

The oxidation of $[\text{Co}(\text{edta})]^{2-}$ by $[\text{Co}(\text{phen})_3]^{3+}$

Robert M.L. Warren, Lars Öhrström, Gregory J. Opiteck, Maoyu Shang,
A. Graham Lappin*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

Received 8 February 1994

Abstract

$[(\text{Co}(\text{phen})_3)[(\text{Sb}(\text{R},\text{R})\text{-tartrate})_2]\cdot 8\text{H}_2\text{O}$, $\text{C}_{44}\text{H}_{44}\text{N}_6\text{O}_{20}\text{CoSb}_2$, crystallizes in the trigonal space group $P3_221$ (No. 154) with $Z=3$, $a=18.861(4)$, $c=11.917(3)$ Å and $R=0.035$ for 1800 reflections. The structure has been determined and the absolute configuration of $(+)_{\text{S89}}\text{[Co}(\text{phen})_3\text{]ClO}_4\cdot 2\text{H}_2\text{O}$ formed from the compound by Cl_2 oxidation is confirmed as Λ . Reduction of $[\text{Co}(\text{phen})_3]^{3+}$ by $[\text{Co}(\text{edta})]^{2-}$ is outer-sphere with a second-order rate constant of $9.6\times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$ at 25 °C and 0.10 M ionic strength. When $\Lambda\text{-[Co}(\text{phen})_3]^{3+}$ is used as oxidant, chiral induction is observed and the $[\text{Co}(\text{edta})]^-$ product shows an enantiomeric excess of 20% of the Λ isomer. This homochiral ($\Lambda\Lambda$) preference contrasts with the heterochiral ($\Delta\Lambda$) preference found previously for reactions of $[\text{Co}(\text{edta})]^{2-}$ with $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Os}(\text{phen})_3]^{3+}$. Interpretation of the results is aided by ^1H NMR relaxation studies of the ion pair $\{[\text{Co}(\text{phen})_3]^{3+}, [\text{Co}(\text{edta})]^{-}\}$.

Keywords: Crystal structures; Oxidation; Electron transfer; Cobalt complexes; Chelate ligand complexes

1. Introduction

Stereoselectivity in outer-sphere electron transfer reactions between metal ion complexes is a widespread phenomenon [1] and serves as an important probe of mechanism. Interpretation of the phenomenon has centered on the relationship between chiral recognition in the assembly of the reactants which forms as a precursor to electron transfer and the chiral induction in the overall reaction process. In some reactions particularly where strong directional forces such as hydrogen bonds are present between the reactants, the overall chiral induction appears to be determined by chiral recognition [2,3]. In others, less well understood factors, attributed to the electron transfer process itself, have been shown to participate [4]. One fascinating observation relating to this topic is the variation in both the sense and magnitude of the chiral induction in reactions of $[\text{Co}(\text{edta})]^{2-}$ ($\text{edta}^{4-}=1,2\text{-diaminoethane-}N,N,N',N'\text{-tetraacetate}(4-)$) with $[\text{Co}(\text{bpy})_3]^{3+}$ ($\text{bpy}=2,2'\text{-bipyridine}$), $[\text{Fe}(\text{bpy})_3]^{3+}$, $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{Os}(\text{bpy})_3]^{3+}$ [5]. The metal complexes have similar shapes, so that discrimination based on shape, chiral recognition, is expected to be similar in all cases. However, with

$[\text{Co}(\text{bpy})_3]^{3+}$ and $[\text{Os}(\text{bpy})_3]^{3+}$, a homochiral ($\Delta\Delta$) preference is reported, while with $[\text{Fe}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$ and the related reaction of $[\text{Co}(\text{edta})]^{2-}$ with $[\text{Ru}(\text{bpy})_3]^{2+}$ [6], the preference is heterochiral ($\Delta\Lambda$).

Stereoselectivity has been found [5] in the reaction of $[\text{Fe}(\text{phen})_3]^{3+}$ ($\text{phen}=1,10\text{-phenanthroline}$) with $[\text{Co}(\text{edta})]^{2-}$ and, in this paper, investigations of the corresponding oxidation by $[\text{Co}(\text{phen})_3]^{3+}$ are reported to discover if the trend observed in complexes with bpy ligands is maintained also with the more rigid phen ligands where the stereoselectivities should be more pronounced [4]. The absolute configuration of $[\text{Co}(\text{phen})_3]^{3+}$ has been assigned only indirectly by analysis of circular dichroism spectra [7]. Since this presents a potential problem for interpretation, the absolute configuration of $[\text{Co}(\text{phen})_3]^{2+}$ is determined by X-ray crystallography as the $[(\text{Sb}(\text{R},\text{R})\text{-tartrate})_2]^{2-}$ ($(\text{Sb}(\text{R},\text{R})\text{-tartrate})_2]^{2-}=\text{diantimony(III)tartrate}(2-)$) salt. Information on the preferred orientation of the ions in the ion pair formed between the inert ions $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Co}(\text{edta})]^-$ is determined from solution NMR measurements. This ion pair serves as a model for the electron transfer precursor assembly

*Corresponding author.

and the orientation information is used to suggest an explanation for differences in chiral induction in these reactions.

2. Experimental

The complexes $\text{Na}[\text{Co}(\text{edta})] \cdot 2\text{H}_2\text{O}$ [8], $\text{Na} \Lambda\text{-}(+)_{546}\text{-}[\text{Co}(\text{edta})] \cdot 4\text{H}_2\text{O}$ ($\epsilon_{535} = 331 \text{ M}^{-1} \text{ cm}^{-1}$, $\Delta\epsilon_{575} = -1.79 \text{ M}^{-1} \text{ cm}^{-1}$) [9], $[\text{Co}(\text{phen})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ [10], $\Lambda\text{-}(+)_{589}\text{-}[\text{Co}(\text{phen})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ ($\epsilon_{455} = 99 \text{ M}^{-1} \text{ cm}^{-1}$, $\Delta\epsilon_{490} = +1.189 \text{ M}^{-1} \text{ cm}^{-1}$) [11,12], $[\text{Cr}(\text{phen})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ [13] and $\text{Na}[\text{Cr}(\text{edta})] \cdot 2\text{H}_2\text{O}$ [14] were prepared by literature methods. Solutions of $[\text{Co}(\text{edta})]^{2-}$ and $[\text{Co}(\text{phen})_3]^{3+}$ were prepared and used under an atmosphere of argon gas as described earlier [10,15,16].

