Because of the relatively low quality of the Cu data set, it was felt that the credibility of the results would be enhanced by direct measurements of the most significant Bijvoet differences, and as an additional benefit we hoped to provide an experimental test of theoretical $\Delta f''$ values. For these measurements a freshly ground crystal was used with monochromatic Mo Kα radiation (graphite crystal).

Table I lists the observed and calculated[9] Bijvoet differences $[F(hkl) - F(\bar{h}\bar{k}\bar{l})]$ for the 48 pairs of reflections with $D > 100$.[7] Both in sign as well as in magnitude the agreement is excellent. If ΔF_{Bij} denotes a Bijvoet difference, we note that the value of $R_{\mathrm{Bij}} = \Sigma|\Delta F_{\mathrm{Bij,obsd}} - \Delta F_{\mathrm{Bij,calcd}}|/\Sigma|\Delta F_{\mathrm{Bij,obsd}}|$ is as low as 0.08. This index, together with the observation that for these reflections the magnitudes of ΔF_{Bij} in general correspond to about 10–20% of F_{obsd}, indicates that the theoretical $\Delta f''$ values are highly accurate.

As a result of this study it has been established with certainty that the absolute configuration of (−)-phenyltriphenylsilylcarbinyl *p*-bromobenzoate from (+)-phenyltriphenylsilylcarbinol is *R*. Comparison of our results with those reported by Biernbaum and Mosher[3] shows that stereochemical deductions based on extensions of Cram's rule to novel systems can be quite misleading.

The fact that Freudenberg's method of rotational shifts led to the incorrect answer, while Fredga's quasi-racemate method and Prelog's atrolactic asymmetric synthesis gave the correct prediction, does not imply that we are in a position to evaluate the relative merits of these methods. They all have the potential for failure, and should be applied with great caution. With present-day methods and equipment we think that an X-ray study very often affords the safest, fastest, and most economic solution to configurational problems.

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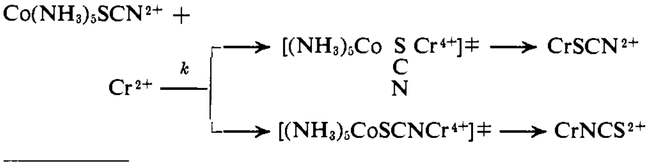
Adjacent and Remote Attacks in the Inner-Sphere Reductions of Thiocyanato- and Isothiocyanatopentaamminecobalt(III) Complexes by Chromium(II)[1]

Sir:

Following the report[2] on the bridged activated complex for electron-transfer reactions, a great deal of effort was devoted to the question of adjacent *vs.* remote attack for polyatomic bridging ligands,[3] but it was not until 1965 that definitive evidence was obtained for the remote-attack mechanism.[4–6] In contrast, direct evidence for adjacent attack in inner-sphere reactions with polyatomic bridging ligands has not been obtained thus far.[7] In the present communication, we report evidence for adjacent attack in the inner-sphere $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction. The discovery of efficient electron transfer by attack of Cr^{2+} on S bound to Co(III) is of particular importance in the context of recent redox work with sulfur-containing ligands.[8,9]

