

DISSERTATIONES

DCC-15 (Univ. Zagreb)

541.486:546.73:541.124

Croat. Chem. Acta 37 (1965)**Kinetics, Mechanism and Stereochemistry of the Octahedral Substitutions on Some Cobalt(III) Complexes**

M. Orhanović

Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

The rate of replacement of chlorine by thiocyanate and chloride-36, respectively, in the *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) ions in absolute methanol was measured. It was found that the rate of the substitution shows only a small dependence on the thiocyanate and chloride ion concentration, respectively. The specific rates of the substitutions by thiocyanate and chloride ion, respectively, on the same isomer are practically equal. The substitution of chlorine in *trans*-isomer proceeds with retention of configuration. The substitution of chlorine in *cis*-isomer proceeded with partial change of configuration yielding about 20% of *trans*-substitution product. The rate of replacement of chlorine by SCN⁻ and ³⁶Cl⁻, respectively, in *trans*-nitrochloro isomer is about 35 times faster than the rate of the similar replacement of chlorine in the *trans*-dichlorobis(ethylenediamine)cobalt(III) ion. The large accelerating influence of the nitro-group suggests that this substitution is an S_N2 process involving methanol as the nucleophilic reagent. The negative electromeric effect of the nitro-group causes polarization of the cobalt atom. The polarization demand of the binding of the methanol seems to be more important than the loosening of the displaced chlorine which the nitro-group makes more difficult. An analogy is drawn with the aquation of the same complexes.

The thesis was reported in part at the 7th International Conference on Co-ordination Chemistry, Stockholm and Uppsala, June 1962 and partly published: *J. Chem. Soc.*, 1961, 2142; *ibid.* 1964, 2969.

Examiners: Professor S. Ašperger, Professor B. Težak and Doc. C. Djordjević.

Oral examination: February 19, 1964. *Degree conferred:* March 21, 1964.

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(92 pages, 15 figures, 18 tables, 87 references, original in Croatian)

M. ORHANOVIC

DCC-15

541.486:546.73:541.124

1. Kinetics, Mechanism and Stereochemistry of the Octahedral Substitutions on Some Cobalt(III) Complexes.

I. Orhanović M.

II. Institute »Ruder Bošković«,
Zagreb, Croatia, Yugoslavia

Chloride-36 exchange
Chloronitrobis(ethylenediamine)-
cobalt(III) ion
Co(III) complexes
Isothiocyanatonitrobis(ethylenediamine)cobalt(III) ion
Substitutions in octahedral
Co(III) Complexes

DCC-16 (Univ. Zagreb)

541.124:546.17.02:546.39-8

Croat. Chem. Acta 37 (1965)**Nitrogen-15 Isotope Effect and Secondary Deuterium Isotope Effect in the Reaction of an Amonium Salt with Base**

L. Klasinc

Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

The mechanism of elimination reaction of 2-phenylethyltrimethylammonium iodide with base in aqueous and alcoholic solutions was studied by nitrogen-15 and secondary α -deuterium kinetic isotope effects. The nitrogen-15 isotope effect determination was performed by mass-spectrometry. It was found that the nitrogen isotope effect is only a fraction (about 10%) of the maximum isotope effect calculated by the Bigeleisen theory. These results suggest that the transition state might possess some carbanion character.

Measurements of the secondary α -deuterium isotope effects performed in aqueous and alcoholic media at 97° and 40° respectively, have shown that there is practically no secondary α -deuterium isotope effect in the elimination in both solvents. On the other hand the secondary α -deuterium isotope effect in the reaction of 2-phenylethyl bromide with ethoxide ion in absolute ethanol amounts to about 9% per deuterium atom at 59.8°. The mechanistic implications of these results were discussed regarding the possibility of existence of a carbanion mechanism.

Thesis was partly reported at the XIX Congress for Pure and Applied Chemistry, London, July 1963.

Examiners: Professor S. Ašperger, Professor M. Karšulin, Dr. D. Sunko, Professor B. Težak.

Oral examination: December 18, 1963. Degree conferred: January 25, 1964.

Thesis deposited at the University Library and Institute »Ruder Bošković«, Zagreb.