Crystals of $[\text{Co}(\text{phen})_3][(\text{Sb}(R,R)\text{-tartrate})_2] \cdot 8\text{H}_2\text{O}$ were obtained as yellow, hollow hexagonal rods [11]. A suitable crystal fragment was examined at 20 °C on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A summary of the crystal data and intensity collection parameters is presented in Table 1. Data were collected by the $\theta\text{-}2\theta$ scan technique to a maximum 2θ value of 46.0°. Data with $F_o > 2\sigma(F_o)$ were considered observed. All calculations were performed on a VAX station 3200 using the SDP/VAX programming system. The systematic absences indicate two possible space groups, $P3_121$ and $P3_221$, and from subsequent least-squares refinement, the space group was determined to be $P3_221$ (No. 154). A total of 1995 reflections was collected, of which 1981 were unique and not systematically absent. The intensities of three representative reflections measured every 120 min remained constant within experimental error throughout data collection. Data reduction was by stan-

dard programs [17]. Lorentz and polarization corrections and an empirical absorption correction based on psi-scans were applied to the data. Transmission coefficients from the absorption corrections ranged from 0.9638 to 0.9988 with an average value of 0.980. The structure was solved by direct methods [18]. The Co and Sb atoms were located initially and the remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms from the phenanthroline ligands and the tartrate were located and added to the structure factor calculations but their positions were not refined. Hydrogen atoms from water molecules could not be located from difference Fourier syntheses. The structure was refined by a full-matrix least-squares process. A secondary extinction correction was applied. The highest peak in the final difference Fourier had a height of 0.43 e/\AA^3 . Refinement on the enantiomorph in the space group $P3_221$ converged with $R_1 = 0.038$, $R_2 = 0.048$, confirming that the correct enantiomorph is reported.

The kinetics of reduction of $[\text{Co}(\text{phen})_3]^{3+}$ by $[\text{Co}(\text{edta})]^{2-}$ were investigated under pseudo-first-order conditions at 0.10 M ionic strength (NaNO_3), 10^{-2} M MES (MES = 2-[*N*-morpholino]-ethanesulfonic acid) pH 6.0 and 25.0 ± 0.2 °C. Typically the oxidant concentration was 1.5×10^{-4} M with the reductant concentration in at least a ten-fold excess. In some experiments a ten-fold excess of $[\text{Co}(\text{edta})]^{2-}$ was also present. The reaction was monitored by absorbance measurements at 535 nm, observing the increase in absorbance due to the formation of $[\text{Co}(\text{edta})]^-$. Plots of $\ln(A_\infty - A)$ were generally linear for at least three half-lives, and pseudo-first-order rate constants k_{obs} were calculated from the slopes by least-squares analysis. Stereoselectivity in the reduction of optically active $[\text{Co}(\text{phen})_3]^{3+}$ with $[\text{Co}(\text{edta})]^{2-}$ was determined at 25 ± 1 °C, 0.10 M ionic strength (NaCl , NaNO_3 or Na_2SO_4) and pH 6.0 (10^{-2} M MES). In a typical experiment a solution of 1.5×10^{-2} M $[\text{Co}(\text{edta})]^{2-}$ was added to an equal volume of a 1×10^{-3} M solution of $\Lambda\text{-}(+)_{589}\text{-}[\text{Co}(\text{phen})_3](\text{ClO}_4)_3$ under an atmosphere of argon gas. Aliquots were withdrawn at 30 to 50 min intervals. Each aliquot was eluted through a Dowex 50W-X8 strong cation exchange column, and the product $[\text{Co}(\text{edta})]^-$ solution was characterized by absorption and circular dichroism spectroscopy. Absorption measurements were made on a Varian Instruments Cary 3 spectrophotometer, and circular dichroism measurements were recorded on an Aviv model 60DS or a model 62DS circular dichroism spectrometer.

NMR spectra were accumulated on a Nicolet NT-300 MHz instrument at 25.0 ± 0.5 °C. T_1 determinations were carried out using an inversion-recovery program. This employs the usual $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence, where τ is the delay time. At least 11 different delay times were used in each experiment. Spin-lattice relaxation times were evaluated by plotting $\ln(I_0 - I)$ against τ and calculating the slopes ($-1/T_1$) by least-squares analysis.

Table 1
Crystal data and experimental details for $[\text{Co}(\text{phen})_3][(\text{Sb}(R,R)\text{-tartrate})_2] \cdot 8\text{H}_2\text{O}$

Empirical formula	$\text{C}_{44}\text{H}_{44}\text{N}_6\text{O}_{20}\text{CoSb}_2$
Formula weight	1279.30
Crystal dimensions (mm)	$0.60 \times 0.12 \times 0.10$
Space group	$P3_221$ (No. 154)
<i>a</i> (Å)	18.861(4)
<i>c</i> (Å)	11.917(3)
<i>V</i> (Å ³)	3671(1)
<i>Z</i>	3
<i>D</i> _{calc} (g cm ⁻³)	1.736
$\mu(\text{Mo K}\alpha)$ (cm ⁻¹)	15.183
Extinction coefficient	3.557×10^{-8}
No. unique data measured	1981
No. unique observed data	1800
Data/variable ratio	5.4
<i>R</i> ₁	0.035
<i>R</i> ₂	0.043
<i>EOF</i>	1.48

All solutions for NMR studies were prepared with Cambridge Isotope Laboratories 99.9% D₂O under an atmosphere of argon gas to eliminate any effect of paramagnetic oxygen on the relaxation times.

