

207. Steric Crowding in Coordination Compounds: Electron-Transfer Kinetics of the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ Couple ($\text{tmen} = 2,3\text{-Dimethylbutane-2,3-diamine}$)

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The $[\text{Co}(\text{tmen})_3]^{3+}$ complex ion ($\text{tmen} = 2,3\text{-dimethylbutane-2,3-diamine}$) has been synthesized and its redox characteristics compared to those of its parent ion $[\text{Co}(\text{en})_3]^{3+}$. The 12 peripheral Me groups significantly affect the properties of the $[\text{Co}(\text{tmen})_3]^{3+}$ ion. The ligand-field bands are shifted to lower energies by about 1700 cm^{-1} compared to $[\text{Co}(\text{en})_3]^{3+}$. The reduction potential for $[\text{Co}(\text{tmen})_3]^{3+}$ is $+0.28\text{ V}$ (vs. NHE) compared to -0.18 V for $[\text{Co}(\text{en})_3]^{3+}$. The rate of the self-exchange reaction for the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ couple, $k = 8.5 \times 10^{-8}\text{ M}^{-1}\cdot\text{s}^{-1}$ was determined by applying the Marcus cross-relation with the reductants Cr^{2+} , V^{2+} , Eu^{2+} , Ru^{2+} , and $[\text{Co}(\text{sepulchrate})]^{2+}$.

Introduction. – Octahedral Co(III) complexes with NH_3 and bidentate aliphatic diamines are the most thoroughly studied coordination compounds. A great wealth of physical data concerning structure and reactivity has been collected over the years for the most prominent example, $[\text{Co}(\text{en})_3]^{3+}$ ($\text{en} = \text{ethylenediamine}$). Typically, Co(III)-amine complexes are yellow salts with the two ligand-field bands peaking around 470 and 340 nm. We have recently prepared the tris(2,3-dimethylbutane-2,3-diamine)cobalt(III) ion, $[\text{Co}(\text{tmen})_3]^{3+}$, and found its physical properties markedly different from its parent compound $[\text{Co}(\text{en})_3]^{3+}$. The most apparent difference is the pink-red color attributed to the two ligand-field bands at 504 and 362 nm with *ca.* twice the intensity compared to the en complex. This preliminary study showed remarkable shifts in the chemical reactivity such as rates of hydrolysis and electron transfer [1].

The classical approach to modelling simple electron-exchange reactions such as $[\text{ML}_6]^{3+/2+}$ relies on internal parameters of the two reactants, the metal-ligand distances and the force constants for the breathing vibration for both oxidation states. In addition, the distance between the two metal centers of different oxidation states and solvent properties should also be considered [2]. The $[\text{Co}(\text{tmen})_3]^{3+}$ complex provides a useful model to probe these effects. The weaker ligand field is expected to be compatible with longer Co–N distances in $[\text{Co}(\text{tmen})_3]^{3+}$ than in $[\text{Co}(\text{en})_3]^{3+}$. It is also expected that the steric crowding would not be as severe in the larger Co(II) ion, and the Co–N bond lengths in the $[\text{Co}(\text{tmen})_3]^{2+}$ ion would be rather similar to those in $[\text{Co}(\text{en})_3]^{2+}$. The corresponding smaller difference in the metal-to-ligand distances in $[\text{Co}(\text{tmen})_3]^{3+/2+}$ should accelerate the self-exchange reaction. The force constants for the breathing vibra-

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tion depend not only on the M–ligand bond strength but also on the ease of deformation of the chelate ring. Steric crowding would produce a more rigid or stiff coordination geometry, and hence lead to a decrease of the exchange rate. Finally, the separation distance of the two metal centers during electron transfer depends on the docking geometry of the precursor complex $\{[\text{Co}(\text{tmen})_3]^{3+} \cdots [\text{Co}(\text{tmen})_3]^{2+}\}$. Again, the 12 peripheral Me groups are expected to strongly influence this geometry.

