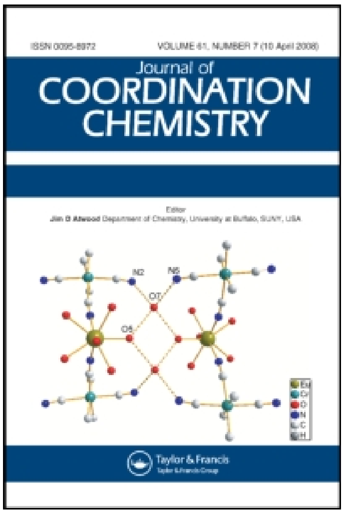

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NICKEL(II) COMPLEXES OF THE TWELVE AND FOURTEEN MEMBERED TETRADENTATE MACROCYCLIC LIGANDS - 2,3,8,9-TETRAPHENYL-1,4,7,10-TETRAAZA-CYCLO-DIDECA-1,3,7,9-TETRAENE AND 2,3,9,10-TETRAPHENYL-1,4,8,11-TETRAAZACYCLO-TETRADECA-1,3,8,10-TETRAENE

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NICKEL(II) COMPLEXES OF THE TWELVE AND FOURTEEN MEMBERED TETRADENTATE MACROCYCLIC LIGANDS – 2,3,8,9-TETRAPHENYL-1,4,7,10-TETRAAZA-CYCLO-DIDECA-1,3,7,9-TETRAENE AND 2,3,9,10-TETRAPHENYL-1,4,8,11-TETRAAZACYCLO-TETRADECA-1,3,8,10-TETRAENE

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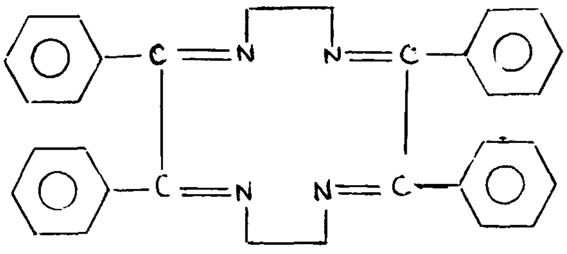
KEY WORDS: Ni(II) complexes – 12 and 14 membered macrocyclic ligands.

A series of nickel(II) complexes of 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclo-di-deca-1,3,7,9-tetraene (I) and 2,3,9,10-tetraphenyl-1,4,8,11-tetraazacyclo-tetradeca-1,3,8,10-tetraene (II) (abbreviated as EBM and TBM) have been synthesized and characterized by magnetic susceptibility and electronic spectral measurements.

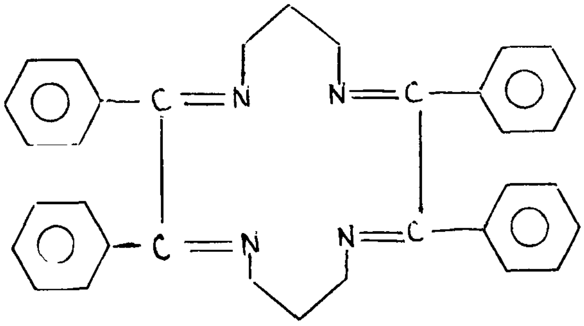
INTRODUCTION

The complexes of metal ions with a variety of synthetic macrocyclic ligands have been extensively investigated in view of the fact that they act as model compounds in certain cases for the various natural systems such as porphyrins and cobalamines. The ligands are also of theoretical interest as they are capable of furnishing an environment of controlled geometry and ligand field strength. The work of Curtis[1] and coworkers produced the first of many new synthetic tetraaza macrocyclic ligands, especially with the hexamethyl tetraazacyclotetradecadiene. These have been followed by cyclam,[2] cyclen,[3] aminobenzaldehyde trimers and tetramers,[4] the bicyclic condensation products of 2,6-diacetylpyridine[5] and various polyamines. Several reviews covering various aspects of the coordination chemistry of metal complexes of macrocyclic ligands have been published.[6–15]

Earlier we reported the copper(II) complexes[16] of EBM which were prepared by the reaction of the synthesized ligand and the copper salts but it failed to form complexes with nickel(II) salt and therefore an attempt was made in synthesizing the nickel(II) complexes of EBM and TBM by a route dependent on *in situ* synthesis of macrocycles-I and II by the condensation of benzil and ethylenediamine and 1,3-diaminopropane respectively in the presence of a suitable nickel(II) salt.