3. Results

3.1. Structural studies

The structure of [Co(phen)₃][(Sb(*R,R*)-tartrate)₂] \cdot 8H₂O is isomorphous with iron analogue [19]. Atomic coordinates and temperature factors are presented in Table 2. The absolute configuration of [Co(phen)₃]²⁺ is Λ (M(C₃)), Fig. 1, and is confirmed

Table 2

Positional and isotropic thermal parameters for [Co(phen)₃][(Sb(*R,R*)-tartrate)₂] \cdot 8H₂O

Atom	x	y	z	B (Å ²)
Co	0.60154(7)	0.00000	0.66667	2.93(3)
N(1)	0.6452(3)	0.0929(3)	0.7913(4)	2.9(1)
N(2)	0.5588(3)	0.0774(3)	0.6044(4)	3.2(1)
C(1)	0.6917(4)	0.1021(4)	0.8803(6)	3.8(2)
C(2)	0.7194(4)	0.1687(4)	0.9502(6)	4.0(2)
C(3)	0.6970(4)	0.2271(4)	0.9349(5)	4.1(2)
C(4)	0.6473(4)	0.2193(4)	0.8436(5)	3.2(1)
C(5)	0.6213(4)	0.2761(4)	0.8171(6)	4.1(2)
C(6)	0.5746(4)	0.2659(4)	0.7280(6)	4.0(2)
C(7)	0.5495(4)	0.1983(4)	0.6518(5)	3.1(1)
C(8)	0.5046(4)	0.1873(4)	0.5534(6)	4.3(2)
C(9)	0.4881(4)	0.1224(4)	0.4834(6)	4.4(2)
C(10)	0.5163(4)	0.0704(4)	0.5107(6)	4.0(2)
C(11)	0.5753(3)	0.1413(4)	0.6737(5)	2.8(1)
C(12)	0.6240(3)	0.1503(3)	0.7720(5)	2.6(1)
N(3)	0.7185(3)	0.0612(3)	0.5928(4)	3.5(1)
C(13)	0.7467(5)	0.1214(5)	0.5179(7)	5.3(2)
C(14)	0.8247(6)	0.1567(6)	0.4762(8)	6.4(3)
C(15)	0.8746(5)	0.1295(7)	0.5110(8)	8.1(3)
C(16)	0.8473(5)	0.0636(6)	0.5892(7)	6.5(3)
C(17)	0.8956(6)	0.0270(8)	0.630(1)	10.1(4)
C(18)	0.7660(4)	0.0313(4)	0.6268(6)	4.3(2)
Sb	0.13064(3)	0.48008(3)	0.94381(4)	5.00(1)
C(19)	0.1128(4)	0.5901(5)	0.7884(6)	4.8(2)
C(20)	0.0391(4)	0.5575(4)	0.8687(6)	4.1(2)
O(1)	0.1611(3)	0.5618(3)	0.8022(4)	5.3(1)
O(2)	0.1217(3)	0.6428(4)	0.7183(5)	6.4(2)
O(3)	0.0391(3)	0.5021(3)	0.9472(4)	4.3(1)
C(21)	0.0149(5)	0.3086(5)	0.9903(7)	6.0(2)
C(22)	0.0382(5)	0.3120(5)	0.8691(7)	5.6(2)
O(4)	0.0485(3)	0.3763(4)	1.0427(4)	6.2(2)
O(5)	-0.0322(4)	0.2418(4)	1.0310(5)	8.2(2)
O(6)	0.0918(3)	0.3934(3)	0.8314(4)	5.4(1)
O(11)	0.9590(5)	0.8887(5)	0.9383(7)	10.4(3)
O(12)	0.9207(6)	1.1946(7)	0.2441(8)	16.3(4)
O(13)	0.3187(8)	1.2533(7)	0.564(1)	18.1(6)
O(14)	0.8444(7)	1.0745(8)	0.964(1)	17.5(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

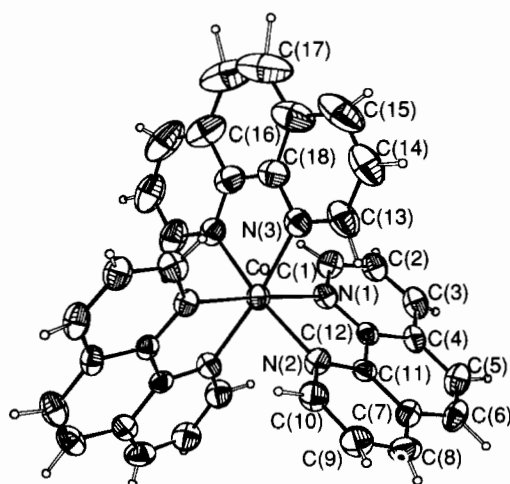


Fig. 1. ORTEP diagram of Λ -[Co(phen)₃]²⁺ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% level for non-hydrogen atoms and arbitrarily small radii are used for the hydrogen atoms.

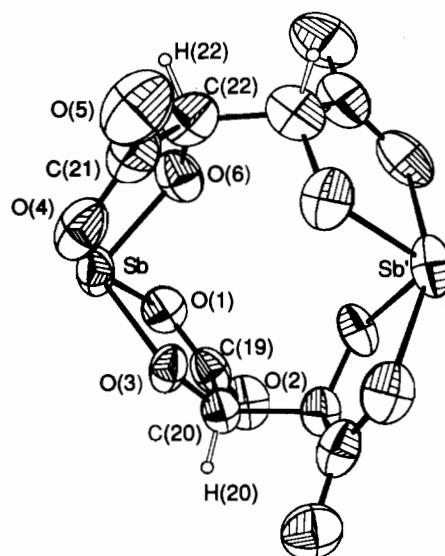


Fig. 2. ORTEP diagram of the [(Sb(*R,R*)-tartrate)₂]²⁻ ion showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% level for non-hydrogen atoms and arbitrarily small radii are used for the hydrogen atoms.

by the known configuration of [(Sb(*R,R*)-tartrate)₂]²⁻, Fig. 2. Oxidation of the salt with Cl₂ gives (+)_{S89}-[Co(phen)₃]³⁺ which has therefore the same, Λ , absolute configuration, confirming the assignment of Mason and Peart [7]. Bond lengths and angles in the complex anion, presented in Table 3, are similar to those reported previously [19]. The structure of the complex cation can be compared with that of the perchlorate salt [20]. Bond lengths and angles within the 1,10-phenanthroline ligands are similar to those of the previously reported structure. Although the coordination of the 1,10-phenanthroline ligands about the metal center is also similar, the Co–N bond lengths average 0.01 Å shorter in the

Table 3

Selected bond distances (Å) and angles (°) for [Co(phen)₃][[Sb(R,R)-tartrate]₂]·8H₂O

