Inorg. Chem. **1988**, *27*, 777-780 777

Contribution from the Department of Chemistry, University College (NSW),
Australian Defence Force Academy, Northcott Drive, Campbell, Canberra, ACT, Australia 2600

(Sulfito)cobalt(III) Chemistry: Synthesis of *cis*-$Co(en)_2(OH_2)SO_3^+$ and the Kinetics of Cis to Trans Isomerization

W. G. Jackson

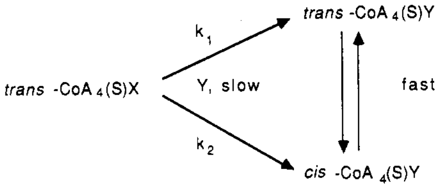
Received December 30, 1986

The cis isomer of $Co(en)_2(SO_3)OH_2^+$ has been identified for the first time, and the kinetics of its isomerization to the trans isomer have been determined: $k = 1.56 \times 10^{-3}$ s^{-1} at 25 °C; 3.5/96.5 cis/trans at equilibrium. The isomerization reaction is not as fast as once believed. The individual cis to trans and trans to cis rates are now known, and from these data and an estimate for the specific rate of exchange of water in the trans ion, the steric course of substitution is defined. The retention/rearrangement ratio so determined is $\geq 7 \times 10^6$, confirming the marked trans specificity afforded by the SO_3^{2-} ion in cobalt(III) chemistry. It is also shown that, as always believed but never proven, the stereochemistries of aquation of *trans*-$Co(en)_2(SO_3)X$ complexes in general ($X = OH_2$, N_3^-, Cl^-, and others) are strictly retentive. Finally, the *cis*-aqua(sulfito) isomer has been isolated and characterized, enabling for the first time the determination of the steric course for some cis substitution reactions, the induced hydrolysis (nitrosation) reaction of *cis*-$[Co(en)_2(SO_3)N_3]$ in particular (43% trans, 57% cis).

Introduction

Complexes of the kind *trans*-$CoA_4(SO_3)X$ are characterized by exceptional lability (A = amine).[1] Indeed, S-bonded SO_3^{2-} is approximately 10^8-fold more effective than NH_3 in activating the X group trans to it.[2] Curiously, the trans specificity has not been directly proven, although inferred with good reason from a number of observations. For example, the X-ray crystal structures of several *trans*-$[Co(en)_2(SO_3)X]$ complexes reveal substantially lengthened Co–X bonds, presumed weakened.[3-5] Also, their substitution products appear to be all in the trans configuration.[1,2] However a more definitive result is the fact that 1 (and just 1) equiv of $^{15}NH_3$ can be rapidly and stereospecifically incorporated into *trans*-$[Co(NH_3)_4(SO_3)OH]$ or $Co(NH_3)_5SO_3^+$, yielding *trans*-$Co(NH_3)_4(SO_3)(^{15}NH_3)^+$.[6]

Ligands such as $S_2O_3^{2-}$ appear[7] to behave like SO_3^{2-}, although they are not as effective in labilizing the trans ligand. However, our observations[8] on the relatively rapid loss of NH_3 from $Co(NH_3)_5S(O)_2R^{2+}$ (R = CH_3 and others) emphasize the danger of *inferred* conclusion about the stereochemistry of the substitution process. Here the first observable product is *cis*- rather than *trans*-$Co(NH_3)_4(S(O)_2R)(sol)^{2+}$ (sol = OH_2, $OS(CH_3)_2$), implying the loss of the NH_3 cis to the S-bonded ligand![8] Clearly a scheme such as



with k_1/k_2 assuming *any* value, is possible when the products can rapidly rearrange and the properties of one of the two product isomers are unknown. Indeed, the apparent contrast between the RSO_2^- and SO_3^{2-} systems could simply reflect the final equilibrium isomer distribution, cis for the sulfinate and trans for the sulfite system.

The vexing questions are obviously the rate of equilibration of the cis and trans substitution products, and the cis/trans equilibrium position. Unequivocal answers to these questions can help pinpoint the origin of both the kinetic and equilibrium specificities for SO_3^{2-}, and also RSO_2^-. Accordingly, we describe herein the synthesis of the putative *cis*-$Co(en)_2(SO_3)OH_2^+$ species, and in addition we describe some observations which resolve the ambiguities for the SO_3^{2-} substitution chemistry. Since very few cis SO_3 species are known and nothing of their substitution stereochemistry is known, we report also new[9] results for the H^+- and NO^+-catalyzed loss of N_3^- from *cis*-$[Co(en)_2(SO_3)N_3]$.

