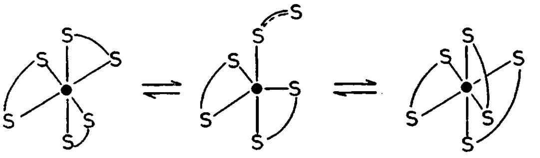
Pressure Dependence of the Racemization of Tris(pyrrolidyldithiocarbamato)-cobalt(III) in Non-aqueous Solvents

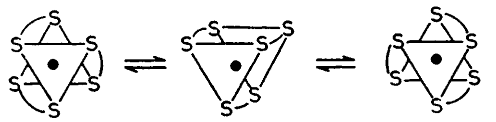
By GEOFFREY A. LAWRANCE,[*†] SURAPONG SUVACHITTANONT, DONALD R. STRANKS, and PETER A. TREGLOAN
(Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia)
and LAWRENCE R. GAHAN[†] and MAXWELL J. O'CONNOR
(Department of Analytical and Inorganic Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia)

Summary From activation volume evidence a twist mechanism incorporating a low-spin → high-spin pre-equilibrium in the transition state is indicated for racemization of $Co(pyrdtc)_3$ (pyrdtc = pyrrolidyldithiocarbamato) in non-aqueous solvents.

THE success of activation volume ($\Delta V^{\ddagger}$) in establishing mechanisms for racemization of octahedral metal complexes has been shown recently.[1-3] We have now applied activation volumes for the first time to mechanistic elucidation in the racemization of a formally neutral tris(dithiocarbamato)cobalt(III) complex in non-aqueous solvents.

A detailed study of solvent and temperature dependence of racemization in a series of $Co(dtc)_3$ complexes (dtc^- = dithiocarbamato) has been completed recently.[4] For any one dtc^- complex an appreciable variation of both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with solvent was observed, but the mechanistic details of the racemization were not forthcoming. Likely intramolecular mechanisms, distinguished by whether or not there is bond breaking in the transition state, are a one-ended dissociative mechanism (equation 1) or a trigonal twist mechanism (equation 2).


(1)


(2)

The former mechanism involves extension of a partially charged dtc^- arm into the solvent in the transition state. While the dissociated chelate arm does not carry a full formal negative charge, the arguments relating to $\Delta V^{\ddagger}$ prediction will be similar to those developed for this mechanism with oxalate^{2-} as chelate.[1] Since the periphery of the molecule is presumably fully solvated, the only change in the intrinsic volume of the molecule in the transition state will arise from extension of the S atom into the solvent. This small positive contribution ($<2\ cm^3\ mol^{-1}$) will be offset by a significant negative contribution to the experimental activation volume due to solvent electrostriction about the new charge centre generated by dissociation. Since it is likely that an appreciable negative charge density would reside on the extended S atom for the short lifetime of the five-co-ordinate intermediate, a negative $\Delta V^{\ddagger}$ is predicted for racemization of $Co(dtc)_3$ by this mechanism. Further, since each solvent will exhibit different solvating properties, partial molar volumes, and compressibility coefficients, both $\Delta V^{\ddagger}$ and the compressibility coefficient of activation ($\Delta\beta^{\ddagger}$) for racemization proceeding *via* a one-ended dissociation with dominant electrostrictive contributions should be markedly solvent dependent.

The arguments relating to racemization *via* a trigonal twist mechanism will be essentially those discussed previously.[1,5] Since this mechanism can be considered to a first approximation to occur without bond lengthening and only with bond angle distortion, a near-zero $\Delta V^{\ddagger}$ is predicted. For $Co(dtc)_3$ complexes the usual intraligand S–Co–S angle of 76·1°[6] approaches the angle for a trigonal intermediate of 81·8°, and hence a twist may be favoured. There is strong evidence from temperature-dependent n.m.r. studies of metal–dtc^- complexes in favour of a twist mechanism in octahedral systems.[7]

In the case of $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline) racemization a trigonal twist mechanism is also favoured.[2] However, a low-spin → high-spin pre-equilibrium with general metal–ligand bond lengthening contributing positively to $\Delta V^{\ddagger}$ is considered to precede twisting in the 'expanded' state. Ready spin equilibria in $Fe(dtc)_3$ complexes have been reported,[8] and the pyrrolidyl dtc^- ligand (pyrdtc) which we have chosen for this study exists as a high-spin iron(III) complex at room temperature. A relationship has been established previously indicating that the ligand field characteristics of the dtc^- ligands in $Fe(dtc)_3$ may be reflected in the $Co(dtc)_3$ analogues,[9] hence a spin-pre-equilibrium twist mechanism can be considered.

TABLE

Activation parameters for racemization of $Co(pyrdtc)_3$ in non-aqueous solvents

Solvent	$\Delta V^{\ddagger}$ $cm^3\ mol^{-1}$	$\Delta\beta^{\ddagger}$ $cm^3\ mol^{-1}\ kbar^{-1}$	$\Delta H^{\ddagger}$ $kJ\ mol^{-1}$	$\Delta S^{\ddagger}$ $J\ K^{-1}\ mol^{-1}$
Acetonitrile	+5·4	+2·5	103	+10
Ethanol	+9·8	+4·0	105	+18
Dimethylformamide	+5·2	+2·2	112	+35
Toluene	+7·8	+3·1	121	+51
(Average error)	(±0·3)	(±0·5)	(±5)	(±15)

Activation parameters for the racemization of $Co(pyrdtc)_3$ in four solvents are shown in the Table. The significantly positive $\Delta V^{\ddagger}$ in all solvents is not consistent with either a one-ended dissociation (negative $\Delta V^{\ddagger}$ predicted) or a

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[†] *Present address:* Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra, ACT, 2600, Australia.

simple twist mechanism (near-zero $\Delta V^\ddagger$ predicted). Subsequently a twist mechanism preceded by a low-spin → high-spin transition is indicated.

This mechanism is also supported by the observed pressure dependence of the activation volume in each solvent. The compressibility of activation ($\Delta\kappa^\ddagger$), defined as $\Delta\beta^\ddagger/\Delta V^\ddagger$,[10] is essentially independent of solvent [$\Delta\kappa^\ddagger = 0{\cdot}42 \pm 0{\cdot}02$ kbar^{-1} (1 bar = 10^5 Pa)]. This need not be the case for a one-ended dissociation since the compressibilities of the solvents are different, and solvent electrostriction dominates the experimental activation volume and compressibility coefficient of activation in that mechanism. Since we are dealing with a formally neutral complex, arguments relating to the essential incompressibility of ionic complexes do not apply.[10] In particular, a spin pre-equilibrium mechanism leading to an 'expanded' high-spin transition state should be associated in the case of a neutral complex with an appreciable change in compressibility from precursor to transition state, which should nevertheless be essentially solvent independent. This is borne out by our experimental results. The spin pre-equilibrium would contribute positively to $\Delta S^\ddagger$ as well as $\Delta V^\ddagger$, and the positive $\Delta S^\ddagger$ for the Co(pyrdtc)$_3$ complex can be compared with a positive $\Delta S^\ddagger$ for racemization of Fe(phen)$_3{}^{2+}$ and a negative $\Delta S^\ddagger$ for racemization of Cr(phen)$_3{}^{3+}$ where a twist mechanism with and without a spin pre-equilibrium is proposed, respectively.[1,2]

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