of these sets of parameters. To within the experimental error the value of the isotropic exchange parameter agrees with that reported by previous works of 5.5[6] and 5.3 K.[4,5]

Conclusion

The present study shows that the three principal crystal susceptibilities of even very small weakly anisotropic single crystals can be conveniently determined by combining magnetic anisotropy and average susceptibility data. The present data of principal susceptibilities of $Cu(pz)(NO_3)_2$ over the entire temperature range was found to conform well by using experimental g values, as expected, with an isotropic Heisenberg chain.

Registry No. $Cu(pz)(NO_3)_2$, 28209-64-5.

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Single-Electron Reactions of Vitamin B_{12s}: Reduction of Chromium(III) Complexes

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Vitamin B_{12s} is a cobalt(I) corrin complex, also known as cob(I)alamin, having a formula we abbreviate as $[Co^I]^-$. Other derivatives referred to in this work are vitamins B_{12r} and B_{12a} (aquocobalamin), $[Co^{II}]$ and $[Co^{III}]^+$, respectively, and organometallic derivatives such as the alkylcobalamins, R[Co]. B_{12s} is a powerful nucleophile toward organic halides[1] (RX) (eq 1) and toward acetylenic compounds[2] (eq 2).

$$[Co^I]^- + RX \rightarrow R[Co] + X^- \quad (1)$$

$$[Co^I]^- + HC{\equiv}CH + H_2O \rightarrow H_2C{=}CH[Co] + OH^- \quad (2)$$

On the other hand, only a very limited amount of work has been done relating to another aspect of the chemistry of B_{12s}, its reactivity as a powerful one-electron reducing agent. Our earlier work[3] on this aspect of B_{12} chemistry included a study of its reaction with aquo- and hydroxocobalamin. Instability of the cobalt(I) compound toward hydrogen evolution in neutral or acidic solution[4,5] has hindered the study of a wider range of metal complexes. We have now found that B_{12s} can be generated electrochemically at pH 2.5–3.2 in aqueous glycine buffers to yield solutions that are reasonably stable over several hours. We report here on the kinetics of reduction of a family of chromium(III) complexes, $(H_2O)_5CrX^{2+}$ with $X = F^-$, Cl^-, Br^-, N_3^-, NCS^-, OAc^-, SH^-, and OH^-. The reaction produces B_{12r} and $Cr^{2+}(aq)$ as shown in eq 3.

$$[Co^I]^- + (H_2O)_5CrX^{2+} \rightarrow [Co^{II}] + Cr^{2+}(aq) + X^- \quad (3)$$

Experimental Section

Solutions of vitamin B_{12a} (Sigma Chemicals Co.) were made up in 0.05 M sodium perchlorate and 0.05 M glycine to which sufficient perchloric acid had been added to adjust the pH to its desired value in the range 2.5–3.2. The B_{12} solutions, under argon, were reduced to B_{12s} at an applied potential of −1.5 V supplied by a Princeton Applied Research potentiostat. The electrochemical cell consisted of a mercury pool cathode, a platinum wire anode, and a saturated calomel reference electrode separated from the cell by a bridge containing 0.05 M sodium perchlorate.

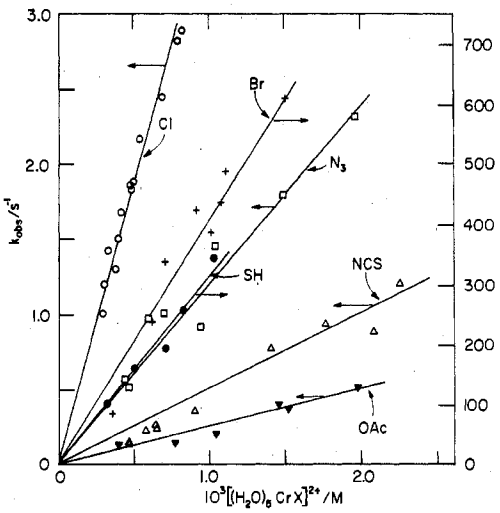

Figure 1. Plots showing the variation of the pseudo-first-order rate constants with the average concentration of the CrX^{2+} complex.