Results and Discussion

Identification of *cis*-$Co(en)_2(SO_3)OH_2^+$. The configuration of the red $[Co(en)_2(SO_3)N_3]$ species has been described as cis.[10] The evidence previously rested with IR data of disputed validity, but nonetheless the assignment is correct since in D_2O it shows the expected four-line ^{13}C NMR spectrum.[11] The brown *trans*-$[Co(en)_2(SO_3)N_3]$ isomer, previously known only in solution,[2] has now been crystallized also.[11] We confirm the report[2] that H^+ induces the loss of N_3^- rather than SO_3^{2-} from the cis (and trans) isomers, and that $Co(en)_2(SO_3)OH_2^+$ is the only product. However, at $[H^+] \geq 0.2$ M, we observe biphasic kinetics for the cis species, at several wavelengths. This was not detected in the original work,[2] for which 0.2 M was the highest $[H^+]$ examined. Our studies[12] with variations of $[H^+]$ have revealed two (consecutive) reaction rates, one dependent and one independent of acid (at constant μ; 1.0 M, $LiClO_4$). The $[H^+]$ independent rate we attribute to *cis-/trans*-$Co(en)_2(SO_3)OH_2^+$ isomerization ($k = 1.60 \times 10^{-3}$ s^{-1}), observed for the first time despite previous[2] attempts, and this reaction is notable for its remarkably long half-life (7.2 min, 25 °C); sulfito substitution reactions are usually on a millisecond time scale.[1,2]

A closer scrutiny of the absorption spectra of $Co(en)_2(SO_3)OH_2^+$ following the very rapid loss of N_3^- from *trans*-$[Co(en)_2(SO_3)N_3]$ in dilute acid revealed very small but reproducible changes in absorbance, especially in the region 390 nm and below. These data conform to a first-order rate law, with $k = (1.45 \pm 0.3) \times 10^{-3}$ s^{-1}, the same within experimental error as that found for the *cis*-azido(sulfito) reactant. Furthermore the same specific rate and spectra were determined, for the initial or subsequent reaction, as appropriate, commencing with *trans*-$[Co(en)_2(SO_3)Cl]$ (1.6×10^{-3} s^{-1}) and also starting with *trans*-$[Co(en)_2(SO_3)OH]$ (1.8×10^{-3} s^{-1}), *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$ (1.85×10^{-3} s^{-1}),

---

[1] Byrd, J. E.; Wilmarth, W. K. *Inorg. Chim. Acta Rev.* **1978**, *5*, 7.

[2] Yandell, J. K.; Tomlins, L. A. *Aust. J. Chem.* **1978**, *31*, 561.

[3] Snow, M. R.; Boomsa, R. F. *Acta Cryst. B.* **1972**, *B28*, 1908.

[4] Raston, C. L.; White, A. H.; Yandell, J. K. *Aust. J. Chem.* **1978**, *31*, 993.

[5] Maslen, E. N.; Raston, C. L.; White, J. H.; Yandell, J. K. *J. Chem. Soc., Dalton Trans.* **1975**, 323, 327.

[6] Richards, L.; Halpern, J. *Inorg. Chem.* **1976**, *5*, 2571.

[7] Cooper, J. N.; Bentsen, J. G.; Handel, T. M.; Strohmaier, K. M.; Porter, W. A.; Johnson, B. C.; Carr, A. M.; Farnath, D. A.; Appleton, S. L. *Inorg. Chem.* **1983**, *22*, 3060 and references therein.

[8] Jackson, W. G.; O'Leary, M.; Fairlie, D. P.; Jurisson, S. S., results to be submitted for publication.

[9] The stereochemical data reported in ref 2 are, as shown in this article, in serious error.

[10] Hargens, R. D.; Min, W.; Henney, R. C. *Inorg. Synth.* **1973**, *14*, 77.

[11] W. Marty (personal communication) first noted this fact. The trans isomer shows a single resonance, which interestingly is distinct from that of *trans*-$Co(en)_2(SO_3)OH_2^+$ with which it is in very rapid equilibrium.

[12] Jackson, W. G., results to be published.

0020-1669/88/1327-0777$01.50/0 © 1988 American Chemical Society

and *trans*-[$Co(en)_2(SO_3)OH_2$]CF_3SO_3 (1.95×10^{-3} s^{-1}) in 0.1–1.0 M $HClO_4$ or CF_3SO_3H.

