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(12) Potassium triisopropoxyhydridoborate in THF shows little or no reaction at ambient temperature with most organic functionality other than ketones and aldehydes. Even alcohols and carboxylic acids liberate hydrogen exceptionally slowly compared with other group 3 hydrides.[1b,4]
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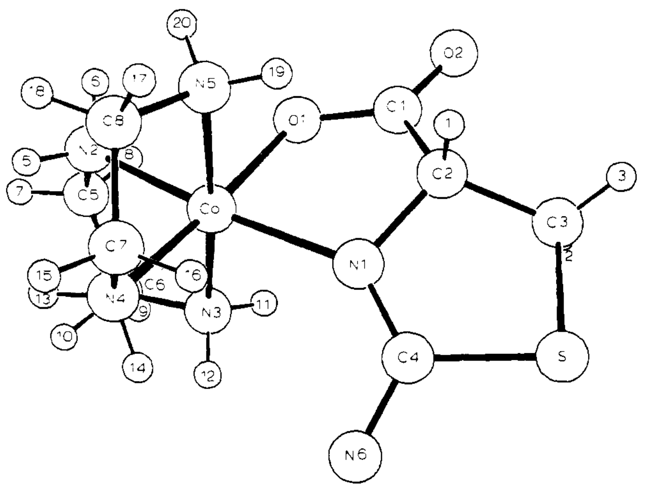


Figure 1. The structure of Δ-[bis(ethylenediamine)-(*R*)-2-aminothiazoline-4-carboxylatocobalt]$^{2+}$. Relevant bond lengths: Co–N(1), 1.96 (1); N(1)-C(4), 1.29 (2); C(4)–N(6), 1.32 (3); S–C(4), 1.76 (3); S–C(3), 1.83 (3); C(2)–N(1), 1.49 (2); mean Co–N, 1.96 Å. Crystal data: $CoCl_2SO_{10}N_6C_8H_{21}$;[4] monoclinic; a = 17.325 (14), b = 14.194 (11), c = 8.295 (8) Å; β = 102.82 (2)°; space group $C2$; M = 523.2 daltons; d_m = 1.77 (±0.02), d_c = 1.75 g cm^{-3}; Z = 4, μ = 13.3 cm^{-1} (Mo Kα). For the 1150 independent reflections collected with a Hilger and Watts four-circle diffractometer with $F_o^2 > 3\sigma(F_o^2)$, the R index is 0.069.

Synthesis and Structure of a 2-Aminothiazolinecobalt(III) Complex Derived from (*R*)-Cysteine

Sir:

The remarkable oxidation-condensation reaction of Δ-[Co(en)$_2$-(*R*)-cysteinato](ClO$_4$)$_2$ (I) to give the sulfenamide product II in a dimethyl sulfoxide-acetic anhydride mixture was described recently.[1] The sulfur in II is very susceptible to both electrophilic and nucleophilic attack and we have reported some nucleophilic reactions of II with $S_2O_4^{2-}$, BH_4^-, and mercaptide ions.[2,3] The CN$^-$ ion also reacts with II in a complex manner herein described.

The Δ-sulfenamide II and aqueous NaCN (1-2 equiv) reacted within the time of mixing (20 °C) to give a deep-red-burgundy-colored solution which on acidification (HClO$_4$) deposited crystals with the stoichiometry $[Co(C_2H_8N_2)_2(C_4H_5N_2SO_2)](ClO_4)_2$.