The chromium(III) complexes were prepared by standard methods:[6-10] (1) reaction of $(NH_3)_5CoX^{2+}$ with Cr^{2+} followed by ion-exchange chromatography for X = F (Bio-Rad Cellex P cation-exchange resin, elution with 0.1 M perchloric acid) and OAc (Sephadex C-25, elution with 0.18 M $LiClO_4$ and 0.02 M $HClO_4$); (2) reaction of X^- with $Cr(H_2O)_6^{3+}$ for $X = Cl^-$ and NCS^- (Dowex 50W-X8, elution with 1 M $(Na,H)ClO_4$); (3) reaction of Cr^{2+} with Br_3^- (Dowex 50W-X8, elution with 0.8 M $NaClO_4$ and 0.05 M $HClO_4$); (4) reaction of Cr^{2+} with polysulfide,[9] volatilization of H_2S, oxygenation to remove excess Cr^{2+}, and separation on Dowex 50W-X8. Additional Cr^{2+} was added to the crude $CrSH^{2+}$, and the separation was repeated, yielding a pure product which was stable for 24 h at pH 2 and 0 °C. The products had UV–visible spectra which matched the published values.[6-10]

The reactions in eq 3 were monitored spectrophotometrically, following the decrease in $[B_{12s}]$ at 385 nm ($\epsilon \sim 3.08 \times 10^4$ M^{-1} cm^{-1}) or the increase in $[B_{12r}]$ at 470 nm ($\epsilon \sim 1.10 \times 10^4$ M^{-1} cm^{-1}) with use of a Cary 219 or a Durrum D-110 stopped-flow spectrophotometer. The conditions in the kinetic determinations were chosen with a large excess of the chromium(III) complex, yielding data which conformed to pseudo-first-order kinetics. Throughout the course of the reactions the solutions were maintained under rigorously oxygen-free conditions.

Results and Discussion

The 1:1 stoichiometry shown in eq 3 was confirmed by spectrophotometric titration, and the quantitative formation of B_{12r} confirmed by the product spectra. The Cr^{2+} formed in the reaction of B_{12s} and $CrNCS^{2+}$ was detected by addition of $Co(NH_3)_5Cl^{2+}$ to convert Cr^{2+} to $CrCl^{2+}$. The resulting solution was first passed through a column of the macroreticular XAD-4 resin to remove all B_{12} species, and subsequently $CrCl^{2+}$ was separated from Co^{2+} by chromatography on a Dowex 50W-X8. The identity of $CrCl^{2+}$ was confirmed by its absorption spectrum, and the yield in two experiments was 68 and 86% of the value expected from eq 3 and the amount of B_{12s} taken. These findings confirm the production of Cr^{2+} and, considering the practical difficulties and separations, especially the problem of quantitative assay of the highly reactive and oxygen-sensitive B_{12s}, also constitute reasonable

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Table I. Kinetic Data[a] for Reactions of Vitamin B_{12s} and $(H_2O)_5CrX^{2+}$ Complexes

X	$10^5[B_{12s}]_0$/M	$10^3[CrX^{2+}]_0$/M	k_X/M^{-1} s^{-1}	K_X[c]/M^{-1}	k_XK_X/M^{-2} s^{-1}
Cl[b]	1.9–3.2	2.90–8.12	$(3.80 \pm 0.30) \times 10^3$	1.1×10^{-1}	4.2×10^2
NCS	3.5–4.0	0.47–4.22	$(4.63 \pm 0.52) \times 10^2$	1.9×10^2	9.1×10^4
N_3	3.3–3.5	0.43–1.95	$(1.31 \pm 0.22) \times 10^3$	1.7×10^3[d]	2×10^6
OAc	3.5	0.39–1.98	$(2.49 \pm 0.50) \times 10^2$		
F	10.0	1.12–2.27	$(8.1 \pm 1.0) \times 10^{-1}$	3.9×10^4	3.2×10^4
Br	3.1	0.36–1.51	$(4.00 \pm 0.75) \times 10^5$	2.3×10^{-3}	9.2×10^2
SH	3.5	0.31–1.02	$(3.08 \pm 0.21) \times 10^5$		
OH[e]	3.0	4.5–8.8	7.3×10^{-1}		
H_2O[e]	3.0	4.5–8.8	1.0×10^{-1}		

[a] At 25.0 °C in 0.05 M sodium perchlorate and 0.05 M glycine (except as noted), pH 2.5–3.2. [b] Includes runs having 0.02–0.15 M glycine. [c] For the equilibrium $Cr^{3+} + X^- = CrX^{2+}$. [d] The value given is that for VN_3^{2+} (assumed equal to K for CrN_3^{2+}): Espenson, J. H.; Pladziewicz, J. R. *Inorg. Chem.* 1970, *9*, 1380. [e] Values determined from eq 5 as described in the text.

evidence for the quantitative occurrence of the reaction given by eq 3.