(84 pages, 7 figures, 8 tables, 74 references, original in Croatian)

L. KLASINC

DCC-16

1. Nitrogen-15 Isotope Effect and Secondary Deuterium Isotope Effect in the Reaction of an Ammonium Salt with Base
 - I. Klasinc L.
 - II. Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

541.124:546.17.02:546.39-6

Elimination reactions
Mass-spectrometry
Co(III) complexes
2-Phenylethyltrimethyl-
ammonium iodide
Nitrogen-15 kinetic isotope effect
Secondary α -deuterium isotope effect

MCC-5

541.486.546.73:541.124

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

Kinetics and Mechanism of the Substitutions on Cobalt Octahedral Complexes. The Substitution of Chlorine by Thiocyanate in *trans*-[Coen₂(NH₃)Cl]⁺⁺ Ion in Methanol

M. Papić

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

The Werner's procedure for the preparation of *trans*-[Coen₂(NH₃)Cl]Cl₂ was modified since it was found that this procedure does not yield a correct product.

The rate of replacement of chlorine in *trans*-[Coen₂NH₃Cl]Cl₂ by thiocyanate in methanolic solution was measured and it was found that the specific rate is practically independent on the thiocyanate ion concentration which excludes the S_N2 replacement mechanism. The specific rates vary with hydrogen ion concentration and nearly linear dependence was obtained by plotting the specific reaction rates *versus* reciprocal perchloric acid concentration. It was concluded that in basic, neutral and weakly acid solutions the replacement of chlorine by thiocyanate ion proceeds with methoxide ion participation. At elevated temperatures the amino group can be also replaced by thiocyanate giving dithiocyanato complex ion, but this substitution is a much slower process than the chlorine substitution.

Examiners: Professor S. Ašperger, Professor B. Težak, Doc. C. Djordjević.

Oral examination: April 4, 1964.

Thesis deposited at the University Library, Zagreb.

(53 pages, 10 figures, 44 references, original in Croatian)

M. PAPIĆ

MCC-5

1. Kinetics and Mechanism of the Substitutions on Cobalt Octahedral Complexes. The Substitution of Chlorine by Thiocyanate in *trans*-[Coen₂(NH₃)Cl]⁺⁺ Ion in Methanol

I. Papić M.

II. Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

541.486:546.73:541.124

Cobalt(III) complexes
Diisothiocyanatobis(ethylenediamine)cobalt(III) ion
Isothiocyanatoaminobis-ethylenediamine)cobalt(III) ion
Substitutions in octahedral cobalt(III) complexes
trans-Chloroaminobis(ethylenediamine)cobalt(III) chloride

MCC-6

541.486:546.73:541.124

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

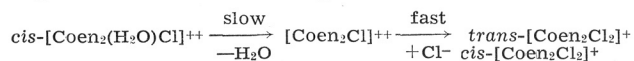
Kinetics, Mechanism and Stereochemistry of Substitutions on Cobalt Octahedral Complexes. The Conversion of *cis*-[Coen₂(H₂O)Cl]Cl₂ to *trans*-[Coen₂Cl₂]Cl in Methanolic and Ethanolic Medium

M. Flögel

Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute of Physical Chemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

In studying the mechanism of replacement of X of [Coen₂AX] ion by nucleophilic reagents in non-aqueous media it was found that the replacement of chlorine of *cis*-[Coen₂(H₂O)Cl]⁺⁺ by a nucleophilic reagent does not take place in methanolic and ethanolic solutions (as it does in aqueous solution) because in alcoholic solutions covalently bounded water is replaced by anion of the complex salt. The replacement proceeds with the change of the stereo-configuration. E. g. violet *cis*-[Coen₂(H₂O)Cl]Cl₂ converts quantitatively to green *trans*-[Coen₂Cl₂]Cl in methanol and ethanol.

The kinetics and mechanism of this reaction was studied spectrometrically and conductometrically. The reaction rate does not depend on the concentration of chlorine ion and shows the mass law retardation which is indicative of a dissociation mechanism. Observed kinetic data are in agreement with the following mechanism:



The specific reaction rates in methanolic and ethanolic solutions are nearly equal.

Examiners: Professor S. Ašperger Professor H. Iveković, Professor K. Weber.