Yandell and Tomlins have reported that *trans*-$Co(en)_2(SO_3)OH_2^+$ is formed in a single observable step when N_3^- is removed rapidly from *cis*-[$Co(en)_2(SO_3)N_3$] with NO^+ or Hg^{2+}.[2] They inferred that if *cis*-$Co(en)_2(SO_3)OH_2^+$ were formed, it isomerized completely and extremely rapidly to the trans isomer. Since we now find that the isomerization is not as rapid as once believed, it would have to be now concluded that the cis isomer is not formed. We reexamined this reaction since it is very unusual in $Co(en)_2AX^{n+}$ substitution chemistry to achieve complete stereochemical change in a single step.[13] Indeed, in direct contradiction to the previous work,[2] we observe two clear steps. The first reaction with 1.1-2.0 equiv of NO_2^- in 0.1–1.0 M$HClO_4$ is effectively instantaneous:

$$cis\text{-}[Co(en)_2(SO_3)N_3] \xrightarrow[H_2O,\ fast]{NO^+} Co(en)_2(SO_3)OH_2^+$$

Subsequent reaction, also characterized by large absorbance changes, displayed four sharp isosbestic points [283.5, 444 (ϵ 127.9), 499 (ϵ 101.0), 588 nm (ϵ 8.9 M^{-1} cm^{-1})], identical with those observed by commencing with *trans*-$Co(en)_2(SO_3)X$. Moreover these absorbance changes are in the reverse sense, and clearly we were observing the reverse *cis*- to *trans*-$Co(en)_2(SO_3)OH_2^+$ isomerization. The absorption spectra indicated that the equilibrium strongly favours the trans form, although not exclusively so. This result contrasts with the predominance of cis isomer for most other $Co(en)_2A(OH_2)^{n+}$ systems at equilibrium (A = Br^-, Cl^-, N_3^-, OH^-, OH_2, NCS^-, NH_3, NO_2^-).[14]

Unlike the nitrosation process, the consecutive reactions of *cis*-[$Co(en)_2(SO_3)N_3$] with H^+ are not so well separated that either step can be easily studied separately. Nonetheless, for absorbance data collected at 503 nm, which we have determined to be one of the isosbestic points for aqua(sulfito) isomerization, the biphasic kinetics disappeared, and the simple rate law $k(obsd) = k[H^+]$ was deduced from the rate data over a range of [H^+], 0.1–1.0 M $HClO_4$ ($k = 4.4 \times 10^{-4}$ s^{-1}; $\mu = 1.0$ M, $LiClO_4$). This substantiates our claim that the acid-catalyzed hydrolysis gives initially a nonequilibrium $Co(en)_2(SO_3)OH_2^+$ isomer distribution that contains considerable cis isomer. The precise composition was not determined because the isomerization is substantially faster than the generating acid-catalyzed reaction.

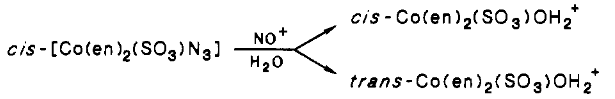
In summary, it has been established directly that the substitution reactions of *trans*-$Co(en)_2(SO_3)X$ are genuinely retentive. Several different sources of the *trans*-$Co(en)_2(SO_3)OH_2^+$ ion has authenticated its absorption spectrum, and it is clearly different from that for the cis isomer. Moreover, it is now obvious that the cis isomer, if formed, *would* be detected since it has been established that *cis-trans*-$Co(en)_2(SO_3)OH_2^+$ isomerization is not overwhelmingly rapid, as once believed.

Quantitative Aspects of the Stereochemistry of Substitution. The substitution reactions of the *cis*-($Co(en)_2(SO_3)X$ species appear to involve some but not complete steric change, in contrast to those for the trans species. This constrast becomes clearer in the following analysis. If the limiting rate of anation of *trans*-$Co(en)_2(SO_3)OH_2^+$ is recognized as a reasonable estimate of the H_2O exchange rate ($k = 400$ s^{-1}),[2] then this number coupled with the now known specific rate of trans to cis isomerization (vide infra), leads to a retention/rearrangement ratio of $\geq 7 \times 10^6$ for the steric course of H_2O exchange. This result emphasizes and now quantifies unambiguously the high trans specificity[1,2] of sulfur-bonded SO_3^{2-}. A similar although less pronounced trans specificity appears to be emerging for S-bonded $S_2O_3^{2-}$.[7]

Table I. Summary of Results for the Nitrosation of *cis*-[$Co(en)_2(SO_3)N_3$]·$1.5H_2O$ and Isomerization of $Co(en)_2(SO_3)OH_2^+$

$$cis\text{-}Co(en)_2(SO_3)OH_2^+ \underset{k_{tc}}{\overset{k_{ct}}{\rightleftharpoons}} trans\text{-}Co(en)_2(SO_3)OH_2^+$$

$10^3(k_{ct} + k_{tc})$, s^{-1}	K (=k_{ct}/k_{tc})		10^5k_{tc}, s^{-1}	10^5k_{ct}, s^{-1}
1.53[a]	96/4[e]			
1.58;[b] 1.56[d]	97/3;[f]	96.5/3.5	5.45[d]	150[d]
1.58[c]	96.5/3.5[g]	= 27.5[d]		
1.70[k]	97.5/2.5[h]			
	96/4[c]			