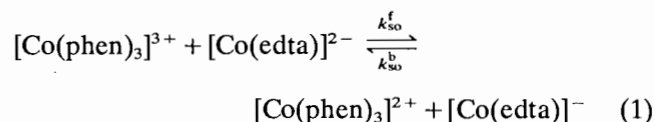
Bond distance			
Co–N(1)	2.123(5)	N(3)–C(13)	1.33(1)
Co–N(2)	2.121(6)	N(3)–C(18)	1.34(1)
Co–N(3)	2.100(5)	Sb–O(1)	2.159(5)
N(1)–C(1)	1.329(9)	Sb–O(3)	1.963(6)
N(1)–C(12)	1.35(1)	Sb–O(4)	2.140(5)
N(2)–C(10)	1.339(9)	Sb–O(6)	1.950(5)
N(2)–C(11)	1.362(8)		
Bond angles			
N(1)–Co–N(1)'	177.1(2)	O(4)–C(21)–O(5)	125.5(8)
N(1)–Co–N(2)	78.4(2)	O(1)–C(19)–O(2)	125.6(7)
N(1)–Co–N(2)'	99.4(2)	O(1)–Sb–O(3)	79.2(2)
N(1)–Co–N(3)	88.5(2)	O(1)–Sb–O(4)	153.5(2)
N(1)–Co–N(3)'	93.9(2)	O(1)–Sb–O(6)	85.2(2)
N(2)–Co–N(2)'	87.4(2)	O(3)–Sb–O(4)	82.7(2)
N(2)–Co–N(3)	97.4(2)	O(3)–Sb–O(6)	101.1(2)
N(2)–Co–N(3)'	171.6(2)	O(4)–Sb–O(6)	79.3(2)
N(3)–Co–N(3)'	78.7(3)	C(21)–C(22)–C(22)'	109.6(7)
Co–N(1)–C(1)	128.5(5)	C(20)–C(19)–O(1)	116.3(7)
Co–N(1)–C(12)	113.3(4)	C(20)–C(19)–O(2)	118.1(9)
Co–N(2)–C(10)	129.4(5)	C(19)–C(20)–O(3)	112.1(7)
Co–N(2)–C(11)	113.6(4)	C(19)–C(20)–C(20)'	108.0(5)
Co–N(3)–C(13)	127.8(6)	C(20)–C(20)–O(3)	111.6(5)
Co–N(3)–C(18)	112.3(4)	C(21)–C(22)–O(6)	112.5(7)
Sb–O(1)–C(19)	114.1(5)	C(22)–C(22)–O(6)	109.3(8)
Sb–O(3)–C(20)	118.1(4)	C(22)–C(21)–O(4)	116.3(6)
Sb–O(4)–C(21)	114.7(5)	C(22)–C(21)–O(5)	118.1(8)
Sb–O(6)–C(22)	117.0(5)		

Numbers in parentheses are e.s.d.s in the least significant digits.

present structure, a difference slightly larger than a standard deviation.

3.2. Kinetics studies

The reduction of [Co(phen)₃]³⁺ by [Co(edta)]²⁻, Eq. (1), has a small thermodynamic driving force. The



equilibrium constant determined from spectrophotometric measurements is 1.3 ± 0.1 . This reversibility complicates the kinetic analysis of the reaction because both forward and reverse rate constants participate in the rate law, and only a limited kinetic study was attempted. Pseudo-first-order rate constants, k_{obs} , for the oxidation of [Co(edta)]²⁻ by [Co(phen)₃]³⁺ in the absence of added [Co(edta)]⁻, were obtained under conditions of a large excess of [Co(edta)]²⁻ where the reaction involves >95% conversion to products and may be considered as an irreversible process [21]. The rate constants are collected in Table 4. In other experiments, an excess of the product, [Co(edta)]⁻, was added to the reaction and the approach to equilibrium

Table 4

Pseudo-first-order rate constants, k_{obs} , for the reaction of [Co(edta)]²⁻ with [Co(phen)₃]^{3+/2+} at 25.0 ± 0.2 °C, pH = 6.0 (MES) and 0.10 M ionic strength (NaNO₃)

[Co(edta)] ²⁻ (M)	[Co(edta)] ⁻ ^a (M)	[edta] ^b (M)	10 ⁵ k_{obs} (s ⁻¹)
7.68×10^{-3}	0.0	3.8×10^{-4}	7.53 ± 0.09
1.54×10^{-3}	0.0	3.8×10^{-4}	1.49 ± 0.05
7.68×10^{-3}	1.5×10^{-3}	3.8×10^{-4}	8.2 ± 0.3
7.68×10^{-3}	4.5×10^{-3}	3.8×10^{-4}	10.6 ± 0.9
7.68×10^{-3}	0.0	15.2×10^{-4}	7.7 ± 0.5

^aConcentration of added [Co(edta)]⁻ at start of reaction.^bConcentration of free edta above that necessary to form 1:1 stoichiometry with cobalt(II).

monitored. The pseudo-first-order rate constants in this case are $k_{\text{obs}} = \{k_{\text{so}}^{\text{f}}[\text{Co(edta)}]^{2-} + k_{\text{so}}^{\text{b}}[\text{Co(edta)}]^{-}\}$ and these two approaches yield $k_{\text{so}}^{\text{f}} = 9.6 \pm 0.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{so}}^{\text{b}} = 7.1 \pm 0.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ with $K = 1.35 \pm 0.06$, in good agreement with the spectrophotometric value. There does not appear to be an appreciable effect of free [H₂edta²⁻] on the rate.

