Ligand Substitution at a Hexa-coordinate Centre.
Part IV. A Kinetic Study of the Reaction of $[Co_2(Et_2dtc)_5] BF_4$ with some Ethylenediamines

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The kinetics of the reaction of $[Co_2(Et_2dtc)_5]$- BF_4 with some N-substituted ethylenediamines has been investigated in CH_2Cl_2 medium by means of spectrophotometric measurements. The results according to those obtained using dithio-oxamides as incoming ligands show that the mechanism involves a rapid equilibrium between the substrate and an intermediate in which $Co(Et_2dtc)_3$ is one-end linked to a $Co(Et_2dtc)_2^+$ unit. This intermediate then undergoes a bimolecular attack from the nucleophilic ligands. The rate constants, related to the substitution reaction by ethylenediamines, are higher than those related to the dithio-oxamides, in agreement with their higher basicity. Moreover a steric effect of the entering group has been demonstrated, since for N-substituted ethylenediamines with nearly the same acid–base dissociation constants we have observed a lowering of the rate constants when the steric bulkiness of the ligands increases.

Introduction

The kinetic studies of octahedral substitution on Co(III) substrates showed that their rates are normally insensitive to most entering ligands [1, 2]. These reactions were generally studied in aqueous or alcoholic solvents, which are simultaneously solvents and nucleophiles. Since any coordinating solvent becomes the most important reactant because of its advantages of continual encounter with the substrate, the role of the entering group may be studied in non-coordinating solvents. Being inert and soluble in CH_2Cl_2, the $[Co_2(Et_2dtc)_5]BF_4$ substrate is suitable for this kind of analysis.

We have recently demonstrated [3] that the substitution reaction of some dithio-oxamides on the above substrate proceeds in CH_2Cl_2 and in CH_2Cl_2/CH_3OH mixtures, with the mechanism given below.

We report here on the reaction of the same complex with some ethylenediamines. In view of studying the entering group effect, we have chosen some N-substituted ethylenediamines with nearly the same basicity but increasing bulkiness on the N atoms. They were: unsubstituted ethylenediamine = H_2enH_2; N-methyl-ethylenediamine = $HMeenH_2$; N-ethyl-ethylenediamine = $HEtenH_2$; N-iso-propyl-ethylenediamine = $HisoPrenH_2$; N,N'-dimethyl-ethylenediamine = $HMeenMeH$; N,N'-diethylethylenediamine = $HEtenEtH$.

Experimental

Reagents

The $[Co_2(Et_2dtc)_5]BF_4$ complex [4] was prepared as described in the literature. The ethylene-

S = dichloromethane
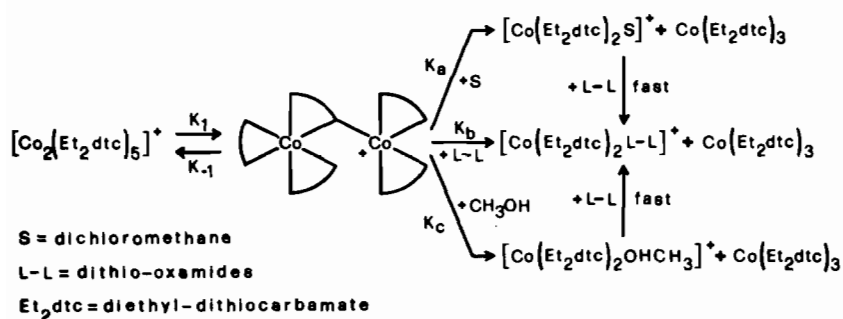L–L = dithio-oxamides
Et_2dtc = diethyl-dithiocarbamate

TABLE I. Rate Constants for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\cong 3 \times 10^{-4}$ M) and H_2enH_2 in CH_2Cl_2. $k_I = sec^{-1}$; $k_{II} = mol^{-1}$ $1 sec^{-1}$. Activation parameters related to k_{II} are calculated from Eyring plot.

10 °C		15 °C		20 °C		25 °C		30 °C	
a	b	a	b	a	b	a	b	a	b
5.99	1.91 ± 0.02	6.95	3.25 ± 0.03	5.99	5.00 ± 0.04	7.48	10.6 ± 0.1	5.99	13.8 ± 0.1
11.97	3.22 ± 0.06	13.90	5.91 ± 0.04	11.97	8.96 ± 0.06	12.87	16.8 ± 0.1	11.97	21.8 ± 0.2
17.96	4.21 ± 0.02	20.86	8.61 ± 0.08	24.44	16.9 ± 0.1	17.46	23.1 ± 0.1	17.96	28.5 ± 0.3
24.44	5.21 ± 0.05	27.81	10.4 ± 0.2			24.94	30.0 ± 0.2	24.44	36.0 ± 0.3

