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Electron Transfer across a Coordinated Azide Group Positioned *trans* to Secondary Nitrogen and Thioether Donors

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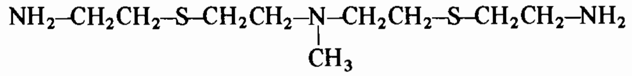
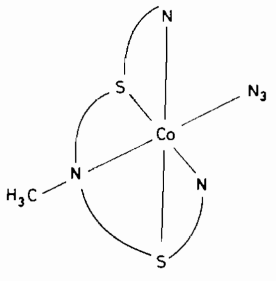
Recent work in our laboratory has centered on the design and synthesis of ligands which when coordinated octahedrally to metal ions, selectively place thioether or secondary nitrogen donors *trans* to a single site suitable for substitution and/or reaction. Two such new ligands are Q and QS [1]. Because of their design and in consideration of stereochemical requirements for coordinated R–S–R and $>$N–CH$_3$ donors, the number of possible cobalt(III) geometric isomers is restricted to the αα topology [2–4]:

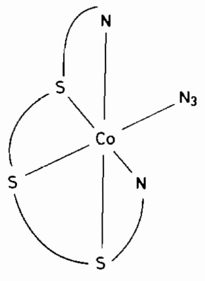


Q: $NH_2–CH_2CH_2–S–CH_2CH_2–\underset{CH_3}{\underset{|}{N}}–CH_2CH_2–S–CH_2CH_2–NH_2$

QS: $NH_2–CH_2CH_2–S–CH_2CH_2–S–CH_2CH_2–S–CH_2CH_2–NH_2$



Co(Q)N$_3^{2+}$



Co(QS)N$_3^{2+}$

This report presents data for the iron(II) reduction of these two complexes, demonstrating a marked rate enhancement when $>$N–CH$_3$ or R–S–R groups are selectively positioned *trans* to the azide bridge and all other non-bridging ligand factors are held constant.

Experimental

Kinetic data were collected (3–6 runs/data point) spectrophotometrically (Cary 14) at the conditions given using standard techniques. All solutions were prepared and standardized as reported earlier [5]. The new complexes were prepared from [Co(Q)Cl]-

TABLE I. Kinetic Data for the Reduction of CoQN$_3^{2+}$ by Iron(II).[a]

10^4 [Co(III)] *M*	[Fe(II)] *M*	[H$_3$O$^+$] *M*	Temp. °C	k$_t$ M^{-1} s^{-1}
3.60	0.005	0.20	25.0	1.31
	0.010	0.20	25.0	1.37
	0.015	0.20	25.0	1.34
	0.020	0.20	25.0	1.34
	0.025	0.20	25.0	1.36
	0.030	0.20	25.0	1.33
	0.010	0.20	17.3	0.663
	0.010	0.20	32.9	2.39
	0.010	0.05	25.0	1.36
	0.010	0.10	25.0	1.37
	0.010	0.20	25.0	1.37
	0.010	0.40	25.0	1.35
	0.010	0.60	25.0	1.33
	0.010	0.80	25.0	1.36
1.80	0.010	0.20	25.0	1.40
			AVE =	1.35 ± 0.02 std. dev.

[a] $\Sigma[ClO_4^-] = 1.00\ M$, maintained with LiClO$_4$.

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TABLE II. Kinetic Data for the Reduction of Co(QS)N_3^{2+} by Iron(II).[a]

10^4 [Co(III)] M	[Fe(II)] M	[H_3O^+] M	Temp. °C	k_t M^{-1} s^{-1}
1.6	0.0108	0.50	25.0	0.925
	0.0146	0.50	25.0	0.879
	0.0183	0.50	25.0	0.928
	0.0222	0.50	25.0	0.914
	0.0146	0.10	25.0	0.898
	0.0146	0.30	25.0	0.910
0.80	0.0146	0.50	25.0	0.932
	0.0146	0.70	25.0	0.919
	0.0146	0.90	25.0	0.908
	0.0146	0.50	18.1	0.504
	0.0146	0.50	18.4	0.512
	0.0146	0.50	33.2	1.59
	0.0146	0.50	33.6	1.70
3.2	0.0146	0.50	25.0	0.930
			AVE =	0.914 ± 0.016 std. dev.