(I)



(II)

EXPERIMENTAL

Physical Measurements

Visible and near infrared spectra were obtained with a Carry model-14 Recording spectrophotometer in alcohol. The electrical resistances of solutions of the complexes were measured using RC 16 B conductivity bridge and a conductance cell with platinum electrodes and a cell constant of 2.116 cm^{-1}. Conductances were measured at 25°C at 1000 cps for approximately 10^{-3} M solutions. The IR spectra of the complexes were recorded on a Perkin–Elmer 621 Grating IR spectrophotometer in KBr pellets.

The magnetic susceptibility measurements were carried out on a Gouy's balance at room temperature (300°K) using $Hg[Co(CNS)_4]$ as the calibrant ($\chi_g = 16.44 \times 10^{-6}$ cgs units).

Analyses

The compounds were analysed for C, H and N in the micro-analytical laboratory, Chemistry Department, University of Birmingham, UK, while the analysis for metal was undertaken by the usual quantitative method for nickel.

Preparation of Nickel(II) Complexes

(i) (2,3,8,9-Tetraphenyl-1,4,7,10-tetraazacyclo-dideca-1,3,7,9-tetraene)Nickel(II) perchlorate To 1 litre of methanol in a 2 litre beaker containing 12 g (0.2 mole) of ethylenediamine was added 19.75 g (0.2 mole) of concentrated hydrochloric acid from a dropping funnel. The solution was cooled to 5°C and 42 g (0.2 mole) of benzil was added to the mixture in an efficient fuming cupboard. The solution was stirred for 30 minutes and then allowed to stand at room temperature. After about half an hour, 24.9 g (0.1 mole) of nickel(II) acetate tetrahydrate was added to the orange solution. The solution darkened to a red–brown colour and after 4 hours of stirring, 19.7 g (0.2 mole) of concentrated hydrochloric acid was added, followed by 13.6 g (0.1 mole) of zinc chloride. The dark brown–red solid form of $[Ni(Ph_4[12]\text{-}1,3,7,9\text{-tetraene}N_4)][ZnCl_4]$ precipitated immediately and was removed by filtration, washed with cold ethanol and diethyl ether, and dried in a vacuum desiccator over P_4O_{10}. The yield was 25 g, $C_{32}N_4H_{28}Cl_4 \cdot ZnNi$ contains C 52.31%, N 7.63%, H 3.81%, Cl 19.34% and Ni 8.90% and was found to have C 52.01%, N 7.42%, H 3.40%, Cl 19.01% and Ni 8.71%.

The tetrachlorozincate salt (7.34 g, 0.01 mole) was dissolved in 60 ml of water and 6.8 g (0.04 mole) of silver nitrate was added. The mixutre was stirred for 30 minutes and was filtered off to remove the precipitated silver chloride. Sodium perchlorate (2.45 g, 0.02 mole) was added to the red–orange filtrate and solution was evaporated to dryness using a rotary evaporator. The solid so obtained was washed with small lots of acetone and cold water. The yellow compound $[Ni(Ph_4[12]\text{-}1,3,7,9\text{-tetraene}N_4)]\ (ClO_4)_2$ so obtained on the funnel was dried in vacuo over P_4O_{10}. Anal. Calcd. for $C_{32}N_4H_{28}Cl_2O_8Ni$: C, 52.91%; N, 7.71%; H 3.86% and Ni 9.01%. Found: C 52.78%; N 7.60%; H 3.52% and Ni 8.46%.