$k_I = (7 \pm 1) \times 10^{-5}$ $(1.0 \pm 0.4) \times 10^{-4}$ $(1.2 \pm 0.1) \times 10^{-4}$ $(2 \pm 1) \times 10^{-4}$ $(7.0 \pm 0.6) \times 10^{-4}$

$k_{II} = (1.85 \pm 0.08) \times 10^{-2}$ $(3.5 \pm 0.2) \times 10^{-2}$ $(6.44 \pm 0.06) \times 10^{-2}$ $(1.12 \pm 0.06) \times 10^{-1}$ $(1.19 \pm 0.03) \times 10^{-1}$

$r = 1.000$ 0.996   1.000   0.997   0.999

$\Delta H^{\neq} = 16 \pm 1$ $Kcal$ mol^{-1}; $\Delta S^{\neq} = -9 \pm 5$ cal K^{-1} mol^{-1}; $r = 0.98$

a $= 10^3$ $[en]$ $(mol$ $1^{-1})$

b $= 10^4$ k_{obs} (sec^{-1}); $r =$ correlation coefficients were alwyas 0.998 or better.

TABLE II. Rate Constants and Reaction Conditions for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\cong 3 \times 10^{-4}$ M) and Some Ethylenediamines in CH_2Cl_2 at 25 °C. Correlation coefficients are always 0.999 or better.

Ligand	10^3 $[en]$ $(mol$ $1^{-1})$	10^4 k_{obs} (sec^{-1})
HMeenH₂	19.67	16.5 ± 0.1
	27.54	21.7 ± 0.1
	37.38	29.0 ± 0.2
HMeenMeH	6.31	4.87 ± 0.05
	12.62	8.22 ± 0.08
	22.08	12.4 ± 0.1
	29.97	17.5 ± 0.1
HEtenH₂	9.49	7.0 ± 0.1
	15.82	10.1 ± 0.1
	22.15	14.5 ± 0.1
	30.07	18.2 ± 0.2
HisoPrenH₂	8.12	6.1 ± 0.1
	13.54	9.5 ± 0.1
	18.95	11.9 ± 0.2
	25.72	15.3 ± 0.1
HEtenEtH	6.95	2.88 ± 0.03
	11.59	3.85 ± 0.04
	16.22	4.7 ± 0.1
	22.01	5.98 ± 0.04

diamines were FLUKA reagent grade and were used after column distillation.

The $[Co(Et_2dtc)_2en]BF_4$ complexes were isolated and characterized as reported in part III [5]. The dichloromethane was Merck analytical reagent grade and was purified as described in part I [3].
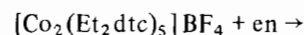
Spectrophotometric Measurements

The reaction was followed on a Perkin Elmer UV-vis mod. 402 spectrophotometer by monitoring the changes in absorbance at a wavelength at which (ϵ products $-$ ϵ reagent) is large (576 nm was a suitable value in all cases) and by using 1 cm glass cells thermostatted at the chosen temperature (±0.1 °C).

At zero time the ethylenediamine was added by means of a Hamilton microsyringe to the prethermostatted solution of $[Co_2(Et_2dtc)_5]BF_4$, directly in the cell. The absorbance values at infinite time (A_∞) were read experimentally and agreed with those calculated from the starting complex concentration multiplied by the molar extinction coefficients of the two products at the chosen wavelength.

Results and Discussion

The kinetics of the substitution reaction:

$[Co_2(Et_2dtc)_5]BF_4 + en \rightarrow$

$$[Co(Et_2dtc)_2en]BF_4 + Co(Et_2dtc)_3$$

where en = ethylenediamines, has been investigated in CH_2Cl_2 medium by spectrophotometric measurements in pseudo first-order condition.

The observed rate constants, k_{obs}, obtained as slopes of straight lines, $\ln(A_\infty - A_t)$ against time (see Tables I and II), obey a two term rate law: $k_{obs} = k_I + k_{II}[en]$.

TABLE III. k_I and k_{II} Values at 25 °C for the Substitution Reactions between $[Co_2(Et_2dtc)_5]BF_4$ ($\cong 3 \times 10^{-4}$ *M*) and Some Ethylenediamines in CH_2Cl_2 at 25 °C.*

Ligand	$10^4 k_I$ (sec^{-1})	$10^2 k_{II}$ (mol^{-1} l sec^{-1})	pK$_{A1}$[a]
H$_2$enH$_2$	2 ± 1	11.2 ± 0.6	9.93
HMeenH$_2$	2.5 ± 0.7	7.1 ± 0.2	10.40
HMeenMeH	1.5 ± 0.6	5.2 ± 0.3	10.29
HEtenH$_2$	1.7 ± 0.6	5.6 ± 0.3	10.56
HisoPrenH$_2$	2.2 ± 0.4	5.2 ± 0.2	10.62
HEtenEtH	1.5 ± 0.1	2.1 ± 0.1	10.46

*Correlation coefficients were always 0.997 or better.
[a]References [7] and [8].

