminobenzaldehyde trimers and tetramers[4], reaction products of various polyamines[5,6] and 2,6-diacetylpyridine[7–9] have been reported. Some α-diketones are also capable of forming macrocyclic ligands.

Here we report the synthesis and characterization of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Pd(II) and Cu(II) complexes of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, abbreviated as Tmtacdte (Fig. 1). Although the Co(II) and Ni(II) complexes of this ligand have been reported earlier by Singh *et al.*[10] but the anions used were different than what we have used in this paper. So the results obtained are also different, As Singh *et al.*[10] have reported the complexes to have low-spin and square-planar geometry while in the present case we found the complexes to have high-spin and six-coordinate geometry.

EXPERIMENTAL

Preparation of Complexes

A tempelate reaction was carried out for the formation of the complexes. A hot ethanolic solution (20 mL) of the metal salt (0.025 mol) was mixed with a hot ethanolic solution (20 mL) of ethylenediamine (3 g,

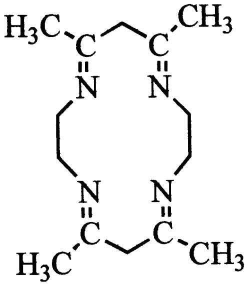

Figure 1. Structure of the macrocyclic ligand tmtacdte.

0.05 mol) and with an ethanolic solution (20 mL) of acetylacetone (5 mL, 0.05 mol) in the presence of a few drops of conc. HCl. The solution was refluxed for about four to five hours in each case. The complexes precipitated out on cooling the reaction mixture overnight. They were filtered, washed with ethanol and dried over P_4O_{10}. Yields, 58–75%.

Physical Measurements

Microanalyses (C, H and N) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Perkin Elmer 137 instrument as Nujol mulls [for (**1**) and (**7**)] or KBr pellets [for (**2**), (**3**), (**4**), (**5**) and (**6**)]. Electronic spectra were recorded in DMF solution on a Shimadzu UV mini-1240 spectrophotometer. The molar conductance was measured on a Elico conductivity bridge (type C M 82 T).

Magnetic susceptibility measurements (Gouy balance) were made at room temperature using $CuSO_4.5H_2O$ as callibrant. EPR spectra of the complexes were recorded as powdered samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker. The molecular weights of complexes were determined cryoscopically in benzene.

RESULTS AND DISCUSSION

The analytical and molar conductance (Table I) values of all the complexes in DMF solution suggest that general formulas of the complexes are $[MLCl_2]$ (where M = Mn(II), Co(II), Ni(II), Cu(II) and L = Tmtacdte), $[M'LCl_2]Cl$ (where M′ = Cr(III) and Fe(III)) and $[PdL]Cl_2$ for the Pd complex. The IR spectra of the ligand and complexes show moderate-intensity absorptions in the range 1600–1700 cm^{-1} attributable to the imine $\nu(C{=}N)$[11] but no bands are observed for free $>C{=}O$ or primary diamine indicating that complete condensation has occurred. A shift in the absorption of the $\nu(C{=}N)$ frequency for the complexes suggests coordination through $>C{=}N$.

The formation of the complexes may be represented by the following equations

$$MCl_2 + 2H_2NCH_2CH_2NH_2 + 2CH_2COCH_2COCH_3$$

$$\xrightarrow[\text{a few drops of conc. HCl}]{\text{Ethanol}} [M(Tmtacde)Cl_2] + 2H_2O$$