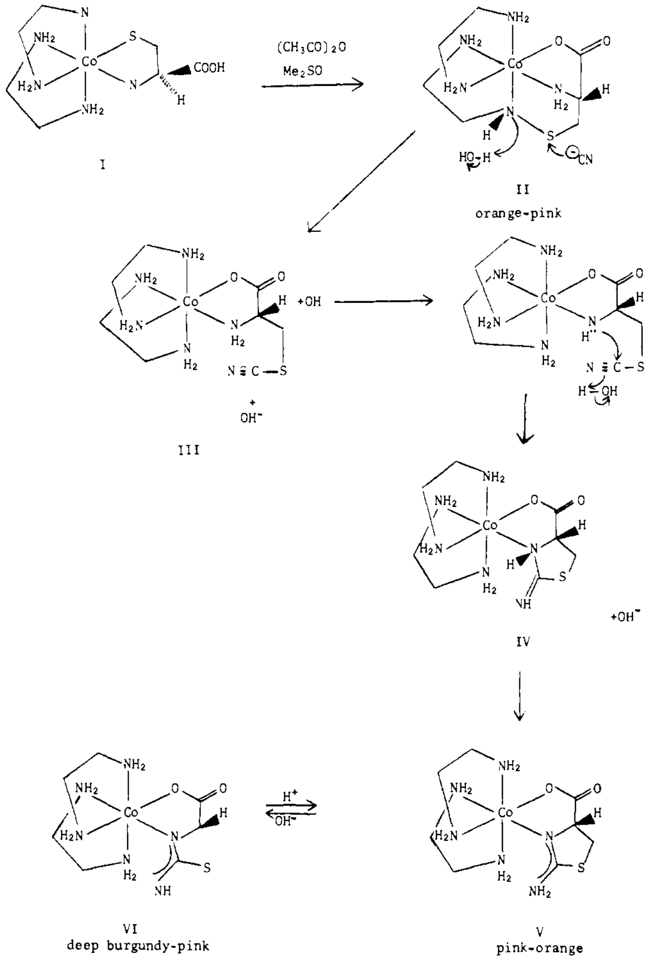
The visible spectrum for this product (0.01 M HClO$_4$) showed two ligand field bands ($\epsilon_{\max}^{497}$ 163, $\epsilon_{\mathrm{sh}}^{350}$ 198 M^{-1} cm^{-1}; $[M]_{436}^{20}$ +7750 deg M^{-1} m^{-1}) indicative of the Co^{III}N$_5$O chromophore. Also the spectrum implies detachment of the sulfur from the Co–N–S moiety of the reactant sulfenamide which has its second ligand field band obscured by the intense charge-transfer absorption associated with the Co–NH(*R*)-$\ddot{S}$: group.

The ^{13}C and ^{1}H NMR spectra and chromatography of the product indicated the formation of a single isomer, while the rotatory dispersion spectrum (10^{-2} M HClO$_4$) suggested the same absolute configuration about cobalt as the starting material (Δ), on comparison with reference spectra of several Λ and Δ (Co(en)$_2$(amino acido)]$^{n+}$ complexes.[5] A similar but chemically distinct product was obtained also from the diastereoisomeric Λ-sulfenamide and CN$^-$.

These results suggested that the CN$^-$ reaction involved neither attack at, nor mutarotation about, cobalt. The data did not allow, however, a conclusive structural assignment and therefore an X-ray crystallographic study was undertaken on the perchlorate salt derived from the Δ-sulfenamide.[4]

The structure (Figure 1) consists of independent divalent cations and ClO$_4^-$ ions linked by H bonds. It indicates that CN$^-$ has attacked the sulfur center and cleaved the sulfenamide linkage. The dangling thiocyanate III so formed is then attacked by the deprotonated amine group of the amino acid chelate to generate finally an unusual amino acid chelate, the 2-aminothiazoline-4(*R*)-carboxylato ion, bound through a N atom of the thiaamidine moiety. Overall the six-membered sulfenamide ring has opened and a new five-membered thi-

Scheme I



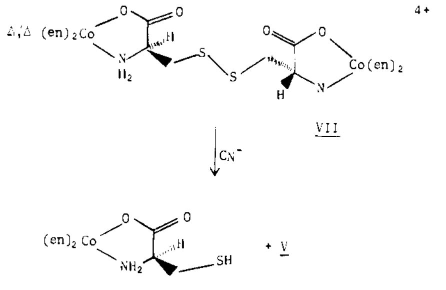
azoline ring has formed at a different site. The rearrangements are depicted in Scheme I which also outlines a plausible mechanism. Note that the five-membered ring formed at the amino acid N atom is preferred to a seven-membered ring involving the N atom of an adjacent ethylenediamine.

