Ligand substitution at a Hexa-coordinate Centre. Reaction of $[Co_2(Et_2dtc)_5]$ BF_4 with some Dithio-oxamides.
Part II. A Kinetic Study

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The reaction $[Co_2(Et_2dtc)_5]BF_4 + DTO \rightarrow [Co(Et_2dtc)_2DTO]BF_4 + Co(Et_2dtc)_3$ *(where* Et_2dtc = *N,N-diethyldithiocarbamate and DTO = substituted dithio-oxamides as N,N,N',N'-tetraethyldithio-oxamide =* Et_4DTO*; N,N'-diisopropyldithio-oxamide =* Pr_2DTOH_2*; N,N'-difurfuryldithio-oxamide =* Fur_2DTOH_2*; N,N'-dimorpholyldithio-oxamide =* Mo_2DTOH_2*) was followed spectrophotometrically in* CH_2Cl_2 *medium. The kinetic expression for this reaction is a two-term rate law and the pseudo-first order rate constants obey the expression:* $k_{obs} = k_I + k_{II}\,[DTO]$ *where* $k_{II} \gg k_I$ *and depends on the nature of the ligand.*

A mechanism involving a one-ended reversible dissociation of the $Co(Et_2dtc)_3$ *unit, preceding the rate determining steps, is invoked. The second order contribution to the rate law (*k_{II}*) is related to the nucleophilic participation of the incoming ligand. The* k_I *term is also probably related to a bimolecular process i.e. the displacement of the* $Co(Et_2dtc)_3$*, one end linked by the solvent, and the process is followed by the fast entry of DTO displacing the solvent. Using more coordinating solvents (like* CH_3OH*), the reaction becomes too fast to be spectrophotometrically followed, but in* CH_3OH/CH_2Cl_2 *mixtures a linear dependence on* CH_3OH *concentration was obtained. Activation parameters are consistent with the proposed mechanism.*

Introduction

We are now extending our interest in dithio- and diselenocarbamato complexes [1–3] to kinetic studies [4]. Only a few cases of substitution reactions on dithioate complexes are reported in the literature [5, 6] and so far only one report on dithio and diselenocarbamato complexes [7] is available, although this class of compounds seems particularly suitable for a comparative analysis of the ligand substitution reactions on a coordinated metal centre with a given geometry.

Such an analysis can also be related to a variation of the structural parameters. In fact, it is possible to synthesize a rich class of dtc or dsc complexes with a central atom having the same coordination number but either (i) a different electronic configuration, or (ii) the same electronic configuration but different size, or (iii) a different oxidation number *etc.* [8].

We report here on the substitution reaction of the octahedrally coordinated diethyldithiocarbamato (Et_2dtc) complex of Co(III) with some substituted dithio-oxamides in CH_2Cl_2 medium. Unlike the tris dithiocarbamato derivatives of Fe(III) [7] and Mn(III) [8], the $Co(dtc)_3$ compound is kinetically inert [9]. However, in its dimeric form $[Co_2(Et_2dtc)_5]^+$, the cation may be considered as a $Co(Et_2dtc)_3$ coordinated in the *cis* position of an octahedral $Co(Et_2dtc)_2^+$ unit [10].

The Co–S bridging distances of the $Co(Et_2dtc)_2^+$ fragment are the longest observed in this structure, and this finding is reflected by rupture of these bonds when the dimer is allowed to react with other ligands [10].

The reaction under investigation (see part I) is:

$$[Co_2(Et_2dtc)_5]BF_4 + DTO \rightarrow [Co(Et_2dtc)_2DTO]BF_4 + Co(Et_2dtc)_3$$

where DTO is: N,N,N',N'-tetraethyldithio-oxamide = Et_4DTO; N,N'-diisopropyldithio-oxamide = Pr_2DTOH_2; N,N'-difurfuryldithio-oxamide = Fur_2DTOH_2; N,N'-dimorpholyldithio-oxamide = Mo_2DTOH_2. In CH_2Cl_2 it virtually runs to completion.

