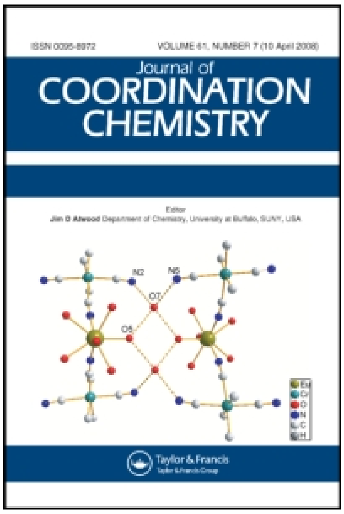

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STEREOSELECTIVITY IN THE REDUCTION OF Λ-[1,4,7-TRIAZACYCLONONANE-1,4,7-TRIS[2′(R)-2′-PROPIONATE]COBALT(III)]

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$[\mathrm{Co((R)\text{-}tacntp)}]\cdot\mathrm{NaBr}$, $C_{15}H_{24}BrCoNaN_3O_6$ crystallizes in the trigonal space group R3(No.146) with $Z = 3$, $a = 9.843(2)$ Å, $c = 15.781(4)$ Å and $R = 0.053$ for 859 reflections. The structure has been determined and the absolute configuration about the complex is $M(C_3)$ (Λ). The second-order rate constant for outer-sphere reduction of Λ-[Co((R)-tacntp)] by $[\mathrm{Co(en)_3}]^{2+}$ is $6.3 \times 10^{-2}\ M^{-1}s^{-1}$ at 25.0 °C and 0.10 M ionic strength. The product, $[\mathrm{Co(en)_3}]^{3+}$, is formed with 11% enantiomeric excess of the Δ isomer. The corresponding reduction of Λ-[Fe((R)-tacntp)] has a rate constant $5 \times 10^{3}\ M^{-1}s^{-1}$ and results in formation of $[\mathrm{Co(en)_3}]^{3+}$ which shows 3% enantiomeric excess of the Δ isomer.

KEYWORDS: absolute configuration, electron transfer, stereoselectivity

INTRODUCTION

In the course of studies of stereoselectivity in electron transfer reactions, interest has focused on reagents which retain chirality in adjacent oxidation states.[1,2] Some, such as $[\mathrm{Ru(en)_3}]^{3+/2+}$ and $[\mathrm{Co(sep)}]^{3+/2+}$,[3–5] rely on low substitution lability of the metal ion in both oxidation states while for others, the best known example of which is $[\mathrm{Co(pdta)}]^{-/2-}$,[6] the binding of a chiral ligand involves stereospecific coordination to the metal center and the chirality is preserved even when one of the complexes is substitution labile. It has been reported that the ligand, 1,4,7-triazacyclononane-1,4,7-tris[2′(R)-2′-propionate], (R)-tacntp^{3-}, also binds stereospecifically.[7] This ligand has the advantage that complexes are readily prepared with a number of different metal ions which are capable of exhibiting redox reactivity. Related complexes of the racemic 1,4,7-triazacyclononane-1,4,7-triacetate, tacnta^{3-}, including $[\mathrm{Co(tacnta)}]^{0/-}$, $[\mathrm{Fe(tacnta)}]^{0/-}$ and $[\mathrm{Ni(tacnta)}]^{0/-}$ have been well characterized.[8–10] For a number of these reagents, structural data are available,[8,10] and there is a dependence of the geometrical arrangement of the atoms coordinated to the central ion with the size of the metal ion.[11] Small ions promote an octahedral arrangement (type I) while, for larger ions, there is a significant distortion towards a trigonal prismatic arrangement (type II). This trend has an effect on the C_3 carboxylate face of these reagents, a feature which has been pinpointed as important in chiral recognition.[12]

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In this paper, the preparation and X-ray structure of the complex, Λ-[1,4,7-triazacyclononane-1,4,7-tris[2′(R)-2′-propionate]cobalt(III)] are described. This is the first X-ray structure of a cobalt(III) complex with a ligand of this type. The reaction with $[Co(en)_3]^{2+}$ (en = 1,2-diaminoethane) has been investigated and is found to exhibit stereoselectivity.

