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Cobalt(III) Complexes in Dipolar Aprotic Solvents. Part XV.* Some Reactions of *trans*-methylbis(dimethylglyoximato)(dimethylsulphoxide)cobalt(III), *trans*-[$CoCH_3(DH)_2(DMSO)$] in Dimethyl Sulphoxide

S.T.D. LO** and D.W. WATTS***
School of Chemistry, The University of Western Australia, Nedlands, 6009 Western Australia
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The anation reactions: trans-[$CoCH_3(DH)_2(DMSO)$] $+ X^- =$ *trans-*[$CoCH_3(DH)_2X$]$^-$ $+$ *DMSO have been studied for* $X^- = NCO^-$, N_3^- *and* NCS^- *in the solvent DMSO. Equilibrium constants and rate constants have been determined over a range of temperature. The reactions are appreciably faster than those in the trans-*[$Co(DH)_2(NO_2)(DMSO)$] *system*[1] *confirming the strong trans labilizing effect of the* CH_3^- *ligand. The results are consistent with a dissociative mechanism, showing correspondence with similar systems in aqueous solutions.*[1,2]

Introduction

These studies are a continuation of our recent work on *trans*-[$Co(DH)_2(NO_2)(DMSO)$] in DMSO and its anation products with Br^- and NCS^-. These systems are under study for comparison with the anation results of cationic complexes of cobalt(III) in dipolar aprotic solvents[3–5] and to confirm the assigned dissociative mechanism of reaction for these complexes in aqueous solution[2,6,7] through studying solvent transfer phenomina.

The analogous aqueous chemistry of *trans*-[$Co(CH_3)(DH)_2(OH_2)$] has been studied by Crumbliss and Wilmarth[6] and more recently by Sakurai, Fox and Ingraham,[7] while a series of alkyl complexes have been studied in mixed solvents by Costa *et al.*[8] as models for the vitamin B_{12} system.[9,10] The consensus is that the mechanisms of all these reactions are dissociative interchange,[6] reaching the extreme of the limiting dissociative mechanism in the *trans*-[$Co(DH)_2SO_3OH_2$]$^-$ system.

A comparison of the *trans*-[$Co(DH)_2CH_3(OH_2)$] and *trans*-[$Co(DH)_2NO_2(OH_2)$] systems in water show the former to be 10^5 times more labile because of the strong *trans* labilizing effect of the CH_3^- ligand.[6,7] In water the nucleophilicities of SCN^- and N_3^- are in the ratio 1.0:0.7.[6] The same labilization by CH_3^- is shown in DMSO. Previously we measured DMSO exchange with *trans*-[$Co(DH)_2NO_2(DMSO)$] by pmr spectroscopy,[1] a technique which is inapplicable to the methyl system where exchange is complete in the time of mixing. This observation of solvent exchange much faster than anation, is not found for the cationic complex of cobalt(III)[3–5] where anation rates approach a limiting value close to that of solvent exchange because of the predominance of ion association pre-equilibria.

Experimental

trans-[$Co(DH)_2CH_3(OH_2)$] was prepared after Schrauzer and Windgassen.[11] *Anal.* Calc. for *trans*-[$Co(DH)_2CH_3(OH_2)$]: C, 33.6; H, 5.9; N, 17.4% Found: C, 33.2; H, 5.8; N, 17.4%.

DMSO was purified as previously[12] and all salts were recrystallized analytical reagent grade except Et_4NClO_4, which was prepared from aqueous Et_4NCl with 70% $HClO_4$ and recrystallized from warm acetone with ether, and Et_4NN_3, which was prepared after Ko and Parker.[13,14]

trans-[$Co(DH)_2CH_3(DMSO)$] resulted immediately, confirmed by pmr spectroscopy, from the introduction of *trans*-[$Co(DH)_2CH_3(OH_2)$] into DMSO. At the concentration used in both the kinetic and equilibrium studies the introduced water (5×10^{-4} mol dm^{-3}) was negligible. Precautions were taken to exclude light in all work.