Experimental

The $[Co_2Et_2dtc)_5]BF_4$ complex [10] and the substituted dithio-oxamides [11] were prepared as described in the literature. The $[Co(Et_2dtc)_2DTO]BF_4$ complexes were isolated and characterized as reported in part I [12].

The solvent was Merck analytical reagent grade and was used after column distillation and drying with molecular sieves (A4). Its purity was verified gas-chromatographically. Great care was taken in purifying the solvent from traces of water or alcohols, which have the effect of accelerating the reactions.

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TABLE I. Rate Constants for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\simeq 3 \times 10^{-4}$ *M*) and Pr_2DTOH_2 in CH_2Cl_2. k_I = sec^{-1}; k_{II} = mol^{-1} l sec^{-1}. Activation parameters related to k_I are calculated from Eyring plots.

10 °C		15 °C		20 °C		25 °C		30 °C	
a	b								
[6.54]	3.1 ± 0.3	[5.65]	4.20 ± 0.08	[6.02]	9.6 ± 0.2	[6.48]	22.7 ± 0.4	[7.16]	35.6 ± 0.5
[11.40]	4.2 ± 0.1	[11.36]	6.53 ± 0.07	[11.67]	13.5 ± 0.1	[13.22]	31.8 ± 0.4	[11.77]	44.9 ± 0.4
[16.95]	5.6 ± 0.2	[15.79]	8.4 ± 0.1	[18.13]	18.0 ± 0.2	[17.67]	36.9 ± 0.6	[17.70]	55.4 ± 0.7
[22.81]	7.5 ± 0.1	[23.30]	10.5 ± 0.1	[22.67]	22.6 ± 0.2	[22.40]	43.5 ± 0.5	[22.54]	63.1 ± 0.8
$k_I = (1.2 \pm 0.2) \times 10^{-5}$		$(2.4 \pm 0.4) \times 10^{-5}$		$(4.7 \pm 0.7) \times 10^{-5}$		$(1.44 \pm 0.05) \times 10^{-4}$		$(2.3 \pm 0.1) \times 10^{-4}$	
$k_{II} = (2.7 \pm 0.2) \times 10^{-3}$		$(3.6 \pm 0.3) \times 10^{-3}$		$(7.7 \pm 0.5) \times 10^{-3}$		$(1.29 \pm 0.03) \times 10^{-2}$		$(1.8 \pm 0.6) \times 10^{-2}$	
r = 0.995		0.995		0.996		0.999		0.999	
$\Delta H^{\neq} = 26 \pm 1$ Kcal mol^{-1}; $\Delta S^{\neq} = 10 \pm 5$ cal K^{-1} mol^{-1}; r = 0.993									

[a] = 10^3 [DTO] (mol l^{-1}). [b] = 10^5 k_{obs} (sec^{-1}); r = correlation coefficients were always 0.999 or better.

Spectrophotometric Measurements

We followed the reaction on a Perkin Elmer UV–Vis. mod. 402 spectrophotometer by monitoring the changes in absorbance at a wavelength at which the value |ε products – ε reagent| is large (576 nm was a suitable value in all cases), and by using 1 cm glass cells, thermostatted (±0.1 °C) at the chosen temperature. At zero time the pre-thermostatted solvent (3 ml) was added to the weighed reagents in the cell. The absorbance values at infinite time (A_∞) were calculated from the starting complex concentration multiplied by the molar extinction coefficients of the two products at the chosen wavelength, and were sometimes verified experimentally.

Under pseudo first-order conditions we obtained good linear plots of ln ($A_\infty - A_t$) against time, having slopes = k_{obs}. By means of the plot of k_{obs} against [DTO], it is possible to identify a positive intercept (k_I) and a slope (k_{II}) of straight lines. Since $k_{II} \gg k_I$, low standard deviations were obtained by working at a [DTO] 20 ÷ 100 times and 200 ÷ 1000 times larger than the starting complex, for k_I and k_{II} respectively (see Table I and II).