By plotting the k_{obs} against the en concentration, k_I and k_{II} were identified as intercepts and as slopes of straight lines respectively (see Tables I and III).

The obtained results, when en = H$_2$enH$_2$, are listed in Table I together with the activation parameters related to k_{II}. Using 0.025/1% vol. CH$_3$OH/CH$_2$Cl$_2$ mixtures as solvent, a linear dependence of the k_{obs} against the CH$_3$OH concentration was obtained: the slope gives k_I^1, and the intercept on the y axis is k_{obs} in absence of CH$_3$OH (Fig. 1).

Comparing these results with those reported when we used dithiooxamides as incoming ligands [3], we observed that:

1) the rate constants k_I fall in the same range obtained for dithio-oxamides, but their values are affected by a larger error, their contribution to the k_{obs} being even lower than in the DTO case.

2) The rate constants k_{II} are about ten times larger on going from DTO to H$_2$enH$_2$, and the activation parameters agree with those reported for the dithio-oxamides.

3) Also the k_I^1 value is in accordance with that previously obtained for the dithio-oxamides.

From this we can see that mechanism (1) is proved further (see discussion in part II) and that it fits the experimental data if L—L = substituted ethylenediamine.

Under steady-state conditions [6] the overall reaction follows pseudo first order kinetics with:

$$k_{obs} = \frac{k_1 K_a[S]}{k_{-1}} + \frac{k_1 K_c[CH_3OH]}{k_{-1}} + \frac{k_1 K_b[en]}{k_{-1}}$$

where

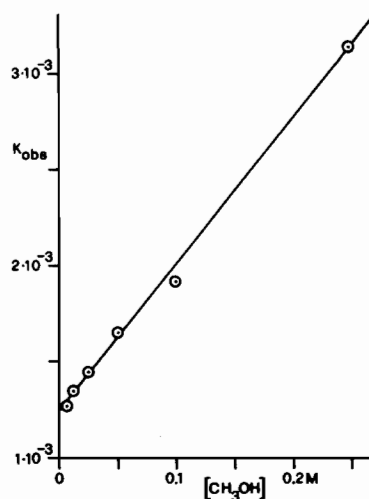$$k_I = \frac{k_1 K_a[S]}{k_{-1}}; \quad k_{II} = \frac{k_1 K_b}{k_{-1}}; \quad k_I^1 = \frac{k_1 K_c}{k_{-1}}$$

Fig. 1. Pseudo-first-order rate constants for the reaction between $[Co_2(Et_2dtc)_5]BF_4$ and H$_2$enH$_2$ ($[H_2enH_2]$ = 9.98 × 10^{-3} mol l^{-1}) in CH$_2$Cl$_2$ as a function of [CH$_3$OH] at 25 °C. Intercept = (12.4 ± 0.2) × 10^{-4} sec^{-1}; slope = k_I^1 = (7.6 ± 0.2) × 10^{-3} sec^{-1} mol^{-1} l (r = 0.998).

Both a dissociative and an associative process contribute to define the constants.

Using N-substituted ethylenediamines with nearly the same acid—base dissociation constants [7, 8] we obtained the rate constants listed in Tables II and III. As expected the k_I values are all of the same order of magnitude, but k_{II} present lowering values as the bulkiness on N atoms increases. It may be admitted that K_b is determined by the first attack of either of the two N atoms of the chelating ligand, and that the closure of the ring is a fast process.

If so each $\rangle$N-group should contribute to define k_{II} with its own specific rate. Now these contributions are easily obtained in symmetrical ethylenediamines [9], being

$$\frac{k_{II}}{2}$$

and if the groups retain their own specific rates unchanged, even if contained in different molecules, these rates may be used to predict k_{II} in unsymmetrical ethylenediamines. Using the partial contribution of H$_2$enH$_2$ and HRenRH we obtained k_{II} = 6.7 × 10^{-2} for HMeenH$_2$ and k_{II} = 8.1 × 10^{-2} for HEtenH$_2$.

The experimental values are slightly lower than calculated. Moreover k_{II} related to H-isoPrenH$_2$ is about fifty percent lower than that related to H$_2$-enH$_2$.

The small differences between the calculated and experimental rate constants (see Table III) should take into account the differences in the reactivity

of each group when it is contained in different molecules (due to steric, electronic and solvatation effects, *etc.*).

However an alternative mechanism may be proposed. If the closure of the chelating ring is not a fast process, the contribution related to this step would affect k_{II}. The first hypothesis seems more convincing to us, since the closure of the chelating ring is generally reported [10–12] as a fast process because it does not require further collision between the reactants. Exceptions are reported when the chelating ligand has one of its coordination sites in an unreactive form [13], but all coordination sites are active in the substituted ethylenediamines of this paper.

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