The equilibrium results were obtained by spectrophotometric analysis on a Perkin Elmer 450 Spectrophotometer, and the equilibrium constants calculated using a modified Newton and Arcand method.[15] The rate constants were obtained using a Durrum–Gibson stopped-flow spectrophotometer. In the cases of N_3^- and NCO^- where anation went to completion under all conditions plots of $\log(\varepsilon - \varepsilon_\infty)$ *versus* time yielded

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* Part XIV: See ref. 1.

** Present address: Department of Chemistry, University of Toronto.

*** To whom correspondence should be sent.

pseudo-first-order rate constants for the anation process. For the SCN^- system where the reverse solvolysis reaction was significant plots of $\log(\varepsilon - \varepsilon_\infty)$ *v.* time gave a combined rate constant (see later).

Results and Discussion

The equilibrium constants for the reactions: *trans*-$[Co(DH)_2CH_3(DMSO)] + X^- = $ *trans*-$[Co(DH)_2CH_3X]^- + DMSO$ presented in Table I are concentration based with no allowance for solution non-ideality. These constants differ from the thermodynamic constants by a factor which is a function of activity coefficients $\left(\frac{\gamma_{[Com^-]}}{\gamma_{[Com]}\gamma_{X^-}}\right)$ where "Com⁻" is the product complex and "Com" the reactant complex. If at the concentration of these experiments ($3–12 \times 10^{-4}$ mol dm^{-3}) the Debye Hückel Limiting Law is taken to account for these activity coefficients then $\gamma_{Com^-} = \gamma_{X^-}$ and $\gamma_{Com} = 1$ and thus the recorded constants can be expected to closely represent the thermodynamic constants. In practice, this has been confirmed by studying each system as a function of ionic strength up to 0.1 mol dm^{-3} and the equilibrium constants thus determined were found to be invariant. That each system was involved in a clean reaction was confirmed by the existence of isosbestic points in the equilibrium spectra at 426 nm for NCO^-, 441 nm for N_3^- and 422 nm for NCS^-.

The thermodynamic functions based on this equilibrium data are collected in Table II. These equilibrium constants are of the order 10 times greater than the values for the analogous aqueous reactions,[6] which is a reflection of the greater anion (X^-) activity in DMSO compared with water, not compensated by increased activity in the larger more polarizable complex anion.[17] In water[6] the anation equilibrium constant for N_3^- is greater than for NCS^- by a factor of 2. This factor is increased to 3 in DMSO.

TABLE I. Equilibrium Constants for the Formation of *trans*-$[Co(DH)_2CH_3X]$ in DMSO.

X^-	Temperature C	ε_o[a]	ε_p[a]	10^{-3}K dm^3 mol^{-1}
NCO^-	32.7	1137	342	3.59
	40.0	1157	350	3.04
	48.0	1162	366	2.59
N_3^-	32.2	1022	538	3.08
	40.0	1034	570	2.73
	49.2	1064	590	2.33
NCS^-	32.5	1168	340	0.102
	42.3	1177	342	0.086
	53.5	1180	344	0.070

[a] ε_o and ε_p refer to the molar extinction coefficients of *trans*-$[Co(DH)_2CH_3(DMSO)]$ and *trans*-$[Co(DH)_2CH_3X]^-$ respectively at the wavelengths 460 nm for NCO^-, 466 nm for N_3^- and 460 nm for NCS^-. Isosbestic points occur in reactant and product spectra at 426 nm, 441 nm and 422 nm for respectively, the NCO^-, N_3^- and NCS^- systems.

TABLE II. Thermodynamic Functions for Reactions *trans*-$[Co(DH)_2CH_3(DMSO)] + X^- = $ *trans*-$[Co(DH)_2CH_3X]^- +$ DMSO in DMSO.

X^-	$\Delta H°$ kJ mol^{-1}	$\Delta S°$ J deg^{-1} mol^{-1}	$\Delta G°$ kJ mol^{-1} (25° C)
NCO^-	−17.6 ± 0.8	13 ± 2	−21 ± 1
N_3^-	−13.5 ± 0.9	23 ± 3	−20 ± 1
NCS^-	−15 ± 1	−10 ± 2	−12 ± 1

