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Mechanism of Octahedral Substitution in non Aqueous Media. I. Isotopic Exchange Reactions of Chloride-36 in *Trans*-Chlorocyanobis(ethylenediamine)Cobalt(III) Cation in Methanol, Dimethylsulfoxide, Ethylene Glycol and N,N-Dimethylformamide

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The first order rate constants of chloride-36 exchange in trans-$[Coen_2CNCl]^+$ *are independent on LiCl concentration in the solvents methanol, dimethylsulfoxide (DMSO), and ethylene glycol, while in dimethylformamide (DMF) the first order rate constants for isotopic exchange are higher than those obtained with other solvents studied and dependent on LiCl concentration in the range* 10^{-3}–10^{-2} *M.*

The activation parameters are $E_a = 21.32$ *Kcal/mol,* $\Delta S^{\ddagger} = -10.94$ *cal* K^{-1} *mol*$^{-1}$*,* $A = 2 \times 10^{10}$ *sec*$^{-1}$ *in methanol;* $E_a = 20.13$ *Kcal/mol,* $\Delta S^{\ddagger} = -12.94$ *cal* K^{-1} *mol*$^{-1}$*,* $A = 8.6 \times 10^{9}$ *sec*$^{-1}$ *in DMSO;* $E_a = 21.96$ *Kcal/mol,* $\Delta S^{\ddagger} = -3.98$ *cal* K^{-1} *mol*$^{-1}$*,* $A = 7 \times 10^{11}$ *in ethylene glycol;* $E_a = 32.5$ *Kcal/mol,* $\Delta S^{\ddagger} = +35.5$ *cal* K^{-1} *mol*$^{-1}$*,* $A = 3 \times 10^{20}$ *sec*$^{-1}$ *in DMF. Bearing in mind that methanol and DMSO are good solvating agents, while ethylene glycol is not, we propose an associative interchange* I_a *stoichiometric mechanism,* via *solvation reaction, in methanol and DMSO, and a dissociative interchange stoichiometric mechanism in ethylene glycol. In DMF the results are consistent with the formation of a strong ion-pair between chloride and* trans-*chlorocyanobis(ethylenediamine)cobalt(III) ions K(IP) = 1870 mol*$^{-1}$ *and seems to indicate the presence of a stoichiometric mechanism of interchange I, where the ion-pair is the activated complex in the transition state. Within the ion-pair the intimate mechanism of isotopic exchange is probably of* I_d *type. Thus we have found that for the complex* trans-$[Coen_2LCl]^+$ *the role of L = CN is not solvent independent.*

Introduction

Ligand substitution reactions in complexes of the general formula $[Coen_2LX]^{n+}$ (where X is the ligand undergoing substitution) in non aqueous media, have been examined to establish whether such reactions are subject to the same distinction that characterizes acid hydrolysis in these species, on the basis of the nature of the non labile ligand L. Indeed, whenever L is an electron donor by way of back donation of π electron, acid hydrolysis through an S_N1 type mechanism is assisted, whenever L is an electron acceptor an S_N2 mechanism prevails [1].

Asperger *et al.* [2] have investigated substitution reactions where Cl^- is replaced by various nucleophiles: NO_2^-, N_3^-, NCS^- within the complex *trans*-$[Coen_2LCl]^{n+}$ where L = NO_2, N_3, CN, and NCS, in methanol. The relative rate of the substitution reaction of chlorine with nitrite, azide, and thiocyanate, is the same in methanol and in water. The electronic effects of directing ligands Ls observed in acid hydrolysis reactions are observed in anionic substitution reactions in methanol as well. These authors deduce from this behaviour that the role of L is solvent independent since similar effects were already observed in dimethylformamide [3] for complexes of formula *trans*-$[Coen_2LCl]^{n+}$ with L = Cl and NO_2.

Non aqueous solvents are well suited for studying the labilizing effect of the directing ligand situated in trans with respect to the labile partner in the octahedral coordination configuration [4].

Preliminary investigations carried out on isotopic exchange reactions between *trans*-$[Coen_2CNCl]^+$ and LiCl with either reagent labelled by ^{36}Cl in the solvents methanol, dimethylsulfoxide, ethylene glycol, and dimethylformamide, have shown that when the ligand CN is involved its role is not solvent independent, but rather different mechanisms seem to be at play in the isotopic exchange reaction depending on the particular solvent utilized.