$$M = Mn,\ Co,\ Ni\ and\ Cu$$

Table I. Analytical and Physical Data of the Complexes Derived from Tmtacde

Complex and Molecular formula	Mol. Wt. Calc (found)	Colour	Yield (%)	M.p. (°C)	M	Molar[a] conductance (Ohm^{-1} cm^{2} mole^{-1})	Elemental analysis (%) Calcd (Found)			
							C	N	H	Cl
(**1**) [Cr(Tmtacdte)Cl$_2$]Cl	406.72	Shiny	75	208	95	12.78	41.34	13.77	5.94	26.15
$C_{14}H_{24}Cl_3CrN_4$	(414)	violet				(12.67)	(41.23)	(13.72)	(5.84)	(26.09)
(**2**) [Mn(Tmtacdte)Cl$_2$]	374.21	Light	72	215	10	14.68	44.93	14.97	6.46	18.94
$C_{14}H_{24}Cl_2MnN_4$	(380)	yellow				(14.65)	(44.89)	(14.95)	(6.37)	(18.92)
(**3**) [Fe(Tmtacdte)Cl$_2$]Cl	410.57	Black	60	222	100	13.60	40.95	13.64	5.89	25.90
$C_{14}H_{24}Cl_3FeN_4$	(405)					(13.57)	(40.89)	(13.56)	(5.78)	(25.93)
(**4**) [Co(Tmtacdte)Cl$_2$]	378.21	Orange	75	216	15	15.58	44.46	14.81	6.39	18.74
$C_{14}H_{24}Cl_2CoN_4$	(381)					(15.54)	(44.35)	(14.79)	(6.28)	(18.71)
(**5**) [Ni(Tmtacdte)Cl$_2$]	377.98	Light	72	210	17	15.53	44.48	14.82	6.40	18.75
$C_{14}H_{24}Cl_2NiN_4$	(384)	purple				(15.45)	(44.42)	(14.75)	(6.29)	(18.74)
(**6**) [Pd(Tmtacdte)]Cl$_2$	425.67	Black	58	215	242	24.99	39.50	13.16	5.68	16.65
$C_{14}H_{24}Cl_2PdN_4$	(421)					(25.01)	(39.39)	(13.12)	(5.33)	(16.62)
(**7**) [Cu(Tmtacdte)Cl$_2$]	382.82	Green	70	208	12	16.60	43.92	14.63	6.31	18.52
$C_{14}H_{24}Cl_2CuN_4$	(375)					(16.53)	(43.81)	(14.51)	(6.19)	(18.43)

[a] Solvent used for molar conductance: DMF

$$\mathrm{M'Cl_3 + 2H_2NCH_2CH_2NH_2 + 2CH_2COCH_2COCH_3}$$

$$\xrightarrow[\text{a few drops}\atop\text{of conc. HCl}]{\text{Ethanol}} \mathrm{[M'(Tmtacde)Cl_2]Cl + 2H_2O}$$