The dissociative model which is favoured for the aqueous system[2,6] and is applicable to the *trans*-$[Co(DH)_2NO_2(DMSO)]$ system in DMSO,[1] is specified in the following equations:

$$trans\text{-}[Co(DH)_2CH_3(DMSO)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(intermediate)}}{[Co(DH)_2CH_3]} + DMSO$$

$$[Co(DH)_2CH_3] + X^- \underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}} trans\text{-}[Co(DH)_2CH_3X]^-$$

for which a steady state treatment yields the following for the observed first order rate constant (plotting $\log(\varepsilon - \varepsilon_\infty)$ against t) provided $[X^-]$ is in large excess:

$$k_{obs} = \frac{k_1k_x[X^-] + k_{-1}k_{-x}}{k_{-1} + k_x[X^-]} \qquad (1)$$

The primary rate data for the three systems (Tables III, IV and V) are presented in Figure 1 and show the plot of k_{obs} against $[X^-]$ to be curved in each case and further, in the case of SCN^-, show a non-zero intercept at $[X^-] = 0$. In the bisethylenediamine cobalt(III) cationic systems such curvatures are due to associative pre-equilibria which are unlikely for these neutral complexes,[1] and further receive no support from the absence of anion concentration dependant charge transfer spectra, and from the absence of any comparable effect in the *trans*-$[Co(DH)_2NO_2(DMSO)]$ system.[1]

Thus the non-linearity here must be explained by (1) as must the intercept in the case of SCN^-. An inspection of (1), since k_{-1} has the same value for all three systems, shows us that the SCN^- intercept must arise from the significantly larger value of k_{-x}, that is from a term which correlates with the observed smaller stability of the SCN^- complex. The curvature of the

TABLE III. Rate Constants for the Anation of *trans*-[Co(DH)$_2$CH$_3$(DMSO)] by NCO$^-$ in DMSO. Initial [*trans*-[Co(DH)$_2$CH$_3$(DMSO)]] = 5.94 × 10^{-4} mol dm^{-3}.

t° C	10^2[KNCO] mol dm^{-3}	10^2[KClO$_4$] mol dm^{-3}	10^{2}I	10^{2}k$_{obs}$ (s^{-1})
25.2	4.60	0	4.60	4.54
29.7	4.60	0	4.60	6.7
34.3	4.60	0	4.60	10.7
40.4	4.60	0	4.60	19.0
45.0	4.60	0	4.60	28.5
25.2	3.44	1.18	4.60	3.51
25.2	2.30	2.30	4.60	2.40
25.2	1.15	3.45	4.60	1.20
25.2	0.92	0	0.918	0.94
25.2	0.92	1.18	2.10	0.92
25.2	0.92	3.60	4.52	0.94
25.2	0.92	4.81	5.73	0.93

TABLE IV. Rate Constants for the Anation of *trans*-[Co(DH)$_2$CH$_3$(DMSO)] by N$_3^-$ in DMSO. Initial [*trans*-[Co(DH)$_2$CH$_3$(DMSO]] = 5.68 × 10^{-4} mol dm^{-3}.

t° C	10^2[Et$_4$NN$_3$] mol dm^{-3}	10^2[Et$_4$NClO$_4$] mol dm^{-3}	I	10^{2}k$_{obs}$ (s^{-1})
25.2	11.5	0	0.115	3.72
30.5	11.5	0	0.115	6.1
35.2	11.5	0	0.115	10.2
40.7	11.5	0	0.115	17.3
45.5	11.5	0	0.115	26.1
25.2	8.65	2.88	0.115	2.97
25.2	5.77	5.76	0.115	2.03
25.2	2.88	8.65	0.115	1.06
25.2	2.88	0	0.029	1.10
25.2	2.88	1.40	0.043	1.06
25.2	2.88	4.23	0.071	1.08

TABLE V. Rate Constants for the Anation of *trans*-[Co(DH)$_2$CH$_3$(DMSO)] by NCS$^-$ in DMSO. Initial [*trans*-[Co(DH)$_2$CH$_3$(DMSO)]] = 4.74 × 10^{-4} mol dm^{-3}.

