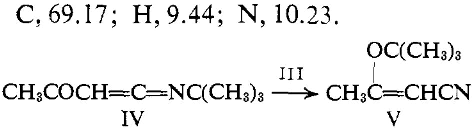
H, 9.41; N, 10.05. Found: C, 68.94; H, 9.42; N, 9.98.

A side reaction was encountered when the method of combining the reagents was reversed in the preparation of IV. Addition of triethylamine to III gave IV along with a contaminant that had a nearly superimposable nmr spectrum, but which could be detected by its infrared absorption at 4.51 μ. Control experiments established that the source of the impurity was a reaction of the ketoketenimine in the presence of the unconsumed isoxazolium salt. In dichloromethane solution containing a small amount of III, compound IV underwent slow isomerization to β-*t*-butoxycrotononitrile (V) which was isolated in 58% yield after distillation and was further purified by recrystallization from a small volume of petroleum ether; mp 36–37°; $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ε 14,300)[7]; $\lambda_{\max}^{\mathrm{CCl_4}}$ 4.51 (conjugated C≡N) and 6.20 μ (conjugated C=O);[9] $\tau_{\mathrm{CCl_4}}$ 5.58 (1 H, singlet), 7.95 (3 H, singlet), and 8.57 (9 H, singlet). *Anal.* Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.05. Found: C, 69.17; H, 9.44; N, 10.23.



$$\underset{\mathrm{IV}}{\mathrm{CH_3COCH{=}C{=}NC(CH_3)_3}} \xrightarrow{\mathrm{III}} \underset{\mathrm{V}}{\mathrm{CH_3}\overset{\mathrm{OC(CH_3)_3}}{\mathrm{C}}\mathrm{{=}CHCN}}$$

The ketoketenimines II and IV are stable below 0°, but both darken on standing at room temperature. The colorless, freshly distilled IV turns pale yellow within a few hours, even under nitrogen in the dark at low temperature. However, the compound shows no further change in its color and shows no change in its infrared and nmr spectra after prolonged storage, with occasional warming to room temperature for removal of samples. The possible use of IV as a reagent for peptide synthesis[10] is under investigation.

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(7) Model, β-*n*-butoxycrotononitrile, $\lambda_{\max}^{\mathrm{MeOH}}$ 228 mμ (ε 14,500).[8]

(8) P. Kurtz, H. Gold, and H. Disselnkötter, *Ann.*, **624**, 1 (1959).

(9) Model,[7] 4.51 and 6.19 μ.

(10) R. B. Woodward, R. A. Olofson, and H. Mayer, *J. Am. Chem. Soc.*, **83**, 1010 (1961).

(11) National Institutes of Health Predoctoral Fellow, 1961–1964. This work was also supported by a grant from the National Institutes of Health.

R. B. Woodward, D. J. Woodman[11]
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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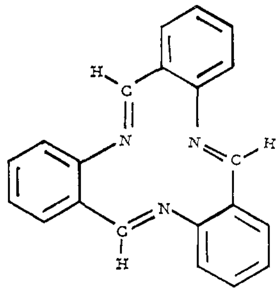
The Coordination Template Effect in *o*-Aminobenzaldehyde–Metal Ion Systems and Formation of a Novel Chelate Sandwich Compound[1]

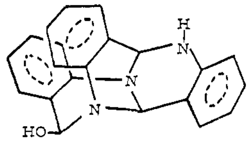
Sir:

In the course of investigations which served to demonstrate the template effects that metal ions exert on the stereochemical course of certain chemical reactions, the self-condensation of *o*-aminobenzaldehyde was reinvestigated.[2] Unlike systems based on the reaction of coordinated mercaptide groups as nucleophiles,[3] the stepwise reaction path and, consequently, the manner of influence of the metal ion have not been clear in the case of *o*-aminobenzaldehyde. It has been shown[2,4] that one of the products of the self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) ion is a complex containing a closed tridentate macrocyclic ligand tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine, structure I.