We have investigated in detail this type of reaction in methanol, and have compared the results obtained with the ones relative to isotopic exchange, in the same solvent, between ^{36}Cl labelled chloride and *trans*-$[Coen_2NO_2Cl]^+$ [5] and *trans*-$[Coen_2Cl_2]^+$ [6] respectively. The study has also been extended to include solvents dimethylsulfoxide and ethylene glycol, so as to allow a comparison with the results reported in [7] regarding chlorine substitution reactions in dichloro- and chloronitro-complexes, and to dimethylformamide, so as to allow a similar comparison with the results reported in [3].

A detailed analysis of the various sets of data shows that a wide gamut of rate constants and of activation related thermodynamical parameters is covered by the compounds examined.

Experimental

Trans-chlorocyanobis(ethylenediamine)cobalt(III) nitrate was prepared according to the method observed in [8], purified and analysed. Lithium chloride was purified and dehydrated by fusion with ammonium chloride. Both compounds were alternatively radioactivated through exchange with $H^{36}Cl$ of high specific activity.

Kinetic experiments

The initial radioactivity of the lithium chloride labelled with ^{36}Cl was determined adding $AgNO_3$ to an aqueous solution of the chloride acidified with nitric acid. The precipitate $Ag^{36}Cl$ was filtered and washed with water, then diluted HNO_3 and zinc in grains were added. Addition of $Hg_2(NO_3)_2$ to the acid solution obtained produced a precipitate of Hg_2Cl_2, which was washed with water, suspended in acetone and finally deposited on plastic discs of predetermined area. Radioactivity measurements were carried out by means of a solid sample G. M. counter. The saturation curve of these samples of calomel has been determined reporting the activity in cts/min *vs.* weight of calomel deposited on the plastic discs. Since the saturation value corresponds to 150 mg of calomel, a quantity which does not allow to obtain samples of the desired surface homogeneity and constant area, we have preferred to express the specific activity through cts min^{-1} mg^{-1} for samples of weight lower than 10 mg, using the proportionality range of the saturation curve.

Little quantities of the reaction mixture, sampled at given times, were treated with 70% $HClO_4$. The precipitate perchlorate of the cobalt(III) complex was filtered, washed with water, and treated with concentrated HNO_3 and $AgNO_3$ solution. Heating of the mixture led to precipitation of AgCl containing the chloride ion initially present as ligand in the complex, and not radioactive at the beginning of the experiment. Silver chloride was transformed into Hg_2Cl_2 according to the procedure described above thus obtaining a series of samples of increasing radioactivity from zero to A_∞, A_∞ being the radioactivity that corresponds to the equilibrium isotopic distribution. In Fig. 1 is presented a typical exchange experiment. It shows that a simple isotopic exchange reaction without an apparent zero-time exchange is operative.

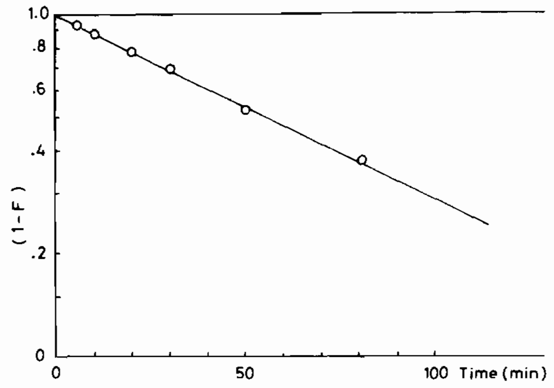


Fig. 1. Typical exchange experiment in 5.57 × 10^{-4} *M trans*-$[Coen_2CN^{36}Cl]^+$ and 10^{-3} *M* LiCl in DMF at 25 °C. Observed time of half-exchange 57 min.

From the original reaction mixture, after precipitation of the complex perchlorate, the chloride ion which was initially radioactive was precipitated by adding a solution of $Hg_2(NO_3)_2$ acidified with HNO_3. A series of calomel samples for which the radioactivity decreased from A_0 to A_∞, A_0 being the initial radioactivity, with the advancement of the exchange reaction was thus obtained. Samples of calomel containing chlorine originally present as ligand, and chlorine originally present as chloride ion, corresponding to the same reaction time, were checked for total specific radioactivity equal to the initial radioactivity of $Li^{36}Cl$ (A_0).

