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Hemant Kumar Sharma [a], Sulekh Chandra [a] & Sunita Gupta [a]

[a] Department of Chemistry, Zakir Husain College, (University of Delhi) J. L. Nehru Marg, New Delhi, 110 002, India

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SYNTHESIS AND SPECTRAL STUDIES OF NICKEL(II) AND COBALT(II) COMPLEXES OF A TWELVE-MEMBERED AND TETRADENTATE MACROCYCLIC LIGAND

Hemant Kumar Sharma, Sulekh Chandra* and Sunita Gupta
Department of Chemistry, Zakir Husain College, (University of Delhi)
J. L. Nehru Marg, New Delhi-110 002, India

ABSTRACT

Nickel(II) and cobalt(II) complexes of the general compositions M(Tptacdte)X_2 (Tptacdte = 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene; X = Cl, Br, SCN for Ni(II) and X = Cl, NO_3, SCN for Co(II) and Co(Tptacdte)SO_4.$(H_2O)_2$ have been synthesized. The complexes have been characterized on the basis of elemental analyses, molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral studies. The complexes were found to stabilize an octahedral geometry for the Ni(II) complexes and a distorted octahedral geometry for the Co(II) complexes.

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 hexamethytetraazacyclotetradecadienes. Since then several other macrocyclic ligands such as cyclam[2], cyclen[3], aminobenzaldehyde trimers and tetramers[4], various polyamines[5-7] and 2,6-diacetylpyridine[8-10] have been reported. Some α-diketones are also capable of forming macrocyclic ligands.

In the present paper, we report the synthesis and characterization of Ni(II) and Co(II) complexes of the macrocyclic ligand 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene abbreviated as Tptacdte and shown in Fig. 1.

EXPERIMENTAL

Preparation of the Ligand

The ligand was synthesized by refluxing an ethanolic solution (20 mL) of benzil (10.5 g, 0.05 mol) with an ethanolic (20 mL) solution of ethylenediamine (3.0 g, 0.05 mol) in the presence of a few drops of conc. HCl for about four hours. A light yellow crystalline compound separated out on cooling of the resulting solution. The precipitate was filtered, washed with ethanol and dried over P_4O_{10}.Analyses: Found: C, 82.23 ; H, 5.83 ; N, 11.76. Calculated for $C_{32}H_{28}N_4$ {M.W. calcd. (found): 468 (472)}:C, 82.05 ; H, 5.98 ; N, 11.96. Observed yield 1.8 g (80%), Mp 154-157°C.

Preparation of the Complexes

A hot ethanolic solution (20 mL) of the metal salt (0.002 mol) was mixed with a hot ethanolic 20 mL solution of the ligand 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (1.178 g, 0.002 mol). The solutions were refluxed for about four hours in each case . The complexes precipitated on cooling the reaction mixture overnight . They were filtered, washed with hot ethanol and dried over P_4O_{10}.

Physical Measurements

Magnetic susceptibility measurements were made on a CAHN-2000 Faraday balance using $Hg[Co(CNS)_4]$ (χ_g = 16.44 x 10^{-6}g/cc at 28° C) as the calibrating agent. Molar conductance measurements were carried out on a Leeds Northrup Conductivity Bridge 4995. IR spectra were recorded on a IR-435 Shimadzu infrared spectrophotometer. The electronic spectra of the complexes were recorded on a Hitachi-3000 UV-Visible spectrophotometer. C, H and N analyses were obtained in the Microanalytical Laboratory at University Science Instrumentation Centre, Delhi University. The metal contents of the complexes were determined by previously reported methods.[11] Molecular weights were determined in benzene (freezing point).

RESULTS AND DISCUSSION

On the basis of elemental analysis data (Table I), the general compositions $M(Tptacdte)X_2$ and $Co(Tptacdte)(H_2O)_2SO_4$ have been suggested for the complexes (Tptacdte = 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene; X = Cl, Br, SCN for Ni(II) and X = Cl, NO_3, SCN for Co(II). Molar conductance measurements in nitrobenzene show that the complexes behave as non-electrolytes except for the complex prepared from $CoSO_4$, which behaves as an electrolyte. Thus, the general formulas $[M(Tptacdte)X_2]$ (where M = Ni(II) or Co(II) and $[Co(Tptacdte)(H_2O)_2]\ SO_4$ may be suggested for the complexes.