$$\mathrm{M' = Cr\ and\ Fe}$$

Chromium(III) Complex

The room temperature magnetic moment (3.78 B.M.) of the Cr(III) complex lies within the range expected for high-spin octahedral Cr(III) complexes. The electronic spectrum of the complex recorded in DMF displays four bands at 18,400 (ν_1) ($\varepsilon = 32\,\mathrm{mole^{-1}\,cm^{-1}}$), 22,500 ($\nu_2$) ($\varepsilon = 43\,\mathrm{mole^{-1}\,cm^{-1}}$), 24,900 ($\nu_3$) ($\varepsilon = 54\,\mathrm{mole^{-1}\,cm^{-1}}$) and 28,900 ($\nu_4$) $\mathrm{cm^{-1}}$ ($\varepsilon = 67\ \mathrm{L\,mole^{-1}\,cm^{-1}}$). Six-coordinate complexes with $\mathrm{O_h}$ symmetry show three spin-allowed bands[12] of which the highest energy band assignable to the $^4\mathrm{A}_{2g} \rightarrow {}^4\mathrm{T}_{1g}(\mathrm{P})$ transition occurs around 30,000 $\mathrm{cm^{-1}}$. The spectrum of the complex under study shows four bands below 30,000 $\mathrm{cm^{-1}}$, which cannot be interpreted in terms of idealized symmetry elements in the complexes. Such six-coordinated chromium(III) complexes can have either $\mathrm{C_{4v}}$ or $\mathrm{D_{4h}}$ symmetry. In the present complex, the four transitions observed may be assigned to $^4\mathrm{B}_{1g} \rightarrow {}^4\mathrm{E}^a_g(\nu_1)$, $^4\mathrm{B}_{1g} \rightarrow {}^4\mathrm{B}_{2g}(\nu_2)$, $^4\mathrm{B}_{1g} \rightarrow {}^4\mathrm{A}_{1g}(\nu_3)$ and $^4\mathrm{B}_{1g} \rightarrow {}^4\mathrm{E}^b_g(\nu_4)$ transitions arising from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in order of increasing energy and assuming $\mathrm{D_{4h}}$ symmetry around the metal ion. In $\mathrm{O_h}$ symmetry, ν_1 and ν_2 are derived from the $^4\mathrm{T}_{2g}$ level, whilst ν_3 and ν_4 from $^4\mathrm{T}_{1g}(\mathrm{F})$. The $\mathrm{C_{4v}}$ symmetry has been ruled out because of the greater splitting of the first band and lower intensity of spectral bands. On the basis of symmetry arguments Lever *et al.*[13] have devised a normalised spherical harmonic Hamiltonion (NSH) theory applicable to molecule of $\mathrm{D_{4h}}$. The newly developed NSH theory relates the classical ligand field parameters to NSH absolute ligand field parameters. For our complex the NSH parameters are $\mathrm{Dq^{xy}} = 2,250$, $\mathrm{D_t} = 469$, $\mathrm{Dq^z} = 1430$, $\mathrm{D_s} = 764$, $\mathrm{DS} = -5348$, $\mathrm{DT} = -6357$, $\mathrm{DQ} = -26746$, $\mathrm{DT/DQ} = 0.237$. DQ is a measure of the average ligand field experienced by the metal ion unlike the classical Dq, which is the measure of the in-plane ligand field. The DT/DQ ratio provides the amount of distortion of the molecule. The value of DT/DQ is 0.237 and thus indicates that the complexes are moderately distorted. The EPR spectrum of the complex has been recorded as a polycrystalline sample at room temperature. The g-value is found to be 1.938. The g-value was calculated using the expression, $\mathrm{g} = 2.0023\ (1 - 4\lambda)/\ (10\mathrm{Dq})$ where λ is the spin orbit coupling constant for the metal ion in the complex. It was noted that the reduction of the spin orbit coupling constant from the free ion value of $90\,\mathrm{cm}^{-1}$ for chromium(III) may be employed as a measure of metal ligand covalency. It is possible to derive a covalency parameter λ, analogous to the nephelauxetic parameter which is the ratio of the spin orbit coupling constant for the complex and the free Cr(III) ion. This also indicates appreciable covalent character in the complex.

Manganese(II) Complex

This complex shows a magnetic moment corresponding to five unpaired electrons *i.e.*, 5.94 B.M., which indicates that Mn(II) is high-spin in this case. The electronic spectrum of the complex displays weak absorption bands at 17,900 ($\varepsilon = 43\,\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$), 24,600 ($\varepsilon = 48\,\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$), 29,400 ($\varepsilon = 63\,\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$) and $31{,}700\,\mathrm{cm}^{-1}$ ($\varepsilon = 106\,\mathrm{L\,mole}^{-1}\,\mathrm{cm}^{-1}$) characteristic of octahedral geometry[20]. These bands may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$, and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (${}^4P$) transitions, respectively. High values of extinction coefficient may be due to lower symmetry or mixing of charge transfer. The value for the ligand field parameters have been calculated ($Dq = 1790\,\mathrm{cm}^{-1}$, $B = 686\,\mathrm{cm}^{-1}$, $\beta = 0.86$ and $C = 3548.6\,\mathrm{cm}^{-1}$). The value of Dq could be evaluated with the help of the curve transition energies *vs.* Dq by Orgel[14] using the energy due to the transition ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (${}^4G$). Parameters B and C were calculated by using the methods reported earlier[15,16]. The calculated value of β indicates that the complex under study has covalent character. The EPR spectrum of the complex has been recorded as polycrystalline sample and in DMF solution. The polycrystalline sample gives one broad isotropic signal centered at approximately the free electron g-value ($g_0 = 2.0023$). The broadening of the spectrum probably is due to spin relaxation[17]. In DMF solution the complex gives an EPR spectrum containing six lines arising due to hyperfine interaction[17–19] between the unpaired electrons with the ^{55}Mn nucleus ($I = 5/2$). The nuclear magnetic quantum number, MI, corresponding to the lines are $-5/2, -3/2, -1/2, +3/2, +5/2$ from low to high field.

