Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843,
and The University of Western Ontario, London, Ontario, Canada

Synthesis and Characterization of Copper(II) and Nickel(II) Complexes of Novel 18-Membered Tetraaza Macrocyclic Ligands

JOHN W. L. MARTIN, JAMES H. TIMMONS,[1] ARTHUR E. MARTELL,* and CHRISTOPHER J. WILLIS

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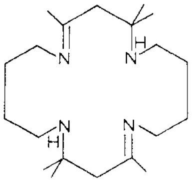
The condensation of acetone with bis(1,4-diaminobutane)copper(II) perchlorate has been shown to produce complexes of two isomeric 18-membered macrocyclic ligands [5*S*(*R*),10*R*(*S*)]-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene and [5*R*(*S*),14*R*(*S*)]-2,4,4,11,13,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene. With nickel as the template a single product, involving an 18-membered macrocyclic ligand which has trans imino moieties, was obtained. The trans macrocycle has also been prepared via the reaction of acetone with 1,4-butanediamine hydroperchlorate. Interconversion between two isomeric nickel(II) macrocycle thiocyanate complexes is discussed. Synthesis, characterization, and the physical and chemical properties of a number of complexes of these novel macrocycles are described.

Introduction

Considerable attention has been given to the characterization of macrocyclic complexes prepared by the condensation of ketones such as acetone with transition-metal complexes of di-, tri-, or tetraamines.[2-4] These complexes have been used as model systems for such biologically important materials as porphyrins and corrins. Geometrical and configurational isomerism in these systems has been studied in depth for a number of 14-membered macrocylic complexes.[5,6] Curtis reported the geometrical isomers [Cu(*trans*-[14]dieneN_4)]$(ClO_4)_2$ and [Cu(*cis*-[14]dieneN_4)]$(ClO_4)_2$ as products of the reaction of acetone with bis(diaminoethane)copper(II) perchlorate and a small excess of diaminoethane.[5] The nickel(II) analogues have been characterized by X-ray crystal structures of their perchlorate salts.[7-9] The effect of varying the macrocyclic ring size has also received some attention, and analogous 15-[2,10] and 16-membered[4,11] tetraaza macrocyclic complexes have been reported. The properties of these complexes are not remarkably different from those of the 14-membered systems, except that they are more susceptible to acid hydrolysis.

Although a majority of the tetraaza macrocyclic ligands described in the literature have been synthesized with a metal ion template, a number of them have also been prepared via nontemplate synthetic routes.[2] Tetraaza macrocycles have been prepared by the reaction of ketones[2,12] or α,β-unsaturated carbonyl compounds[2,13,14] with the mono(hydroperchlorate) salts of ethylenediamine[2,13,14] or 1,2-diaminopropane.[15] These reactions have all yielded macrocycles having trans imino groups. The macrocycles are considered to be formed via the condensation of two diamino-β-amino ketone molecules.[2]

In the present paper the synthesis and properties of a number of copper(II) and nickel(II) complexes of the 18-membered macrocycles, *trans*-[18]dieneN_4, **1**, and *cis*-[18]dieneN_4, **2**, are reported. The X-ray crystal structures of the copper(II) complexes of these ligands [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$ and [Cu(*cis*-[18]dieneN_4)]$(ClO_4)_2$, described elsewhere,[16] show a large tetrahedral distortion (dihedral angle 36.6°) for the cis complex and a close to square-planar geometry about the Cu(II) but with a 10° twist for the trans complex. The nontemplate synthesis of the dihydroperchlorate of (*trans*-[18]dieneN_4) is also described.



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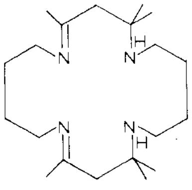

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Experimental Section

General Information. All chemical reagents were obtained commercially and were of high purity. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer, and UV-visible spectra on Cary 14, Cary 118, and Cary 219 spectrophotometers. Magnetic moments were determined by the Gouy and Faraday methods, with $HgCo(NCS)_4$ as standard. Microanalyses were carried out by Malissa-Reuter Laboratories and by the Center for Trace Characterization, Texas A&M University.

