Conformational Effects in Stereoselective Electron Transfer between Metal Ion Complexes

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The oxidation of cobalt(II) in racemic *trans*-1,2-diaminocyclohexane (chxn) solution by [Δ-Co(edta)]$^-$ (edta^{4-} = 1,2-diaminoethane-*N,N,N',N'*-tetra-acetate) is a stereoselective reaction resulting in the formation of three conformational isomers of [Co(chxn)$_3$]$^{3+}$ in the ratios: (*lel*)$_3$ 36%, (*lel*)$_2$(*ob*) 37%, (*lel*)(*ob*)$_2$ 27% [where (*lel*) and (*ob*) refer to the conformation of the five-membered chelate ring, parallel or oblique to the C$_3$ axis] for which stereoselectivities are 25% Δ, 5% Δ, and 11% Λ respectively.

The modest chiral induction observed[1,2] in electron transfer reactions between metal ion complexes in solution promises to be an important probe of mechanism. In favourable cases, this stereoselectivity can be correlated with the stereoselectivity of the precursor ion pair.[3] Sargeson and coworkers postulate[4] that chelate ring conformation may be a factor in determining stereoselectivity. In this communication, the importance of this factor is demonstrated.

In the oxidation of [Co(en)$_3$]$^{2+}$ (en = 1,2-diaminoethane) by [Δ-CO(edta)]$^-$ (edta^{4-} = 1,2-diaminoethane-*N,N,N',N'*-tetra-acetate) studied by Geselowitz and Taube,[1] the [Co(en)$_3$]$^{3+}$ formed shows an excess of 10% of the Λ isomer† indicating a preferred $\Delta\Lambda$ interaction. Information on the precursor ion pair can be deduced from ion-exchange studies[5] with [Co(en)$_3$]$^{3+}$ and [Co(edta)]$^-$ where a preferred $\Delta\Lambda$

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† Quoted as % optical purity. The absolute configuration of [(+)-Co(en)$_3$]$^{3+}$ is mis-assigned in ref. 1.

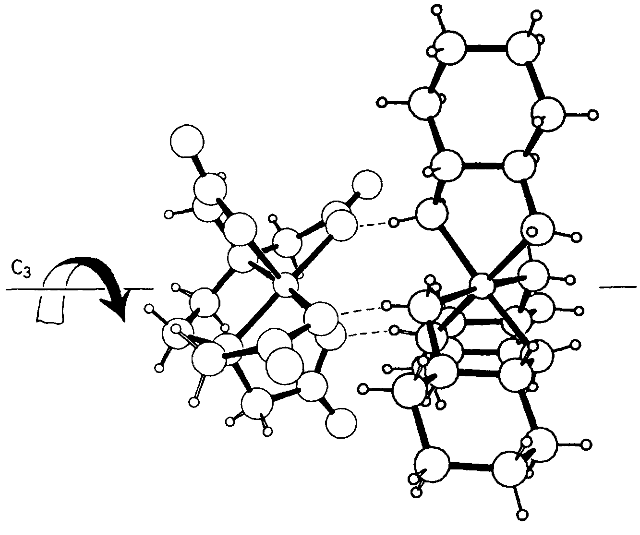

Figure 1. Ortep diagram viewed perpendicular to the C_3 axis of the proposed C_3C_3 interaction of [Δ-Co(edta)]$^-$ with [Δ-Co(chxn)$_3$-(*lel*)$_3$]$^{2+}$ showing the hydrogen bonding interaction (dashed lines) and the homochiral pairwise interaction. Structural data are taken from H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, 1959, **81**, 549, and F. Marumo, Y. Utsumi, and Y. Saito, *Acta Crystallogr., Sect. B*, 1970, **26**, 1492.

interaction is also indicated. In an octahedral complex, the chelate rings describe different helicities along the C_2 and C_3 axes [plus (P) or minus (M)] providing a structural basis for chiral discrimination. Thus [Δ-Co(edta)]$^-$ is designated P(C_3)M(C_2) while [Λ-Co(en)$_3$]$^{3+}$ is designated M(C_3)P(C_2).[6] Yoneda and coworkers[5] assert that homochiral pairwise interactions (PP or MM) are favoured and suggest a model for the preferred ion pair in which the pseudo-C_3 axis of [Co(edta)]$^-$ with three localized carboxylate charges is presented to the C_2 axis of [Co(en)$_3$]$^{3+}$ in an interaction in which hydrogen bonding is important. A similar structure for the precursor ion pair formed between [Co(edta)]$^-$ and [Co(en)$_3$]$^{2+}$ is attractive.