Iron(III) Complex

The iron(III) complex was found to have the composition $FeLCl_3$. This complex shows a magnetic moment corresponding to five unpaired electrons (*i.e.*, 6.0 B.M.), indicating the presence of high-spin Fe(III) ion.

The electronic spectrum of this complex shows two electronic spectral bands at 19,200 ($\varepsilon = 76\,\text{mole}^{-1}\,\text{cm}^{-1}$) and 23,000 ($\varepsilon = 89\,\text{L mole}^{-1}\,\text{cm}^{-1}$) which are characteristic of octahedral geometry.

Cobalt(II) Complex

The magnetic moment (4.9 B.M.) of the cobalt(II) complex lies within the range expected for high-spin octahedral Co(II) complexes[20]. The electronic spectrum exhibits a broad band at *ca.* 8,850 cm^{-1} ($\varepsilon = 65\,\text{mole}^{-1}\,\text{cm}^{-1}$) and two shoulders at 14,300 ($\varepsilon = 73\,\text{mole}^{-1}\,\text{cm}^{-1}$) and 20,600 cm^{-1} ($\varepsilon = 93\,\text{L mole}^{-1}\,\text{cm}^{-1}$) on the rising charge transfer band, tentatively assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ $(P)(\nu_3)$, transitions, respectively. The low value of ν_2/ν_1 (1.75) may be due to distortion of the octahedral structure[20,21]. This is consistent with the very broad nature of the ν_1 band, which may be assigned to the envelope of the transitions from ${}^4E_g({}^4T_{1g})$ to the components ${}^4B_{2g}$ and ${}^4E_g$ of ${}^4T_{2g}$, characteristic of tetragonally-distorted octahedral environment. A complex of this ligand reported by Singh *et al.*[10] with cobalt nitrate is low-spin in nature while we observed a high-spin nature of the complex reported by us. The reason for this difference is yet not certain, but it might be due to the bulky nature of ligand. The EPR spectrum of the complex under study was recorded at liquid nitrogen temperature because the rapid spin lattice relaxation of Co(II) broadened the lines at higher temperatures ($g_{11} = 3.109$ and $g_{\perp} = 2.6122$). The large deviation of the g-values from the spin-only value ($g = 2.0023$) is due to the large angular momentum contribution.

Nickel(II) Complex

This complex shows a magnetic moment corresponding to two unpaired electrons. The electronic spectrum of the nickel complex shows two well defined bands at 10,570 ($\varepsilon = 34\,\text{L mole}^{-1}\,\text{cm}^{-1}$) and 16,400 ($\varepsilon = 68\,\text{L mole}^{-1}\,\text{cm}^{-1}$) cm^{-1} assignable to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ $(F)(\nu_2)$, transitions, respectively. Here splitting of the ν_1 band is not observed which is generally observed in D_{4h} symmetry. So D_t, Dq^E and Dq^A cannot be calculated. The third d-d transition band (ν_3) which may be obscured by the more intense charge transfer band, is calculated to be at 25,780 cm^{-1}. The value of ν_2/ν_3 is 1.52 and the ligand field parameters Dq, B and β have been found[20] to be 1057 cm^{-1}, 630 cm^{-1} and 0.605, respectively. All of these values, together with the magnetic moment

(3.1 B.M), are characteristic of an octahedral geometry for this complex. Though a complex of this ligand already have been prepared from nickel acetate, as reported by Singh *et al.*[10], it was found to be diamagnetic, low-spin, square-planar. While our complex is paramagnetic, high-spin and octahedral. This difference also might be due to the bulky nature of the acetate group.