t° C	10^2[KNCS] mol dm^{-3}	10^2[KClO$_4$] mol dm^{-3}	10^{2}I	10^{2}k$_{obs}$ (s^{-1})	10^{2}k$_{-1}$ (s^{-1})[a]
25.2	7.85	0	7.85	12.0	
25.2	5.88	1.95	7.85	9.7	
25.2	3.92	3.93	7.85	6.8	
25.2	1.96	5.89	7.85	4.01	
25.2	1.96	4.48	6.44	4.02	
25.2	1.96	9.09	11.0	4.05	
25.2	0.98	6.87	7.85	2.57	1.2 ± 0.2
31.0	5.88	1.97	7.85	16.6	
31.0	3.92	3.93	7.85	12.2	
31.0	1.96	5.89	7.85	7.9	
31.0	0.98	6.87	7.85	4.43	2.4 ± 0.4
37.3	5.88	1.97	7.85	30.7	
37.3	3.92	3.93	7.85	23.2	
37.3	1.96	5.89	7.85	14.2	6 ± 1

[a] Obtained from the intercept of a plot of k$_{obs}$ *versus* added NCS$^-$ concentration.

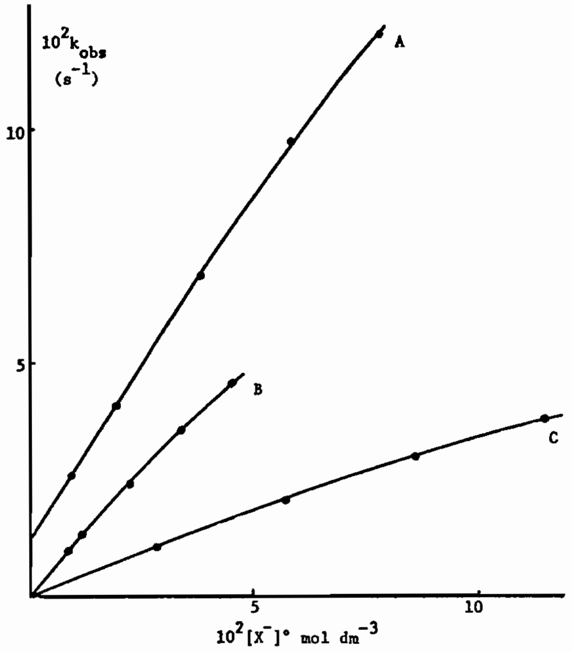

Figure 1. Plots of k_{obs} *versus* added X^- concentration (where X^- = NCS^-(A), NCO^-(B) and N_3^-(C)) at 25.2° C.

plots arises from the fact that $k_x[X^-]$ for this intermediate is significant compared with k_{-1}. This was not found under comparable conditions in the *trans*-$[Co(DH)_2NO_2(DMSO)]$ system. Thus in the present system the anions have improved reactivity for the intermediate compared with the solvent (DMSO).

From (1) the intercept for SCN^- gives a value for k_{-x} of 1.2×10^{-2} s^{-1} while k_{-x} for NCO^- and N_3^- are effectively zero ($<10^{-3}$ s^{-1}).

Reorganizing (1) yields:

$$\frac{1}{k_{obs}-k_{-x}} = \frac{1}{k_1-k_{-x}} + \frac{k_{-1}}{k_x(k_1-k_{-x})[X^-]}$$

which for N_3^- and NCO^- gives:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_xk_1[X^-]}$$

A plot of $1/k_{obs}$ against $[X^-]$ (Figure 2) for these two systems gives an intercept of $1/k_1$ which yields k_1 = 0.6 ± 0.1 s^{-1} at 25.2° C (Table V). The ratio of the intercept to the slope gives (k_x/k_{-1}) the values of which are recorded in Table VI. A combination of the equilibrium constants $K_x = \frac{k_1k_x}{k_{-1}k_{-x}}$ and the slope yields values for k_{-x} which are also in Table VI. The value for SCN^- of $k_{-x} = 1.33 \times 10^{-2}$ s^{-1} compares reasonably well with intercept of Figure 1 of 1.20×10^{-2} s^{-1}. The values for N_3^- and NCO^- are substantially less than 10^{-3} s^{-1}, the minimum value for Figure 1 to show a non-zero intercept for these ions.