Preparation of Macrocyclic Ligand 2,4,4,11,13,13-Hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene Bis(hydroperchlorate), H_2(*trans*-[18]dieneN_4)$(ClO_4)_2$. In a typical reaction 11.65 mL of 70% $HClO_4$ (0.134 mol), diluted to 25 mL with water, was added dropwise with stirring to 11.8 g (0.134 mol) of 1,4-diaminobutane in 25 mL of water. The resultant solution was evaporated (rotary evaporation) until an oil remained (*Caution*!). To the chilled oil was added 50 mL of 2-propanol followed by 250 mL of dry acetone, and the resultant solution was placed in a sealed flask at 10 °C for ca. 3 days. Colorless crystals of product were filtered off and washed with cold acetone. The filtrate was then cooled at 10 °C for 2 days, and an additional yield of product was isolated. The product was dried at 35 °C under vacuum. This material was used in subsequent synthetic work in freshly prepared form, as it was found to deteriorate to a brown tar over a period of ca. 4 days in the presence of atmospheric moisture and more slowly under an atmosphere of dry nitrogen (yield 35 g, 95%). The trans structure has been assigned on the basis of the crystal structure of the complex [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$, which can be formed from H_2(*trans*-[18]dieneN_4)$(ClO_4)_2$. An NMR spectrum of the product was not obtained because it decomposed in solution.

The structure **3** may also be proposed for the product of this

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* To whom correspondence should be addressed at Texas A&M University.

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(2) Curtis, N. F. Coord. *Chem. Rev.* **1968**, *3*, 3. Busch, D. H. *Helv. Chim. Acta* **1967**, 174.

(3) Martin, J. W. L.; Johnston, J. H.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1978**, 68.

(4) Cook, D. F.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1076.

(5) Curtis, N. F.; Curtis, Y. M.; Powell, H. K. J. *J. Chem. Soc. A* **1966**, 1015.

(6) Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *9*, 703.

(7) Bailey, M. F.; Maxwell, I. E. *Chem. Commun.* **1966**, 908.

(8) Kilbourn, B. T.; Ryan, R. R.; Dunitz, J. D. *J. Chem. Soc. A* **1969**, 2407.

(9) Bailey, M. F.; Maxwell, I. E. *J. Chem. Soc., Dalton Trans.* **1972**, 938.

(10) Love, J. L.; Powell, H. K. J. *Chem. Commun.* **1968**, 39.

(11) House, D. A.; Curtis, N. F. *J. Am. Chem. Soc.* **1964**, *86*, 223.

(12) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1357.

(13) Kolinski, R. A.; Korybut-Daskiewicz, B. *Bull. Acad. Pol. Sci., Ser. Sci. Biol.* **1969**, *17*, 13.

(14) Hay, R. W.; Jeragh, B. *J. Chem. Soc., Dalton Trans.* **1977**, 1261.

(15) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1973**, 863.

(16) Timmons, J. H.; Rudolf, P.; Martell, A. E.; Martin, J. W. L.; Clearfield, A. *Inorg. Chem.*, following paper in this issue. Martin, J. W. L.; Timmons, J. H.; Rudolf, P.; Clearfield, A; Martell, A. E.; Willis, C. J. *J. Chem. Soc., Chem. Commun.* **1979**, 999.

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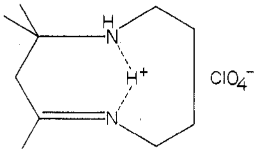

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reaction. In the presence of a small amount of water **3** could ring open, and then the "open" form of it could recombine via a metal template reaction to give the corresponding trans macrocyclic complex. This mechanism might explain the slow reaction of the ligand with nickel(II) acetate.