ϵ_{380} 173.4[i]	43%[j]
ϵ_{470} 143.4[i]	44%[j]
ϵ_{530} 46.5[i]	39.5%[j]
	43% trans[d]

[a] Cis reactant; result is the mean of several runs for wavelengths in the range 350–470 nm. [b] Trans reactant; result is the mean of several runs for wavelengths in the range 350–390 nm. [c] Isomerization studied subsequent to the nitrosation of *cis*-[$Co(en)_2(SO_3)N_3$] in dilute $HClO_4$. [d] Weighted mean value. [e] First and second figures are, respectively, the determined % trans and % cis isomer at equilibrium. *cis*-(sulfito)aqua isomer reactant; 380 nm data, ϵ(equil) 45.1; % trans obtained by using the following ϵ data for the pure *cis*- and *trans*-$Co(en)_2(SO_3)OH_2^+$ isomers: ϵ(cis) 276.3, ϵ(trans) 35.6. [f] *trans*-(sulfito)aqua isomer reactant; 380 nm data, ϵ(equil) 43.0; % trans obtained by using the following ϵ data for the pure *cis*- and *trans*-$Co(en)_2(SO_3)OH_2^+$ isomers: ϵ(cis) 276.3, ϵ(trans) 35.6. [g] Calculated from ϵ_{530} 31.1, the mean result for cis and trans reactants; ϵ for the pure component isomers used in the analysis: ϵ(cis) 57.2, ϵ(trans) 30.1. [h] Calculated from ϵ_{470} 162.0, the mean result for cis and trans reactants; ϵ for the pure component isomers used in the analysis: ϵ(cis) 127.8, ϵ(trans) 162.9. [i] Mean of triplicate determinations. [j] Calculated by using the ϵ data recorded in *f*, *g*, and *h*. [k] Average value for all the *trans*-$Co(en)_2(SO_3)X$ data.

The observations reported herein prompted an attack on the synthesis of pure *cis*-$Co(en)_2(SO_3)OH_2^+$. This was achieved by the rapid nitrosation of *cis*-[$Co(en)_2(SO_3)N_3$] and selective removal of the trans component of the aqua product, followed by crystallization of the cis form with $S_2O_6^{2-}$. The ClO_4^- salt was also characterized, and the reproducibility of the zero time absorption spectra with the nature of the counterion and independent syntheses testify to (although they do not prove) the isomeric purity. The final proof of isomeric purity came from the ^{13}C NMR spectra in D_2O and 1 M NaOD. In each medium the cis and trans ions are clearly distinguished; moreover, the isomerization reaction is frozen in OH^- media.

The steric course for the nitrosation reaction above, and also the precise *cis-/trans*-$Co(en)_2(SO_3)OH_2^+$ equilibrium position and individual cis to trans and trans to cis isomerization rates could then be determined. Results are recorded in Table I, together with other data to support the analyses.

The principal results are (i) there is detectable cis isomer, 3.5%, for the $Co(en)_2(SO_3)OH_2^+$ equilibrium, and (ii) the nitrosation of *cis*-[$Co(en)_2(SO_3)N_3$] gives 43% *trans*- and 57% *cis*-$Co(en)_2(SO_3)OH_2^+$; this result is consistent with the "gravimetric" result (ca. 40% trans) observed for the synthesis of the *cis*-aqua(sulfito) complex (see Experimental Section).

Having established some kinetic and equilibrium properties of a cis sulfito species, it is appropriate to comment further on previous work[2] where the intervention of *cis*-$Co(en)_2(SO_3)OH_2^+$ was denied. First, it is clear that the 3.5% cis isomer at $Co(en)_2(SO_3)OH_2^+$ equilibrium will have no serious effect on the kinetics of anation of *trans*-$Co(en)_2(SO_3)OH_2^+$ unless the cis isomer is extraordinarily reactive and substitutes with complete rearrangement (since the products are essentially trans). We have shown that at least one cis reactant substitutes with some, but not complete, rearrangement. Also, it is known[2] that, for $Co(en)_2(SO_3)N_3$ and $Co(en)_2(SO_3)_2^-$, the trans isomer is substantially more reactive than the cis. Furthermore, we have observed that *cis*-$Co(en)_2(SO_3)OH_2^+$ reacts only slowly with anions such as NCS^- and Cl^-, in contrast to the trans isomer. This is consistent with our analysis for water exchange.

---

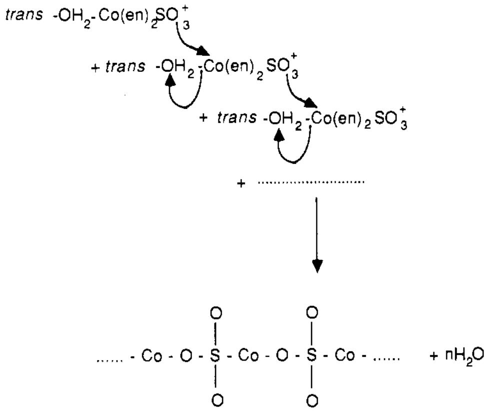
[13] Jackson, W. G. In *The Stereochemistry of Organometallic and Inorganic Reactions*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, pp 255–357.