3.3. Stereoselectivity studies

The determination of stereoselectivity in this electron transfer reaction is most readily accomplished by measuring optical activity in [Co(edta)]⁻ produced in the reaction of an excess of racemic [Co(edta)]²⁻ with optically active [Co(phen)₃]³⁺. The rate of racemization of [Co(edta)]²⁻ is rapid in comparison with the electron transfer rate [22], ensuring that this reactant remains a racemic mixture throughout the reaction. Racemization of the product [Co(edta)]⁻ is much slower than the electron transfer reaction, even in the presence of an excess of [Co(edta)]²⁻ where racemization by self-exchange can participate, and so optical activity induced in the product can be determined. However, the slowness of the reaction does present a problem. Racemization of the reactant, $\Lambda - (+)_{\text{S89}} - [\text{Co(phen)}_3]^{3+}$, takes place by a self-exchange mechanism in the presence of the product [Co(phen)₃]²⁺ [10,23]. Although the racemization process is initially slow since the concentration of [Co(phen)₃]²⁺ involved is small, the optical purity of the [Co(edta)]⁻ produced shows a steady decrease with increasing extent of reaction. Stereoselectivities determined at different conversion times after the start of the reaction between $\Lambda - [\text{Co(phen)}_3]^{3+}$ and [Co(edta)]²⁻ at 0.10 M ionic strength and 25 ± 1 °C are shown in Table 5. Extrapolation to 0% conversion gives a good estimate of the true stereoselectivity of the reaction and values are $20 \pm 2\%$ $\Lambda\Lambda$ in 0.10 M NaNO₃, $22 \pm 2\%$ $\Lambda\Lambda$ in 0.10 M Na₂SO₄ and $22 \pm 2\%$ $\Lambda\Lambda$ in 0.10 M NaCl.

Table 5
 Stereoselectivity results for the reduction of $\Lambda-(+)\text{-}_{\text{S89}}[\text{Co}(\text{phen})_3]^{3+}$ with $[\text{Co}(\text{edta})]^{2-}$ at 25 ± 1 °C and 0.10 M ionic strength

Medium	Stereoselectivity ^a	% Reaction	Medium	Stereoselectivity ^a	% Reaction
NaNO ₃	20.2% $\Lambda\Lambda^b$	0	NaNO ₃	20.7% $\Lambda\Lambda^b$	0
	15.9% $\Lambda\Lambda$	9.5		14.9% $\Lambda\Lambda$	10.5
	12.9% $\Lambda\Lambda$	16.2		11.1% $\Lambda\Lambda$	17.4
	9.2% $\Lambda\Lambda$	27.3		8.4% $\Lambda\Lambda$	26.7
	6.7% $\Lambda\Lambda$	35.5		6.1% $\Lambda\Lambda$	35.1
Na ₂ SO ₄	21.6% $\Lambda\Lambda^b$	0	NaCl	22.2% $\Lambda\Lambda^b$	0
	19.1% $\Lambda\Lambda$	15.3		18.8% $\Lambda\Lambda$	12.1
	17.3% $\Lambda\Lambda$	26.4		16.1% $\Lambda\Lambda$	21.8
	14.2% $\Lambda\Lambda$	41.9		11.2% $\Lambda\Lambda$	22.7
	11.5% $\Lambda\Lambda$	51.3		9.2% $\Lambda\Lambda$	42.9

^aEnantiomeric excess of $\Lambda\text{-}[\text{Co}(\text{edta})]^-$ formed in the reaction.

^bExtrapolation to 0 reaction completed to take account of racemization of $\Lambda\text{-}[\text{Co}(\text{phen})_3]^{3+}$.

3.4. NMR relaxation studies

Structure in the interactions between $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Co}(\text{edta})]^-$ was probed in a series of ¹H relaxation experiments involving paramagnetic analogues [4,24]. Studies were carried out on the interaction of $[\text{Co}(\text{phen})_3]^{3+}$ with $[\text{Cr}(\text{edta})]^-$, a paramagnetic analogue for $[\text{Co}(\text{edta})]^-$, and the interaction of $[\text{Co}(\text{edta})]^-$ with $[\text{Cr}(\text{phen})_3]^{3+}$, a paramagnetic analogue for $[\text{Co}(\text{phen})_3]^{3+}$. Four ¹H environments are readily distinguished in the spectrum of $[\text{Co}(\text{phen})_3]^{3+}$ and the assignments and observed T_1 relaxation times are shown in Table 6. In a structured ion pair with the paramagnetic ion, $[\text{Cr}(\text{edta})]^-$, the ¹H NMR relaxation times (T_1) for $[\text{Co}(\text{phen})_3]^{3+}$ decrease according to Eq. (2), where M_{diam} is the mole fraction of $[\text{Co}(\text{phen})_3]^{3+}$ free in solution, M_{para} is the mole

$$(1/T_1)_{\text{obs}} = M_{\text{diam}}(1/T_1)_{\text{diam}} + M_{\text{para}}(1/T_1)_{\text{para}} \quad (2)$$

fraction in the structured ion pair, $(1/T_1)_{\text{diam}}$ is the relaxation rate in the absence of the paramagnetic ion and $(1/T_1)_{\text{para}}$ is the relaxation rate in the isolated structured ion pair. When the diamagnetic complex is present in large excess, Eq. (2) can be modified to Eq. (3) where the term $\{K_0/(1+K_0[\text{Co}(\text{III})]_T)\} (1/T_1)_{\text{para}} = R_{\text{struct}}$ is defined as the relaxivity due to

$$(1/T_1)_{\text{obs}} = (1/T_1)_{\text{diam}} + \frac{K_0}{1+K_0[\text{Co}(\text{III})]_T} (1/T_1)_{\text{para}} [[\text{Cr}(\text{edta})]^-] \quad (3)$$

the structured ion pair. Additional contributions to the relaxivities from unstructured interactions, R_{unstruct} , will also occur. These will also show a linear dependence on $[[\text{Cr}(\text{edta})]^-]$ [24]. A similar scheme applies for the interaction of the six distinguishable ¹H environments of $[\text{Co}(\text{edta})]^-$ with $[\text{Cr}(\text{phen})_3]^{3+}$, Table 6. The dependence of $(1/T_1)_{\text{obs}}$ on the paramagnetic probe concentration is linear in all cases, and values vary with

the position of ¹H on the ligand backbone, Table 6, a characteristic of well structured ion-pairing interactions. The components, R_{struct} and R_{unstruct} can be separated by least-squares optimization of the Solomon–Bloembergen [26,27] correlation between R_{struct} and $(1/N)\sum(1/r_i^6)$ where r_i is the distance between the paramagnetic center and the i th equivalent proton and N is the number of equivalent proton environments in the complex. However, unconstrained analysis of this correlation failed to result in convergent fits at chemically sensible separations in either system. A consistent Co–Cr distance of 7 Å was imposed on both systems and the orientation of the paramagnetic centers relative to the protons was determined. It should be noted that while this constraint is a serious limitation, the orientations of the paramagnetic centers to the protons are relatively insensitive to the Co–Cr distance. The paramagnetic center $[\text{Cr}(\text{edta})]^-$ is close to the C_3 axis of $[\text{Co}(\text{phen})_3]^{3+}$, Fig. 3(a), while for $[\text{Co}(\text{edta})]^-$, the $\text{Cr}(\text{phen})_3]^{3+}$ paramagnetic center lies on the carboxylate face offset from the C_2 axis of the molecule, Fig. 3(b).