Anal. Calcd for H_2(*trans*-[18]dieneN_4)$(ClO_4)_2$, $C_{20}H_{42}Cl_2N_4O_8$: C, 44.7; H, 7.90; N, 10.4. Found: C, 44.5; H, 7.64; N, 10.6.

Preparation of Copper(II) Complexes. **{[5*S*(*R*),10*R*(*S*)]-2,4,4,11,11,13-Hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene}copper(II) Diperchlorate, [Cu(*cis*-[18]dieneN_4)]$(ClO_4)_2$, and {[5*R*(*S*),14*R*(*S*)]-2,4,4,11,13,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene}copper(II) Diperchlorate, [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$.** Blue crystals of bis(1,4-butanediamine)copper(II) diperchlorate ethanolate were prepared by the addition of copper(II) perchlorate hexahydrate in hot ethanol to a stirred solution containing a 2:1 molar proportion of 1,4-butanediamine in ethanol. The crystalline material was filtered, washed with cold absolute ethanol to remove excess diamine, and air-dried. *Caution! Although these complexes have not been found to be shock sensitive, perchlorates of this type may detonate if heated above 100 °C. Preparative reactions should be limited to small quantities to minimize risk.* In a typical reaction 15 g of bis(1,4-butanediamine)copper(II) diperchlorate was placed in a flask, a large excess of acetone was added (500 mL) and the vessel was tightly stoppered and placed in a refrigerator. After 3–6 days of reaction a mixture of red-orange crystals and small purple crystals was obtained. The relative yields of the two products differed considerably in successive reactions but the red-orange material [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2 \cdot CH_3COCH_3$ always formed in higher yield. The reaction proceeded more rapidly at 30 °C, and after ca. 12 h a low yield of almost pure trans isomer was filtered, washed with cold acetone and recrystallized from acetone as [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2 \cdot CH_3COCH_3$.

Anal. Calcd for [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2 \cdot CH_3COCH_3$, $C_{23}H_{46}Cl_2CuN_4O_9$: C, 42.0; H, 7.06; N, 8.52. Found: C, 42.0; H, 6.75; N, 8.56.

The filtrate was returned to the reaction vessel which was again stoppered. A further yield of the mixed cis and trans isomers was obtained after 3 days of reaction at 30 °C, but considerable tarry byproduct was also present. The purple cis isomer was separated from the isomeric mixture by extraction with methylene chloride, in which the red trans isomer is nearly insoluble. The pure cis complex was then obtained as purple crystals by evaporation and subsequent recrystallization from methanol.

Anal. Calcd for [Cu(*cis*-[18]dieneN_4)]$(ClO_4)_2$, $C_{20}H_{40}Cl_2CuN_4O_8$: C, 40.1; H, 6.73; N, 9.35. Found: C, 40.6; H, 6.51; N, 9.35.

The trans isomer was isolated as a red dihydrate from water, as an orange-red acetonate from acetone, and as a red nonsolvated product from methanol.

Anal. Calcd for [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2 \cdot 2H_2O$, $C_{20}H_{44}Cl_2CuN_4O_{10}$: C, 37.8; H, 6.98; N, 8.82. Found: C, 37.6; H, 6.73; N, 8.82. Calcd for [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$, $C_{20}H_{40}Cl_2CuN_4O_8$: C, 40.1; H, 6.73; N, 9.35. Found: C, 40.0; H, 6.58; N, 9.22.

(2,4,4,11,11,13-Hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene)copper(II) Perchlorate, [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$. A 0.98 molar proportion of copper(II) acetate tetrahydrate in dry methanol was added to a suspension of H_2(*trans*-[18]dieneN_4)$(ClO_4)_2$ in dry methanol. The mixture was then stirred until the reactants had dissolved and the solution was filtered. A little absolute ethanol was added, and the solution was refrigerated overnight. Red needlelike crystals of [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$ were filtered off and recrystallized from dry methanol.