EXPERIMENTAL DETAILS

1,4,7-Triazacyclononane[13,14] and 2(S)-bromopropionic acid[15] were prepared by modifications of published procedures. The optical purity of the latter reagent was determined by NMR using the chiral shift reagent (1R,2R)-1,2-diphenyl-1,2-diaminoethane in $CDCl_3$.[16] The ligand 1,4,7-triazacyclononane-1,4,7-tris[2′(R)-2′-propionate] was prepared as described by Parker and coworkers,[7] but was not isolated and complexes were prepared directly from aqueous solutions of the ligand adjusted to neutral pH. Procedures used were analogous to those described for the tacnta complexes.[8,9]

For [Co((R)-tacntp)], an oxygen-free solution (20 mL) of (R)-tacntp (0.010 moles) was added to a solution (10 mL) of $Co(ClO_4)_2 \cdot 6H_2O$ (3.7 g, 0.010 moles) under argon. After the addition of argon-purged ethanol (140 mL), the solution was heated to 80°C and 20 mL of 30% H_2O_2 added dropwise. The resulting solution of the complex was cooled and 3.5 g of crude product which was heavily contaminated with salt was collected. Analysis indicates this product contains around 87% of the desired complex and that the major contaminant is NaBr. Small amounts of cationic complex ion impurities were removed by chromatography on SP-sephadex but the neutral complex which eluted remained contaminated with NaBr. The ^1H NMR of [Co((R)-tacntp)] (1.44 (*d*, 3), 3.01 (*m*, 2), 3.53 (*m*, 2), 3.94 (*q*, 1)) indicates a single isomer present. Purple crystals of [Co((R)-tacntp)]·NaBr were grown by vapor diffusion of 2-propanol into a concentrated aqueous solution of the complex containing NaBr. *Anal* calcd. for [Co((R)-tacntp)]·NaBr(%): Co 11.7; C 35.7; H 4.81; N 8.3. Found: Co 11.5; C 36.6; H 5.05; N 8.4. Spectroscopic data: (absorbance ε_{max}, $M^{-1}cm^{-1}$) $\varepsilon_{512} = 430$, $\varepsilon_{373} = 280$, $\varepsilon_{232} = 2.22 \times 10^4$; (circular dichroism $\Delta\varepsilon_{max}$, $M^{-1}cm^{-1}$) $\Delta\varepsilon_{540} = -1.02$, $\Delta\varepsilon_{487} = +0.10$, $\Delta\varepsilon_{449} = -0.11$, $\Delta\varepsilon_{368} = -1.21$, $\Delta\varepsilon_{256} = -8.57$, $\Delta\varepsilon_{226} = +14.6$.

For [Fe((R)-tacntp)], 2 g (0.010 moles) of $FeCl_3 \cdot 6H_2O$ in 30 mL water was added slowly at 80°C to a solution (20 mL) of (R)-tacntp (0.010 moles). The resulting yellow precipitate was recrystallized from dilute HCl (pH 3) to give 2.40 g of $[Fe((R)\text{-tacntp})] \cdot H_2O$. *Anal.* calcd. for $[Fe((R)\text{-tacntp})] \cdot H_2O$(%): C 43.28; H 6.31; N 10.10. Found: C 43.59; H 6.31; N 10.10. Spectroscopic data: (absorbance ε_{max}, $M^{-1}cm^{-1}$) $\varepsilon_{258} = 1.1 \times 10^4$; (circular dichroism $\Delta\varepsilon_{max}$, $M^{-1}cm^{-1}$) $\Delta\varepsilon_{366} = +0.66$, $\Delta\varepsilon_{298} = -1.1$, $\Delta\varepsilon_{250} = +2.50$, $\Delta\varepsilon_{225} = +4.8$.

