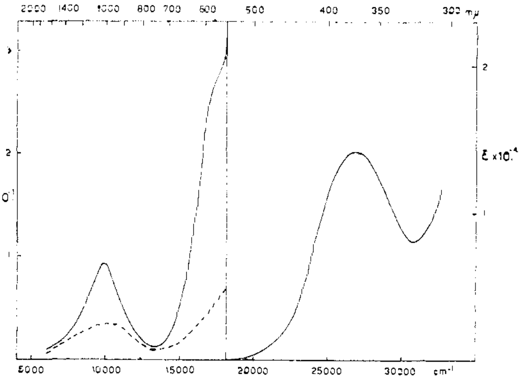

Fig. 2.—Absorption spectrum of bis-(N-phenylsalicylaldimino)-cobalt(II) in pyridine: ———; reflectance spectrum of bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine, absorbance scale arbitrary: ---------.

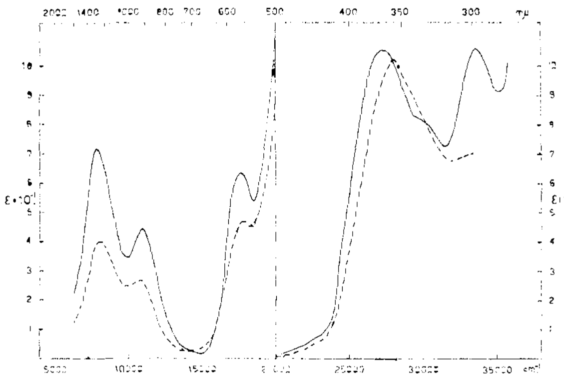

Fig. 3.—Absorption spectra of bis-(N-cyclohexylsalicylaldimino)-cobalt(II): ———, in benzene; ---------, in pyridine.

and shoulders at about 17,000 and 28,000 cm.$^{-1}$. The bands beyond 20,000 cm.$^{-1}$ are very intense (log $\epsilon > 4$) and occur at frequencies which are almost identical with those of the corresponding bands of the bis-(N-alkylsalicylaldimino)-copper(II) compounds.[1] They may be attributed either to intraligand transitions or to charge transfer between the ligands and the cation. The weaker bands (log $\epsilon < 2$) occurring at lower wave numbers may be ascribed to crystal-field transitions.

The magnetic moment of the complex bis-(N-phenylsalicylaldimino)-cobalt(II) in pyridine solution (4.78 B.M., see Table I) is higher than in benzene solution. This suggests that in pyridine the complex coördinates two molecules of solvent becoming six-coördinate and octahedral. This is confirmed by the isolation of the solid adduct bis-(N-phenylsalicylaldimino)-cobalt(II)·2 pyridine with a μ_{eff} = 4.81 B.M. Further evidence for the formation of this adduct is provided by the reflection spectrum of the di-pyridine derivative and that of a pyridine solution of the unsolvated complex (Fig. 2). These two are very similar. The latter shows maxima at 10,000, 26,000, 33,100 cm.$^{-1}$ and a shoulder at about 17,000 cm^{-1}. This differs from the spectrum of a benzene solution of the tetrahedral complex, the major difference being the markedly higher extinction coefficients of the crystal-field bands in the tetrahedral complex.

The magnetic moment of the complex bis-(N-cyclohexylsalicyl-aldimino)-cobalt(II) in pyridine is 4.62 B.M. (see Table I). This value can be accounted for if it is assumed that only approximately 50% of the molecules of this complex are in the octahedral form. Spectrophotometric measurements are in agreement with this hypothesis. Thus it is evident from Fig. 3 that the spectrum of this complex in pyridine shows the same maxima as that in benzene, at least in the region 6,000–20,000 cm.$^{-1}$, but lower extinction coefficients. This is due to the fact that the tetrahedral complex has extinction coefficients which are larger than those for the bands of the octahedral complex. If one makes use of the observation that the dipyridine adduct has a negligible absorption at 7,700 cm.$^{-1}$, where the tetrahedral complex shows its maximum absorption, from the ratio of the extinction coefficients in both solvents one obtains a value of about 50% for each form.