Preparation of Nickel(II) Complexes. When a methanolic solution of nickel(II) perchlorate hexahydrate was added to a stirred solution containing a 3:1 molar ratio of 1,4-butanediamine in methanol, a flocculent blue-green precipitate formed. This precipitate was filtered, washed with methanol, and air-dried. The solid (10 g) was warmed with 300 mL of acetone in a flask which was then stoppered and placed in the refrigerator. After 3 days of refrigeration, the reaction mixture was filtered and the yellow solution was again refrigerated in a tightly stoppered reaction vessel. After further reaction for 1–2 weeks, yellow needles of [Ni([18]dieneN_4)]$(ClO_4)_2(CH_3COCH_3)$ separated in low yield. Pure [Ni([18]dieneN_4)]$(ClO_4)_2$ was prepared by recrystallization from methanol or water.

Table I. Visible (d–d) Spectra (nm)

compd	λ_{max} (ϵ)	solvent or method
[Cu(*trans*-[18]dieneN_4)]-$(ClO_4)_2$	488 (104)	acetone
[Cu(*trans*-[18]dieneN_4)]-$(ClO_4)_2$	482	reflectance
[Cu(*cis*-[18]dieneN_4)]-$(ClO_4)_2$	582 (br)	reflectance
[Cu(*cis*-[18]dieneN_4)]-$(ClO_4)_2$	578 (451), charge transfer	dichloromethane
[Ni([18]dieneN_4)]$(ClO_4)_2$	470 (56)	acetone
[Ni([18]dieneN_4)]$(ClO_4)_2$	465	reflectance
[Ni([18]dieneN_4)]$(NCS)_2$	473 (60)	water
[Ni([18]dieneN_4)$(NCS)_2$]	365 (17), 585 (8), 788 (3)	chloroform

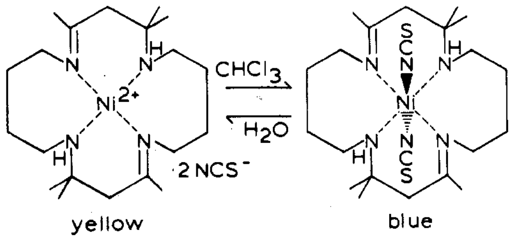
Anal. Calcd for [Ni([18]dieneN_4)]$(ClO_4)_2$, $C_{20}H_{40}Cl_2N_4NiO_8$: C, 40.4; H, 6.79; N, 9.42. Found: C, 40.7; H, 7.01; N, 9.74.

The [Ni([18]dieneN_4)]$(ClO_4)_2 \cdot (CH_3)_2CO$ adduct was also prepared in low yield from the reaction of a large excess of H_2(*trans*-[18]dieneN_4)$(ClO_4)_2$ suspended in methanol and nickel(II) acetate in methanol–pyridine. Yellow needles separated after ca. 1 week of reaction at 10 °C.

The yellow complex [Ni([18]dieneN_4)]$(NCS)_2$, **4**, was prepared by addition of sodium thiocyanate to an aqueous solution of [Ni([18]dieneN_4)]$(ClO_4)_2$. This complex was also prepared by reaction of nickel(II) thiocyanate with a 3:1 molar ratio of 1,4-butanediamine in ethanol to obtain a blue solid which was then reacted with acetone at room temperature for ca. 1 week. The product from the acetone condensation reaction was recrystallized from water to yield [Ni([18]dieneN_4)]$(NCS)_2$.

Anal. Calcd for [Ni([18]dieneN_4)]$(NCS)_2$, $C_{22}H_{40}N_6NiS_2$: C, 51.7; H, 7.88; N, 16.4. Found: C, 51.6; H, 7.82; N, 16.4.

