ther work will be undertaken along these lines. A most important point to be investigated is the precise ratio of cis and trans products to be found for specific systems involving stereomobility, since its extent is not certain either from our work or the studies of $[CrCl(NH_3)_5]^{2+}$. Resolution of the question of which ammonia molecule is lost in the photoaquation of $[CrX(NH_3)_5]^{2+}$ will have to depend not on product characterization but on experiments such as the photolysis of *trans*-$[CrX(NH_3)_4(^{15}NH_3)]^{2+}$.

It is the sincere hope of the author that this note helps resolve any confusion about the stereochemical implications of Adamson's rules and will also suggest new directions for future investigations.

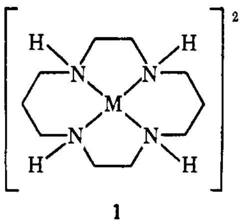
Acknowledgment. I wish to express my thanks to A. W. Adamson and V. Balzani for useful past discussions and for supplying preprint copies of their work, and to my coworkers, K. C. Moss and J. G. Valentin, for their contributions to the experimental work quoted in this note.

A. D. Kirk
Department of Chemistry, University of Victoria
Victoria, British Columbia
Received October 30, 1970

Nontemplate Synthesis of an Unsaturated Tetraaza[14]macrocycle and Its Metal(II) Complexes

Sir:

In recent years considerable effort has been directed toward development of convenient synthetic routes to macrocyclic polydentate ligands and their metal complexes.[1] The general class of compounds which has attracted the most interest is composed of 14-membered tetraaza ring systems, which are readily classified according to their degree of unsaturation: 1,4,8,11-tetraazacyclotetradecane complexes[2] (1) and C-methyl derivatives thereof,[3] *cis-* and *trans-* (2) -tetraazadiene complexes and their tetraimino oxidation products[3] (*e.g.*, 3), substituted tetraazatetraene species[4] (4), and the "tetraazaannulenes" (5) of Jäger[5] and Hiller, *et al.*[6] The macrocycles shown in 2 and 5 are most efficiently synthesized by metal-ion-assisted reactions; but can be obtained in lower yield in the absence of metal ions.[3,6] The species 4 have thus far been obtained only by template reactions involving as the most common precursor a tetradentate ketoamine complex substituted with a carbonyl-containing group (R = alkyl, aryl, OEt) at the β positions.



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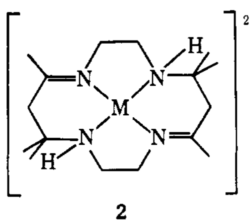

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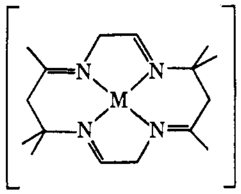

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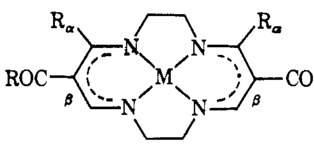

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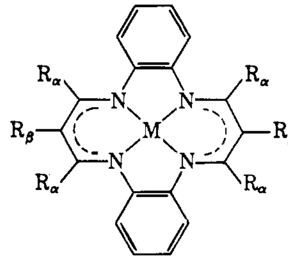

5

In the course of a systematic investigation of the electronic properties and electrochemical and chemical redox reactions (including oxidative addition and reaction with molecular oxygen) of d^4–d^{10} metal ions in a planar N_4 ligand field, soluble neutral complexes with the degree of unsaturation in 4 or 5 but lacking potentially reactive functional groups were required. The low solubility of the parent complex[6] 5 ($R_\alpha = R_\beta = H$) and several substituted derivatives render them unattractive. Template reactions analogous to those[5,6] affording 5 (R_α, R_β = Me, Ph, H) have thus far not yielded the corresponding diethylene-bridged complexes lacking carbonyl-containing substituents at the β positions.[7] We report here a facile nontemplate synthesis of the basic macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13- tetraene (H_2(MeHMe-(en)$_2$, 7) and its first row d^6–d^{10} complexes 8.