Palladium(II) Complex

This complex is diamagnetic as expected for a low-spin d^8 system. The low-spin square-planar metal complexes are characterized by three spin-allowed d-d bands, corresponding to the $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_g$, and $^1A_{1g} \rightarrow {}^1E_g$ transitions, respectively. The complex under study display two bands at 21,500 ($\varepsilon = 98\,\mathrm{L\,mole^{-1}\,cm^{-1}}$) and 27,500 ($\varepsilon = 123\,\mathrm{L\,mole^{-1}\,cm^{-1}}$) $\mathrm{cm^{-1}}$, respectively. These bands may be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}(\nu_1)$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) transitions, respectively.

Copper(II) Complex

The magnetic moment of the complex was found to be 1.98 B.M. The electronic spectrum of the complex displays two bands at 16,000 ($\varepsilon = 54\,\mathrm{L\,mole^{-1}\,cm^{-1}}$) and 14,085 ($\varepsilon = 63\,\mathrm{L\,mole^{-1}\,cm^{-1}}$) $\mathrm{cm^{-1}}$. The electronic spectrum of six-coordinate Cu(II) complexes have either D_{4h} or C_{4v} symmetry, and the E_g and T_{2g} levels of the ^2D free ion will split into B_{1g}, A_{1g}, B_{2g} and E_g levels, respectively. Thus, three spin-allowed transitions are expected in the visible and near-IR region, but only few complexes are known, in which such bands are resolved either by "Gaussian analysis" or by "Single Crystal Polarization" studies[21]. These bands have been assigned to the following transitions, in order of increasing energy, $^2B_{1g} \rightarrow {}^2A_{1g}$ $(d_{x^2-y^2} \leftarrow d_z^2)$, $^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} \leftarrow d_{xy})$, and $^2B_{1g} \rightarrow {}^2E_g$ $(d_{x^2-y^2} \leftarrow d_{xz,yz})$. The energy level sequence will depend on the amount of tetragonal distortion due to ligand-field and Jahn-teller effects[22–24]. The electronic spectrum of the complex shows a band at $14{,}085\,\mathrm{cm^{-1}}$ ($\varepsilon = 78\,\mathrm{L\,mole^{-1}\,cm^{-1}}$) and a well defined shoulder at $16{,}000\,\mathrm{cm^{-1}}$($\varepsilon = 89\,\mathrm{L\,mole^{-1}\,cm^{-1}}$). These may be assigned to the $^2B_{1g} \leftarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. The EPR spectrum[22–24] of the present complex exhibits a well resolved anisotropic signals in the parallel and perpendicular ^{63}Cu region. The observed data show that $g_{11} = 2.36$ and $g_{\perp} = 2.08$ and the g_{11} and $g_{\perp}$ values are closer to 2 and $g_{11} > g_{\perp}$. This suggests major distortion in the copper(II) complex from O_h symmetry *i.e.*, D_{4h} symmetry.