The known absolute configuration of (R)-cysteine, coupled with the known configurations of the reactant, fixes the chirality about cobalt as Δ which confirms the suspected retention of configuration at both centres during the reaction. The X-ray anomalous dispersion results are also consistent with this assignment (weighted R values for the Δ and Λ configurations 0.0960 and 0.0968, respectively). The thiaamidine moiety is delocalized over both N atoms since the C-N bond lengths are almost the same (1.32 (3) and 1.29 (2) Å) and the atoms Co, N(1), C(2), C(4), and N(6) are essentially coplanar (mean deviation 0.015 Å). This indicates that both N protons should be found on the N atom exo to the ring even though they were not located crystallographically unambiguously. Such an assignment is in keeping with other coordinated amidine structures where the protons have always been found on the uncoordinated N atom.[6-8] Furthermore, the ^{1}H NMR spectrum in MeSO-d_6 showed an isolated NH_2 resonance (δ 7.25, 2 protons) which indicates the N-proton distribution in the crystal is retained in solution. In D_2O or DCl, however, exchange was too rapid to allow the observation of the NH_2 signal. Isomer V was deprotonated by OH^- and the isolated perchlorate salt[9] gave an NH signal at δ 5.33 (1 H) in Me_2SO-d_6. Deprotonation of the exo NH_2 is implicated (VI).

Under the basic conditions of the CN^- addition (pH ~9), mutarotation of the configuration about cobalt in the reactant sulfenamide would be rapid ($t_{1/2} \sim 20$ s).[3] The results show however that the Δ configuration is retained and therefore nucleophilic attack at S must be exceedingly rapid under the conditions (0.1 M CN^-, $t_{1/2} \lesssim 1$ s, 20 °C). This conclusion is in keeping with previously reported reductions and additional observations on the sulfenamide II using BH_4^-, $S_2O_4^{2-}$, SO_3^{2-}, and RS^- ions.[2,3] All of the reagents react rapidly and cleave the sulfenamide bond without mutarotation about cobalt.

An alternative stereospecific synthesis of the 2-aminothiazoline-4-carboxylato chelate, V, was found through the action of CN^- on the cystine dimer, VII, Scheme II, of known structure and absolute configuration.[2] Half of the dimer yields the thiazolinecarboxylato chelate; the other half yields the N,O-bound cysteinato complex, VIII. This result also confirms the absolute configuration derived from the sulfenamide and lends support to the mechanistic proposals in Scheme I. Both reactions should take place through the dangling thiocyanate intermediate III. Also it supports earlier observations[10] on the reaction between CN^- and uncoordinated (R,R)-cystine which was believed to give the aminothiazoline carboxylate reported here.

Scheme II



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Supplementary Material Available. Atomic parameters (Table 1), bond distances, angles, dihedral angles, and mean planes (Table 2), and listings of observed and calculated structure factors (Table 3) (5 pages). Ordering information is given on any current masthead page.

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(4) Anal. Calcd for $CoC_8H_{21}N_6SCl_2O_{10}$: C, 18.4; H, 4.1; N, 16.1; S. 6.1; Cl, 13.6.Found: C, 18.5; H, 4.2; N, 16.1; S, 6.0; Cl, 13.6.
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Vinylic Cations from Solvolysis. 28.[1] Solvent Dependency of the Solvolytic Site of 9-(α-Bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene

Sir:

In a recent communication[1] we reported the preparation and the rates of solvolysis (k_t) and loss of optical activity (k_α) of an optically active vinylic compound, 9-(α-bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene (**1**), in TFE. It was concluded that ion pairs are not involved in the solvolysis, indicating the suitability of **1** and its analogues for studying the selectivities of solvolytically generated free cations. A competing initial solvolysis of the 10-hydroxy group was excluded, among other evidence, by the lower solvolytic rearrangement rate (k_{rear}) of the nonbromo analogue **2** to **3**. We now report that the initial solvolytic site of **1** is solvent dependent.

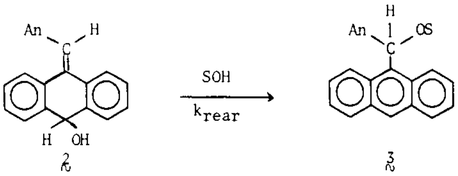

Table I gives k_t values (measured either by UV or titrimetrically) and k_α values for **1** and k_{rear} values for **2** in 80% EtOH and AcOH. In 80% EtOH $k_\alpha/k_t = 1.02 \pm 0.04$ and common ion rate depression[2] within a run was not detected, although k_t in the presence of Bu_4NBr (k_d) is reduced. Combination of