When $Co(NH_3)_5SCN^{2+}$ [10] is mixed with an *excess* of Cr^{2+} in a rapid-flow apparatus, two reactions can be detected. The first is the rapid redox reaction between $Co(NH_3)_5SCN^{2+}$ and Cr^{2+} to produce a mixture of $CrSCN^{2+}$ and $CrNCS^{2+}$. The second, slower reaction is the chromium(II)-catalyzed isomerization[6] of $CrSCN^{2+}$ to $CrNCS^{2+}$. The rate constant for the first reaction ($[H^+] = 1.0\ M$, $[Co(III)] = 5.0 \times 10^{-5}\ M$, and $[Cr(II)] = 2.8\text{–}4.5 \times 10^{-5}\ M$) is $(2.7 \pm 0.1) \times 10^5\ M^{-1}\ sec^{-1}$ at 25°. The $CrSCN^{2+}$ produced was identified by its spectrum[7] and by its rate of chromium(II)-catalyzed isomerization to $CrNCS^{2+}$ (found, $40 \pm 1\ M^{-1}\ sec^{-1}$ at 25°, $[H^+] = 1.0\ M$, to be compared with the literature[6] value of $42 \pm 2\ M^{-1}\ sec^{-1}$). The yield of $CrSCN^{2+}$ was determined in three different manners. In the first method, $Co(NH_3)_5SCN^{2+}$ was mixed with an excess of Cr^{2+} in the rapid-flow apparatus. At 25° ($[H^+] = 1.0\ M$, $[Co(III)] = (1.3\text{–}1.6) \times 10^{-4}\ M$, $[Cr(II)] = (7.5\text{–}17.0) \times 10^{-3}\ M$) the Co(III)–Cr(II) reaction had a half-life shorter than 0.3 msec, and therefore the observed absorbance changes were associated with the Cr^{2+}-catalyzed isomerization of the $CrSCN^{2+}$ produced in the first stage. From the measured absorbance changes and the known extinction coefficients of $CrSCN^{2+}$ and $CrNCS^{2+}$, the fraction of $CrSCN^{2+}$ formed in the $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction was found to be 0.30 ± 0.02. In the second method, Cr^{2+} ($4.8 \times 10^{-5}\ M$) and an excess of $Co(NH_3)_5SCN^{2+}$ ($1.9 \times 10^{-4}\ M$) were mixed ($[H^+] = 1.0\ M$, 25°) in the flow machine. The resulting solution was analyzed for $CrSCN^{2+}$ and $CrNCS^{2+}$ by ion-exchange and spectrophotometric techniques.[6,7] The fraction of $CrSCN^{2+}$ produced was 0.29. In the third method, the Cr^{2+} was mixed with an excess of $Co(NH_3)_5SCN^{2+}$ at 0° by conventional syringe techniques, and the resulting solution was analyzed as indicated above. The fraction of $CrSCN^{2+}$ produced was 0.26 ± 0.02. From these measurements, we conclude that the $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction proceeds *via* parallel adjacent and remote attack mechanisms according to the scheme



$$Co(NH_3)_5SCN^{2+} + Cr^{2+} \xrightarrow{k} \begin{cases} [(NH_3)_5Co\overset{}{\underset{\substack{C\\N}}{S}}Cr^{4+}]^{\ddagger} \longrightarrow CrSCN^{2+} \\ [(NH_3)_5CoSCNCr^{4+}]^{\ddagger} \longrightarrow CrNCS^{2+} \end{cases}$$

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(1) This work was supported by the National Science Foundation under Grant No. GP-9669.

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Table I. Rate Constants[a] for Reductions of Cobalt(III) and Chromium(III) Thiocyanate and Isothiocyanate Complexes

Reaction	M^{2+}		Ref
	Cr^{2+}	Fe^{2+}	
$(NH_3)_5CoSCN^{2+} + M^{2+} \rightarrow [(NH_3)_5CoSCNM^{4+}]^{\ddagger}$	1.9×10^5	1.2×10^{-1}	*b, c*
$(NH_3)_5CoSCN^{2+} + M^{2+} \rightarrow [(NH_3)_5Co\underset{\underset{N}{C}}{S}M^{4+}]^{\ddagger}$	0.8×10^5		*b*
$(NH_3)_5CoNCS^{2+} + M^{2+} \rightarrow [(NH_3)_5CoNCSM^{4+}]^{\ddagger}$	1.9×10^1	$<3 \times 10^{-6}$	*d, e*
$(H_2O)_5CrSCN^{2+} + M^{2+} \rightarrow [(H_2O)_5CrSCNM^{4+}]^{\ddagger}$	40		*f*
$(H_2O)_5CrNCS^{2+} + M^{2+} \rightarrow [(H_2O)_5CrNCSM^{4+}]^{\ddagger}$	1.4×10^{-4}		*g*

[a] At 25° and $\mu = 1.0\ M$. [b] This work. [c] Reference 13. [d] Reference 12. [e] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965). [f] Reference 6. [g] D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80**, 1091 (1958).