When [Ni([18]dieneN_4)]$(NCS)_2$ was stirred overnight in chloroform, a blue solution was obtained, along with some undissolved yellow solid. Blue-purple crystals of [Ni([18]dieneN_4)$(NCS)_2$], **5**, were isolated from a mixture of the filtered solution and petroleum ether upon chilling. This purple isomer reverted to the yellow form in polar solvents (e.g., methanol or water) and more slowly in the presence of atmospheric moisture.



4 **5**

Anal. Calcd for [Ni([18]dieneN_4)$(NCS)_2$], $C_{22}H_{40}N_6NiS_2$: C, 51.7; H, 7.88; N, 16.4. Found: C, 51.2; H, 7.60; N, 16.1.

Results and Discussion

The condensation of acetone with 1,4-butanediamine in the presence of copper(II) yields two isomeric macrocyclic complex cations, $[Cu(\textit{cis}\text{-}[18]dieneN_4)]^{2+}$ and $[Cu(\textit{trans}\text{-}[18]dieneN_4)]^{2+}$. However when nickel is the template, only one product is obtained (Figure 1). Complexes of these novel macrocycles have been characterized by the use of elemental analyses, infrared spectra, magnetic moments, and UV-visible solution and reflectance spectra. Structures of the Cu(II) complexes have been confirmed by X-ray crystallography.[16]

Copper(II) Complexes. The purple [Cu(*cis*-[18]dieneN_4)]$(ClO_4)_2$ and red [Cu(*trans*-[18]dieneN_4)]$(ClO_4)_2$ complexes are both paramagnetic with magnetic moments

Table II. Infrared Spectra (cm^{-1}, Nujol Mulls)[a]

compd	ν(C=N)	ν(N–H)	other
[Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$	1643 s, sp	3222 s, sp	
[Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$·2H$_2$O	1644 s, sp	3183 s, sp	ν(O–H) 3565 s; 3496 s
[Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$·CH$_3$COCH$_3$	1644 s, sp	3211 s, sp	ν(C=O) 1708 s, sp
[Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$	1641 s, sp	3214 s, sp; 3254 s, sp	
[Ni([18]dieneN$_4$)](ClO$_4$)$_2$	1641 s, sp	3208 s, sp	
[Ni([18]dieneN$_4$)](NCS)$_2$	1639 s, sp	3080 s, sp	ν(C≡N) 2048 vs, sp; ν(C–S) 760 m
[Ni([18]dieneN$_4$)(NCS)$_2$]	1659 s, sp	3279 s, sp	ν(C≡N) 2079 vs, sp; ν(C–S) 790 m
$\overline{H}_2$(*trans*-[18]dieneN$_4$)(ClO$_4$)$_2$	1662 s, sp		ν(NH$_2^+$) 3190 s; δ(NH$_2^+$) 1536 m, br

[a] Abbreviations: s, strong; m, medium; sp, sharp; br, broad.