A suitable crystal of [Co((R)-tacntp)]·NaBr was examined at 20°C on an Enraf-Nonius CAD4 computer-controlled diffractometer equipped with a graphite crystal, incident beam monochromator using Mo K*α* radiation (λ = 0.71073 Å). A summary of the crystal data and intensity collection parameters is presented in Table 1.[17] The space group was determined to be R3 (No. 146). A total of 997 reflections were collected, of which 859 were unique. The intensities of three representative reflections measured every 2h of X-ray exposure remained constant within experimental error throughout data collection. Lorentz and polarization

Table 1 Crystal data and experimental details for Λ[Co((R)-tacntp)]·NaBr.

formula	$C_{15}H_{24}BrCoNaN_3O_6$
F.W.	504.21
crystal dimensions	0.35 × 0.22 × 0.13 mm
space group	R3 (No. 146)
a	9.843(2) Å
c	15.781(4) Å
V	1324.1(4) $Å^3$
Z	3
cal. density	1.897 g/cm^3
μ(Mo Kα)	32.737 cm^{-1}
No. of refl. measured	997 total, 859 unique
reflections included	816
parameters refined	81
unweighted agreement factor[a]	0.03475
weighted agreement factor[b]	0.05308
esd of obs. of unit weight	1.684

[a] $R_1 = (\Sigma|F_0 - F_c|/\Sigma|F_0|)$, [b] $R_2 = (\Sigma w|F_0 - F_c|^2/\Sigma w|F_0|^2)^{1/2}$

corrections and an empirical absorption correction based on a series of psi-scans were applied to the data. Relative transmission coefficients from the absorption corrections ranged from 0.8483 to 0.9986 with an average value of 0.941. Data reduction was done by standard programs[18] and the structure was solved by direct methods.[19] The Co and Br atoms were located initially and the remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined by a full-matrix least-squares process. Anomalous dispersion effects were included in F_c.[20] Final cycles of least-squares refinement assigned anisotropic displacement parameters to all non-hydrogen atoms and included hydrogen atom coordinates and isotropic displacement parameters as fixed parameters. The highest peak in the final difference electron density Fourier map was 1.11 e/$Å^3$. The coordinates are presented in Table 2. Refinement on the other enantiomorph resulted in poorer agreement factors: 0.060 for R_1 and 0.090 for R_2, indicating the veracity of the enantiomorph reported.

The kinetics of oxidation of $[Co(en)_3]^{2+}$ by [Co((R)-tacntp)] were investigated under pseudo-first-order conditions using an excess of reductant. The decrease in

Table 2 Positional and equivalent isotropic thermal parameters for Λ-[Co((R)-tacntp)]·NaBr.

Atom	*x*	*y*	*z*	B($Å^2$)
Co	1.000	1.000	0.681	0.843(8)
Na	1.000	1.000	0.1571(2)	1.96(4)
Br	1.000	1.000	0.33123(6)	3.14(1)
O(1)	0.8318(3)	0.9846(3)	0.7481(2)	1.52(5)
O(2)	0.5814(4)	0.8224(4)	0.7774(2)	2.40(7)
N	0.8369(3)	0.8456(3)	0.6094(2)	1.22(5)
C(1)	0.9036(4)	0.7523(4)	0.5706(3)	1.64(7)
C(2)	0.7991(4)	0.9307(4)	0.5426(2)	1.56(7)
C(3)	0.7046(4)	0.7478(4)	0.6695(3)	1.62(7)
C(4)	0.5476(5)	0.6409(6)	0.6266(4)	2.51(9)
C(5)	0.7021(4)	0.8578(4)	0.7366(3)	1.50(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