[14] Jackson, W. G.; Begbie, C. M. *Inorg. Chim. Acta* **1982**, *61*, 167.

We should note in passing that Cl^- anation of *trans*-$Co(en)_2(SO_3)OH_2^+$, in an equilibrium sense, is not as insignificant as previously believed.[2] For example, in 1 M HCl as opposed to dilute $HClO_4$, the first absorption maximum is shifted 7 nm (ϵ_{473} 178; ϵ_{399}(min) 29.5, ϵ_{360} 123), and at several particular wavelengths in the visible region, there are ϵ differences well in excess of 20%. Attempts to confirm this by ^{13}C NMR were prevented by the observation of an exchange-averaged signal for the *trans*-$Co(en)_2(SO_3)OH_2^+$ and *trans*-$[Co(en)_2(SO_3)Cl]$ species.

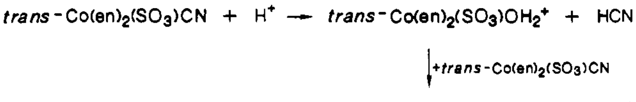
Finally, Baldwin has reported[15] (without details) the synthesis of materials $[Co(en)_2(SO_3)]Z$ ($Z = ClO_4^-, I^-, NO_2^-, NCS^-$) believed to contain SO_3^{2-} chelated through two oxygen atoms. The published electronic absorption spectrum for this compound is different, but not greatly different, from that of our authentic *cis*-$[Co(en)_2(SO_3)OH_2]ClO_4{\cdot}H_2O$ in water. If their species is the genuine chelate, then it is most likely S,O- rather than O,O-bonded because of the characteristically[20] intense Co–S charge-transfer absorption at ca. 270 nm.

Other Cobalt(III)–Sulfite Chemistry. It has been reported that the golden-brown *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4{\cdot}H_2O$ salt is readily dehydrated to yield a red material.[2,15] We can confirm this, and we note that simply stirring the salt in methanol effects the same transformation. On dissolution in water, the *trans*-$Co(en)_2(SO_3)OH_2^+$ ion is instantly regenerated, after which there is the small (but real) change in absorption spectrum mentioned above. The same equilibrium spectrum is observed, and it is attained with the same specific rate ($(1.55 \pm 0.15) \times 10^{-3}\ s^{-1}$) as before. There is some parallel here to the analogous $S_2O_3^{2-}$ chemistry,[7] and a red chelated thiosulfato complex has been structurally characterized.[16] However, our observations effectively eliminate a chelated sulfite (whether it be S, O- or O,O-bound) for the structure of the red $[Co(en)_2(SO_3)]ClO_4$ material, since this necessarily must be a cis complex; ring opening on redissolution in water must yield at least some if not all *cis*-$Co(en)_2(SO_3)OH_2^+$, which we now know does *not* instantly isomerize to the trans form. Thus the alternative and more likely structure [15] is an all-trans, sulfite-bridging polymer, with alternating S- and O-bonding, formed by self-substitution under dehydrating conditions:



The cobalt–oxygen bond would be quite labile under the trans influence of the S-bonded sulfite, and hence the *trans*-(sulfito)aqua ion is rapidly regenerated in solution.

This chemistry is not without precedent. Both the orange-yellow *cis*-[17] and yellow *trans*-$[Co(en)_2(SO_3)CN]$[18] complexes are known. They are useful synthetic precursors to aquacyano and cyanohalogeno species, the sulfite group being removed with concentrated mineral acid.[17,18] Interestingly, in *dilute* acid it is the CN^- group that reacts, leaving as HCN, a process not unlike what we have described for the azidosulfito species. Indeed, a solution of the *trans*-$[Co(en)_2(SO_3)CN]$ complex in 4 M $HClO_4$ on standing leads to the crystallization of an insoluble yellow substance that still contains CN^-, but only half the original amount. A plausible explanation



is consistent with the ambidentate nature of the CN^- ligand,[19] the lability of the aqua group in *trans*-$Co(en)_2(SO_3)OH_2^+$, and the self-substitution (or condensation) process advanced earlier. The mechanism for the formation of this "double salt" or dimer was confirmed by an independent synthesis, simply by mixing authentic specimens of *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$ and *trans*-$[Co(en)_2(SO_3)CN]$ in a 1:1 ratio in water.