Results

Methanol

As it appears from the data in Table I the rate constant for isotopic exchange in methanol is independent on LiCl concentration within the interval 1–7 × 10^{-3} *M* (and also independent on acidity as for the *trans*-$[Coen_2NO_2Cl]^+$ [5]). Activation energy is found to be E_a = 21.32 Kcal/mol, activation entropy $\Delta S^\ddagger$ = −10.94 cal K^{-1} mol^{-1}, and frequency factor A = 2 × 10^{10} sec^{-1}.

TABLE I. First Order Constants for the Chloride-36 Exchange in 1.36 × 10^{-3} *M trans*-$[Coen_2CNCl]^+$ in Methanol.

No.	10^3[LiCl]	t °C	10^5k sec^{-1}
1	1.36	25	0.51
2	1.36	30	1.06
3	1.36	40	2.87
4	2.72	40	2.80
5	6.80	40	2.86
6*	1.36	40	3.11
7	1.36	50	9.55

*Acid solution for $HClO_4$.

Dimethylsulfoxide

From Table II one sees that the rate constant for isotopic exchange in DMSO is independent on LiCl concentration in the range 8.3–41.5 × 10^{-3} *M*. Probably in this range the reagents are completely associated as ion-pairs as verified by Tobe [9] for the system *trans*-$[Coen_2Cl_2]^+$–Cl^- in DMSO. The rate constants for isotopic exchange in the latter solvent are slightly higher than in methanol. Activation energy E_a = 20.13 Kcal/mol, activation entropy $\Delta S^\ddagger$ = –12.74 cal K^{-1} mol^{-1}, and frequency factor A = 8.6 × 10^9 sec^{-1} are obtained.

TABLE II. First Order Constants for the Chloride-36 Exchange in 8.3 × 10^{-4} *M* *trans*-$[Coen_2CNCl]^+$ in Dimethylsulfoxide.

No.	10^3[LiCl]	t °C	10^5k sec^{-1}
1	8.3	25	1.58
2	8.3	30	2.57
3	8.3	40	7.41
4	16.6	40	7.40
5	41.5	40	7.43
6	8.3	50	20.89

Ethylene glycol

Table III shows that the rate constant for isotopic exchange in ethylene glycol is independent on LiCl concentration in the range 5.41–82 × 10^{-3} *M*. Higher rate constants are found here than in the solvents methanol and DMSO. The values of the rate parameters are E_a = 21.96 Kcal/mol, $\Delta S^\ddagger$ = –3.98 cal K^{-1} mol^{-1}, A = 7 × 10^{11} sec^{-1}.

TABLE III. First Order Constants for the Chloride-36 Exchange in 5.41 × 10^{-3} *M* *trans*-$[Coen_2CNCl]^+$ in Ethylene Glycol.

No.	10^3[LiCl]	t °C	10^5k sec^{-1}
1	5.41	25	5.62
2	5.41	30	8.81
3	5.41	40	37.33
4	27.10	40	37.65
5	82.31	40	38.01
6	5.41	50	87.51

Dimethylformamide

The visible absorption spectrum of a solution of the complex in DMF, measured at the highest temperature explored and over a length of time equal to the maximum time necessary for isotopic exchange experiments, remains unaltered and identical to the one observed on an aqueous solution of the complex, freshly prepared. This behaviour allows the ruling out of any chemical transformation that might, in principle, be expected to take place during isotopic exchange experiments, *e.g.* *cis–trans* isomerization of the complex or solvolysis of the complex giving rise to a stable $[Coen_2CN(DMF)]^{2+}$ species. In Table IV are collected the results obtained in a series of isotopic exchange experiments in DMF over the temperature range 20–40 °C with constant concentration of reagents. From the k_{obs} *vs.* 1/T plot, activation energy E_a = 32.5 Kcal/mol, activation entropy $\Delta S^\ddagger$ = +35.5 cal K^{-1} mol^{-1}, and frequency factor A = 3 × 10^{20} sec^{-1} obtain. When reported against LiCl concentration, as shown in Table V, the isotopic exchange rate constant appears to be a function of concentration over the range 0 to 4 × 10^{-3} *M*. Such

TABLE IV. First Order Constants of Chloride-36 Exchange by 0.01 *M* LiCl in 5.57 × 10^{-4} *M* *trans*-$[Coen_2CN^{36}Cl]^+$ Ion in DMF.