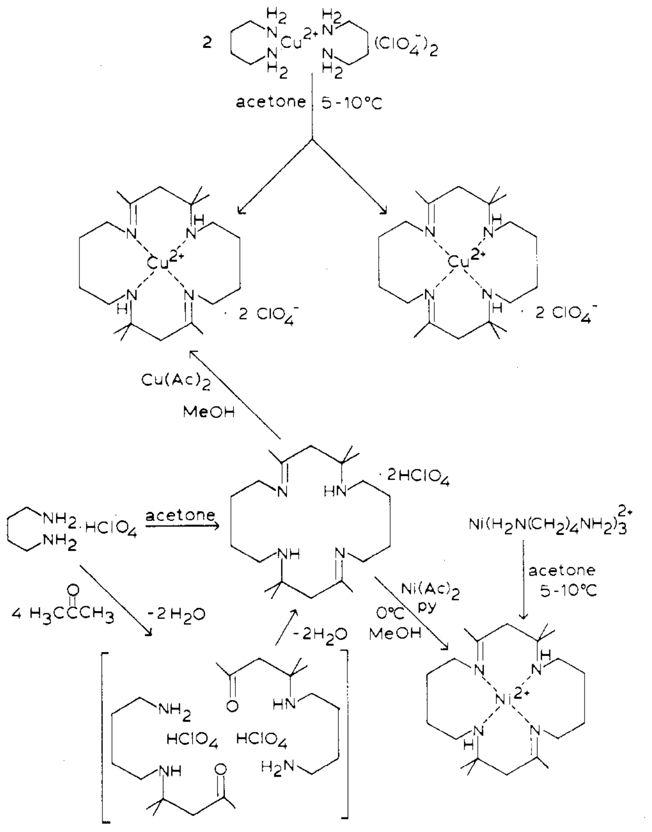


Figure 1. Synthesis and reactions of the 18-membered macrocycles derived from 1,4-butanediamine and acetone.

(1.87 and 2.10 μ_B, respectively, at 300 K) within the normal range for Cu(II) complexes lacking metal–metal interactions.[17] The large difference in the visible (d–d) metal ion spectra (Table I) of these complexes is attributed to a change in coordination geometry from a distorted tetrahedron for the cis isomer to a nearly square-planar arrangement for the trans isomer.[16] The d–d spectrum of the trans isomer in methanol or acetone is very similar to that observed for [Cu(*trans*-[14]dieneN$_4$)](ClO$_4$)$_2$ in acetone.[2,18] The nearly square-planar geometry in [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$ also is in good agreement with the square-planar structure implied for the "orange" modification of [Cu(*trans*-[14]dieneN$_4$)](ClO$_4$)$_2$ which is isostructural with square-planar [Ni(*ms-trans*-[14]dieneN$_4$)](ClO$_4$)$_2$.[19]

The purple [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$ complex has an intense band at 578 nm (ϵ = 451) in 1,2-dichloromethane solution, corresponding to an absorption at 582 nm in the reflectance spectrum. It is interesting to note that a characteristically intense electronic absorption band ($\epsilon \approx$ 1300–5000) is observed at about 600 nm for the "blue" copper proteins[20] and that some authors recently have suggested a pseudotetrahedral geometry[20,23] for the copper site in these proteins. A crystal structure determination has confirmed the presence of distorted tetrahedral geometry in the blue copper protein plastocyanin.[21] In addition to the d–d visible absorption bands the complexes exhibit an intense UV absorption band at 300 nm (for example, 301 nm (ϵ = 6030) for [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$ in 1,2-dichloroethane). This absorption is attributed to a charge-transfer transition.[24]

Nickel(II) Complexes. Both [Ni([18]dieneN$_4$)](ClO$_4$)$_2$ and [Ni([18]dieneN$_4$)](NCS)$_2$ are yellow and diamagnetic with d–d electronic spectra (Table I) typical of square-planar NiN$_4$ chromophores.[2,25,26] The IR spectra of these complexes have a singlet at 3208 and 3090 cm^{-1}, respectively, which is assigned to the N–H stretch of coordinated secondary amino groups. A singlet in this region is observed also in [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$ and its various solvates whereas a doublet is observed in the IR spectrum of [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$. This fact, along with the observation that the copper(II) complexes of the trans rather than the cis isomer of the macrocycle adopt close to square-planar geometry, suggests that the trans macrocycle is present in the nickel complexes. The extinction coefficients of the Ni(II) complexes are indicative of regular coordination geometry, further supporting this suggestion. We thus assign the structures [Ni(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$ and [Ni(*trans*-[18]dieneN$_4$)](NCS)$_2$ to the two yellow nickel(II) complexes, although the cis isomeric forms cannot be completely ruled out for these compounds.