Oral examination: June 6, 1964.

Thesis deposited at the University Library, and at the Faculty of Pharmacy and Biochemistry, University of Zagreb.

(58 pages, 12 figures, 30 references, original in Croatian)

M. FLÖGEL

MCC-6

541.486:546.73:541.124

1. Kinetics, Mechanism and Stereochemistry of Substitutions on Cobalt Octahedral Complexes. The Conversion of *cis*-[Coen₂(H₂O)Cl]Cl₂ to *trans*-[Coen₂Cl₂]Cl in Methanolic and Ethanolic Medium

cis-Chloroquoobis (ethylenediamine) cobalt (III) chloride
Cobalt (III) complexes
Substitutions in octahedral cobalt (III) complexes
trans-Dichlorobis (ethylenediamine) cobalt (III) chloride

I. Flögel M.

II. Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute of Physical Chemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

MCC-7

541.486:546.73:541.124

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

Kinetics, Mechanism and Stereochemistry of Octahedral Substitutions on Cobalt Complexes. The Influence of the Solvent on the Substitution of Chlorine by Thiocyanate in *trans*-[Coen₂(NO₂)Cl]NO₃

V. Reić

Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

The rate of replacement of chlorine of *trans*-[Coen₂(NO₂)Cl]⁺ ion by thiocyanate in absolute ethanol was measured and compared with the rate of the analogous reaction in methanol. The rate in ethanol is approximately 1.22 times slower than in methanol. The rates of replacements in both alcohols are independent of the thiocyanate ion concentration.

The rates of replacement of chlorine of *trans*-[Coen₂Cl]⁺ ion by thiocyanate ion in methanol and ethanol were also determined and it was found that the replacement reaction in ethanol is 1.48 times slower than in methanol. Since the substitution of chlorine in dichloro-complex is generally considered to be S_N1 reaction it is likely that the substitution of chlorine in nitro-chloro complex is basically of the same type. This should mean that the nitro group has not the analogous directing effects in octahedral substitutions as it has in organic substitution reactions.

Examiners: Professor S. Ašperger, Professor H. Iveković, Doc. M. Pećar.

Oral examination: October 8, 1964.

Thesis deposited at the University Library, and at the Faculty of Pharmacy and Biochemistry, University of Zagreb.

(41 pages, 8 figures, 25 references, original in Croatian)

V. REIC

MCC-7

541.486:546.73:541.124

1. Kinetics, Mechanism and Stereochemistry of Octahedral Substitutions on Cobalt Complexes. The Influence of the Solvent on the Substitution of Chlorine by Thiocyanate in *trans*-[Coen₂(NO₂)Cl]NO₃

I. Reić V.

- II. Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb Zagreb, Croatia, Yugoslavia

Cobalt(III) complexes
Substitutions in octahedral cobalt(III) complexes
trans-Chloroisothiocyanatobis(ethylenediamine)cobalt(III) ion
trans-Dichlorobis(ethylenediamine)cobalt(III) chloride
trans-Dichlorobis(ethylenediamine)cobalt(III) nitrate

MCC-8

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*Master of Science Thesis**Croat. Chem. Acta* **37** (1965)**Kinetics and Mechanism of the Substitutions on Cobalt Octahedral Complexes. The Substitution of Chlorine by Azide Ion in *trans*-[Coen₂(NO₂)Cl]NO₃***M. Pribanić**Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute of Physical Chemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia*

The replacement of chlorine of *trans*-[Coen₂(NO₂)Cl]⁺ by azide ion in absolute methanol was studied spectrometrically and was found that the replacement proceeds with retention of configuration. The specific reaction rate is nearly independent of the azide ion concentration which strongly suggests that azide does not participate in the transition state of the reaction.

The specific rate was found to be equal to that of the replacement of chlorine by thiocyanate and chloride-36, respectively, though the azide ion is a stronger nucleophile than chloride and thiocyanate. These results exclude the S_N2 replacement mechanism.

Examiners: Professor S. Ašperger, Professor H. Iveković, Professor K. Weber.

Oral examination: November 10, 1964.

Thesis deposited at the University Library, and at the Faculty of Pharmacy and Biochemistry, University of Zagreb.