No.	t °C	10^4k_{obs} sec^{-1}
1	20	2.11
2	25	4.42
3	30	13.03
4	35	34.67
5	40	63.09

TABLE V. First Order Constants of Chloride-36 Exchange in 5.57 × 10^{-4} *M* *trans*-$[Coen_2CN^{36}Cl]^+$ Ion in DMF at 25 °C.

No.	10^3[LiCl]	10^4k_{obs} sec^{-1}
1	1.0	1.30
2	2.0	2.45
3	4.0	3.81
4	4.7	4.14
5	6.0	4.20
6	7.5	4.30
7	10.0	4.30

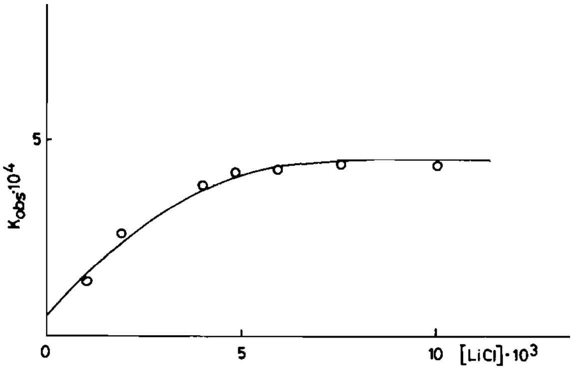
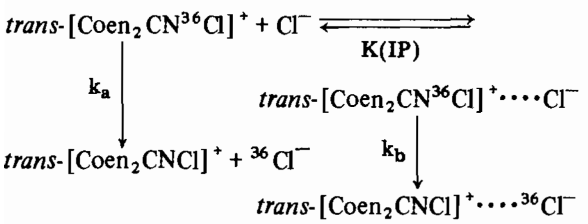


Fig. 2. Rates of chloride-36 exchange reactions in 5.57 × 10^{-4} *M* *trans*-$[Coen_2CNCl]NO_3$ in DMF at 25 °C.

dependence is also illustrated in Fig. 2, and the profile of the curve is found to be similar to the one observed by other authors [6] in cases where nucleophilic substitution reactions in non aqueous media occur with an ion association pre-equilibrium. In view of this similarity we can propose for the present case the following mechanism:



The rate equation for isotopic exchange, as obtained from the experimental data with the aid of McKay's equation, can be thus formulated:

$$R = k_a[C] + k_b[IP] \qquad (1)$$

where R is the rate of the isotopic exchange, [C] the concentration of the complex in its free-ion configuration and [IP] is the concentration of the complex in the ion-pair configuration. The equilibrium constant for ionic association is:

$$K = \frac{[IP]}{[C][Cl^-]} \qquad (2)$$

If $[C^x]$ is the initial concentration of the complex, it follows that:

$$[C^x] = [C] + [IP] = [C] + K[C][Cl^-]$$

$$[C] = \frac{[C^x]}{1 + K[Cl^-]} \qquad (3)$$

If the initial concentration of Cl^- ions is high enough for the relation $[Cl^-] = [LiCl]$ to hold, it follows that

$$R = k_a\frac{[C^x]}{1 + K[LiCl]} + k_b\frac{[C^x][LiCl]K}{1 + [LiCl]} \qquad (4)$$

Since in every isotopic exchange experiment [LiCl] stays constant with time (4) can be rewritten as:

$$R = k_{obs}[C^x] \qquad (5)$$

where

$$k_{obs} = \frac{k_a + Kk_b[LiCl]}{1 + K[LiCl]} \qquad (6)$$

Finally:

$$\frac{1}{k_{obs} - k_a} = \frac{1}{(k_b - k_a)K[LiCl]} + \frac{1}{k_b - k_a} \qquad (7)$$

