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Cobalt(III) Complexes in Dipolar Aprotic Solvents.
Part XIV*. Some Reactions of *trans*-nitrobis(dimethylglyoximato)(dimethyl sulphoxide)cobalt(III), *trans*-[Co(DH)$_2$(NO$_2$)(DMSO)], in Dimethyl Sulphoxide

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The anation reactions: trans-[Co(DH)$_2$NO$_2$DMSO] + X$^-$ = trans-[Co(DH)$_2$(NO$_2$)X]$^-$ + DMSO have been studied for X$^-$ = Br$^-$ and SCN$^-$ in the solvent dimethyl sulphoxide (DMSO). These rates are compared with the DMSO exchange rate measured by pmr spectroscopy. The results are interpreted in terms of a limiting dissociative mechanism and this is supported by a study of the solvolysis reaction: trans-[Co(DH)$_2$NO$_2$Br]$^-$ + DMSO = trans-[Co(DH)$_2$NO$_2$DMSO] + Br$^-$ the mechanism of which is confirmed using solvent transfer activity data in comparing the analogous hydrolysis reaction.

Introduction

The great volume of data on the aqueous reactions of cobalt(III) compounds,[1–2] particularly with ethylenediamine ligands, led naturally to study of these complexes in non-aqueous and particularly aprotic media.[1–4] In dipolar aprotic media, where almost all the complex ions studied have been cationic in nature, the mechanisms are dissociative in nature, but dominated by the role of very substantial ion association.[3,4] It is time that comparative data be collected for the reactions of anionic and neutral species where ion aggregation is minimal and thus where the complex substrate exists in a solvation sphere occupied only by solvent molecules.

We have chosen for this initial work two dimethylglyoximate complexes of cobalt(III), *trans*-[Co(DH)$_2$NO$_2$Br]$^-$ and *trans*-[Co(DH)$_2$NO$_2$DMSO] because some results exist here for their aqueous chemistry[5–16] and because of the geometrical simplicity of the reactions which are dominated by the stability of the planar (DH)$_2$ arrangement giving the overwhelming dominance of *trans* structures.

A number of relevant studies of bisdimethylglyoximate complexes exist[5–16] mostly for anation and solvolysis reactions in aqueous solution. The results show strong evidence particularly in the reactions of *trans*-[Co(DH)$_2$SO$_3$(OH$_2$)]$^-$ that a limiting dissociative mechanism (S$_N$1(lim)) can operate for these complexes. Some of these results have been reviewed recently by Byrd and Wilmarth.[16]

The aquation of a number of *trans*-[Co(DH)$_2$X$_2$]$^-$ complexes has been studied by Ablov *et al.*[9,10] and also by Zsako *et al.*[11–14] Complexes with X = Cl$^-$, Br$^-$ and I$^-$ show two stage hydrolysis reactions in equilibria which favour the diaqua-species.

The use of solvent transfer activity coefficients[17] in the interpretation of the mechanism of the reactions of transition metal complexes has been very limited to date[17–21] because of the complicating predominance of ion association in non-aqueous chemistry, because hydrolysis dominates reactions in water, and because in many cases they are less applicable to dissociative mechanism. In support of our recent statements,[18,21] the present work shows that solvent transfer data can be of considerable use in the diagnosis of the nature of the mechanism of some dissociative reactions in cobalt(III) systems.

Experimental

Preparation of Complexes

trans-[Co(DH)$_2$NO$_2$DMSO] was prepared from *trans*-[Co(DH)$_2$NO$_2$(OH$_2$)][22] by dissolving this complex in a minimum volume of DMSO at 70° C and heating at this temperature for 10 minutes. On cooling to room temperature acetone and ether was added to induce product precipitation. Recrystallization was from DMSO with acetone and ether. *Anal.* Calc. for *trans*-

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$[Co(DH)_2NO_2(DMSO)]$: C, 29.1; H, 4.9; N, 17.8; S, 7.8%. Found: C, 29.2; H, 5.0; N, 17.5; S, 7.8%.

$(n\text{-}Bu)_4N$ *trans*-$[Co(DH)_2NO_2Br]$ was prepared by the addition of stoichiometric amounts of $(n\text{-}Bu)_4NBr$ to *trans*-$[Co(DH)_2NO_2H_2O]$[22] in a minimum volume of ethanol at 60° C. The solution was heated for 30 minutes and the product precipitated with ether. Recrystallization was from ethanol with ether. *Anal.* Calc. for $(n\text{-}Bu)_4N$ *trans*-$[Co(DH)_2NO_2Br]$: C, 43.8; H, 7.7; N, 12.8; Br, 12.2%. Found: C, 44.1; H, 7.7; N, 12.5; Br, 12.3%. The potassium salt of this complex could be made using KBr as the source of nucleophile and gave the same spectrum.