In the ion pairing interaction between [Co(edta)]$^-$ and [Co(chxn)$_3$-(*lel*)$_3$]$^{3+}$ (chxn = *trans*-1,2-diaminocyclohexane) the stereoselectivity is ΔΔ, consistent with a homochiral interaction along the C_3 axis of the latter complex since the C_2 axis is sterically constrained by the cyclohexane rings.[5] The ligand *trans*-1,2-diaminocyclohexane is chiral and the structural constraints of tris-chelate formation are such that the conformational isomers are diastereoisomers, not interconvertible by rotational processes. Four pairs of optical isomers of [Co(chxn)$_3$]$^{3+}$ are possible; (*lel*)$_3$, (*lel*)$_2$(*ob*), (*lel*)(*ob*)$_2$, and (*ob*)$_3$ where (*lel*) refers to a conformation of the five membered ring with the C–C bond parallel to the C_3 axis while in the (*ob*) conformation this bond is oblique to the C_3 axis.

Oxidation of [Co(chxn)$_3$]$^{2+}$ by [Δ-Co(edta)]$^-$ is, like the corresponding oxidation[1] of [Co(en)$_3$]$^{2+}$, a rapid process, likely to be outer-sphere in nature. It is also a stereoselective reaction. When [Δ-Co(edta)]$^-$ (1.9×10^{-3} M) is mixed with cobalt(II) (1.9×10^{-2} M) in racemic *trans*-1,2-diaminocyclohexane (1.9×10^{-1} M), the resulting [Co(chxn)$_3$]$^{3+}$ is optically active and consists of a mixture of diastereoisomers. Separation of the diastereoisomeric mixture was carried out on a Sephadex SP-C25 column using 0.1 M Na_2SO_4 as eluant.[7,8] Three pairs of optical isomers are readily separated‡ and were identified as (*lel*)$_3$: 36%, (*lel*)$_2$(*ob*) : 37%, and (*lel*)(*ob*)$_2$: 27% from their elution order and subsequent c.d. measurements.[7] Small amounts of the (*ob*)$_3$ isomer (<2%) may be present but were not identified. The isomer distribution differs from that found for [Co(chxn)$_3$]$^{3+}$ equilibrated over charcoal at 100 °C[7] and may reflect differences in the isomer distribution between cobalt(III) and cobalt(II) and differences in the electron transfer reactivities of the various isomers.[9]

Each of the isomer pairs shows evidence for stereoselective formation, presumably reflecting the stereoselectivity of the precursor complexes with (*lel*)$_3$: 25±2% Δ, (*lel*)$_2$(*ob*) : 5±1% Δ, (*lel*)(*ob*)$_2$: 11±1% Λ.[7] Not only do the stereoselectivities vary with ring conformation but the preferred isomeric form changes from Δ to Λ as the number of (*ob*) conformations increases. In the (*lel*)$_3$ isomer, amine protons on each co-ordinated nitrogen lie with the N–H bond almost parallel to the C_3 axis, readily available for hydrogen bonding along this axis as shown in Figure 1. Thus a C_3C_3 interaction is promoted in the precursor complex giving ΔΔ stereoselectivity as is observed in the ion-pairing experiments.[5] In the (*ob*) conformation, the N–H bonds are oblique to the C_3 axis and, combined with some steric relief along the C_2 axis, ΔΛ stereoselectivity is promoted.

The low stereoselectivity shown by the (*lel*)$_2$(*ob*) isomer of [Co(chxn)$_3$]$^{2+}$ is of some interest since [Co(en)$_3$]$^{3+}$ is thought to exist primarily in this form in solution[10] and reaction of [Co(en)$_3$]$^{2+}$ shows a larger stereoselectivity of the opposite sign. Despite the fact that the steric hindrance of the cyclohexane rings has little effect on electron transfer reactivity,[11] it does affect the mode of interaction with [Co(edta)]$^-$.

Certain reagents, notably $PO_4{}^{3-}$ are known to modify tris(1,2-diaminoethane) chelate conformation in solution.[12,13] Specifically, addition of $PO_4{}^{3-}$ to [Co(en)$_3$]$^{3+}$ induces the (*lel*)$_3$ conformer by hydrogen bonding along the C_3 axis.[14] This should promote an increase in the ΔΔ interaction. Consistent with this, the stereoselectivity of the reaction between [Δ-Co(edta)]$^-$ and [Co(en)$_3$]$^{2+}$ measured at 1.0 M ionic strength is 0.5% Λ in $PO_4{}^{3-}$ media, much smaller when compared with 8.5% Λ in $ClO_4{}^-$ media.

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‡ Greater than 97% of the [Co(chxn)$_3$]$^{3+}$ was recovered from the elution experiments.