4. Discussion

Reduction potentials reported for $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Co}(\text{edta})]^-$ are both quoted as 0.37 V [28,29] and consequently the reaction of $[\text{Co}(\text{phen})_3]^{3+}$ with $[\text{Co}(\text{edta})]^{2-}$ is studied under reversible conditions. The equilibrium constant determined in this study, $K=1.3$, is in good agreement with the published potentials. Rate studies indicate that electron transfer between $[\text{Co}(\text{edta})]^{2-}$ and $[\text{Co}(\text{phen})_3]^{3+}$ is slow. The rate and products of the reaction are consistent with an outer-sphere mechanism. Self-exchange rate constants for $[\text{Co}(\text{phen})_3]^{3+/2+}$ and $[\text{Co}(\text{edta})]^{-/2-}$ are $12 \text{ M}^{-1} \text{ s}^{-1}$ [10,23] and $2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ [30], respectively, and

Table 6

Relaxivities obtained for the protons in $[\text{Co}(\text{phen})_3]^{3+}$ (a) and $[\text{Co}(\text{edta})]^{-}$ (b) in the presence of the paramagnetic relaxants $[\text{Cr}(\text{edta})]^{-}$ and $[\text{Cr}(\text{phen})_3]^{3+}$, respectively, at 25.0 ± 0.5 °C and 0.10 M ionic strength^a

(a) $10^4[[\text{Cr}(\text{edta})]^{-}]$ (M)	$(1/T_1)_{\text{obs}}$ (s^{-1})					
	$\text{H}_{2,9}$	$\text{H}_{3,8}$	$\text{H}_{4,7}$	$\text{H}_{5,6}$		
0.0	1.0	1.0	0.9	0.9		
3.3	33	31	16	15		
8.3	65	57	32	27		
11.6	91	87	44	43		
16.5	135	118	57	57		
24.8	199	189		84		
Relaxivity ($\text{M}^{-1} \text{s}^{-1}$) ^b	79200	74100	33800	33200		
(b) $10^4[[\text{Cr}(\text{phen})_3]^{3+}]$ (M)	$(1/T_1)_{\text{obs}}$ (s^{-1})					
	H_a	H_b	H_c	H_d	H_e	H_f
0.0	2.4	2.4	2.1	1.8	2.0	1.9
1.6	2.9	2.7	2.6	3.0	2.7	2.8
3.9	3.6	3.0	3.2	4.9	3.6	3.9
7.8	5.0	3.8	4.5	6.7	5.6	5.9
11.7	5.5	4.2	5.0	7.6	6.2	6.8
25.0	9.5	6.6	8.6	13.0	11.4	12.3
36.7	13.1	8.9	12.2		15.8	17.3
50.0	17.9	11.4			22.1	24.2
61.7	22.6	13.9			27.2	30.5
75.0		17.4			35.1	
100.0		22.7			43.2	
Relaxivity ($\text{M}^{-1} \text{s}^{-1}$) ^c	3180	2010	2690	4300	4190	4490

^aProtons assigned and labelled according to Ref. 25.

^bObtained from slopes of $(1/T_1)_{\text{obs}}$ against $[[\text{Cr}(\text{edta})]^{-}]$ at 25 ± 0.5 °C and 0.10 M ionic strength.

^cObtained from slopes of $(1/T_1)_{\text{obs}}$ against $[[\text{Cr}(\text{phen})_3]^{3+}]$ at 25 ± 0.5 °C and 0.10 M ionic strength. Values for R_{unstruct} are 1370 and 28200 $\text{M}^{-1} \text{s}^{-1}$, respectively, for the interactions of $[\text{Cr}(\text{phen})_3]^{3+}$ and $[\text{Cr}(\text{edta})]^{-}$ with the diamagnetic partners with Co–Cr separation 7 Å.

Marcus theory [31] can be used to calculate the rate of the forward reaction as $1.6 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$ at 0.10 M ionic strength and 25 °C, in fair agreement with the observed value of $9.6 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$. There is no evidence from the product analysis that species such as $[\text{Co}(\text{edta})(\text{H}_2\text{O})]^{2-}$ participate in the reaction [32].

The stereoselectivity determined in the reduction of $[\text{Co}(\text{phen})_3]^{3+}$ by $[\text{Co}(\text{edta})]^{2-}$, 20% $\Delta\Delta$, shows a preference for the homochiral reactant pair. A comparable result, 25% $\Delta\Delta$, again favoring the homochiral pair, was found in the reduction of $[\text{Co}(\text{ox})_3]^{3-}$ by $[\text{Co}(\text{phen})_3]^{2+}$, where the magnitude of the stereoselectivity was shown to be related to the rigidity of the phen ligand. There appears to be little effect of the anion of the supporting electrolyte on the stereoselectivity in the reaction although there are changes in both the rate of the electron transfer reaction and rate of racemization of $[\text{Co}(\text{phen})_3]^{3+}$ in the different media.

Stereoselectivities in the reactions of $[\text{Fe}(\text{phen})_3]^{3+}$ [5] and $[\text{Os}(\text{phen})_3]^{3+}$ [33] with $[\text{Co}(\text{edta})]^{2-}$ have been determined previously and it is of interest to note that in both cases a heterochiral or $\Delta\Delta$ preference is observed, contrasting with the homochiral preference in the reaction with $[\text{Co}(\text{phen})_3]^{3+}$. This difference cannot be

ascribed to mis-assignment of the absolute configurations of the complexes since these have been established directly by X-ray crystallography. Although the reactions of $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Os}(\text{phen})_3]^{3+}$ were studied in the pH range 2–3 where substantial amounts of the reductant are present as $[\text{Co}(\text{Hedta})(\text{H}_2\text{O})]^{-}$ [5,33], the reaction of $[\text{Co}(\text{edta})]^{2-}$ appears to dominate [32]. The differences in stereoselectivity between the reactions of $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$ with $[\text{Co}(\text{edta})]^{2-}$ are similar to those for the corresponding bpy complexes [5], and this observation requires some comment. However, before meaningful comment can be made, some understanding of the origins of stereoselectivity in these reactions must be presented.