$(n\text{-}Bu)_4N$ *trans*-$[Co(DH)_2NO_2(SCN)]$ was prepared by first reacting stoichiometric amounts of KSCN and *trans*-$[Co(DH)_2NO_2(OH_2)]$[22] in ethanol at 60° C. The yellow precipitate of crude K *trans*-$[Co(DH)_2NO_2(SCN)]$ was dissolved in a minimum of cold water to which was added a stoichiometric quantity of $(n\text{-}Bu)_4NBr$. The product separated as an oil which following decantation was dissolved in ethanol and precipitated with ether. The compound was recrystallized from ethanol with ether. *Anal.* Calc. for $(n\text{-}Bu)_4N$ *trans*-$[Co(DH)_2NO_2(NCS)]$; C, 47.2; H, 7.9; N, 16.4; S, 5.0. Found: C, 47.0; H, 7.9; N, 16.7; S, 5.4%.

All the above analyses except halides, which were by titration, were carried out by Australian Microanalytical Services. DMSO was purified as previously.[23] All other chemicals were recrystallized Analytical Reagent Grade, except hexadeutero-DMSO (d_6-DMSO) which was supplied 99.9% pure by Merck, Sharpe and Dohme.

Spectral results for both the kinetic and solubility data was recorded in a thermostatted cell block in a Perkin Elmer 450 spectrophotometer using the following extinction coefficients: for *trans*-$[Co(DH)_2NO_2(DMSO)]$, at 330 nm, $\varepsilon = 5690$ and at 370 nm, $\varepsilon = 4004$; for *trans*-$[Co(DH)_2NO_2SCN]^-$ at 330 nm, $\varepsilon = 6730$; for *trans*-$[Co(DH)_2NO_2Br]$ at 370 nm, $\varepsilon = 6130$; and an isosbestic point in the spectra of the *trans* solvent species and the *trans* thiocyanate species at 360 nm, $\varepsilon = 4720$.

The DMSO exchange rate was measured on a Varian A60 Spectrometer in a thermostatted probe at 26.5° C using the same procedure as Lantzke and Watts.[24,25]

Anation rate constants were calculated as second order constants for $\log(\varepsilon - \varepsilon_\infty)$ data plotted against time for reactions studied under pseudo-first-order conditions of excess anion concentration. All rate constants are initial rate constants calculated on the basis of an ε_∞ for completion of the forward process.

Results and Discussion

The anation results for both the systems: *trans*-$[Co(DH)_2NO_2(DMSO)] + X^- =$ *trans*-$[Co(DH)_2NO_2(X)]^- + DMSO$ in DMSO where $X^- = Br^-$ and SCN^- are accumulated in Tables I and II and show excellent second order kinetics comparable with other systems of this type.[5,16] The rate data is presented both as the primary pseudo-first order rate constants measured in vast excess of anion and the calculated second order constants. The rate data in each case were measured at constant ionic strengths maintained by Et_4NClO_4 in the Br^- system (ionic strength = 6.08×10^{-2} mol dm^{-3}) and by $KClO_4$ in the SCN^- system (ionic strength = 5.6×10^{-3} mol dm^{-3}). The activation parameters calculated for 26.5° C are $\Delta H^* = 109 \pm 4$ and 87 ± 2 kJ mol^{-1} and $\Delta S^* = 50 \pm 20$ and 0 ± 8 JK^{-1} mol^{-1} for the Br^- and SCN^- system respectively.

As previously discussed[5,14] the observation of second order kinetics in such systems is equivocal and is equally compatible with both a bimolecular mechanism or a dissociative process in which the anion competes unfavourably with the solvent for entry into the dissociative intermediate. Such a dissociative mechanism may be represented as:

TABLE I. Rate Constants for the Anation of *trans*-$[Co(DH)_2NO_2(DMSO)]$ by Br^- in DMSO. Initial [*trans*-$[Co(DH)_2NO_2(DMSO)]$] = 5.19×10^{-5} mol dm^{-3}, Ionic Strength = 6.08×10^{-2}.

t° C	$10^2[Et_4NBr]$ mol dm^{-3} [a]	$10^4 k_{obs}{}^{\circ}(s^{-1})$[a]	$10^3 k_2(dm^3\ mol^{-1}\ s^{-1})$
65.0	6.08	1.10	1.81
65.0	4.86	0.90	1.85
65.0	3.65	0.64	1.75
65.0	2.43	0.413	1.70
70.5	6.08	2.23	3.67
75.3	6.08	3.73	6.1
60.7	6.08	0.70	1.16
56.0	6.08	0.38	0.63
51.0	6.08	0.205	0.34

[a] Values at time zero.

