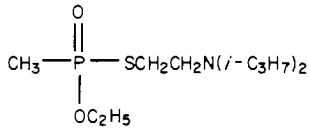
Table I. Reaction of Zinc(II)-NMF Complexes with *O*-Ethyl *S*-[(Diisopropylamino)ethyl]methylphosphonothioate in NMF

compd	result[a]	compd	result[a]
$Zn(NMF)_6(ClO_4)_2$	neg	$ZnCl_2 \cdot nH_2O$	++
$ZnCl_2(NMF)_2$	+++	10% aqueous $ZnCl_2$	+
$ZnBr_2(NMF)_{2.3}$	++++	$Zn(ClO_4)_2$ + NaI	++++
$ZnI_2(NMF)_2$	+++++	$Zn(ClO_2)_2$ + KF	+

[a] The intensity is indicated by the number of + signs. The test was performed after a reaction time of 1 min.

synthesized,[3] and it was discovered that the $ZnCl_2(NMF)_2$ complex did in fact react with tosyl chloride in 1-butanol. Since some of the complexes tend to dissociate to various extents when dissolved in solvents such as butanol or nitromethane and since NMF reacts directly with tosyl chloride, the results were questionable. Therefore, another electrophile was chosen which does not react directly with the free ligand. This electrophile is *O*-ethyl *S*-[(diisopropylamino)ethyl]methylphosphonothiolate (III).



III

A number of metal chloride complexes of NMF were allowed to react with III without solvent in one case and in NMF in the other. These are $MgCl_2(NMF)_4 \cdot 2H_2O$, $MnCl_2(NMF)_2$, $FeCl_2(NMF)_{2.5}$, $CoCl_2(NMF)_3$, $NiCl_2(NMF)_4$, $CuCl_2(NMF)_2$, and $ZnCl_2(NMF)_2$. (It should be noted that III does not react with any of the octahedral nitrate or perchlorate salts or the copper perchlorate salt.) Again, there is no reactivity of any of the (psuedo) *octahedral* chloride complexes or of the copper complex. However, the zinc complex, which is presumably tetrahedral, promotes the dehydration of NMF by III. The only other positive result, albeit weak, is for $CoCl_2(NMF)_3$ in NMF. In the solid, this compound has the structure $[Co(NMF)_6][CoCl_4]$,[3] and its lack of reactivity is therefore not surprising. In nitromethane, conductance data indicate that disproportionation to a tetrahedral species is occurring (eq 2). Dissolution in NMF leads to $Co(NMF)_6^{2+}$

$$\underset{\text{solid}}{[Co(NMF)_6][CoCl_4]} \xrightarrow{CH_3NO_2} \underset{\text{tetrahedral}}{2[Co(NMF)_2Cl_2]} + 2NMF \quad (2)$$

in dilute solution and a mixture containing some tetrahedral species $[Co(NMF)_xCl_{4-x}]^{2-x}$ in more concentrated solution.[3] This again leads to the conclusion that a tetrahedral species is a necessary (but not sufficient) condition for reaction.

Zinc Halide Complexes. Since only the zinc chloride complex exhibited appreciable reactivity, attempts were made to synthesize the set of complexes $ZnX_2(NMF)_2$ (X = F, Cl, Br, I) in order to gain additional information on the reaction mechanism. The iodide and bromide complexes were prepared, the latter apparently containing some lattice NMF. Attempts to isolate a fluoride complex were unsuccessful. The results of the reaction of the zinc halide compounds with III in NMF are given in Table I. A few points are immediately evident. First, the order of reactivity, perhaps initially somewhat surprising, is I > Br > Cl. Second, formation of a complex in situ by adding the ZnX_2 salt directly to NMF gives essentially the same result. This indicates that the complete order is I > Br > Cl > F. Third, increasing the water content decreases the reactivity. Presumably this is a result of displacement of ligand by water.

Reaction Mechanism. The above results permit us to draw some conclusions concerning the mechanism of the reaction between electrophile and coordinated (NMF) ligand. We consider the following three principal mechanisms: (i) direct attack on (formamide) oxygen; (ii) coordination to zinc, followed by attack on oxygen; (iii) coordination to zinc by displacement of halide, followed by attack on oxygen. Mechanism i should result in enhanced reactivity with increasing electronegativity of X (F > Cl > Br > I), while the reverse order is observed. Also, it does not explain the lack of reactivity of the copper complexes. Mechanism ii is consistent with the latter, since coordination of a fifth (weak) ligand is not expected. However, for the zinc complexes, this would lead to a five-coordinate complex which from both electronic and steric considerations should become more reactive as the halide becomes more electronegative. Thus, mechanism iii seems to be the best candidate at present since it is consistent not only with the copper result but also with the expected ease of displacement of the halide leaving group.