The k_a value is the value of k_{obs} extrapolated to a zero concentration of LiCl in the curve of Fig. 3. Plotting $1/(k_{obs} - k_a)$ against $1/[LiCl]$ one obtains the straight line in Fig. 4 having a slope $1/(k_b - k_a)K$ and an intercept at the origin $1/(k_b - k_a)$. The points corresponding to low [LiCl] have not been plotted since in this region the approximation $[Cl^-] = [LiCl]$ is not valid. From the plot, at 25 °C, the following constants have been calculated: $K = 1870\ mol^{-1}$, $k_a = 4 \times 10^{-5}\ sec^{-1}$ and $k_b = 4.5 \times 10^{-4}\ sec^{-1}$ from which the rate equation (8) follows:

$$R = 4 \times 10^{-5}[C] + 4.5 \times 10^{-4}[IP] \qquad (8)$$

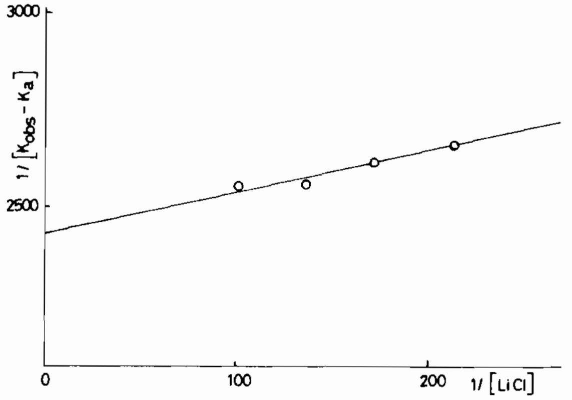


Fig. 3. Dependence of rate constant on dielectric constant

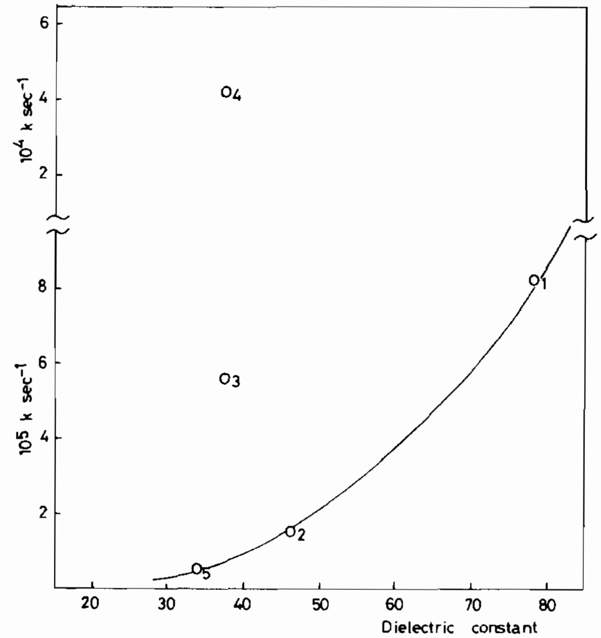


Fig. 4. Rates of isotopic exchange of chloride-36 in *trans*-$[\mathrm{Coen_2CNCl}]^+$ ion against dielectric constant of the solvents at 25 °C: 1, H_2O; 2, DMSO; 3, ethylene glycol; 4, DMF; 5, MeOH.

Discussion

In Fig. 4 the isotopic exchange rate constants for *trans*-[Coen$_2$CNCl]$^+$ are reported against the dielectric constants of the solvents at 25 °C for the four solvents investigated, along with the rate constant of acid hydrolysis as reported in [8]. The behaviour of the complex investigated here could be assimilated to the one observed for *trans*-dichloro in methanol, DMSO and water [7], leading to the conclusion that in the first two solvents, a dissociative interchange I$_d$ is operative here. Indeed the increase of rate constant with increasing dielectric constant of the medium indicates that the more dielectric solvent favours charge separation in the transition state. A different situation, on the other hand, prevails when the solvent is ethylene glycol. It is well known, that both methanol and DMSO are good solvating agents [9], while ethylene glycol is fairly inert with regard to solvation complexes formation. Furthermore the value of the rate constant of isotopic exchange between *trans*-[Coen$_2$CNCl]$^+$ and LiCl labelled with ^{36}Cl in DMF falls beyond the range of the other values, as shown in Fig. 4. In view of this the fitting of its data to the curve illustrated there would be meaningless. One can assume that two different mechanisms for isotopic exchange are operative in the solvents ethylene glycol on one side and methanol and DMSO on the other, the first being direct chloride exchange (*d* process), the latter chloride exchange by solvolysis-anation combination (*a* process). In particular we propose that in these two solvents an associative interchange I$_a$ takes place for which the rate determining step is solvation of the complex followed by fast anation reaction in agreement with the results obtained by Asperger for chloride exchange in *trans*-[Coen$_2$NO$_2$Cl]$^+$ [5].