TABLE II. Rate Constants for the Anation of *trans*-[Co(DH)$_2$NO$_2$(DMSO)] by NCS$^-$ in DMSO. Initial [*trans*-[Co(DH)$_2$NO$_2$(DMSO)]] = 5.19 × 10^{-5} mol dm^{-3}, Ionic Strength = 5.6 × 10^{-3}.

t° C	10^3[KNCS] mol dm^{-3} [a]	10^{4}k$_{obs}$°(s^{-1})[a]	10^{3}k$_2$(dm^3 mol^{-1} s^{-1})
65.1	5.61	0.490	8.7
70.3	5.61	0.82	14.6
75.5	5.61	1.28	22.3
80.0	5.61	1.87	33.3
80.0	4.21	1.41	33.4
80.0	2.81	0.94	33.3
80.0	1.40	0.473	33.5

[a] Values at time zero.

$$\textit{trans}\text{-}[\mathrm{Co(DH)_2NO_2(DMSO)}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Intermediate)}}{[\mathrm{Co(DH)_2NO_2}]} + \mathrm{DMSO}$$

$$[\mathrm{Co(DH)_2NO_2}] + \mathrm{X^-} \xrightarrow{k_x} \textit{trans}\text{-}[\mathrm{Co(DH)_2NO_2(X)}]^-$$

where full expression for the anation rate is:

$$\mathrm{Rate} = \frac{k_1[\mathrm{complex}][X^-]}{k_{-1}/k_x + [X^-]} = \frac{k_1[\mathrm{complex}]}{1 + k_{-1}/k_x[X^-]}$$

where [complex] is the reactant complex concentration. Such a dissociative mechanism will yield first order kinetics only if the anions compete favourably with the solvent for the intermediate (if $k_{-1}/k_x[X^-] \ll 1$).

In the present systems the anation rates and the solvent exchange rate (k_1, since the intermediate is an insignificant part of the system) could not be measured at the same temperature but extrapolation of the anation rates to 26.5° C yields the following comparative values: $k_1 = 1.90 \times 10^{-4}$ s^{-1},* $k_{Br^-} = 6.5 \times 10^{-8}$ s^{-1} and $k_{SCN^-} = 9 \times 10^{-7}$ s^{-1}, for $[X^-] = 5.6 \times 10^{-3}$ mol dm^{-3}, indicating the exchange rate, which is itself less than k_{-1}, to be substantially greater than $k_x[X^-]$ in both cases. A limiting rate, which in theory could be diagnostic of a dissociative mechanism (where $k_{-1}/k_x[X^-]$ becomes less than unity) is not attainable in either system because of the great difference between k_x and k_{-1}. Any tendency towards lack of linearity in the plots of the first order rate constants against [X$^-$] would be confused by ion association between X$^-$ and its accompanying cation as the concentration of this salt is increased.

The major difference between the anation rates here and those determined for the bisethylenediamine cobalt(III) complexes is the absence of a limiting rate which in the [CoX(SOL)(en)$_2$]$^{2+}$ is characteristic of substrate–anion association in a pre-equilibrium. The total absence of any tendancy to a limiting rate is in itself evidence of the absence of pre-equilibria in the anation of these neutral species, which further, do not have acidic proton sites (*c.f.* N-protons on ethylenediamine) to enhance such pre-association. The only acid protons in the bisdimethylgloximate complexes are presumably well insulated from outer sphere interaction in the (DH)$_2$ plane. The absence of outer sphere association is supported by total independence of the ultraviolet spectrum of *trans*-[Co(DH)$_2$NO$_2$(DMSO)] of high concentrations of Br$^-$ ion. In those cases in DMSO where aggregation was found in cobalt(III)–ethylenediamine systems substantial anion dependent charge transfer spectra were observed.[26]

If the limiting dissociative model is accepted as appropriate, then competition of DMSO, Br$^-$ and SCN$^-$ for the intermediate gives nucleophilicities (corrected to equal concentrations) of Br$^-$:DMSO:SCN$^-$ of 1:1.1:15. A greater nucleophilicity for SCN$^-$ compared with Br$^-$ has also been recorded for similar limiting dissociative mechanisms in water,[5, 16] although it is surprising that these values in DMSO, in which increased Br$^-$ activity compared with SCN$^-$ could be expected,[17] should show a widening of the gap in reactivity. However comparisons of this type are inevitably dangerous because of the unknown changes in transition state solvation induced.