The reaction was also followed in 0.5 ÷ 4% vol. CH_3OH/CH_2Cl_2 mixtures at a constant known excess of DTO, and a linear dependence of k_{obs} on [CH_3OH] was observed (Table III).

The [CH_3OH] were about 12 ÷ 100 times larger than those of DTO and the contribution of [DTO] to k_{obs} was too low to be detected. This contribution, however, exists and can be observed when working in 0.01% vol. CH_3OH in CH_2Cl_2 at different DTO concentrations.

The results of the reaction at 25 °C with Et_4DTO, Fur_2DTOH_2, Mo_2DTOH_2 are reported in Table (IV).

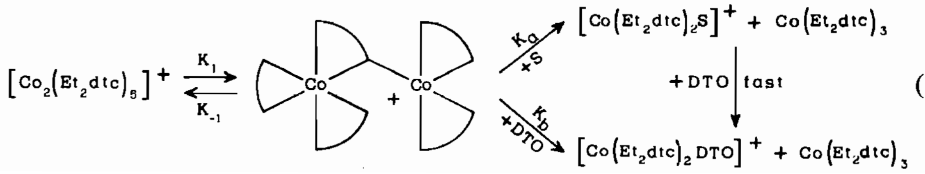
Results and Discussion

The pseudo first-order rate constants (Table I and II) obtained as the slope of ln($A_\infty - A_t$) against time, obey the expression:

$$k_{obs} = k_I + k_{II}[DTO] \tag{1}$$

In fact by plotting the k_{obs} against the DTO concentrations, straight lines with positive intercepts were obtained. The k_I and k_{II} values, together with the activation parameters, are listed respectively in Table I and II. On varying the parent amine of the ligand, the k_I and k_{II} values result respectively 'independent of' and 'dependent on' the nature of the ligand (Table IV). At first sight, these results may be explained by assuming that the substrate proceeds in two paths: a dissociative path, (k_I), and an associative one, related to the nucleophilic attack of DTO on the Co(III) centre (k_{II}). This mechanism seems unlikely, since the associative nucleophilic substitution on the octahedrally coordinated Co(III) would involve an elementary step with an intermediate having 20 metal valence electrons, while the dissociative one would involve an intermediate having 14 metal valence electrons. Now, Tolman's rule [13] states that organometallic reactions proceed by steps involving only intermediates with 16 or 18 metal valence electrons. In fact substitution reactions on Co(III) substrates are generally dissociative processes [14].

An alternative mechanism that fits our experimental data is proposed:



(2)

TABLE II. Rate Constants for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\simeq 3 \times 10^{-4}$ *M*) and Pr_2DTOH_2 in CH_2Cl_2. k_I = sec^{-1}; k_{II} = mol^{-1} 1 sec^{-1}. Activation parameters related to k_{II} second order constant are calculated from Eyring plots.

10 °C		15 °C		20 °C		25 °C		30 °C	
a	b								
[6.63]	2.07 ± 0.03	[6.56]	3.54 ± 0.05	[8.11]	6.56 ± 0.05	[5.95]	10.2 ± 0.2	[5.62]	15.5 ± 0.1
[13.15]	3.76 ± 0.07	[12.86]	6.64 ± 0.07	[11.22]	8.77 ± 0.09	[11.68]	18.8 ± 0.2	[11.71]	29.6 ± 0.4
[19.59]	5.49 ± 0.06	[19.12]	9.59 ± 0.08	[16.03]	12.7 ± 0.1	[17.09]	24.9 ± 0.3	[17.23]	36.6 ± 0.3
[25.73]	7.04 ± 0.06	[25.72]	12.2 ± 0.1	[23.64]	20.4 ± 0.2	[22.90]	34 ± 0.3	[22.81]	51.5 ± 0.3
k_I = (3.4 ± 0.4) × 10^{-5}		(7 ± 3) × 10^{-5}		(1.1 ± 0.7) × 10^{-4}		(2.1 ± 0.9) × 10^{-4}		(5 ± 3) × 10^{-4}	
k_{II} = (2.61 ± 0.02) × 10^{-3}		(4.5 ± 0.2) × 10^{-3}		(9.0 ± 0.5) × 10^{-3}		(1.38 ± 0.06) × 10^{-2}		(2.0 ± 0.2) × 10^{-2}	
r = 1.000		0.999		0.997		0.998		0.991	
$\Delta H^{\neq}$ = 17.1 ± 0.7 Kcal mol^{-1}; $\Delta S^{\neq}$ = −10 ± 2 cal K^{-1} mol^{-1}; r = 0.995.									