Yellow [Ni(*trans*-[18]dieneN$_4$)](NCS)$_2$ changes to a blue isomeric complex in chloroform. The blue complex is paramagnetic with an effective magnetic moment of 2.96 μ_B at 300 K. The visible (d–d) spectrum (in chloroform) is typical of an octahedral complex of nickel(II) (λ_{max} (ϵ) = 788 (3), 585 (3), 365 (17) nm). Further information concerning the structure of this complex is derived from the ν(C≡N) stretching vibration, observed as a singlet at 2078 cm^{-1}, and from the ν(C—S) band at 790 cm^{-1}. These bands are charactistic of N bound, isothiocyanate groups.[3,27] The isothiocyanate groups are probably bound trans above and below the coordination plane of the macrocyclic ligand. The cis arrangement would give a doublet in the ν(C≡N) region of the spectrum.[25] The yellow isomer has a singlet ν(C≡N) stretch

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(17) Cotton, F. A.; Wilkinson, G. A. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 916.

(18) Blight, M. M.; Curtis, N. F. *J. Chem. Soc.* **1962**, 3016.

(19) Curtis, N. F.; Curtis, Y. M.; Powell, H. K. J. *J. Chem. Soc. A* **1966**, 1015.

(20) Siiman, O.; Young, N. M.; Carey, P. R. *J. Am. Chem. Soc.* **1976**, *98*, 744.

(21) Colman, R. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *272*, 319

(22) Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341. Sakaguchi, U.; Addison, A. W. *J. Am. Chem. Soc.* **1977**, *99*, 5189.

(23) McLendon G.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1977**, *39*, 191.

(24) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.

(25) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1974**, 347.

(26) Hay, R. W., Piplani, D. P.; Jeragh, B. *J. Chem. Soc., Dalton Trans.* **1977**, 1951.

(27) Curtis, N. F.; Curtis, Y. M. *Aust. J. Chem.* **1966**, *19*, 1423.

at 2048 cm^{-1} and a weak ν(C—S) stretch at 760 cm^{-1} in its IR spectrum, characteristic of ionic thiocyanate.[2,25]

The blue and yellow isomers **4** and **5** are readily interconvertible in a fashion very similar to that observed by Busch et al.[28] between [Ni(*ms-trans*-[14]dieneN$_4$)(NCS)$_2$] (also prepared in chloroform as a metastable solid) and [Ni(*ms-trans*-[14]dieneN$_4$)](NCS)$_2$.

Butanediamine–Acetone Reaction. Attempts to prepare the [18]dieneN$_4$ macrocycle by reacting 1,4-butanediamine with acetone were unsuccessful. When 1,4-butanediamine and acetone were reacted at room temperature, the solution turned dark brown after 1 week and only tarry aldol condensation products were isolated. The same reaction at 0 °C also yielded no crystalline products even after 2 weeks of reaction. When copper(II) perchlorate hexahydrate in methanol was added to a reaction mixture 4 days aged at 25 °C, only bis(1,4-butanediamine)copper(II) perchlorate could be isolated.

Reactivity of Macrocyclic Complexes. The [18]diene macrocylic complexes are generally less resistant to acid- and base-catalyzed hydrolysis than are the [16]diene analogues and much less resistant than the [14]diene complexes of nickel(II) and copper(II). The [Cu(*cis*-[18]dieneN$_4$)]$^{2+}$ ion has greater resistance to nucleophilic attack by water than the [Cu(*trans*-[18]dieneN$_4$)]$^{2+}$. Attempts to reduce the imino group double bonds in [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, in [Ni(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, or in the free ligand bis(hydroperchlorate) salt[20] by using BH$_4^-$ or H$_2$ with Pd/charcoal catalyst in anhydrous methanol solvent resulted in the breakdown of the macrocycle to 1,4-butanediamine. Reduction of the Cu^{II}(*cis*-[18]diene) complex is presently being investigated.

Conclusions

The preparation of copper(II) and nickel(II) complexes of novel 18-membered macrocycles by the template reaction of 1,4-butanediamine indicates that large-ring macrocycles can be synthesized by reaction of acetone with α,ω-diamine complexes. We are currently working on the extension of this preparative method to larger macrocycles which may exhibit further interesting effects on the coordination geometry of their metal chelates and about copper(II) in particular.