To give a greater insight into the nature of the transition state in these reactions the solvolysis of the product *trans*-[Co(DH)$_2$NO$_2$Br]$^-$ has been studied:

$$\textit{trans}\text{-}[\mathrm{Co(DH)_2NO_2Br}]^- + \mathrm{DMSO} = \textit{trans}\text{-}[\mathrm{Co(DH)_2NO_2(DMSO)}] + \mathrm{Br^-}$$

The rate constants recorded in Table III yield an activation energy (E$_a$) of 115 ± 2 kJ mol^{-1}.

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* The pmr spectrum of *trans*-[Co(DH)$_2$NO$_2$(DMSO)] in d$_6$-DMSO shows one absorption at $\delta = 2.41$ ppm relative to NaTMS integrating to 18 protons (6 methyl-protons on coordinated DMSO and 12 methyl-protons on (DH)$_2$). With reaction this absorption reduces to 12 protons on the (DH)$_2$ and a new absorption (6 protons) arises due to free DMSO at $\delta = 2.57$ ppm. No signal is found for the two bridging protons in the (DH)$_2$ plane.

TABLE III. Rate Constants for the Solvolysis of *trans*-$[Co(DH)_2NO_2Br]^-$ in DMSO.

t° C	10^5[Complex] mol dm^{-3}	$10^5 k_{SOL}{}^{o}(s^{-1})^{a}$
70.3	6.22	3.10
75.7	6.22	5.6
78.8	6.22	8.0
81.5	6.22	10.8

[a] Values at time zero.

A comparison of the hydrolysis of *trans*-$[Co(DH)_2NO_2Br]^-$ in water[5] shows the hydrolysis reaction to be 1.7×10^3 times faster at 25° C ($k_{H_2O} = 1.15 \times 10^{-4}\ s^{-1}$ and $k_{DMSO} = 6.8 \times 10^{-8}\ s^{-1}$). Assuming a dissociative model for both these reactions then:[17]

$$\log \frac{k_{DMSO}}{k_{H_2O}} = \log {}^{H_2O}\gamma_{Com^-}^{DMSO} - \log {}^{H_2O}\gamma_{TS}{}^{DMSO}$$

where $Com^- \equiv$ *trans*-$[Co(DH)_2NO_2Br]^-$ and TS ≡ the dissociative transition state. Using the solubility products at 25° of K*trans*-$[Co(DH)_2NO_2Br]$ in DMSO ($7.3 \times 10^{-1}\ mol^2dm^{-6}$) and H_2O ($1.9 \times 10^{-2}\ mol^2dm^{-6}$) and ${}^{H_2O}\gamma_{K^+}^{DMSO} = -2.7$[17], the value of ${}^{H_2O}\gamma_{Com^-}^{DMSO}$ is 1.1. Substitution of the rate constants and ${}^{H_2O}\gamma_{Com^-}^{DMSO}$ in the above relationship yields $\log {}^{H_2O}\gamma_{TS}{}^{DMSO} = 4.3$ (*c.f.* $\log {}^{H_2O}\gamma_{Br^-}{}^{DMSO} = 5.7$).[17]

The transition state is clearly not closely related in character to the reactant complex ($\log {}^{H_2O}\gamma_{TS}{}^{DMSO} = 4.3$, $\log {}^{H_2O}\gamma_{Com^-}^{DMSO} = 1.1$). On the other hand if the transition state for the sake of argument is equated to the intermediate (a neutral penta-coordinated complex and free bromide ion) then one expects a $\log {}^{H_2O}\gamma_{TS}{}^{DMSO}$ to be the net result of $\log {}^{H_2O}\gamma_{Br^-}{}^{DMSO} = 5.7$, and a $\log {}^{H_2O}\gamma_{Int}{}^{DMSO}$ which is slightly negative due to the tendency of DMSO to better solvate large polarizable neutral species.[17] This dissociative model clearly is compatible the measured value of $\log {}^{H_2O}\gamma_{TS}{}^{DMSO}$ indicating something approaching total charge separation in the transition state and confirming the applicability of the limiting dissociative model. The law of microscopic reversibility dictates then that both the previous anation process and this solvolysis reaction are at least close to limiting dissociative processes.

The activation energy measured for this solvolysis reaction in DMSO (115 kJ mol^{-1}) is higher than the values recorded for the aqueous system (~94 kJ mol^{-1})[5] which is also compatible with a dissociative process generating free Br^- which is poorly solvated in DMSO.

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