Experimental Section

Electronic spectra were measured on Kontron 810 and Cary 210 instruments, thermostated to 25.0 ± 0.1 or 10.0 ± 0.1 °C by water circulation from Lauda baths. Details of our kinetic techniques and data analysis are described elsewhere.[21] All reactions were sufficiently slow to follow in situ in a cell thermostated within the spectrophotometer; kinetic data were analyzed by a nonlinear least-squares analysis using the appropriate functions. Carbon-13 NMR spectra were obtained with a Varian XL-300 instrument, for D_2O solutions with dioxane as the internal reference. Chemical shifts are reported as positive downfield from this signal. Chemicals were AnalaR grade or the equivalent. All compounds analyzed satisfactorily for three or more elements.

The nitrosation experiments on *cis*-$[Co(en)_2(SO_3)N_3]{\cdot}1.5H_2O$ were performed as follows. Accurately weighed samples of the azido complex (ca. 90 mg) were dissolved in ca. 20 mL of water (25 °C) and treated with 0.10 M $NaNO_2$ (ca. 5 mL). Perchloric acid (1.0 M, 10 mL) was then added as timing was commenced. The initial reaction was essentially instantaneous. After 30 s, sodium azide solution (0.10 M, 5 mL) was added to destroy excess HNO_2, and the mixture was made to the mark (50.00 mL) with H_2O. An ultrasound bath was employed to quickly degas the solution of liberated N_2 and N_2O, bubbles of which seriously interfered with the subsequent spectrophotometric measurements. Several scans were made on the Cary instrument and the spectra extrapolated to zero time.

cis-$[Co(en)_2(SO_3)N_3]{\cdot}1.5H_2O$ was synthesized by the published route,[10,22] the following modifications of which led to more than treble the yield: *cis*-$[Co(en)_2(N_3)_2]NO_3$ (63 g)[23] suspended in water (250 mL, 40 °C) was treated with Na_2SO_3 (24.6 g; 1 equiv) in water (100 mL, 40 °C) by uniform addition over 1 min while being well magnetically stirred. The violet solution/crystals were quickly replaced by orange/brown crystals; after 10 min, ethanol was added slowly to a total volume of 2 L. After 2 h, the crystals were collected, washed with ethanol and ether, and dried in air. Yield: 59 g (crude). This material contains a little of the yellow *cis*-$Na[Co(en)_2(SO_3)_2]$ salt, readily removed by recrystallization as follows. The crude product in saturated solution in warm water (ca. 150 mL/g) was filtered, and double the volume of acetone was added slowly. After the mixture was cooled overnight, the resultant red plates were collected and washed and dried as above. Yield: 50.5 g (80% overall). ϵ_{498}(max) 406, ϵ_{426}(min) 136.5 in H_2O. ^{13}C NMR (D_2O): δ – 21.70, –22.10, –22.93, –23.05.

cis-$Co(en)_2(SO_3)OH_2^+$ salts were obtained as follows. Concentrated $HClO_4$ (30 mL) was mixed with an equal volume of ice (–10 °C) to yield 5 M $HClO_4$ at ca. –20 °C. While the mixture was being well stirred, the complex *cis*$[Co(en)_2(SO_3)N_3]{\cdot}1.5H_2O$ (10.0 g) was added in portions over 1 min. Sodium nitrite (3.15 g; 1.5 equiv) was then added slowly to this suspension (over ca. 1 min); this resulted in the dissolution of the azido complex (as $Co(en)_2(SO_3)OH_2^+$) and the rapid liberation of gaseous N_2 and N_2O. At this time some yellow-brown crystalline material remained, identified from its electronic spectrum as *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4{\cdot}H_2O$ (4.8 g, 40%). This was quickly removed by filtration, and after the mixture was stirred for a further 5 min at ca. 0 °C,

---

(15) Baldwin, M. E. *J. Chem. Soc.* **1961**, 3123.

(16) Murdock, A. R.; Tyree, T.; Otterbein, W.; Kinney, L.; Carreras, M.; Cooper, J. N.; Elder, R. C. *Inorg. Chem.* **1985**, *24*, 3674.

(17) Ohkawa, K.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1715.

(18) Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1963**, 966.

(19) Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 2, pp 273–378.

(20) Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1982**, *21*, 3186.

(21) Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P. C.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473.

(22) $[Co(en)_2(SO_3)N_3]$ is reported as anhydrous; we find 1.5 H_2O/Co, as revealed by the ^1H NMR spectrum in dry Me_2SO-d_6. The single-crystal X-ray structure confirms the lattice water: Bernal, I., personal communication.