The (–T) electromeric effect of cyano group and nitro group in *trans* with respect to the labile ligand should inhibit heterolysis of the Co–Cl bond, favour an *a* type substitution operated from the solvent.

The analysis of the results illustrated in Table VI shows that a different behaviour characterizes chloride exchange in the dichloro and in the chloro-cyano-complex respectively. In the first case, k_{obs} has the value intermediate between k_a and k_b, *i.e.* both isotopic exchange between free ions and isotopic exchange within an ion-pair give a contribution to k_{obs}, due to the low value of K(IP). In the second case, however, k_{obs} and k_b coincide, meaning that, due to the high value of the association equilibrium constant, the contribution of k_a to k_{obs} drops to a negligible figure.

The results illustrated in Table VII point to a remarkable difference between the rate constants of complexes dichloro- and chloronitro- on one side, and chlorocyano-complex on the other. The former exhibit furthermore very typical values of activation energies and of frequency factors, and negative values of activation entropies such as apply to the cases where the (activated) transition state carries an increased ionic charge [10], both due to a stoichiometric mechanism of d type [3] or due to the formation of a solvated complex where the cation charge is more positive by one unity as hypothesized by Langford [3, 11].

As far as *trans*-[Coen$_2$CNCl]$^+$ is concerned we find on the other hand a very high isotopic exchange rate constant, as consequence of an high A value (exchange taking place within the ion-pair) even though the E$_a$ value is higher than usual. These results, together with the observation of a large positive value for activation entropy, as expected for charge neutralization in the (activated) transition state [10], seems to indicate the presence of a stoichiometric mechanism of I type, where the ion-pair is the activated complex in the transition state. Within the ion-pair, the intimate mechanism of isotopic

TABLE VI. First Order Constants for Chloride-36 Exchange in *trans*-[Coen$_2$LCl]$^+$ in DMF.

L	k_a sec^{-1}	k_b sec^{-1}	k_{obs} sec^{-1}	K (IP) mol^{-1}	t °C
Cl	5×10^{-5}	1.5×10^{-3}	2×10^{-4}	30	60
CN	4×10^{-5}	4.5×10^{-4}	4.4×10^{-4}	1870	25

TABLE VII. Rates of Nucleophilic Substitution in DMF, Arrhenius Activation Energies, Activation Entropies and Frequency Factors for: *trans*-[Coen$_2$LCl]$^+$ + X$^-$ $\longrightarrow$ *trans*-[Coen$_2$LX]$^+$ + Cl$^-$ at 35 °C.

L	X	k_{obs} sec^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}	A sec^{-1}	E$_a$ Kcal/mol
Cl	SCN	5.8×10^{-6}	–4.26	6.2×10^{11} (a)	24.0
NO$_2$	SCN	5.4×10^{-5}	–1.46	2.5×10^{12} (a)	23.5
CN	^{36}Cl	3.4×10^{-3}	+35.52	3.9×10^{20}	32.5

[a] Calculated from data in ref. [4].

exchange is probably of I_d type, in line with what suggested by Langford and Gray [12] for the complexes of general formula *trans*-$[Coen_2NO_2X]^+$.

In opposition to the deduction of Asperger [2] we have found that for the complex *trans*-$[Coen_2CNCl]^+$, the role of L = CN is not solvent independent but rather that cyano groups induce a mechanism of I_a type in methanol and DMSO via solvation reaction, one of I_d type in ethylene glycol, and one of I_d type in DMF via an ion association preequilibrium.

Considering now the labilizing effect in *trans* position in an octahedric coordinated system, our results are well in agreement with those obtained in acid hydrolysis reactions. The labilizing power decreases in the order: $SO_3^= \gg NO_2^- > CN^- \simeq Cl^-$. The complex *trans*-$[Coen_2SO_3Cl]^0$ undergoes rapid and complete hydrolysis in water [13] and gives rise to exhaustive ^{36}Cl isotopic exchange within the time of separation of the reagents in ethylene glycol (this particular complex is not soluble in methanol) [14]. This behaviour accounts for the position of the sulphite group in the sequence of labilizing power.

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