[a] $\Sigma[ClO_4] = 1.0\ M$, maintained with $LiClO_4$.

$(ClO_4)_2$ and $[Co(QS)Cl](ClO_4)_2$ by treatment with aqueous NaN_3 followed by recrystallization from aqueous $NaClO_4$. *Anal.* Calcd. for $[Co(Q)N_3](ClO_4)_2$: C, 20.1; H, 4.32; N, 15.6. Found: C, 20.0; H, 4.26; N, 15.6% (λ_{max} = 547 nm, ϵ = 778). *Anal.* Calcd. for $[Co(QS)N_3](ClO_4)_2$: C, 17.8; H, 3.73; N, 12.9. Found: C, 17.9; H, 3.88; N, 12.7% (λ_{max} = 537 nm, ϵ = 1150).

Results and Discussion

Tables I and II present the Co(III), Fe(II), H_3O^+ and temperature dependence data for the reduction of Co(Q)N_3^{2+} and Co(QS)N_3^{2+} respectively. The reduction path is acid independent for both complexes over the range $0.05\ M < H_3O^+ > 0.80\ M$, and first order in Co(III) and Fe(II). The data are consistent with a mixed second-order rate law:

$$\frac{-\,d[\mathrm{Co(III)}]}{dt} = k_t\,[\mathrm{Co(III)}]\,[\mathrm{Fe(II)}]$$

Reduction activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined to be +14.1 ± 0.2 kcal/mol and −10.8 ± 0.8 eu for Co(Q)N_3^{2+} and +13.2 ± 0.2 kcal/mol and −14.7 ± 0.8 eu for Co(QS)N_3^{2+}.

Table III summarizes the iron(II) reduction rates for several cobalt(III) azide complexes. In earlier work [6], Haim and co-workers attributed the particular reactivity trends in k_t simply to the circumstance that the d_{z^2} orbital that accepts the electron is made more available by simultaneously removing the bridging ligand and the donor group *trans* to it [7]. Increased chelation in going from NH_3's, to en's, to trien, to tetren reduces k_t significantly [8, 9]. Presumably increased chelation reduces the ability of a *trans* donor to stretch along the axis of inner-sphere interactions and thus we would expect complexes derived from a pentadentate ligand to exhibit a further reduction in k_t.

TABLE III. Fe(II) Reduction Rates for Several Azido Cobalt(III) Complexes.[a]

Complex	k_t, M^{-1} s^{-1}	Ref.
$Co(NH_3)_5N_3^{2+}$	0.0087	6
Co(Q)N_3^{2+}	1.35	this work
Co(QS)N_3^{2+}	0.914	this work
cis-Co(NSSN)$(N_3)_2^+$	0.145[b]	8
cis-$Co(NH_3)_4(N_3)_2^+$	0.185	6
cis-$Co(NH_3)_4(H_2O)N_3^{2+}$	0.355	6

[a] 25 °C, $\Sigma[ClO_4^-] = 1.0\ M$. [b] NSSN = $H_2N–CH_2CH_2–S–CH_2CH_2–S–CH_2CH_2–NH_2$.

In this work, the presence of R–S–R donors both *cis*-(CO(Q)N_3^{2+}) and *cis* and *trans*-(Co(QS)N_3^{2+}) enhance k_t dramatically even with increased chelation when compared to the reduction rate for $Co(NH_3)_5N_3^{2+}$. Other specific enhancement factors may also be of importance such as solvation, low lying electronic states due to R–S–R, ease of Co–N_3 bond breakage and π/σ bonding features. The similarity of thermodynamic activation parameters indicate a common activation step in the iron(II) reduction of both $Co(Q)N_3^{2+}$ and $Co(QS)N_3^{2+}$. The greater k_t observed for the former may be due to the $CH_3{-}N\langle$ group disruption of the primary solvation sphere, thus facilitating elongation along the inner-sphere reduction axis.

References

1 Q = 7-methyl-4,10-dithia-1,7,13-triazatridecane; QS = 1,11-diamino-3,6,9-trithiaundecane.
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