(23) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

a second fraction was collected (3.9 g); this proved to be very largely the cis isomer. The remaining solution was discarded. The cis isomer was recrystallized as the $S_2O_6^{2-}$ salt by dissolution of the crude ClO_4^- salt in H_2O at 0 °C (ca. 90 mL/g; 180 mL) and the addition of $Li_2S_2O_6\cdot 3H_2O$ in ice–water (2 g/10 mL). The resulting mixture was kept on an ice–salt bath, and cold acetone (200 mL, 0 °C) was added. After 10 min, the purified orange-pink cis isomer (1.1 g) was collected, washed with ethanol and ether, and dried in air. The crystals analyzed as the monohydrate, *cis*$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)\cdot 2H_2O$. The perchlorate salt was obtained from the dithionate (1 g) by trituration with cold 4 M $HClO_4$ (10 mL); it dissolved readily only to crystallize shortly thereafter as *cis*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ on addition of cold ethanol (15 mL). It was quickly collected, washed with ethanol and ether, and air dried. ϵ_{456}(max) 129.5 in H_2O. ^{13}C NMR (D_2O/D^+): δ −21.22, −21.71, −22.86, −23.05.^{13}C NMR for the aqua salts in 1 M NaOD ($[Co(en)_2(SO_3)OH]$): δ −22.23, −22.39, −23.27 (2).

trans-$[Co(en)_2(SO_3)Cl]$,[15] *trans*-$[Co(en)_2(SO_3)OH]$,[15] *trans*-$[Co(en)_2(SO_3)CN]$,[18] and *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$[15] were prepared by minor modifications to published procedures. Recrystallizations were from H_2O/CH_3OH, H_2O/CH_3OH, and $H_2O/HClO_4$, respectively. *trans*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)\cdot 2H_2O$ crystallized as large khaki-colored from a concentrated aqueous solution of the perchlorate containing $Li_2S_2O_6$, on the slow addition of acetone and cooling. The triflate salt was also characterized by using CF_3SO_3H as the precipitant. For *trans*-$Co(en)_2(SO_3)OH_2^+$: ϵ_{467}(max) 164.0, ϵ_{397}(min) 21.6, ϵ_{360} 98.0 in 0.01 M $HClO_4$. ^{13}C NMR (D_2O/D^+) δ −22.73. ^{13}C NMR for the aqua salts in 1 M NaOD ($[Co(en)_2(SO_3)OH]$): δ −23.22. *trans*-$[Co(en)_2(SO_3)N_3]$ was obtained by dissolving *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ in 2 M NaN_3 to the point of saturation, filtering, and carefully adding an equal volume of methanol. Brown needles deposited on standing in a refrigerator overnight; these were filtered, sucked semidry at the pump, washed with methanol and ether, and air dried. ^{13}C NMR (1 M NaN_3): δ −22.97.

trans-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ was dehydrated to a red power by drying it under vacuum over P_2O_5 for 24 h. The same red material, *trans*-$[Co(en)_2SO_3)]_n(ClO_4)_n$, was synthesized by stirring *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ (2 g) for 1 h in methanol (500 mL), in which the reactant is partially soluble. Although the additional possibility of SO_3^{2-} chelation existed, similar experiments on the cis isomer did not lead to any detectable dehydration of the $Co(en)_2(SO_3)OH_2^+$ moiety.

The sparingly soluble dimeric yellow *trans,trans*-$[(en)_2(SO_3)CoCNCo(en)_2(SO_3)]ClO_4$ salt was obtained by adding a solution of *trans*-$[Con(en)_2(SO_3)CN]$ to an equimolar one of *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ in water. It crystallized immediately and was collected and washed with methanol and ether and dried in air. The same material was obtained less conveniently by dissolving *trans*-$[Co(en)_2(SO_3)CN]$ in 5 M $HClO_4$; the dimer slowly crystallized on standing. [*Caution! Liberated HCN is toxic.*]

The "double salts" *trans,trans*-$[Co(en)_2A(OH)]_2H\cdot(ClO_4)_3$ are known for several A groups.[23,24] The examples A = N_3^- and NCS^- have been structurally characterized by single-crystal X-ray crystallography, and these ions contain the symmetrical H-bonded bridging ion $H_3O_2^-$.[24] Half-neutralization of *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$ with aqueous NaOH merely solubilized half of the salt, and presumably for the sulfito species the double salt is more soluble than its individual aqua and hydroxo components. The H-bonding structural feature no doubt is weakened by the trans influence of two SO_3^{2-} groups in the dimer, preventing its ready crystallization.

The visible spectra of the *cis*- and *trans*-$Co(en)_2(SO_3)OH_2^+$ ions were measured in both dilute acid (0.01 M $HClO_4$) and dilute base (0.03 M NaOH). The determination of the pure absorption spectra for the *trans*- and especially the *cis*-(sulfito)aqua ions required repetitive scanning and extrapolation to zero time; a slight temperature dependence was noted, particularly for the tail of the UV band, even over the narrow range 10–25 °C. Quoted data refer to 25 °C. The spectra of the generated *cis*- and *trans*-$[Co(en)_2(SO_3)OH]$ species did not change rapidly with time; indeed, neither showed significant change over 2 days at ambient temperature, as shown by ^{13}C NMR and visible absorption spectrometry (trans: ϵ_{467}(max) 180.5, ϵ_{401}(min) 38.0, ϵ_{360} 138.5. cis: ϵ_{461}(max) 177, ϵ_{404}(min) 70, ϵ_{360} 225).