In a general form, the rate of outer-sphere electron transfer between metal ion complexes can be represented by Eq. (4), where $g(r, \phi)$ is a distribution function describing the precursor association and dependent

$$k = \int_0^{\infty} g(r, \phi) 4\pi r^2 v_{\text{eff}}(r, \phi) \kappa_{\text{el}}(r, \phi) \kappa_{\text{nuc}}(r, \phi) dr d\phi \quad (4)$$

on the reaction distance, r , and an orientation parameter ϕ [34]. The terms describing electron transfer within

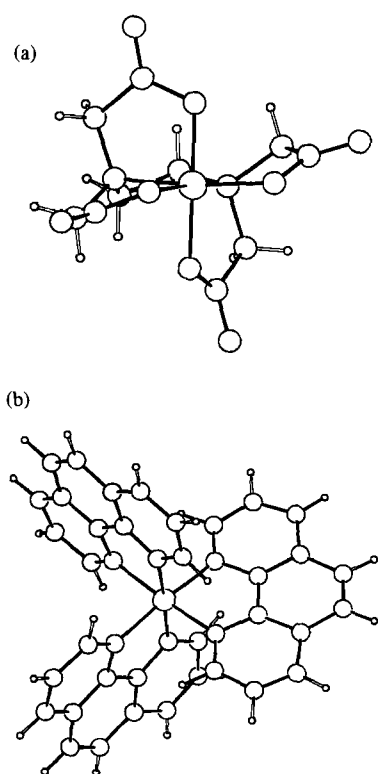


Fig. 3. Ion pair structure determined by ^1H NMR relaxation studies. (a) The relative orientation of the paramagnetic center $[\text{Cr}(\text{edta})]^-$ close to the C_3 axis of $[\text{Co}(\text{phen})_3]^{3+}$, and (b) the relative orientation of the paramagnetic center $[\text{Cr}(\text{phen})_3]^{3+}$ on the carboxylate face offset from the C_2 axis of $[\text{Co}(\text{edta})]^-$.

the precursor are an effective frequency, $\nu_{\text{eff}}(r, \phi)$, which carries the reaction from the precursor reaction surface to the successor reaction surface, and electronic factor, $\kappa_{\text{el}}(r, \phi)$, equal to 1 for an adiabatic reaction but otherwise dependent on the extent of coupling between the donor and acceptor orbitals, and a nuclear factor, $\kappa_{\text{nuc}}(r, \phi)$, associated with the energetics of reorganization of the reactants and the surrounding solvent to obtain a configuration of the transition state. It is useful to divide the overall process into a sequence of two steps; the formation of the precursor complex and the subsequent electron transfer within this precursor, particularly when as, in this case, the time frame associated with precursor formation is much more rapid than that for electron transfer. However, it must be remembered that this assembly is not represented by a single structure, but rather a statistical distribution of microstructures each with its own thermodynamic stability and electron transfer reactivity. The results of the NMR studies on the ion pair $\{[\text{Co}(\text{phen})_3]^{3+}, [\text{Co}(\text{edta})]^{-}\}$ strongly suggest that this distribution is very anisotropic.

Stereoselectivity in the electron transfer reactions arises from a number of sources. When the distribution functions for the homochiral and heterochiral reaction pairs differ, $\{g(r, \phi)\}_{\text{homo}} \neq \{g(r, \phi)\}_{\text{hetero}}$, then there is chiral recognition in the precursor assembly. In addition,

there are contributions to stereoselectivity from the electron transfer within this assembly. In the reactions of interest, the component $\nu_{\text{eff}}(r, \phi)$ is predominantly a metal–ligand stretching vibration, and consequently chiral induction from this source should be small. If the reactions are adiabatic $\{\kappa_{\text{el}}(r, \phi)\}_{\text{homo}} = \{\kappa_{\text{el}}(r, \phi)\}_{\text{hetero}} = 1$. The primary source for stereoselectivity is the nuclear factor, $\kappa_{\text{nuc}}(r, \phi)$, which classically is represented in Eq. (5), where λ_{in} and λ_{out} are parameters describing the respective rearrangements of the inner and outer coordination spheres to attain

$$\kappa_{\text{nuc}}(r, \phi) = \exp \left\{ \frac{\lambda_{\text{in}} + \lambda_{\text{out}}}{4} \left[1 + \frac{\Delta G^{\circ'}}{\lambda_{\text{in}} + \lambda_{\text{out}}} \right] \right\} \quad (5)$$

the transition state for electron transfer, and $\Delta G^{\circ'}$ is the thermodynamic driving force for electron transfer within the precursor–successor assembly. While internal reorganization of the complexes is expected to be similar for diastereomeric pairs, rearrangement of the outer coordination sphere can be an important source of stereoselectivity. Stereoselectivity from the driving force term, $\Delta G^{\circ'}$, will also arise where the ratios of the thermodynamic stabilities for precursor and successor assemblies differ for homochiral and heterochiral pairs.

In comparing stereoselectivities in the reductions of $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$ by $[\text{Co}(\text{edta})]^{2-}$, advantage of the superficial structural similarity of the reactants can be taken to more closely define the origins of chiral induction. It can be argued that chiral recognition in the formation of the precursor and successor assemblies and that chiral discrimination resulting from solvent reorganization in the electron transfer step should be similar for both reactions. Hence, very similar stereoselectivities might be expected. The observation that the selectivities are in opposite senses can be explained only if this argument is incorrect or if there is an additional source for chiral induction in at least one of the reactions. One possible source is the term $\kappa_{\text{el}}(r, \phi)$. If there is significant non-adiabaticity, then $\{\kappa_{\text{el}}(r, \phi)\}_{\text{homo}} \neq \{\kappa_{\text{el}}(r, \phi)\}_{\text{hetero}}$. Thus, it is argued that the metal ion dependence of the stereoselectivity originates in non-adiabaticity in at least one of the reactions.