The reaction between vitamin B_{12s} and each of the CrX^{2+} species follows a second-order rate equation (eq 4). The value

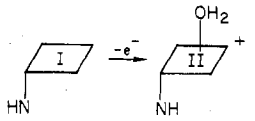
$$-d[B_{12s}]/dt = k_X[B_{12s}][CrX^{2+}] \quad (4)$$

of k_X was determined from the slope of the pseudo-first-order rate constant vs. $[CrX^{2+}]_{av}$ as shown in Figure 1. Rate constants were independent of glycine variation (0.02–0.15 M). Table I summarizes the reaction conditions and rate constants for all the complexes. The kinetic data for $Cr(H_2O)_6^{3+}$ deserve special comment, since it is the only complex for which the rate is pH dependent. The reaction occurs quite slowly, and the rate increases with decreasing $[H^+]$. If we assume both $Cr(H_2O)_6^{3+}$ and $(H_2O)_5CrOH^{2+}$ react with B_{12s}, then the variation of k_2 ($=k_{obsd}/[Cr(III)]_{total}$) with $[H^+]$ is given by eq 5, where K_{Cr} is the acid ionization constant of $Cr(H_2O)_6^{3+}$,

$$k_2 = \frac{k_{H_2O} + k_{OH}K_{Cr}[H^+]^{-1}}{1 + K_{Cr}[H^+]^{-1}} \quad (5)$$

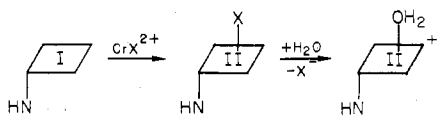
taken as 1.05×10^{-4} M.[11] A fit of the kinetic data to eq 5 was accomplished by a plot of $k_2(1 + K_{Cr}[H^+]^{-1})$ vs. $[H^+]^{-1}$, yielding the values of k_{H_2O} and k_{OH} given in Table I.

Following the notation of Saveant and co-workers,[12,13] the major species of B_{12s} and B_{12r} at pH 2.3 are shown in eq 6.



B_{12s} (IOH) B_{12r} (IIOH$^+$) (6)

The observed pH independence of the reaction rates establishes that the B_{12s} species shown is the reactive species. It is reasonable to suggest that electron transfer may occur via an inner-sphere activated complex, as depicted in eq 7, and to



(7)

enquire what evidence might be cited to support or refute this notion. We note first that the rates do change markedly with variation of group X. Were X involved less directly in the activation process, such as in an outer-sphere electron transfer, comparatively minor variations might be expected. Substitution at the Co(II) complex B_{12r} occurs far too rapidly to permit detection of the X-bound intermediate of eq 7, however, and thus one seeks less direct criteria by which the mechanism might be established. One possibility, following Haim,[14] is to examine the "stability order" of the activated complexes, which is done by computation of the equilibrium constant for the hypothetical process in which one potential bridging ligand X is replaced by another (eq 8). The equilibrium constant

$$[(H_2O)_5CrXCo(corrin)]^* + Y^- = [(H_2O)_5CrYCo(corrin)]^* + X^- \quad (8)$$

for eq 8 is related to the rate constants for the two individual reactions (k_X, k_Y) and the stability constants for the chromium(III) complexes (K_X, K_Y) by eq 9. One way of exam-

$$K_8 = \frac{k_XK_X}{k_YK_Y} \quad (9)$$

ining a series of reactions is thus to compare relative values of the product k_XK_X for each CrX^{2+} complex. These values are also cited in Table I, showing the following trends in the "stability order": (a) for halide-containing activated complexes, values of the quantity k_XK_X decrease in the order $F^- \gg Cl^- \approx Br^-$; (b) for azide and thiocyanate the order is $N_3^- \gg NCS^-$. These trends may be taken as mildly suggestive of an inner-sphere mechanism but are not particularly definitive since the expectation is colored by the degree of hard- or soft-acid character of vitamin B_{12s}. The latter does not appear to have been established directly but probably shows soft-acid character in view of its low-spin d^8 electronic structure.

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Registry No. $[Co^I]^-$, 18534-66-2; $(H_2O)_5CrCl^{2+}$, 14404-08-1; $(H_2O)_5CrNCS^{2+}$, 22258-89-5; $(H_2O)_5CrN_3^{2+}$, 18517-09-4; $(H_2O)_5CrOAc^{2+}$, 18894-45-6; $(H_2O)_5CrF^{2+}$, 19559-07-0; $(H_2O)_5CrBr^{2+}$, 26025-60-5; $(H_2O)_5CrSH^{2+}$, 18518-22-4; $(H_2O)_5CrOH^{2+}$, 27454-20-2; $(H_2O)_6Cr^{2+}$, 20574-26-9; $[Co^{II}]$, 14463-33-3.

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