TABLE I

Elemental Analyses, Colour and Composition of the Complexes

Complex	*Molecular weight found (calculated)*	*% Yield*	*Mp (°C)*	*Colour*	*% Calculated (% found)*			
					M	*C*	*H*	*N*
$[\mathrm{Ni(Tptacdte)Cl_2}]$	599	70	210	Light brown-red	9.82	64.24	4.68	9.36
$\mathrm{NiC_{32}H_{28}N_4Cl_2}$	(598.2)				(9.72)	(64.14)	(4.71)	(9.17)
$[\mathrm{Ni(Tptacdte)Br_2}]$	685	72	218	"	8.55	55.93	4.08	8.16
$\mathrm{NiC_{32}H_{28}N_4Br_2}$	(687.1)				(8.41)	(55.72)	(4.01)	(8.14)
$[\mathrm{Ni(Tptacdte)(SCN)_2}]$	640	60	220	"	9.02	63.48	4.30	13.07
$\mathrm{NiC_{34}H_{28}N_6S_2}$	(643.4)				(8.93)	(63.33)	(4.21)	(13.06)
$[\mathrm{Co(Tptacdte)Cl_2}]$	596	68	216	Green	9.85	64.22	4.66	9.37
$\mathrm{CoC_{32}H_{28}N_4Cl_2}$	(598.4)				(9.74)	(64.63)	(4.35)	(9.28)
$[\mathrm{Co(Tptacdte)(SCN)_2}]$	645	62	221	Black	9.16	63.46	4.35	13.06
$\mathrm{CoC_{34}H_{28}N_6S_2}$	(643.7)				(9.14)	(63.53)	(4.27)	(13.96)
$[\mathrm{Co(Tptacdte)(NO_3)_2}]$	658	70	212	Black	9.05	58.90	4.30	10.61
$\mathrm{CoC_{32}H_{28}N_6O_6}$	(651.5)				(8.97)	(58.97)	(4.21)	(10.60)
$[\mathrm{Co(Tptacdte)(H_2O)_2]SO_4}$	662	75	218	Dull red	8.94	58.28	4.25	8.45
$\mathrm{CoC_{32}H_{32}N_4SO_6}$	(659.6)				(8.82)	(58.43)	(4.09)	(8.39)

The Ni(II) complexes show magnetic moments in the range of 3.1 to 3.25 B.M., while the Co(II) complexes show magnetic moments in the range of 4.6 to 4.9 B.M. at room temperature (Table II). The values are in tune with a high-spin configuration and show the presence of an octahedral environment around the Ni(II) ion and a distorted octahedral environment around the Co(II) ion in the complexes[12]. However, the geometry of the complexes can hardly be decided on the basis of magnetic moments alone. The conclusive proof regarding the geometry of the complexes is supplied by vibrational and electronic spectral data.

TABLE II

Electronic Spectral Data and Magnetic Moments of the Complexes

Complex	μ_{eff} *(B.M).*	*Electronic spectral bands (cm^{-1})*			
[Ni(Tptacdte)(SCN)$_2$]	3.13	8561	13681	28531	40213
[Ni(Tptacdte)Cl$_2$]	3.23	8530	13624	28409	39682
[Ni(Tptacdte)Br$_2$]	3.12	8581	13736	28963	
[Co(Tptacdte)(SCN)$_2$]	4.81	8120	16040	16213	30208
[Co(Tptacdte)Cl$_2$]	4.91	7564 29585	15385	17094	22522
[Co(Tptacdte)(NO$_3$)$_2$]	4.87	8902 31160	1596	17511	18860
[Co(Tptacdte)(H$_2$O)$_2$SO$_4$]	4.69	7560 30128	15315	17114	18860

IR SPECTRA

Ligand. The IR spectrum of the ligand[13a] shows the absence of an absorption at around 3400 cm^{-1} amounting to lack of a free amino group. The absence of a strong band in the vicinity of 1700 cm^{-1} indicates that the free carbonyl group in benzil is no more there and that the condensation of the carbonyl groups has taken place. Phenyl groups show absorptions in the range of 700-780 cm^{-1} and 1400-1600 cm^{-1}. The absorption at ~ 1600 cm^{-1} may be assigned to the azomethine group >C=N-. The fact that this strong band in the complexes has shifted position to the range of 1575-1650 cm^{-1} confirms the coordination of the metal ions with the azomethine group and also makes it clear that the ligand behaves as a tetradentate one.