The objective of our work is to determine the rate of the self-exchange for the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ couple and to assess the relative importance of the factors mentioned above in this structure-reactivity relationship. In this paper, we report the synthesis of $[\text{Co}(\text{tmen})_3]^{3+}$ and the investigation of the electron-transfer process by measuring a series of cross reactions. Further contributions will address the structural properties of the two reactants in conjunction with molecular-mechanics calculations and a detailed study of hydrolysis and racemization kinetics.

Experimental. – *Syntheses.* 2,3-Dimethylbutane-2,3-diamine (*tmen*). 2-Nitropropane (22.5 g) was dissolved in 125 ml of 10% NaOH by heating to $\sim 80^\circ$. The soln. was cooled to 10° , and a slurry of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (112.5 g) in 375 ml of sat. KH_2PO_4 was added in portions over 2 min. The resulting mixture was stirred for 10 min, the solid 2,3-dinitro-2,3-dimethylbutane isolated by filtration, washed with H_2O , and dried *in vacuo*. Yield: 15 g (68%). The reduction of the dinitro compound with Sn/HCl [3] yielded *tmen* · 2 HCl. A further sample of ligand was supplied by *Ciba-Geigy*, Marly.

trans- $[\text{Co}(\text{tmen})_2(\text{H}_2\text{O})_2]\text{Cl}_3$. $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (0.94 g, 4 mmol) and *tmen* · 2 HCl (1.5 g, 8 mmol) were dissolved in 20 ml of H_2O , 0.54 g (13.5 mmol) of NaOH was added and the soln. stirred at r.t. and air bubbled through it for 30 h. Conc. HCl (2 ml) was then added and the soln. evaporated to dryness. The solid was extracted with MeOH and filtered. The resulting green soln. was evaporated to yield ~ 1.7 g of crude product, which was dissolved in 20 ml of warm H_2O and filtered. An equal volume of conc. HCl was added. The volume of the soln. was reduced to 10 ml and cooled to 4° . The red solid was filtered and washed with cold 2M HCl (2×5 ml), and dried *in vacuo*. Yield: 0.775 g (45%). Further product could be obtained by concentration of the filtrate. UV/VIS (0.1M $\text{CF}_3\text{SO}_3\text{H}$, $\lambda_{\text{max}}(\epsilon)$ [nm, $\text{M}^{-1} \cdot \text{cm}^{-1}$]): 226 (14300), 372 (77), 514 (96). $^1\text{H-NMR}$ (60 MHz, D_2O): 1.33 (br. *m*). Anal. calc. for $\text{C}_{12}\text{H}_{36}\text{Cl}_3\text{CoN}_4\text{O}_2$: C 33.23, H 8.37, N 12.92, Cl 24.52; found: C 33.1, H 8.3, N 12.9, Cl 24.4.