Structure in the precursor assembly, $\{[\text{Co}(\text{phen})_3]^{3+}, [\text{Co}(\text{edta})]^{2-}\}$, is described by the distribution function, $g(r, \phi)$, and some insight into the nature of this distribution is obtained from the NMR relaxation studies with the analogue systems $\{[\text{Co}(\text{phen})_3]^{3+}, [\text{Cr}(\text{edta})]^{-}\}$ and $\{[\text{Cr}(\text{phen})_3]^{3+}, [\text{Co}(\text{edta})]^{-}\}$. Semiquantitative analysis of the relaxation data indicates that there is an orientational preference for the association between the ions and that the C_3 axis of $[\text{Co}(\text{phen})_3]^{3+}$ is presented to the pseudo- C_3 carboxylate face of $[\text{Co}(\text{edta})]^{2-}$. This mutual orien-

tation is reasonable since it allows the closest approach of the oppositely charged complex ions, maximizing the electrostatic attraction. A similar orientation for $[\text{Co}(\text{phen})_3]^{3+}$ was found in the interaction with $[\text{Cr}(\text{ox})_3]^{3-}$ [4], while the pseudo- C_3 carboxylate face of $[\text{Co}(\text{edta})]^-$ has been shown to be involved in interactions with a number of cationic species [24,35]. It is noteworthy that this favored juxtaposition of the reactant ions produces poor orbital overlap between the σ^* orbital of the donor and the σ^* orbital of the acceptor in the reaction between $[\text{Co}(\text{edta})]^{2-}$ and $[\text{Co}(\text{phen})_3]^{3+}$ but that this restriction is not as critical in the reaction with $[\text{Fe}(\text{phen})_3]^{3+}$ where the acceptor orbital has π symmetry. This simple observation may account for the difference in stereoselectivity in the reactions of $[\text{Co}(\text{edta})]^{2-}$ with $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$ where the favored orientation is reactive only for the latter reagent.

Acknowledgement

The support of the National Science Foundation (Grant No. CHE 90-16682) is gratefully acknowledged.

References

- [1] A.G. Lappin and R.A. Marusak, *Coord. Chem. Rev.*, 109 (1991) 125.
- [2] P. Osvath and A.G. Lappin, *Inorg. Chem.*, 26 (1987) 195.
- [3] R.M.L. Warren, K.J. Haller, A. Tatehata and A.G. Lappin, *Inorg. Chem.*, 33 (1994) 227.
- [4] R.M.L. Warren, A.G. Lappin and A. Tatehata, *Inorg. Chem.*, 31 (1992) 1566.
- [5] D.A. Geselowitz and H. Taube, *J. Am. Chem. Soc.*, 102 (1980) 4525.
- [6] Y. Kaizu, T. Mori and H. Kobayashi, *J. Phys. Chem.*, 89 (1985) 332.
- [7] S.F. Mason and B.J. Peart, *J. Chem. Soc., Dalton Trans.*, (1973) 949.
- [8] F.P. Dwyer, E.C. Gyrfas and D.J. Mellor, *J. Phys. Chem.*, 59 (1955) 296.
- [9] R.D. Gillard, P.R. Mitchell and C.F. Weick, *J. Chem. Soc., Dalton Trans.*, (1974) 1635.
- [10] R.M.L. Warren, A.G. Lappin, B. Dev Mehta and H.M. Neumann, *Inorg. Chem.*, 29 (1990) 4185.
- [11] C.S. Lee, E.M. Gorton, H.M. Neumann and H.R. Hunt, *Inorg. Chem.*, 5 (1966) 1397.
- [12] J. Ferguson, C.J. Hawkins, N.A.P. Kane-Maguire and H. Lip, *Inorg. Chem.*, 8 (1969) 771.
- [13] A.G. Lappin, M.G. Segal, D.C. Weatherburn and A.G. Sykes, *J. Am. Chem. Soc.*, 101 (1979) 2297.
- [14] D.T. Sawyer and J.M. McKinnie, *J. Am. Chem. Soc.*, 82 (1960) 4191.
- [15] G. Anderegg, *IUPAC Chem. Data Ser.*, 14 (1975) 5, 25.
- [16] W.A.E. McBryde, *IUPAC Chem. Data Ser.*, 17 (1978) 18.
- [17] B.A. Frenz, The Enraf-Nonius CAD 4 SDP – a real-time system for concurrent X-ray data collection and crystal structure determination, in H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G.C. Bassi (eds.), *Computing in Crystallography*, Delft University Press, Delft, Netherlands, 1978, p. 64.
- [18] P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.-J. Declercq and M.M. Woolfson, *MULTAN 11/82*, University of York, UK, 1982.
- [19] A. Zalkin, D.H. Templeton and T. Ueki, *Inorg. Chem.*, 12 (1973) 1641.
- [20] D. Boys, C. Escobar and O. Wittke, *Acta Crystallogr., Sect. C*, 40 (1984) 1359.
- [21] D. Cummins and H.B. Gray, *J. Am. Chem. Soc.*, 99 (1979) 5158.
- [22] S. Harada, Y. Funaki and T. Yasunaga, *J. Am. Chem. Soc.*, 102 (1980) 136.
- [23] M.R. Grace and T.W. Swaddle, *Inorg. Chem.*, 32 (1993) 5597.
- [24] R.A. Marusak and A.G. Lappin, *J. Phys. Chem.*, 93 (1989) 6856.
- [25] O.W. Howarth, *Polyhedron*, 2 (1983) 853.
- [26] I. Solomon, *Phys. Rev.*, 99 (1955) 559.
- [27] N. Bloembergen, *J. Chem. Phys.*, 27 (1957) 572.
- [28] R. Farina and R.G. Wilkins, *Inorg. Chem.*, 7 (1968) 514.
- [29] H. Ogino and K. Ogino, *Inorg. Chem.*, 22 (1983) 2208.
- [30] Y.A. Im and D.H. Busch, *J. Am. Chem. Soc.*, 83 (1961) 3357.
- [31] G.M. Brown and N. Sutin, *J. Am. Chem. Soc.*, 101 (1979) 883.
- [32] R.G. Wilkins and R. Yelin, *J. Am. Chem. Soc.*, 89 (1967) 5496.
- [33] D. Geselowitz, *Ph.D. Dissertation*, Stanford University, USA, 1982.
- [34] R.A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 811 (1985) 265.
- [35] R.A. Marusak, C. Sharp and A.G. Lappin, *Inorg. Chem.*, 29 (1990) 4453.