4-Amino-3-penten-2-one (6, 0.30 mol) in 200 ml of dry dichloromethane was O alkylated by treatment with an equimolar amount of triethyloxonium tetrafluoroborate in 150 ml of dry dichloromethane under nitrogen for 30 min at ~25°. After dropwise addition of 0.15 mol of ethylenediamine over 30 min, the reaction was allowed to proceed at 25° for an additional 3 hr, the solvent removed (reduced pressure), and 400 ml of absolute methanol added. Sodium methoxide (0.30 mol) in 150 ml of methanol and 0.15 mol of ethylenediamine were introduced, and the reaction mixture was stirred (4 hr) as ammonia was evolved. After removal of methanol, extraction of the residue with absolute ethanol and recrystallization of the separated product from this solvent afforded pure 7[9] (30–35%) as cream-colored platelets: mp 226–228°; pmr ($CDCl_3$, TMS reference) −1.95 (12, Me), −3.51 (8, CH_2), −4.58 (2, =CH–),

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(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinatius Alfred Werner*, 174 (1967); J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier, Amsterdam, 1968, pp 83–99.

(2) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(3) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968), and references therein.

(4) E.-G. Jäger, *Z. Chem.*, **8**, 30, 470 (1968).

(5) E.-G. Jäger, *Z. Anorg. Allg. Chem.*, **364**, 177 (1969), and references therein.

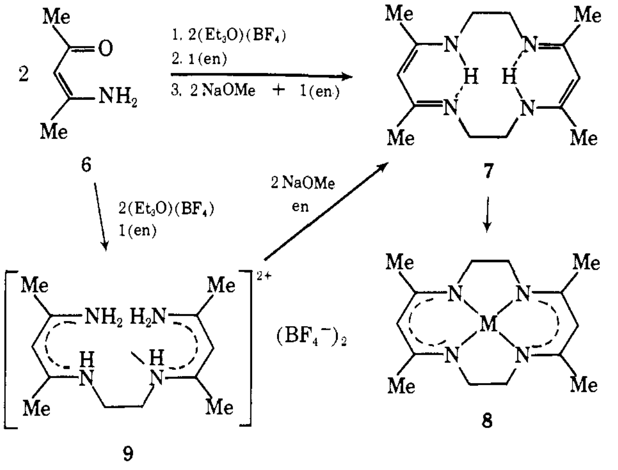
(6) H. Hiller, P. Dimroth, and H. Pfitzner, *Justus Liebigs Ann. Chem.*, **717**, 137 (1968).

(7) For example, reactions of bis(acetylacetone)ethylenediiminemetal-(II) complexes with ethylenediamine under forcing conditions (*i.e.*, refluxing in neat ethylenediamine for 2 days) did not result in cyclization. Failure to form ethylene-bridged macrocycles from these complexes has also been noted briefly by Bamfield,[8] whose work on template reactions of complexes derived from 2-hydroxymethylenecyclohexanone and 2-hydroxymethylenecyclohexa-1,3-dione further emphasizes the apparent necessity of β-carbonyl substituents for cyclization reactions involving ethylenediamine.

(8) P. Bamfield, *J. Chem. Soc. A*, 2021 (1969).

(9) *Anal.* Calcd for $C_{14}H_{24}N_4$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.83; H, 9.70; N, 22.65. All other new compounds also gave satisfactory elemental analyses.