I

The principal products from the self-condensation of *o*-aminobenzaldehyde in the absence of metal ions are a bisanhydro trimer and a trisanhydro tetramer.[5] Recently, McGeachin[6] has reexamined this system and assigned structure II to the bisanhydro trimer, 13-hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline.



II

We have found that in a 1 : 1 mole ratio, 13-hydroxy-6,-12-benzo-6H-quinazolino[3,4-*a*]quinazoline (II) rearranges under the influence of nickel(II) nitrate to give the complex of the tridentate ligand of I. Further, no tetrameric condensate is formed, in contrast to the result when *o*-aminobenzaldehyde undergoes self-condensation in the presence of nickel(II) nitrate.[2] The rearrangement is accomplished by heating a suspension of the quinazoline with an equimolar amount of nickel(II) nitrate hexahydrate in absolute ethanol for 3 hr. During this time, the quinazoline slowly dissolves and the bright orange-yellow dinitratoaquo-(tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine)nickel(II) precipitates.

The art of the self-condensation reaction of *o*-aminobenzaldehyde under the influence of metal ions requires that the condensation be initiated several minutes before the metal ion is added. This provides adequate opportunity for the prior formation of the free bisanhydro trimer and trisanhydro tetramer, both of which may then rearrange under the influence of the metal ion. In fact, free trimeric condensate has been isolated from the self-condensation reaction. The formation of the tridentate ligand alone in the case of the reaction of nickel(II) ion with the bisanhydro trimer indicates that the tetradentate macrocyclic ligand is produced by rearrangement of the trisanhydro tetramer.

In the case of copper(II) the self-condensation reaction produces only the complex of the tetrameric Schiff base, $\mathrm{Cu(TAAB)^{2+}}$. This result was ascribed to the usual stereochemistry of the copper(II) ion. The fact that the quinazoline reacts with copper(II) ion to form the complex containing the tetrameric Schiff base shows that the rearrangement process involves

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(1) This investigation was supported in part by Public Health Service Fellowship 1-F2-GM-28, 091-01 and Public Health Service Grant GM 10040 from the National Institute of General Medical Sciences.

(2) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

(3) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 3651 (1964).

(4) E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

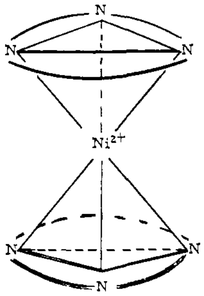
(5) F. Seidel and W. Dick, *Ber.*, **60**, 2018 (1927).

(6) Private communication.

extreme labilization of the organic substrate, terminating in formation of a stable product. In the self-condensation reaction, the yield of copper(II) complex of tetrameric ligand slightly exceeds the combined yields of the nickel(II) complexes of trimeric and tetrameric ligands.

This metal ion induced rearrangement has been used to synthesize a complex containing two trimeric condensates bound to each nickel ion. This compound is prepared by heating a suspension of 2 equiv of the quinazoline in methanol with 1 equiv of nickel(II) nitrate for 2 hr under reflux. The quinazoline dissolves with reaction, first giving an orange-yellow colored solution which slowly turns wine-red. When the homogeneous solution cools to room temperature, red-brown clusters of needles of bis(tribenzo[*b*,*f*,*j*]-[1,5,9]triazacycloduodecine)nickel(II) nitrate monohydrate are deposited on the walls of the reaction vessel. *Anal.* Calcd for $Ni(C_{21}H_{15}N_3)_2(NO_3)_2 \cdot H_2O$: C, 61.56; H, 3.94; N, 13.68. Found: C, 61.63; H, 4.01; N, 13.45. The infrared spectrum of $Ni(TRI)_2(NO_3)_2 \cdot H_2O$ is identical with the spectrum of $Ni(TRI)(NO_3)_2 \cdot H_2O$ except for the absence from the spectrum of $Ni(TRI)_2(NO_3)_2 \cdot H_2O$ of bands which have been attributed to coordinated nitrate.[2] The same material can be formed by reaction of $Ni(TRI)(NO_3)_2 \cdot H_2O$ with 1 mole of the quinazoline.