[a] = 10^2[DTO] (mol l^{-1}). [b] = 10^4 k_{obs} (sec^{-1}); r = correlation coefficients were always 0.999 or better.

TABLE III. Rate Constants and Reaction Conditions for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\simeq 3.5 \times 10^{-4}$ *M*) and Pr_2DTOH_2 ($\simeq 1 \times 10^{-2}$ *M*) in CH_3OH/CH_2Cl_2 Mixtures*. $k_{obs} = k'_I[CH_3OH]$; k'_I (mol^{-1} l sec^{-1}) are estimated from the plot of k_{obs} against $[CH_3OH]$.

% Vol CH_3OH**	T °C	10^4 k_{obs} (sec^{-1})	T °C	10^4 k_{obs} (sec^{-1})	T °C	10^4 k_{obs} (sec^{-1})
0.5	10°	3.0 ± 0.1	20°	9.4 ± 0.1	30°	20.6 ± 0.2
1.0		5.6 ± 0.2		16.7 ± 0.2		34.0 ± 0.4
2.0		11.2 ± 0.5		34.0 ± 0.6		60 ± 1
4.0		27 ± 1		65.2 ± 0.8		121 ± 2
	k'_I = (2.8 ± 0.2) × 10^{-3}		(6.5 ± 0.3) × 10^{-3}		(1.16 ± 0.03) × 10^{-2}	
$\Delta H^{\neq}$ = 11.6 ± 0.7 Kcal mol^{-1}		$\Delta S^{\neq}$ = −29 ± 2 cal K^{-1} mol^{-1}		r = 0.996		

*Correlation coefficients are always 0.995 or better. **The intercept on y axis, that should give k_{obs} in absence of CH_3OH, was not detectable, because the error is of the same order as its magnitude, being $[CH_3OH]$ 10 ÷ 100 times higher than [DTO]. The contribution of DTO concentration was determined working in CH_3OH/CH_2Cl_2 0.01% at 20 °C obtaining $k_{obs} = k''_I + k_{II}[DTO]$; $k''_I = (1.2 \pm 0.1) \times 10^{-4}$ sec^{-1}; $k_{II} = (8.1 \pm 0.1) \times 10^{-3}$ sec^{-1} mol l^{-1}.

TABLE IV. Rate Constants and Reaction Conditions for the Substitution Reaction between $[Co_2(Et_2dtc)_5]BF_4$ ($\simeq 2 \times 10^{-4}$ *M*) and some DTO in CH_2Cl_2.

Ligand	T	10^3[DTO] mol l^{-1}	10^4 k_{obs} sec^{-1}		10^4 k_I (sec^{-1})	10^2 k_{II} (mol^{-1} l sec^{-1})	
Et_4DTO	25°	[5.85]	2.72 ± 0.02	(1.000)	1.8 ± 0.2	1.8 ± 0.1	(0.997)
		[12.14]	3.89 ± 0.05	(0.999)			
		[16.61]	5.1 ± 0.1	(0.998)			
		[23.40]	5.7 ± 0.1	(0.998)			
Fur_2DTOH_2		[5.17]	2.31 ± 0.01	(1.000)	1.65 ± 0.05	1.21 ± 0.04	(0.999)
		[10.24]	2.85 ± 0.01	(1.000)			
		[14.10]	3.36 ± 0.03	(0.999)			
		[20.46]	4.15 ± 0.03	(0.999)			
Mo_2DTOH_2		[5.38]	2.24 ± 0.05	(0.998)	1.68 ± 0.04	1.10 ± 0.03	(0.999)
		[9.74]	2.78 ± 0.06	(0.998)			
		[16.04]	3.5 ± 0.1	(0.996)			
		[21.04]	3.97 ± 0.07	(0.999)			