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[Contribution from the Chemistry Department, Victoria University of Wellington, Wellington, New Zealand]

Transition-metal Complexes with Aliphatic Schiff Bases. IV. Compounds Formed by the Reaction of Copper(II) and Nickel(II) Triethylenetetramine Complexes with Acetone

By D. A. House and N. F. Curtis

Received February 1, 1962

Coördination compounds containing a cyclic quadridentate ligand having three secondary amine and one azomethine donor groups have been prepared by the reaction of copper(II) and nickel(II) triethylenetetramine chlorides with acetone.

It has been reported[1-3] previously that acetone can condense with 1,2-diamine complexes of nickel(II) and copper(II). This paper describes compounds prepared similarly from the triethylenetetramine metal(II) complexes.

If copper(II) or nickel(II) complex chlorides of triethylenetetramine are heated in sealed tubes with acetone, reaction occurs, and an acid stable material can be isolated. Analytical data indicate

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(1) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

(2) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1204 (1962).

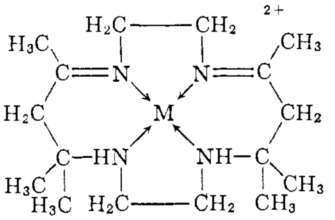
(3) M. M. Blight and N. F. Curtis, in press.

that two moles of acetone have condensed with the polyamine complex and two moles of water have been eliminated.

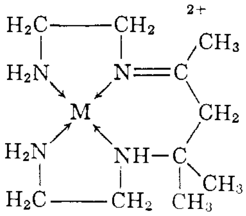
$$MC_6H_{18}N_4^{2+} + 2C_3H_6O \longrightarrow MC_{12}H_{26}N_4^{2+} + 2H_2O \text{ (M = Ni or Cu)}$$

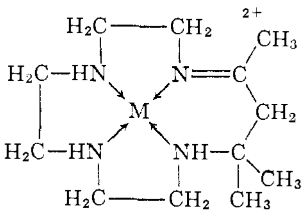
These compounds are similar to the ones prepared from the ethylenediamine[1,3] and propylenediamine[2,3] metal(II) complexes. However, with the nickel(II) ethylenediamine complexes, compounds with two, three or four condensed acetone groups can be isolated.[1]

The metal complexes formed from the 1,2-diamine complexes and acetone were originally assigned N-isopropylidine structures,[1,2] but in the light of further degradative studies together with further infrared and nuclear magnetic resonance data, isomeric bridged structures (I) and (II) were proposed.[4]


M = Ni, Cu

I


II


III

The properties of the compounds formed by the reaction of acetone with the metal(II) triethylenetetramine complexes are also in complete agreement with a cyclic structure (III), being salts of the 1,5,8,11-tetrazo-2,4,4′-trimethylcyclotrideca-1-ene metal(II) ion.

Preparation and Properties.—The ions (III) have been prepared from the triethylenetetramine metal (II) chlorides by heating with acetone at 100° in the presence of a dehydrating agent. In the case of nickel, the crystalline complex $Ni_2trien_3Cl_4 \cdot 2H_2O$ (trien = triethylenetetramine) was used as the starting material with anhydrous zinc chloride as the dehydrating agent. The use of this reagent has the added advantage that the tetrachlorozincate(II) salt of the cyclic complex is insoluble in the acetone solvent and the product crystallizes out as the reaction proceeds. With copper, no crystalline triethylenetetramine complex had been reported in the literature, and an attempt to prepare the chloride of the $Cutrien^{+2}$ ion gave only a blue gum. However, the compound $CutrienZnCl_4$ was isolated as a well-crystallized material by addition of zinc chloride to the blue $CutrienCl_2$ solution. Unfortunately this proved to be too insoluble in acetone to be of any value in the preparation of the desired cyclic complex. Consequently the blue, ill defined gum of $CutrienCl_2 \cdot xH_2O$ mixed with anhydrous calcium sulfate was used as the starting material and proved quite satisfactory.

The ions (III) have been isolated as the tetrachlorozincate(II) salts, the nickel derivative being bright yellow and the copper salt violet (almost black in large crystals). Both the tetrachlorozincate(II) salts are insoluble in acetone, methanol and ethanol but readily soluble in water. They are stable to boiling water and dilute acids. The copper compound is slowly decomposed by concentrated acids (rapidly by concentrated hydrochloric), but the nickel compound is stable to these reagents, even when heated. In aqueous solution the salts give no reactions for simple copper(II) or nickel(II) ions but give positive tests for the zinc(II) ion. Thus there is no visible reaction with ammonical dimethylglyoxime, potassium iodide or salicylaldoxime, but hydrogen sulfide and sodium hydroxide give white precipitates of the zinc compounds, the color of the complex cation being unaffected. Both compounds are slowly decomposed by peroxydisulfate and by cyanide ions in the cold and more rapidly on warming. Reduction with zinc and acetic acid also effects decomposition of the copper complex. Work on the reduction products using hydrogen gas and platinum catalyst is in progress.