The absorption bands in the 900-700cm^{-1} region give important information regarding the geometry of the complexes. The bands in this region can be exclusively assigned to the CH$_2$ absorption of the macrocycle and the multiplicity of the bands is dependent on the geometry of

TABLE III

Ligand Field Parameters

Complex	*Dq (cm⁻¹)*	*B (cm⁻¹)*	β	*L.F.S.E. (KJ mole⁻¹)*
$[Ni(Tptacdte)(SCN)_2]$	856	802	0.77	122.67
$[Ni(Tptacdte)Cl_2]$	853	799	0.77	122.24
$[Ni(Tptacdte)Br_2]$	858	804	0.77	122.96
$[Co(Tptacdte)(SCN)_2]$	812	750	0.67	77.58
$[Co(Tptacdte)Cl_2]$	756	698	0.62	72.24
$[Co(Tptacdte)(NO_3)_2]$	890	822	0.74	85.05
$[Co(Tptacdte)(H_2O)_2]SO_4$	756	698	0.62	72.27

these complexes. In these macrocycles the CH_2 absorption shows two bands and this supports the proposed cis geometry of the complexes.

Anions. The IR spectra of the thiocyanato complexes show a number of characteristic peaks. Absorptions at ~ 2060-2080 cm^{-1}, ~ 820-865 cm^{-1} and 470-485 cm^{-1} could be assigned to ν(N=C), ν(C=S) and ν(NCS) (bending) vibrations, respectively. The position of the bands is in favour of monodentate coordination through the atom N of the -SCN group[14]. Halide complexes show a number of bands characteristic of metal-ligand vibrations in the region 200-690 cm^{-1}. In $[Co(Tptacdte)Cl_2]$ the bands in the vicinity of ~300 cm^{-1} could be assigned to ν(Co-Cl) stretches. The appearance of a single band in this region is in tune with a distorted octahedral geometry of the complex[15]. The IR spectrum of the nitrato complex exhibits bands at ~ 1250, 1010 and 860 cm^{-1} which are consistent with the monodentate coordination of this group. The IR spectrum of the complex prepared from $CoSO_4$ shows the presence of ionic sulphate. The broad band at ~1065 cm^{-1} and a weak band at ~700 cm^{-1} characterize the presence of an uncoordinated sulphato group[16]. The presence of coordinated water molecules in complex is indicated by the presence of a band at ~725 cm^{-1}. The band at ~3200 cm^{-1} might be due to the presence of some water of coordination in the complex[16].

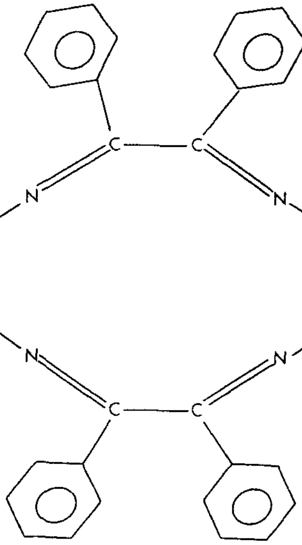
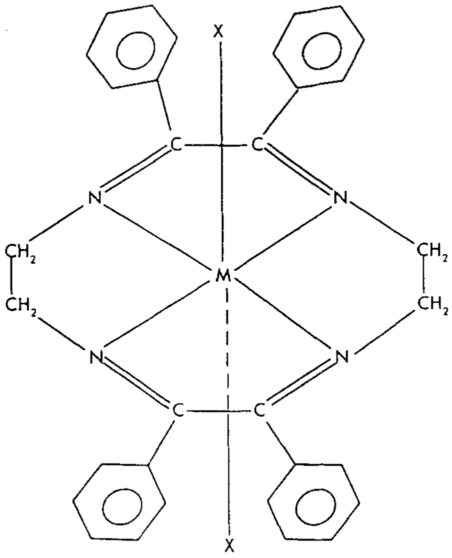