In the proposed mechanism (2), a rapid equilibrium between the substrate and an intermediate in which $Co(Et_2dtc)_3$ is one-end linked to the $Co(Et_2dtc)_2^+$ unit, precedes the rate determining steps. This intermediate (16 metal valence electrons) then undergoes the bimolecular attack of DTO, (path b), and the displacement by the solvent of $Co(Et_2dtc)_3$ one-end linked (path a). The latter is followed by the fast entry of DTO.

If the intermediate is at low concentration, the steady state approximation will be applied [15], and it is possible to obtain the expression for the pseudo-first order kinetics where:

$$k = \frac{k_1 k_a [S]}{k_{-1}} + \frac{k_1 k_b}{k_{-1}} [DTO],$$

and by comparing it with (1)

$$k_I = \frac{k_1 k_a [S]}{k_{-1}} \; ; \; k_{II} = \frac{k_1 k_b}{k_{-1}} ,$$

therefore a dissociative step and an associative one contribute to k_I and k_{II}. The low coordinating ability of the CH_2Cl_2 solvent yields a small contribution of path a to the observed rate constants. Using more coordinating solvents, like CH_3OH, the reaction becomes too fast to be followed spectrophotometrically. On the other hand, using low CH_3OH concentrations in CH_2Cl_2 and a constant excess of DTO, a linear dependence on the CH_3OH concentration of k_{obs} is obtained.

These results suggest that CH_3OH participates in an activated complex formation (*i.e.* $Co(Et_2dtc)_2$-$OHCH_3$) via an S_N2 mechanism with subsequent rapid substitution of methanol by DTO. This intermediate is not improbable because it is known that methanol forms comparatively stable compounds with Co(III) derivatives [16]. Although k_{II} is not very sensitive to the nature of the DTO ligand, because the observed overall change is only within a factor of 1.6, a certain amount of dependence of the k_{II} constants on the donor ability of the sulphur atom was observed. We can assume that for the DTO ligands, if we neglect the influence due to the different steric hindrances, the pK_A of the parent amine will give an indicative measure of the donor ability of the ligand. In fact the more basic the parent amine, the greater the contribution of the $R_2\overset{+}{N}=\underset{|}{C}-S^-$ structure to the resonance hybrid of the molecule. In a class of reagents of the same type, a free energy relationship of the general formula $\ln k = ApK_A + \text{const}$ [17] has been observed. By plotting $\ln k_{II}$ against the pK_A of the parent amine of the DTO, a rough linear dependence was obtained (Fig. 1).

The activation entropy values related to k_I, k_{II} and k_I' are reported in Tables I, II, III. Because in the proposed mechanism (2), a dissociative process and a substitutive one contribute to define the k values, the overall entropy values related to each constant are indicative of the predominant process. The $\Delta S^{\neq}$ value related to k_I suggests that the dissociative step is prevailing, whereas the values related to k_{II} and k_I' indicate that the associative step becomes more important.

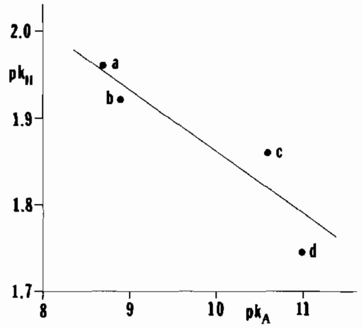


Fig. 1. Plot of pk_{II} at 25 °C against the pK_A of the parent amines in the protonated form [18]: a) $MoNH_2 = 8.70$; b) $FurNH_2 = 8.89$; c) $PrNH_2 = 10.63$; d) $Et_2NH = 10.98$.

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