Steam distillation of the products from the hydrochloric acid decomposition of the copper complex yields only mesityl oxide which was isolated as the 2,4-dinitrophenylhydrazine derivative and characterized by X-ray powder diffraction. Cyanide ion decomposition of the nickel complex also yields mesityl oxide. No acetone could be detected in the hydrolysis products. Triethylenetetramine was isolated from the decomposition of the copper complex as the compound[5] $trien4HCuCl_6$ and characterized by X-ray powder diffraction. The hydrolysis to mesityl oxide supports the cyclic structure, the azomethine link being broken to form an intermediate β amino ketone. This would be unstable under the hydrolysis conditions,[6] forming an unsaturated ketone (mesityl oxide) and regenerating the original amine. The high stability of the complex cation also supports a caged cyclic structure as amine complexes of copper and nickel are usually decomposed by acid.

Spectra.—The visible and ultraviolet spectra of (III) in aqueous solution are very similar to those of (I) and (II) (see Table I) but with some slight shifts due to the structural modifications of the ligand.

The infrared spectra show a strong band at 3070 cm.$^{-1}$ due to the coördinated NH group[3,4] and the NH_2 bands present in the original amine complex are absent. There is also a strong band at 1658 cm.$^{-1}$ due to the —C=N— system.

Experimental

1,5,8,11-Tetrazo-2,4,4′-trimethylcyclotrideca-1-ene Nickel (II) tetrachlorozincate(II).—$Ni_2trien_3Cl_4 \cdot 2H_2O$ was pre-

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[4] N. F. Curtis and D. A. House, *Chem. and Ind.* (London), **42**, 1708 (1961).

[5] H. B. Jonassen, T. B. Crumpler and T. D. O'Brien, *J. Am. Chem. Soc.*, **67**, 1709 (1945).

[6] N. H. Cromwell, *Chem. Revs.*, **38**, 124 (1946).

TABLE I

ULTRAVIOLET SPECTRA IN AQUEOUS SOLUTION

Nickel Compounds			Copper Compounds		
	$\lambda_{max.}$ (mμ)	ε		$\lambda_{max.}$ (mμ)	ε
(I)[1]	436	104	(I)[3]	505	126
	282	5,400		260	6400
	213	17,300			
(II)[1]	436	70	(II)[3]	525	88
	268	2,100		244	5200
	205	15,000			
(III)	420	110	(III)	547	200
	265	2,260		263	5200
	218	14,000			

pared by the method of Jonassen and Douglas.[7] This material (3 g.), anhydrous acetone (100 ml.) and anhydrous zinc chloride (5 g.) were heated in a sealed tube at 110° for four days. On mixing the reactants the pink-violet crystals partially dissolved and the acetone solution became yellow. During the heating period yellow crystals of the cyclic tetrachlorozincate(II) complex formed on the walls of the tube. These yellow crystals were dissolved in a small amount of water, boiled with absorbing charcoal to remove any acetone polymers and, after filtration and evaporation to a small volume, poured into excess acetone. The precipitated bright yellow crystals were recrystallized from water–acetone solution; yield 30%.

Anal. Calcd. for $C_{12}H_{26}N_4NiZnCl_4$: Ni, 11.9; C, 29.3; H, 5.32; N, 11.4; Cl, 28.8. Found: Ni, 11.9; C, 29.0; H, 5.22; N, 11.3; Cl, 28.5.