ii) (2,3,8,9-Tetraphenyl-1,4,7,10-Tetraazacyclo-dideca-1,3,7,9-tetraene)Nickel(II) hexafluorophosphate The complex was prepared by the addition of aqueous solution of sodium hexafluorophosphate to the aqueous solution of $[Ni(Ph_4[12]\text{-}1,3,7,9\text{-tetraene}N_4)]\ (NO_3)_2$ obtained in the above procedure after the removal of precipitated silver chloride. Anal. Calcd. for $C_{32}N_4H_{28}P_2Ni$: C, 47.01%; N 6.85%; H 3.43% and Ni 8.00%. Found: C, 46.84%; N 6.71%; H 6.71%; and Ni 7.85%.

iii) Bis(isothiocyanato)(2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclo-dideca-1,3,7,9-tetraene)nickel(II) One hundredth mole (7.25 g) of $[Ni(Ph_4[12]\text{-}1,3,7,9\text{-tetraene}N_4]\ (ClO_4)_2$ was slurried in 100 ml of absolute alcohol and 2 ml of saturated aqueous solution of potassium thiocyanate was added. The solution was refluxed for 30 minutes and the precipitated potassium perchlorate was removed from the cold solution by filtration. The red–violet filtrate was evaporated to dryness on a rotary evaporator and 100 ml of chloroform added to the solid mass. The solution was filtered and diethyl ether was added to precipitate the complex. The red–brown solid was washed with ether and dried in vacuo over P_4O_{10}.

Anal. Calcd. for $Ni(Ph_4[12]\text{-}1,3,7,9\text{-tetraene}N_4)\text{-}(NCS)_2$: Ni 10.17%; C 59.74%; N 8.71%; H 4.3% and S 9.95%.

Found: Ni 9.84%; C 59.48%; N 8.54% and S 9.47%.

The corresponding nickel(II) complexes of TBM were prepared following exactly the same procedure. All the compounds prepared were recrystallised from ethanol. The results of elemental analysis are presented in Table I.

TABLE I
Elemental analysis

Complex	% Ni Calcd. (Found)	% C Calcd. (Found)	% N Calcd. (Found)	% H Calcd. (Found)	% Cl Calcd. (Found)
[Ni(TMB)]ZnCl$_4$	8.55	53.39	7.32	4.18	18.56
	(8.41)	(53.21)	(7.21)	(4.01)	(18.40)
[Ni(TBM)] (PF$_6$)$_2$	7.73	48.30	6.63	3.78	–
	(7.51)	(48.12)	(6.41)	(3.61)	
[Ni(TBM)] (ClO$_4$)$_2$	8.67	54.13	7.42	4.24	–
	(7.98)	(54.07)	(7.38)	(4.10)	
[Ni(TBM)(NCS)$_2$]	9.60	59.93	8.22	4.70	–
	(9.40)	(59.81)	(8.12)	(4.61)	
[Ni(EBM)] ZnCl$_4$	8.90	52.31	7.63	3.81	19.34
	(8.71)	(52.01)	(7.42)	(3.40)	(19.01)
[Ni(EBM)] (PF$_6$)$_2$	8.00	47.01	6.85	3.43	–
	(7.85)	(46.81)	(6.71)	(3.41)	
[Ni(EMB)] (ClO$_4$)	9.01	52.91	7.71	3.86	–
	(8.46)	(52.68)	(7.60)	(3.52)	
[Ni(EBM)(NCS)$_2$]	10.17	59.74	8.71	4.30	–
	(9.84)	(59.48)	(8.54)	(4.20)	

TABLE II
Electronic spectra of planar Nickel(II) complexes.