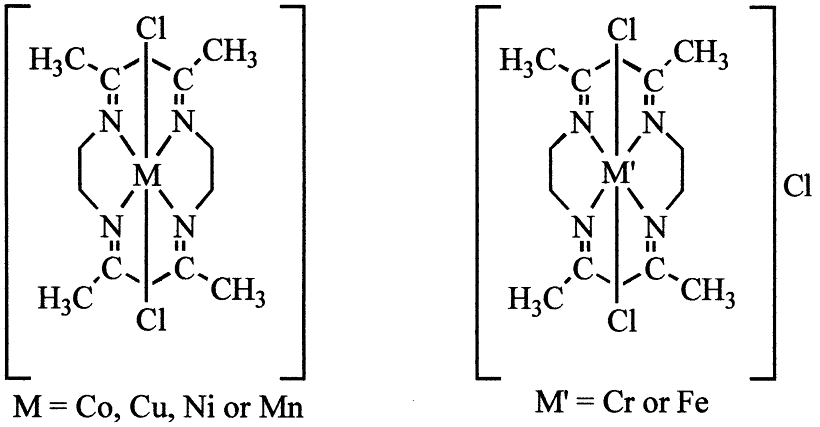

Figure 2. Suggested structures of the complexes.

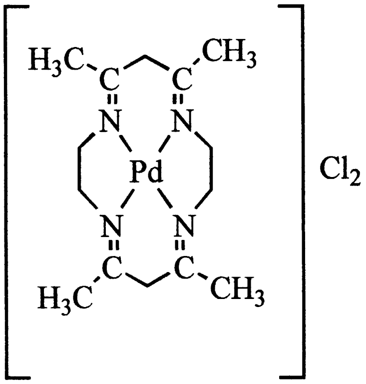

Figure 3. Suggested structure of Pd complex.

On the basis of the above studies the following structures may be suggested for the complexes (Figs. 2 and 3).

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REFERENCES

1. Curtis, N.F. Macrocyclic Coordination Compounds Formed by Condensation of Metal Amine Complexes with Aliphatic Carbonyl Compound. Coord. Chem. Rev. **1968**, *3*, 3–53.
2. Kist, L.T.; Fernandez; M.J.; Scpoganicsz, B.; Manez, M.A.; Basallote, M.G. Kinetics of Reaction of the Fe(II) Cyclam Complex with H_2O_2 in Acetonitrile and the Mechanism of Catalyzed Epoxidation of Cyclohexene. Polyhedron **1997**, *16* (21), 3827–3833.
3. Collman, J.P.; Schneider, P.W. Complexes of Cobalt(III) and Rhodium(III) with a Cyclic Tetradentate Secondary Amine. Inorg. Chem. **1966**, *5*, 1380–1382.
4. Melson, G.A.; Busch, D.H. Reactions of Coordinated Ligands. X. The Formation and Properties of a Tetradentate Macrocyclic Ligand by the Self-condensation of *o*-Aminobenzaldehyde in the Presence of Metal ions. J. Am. Chem. Soc. **1964**, *86*, 4834–4837.
5. Curry, J.D.; Busch, D.H. The Reactions of Coordinated Ligands. VII. Metal Ion Control in Synthesis of Chelate Compounds Containing Pentadentate and Sexadentate Macrocyclic Ligand. J. Am. Chem. Soc. **1964**, *86*, 592–594.
6. Lee, K.J.; Suh, J. Cooperation of Macrocyclic Metal Centers with 4-Dialkylaminopyridines in Catalysis by Poly(ethylenimine)-Based Artifical Metalesterases. Bioorg. Chem. **1994**, *22*, 95–108.
7. Cook, D.H.; Fenton, D.E. Calcium, Strontium, and Barium Complexes of Pyridyl-Containing Macrocyclic Schiff Bases. J. Chem. Soc., Dalton Trans. **1979**, 266–272.
8. Arif, A.M.; Backes-dirks, J.D.J.; Gray, C.J.; Hart, F.A.; Hursthouse, M.B. Synthesis, X-ray Structures, and Properties of Complexes of Macrocyclic Hexaimines with Lanthanide Nitrates. J. Chem. Soc., Dalton Trans. **1987**, 1665–1668.
9. Bastida, R.; Blas, A.; Castro, P.; Fenton, D.E.; Macias, A.; Rial, R.; Rodriguez, A. Complexes of Lanthanide(III) Ions with Macrocyclic Ligands Containing Pyridine Head Units. J. Chem. Soc., Dalton Trans. **1996**, 1493–1497.
10. Singh, A.K.; Chandra, S.; Bainwal, S. Synthesis of 5,7,12,14-Tetramethyl-1,4,8,11-Tetraazacyclotetradeca-4,7,11,14-tetrane and its Metal Complexes with Chromium-, Nickel-, Cobalt-, and Iron(II) Metal Ions. J. Indian Chem. Soc. **1998**, *75*, 84–86.
11. Rao, C.R.K.; Zacharias, P.S. Studies on Dinuclear Metal Complexes of Macrocyclic Ligands with Varying Chelate Ring Size. Polyhedron. **1997**, *16* (7), 1201–1209.