Thioformamide Complexes. The two thioformamide $ZnCl_2$ complexes are coordinated via the sulfur atom as shown by their infrared spectra. The spectra are consistent with those expected for N-substituted thioformamides.[7,8] The observed shift of the C=S bond is from 957 ± 4 cm^{-1} in free TBTF to 915 ± 4 cm^{-1} in the complex. Similar directional shifts have been reported for transition metal-thioacetamide complexes.[8] Thioformamides are weaker nucleophiles and even complexation does not lead to reactivity of either the TBTF or the NMTF complex with III. The NMTF does react with tosyl chloride but not to produce isocyanide. However, the $ZnCl_2(NMTF)_2$ complex in DMF does react with tosyl chloride to produce some isocyanide.

In summary, a number of metal nitrate, perchlorate, and chloride complexes (M = Mg, Mn, Co, Ni, Cu, Zn) of *N*-methylformamide have been reacted with the electrophile *O*-ethyl *S*-[(diisopropylamino)ethyl]methylphosphonothioate (III). Only the $ZnCl_2$ complex reacted to produce isocyanide. For the series of $ZnX_2(NMF)_2$ complexes (X = halogen) the order of reactivity was I > Br > Cl > F. It is concluded that the mechanism of reaction involves coordination of the electrophile with displacement of the halide, followed by reaction of the two coordinated ligands.

Registry No. III, 50782-69-9; $ZnBr_2(NMF)_2$, 32371-45-2; $ZnCl_2(NMF)_2$, 26250-62-4; $ZnI_2(NMF)_2$, 26250-63-5; $ZnF_2(NMF)_2$, 77827-60-2; $ZnCl_2(NMTF)_2$, 77827-61-3; $ZnCl_2(TBTF)_2$, 77827-62-4; TBTF, 20278-31-3; *tert*-butylformamide, 2425-74-3.

(7) C. N. R. Rae, R. Venkataraghavan, and T. R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
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(9) C. D. Flint and M. Goodgame, *J. Chem. Soc A*, 750 (1968).

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Formation of $[Co(en)_2(glyO)]^{2+}$ from Monodentate *trans*-$[Co(en)_2(H_2O/OH)(glyO/H)]^{3+/2+/+}$ Species

C. J. Boreham and D. A. Buckingham*

Received November 20, 1980

Recently we have shown[1] that *cis*-$[Co(en)_2(OH_2)(gly-OH)]^{3+}$, *cis*-$[Co(en)_2(OH_2)(gly-O)]^{2+}$, and probably *cis*-$[Co(en)_2(OH)(gly-O)]^{+}$ react intramolecularly, with the ad-

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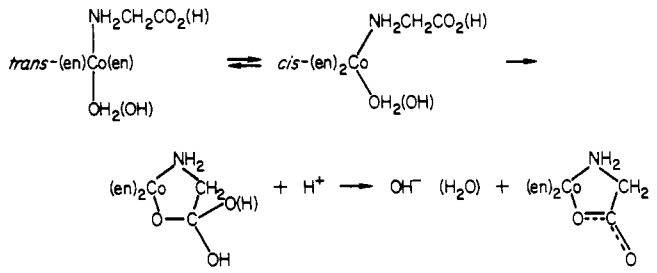
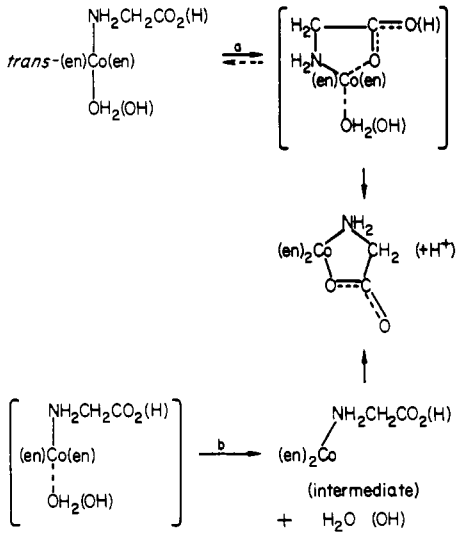
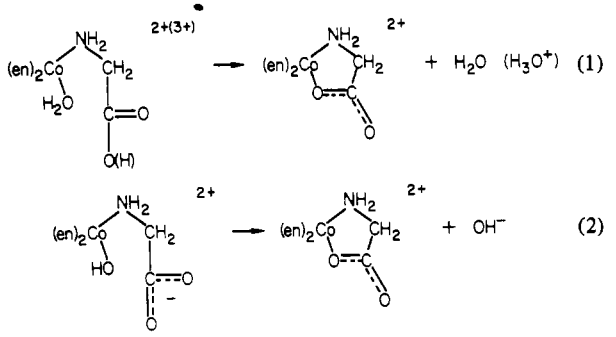
Scheme I



Scheme II



jacent coordinated water or hydroxide ion attacking the carboxylate center to form the chelated acid (reactions 1 and 2).



