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THE SYNTHESIS AND CHARACTERIZATION OF COPPER(II) AND NICKEL(II) COMPLEXES OF NOVEL 16-MEMBERED MACROCYCLIC LIGANDS HAVING VARYING DEGREES OF SATURATION

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Novel tetraaza[16]diene macrocyclic complexes of nickel(II) and copper(II) have been synthesized by the reaction of 4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dione with 1,4-butanediamine in the presence of the corresponding metal ion. The C=N double bonds of the macrocycle have been hydrogenated using NaBH₄ for both the nickel(II) and copper(II) complexes. The preparation and properties of a series of complexes of macrocycles having a varying degree of saturation are described.

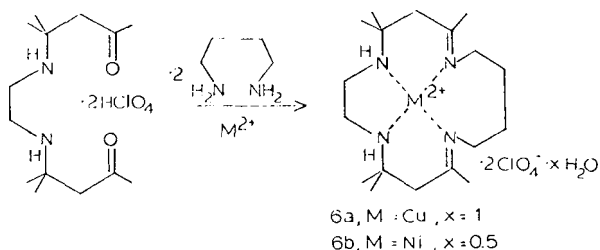
INTRODUCTION

In recent years considerable interest has been shown in the preparation and chemistry of tetraazamacrocyclic ligands and their transition metal complexes.¹⁻³ Most published works have involved 14-membered macrocycles. Recent studies on the effects of seven-membered chelate rings on the structure of transition metal complexes have yielded some interesting results.^{4,5} Two isomeric 18-membered macrocyclic complexes of copper(II), prepared by the reaction of bis(1,4-diaminobutane)-copper(II) perchlorate with acetone⁴ have been shown to have widely differing geometry about the central copper atom.⁵ The complex [Cu(*cis*[18]dieneN₄)](ClO₄)₂, **1**, has a 36.6° distortion from a square-planar coordination geometry whereas the less-strained [Cu(*trans*[18]dieneN₄)](ClO₄)₂, **2**, has essentially square-planar coordination geometry. It was considered desirable to investigate the causes of the pseudo-tetrahedral geometry in the *cis* isomer, **1**. It seemed probable that the steric interactions caused by the presence of the four carbon chain between the imino nitrogen donors in this complex was the primary cause of the tetrahedral distortion about the copper(II). We have therefore prepared a number of macrocyclic complexes which incorporate a four carbon chain between imino donors, and have

characterized some of these by X-ray determination of molecular structure.^{6,7} In the complexes **3** and **4** the macrocyclic ligands are coordinated in a non-planar fashion but the geometry about the copper(II) ion in each case is five-coordinate with a water molecule as the fifth donor.^{6,7} The X-ray crystal and molecular structure of dibenzo[*c, i*]-1;5,8,12-tetraazacyclohexadec-1,11-dienato(2)-copper(II), **5**, shows the geometry about the central Cu(II) ion to be distorted by 20° from regular square-planar geometry.⁸ This distortion is intermediate between that observed in the complexes **1** and **2**.