		Transition, cm^{-1} (log ε) M $\longrightarrow$ L	
Complex	$^1A_{1g} \xrightarrow{\text{d-d}} {}^1B_{1g}$	$^1A_{1g} \longrightarrow {}^1B_{2u}$	$^1A_{1g} \longrightarrow {}^1B_{3u}$
Ni(EBM)ZnCl$_4$	16045(1.90)	21280(3.19)	25000(3.94)
Ni(EBM)(PF$_6$)$_2$	16100(1.89)	21200(3.09)	25040(3.87)
Ni(EBM)(ClO$_4$)$_2$	16090(1.87)	21240(3.16)	25020(3.89)
Ni(TBM)ZnCl$_4$	16080(1.88)	21230(3.18)	24980(3.94)
Ni(TBM)(PF$_6$)$_2$	16130(1.90)	21270(3.16)	24970(3.88)
Ni(TBM(ClO$_4$)$_2$	16060(1.91)	21290(3.15)	24980(3.96)

RESULTS AND DISCUSSION

All the complexes except [Ni(Ph$_4$[12]-1,3,7,9-tetraene N$_4$)(NCS)$_2$] and [Ni(Ph$_4$[14]-1,3,8,10-tetraene-N$_4$)(NCS)$_2$] are diamagnetic and are thus confirmed to be planar. The electronic spectra of these complexes exhibit intense bands assignable to the transitions in planar nickel(II) complexes.[17-22] The position and the assignments of these bands are presented in Table II. However, the complexes [Ni(Ph$_4$[12]-1,3,7,9-tetraeneN$_4$)(NCS)$_2$] and [Ni(Ph$_4$[14]-1,3,8,10-tetraene N$_4$)(NCS)$_2$] are paramagnetic and susceptibility measurements yield the magnetic moments to be 3.20 and 3.30 BM respectively. The molar conductance measurements for these complexes carried out in nitromethane solution confirm them to be nonelectrolyte indicating the participation of the isothiocyanato groups in the coordination sphere and, therefore, unlike the other salts (ClO$_4^-$, PF$_6^-$ and ZnCl$_4^{2-}$) they may be proposed to have octahedral structure where the isothiocyanato groups take the axial position. The infrared spectra of the complexes [Ni(EBM)(NCS)$_2$] and [Ni(TBM)(NCS)$_2$] exhibit strong doublets at 2101, 2114 and 2103, 2116 cm^{-1} respectively corresponding to $\nu_{C\equiv N}$ and another doublet of moderate intensity at 815, 801 and 816, 803 cm^{-1} (ν_{C-S}) which are characterisitcs of N-bonded thiocyanate.[23] Positive identification of the *cis* and *trans* position of the thiocyanato groups in these complexes could not be made on the basis of IR spectrometry due to presence of the various modes of vibrations in the phenyl rings and since the four nitrogen atoms of the macrocycle will take the planar position of the octahedron, the other two axial positions are assumed to be occupied by the thiocyanato groups and so the thiocyanato complexes could be taken as *trans* isomer rather than *cis*, the possibility for which may be ruled out on the ground of the high steric strain in the macrocyclic ring. This gets a support from the study of the electronic spectra of these complexes which show characteristic bands of of nickel(II) octahedral geometry. The visible spectra of the complexes $[Ni(EBM)_2(NCS)_2]$ and $[Ni(TBM)_2(NCS)_2]$ show a group of three bands at 12465, 16758, 23821 and 12805, 16870, 2500 cm^{-1} respectively which are assignable to the $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$, $\nu_2(^3T_{1g} \leftarrow {}^3A_{2g})$ and $\nu_3(^3T_{1g} \leftarrow {}^3A_{2g})$ bands observed in nickel(II) octahedral compounds. 10 Dq has been calculated to be 12465 and 12805 cm^{-1} respectively. High magnitude of DQ speaks of the high strength of ligand fields produced by these cyclic ligands.

The infrared spectra of all these complexes show weak imine $\nu_{C=N}$ in the 1600 cm^{-1}–1500 cm^{-1} region with a very strong sharp band near 1210 cm^{-1} which could be assigned to the N=C—C=N function.

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