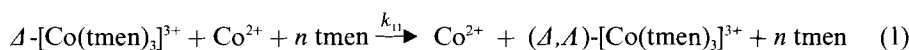
$[\text{Co}(\text{tmen})_3]^{3+}$. $[\text{Co}(\text{tmen})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ (1.0 g) was dissolved in 30 ml of MeOH to yield a green soln. from the initially pink solid. The green soln. contains the *trans*- $[\text{Co}(\text{tmen})_2\text{Cl}_2]^+$ ion; its spectrum, $\lambda_{\text{max}} \sim 615$ nm, $\epsilon = 42 \text{ M}^{-1} \cdot \text{cm}^{-1}$, is in good agreement with the published spectrum [4]. $[\text{Co}(\text{tmen})_2\text{Cl}_2]^+$ is rapidly hydrolyzed upon the addition of H_2O [5]. To this soln. was added 0.5 g of *tmen* (free base) in 10 ml of MeOH. The soln. was stirred at r.t. for 2 h, whereupon a large amount of precipitate had formed. The solid was collected and washed with MeOH, (3×10 ml) and Et_2O , (3×10 ml) to yield anal. pure racemic $[\text{Co}(\text{tmen})_3]\text{Cl}_3$. Yield 0.88 g (74%). Other salts of the complex could be prepared either by precipitation with the appropriate acid ($\text{CF}_3\text{SO}_3\text{H}$, TsOH, HClO_4 , HBr, or HBF_4) or by ion exchange. UV/VIS (H_2O ; $[\text{Co}(\text{tmen})_3]\text{Cl}_3$: $\lambda_{\text{max}}(\epsilon)$ [nm, $\text{M}^{-1} \cdot \text{cm}^{-1}$]): 224 (53000), 362 (177), 504 (177). $^1\text{H-NMR}$ ($[\text{Co}(\text{tmen})_3](\text{Ts})_3$; 400 MHz; D_2O): 7.69 (*d*, *J* = 8.5, 6 H); 7.36 (*d*, *J* = 8.5, 6 H); 2.39 (*s*, 9 H); 1.35, 1.32 (*s*, 36 H). $^1\text{H-NMR}$ (CD_3OD): 7.47 (*d*, *J* = 7, 6 H); 7.25 (*d*, *J* = 7, 6 H); 2.39 (*s*, 9 H); 1.39 (*s*), 1.35 (*s*), 1.24 (*s*) (~ 36 H). $^{13}\text{C-NMR}$ ($[\text{Co}(\text{tmen})_3](\text{Ts})_3$; 25.2 MHz, MeOH, *vs.* TMS): 140.3, 128.1, 125.8, 19.5 (Ts); 63.9, 25.2, 24.1 ($[\text{Co}(\text{tmen})_3]^{3+}$). Anal. of the triflate salt: calc. for $\text{C}_{21}\text{H}_{48}\text{CoF}_9\text{N}_6\text{O}_9\text{S}_3$: C 29.51, H 5.55, N 9.83, F 20.00; found: C 29.6, H 5.7, N 9.8, F 20.2.

Solns. Employed for the Reduction of $[\text{Co}(\text{tmen})_3]^{3+}$. $[\text{Co}(\text{sepulchrate})]^{2+}$ (sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) was prepared by Zn reduction of a $[\text{Co}(\text{sepulchrate})]^{3+}$ [6] soln. Cr^{2+} was obtained by reducing a soln. of $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ or $\text{Cr}(\text{ClO}_4)_3$ (from H_2O_2 reduction of CrO_3 in HClO_4) with amalgamated Zn. The same reducing agent was used to produce V^{2+} solns. from a stock soln. of V_2O_5 in HClO_4 . In all cases, the concentration of M^{2+} was assumed to match the concentration of the stock soln. before reduction. Eu^{2+} solns. were prepared by dissolving EuCO_3 [7] in deaerated HClO_4 , $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ by dissolving solid $[\text{Ru}(\text{H}_2\text{O})_6]$ (Ts)₂ [8] in deaerated aq. HTfl. All air-sensitive reactions were carried out under Ar using *Schlenk* or syringe techniques.

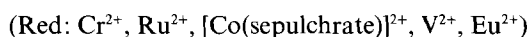
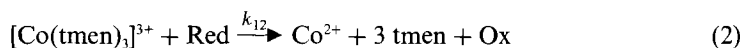
The reduction of $[\text{Co}(\text{tmen})_3]^{3+}$ was followed in thermostatted cuvettes (25°). All the reactions were carried out with a large excess (> 10 -fold) of the reductant over the Co(III) complex so that the reactions were pseudo-first-order. One exception to this generalization is the reduction by Ru^{2+} , where in one instance the rate of the reaction required the use of only a 5-fold excess of reductant. The reactions were monitored spectrophotometrically (*Cary 17 D*) at or near the extinction maximum of the $[\text{Co}(\text{tmen})_3]^{3+}$ complex, 504 nm.

Results and Discussion. – The $[\text{Co}(\text{tmen})_3]^{3+}$ ion is reduced at a potential of *ca.* 450 mV more positive than $[\text{Co}(\text{en})_3]^{3+}$, for which a reduction potential of -0.18 V (*vs.* hydrogen electrode) is reported [9]. Cyclic voltammetry with scan rates up to 100 mVs^{-1} showed only irreversible reduction of $[\text{Co}(\text{tmen})_3]^{3+}$ in H_2O , DMF, and MeOH. DC polarography in MeOH and DMF, however, produced data satisfying the criteria for reversibility. From these experiments, we obtained a value of $+0.28$ V for the standard potential of the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ couple.