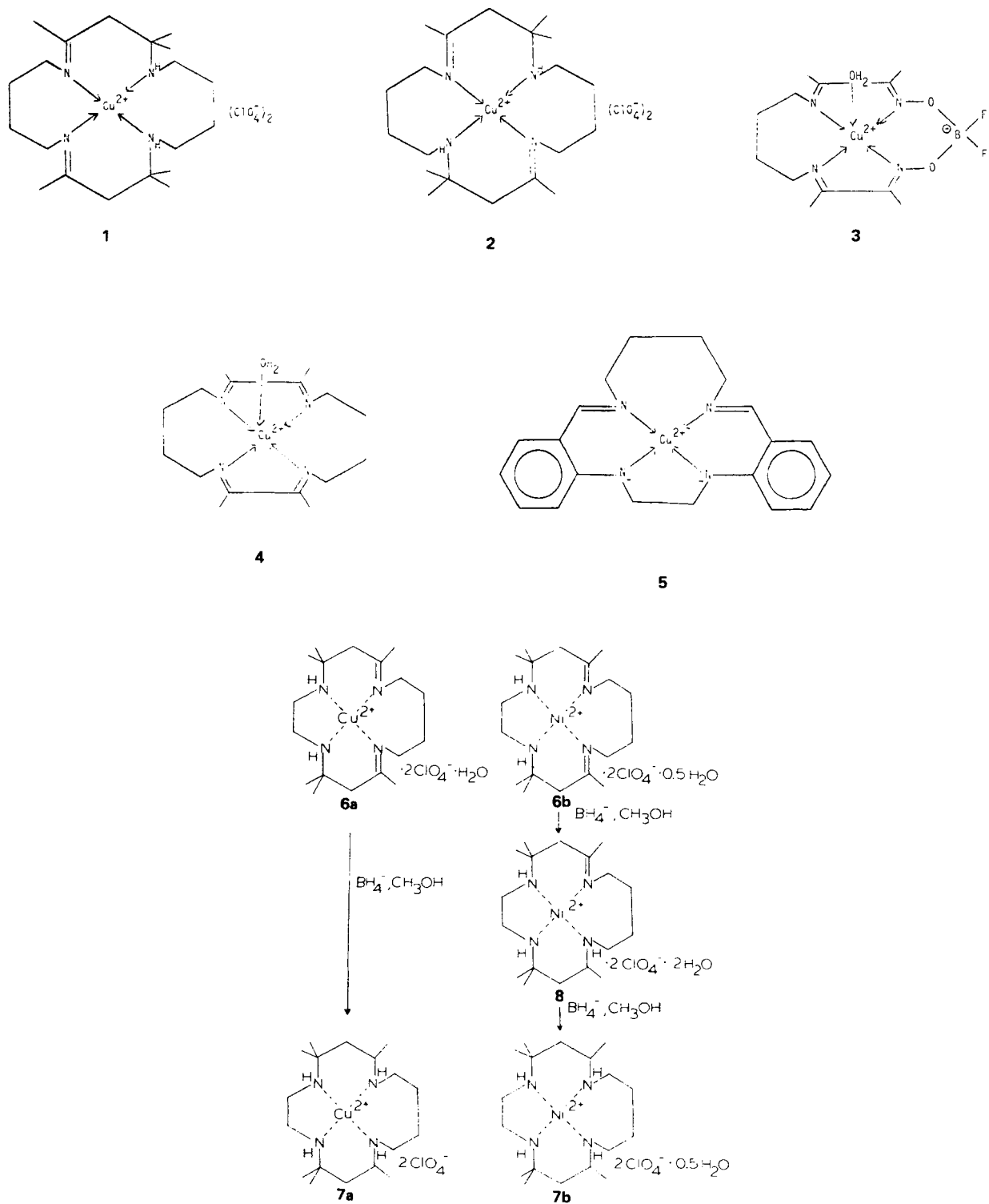
In this paper we report the synthesis of a novel 16-membered macrocycle by reaction of 1,4-butanediamine with 4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dionedihydroperchlorate⁹ in the presence of copper(II) and nickel(II) (Scheme 1) to yield complexes **6a** and **6b** respectively.

The hydrogenation of the coordinated C=N



SCHEME 1 Preparation of the tetraaza[16]diene macrocyclic complexes.

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SCHEME 2 Preparation of a series of 16-membered tetraazamacrocyclic complexes having varying degrees of saturation

double bonds of the complex **6a** yielded the complex **7a**, while the stepwise hydrogenation of the corresponding bonds in the nickel(II) complex **6b** yielded **7b** via the complex **8** (Scheme 2). The X-ray crystal structure of complex **7a** was attempted to help ascertain the effects of a four carbon chain between secondary amino donors on the expected square-planar geometry about copper(II).

EXPERIMENTAL

The compounds employed were all of reagent grade and were used without further purification.

4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dionedihydroperchlorate·2(HClO₄), **9**. This compound may be prepared by the method of Powell and Love.⁹ A more convenient method (details to be published by Curtis)¹⁰ was used in this work. This improved method involves the reaction of acetone with ethylenediamine dihydroperchlorate in the presence of a catalytic quantity of base. **CARE MUST BE TAKEN IN HANDLING AMINE HYDROPERCHLORATES!**

4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dionedihydrotetrafluoroborate·2(HBF₄), **9**. The preparation of this salt of the Powell² diketone is based upon the modification by Curtis.¹⁰ The replacement of the perchloric acid by tetrafluoroboric acid in this preparation gives a similar yield of product, and avoids the dangers inherent in the use of perchlorates.

Copper Complexes

2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclohexadeca-1,11-diene)copper(II) perchlorate, monohydrate, **6a** [Cu(cis[16]dieneN₄)](ClO₄)₂·H₂O. In a typical reaction 3.0 g (6.6 mmol) of the diketone **9** 2(HClO₄) was suspended in 50 ml of methanol and to this was added 2.8 g (6.5 mmol) of bis(1,4-butanediamine)copper(II)perchlorate. The mixture was heated for 1/2 hr and the resulting blue solution was filtered and allowed to stand overnight. Water (10 ml) and sodium perchlorate (2.0 g) were added and the product crystallized after ca. 3 days of reaction at room temperature. Yields of up to 50% were obtained. The blue-purple product was recrystallized from methanol/water.