Acknowledgment. We thank Steve Vallêlian for repeating some experiments, and we are grateful to (the late) Professor Werner Marty for stimulating discussion and for his gracious hospitality at the University of Neuchâtel where some of the preliminary work was performed. Financial assistance from the Australian Research Grants Scheme is gratefully acknowledged.

Registry No. *cis*-$[Co(en)_2(SO_3)N_3]$, 112571-09-2; *trans*-$[Co(en)_2(SO_3)N_3]$, 112459-43-5; *cis*-$[Co(en)_2(N_3)_2]NO_3$, 22651-44-1; *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$, 49727-17-5; *trans*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)$, 112459-42-4; *trans*-$Co(en)_2(SO_3)OH_2^+$, 24458-52-4; *trans*-$[Co(en)_2(SO_3)OH_2]CF_3SO_3$, 112459-44-6; *cis*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)$, 112571-10-5; *cis*-$[Co(en)_2(SO_3)OH_2]ClO_4$, 112571-11-6; *cis*-$Co(en)_2(SO_3)OH_2^+$, 112529-94-9; *cis*-$[Co(en)_2(SO_3)OH]$, 112459-40-2; *trans*-$[Co(en)_2(SO_3)OH]$, 112529-92-7; *trans*-$[Co(en)_2(SO_3)Cl]$, 112459-41-3; *trans*-$[Co(en)_2(SO_3)CN]$, 112529-93-8; *trans*-$[Co(en)_2(SO_3)]_n(ClO_4)_n$, 92130-08-0; *trans,trans*-$[(en)_2(SO_3)CoCNCo(en)_2(SO_3)]ClO_4$, 112459-46-8; NO_2^-, 14797-65-0.

---

[24] Ardon, M.; Bino, A.; Jackson, W. G. *Polyhedron* **1987**, *6*, 181.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 90. Further Oxidations of Vitamin B_{12r} (Cob(II)alamin)[1]

P. N. Balasubramanian, G. Chithambarathanu Pillai, R. R. Carlson, D. E. Linn, Jr., and E. S. Gould*

Received July 27, 1987

Vitamin B_{12r} (cob(II)alamin), the Co(II) derivative of vitamin B_{12}, reduces Fe^{III} (to Fe^{II}), V^V (to V^{IV}), and BrO_2^- (to Br^-) in aqueous solution. The rate law for reaction with Fe^{III}(aq) features an inverse-$[H^+]$ term and, in the presence of added Cl^- or Br^-, a sizable halide-proportional term as well. These kinetic dependencies point to specific redox bridging roles for Fe(III)–bound hydroxide and halide. The very high specific rates for oxidations by $Fe(NCS)^{2+}$ (1.1×10^5) and $Fe(N_3)^{2+}$ ($>1 \times 10^7$ M^{-1} s^{-1}) are in accord with this assignment. Oxidation by Fe^{III}(aq) is inhibited by fluoride, reflecting the conversion of Fe(III) to inactive FeF^{2+}. The specific rate pertaining to the $[H^+]$-independent component in the oxidation by Fe^{III}(aq) corresponds to a self-exchange rate for the cob(II,III)alamin couple of $10^{-4.5}$ M^{-1} s^{-1}, or about 10^{-8} times the corresponding value for cob(I,II)alamin. The acidity pattern for oxidation by vanadium(V) is consistent with partition of V(V) into a reactive protonated form ($pK_A = 3.5$) and an unreactive deprotonated species. The limiting specific rate (4.4×10^5 M^{-1} s^{-1}) points to a predominant inner-sphere path for this reaction. Oxidations by bromite (BrO_2^-) exhibit a prominent $[H^+]$-proportional term, attributed to reaction of B_{12r} with $HBrO_2$, proceeding at a specific rate of 4×10^6 M^{-1} s^{-1}, i.e. about as rapidly as the analogous reaction with $HClO_2$. Oxidations of B_{12r} by $IrCl_6^{2-}$, $Fe(CN)_6^{3-}$, and $Fe(bpy)_3^{3+}$ are too rapid to measure ($k > 7 \times 10^6$ M^{-1} s^{-1} at 25 °C and $\mu = 1.0$ M) by our methods.

We have been interested for some time in the redox reactions of the reduced forms of the coenzyme vitamin B_{12}.[2] The cobalt(I) derivative (B_{12s} or cob(I)alamin) reduces an impressive assortment of organic[3] and inorganic[4] species, and its versatility is enhanced

0020-1669/88/1327-0780$01.50/0 © 1988 American Chemical Society