Fig. 1. Structure of the Macrocyclic Ligand Tptacdte

Complexes. In all the compalexes, a strong band appearing at about 1575-1650 cm^{-1} may be assigned to V(C=N) vibration. Various bands appearing at ~430-490 cm^{-1} indicate V(M-N) vibrations. Both of these bands confirm the coordination of the azomethine group of the ligand with the metal ions[17]. Coupled with the monodentate coordination of the anions as has been discussed above, an octahedral configuration may be proposed for these complexes, with the ligand forming a square plane and the anions residing in axial positions.

ELECTRONIC SPECTRA

Ni(II) Complexes. The electronic spectra of the complexes show two bands in the range of 8,500-8,600 cm^{-1} (intensity 3-5 L mol^{-1} cm^{-1}) and 13,600-13,800 cm^{-1} (intensity 5-12 L mol^{-1} cm^{-1}) before the charge transfer sets in (Table II). An examination of these bands indicates that the complexes have octahedral geometries and might possess D_{4h} symmetry.[12,18,19] The ground state of Ni(II) in an octahedral coordination is $^3A_{2g}$. Thus three spin-allowed transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$,$V_1$; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, V_2 ; and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, V_3, should be observed in the electronic spectra of the complexes. Thus, the band at ~8,500-8,600 cm^{-1} is assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and the band at ~13,600-13,800 cm^{-1} is $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, respectively. The third spin-allowed band $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, appears too high at 28500 cm^{-1} and is probably enveloped



M = Co(II) or Ni(II)

X = Cl, Br, NO_3 and SCN

Fig. 2. Structure of the Complexes

into a strong charge transfer. Various ligand field parameters for the complexes have been calculated (Table III). V_1 directly gives the value of 10 Dq. The nephelauxetic parameter β is obtained by using the relation

$$\beta = \frac{B\ (\text{complex})}{B\ (\text{free ion})}$$

where B is the Racah interelectronic repulsion parameter. The value of B for the free ion is 1041 cm^{-1}, hence, β comes out to be 0.77 for the complexes. The β value indicates that the covalent character of the M-ligand 'σ ' bond is low.

Co(II) Complexes. The electronic spectra of the complexes prepared from $CoCl_2$, $CoSO_4$ and $Co(SCN)_2$ show bands in the ranges of 7,550-8,120 cm^{-1} (intensity 3-8 L mol^{-1} cm^{-1}), 17,100-18,200 cm^{-1}, (intensity 8-15 L mol^{-1} cm^{-1}), 20,000-22,500 cm^{-1} (intensity 15-22 L mol^{-1} cm^{-1}) and at ~30,000 cm^{-1} and a shoulder at 15,400 - 16,000 cm^{-1}. The complex prepared from $Co(NO_3)_2$ shows bands at ~8,900, 17,500, 18,800 and 31,000 cm^{-1} (Table II).

An investigation of these electronic spectral data indicates that these complexes possess distorted octahedral geometries and might be having D_{4h} symmetry[12,18,19]. The assignments for spectral bands may be given as $^4A_{2g} \rightarrow {}^4E_g(F)$, $^4A_{2g} \rightarrow {}^4E_g(P)$, $^4A_{2g} \rightarrow {}^4B_{1g}(P)$, $^4A_{2g} \rightarrow {}^4B_{2g}(F)$ transitions respectively. The band at about ~30000 cm^{-1} might have arisen due to intraligand charge transfer. The absence of a band at about 5,000 cm^{-1} in all the complexes may be used to rule out tetrahedral geometry for these complexes.

Various ligand field parameters for the complexes have been calculated (Table III). V_1 directly gives the value of 10 Dq. The nephelauxetic parameter β has been obtained as in the case of the Ni(II) complexes. B(free ion) for Co(II) is 1120 cm^{-1}, the β values indicate appreciable covalent character in these complexes. Various anions in the Co(II) complexes can be arranged in decreasing order of ligand field strength on the basis of Dq values as: NO_3 > SCN > Cl.

On the basis of the above spectral studies the following structure (Fig. 2) may be suggested for the complexes.

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Referee I: C. Cairns
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