1,5,8,11-Tetrazo-2,4,4′-trimethylcyclotrideca-1-ene Copper (II) tetrachlorozincate(II).—Equimolar amounts of copper-(II) chloride dihydrate and triethylenetetramine were mixed in a 50-50 ethanol–water solution. A bright blue solution resulted, and much heat was evolved, but on cooling and evaporation only a blue gum could be isolated. About 5 g. of this gum was stirred with anhydrous calcium sulfate until a thick paste was formed and as much water as possible was removed by storing this over concentrated sulfuric acid. The dry paste was heated with a further amount of anhydrous calcium sulfate and 100 ml. of anhydrous acetone in a sealed tube at 100° for 40 hr. (Heating at higher temperatures caused decomposition to copper metal.) At the end of the heating period the tube was cooled rapidly and the acetone poured from the solid gum. The acetone solution was evaporated and the residue boiled with water. After four treatments with decolorizing charcoal, a violet solution was obtained. On slow evaporation in the presence of excess zinc chloride solution, violet-black crystals of the tetrachlorozincate(II) salt were isolated. The gum remaining in the tube also contained some of the required product but was difficult to isolate from the starting material. The gum was dissolved in water, boiled with decolorizing charcoal and zinc chloride added to the resulting blue-violet solution. Dilute hydrochloric acid was added until the solution was just acid and on slow evaporation a further quantity of the final product was isolated. The combined products were dissolved in a little hot water and poured into a large excess of acetone. A fine violet powder was immediately precipitated; yield 40%.

Anal. Calcd. for $C_{12}H_{26}N_4CuZnCl$: Cu, 12.9; C, 29.0; H, 5.27; N, 11.2; Cl, 28.45. Found: Cu, 13.0; C, 28.9; H, 5.19; N, 11.0; Cl, 28.4.

Analysis.—Nickel was determined as its dimethylglyoxime derivative and copper as the salicylaldoxime complex, the complex cations (III) being decomposed by boiling peroxydisulfate solution. The Dumas method gave rather unsatisfactory nitrogen analyses and better results were obtained using the Kjeldahl method.

Spectra.—The visible and ultraviolet spectra were determined in aqueous solution using a Unicam model S.P. 500 spectrophotometer. The infrared spectra were determined in mulls, a Perkin–Elmer model 21 infrared spectrophotometer being used.

X-Ray Powder Diffraction Patterns.—These were obtained from a Phillips X-ray spectrograph coupled to a Brown recording potentiometer.

Acknowledgments.—The authors thank Dr. B. Cleverly of the Dominion Laboratory, Wellington, and the Chemistry Department, Canterbury University, Christchurch, for the infrared spectra determinations.

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(7) H. B. Jonassen and B. E. Douglas, *J. Am. Chem. Soc.*, **71**, 4094 (1949).

[CONTRIBUTION 1688 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT]

The Kinetics of the Thermal *cis-trans* Isomerization of 2-Methyl[2.1.0] bicyclopentane

BY JOHN P. CHESICK

RECEIVED JANUARY 30, 1962

The kinetics of the reversible *cis–trans* isomerization reaction of 2-methyl[2.1.0]bicyclopentane have been studied between 203.3 and 231.7° and at reactant pressures between 0.08 and 1.7 mm. If the lower boiling isomer is tentatively identified as *trans*, then $K = k_{trans}/k_{cis} = 0.58$ at 220° for the *trans* → *cis* reaction. $/\Delta H/ \leq 0.5$ kcal./mole. $(k_{trans} + k_{cis}) = 10.^{14.45} \exp((-38.9 \pm 0.8 \text{ kcal.})/RT)\text{sec.}^{-1}$. The transition state is concluded to be one of incomplete rupture of the bridgehead–bridgehead bond corresponding to considerable residual bicyclic strain energy. The first order rate constants have decreased less than 10% on lowering the reactant pressure to 0.1 mm.

Introduction

As a consequence of a study of the kinetics of thermal isomerization of [2.1.0]bicyclopentane to cyclopentene,[1] it was observed that the activation energy was 46.6 kcal./mole, a number considerably larger than the value of 19 ± 4 kcal. calculated for the strength of the bridgehead–bridgehead bond assuming the extra bicyclic strain energy to be released in the transition state. A substituted bicyclo compound, such as the hitherto unreported 2-methyl[2.1.0]bicyclopentane (sometimes referred to as floor-methylhousane) would permit the observation of a probable *cis–trans* reaction which must require at least some loosening of the central bond. Since some low pressure drop-off of the first order rate constant was observed for the unimolecular reaction of the unsubstituted compound,[1] it was also of interest to study any *cis–trans* reaction at the lowest possible pressures to see whether methyl substitution had the expected effect

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(1) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, to be published.