Preliminary investigations of the kinetics of racemization as well as hydrolysis of $[\text{Co}(\text{tmen})_3]^{3+}$ in basic solution showed the half-lives for these reactions to be very short [1]. This reactivity is in striking contrast to $[\text{Co}(\text{en})_3]^{3+}$ where the same half-lives are of the order of years [10]. For that reason, the direct determination of the self-exchange rate for the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ couple by monitoring (*Eqn. 1*)



the loss of optical activity of the Δ - (or A -) Co(III) species in a solution containing an excess of the free ligand and Co(II) is not feasible. Instead, the *Marcus* cross relation has been employed to extract the self-exchange rate for our complex ion from the study of several heteronuclear redox processes of the general reaction (*Eqn. 2*)



For cross reactions with a small driving force, this approach offers a reliable method to calculate self-exchange rates [11]. In this context, the relevant equations are:

$$k_{11} = k_{12}^2/k_{22} \cdot K_{12} \cdot f_{12} \quad (3)$$

$$\ln f_{12} = (\ln K_{12})^2/4 \ln (k_{11} \cdot k_{22}/Z^2) \quad (4)$$

The rates k_{11} and k_{12} are defined by *Eqns. 1* and *2*, k_{22} is the self-exchange rate for the redox partner of $[\text{Co}(\text{tmen})_3]^{3+}$ in the cross reaction (*Eqn. 2*), K_{12} is the equilibrium constant for *Reaction 2*, and Z is the collision frequency, usually taken as $10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$ [2]. The application of these equations to the experimental data collected in *Table 1* offers a reasonably consistent estimate for the self-exchange rate k_{11} for the $[\text{Co}(\text{tmen})_3]^{3+}$ couple.

Table 1. *Experimental Rates for the Reduction Kinetics of $[\text{Co}(\text{tmen})_3]^{3+}$*

Reducing agent	Medium	$k_{12} [\text{M}^{-1} \cdot \text{s}^{-1}]$
$\text{V}_{\text{aq}}^{2+}$	1M HClO_4	$(6.6 \pm 0.1) \times 10^{-1}$
$\text{Cr}_{\text{aq}}^{2+}$	1M $\text{NaTfI} + 0.1\text{M Htfl}^{\text{a}}$	$(1.04 \pm 0.3) \times 10^{-2}$
$\text{Ru}_{\text{aq}}^{2+}$	1M $\text{NaTfI} + 0.1\text{M Htfl}$	$(5.6 \pm 0.5) \times 10^{-3}$
$\text{Eu}_{\text{aq}}^{2+}$	1M HClO_4	$(4.9 \pm 0.5) \times 10^{-1}$
$[\text{Co}(\text{sep})]^{2+\text{b}}$	0.2M NaCl	87 ± 10

^a) tfl = Triflate, CF_3SO_3^- . ^b) sep = Sepulchrate.

Table 2. Calculated Self-Exchange Rates for $[\text{Co}(\text{tmen})_3]^{3+/2+}$ (k_{11} , k_{12} , k_{22} in $\text{M}^{-1} \cdot \text{s}^{-1}$)

Reducing agent		k_{22}	E [V]	$\log K_{12}$	k_{12}	k_{11}
$\text{V}_{\text{aq}}^{2+}$	[12]	10^{-2}	-0.255	9.04	6.6×10^{-1}	2×10^{-7}
$\text{Cr}_{\text{aq}}^{2+}$	[13]	2×10^{-7}	-0.41	11.7	1.04×10^{-2}	10^{-8}
$\text{Ru}_{\text{aq}}^{2+}$	[14]	20	+0.205	1.27	5.6×10^{-3}	9×10^{-8}
$\text{Eu}_{\text{aq}}^{2+}$	[15]	4×10^{-4}	-0.38	11.15	4.9×10^{-1}	4×10^{-8}
$[\text{Co}(\text{sep})]^{2+}$	[6]	5.1	-0.26	9.12	87	7×10^{-6}