absorbance of the oxidant at 430 nm was monitored with a Varian Instruments Cary 3 spectrophotometer thermostated at 25.0±0.2°C. Ionic strength was maintained at 0.10 M ($NaClO_4$) and the pH was varied over the range 10.0–11.5. Typically, oxidant concentrations were 1×10^{-4} M, with $[Co(en)_3]^{2+}$ concentrations in the range $(1-13) \times 10^{-3}$ M. The corresponding oxidation by [Fe((R)-tacntp)] was also studied under comparable conditions and the reaction was monitored at 467 nm, the absorbance maximum of the $[Co(en)_3]^{3+}$ product, with a Durrum Model D-110 stopped-flow spectrophotometer thermostated at 25.0± 0.1°C. In both studies, an excess of enH^+/en was used to provide buffering capacity. All solutions were prepared and used under an atmosphere of argon gas. Plots of $\ln(A-A_\infty)$ against time were generally linear for at least three half-lives, and pseudo-first-order rate constants k_{obsd} were calculated from the slopes by least squares analysis.

Stereoselectivities in the reactions of [Co((R)-tacntp)] and [Fe((R)-tacntp)] with $[Co(en)_3]^{2+}$ were determined at 23±1°C, pH 11.5 and 0.10 M ionic strength under an atmosphere of argon gas. The oxidant concentration was 10^{-4} M and $[Co(en)_3]^{2+}$ concentration was 10^{-3} M with [en] in excess, 0.13 M. After the reaction was run to completion, the solution was acidified with HCl to pH 1, the $[Co(en)_3]^{3+}$ product was isolated and purified on DEAE Sephadex C-25 as described previously,[21] and the optical purity determined by comparison with an optically pure sample of $[\Delta\text{-}(+)\text{-}Co(en)_3]Cl_3$ ($\Delta\varepsilon_{493} = 1.90\ M^{-1}\ cm^{-1}$).[22] Stereoselectivities are quoted as the % optical purity of the product (enantiomeric excess).

Absorption measurements were made on a Varian Instruments Cary 3 spectrophotometer, and circular dichroism measurements were recorded on an Aviv Model 62DS circular dichroism spectrometer. Metal ion analyses were made on a Perkin Elmer Model 400 Plasma Emission Spectrometer. NMR spectra were accumulated on a General Electric GN-300 MHz instrument at 25.0°C.

RESULTS AND DISCUSSION

The structure of [Co((R)-tacntp)] has crystallographically imposed C_3 symmetry, Figure 1. The ligand binds stereospecifically to the metal and the absolute configuration is $M(C_3)$ or Λ. Bond distances and angles of the ligand are normal, Table 3, and the Co-O and Co-N distances are within expected limits. The N-Co-N angle in the triazacyclononane ring is close to 90° and the conformation is δ. The N-Co-O bite angle of the amino-carboxylate chelate ring is 85.1° resulting in slight compression of the octahedral environment, and the ring has a λ envelope conformation. The overall configuration is therefore described as $\Lambda(\delta\lambda)$.[23] The twist angle, θ, between the nitrogen and oxygen planes is 7.5° from the octahedral value, consistent with the expected type I structure.[11] An NaBr of co-crystallization is aligned along the C_3 axis and the Na-Br distance is 2.75 Å, intermediate between the gas phase value (2.50 Å) and the value in crystalline NaBr (2.98 Å).[24] The Na^+ ion is four coordinate with Br^- and three terminal carboxylate oxyten atoms as donors in an arrangement which is close to tetrahedral. The Br^- ion is located on the C_3 axis within contact distance of the van der Waals radii of hydrogen atoms on the ligand backbone (Br-H(22) 2.76 Å, Br-H(3) 2.95 Å).[25]

The UV-visible spectrum of Λ[Co((R)-tacntp)], Figure 2, is similar to that reported[8,9] for the [Co(tacnta)] with absorption maxima at 512 nm (ε_{512} = 430