This compound has a magnetic moment of 2.94 BM, which is consistent with the presence of a pseudo-octahedral environment about the nickel(II). This interesting chelate sandwich compound (structure III) offers an excellent example of strong trigonal distortion from O_h symmetry.



III

Absorption spectra (methanol and Nujol mull) were measured from 7400 to 33,000 cm^{-1}. Bands occur at ν_1 11,300 cm^{-1} (sh) (ϵ 1.1), ν_2 14,500 cm^{-1} (ϵ 18.7), ν_3 20,200 cm^{-1} (ϵ 212). The relatively intense color may be attributed to low-energy charge-transfer bands. The absorption bands have been assigned to the following transitions in D_{3d} symmetry: ν_1, $^3A_{2g} \rightarrow {}^3A_{1g}$; ν_2, $^3A_{2g} \rightarrow {}^3E_g$; ν_3, $^3A_{2g} \rightarrow {}^3A_{2g}$, ^3E_g (plus charge transfer). A *Dq* value of 1340 cm^{-1} for the Schiff base chelate has been calculated assuming it to be the weighed average of ν_1 and ν_2. This agrees quite well with the *Dq* value of 1320 cm^{-1} which is obtained by applying the rule of average environment[7] to the aqueous solution spectrum of $[Ni(TRI)(H_2O)_3]^{2+}$.

Two geometric isomers can be envisioned for this complex based on the relative clockwise or counterclockwise progression of the repeating unit in each Schiff base chelate ring. The two isomers would be a *meso* form, in which the repeating unit progresses in opposite directions on each Schiff base chelate ring, and a *racemic* form, in which the repeating unit progresses in the same direction. From a study of the Dreiding stereomodels, the *racemic* form appears to be improbable in that the nonbonded distance between benzene rings would be 2.8 A. The minimum distance between the benzene rings in [2.2′]paracyclophane is 2.83 A.[8,9] Differences in the ultraviolet spectra of [2.2′]paracyclophane and certain model compounds have indicated considerable interaction between benzene rings in this system.[10,11] The ultraviolet spectra of $Ni(TRI)^{2+}$ and $Ni(TRI)_2{}^{2+}$ in methanol are practically identical; therefore, it appears that little or no interaction exists between benzene rings. In the *meso* form, the nonbonded distance between benzene rings is approximately 3.5 A. Consequently, no interaction is expected and the compound in question is of this structure.

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Larry T. Taylor, Sharon C. Vergez, Daryle H. Busch
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received April 20, 1966

Single-Crystal Preparation of Cubic Rare Earth Tungsten Bronzes

Sir:

The crystal growth of rare earth tungsten bronzes[1] by electrolytic reduction of a fused mixture of rare earth tungstate and tungsten trioxide is possible. The process is, however, complicated by the necessity to operate at relatively high temperatures. Suitable mixtures of rare earth tungstate and tungsten trioxide were found to melt between 1000 and 1200°. These temperatures are considerably higher than those employed for the well-developed technique of growing alkali tungsten bronzes or alkali molybdenum bronzes (around 600°). Several modifications on established crystal-growing methods of bronzes[2-5] were necessary in order to overcome the difficulties of an electrolysis around 1200°. Optimum conditions were determined empirically and represent numerous compromises. Major difficulties were the following: tungsten trioxide sublimes increasingly above 800°, thus changing continuously the composition of the melt; ceramic tubes, recommended to insulate the lead wire of the cathode from the melt,[3] become conducting (it was, for example, observed that little crystals grew on a shielding Degussite tubing). At 1200°, the temperature gradient can be severe, and isotherm profiles in the crystals are difficult to control. Container materials for the highly aggressive melt are hard to find.

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