Table 2 summarizes the results obtained by a self-consistent application of the Marcus cross relation, Eqns. 3 and 4 to various heteronuclear electron-transfer processes. Whereas the results obtained from reduction by aqua ions with k_{22} between 10^{-7} and $20 \text{ M}^{-1} \cdot \text{s}^{-1}$ are in a close range between 10^{-7} and $10^{-8} \text{ M}^{-1} \cdot \text{s}^{-1}$ (25° , $\mu = 1.0$), the value for the $[\text{Co}(\text{sepalchrate})]^{2+} + [\text{Co}(\text{tmen})_3]^{3+}$ reaction produces a faster self-exchange rate. There is no obvious simple explanation for this deviation, possibly the more hydrophobic sepulchrate periphery may affect the solvent reorganization of the activation energy [2]. Excluding this value, we obtain a self exchange rate of $8.5 \times 10^{-8} \text{ M}^{-1} \cdot \text{s}^{-1}$ for the $[\text{Co}(\text{tmen})_3]^{3+/2+}$ couple, three orders of magnitude smaller than the corresponding rate for the parent $[\text{Co}(\text{en})_3]^{3+/2+}$ pair [16].

The redox kinetics of the two couples $[\text{Co}(\text{en})_3]^{3+/2+}$ and $[\text{Co}(\text{tmen})_3]^{3+/2+}$ are compared by considering the three crucial parameters briefly mentioned in the Introduction. Differences Δr of the Co–N distances in the two oxidation states are estimated from molecular-mechanics calculations [17]²⁾, because only for the $[\text{Co}(\text{en})_3]^{3+/2+}$ couple an experimental figure, $\Delta r = 0.19 \text{ \AA}$ [18] is known. The calculated values of 0.185 \AA for $[\text{Co}(\text{en})_3]$ and 0.191 \AA for $[\text{Co}(\text{tmen})_3]$ are virtually identical and do not offer a rationalization of the different exchange rates. Since no normal coordinate analyses have been carried out for the complex ions considered in this study, it is not possible to estimate the vibrational contribution. However, the stiffness caused by the steric crowding of the Me groups is assumed to raise the activation energy, hence to decrease the exchange rate of the tmen complexes relative to their en analogues. Also a rate-decreasing effect is expected to arise from the overall geometry compatible with a larger metal–metal distance for the tmen system. The approximately spherical $[\text{Co}(\text{en})_3]^{n+}$ ions can associate in various relative orientations to form precursor complexes with a narrow range of Co–Co distances. The tmen complexes have disc-like shapes with the three-fold axis perpendicular to the disc plane. The Co^{3+} -to- Co^{2+} distance within the precursor complex is roughly identical for both ligands, if the complex ions approach one another along their trigonal axes, *i.e.* if the docking geometry corresponds to a stacking of discs. For all the other relative orientations of the tmen complexes, the 12 Me groups of each plate-like $[\text{Co}(\text{tmen})_3]^{n+}$ lead to a considerably larger average separation of the metal centers, thus to a smaller self-exchange rate. In a comparative study of tris(cyclohexanediamine)cobalt(III) ($[\text{Co}(\text{chxn})_3]^{3+}$) and $[\text{Co}(\text{en})_3]^{3+}$, it was found that there was virtually no difference between the rates of reduction of the two Co complexes by $[\text{Cr}(\text{bipy})_3]^{2+}$, V^{2+} , and $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^+$. $[\text{Co}(\text{chxn})_3]^{3+}$, like $[\text{Co}(\text{tmen})_3]^{3+}$, has a plate-like molecular shape leading to the conclusion that for both complex ions the reduction proceeds *via* approach of the reactants

²⁾ Molecular-mechanics calculations were performed using the program MOMECS85 kindly supplied by Dr. T. W. Hambley, University of Sydney.

along their trigonal axes [19]. This geometrical aspect has been qualitatively taken into account by the introduction of a steric factor for reactions involving metallo-enzymes [20]. Crystallographic studies on the Co system as well as investigations of the analogous Ru complexes in our laboratory are expected to quantify the various contributions in order to map the redox pathway for these coordination compounds.

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