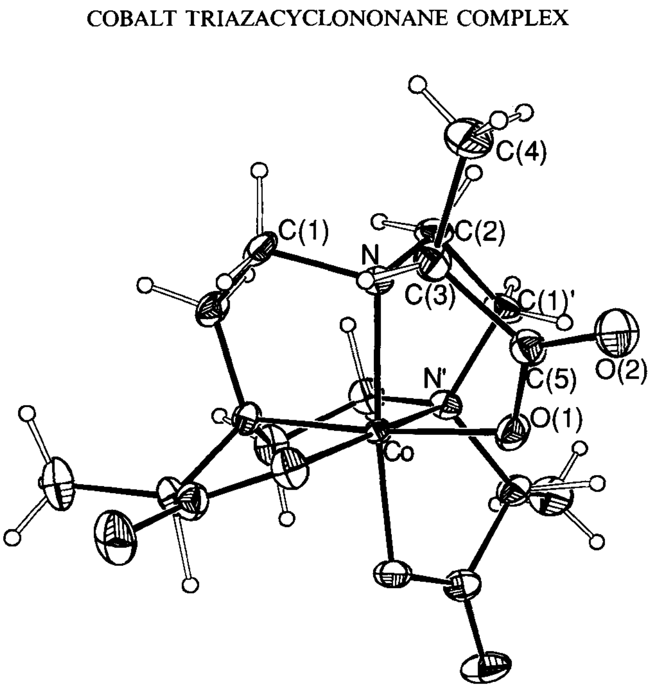

Figure 1 Ortep drawing of Λ-[Co((R)-tacntp)] showing the numbering scheme. Thermal ellipsoids are drawn to illustrate 50% probability surfaces. Hydrogen atoms are drawn arbritrarily small for clarity.

$M^{-1}cm^{-1}$) and 373 nm ($\varepsilon_{373} = 280\ M^{-1}cm^{-1}$) corresponding to the $^1A \rightarrow {}^1(A,E)$ $\{^1T_{1g}\}$ and $^1A \rightarrow {}^1(A,E)$ $\{^1T_{2g}\}$ transitions respectively, where the octahedral labels of the bands are given in curly parentheses. The A and E components of both bands must have opposite signs in their circular dichroism spectra and although much has been written concerning the assignment of the spectrum in D_3 and C_3 complexes,[26] it is difficult to do this unambiguously. The circular dichroism spectrum can be

Table 3 Selected bond distances (Å) and angles (deg) for Λ-[Co((R)-tacntp)]·NaBr.

			Distance				Distance				Distance
Co	O(1)		1.910(3)	C(3)	C(4)		1.525(5)	N	C(3)		1.505(5)
Co	N		1.925(3)	C(3)	C(5)		1.524(6)	C(1)	C(2)		1.515(5)
O(1)	C(5)		1.275(4)	N	C(1)		1.501(6)	Na	O(2)		2.259(3)
O(2)	C(5)		1.238(5)	N	C(2)		1.506(6)	Na	Br		2.747(3)
			Angle				Angle				Angle
O(1)	Co	O(1)′	91.9(1)	Co	N	C(3)	104.6(2)	C(4)	C(3)	C(5)	115.4(4)
O(1)	Co	N	85.1(1)	C(1)	N	C(2)	111.1(3)	O(1)	C(5)	O(2)	123.5(4)
O(1)	Co	N′	173.6(1)	C(1)	N	C(3)	111.7(3)	O(1)	C(5)	C(3)	115.5(3)
O(1)	Co	N″	93.8(1)	C(2)	N	C(3)	114.9(3)	O(2)	C(5)	C(3)	121.0(3)
N	Co	N	89.5(1)	N	C(1)	C(2)′	107.0(3)	Br	Na	O(2)	108.9(1)
Co	O(1)	C(5)	113.8(3)	N	C(2)	C(1)′	111.0(3)	O(2)	Na	O(2)′	110.1(2)
Co	N	C(1)	105.9(2)	N	C(3)	C(4)	114.6(4)				
Co	N	C(2)	108.0(2)	N	C(3)	C(5)	107.4(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