(2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclohexadecanecopper(II)perchlorate, **7a**, [Cu(cis[16]aneN₄)](ClO₄)₂. A ten-fold molar excess of sodium tetrahydroborate was added to a methanolic solution

of the diene complex, **6a**. After the effervescence of gas (1 hr) a small amount of brown solid was removed by filtration and water was added to the filtrate. The resultant solution was boiled with activated charcoal and the product was crystallized from the filtrate upon addition of a little sodium perchlorate. The red product was recrystallized twice from water.

Nickel Complexes

(2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclohexadeca-1,11-diene)nickel(II)perchlorate hemihydrate, **6b**, [Ni(cis[16]dieneN₄)](ClO₄)₂·1/2H₂O. This complex was formed in low yield (often as low as 20%) by the slow addition of a 2 molar proportion of 1,4-butanediamine in methanol to a stirred mixture of the diketone **9**, 2(HClO₄), and nickel perchlorate hexahydrate in methanol at 40°C. The resulting mixture was filtered, and the filtrate boiled for 5 minutes with activated charcoal and the orange-yellow product was isolated following evaporation. The product was recrystallized from methanol/water.

(2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclohexadeca-1-ene)nickel(II)perchlorate dihydrate, **8**, [Ni(cis[16]eneN₄)](ClO₄)₂·2H₂O. To a methanolic solution of the diene complex **6b** was added a 4 molar proportion of sodium tetrahydroborate. After 3 hr of reaction the solution was filtered and 5 ml of a saturated aqueous solution of sodium perchlorate was added. Yellow crystals of the product separated on evaporation. The product was twice crystallized, unchanged, from water/methanol solvent.

(2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclohexadecane)nickel(II)perchlorate hemihydrate, **7b**, [Ni(cis[16]aneN₄)](ClO₄)₂·1/2H₂O. The yellow complex was prepared by reaction of a 5 molar proportion of sodium tetrahydroborate with the complex **8** in methanol. Following filtration and the addition of a little sodium perchlorate, the product crystallized upon standing. The golden yellow product was recrystallized from hot water.

Infrared Spectra

All the compounds reported show a strong broad absorption near 1050 cm⁻¹ attributed to ν(Cl—O) of the free ClO₄⁻ ion. The most significant bands are those attributed to the ν(C=N) stretch of the coordinated imino groups and the ν(N—H) stretch of the coordinated secondary amino groupings. The frequencies of these absorption bands are shown in Table I. The IR spectrum of the diketone **9**,

TABLE I
Infrared frequencies for the 16-membered macrocyclic complexes^a

Compound	$\nu(\text{C}=\text{N}) \text{ cm}^{-1}$	
[Cu(<i>cis</i> [16]dieneN ₄)](ClO ₄) ₂ ·H ₂ O	1642(s)	3214(s)
[Cu(<i>cis</i> [16]aneN ₄)](ClO ₄) ₂	—	3216(s), 3265(m)
[Ni(<i>cis</i> [16]dieneN ₄)](ClO ₄) ₂ ·1/2H ₂ O	1640(m)	3172(s)
[Ni(<i>cis</i> [16]eneN ₄)](ClO ₄) ₂ ·H ₂ O	1636(m)	3247(s)
[Ni(<i>cis</i> [16]aneN ₄)](ClO ₄) ₂ ·1/2H ₂ O	—	3202(s), 3266(m)

^aSpectra all from Nujol mulls.

2(HClO₄), is in agreement with the data of Love and Powell.⁹ The hydrated salts show $\nu(\text{O}-\text{H})$ doublets in the 3400–3550 cm⁻¹ region of the spectrum.

Electronic Spectra

The electronic spectrum of the [Cu(*cis*[16]dieneN₄)](ClO₄)₂·H₂O, **6a**, complex in methanol shows a d–d absorption band at somewhat higher energy than for the [Cu(*cis*[18]dieneN₄)](ClO₄)₂ complex, which has a pseudo-tetrahedral geometry⁵ ($\lambda_{\text{max}} = 555$ and 578 nm, respectively). This d–d band is less intense than that observed in the 18-membered macrocycle complex. ($\epsilon = 225$ and 451 M⁻¹ cm⁻¹, respectively for the two compounds.)