Although the $Co(NH_3)_5NCS^{2+}$–Cr^{2+} reaction has been examined previously both stoichiometrically[11] and kinetically,[12] there is no direct evidence on the question of adjacent or remote attack. We have reexamined this system in order to determine the yields of $CrSCN^{2+}$ and $CrNCS^{2+}$. The measurements were carried out in the rapid-flow apparatus at 262 nm with chromium(II) in excess. At this wavelength the absorbance first increases (disappearance of $Co(NH_3)_5NCS^{2+}$, ϵ 512, appearance of $CrSCN^{2+}$, ϵ 8.0×10^3), goes through a maximum, and then decreases (Cr^{2+}-catalyzed isomerization of $CrSCN^{2+}$ to $CrNCS^{2+}$, ϵ 2.7×10^3). The time, t_{max}, for maximum absorbance is

$$t_{max} = \frac{1}{[Cr(II)](k_1 - k_2)} \ln\left[\frac{(k_2 - k_1)(\epsilon_1 - \epsilon_2)}{f_s k_2(\epsilon_3 - \epsilon_2)} + \frac{k_1}{k_2}\right]$$

where f_s is the fraction of reaction that proceeds *via* attack at S (remote), k_1 and k_2 are the second-order rate constants for the $Co(NH_3)_5NCS^{2+}$–Cr^{2+} and $CrSCN^{2+}$–Cr^{2+} reactions,[6,12] respectively, and ϵ_1, ϵ_2, and ϵ_3 are the extinction coefficients of $Co(NH_3)_5NCS^{2+}$, $CrNCS^{2+}$, and $CrSCN^{2+}$, respectively. At 25°, $[H^+] = 1.0\ M$, $[Cr^{2+}] = 8.47 \times 10^{-3}\ M$, and $[Co(NH_3)_5NCS^{2+}] = 3.61 \times 10^{-4}\ M$; t_{max} was 9.5 ± 0.3 sec. Under the same conditions but with $[Cr^{2+}] = 1.7 \times 10^{-2}\ M$, t_{max} was 4.0 ± 0.3 sec. The values of f_s calculated from these t_{max} values are 0.97 ± 0.03 and 1.04 ± 0.09, respectively, and we conclude that the $Co(NH_3)_5NCS^{2+}$–Cr^{2+} reaction proceeds quantitatively by the remote-attack mechanism.

$$Co(NH_3)_5NCS^{2+} + Cr^{2+} \longrightarrow [(NH_3)_5CoNCS\ Cr^{4+}]^{\ddagger} \longrightarrow CrSCN^{2+}$$

The results of the investigations on the present and related systems are summarized in Table I. It will be seen that the thiocyanate complexes are reduced at a much faster rate than the isothiocyanate complexes. Since all the metal centers involved in the redox reactions under consideration display a preference for nitrogen over sulfur, the reactivity order $SCN^- \gg NCS^-$ for reaction *via* remote attack is expected on the basis of free energy considerations.[13]

However, the high reactivity of $Co(NH_3)_5SCN^{2+}$ for reaction with Cr^{2+} *via* adjacent attack is, in our opinion, a most remarkable finding. On the basis of thermodynamic considerations,[13] the Cr–S bond being 3×10^5 less stable than the Cr–N bond, adjacent attack would be expected to proceed at a rate ~500 times slower than remote attack. Moreover, on the basis of steric effects we would expect the adjacent S to be less available than the remote N for precursor binuclear complex formation. Based on these considerations, a value of 10^3 for the ratio of remote to adjacent attack by Cr^{2+} on $Co(NH_3)_5SCN^{2+}$ would appear to be a reasonable (and perhaps conservative) estimate. The observed ratio of 2.4 is substantially smaller than the estimated value, and therefore an additional factor must be invoked to explain the unusually high reactivity of $Co(NH_3)_5SCN^{2+}$ for reaction with Cr^{2+} *via* adjacent attack. As noted previously,[6] this factor may be the high electron-mediating ability of the sulfur bound to the oxidizing center for reaction *via* an inner-sphere mechanism. Additional work with other reducing agents and with other sulfur-containing ligands is planned.[14]

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A Stereoselective Synthesis of *cis*-Zeatin

Sir:

Zeatin, the highly active stimulant of cell division in plant tissue cultures, which was first isolated from *Zea mays*, has the structure 6-(4-hydroxy-3-methyl-*trans*-2-butenylamino)purine (**1**).[1–5] Although this trans isomer has been synthesized,[6–9] previous attempts to obtain the corresponding cis isomer have been unsuccessful mainly because of cis–trans isomerization encountered with the types of intermediates employed. Interest in the synthesis of *cis*-zeatin (**2**) stems from the isolation of a cytokinin assigned the structure ribosyl-*cis*-zeatin (9-ribosyl-**2**) from the tRNA of certain plant tissue, *e.g.*, peas, spinach, corn,[10–12] and from the finding that cy-

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