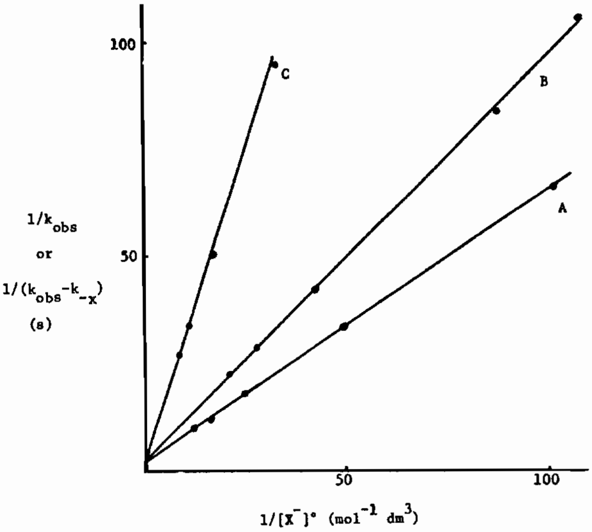

Figure 2. Plots of $\frac{1}{k_{obs}}$ (or $\frac{1}{k_{obs}-k_{-x}}$) *versus* $\frac{1}{[X^-]}$ (where X^- = NCS^-(A), NCO^-(B) and N_3^-(C)) at 25.2° C.

The values of (k_x/k_{-1}) yields the relative reactivities of the nucleophiles NCS^-, NCO^-, N_3^- and DMSO for the intermediate, which decrease in the order given provided the DMSO comparison is made at equal concentrations. The relative nucleophilicities thus calculated are NCS^- : NCO^- : N_3^- : DMSO : 42 : 28 : 9.6 : 1, or alternatively expressed, at an initial anion concentration of 0.5 mol dm^{-3}, NCS^- would gain 58% of the intermediates competing only with solvent, NCO^-, 48% and N_3^-, 24%.

The value of k_1 calculated here to be 0.6 s^{-1} ($t_{1/2}$~1 s) is consistent with the observation that exchange of DMSO is complete before mixing in a pmr experiment. When compared with k_1 measured for *trans*-$[Co(DH)_2NO_2(DMSO)]$ of 1.90×10^{-4} s^{-1}, the increased rate

TABLE VI. Calculated Rate Constants for the Reaction *trans*-$[Co(DH)_2CH_3(DMSO)]$ + X^- = *trans*-$[Co(DH)_2CH_3X]^-$ + DMSO at 25.2° C.

X^-	k_{-x}[a] s^{-1}	k_x/k_{-1}	$10^3K_{X^-}$[b] dm^3 mol^{-1}
NCO^-	2.53×10^{-4}	1.82	4.32
N_3^-	1.10×10^{-4}	0.63	3.50
NCS^-	1.33×10^{-2}	2.76	0.124

[a] Values obtained from $K_x = \frac{k_1k_x}{k_{-1}k_{-x}}$ and the slope (Figure 2) of the plot of $1/k_{obs}$ against $1/[X^-]$. [b] Values calculated from the results in Tables I and II.

(5000 fold) points to the already established strong *trans* labilizing influence of the CH_3^- ligand.[2,6,9]

The relative nucleophilicity of SCN^- and N_3^- (here 4.4 : 1) is slightly greater than in water (1.4 : 1).[6]

The activation energies (E_a) calculated on the basis of the temperature dependence of k_{obs} for the three reactions are 77 ± 2 kJ mol^{-1} (NCO^-), 77 ± 2 kJ mol^{-1} (N_3^-) 69 ± 8 kJ mol^{-1} (SCN^-), are composite of the temperature dependance of $(\frac{k_1k_x}{k_{-1}})$ for the cases of NCO^- and N_3^- and a more complicated function still for SCN^-. These values however are considerably lower than the activation energies for the *trans*-[Co(DH)$_2$NO$_2$(DMSO)] reactions,[1] which is again consistent with the *trans* labilizing effect of the CH_3^- ligand.

The imprecise values of k_{-x}, Table V, yield an activation energy of 100 ± 15 kJ mol^{-1} which is not accurate enough to be fruitfully compared to other work.

In conclusion it can be said that the results on this system in DMSO, like those for *trans*-[Co(DH)$_2$NO$_2$(DMSO)] in DMSO[1] and the results in water[2,6] are compatible with a reaction of dissociative character in which a pentacoordinated square pyramidal intermediate is close to fully developed.

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