(54 pages, 4 figures, 51 references, original in Croatian)

M. PRIBANIĆ

MCC-8

541.486:546.73:541.124

I. Kinetics and Mechanism of the Substitutions on Cobalt Octahedral Complexes. The Substitution of Chlorine by Azide Ion in *trans*-[Coen₂(NO₂)Cl]NO₃

I. Pribanić M.

II. Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute of Physical Chemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

Azidonitrobis(ethylenediamine)cobalt(III) azide
Cobalt(III) complexes
Substitutions in octahedral cobalt(III) complexes
trans-Chloronitrobis(ethylenediamine)cobalt(III) nitrate

MCC-9

541.486:541.124.03

*Master of Science Thesis**Croat. Chem. Acta* **37** (1965)**Studies on Octahedral Complexes and Mass-Spectrometry of Solids**

M. Vidović

Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

The rate of aquation of *trans*-[Coen₂(NO₂)Cl]⁺ ion in solvent formic acid was studied spectrometrically. Formic acid was dried with boron trioxide and known quantities of water were added. The reaction proceeded with complete retention of configuration. The product was *trans*-[Coen₂(NO₂)(H₂O)]⁺⁺ ion. The reaction rate increased almost proportionally with the water concentration in the whole concentration range from zero up to 100 per cent of water. These results suggest that the aquation is a second order reaction and bimolecular (S_N2). This conclusion is a part of a general mechanistic account of reactions of the complexes Coen₂AX where A was varied in order of the decreasing electron donating power, from OH over NCS to NO₂, which seemed to change the mechanism from S_N1 to S_N2, but no direct evidence for the mechanism of the aquation of the nitro-chloro complex ion was reported as yet.

In the second part of the thesis the mass-spectrometric determinations of the ratios of the cadmium isotopes were determined after electrophoresis of cadmium halides samples*. The measurements could not show significant separations of cadmium isotopes in the samples investigated.

Examiners: Professor S. Ašperger, Professor H. Iveković, Doc. M. Pečar.

Oral examination: January 28, 1965.

Thesis deposited at the University Library, and at the Faculty of Pharmacy and Biochemistry, University of Zagreb.

(62 pages, 14 figures, 23 references, original in Croatian)

M. VIDOVIĆ

* Samples were analyzed for Dr. Z. Pučar, Institute »Ruder Bošković«, who did the electrophoretic experiments.

MCC-9

541.486:541.124.03

1. Studies on Octahedral Complexes and Mass-Spectrometry of Solids

I. Vidović M.

II. Department of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, and Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

Cadmium

Cobalt(III) complexes

Mass-spectrometry of solids

Substitutions in octahedral cobalt(III) complexes

trans-Chloronitrobis(ethylenediamine)cobalt(III) nitrate

trans-Nitroaquobis(ethylenediamine)cobalt(III) ion

MCC-10

541.082

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

A New Apparatus for Dielectric Constant Determination

Z. Balenović

*Institute of Inorganic and Physical Chemistry, Faculty of Pharmacy
and Biochemistry, Zagreb, Croatia, Yugoslavia*

A new apparatus for dielectric constant determination was constructed. The modification of Jones's method for measurement of small capacities is employed, where R. F. - voltage is imposed on the combination of an unknown capacity and a small capacity of known value. A part of R. F. - voltage appearing on the unknown capacity was measured, and the value of unknown capacity was determined by the substitution method. The advantages of this method are its simplicity and its being independent of the frequency. The application is limited, similarly to the resonance method, to low conductivity samples. The precision obtained is equal to that of the other commercial apparatus.

Examiners: Prof. H. Iveković, Prof. B. Lovreček, Prof. S. Ašperger.

Oral examination: January 30, 1964.

Thesis deposited at the University Library and Faculty of Pharmacy and Biochemistry, Zagreb.

(60 pages, 19 figures, 50 references, original in Croatian)

Z. BALENOVIĆ

MCC-10

541.082

1. A New Apparatus for Dielectric Constant Determination

Dielectric constant
— , apparatus for

I. Balenović Z.

II. Institute of Inorganic and Physical Chemistry, Faculty of Pharmacy and Biochemistry, Zagreb, Croatia, Yugoslavia