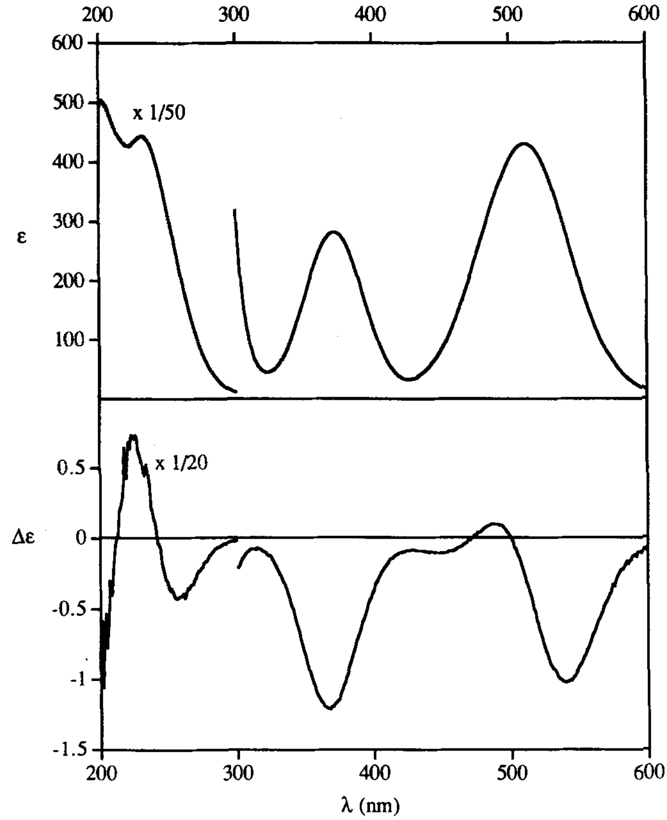

Figure 2 Absorption and circular dichroism spectra for Λ-[Co((R)-tacntp)] in unbuffered aqueous solution.

compared to that for *fac*-Λ-[Co((R)-alanine)$_3$] where the signs of the low energy components of both bands are negative.^{27} The spectrum is also similar to that for the cobalt(III) complex with the saturated ligand 1,4,7-tris{(2′S)-2′-hydroxypropyl} -1,4,7-triazacyclononane, where it is proposed that the $^1A \rightarrow {}^1A\{^1T_{1g}\}$ is the lowest energy transition on the basis of the twist angle of the ligating atoms in the C_3 complex.^{28} A similar conclusion is not unreasonable in the present case. Unusually, the propensity for the $^1A \rightarrow {}^1(A,E)$ $\{^1T_{2g}\}$ band to reflect the weak circular dichroism expected of a magnetic dipole-forbidden transition in octahedral symmetry is not observed for [Co((R)-tacntp)].

[Co((R)-tacntp)] is a modest oxidant with a reduction potential around 0.00 V (measured against n.h.e.)^8. The complex contains a C_3 carboxylate motif which has been shown,^{12} in reactions of related reagents, to be important for chiral discrimination in reactions with reductants such as $[Co(en)_3]^{2+}$. Reduction of [Co((R)-tacntp)] by $[Co(en)_3]^{2+}$ is first-order in both reactants, (Table 4) with a second-order rate constant of $6.3 \pm 0.2 \times 10^{-2}$ $M^{-1}s^{-1}$ at 0.10 M ionic strength and 25°C. The rate is independent of pH over the range 10.21 – 11.6. The rate constant and product are consistent with an outer-sphere process from which a self-exchange rate constant

Table 4 Pseudo-first-order rate constants for the reactions of Λ-[Co((R)-tacntp)] and Λ-[Fe((R)-tacntp)] with $[Co(en)_3]^{2+}$ at 25°C and 0.10 M ionic strength ($NaClO_4$).