The (d–d) spectra of the nickel(II) complexes are typical of square-planar NiN₄ chromophores,¹ with d–d band maxima at 452 nm ($\epsilon = 190$), 460 nm ($\epsilon = 252$) and 465 nm ($\epsilon = 143$) respectively for the complexes **6b**, **8**, and **7b**. The d–d band maximum for complex **6b** is at lower energy than observed for most of the previously studied square-planar nickel(II) complexes of tetraazamacrocyclic ligands.¹

Magnetic Moments

The nickel(II) complexes are all diamagnetic as expected for square planar, singlet ground state complexes. The copper(II) complexes **6a** and **7a**

have magnetic moments in the range expected for high spin copper(II) with a value of $\mu_{\text{eff}} = 1.95$ B.M. for **6a** and a value of $\mu_{\text{eff}} = 1.86$ B.M. for **7a**, measured at 298°K.

RESULTS AND DISCUSSION

Synthesis of the Complexes

Analytical data (Table II) indicate that the expected stoichiometries have been achieved for these novel macrocyclic complexes. The hydrogenation of the C–N double bonds of the macrocycle coordinated to copper(II) is the first reported for a macrocycle bound to that metal, although numerous examples of the analogous reaction using nickel(II) complexes have been reported.^{1–3} Hydrogenation of the C–N double bonds in a series of non-cyclic Schiff base copper(II) complexes has recently been reported by Martin and Willis,¹¹ and by Loeb et al.¹² who used LiAlH₄ as the reducing agent.

Configuration of the Macrocycles

Although the hydrogenation of the coordinated imino groups in the complexes **6a** and **6b** gives rise to centers of asymmetry,^{1–3} no separation of isomers has been achieved. Repeated recrystallization

TABLE II
Analytical data for the 16-membered macrocyclic complexes

Compound	%C		%H		%N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Cu(<i>cis</i> [16]dieneN ₄)](ClO ₄) ₂ ·H ₂ O, 6a	36.7	36.8	6.50	6.29	9.51	9.48
[Cu(<i>cis</i> [16]aneN ₄)](ClO ₄) ₂ , 7a	37.6	37.6	7.01	6.85	9.85	9.62
[Ni(<i>cis</i> [16]dieneN ₄)](ClO ₄) ₂ ·1/2H ₂ O, 6b	37.6	37.8	6.48	6.19	9.74	9.53
[Ni(<i>cis</i> [16]eneN ₄)](ClO ₄) ₂ ·2H ₂ O, 8	35.8	35.4	7.00	6.97	9.27	8.98
[Ni(<i>cis</i> [16]aneN ₄)](ClO ₄) ₂ ·1/2H ₂ O, 7b	37.3	37.1	7.14	7.02	9.68	9.52
9 , 2(HBF ₄)	38.9	38.4	6.49	6.65	7.00	6.67

of **7a** and **7b** from water or methanol gave only one product. None of the nickel(II) complexes **6b**, **7b**, or **8** form triplet ground state oxalato complexes in the presence of oxalate ions. This indicates that the three macrocyclic ligands are incapable of folding,¹ probably because of steric crowding.

Structural Attempt

An attempt to refine the X-ray structure of well-formed crystals of $[\text{Cu}(\text{cis}[16]\text{aneN}_4)](\text{ClO}_4)_2$, **7a**, grown from aqueous solution by slow evaporation was unsatisfactory. An essentially square-planar geometry about the copper(II) ion was indicated from a refinement to $R = 0.19$. Work is presently in progress on X-ray crystal structural determination for a different salt of the complex cation, $[\text{Cu}(\text{cis}[16]\text{aneN}_4)]^{2+}$, in an attempt to avoid the refinement problems inherent in the diperchlorate salt.

Geometrical Effects

The copper(II) complex **7a** of the saturated tetraaza macrocyclic ligand, has a visible (d-d) spectrum very similar to that of the essentially square-planar⁵ complex **2**. This geometry will hopefully be confirmed by future crystallographic data. The complex **6a** is probably five-coordinate with an axial coordinated water molecule, although a distorted four-coordinate structure similar to that of **1** cannot be ruled out at this stage.

Work is continuing on the further characterization of these interesting new compounds. The chemistry of the saturated tetraazamacrocyclic in complexes **7a**

and **7b** should be of particular interest when compared to that of the analogous 14-membered tetraazamacrocyclic ligands which have been studied in detail by a number of workers.¹⁻³

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