12. Perumareddi, J.R. Electronic Spectra of Quadrate Chromium(III) Complexes. Coord. Chem. Rev. **1969**, *4*, 73–105.
13. Doinini, J.C.; Hollebone, B.R.; Lever, A.B.P. The Derivation and Application of Normalized Spherical Harmonics. Progr. Inorg. Chem. **1977**, *22*, 225–307.
14. Orgel, L.E. Spectra of Transition Metal Complexes. J. Chem. Phys. **1955**, *23* (6), 1004–1014.
15. Chandra, S.; Pandeya, K.B.; Singh, R.P. Manganese(II) Complexes of Cyclohexanone Semicarbazone and Cyclohexanone Thiosemicarbazone. Gazz. Chem. Ital. **1980**, *110*, 207–210.
16. Chandra, S. Complexes of Some Semicarbazones and Thiosemicarbazones with Chromium(III). Acta Chim. Scand **1982**, *111*, 155–165.
17. Hong, D.M.; Wei, H.H.; Gan, L.L.; Lee, G.H.; Wang, Y. Synthesis, Structure and Magnetic Properties of Mononuclear [Mn(2,2′-Bipyrimidine)$_2$(H$_2$O)][ClO$_4$]$_2$ and Polynuclear [Mn(2,2′-Bipyrimidine)(NO$_3$)$_2$] Complexes. Polyhedron. **1996**, *15* (14), 2335–2340.
18. Rajan, R.; Rajaram, R.; Nair, B.U.; Ramasami, T.; Mandal, S.K. Synthesis, Characterization and Superoxide Dismutase Activity of Manganese(II) Complex. J. Chem. Soc. Dalton Trans. **1996**, 2019–2021.
19. Chandra, S.; Kumar, Y. Manganese(II) Complexes of Nitrogen-Oxygen and Nitrogen-Sulphur Donor Ligands. Proc. Ind. Academy of Science, Banglore. **1983**, *92*, 249–255.
20. Lever, A.B.P. Crystal Field Spectra. In *Inorganic Electronic Spectroscopy*; 1st Edn; Elsevier: Amsterdam, 1968; 249–360.
21. Figgis, B.N.; Lewis, J. The Magnetic Properties of Transition Metal Complexes. Progress Inorg. Chem. **1964**, *37* (6), 37–239.
22. Procter, I.M.; Hathaway, B.J.; Nicholls, P. The Electronic Properties and Stereochemistry of the Copper(II) Ion. Part I. Bis(ethylenediamine)copper(II) Complexes. J. Chem. Soc. A. **1968**, 1678–1684.
23. Tomilnson, A.A.G.; Hathaway, R.J.; Billing, D.E.; Nicholls, P. The Electronic Properties and Stereochemistry of Copper(II) Ion. Part V. The Tetraamine Complexes. J. Chem. Soc. A. **1965**, 65–71.
24. Choi, S.N.; Menzel, E.R.; Wasson, J.R. Electronic Spectra of Copper(II) Dithiocarbamates. J. Inorg. Nucl. Chem. **1977**, *39*, 417–422.

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