Λ-[Co((R)-tacntp)] 10^2[Co(II)] (M)	pH	10^4 $k_{obsd}(s^{-1})$
1.19	10.24	7.33(5)
1.19	10.39	7.23(3)
1.19	10.64	7.33(3)
1.19	10.75	7.6(2)
1.19	11.56	7.1(2)
0.82	10.84	5.2(1)
0.61	10.90	4.04(8)
0.41	10.93	2.4(1)
0.20	10.94	1.35(6)
Λ-[Fe((R)-tacntp)] 10^2[Co(II)] (M)	pH	$k_{obsd}(s^{-1})$
0.84	12.85	42(5)
0.67	12.88	32(4)
0.51	12.82	25(3)
0.34	12.82	19(1)
0.186	12.86	7.4(3)
0.093	12.80	4.3(4)
0.25	12.92	11.6(3)
0.25	11.26	12.1(2)
0.25	9.88	12.1(5)

around 10^{-5} $M^{-1}s^{-1}$ for $[Co((R)\text{-tacntp})]^{0/-}$ can be estimated. The reaction exhibits stereoselectivity with an 11 ± 1% enantiomeric excess of the Δ form of product $[Co(en)_3]^{3+}$, an 11% $\Delta\Lambda$ process. This is in line with values for other complexes which contain the C_3 motif: $[Co(ox)_3]^{3-}$ 9%, $[Co(gly)(ox)_2]^{2-}$ 9%, $[Co(edta)]^-$ 10%, *cis*-β-$[Co(edda)(ox)]^-$ 8%, C_1-*cis*N-$[Co(gly)_2(ox)]^-$ 9%, all $\Delta\Lambda$ processes.[29] It is remarkable that the stereoselectivity is relatively insensitive to the change in charge on the complexes from −3 to 0, and the change in rate over four orders of magnitude. This observation stresses the importance of the hydrogen-bonding interaction involving the C_3 carboxylate face.

Studies were also carried out with the complex [Fe((R)-tacntp)] as oxidant ($E^\circ \approx 0.20$ V).[8] The reaction rate is much faster and first-order in both reagents with a second-order rate constant of $5.0 \pm 0.3 \times 10^3$ $M^{-1}s^{-1}$. Stereoselectivity measured in the $[Co(en)_3]^{3+}$ formed is 3 ± 1% again with an enantiomeric excess of the Δ isomer. [Fe((R)-tacntp)] is expected to have a type II structure with a distortion of the ligand donor atoms close to a trigonal prismatic structure,[8,11] but also with an $M(C_3)$ or Λ configuration.[7] Limited studies with [Ni(R)-tacntp)], which is a more potent type I oxidant,[10] reveal stereoselectivity of ≤2% $\Delta\Lambda$.[30]

With these structurally related complexes, the largest stereoselectivity is observed in the reaction between [Co((R)-tacntp)] and $[Co(en)_3]^{2+}$ which is also the most sluggish electron transfer reaction. This observation may be a reflection of a dependence of stereoselectivity on the electronic properties of the oxidant which change on changing the metal ion, or may be related to the sampling of precursor complex structures which changes with the rate of the reaction. In the related reductions of $[Co(edta)]^-$ by $[Co(en)_3]^{2+}$ and $[Ru(en)_3]^{2+}$,[3] again the less reactive $[Co(en)_3]^{2+}$ shows the higher stereoselectivity but in this case the differences can be explained by changes in chelate ring conformations as a result of the larger radius of cobalt(II) over ruthenium(II). In the present reactions also, structural variations are expected. The geometry of the C_3-carboxylate face varies with the ionic radius of the oxidant.[11] For small ions such as Co(III) and nickel(III),[10] the radii promote small distortions from idealized octahedral arrangement (type I structures) with $\theta = 7.5$ and 6.9°, respectively, whereas for iron(III),[8] the distortion is much larger with $\theta = 35°$, closer to an idealized trigonal prismatic arrangement (type II structure). It is not possible at this point to evaluate the effect of this structural change on stereoselectivity but the very small stereoselectivity found with [Ni((R)-tacntp)] suggests that this is a secondary factor.

Supplementary data

Additional material available from A. Graham Lappin.

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30. The complex [Ni((R)-tacntp)] decomposes under the reaction conditions with only 4% recovery of $[Co(en)_3]^{3+}$. Saenz, G.L. Thesis, University of Notre Dame, 1993.