—11.61 ppm (2, NH); mol wt 244 (toluene, osmometry), calcd 248; mass spectrum (70 eV) m/e 248 (P). Nickel(II) and copper(II) complexes (**8**) were prepared from **7** and the metal acetate in ethanol, while the remaining complexes were obtained by nonaqueous chelation reactions in *tert*-butyl alcohol[10] (Fe(II), Co(II)) or THF[11,12] (Zn(II)). As a class the complexes M(MeHMe(en)$_2$) are easily crystallized and moderately soluble in weakly polar solvents. As solids, all are stable to dry oxygen except the Fe(II) species; this complex and Co(MeHMe(en)$_2$) react with oxygen in solution. The spectral and magnetic properties are consistent with a planar stereochemistry.[13]



The reaction sequence in the conversion **6** → **7** is under further investigation. Interruption of the reaction after addition of the first equivalent of ethylenediamine has allowed isolation of the intermediate salt **9**, the exact tautomeric structure of which is uncertain. This material was purified by recrystallization from dry methanol and isolated as a very hygroscopic white solid (34%, mp 175–180°). Neutralization of **9** followed by reaction with 1 equiv of ethylenediamine in dry methanol gives the macrocycle **7** in 50% yield. The use of **9** as an intermediate in the preparation of unsymmetrical macrocycles is under study. The synthetic scheme described here represents a particularly clear example of the utility of *O*-alkyl-β-ketoamine cations as intermediates in the synthesis of open[12,14] or cyclic ligand systems by nucleophilic reactions at the >COR carbon, and should be suggestive of further applications.

Details of the electronic and redox properties and the oxidative reactivities of M(MeHMe(en)$_2$) and related complexes, as well as additional experiments directed toward a useful template synthesis of **7** and **8**, will be reported subsequently.

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T. J. Truex, R. H. Holm*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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[10] R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, **11**, 72 (1968).

[11] W. R. McClellan and R. E. Benson, *J. Amer. Chem. Soc.*, **88**, 5165 (1966).

[12] D. H. Gerlach and R. H. Holm, *ibid.*, **91**, 3457 (1969).

[13] Magnetic moments of crystalline solids (**8**) at ~25°: M = Ni(II), Zn(II) diamagnetic; Cu(II), 1.78 BM; Co(II), 2.08 BM; Fe(II), 3.95 BM.

[14] S. G. McGeachin, *Can. J. Chem.*, **46**, 1903 (1968).

Additions and Corrections

Kinetics and Mechanism of the Osmium Tetroxide Catalyzed Oxidation of Acetone and Ethyl Methyl Ketone by Alkaline Hexacyanoferrate(III) Ion [*J. Amer. Chem. Soc.*, **91**, 2643 (1969)]. By V. N. SINGH, H. S. SINGH, and B. B. L. SAXENA, Department of Chemistry, University of Allahabad, Allahabad, India.

The right-hand side of eq 1–4, 6, and 7 should be multiplied by 2 and that of eq 5 by $^1/_2$. The resulting rate expressions thus would be valid for the first stage of oxidation. The k_1 values calculated should be read as $2k_1$. The species of osmium(VIII) and osmium(VI) should be taken as $OsO_4(OH)_2{}^{2-}$ and $OsO_2(OH)_4{}^{2-}$.

On the Mechanism of Interaction between Tertiary Amines and Trichlorosilane [*J. Amer. Chem. Soc.*, **92**, 699 (1970)]. By STANLEY C. BERNSTEIN, Department of Chemistry, Wright State University, Dayton, Ohio 45431

The rate equation on page 699 should read

$$4AIk_{FD}t = 2(I - 1)(x - 1) - (I + 1)\ln(2x - 1)$$

The calculations in the communication are based on this correct equation.

Conformational Analysis. XXII. Conformational Equilibria in 2-Substituted 1,3-Dioxanes [*J. Amer. Chem. Soc.*, **92**, 3050 (1970)]. By FRANZ W. NADER and ERNEST L. ELIEL, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

In Table VI, column 1, compound II should read III and III should read IV. The first two footnotes to the table should read: [a] Axial isomer/equatorial isomer. [b] Equatorial isomer/axial isomer.

A Model for the Biogenesis of the Spirobenzylisoquinoline Alkaloids [*J. Amer. Chem. Soc.*, **92**, 4943 (1970)]. By