The chemistry of the [18]diene complexes described in this paper involves interesting cases of isomerism. Similarities of these complexes to the well-known [14]diene analogues have been observed, but also significant differences have been noted, the most important of which is the large tetrahedral distortion observed for the Cu^{II}(*cis*-[18]diene) complex.[12] Studies are under way to determine the factors causing tetrahedral distortions in copper(II) macrocyclic complexes.

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Registry No. 3, 73531-91-6; **4**, 73544-67-9; **5**, 73557-34-3; H$_2$-(*trans*-[18]dieneN$_4$)(ClO$_4$)$_2$, 73531-93-8; 1,4-diaminobutane, 110-60-1; acetone, 67-64-1; [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$, 73429-78-4; [Cu-(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, 72765-21-0; bis(1,4-butanediamine)-copper(II) diperchlorate, 73429-80-8; [Ni([18]dieneN$_4$)](ClO$_4$)$_2$, 73544-68-0.

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(28) Warner, L. G.; Rose, N. J.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 703.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Crystal and Molecular Structures of Complexes of Two Isomeric 18-Membered Tetraaza Macrocylic Ligands Having the Empirical Formula [CuC$_{20}$H$_{40}$N$_4$](ClO$_4$)$_2$. Effects of Chelate Ring Size and Double-Bond Placement on Coordination Geometry about Copper(II)

JAMES H. TIMMONS,[1] PHIL RUDOLF, ARTHUR E. MARTELL,* JOHN W. L. MARTIN, and ABRAHAM CLEARFIELD

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Crystal and molecular structures are reported for two isomeric compounds, {[5*S*(*R*),10*R*(*S*)]-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene}copper(II) perchlorate, [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$, I, and {[5*R*-(*S*),14*R*(*S*)]-2,4,4,11,13,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene}copper(II) perchlorate, [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, II, having the empirical formula [CuC$_{20}$H$_{40}$N$_4$](ClO$_4$)$_2$. This is the first reported structural characterization of an 18-membered tetraazamacrocyclic ligand complex and only the second structural characterization of cis/trans isomerism in tetraazamacrocyclic complexes. Compound I forms purple monoclinic crystals, space group $C2/c$ (No. 15): a = 29.132 (16), b = 14.021 (8), c = 14.838 (9) Å; β = 113.89°; Z = 8; D_{calcd} = 1.44, D_{obsd} = 1.45 (2) g/cm^3. The nitrogens coordinate copper(II) in a pseudotetrahedral manner, with a dihedral angle of 36.6° between the N(1)CuN(2) and N(3)CuN(4) planes. Compound II forms orange-red orthorhombic crystals, space group $P2_12_12$ (No. 18): a = 14.720 (2), b = 12.308 (2), c = 7.982 (1) Å; Z = 2; D_{calcd} = 1.38, D_{obsd} = 1.39 (2) g/cm^3. The tetrahedral distortion in this complex is rather small, with a dihedral angle between the N(1)CuN(2) and N(1)′CuN(2)′ planes of 11.5°. The extent of tetrahedral distortion about Cu(II) and the amount of strain in the macrocyclic ligand (as determined by deviation of bond angles and torsional angles from ideal values) depend on both the chelate ring size and the C–N double-bond placement. It appears that a variety of tetrahedral distortions about Cu(II) may be obtained if these features of the ligand are modified.

Introduction

The chemistry of 14-membered tetraaza macrocycles has been studied extensively in the recent past.[2-8] These compounds are useful ligands for complexing metal ions and are interesting organic compounds as well. Complexes of tetraaza

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(2) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3.
(3) Busch, D. H. *Helv. Chim. Acta.* **1967**, 174.
(4) Restivo, R. J.; Ferguson, G.; Hay, R. W.; Piplani, D. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1131.

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