We now report on the corresponding reactions of the trans ions. Three possibilities arise: that water or hydroxide exchange results in isomerization to, or equilibration with, the corresponding cis species with the latter reacting intramolecularly as before[1] (Scheme I) or that entry of the carboxyl oxygen into the coordination sphere is accompanied by (Scheme II, path a) or is preceded by (Scheme II, path b) loss of water or hydroxide.

Experimental Section

Preparation of Complexes. *cis*-$[Co(en)_2X(glyOCH_3)]X_2$ (X = Cl, Br) was prepared as described by Alexander and Busch.[2] For X = Br the complex was resolved into the optical enantiomers as described previously.[3]

cis-$[Co(en)_2Br(glyOH)]Br_2$ (or $(ClO_4)_2$) was prepared from the ester as detailed recently.[4] The optically pure forms, Δ- and Λ-$[Co(en)_2Br(glyOH)]Br_2$, were similarly prepared.

***trans*-$[Co(en)_2(OH)(glyO)]^+$.** A solution of *trans*-$[Co(en)_2OH(glyO)]^+$ was prepared in two ways. A mixture of (cis and trans) $[Co(en)_2OH(glyO)]^+$ was obtained by alkaline hydrolysis of *cis*-$[Co(en)_2Br(glyOH)]Br_2$ at pH 10 (10 min, pH stat)[4] and removal of the $[Co(en)_2(glyO)]^{2+}$ chelate (which immediately forms ~46%) by column chromatography on SP-Sephadex C25 resin at 0 °C (0.2 mol dm^{-3} $NaClO_4$, pH 10).[4] The resulting 1+ band was quenched into acetic acid (pH 4) and after 10 min sorbed onto Dowex 50 W × 2 (Na^+ form) and the trans-OH product separated from $[Co(en)_2(glyO)]^{2+}$ (formed from the *cis*-OH ion)[1] by elution with 1.0 mol dm^{-3} $NaClO_4$ (pH ~8). Alternatively, the combined product of the alkaline hydrolysis of *cis*-$[Co(en)_2Br(glyOH)]Br_2$ (as above) was immediately quenched into acetic acid (pH ~4), and after 10 min the remaining trans-OH product was isolated as before. This latter procedure was preferred in later runs and was used in the ^{18}O-tracer experiments.

^{18}O-Tracer Experiments. ^{18}O-Labeled glycine methyl ester and carbonyl-^{18}O-labeled *cis*-$[Co(en)_2Br(glyOCH_3)]Br_2$ were prepared as described previously.[5] The latter was converted into carboxyl-^{18}O-labeled *cis*-$[Co(en)_2Br(glyOH)]Br_2$ as before,[4] and 20.2 g of this complex was converted into carbonyl-^{18}O-labeled *trans*-$[Co(en)_2(OH)(glyO)]^+$ as above. The resulting solution (pH ~8, 500 cm^3) was divided into four equal parts which were treated as follows. (1) The solution was added to 125 cm^3 of 0.01 mol dm^{-3} $HClO_4$, left for 10 days, and then readsorbed on Sephadex C25 exchange resin. The $[Co(en)_2(glyO)]^{2+}$ band was eluted with 0.5 mol dm^{-3} $NaClO_4$ (pH ~6) and recovered as the insoluble HgI_4^{2-} salt as described previously.[6] (2) The solution was added to 100 cm^3 of citrate (0.2 mol dm^{-3})–phosphate (0.1 mol dm^{-3}) buffer (pH 3.7), left for 3 days, and then treated as in part 1. (3) The solution was pH statted against 1.0 mol dm^{-3} $HClO_4$ at pH 8.0 for 12 h and treated as in part 1. (4) The solution was pH statted at pH 10.0 for 5 h and treated as in part 1.

All $[Co(en)_2(glyO)]HgI_4$ samples were pyrolyzed to recover glycine, and this converted to CO_2, as described previously.[5]

Rate Studies and Product Analysis. Kinetic data were obtained spectrophotometrically (560 nm) with use of a Cary 16K spectrophotometer fitted with a thermostated cell (3.2-cm path length) which allowed for pH-stat control (±0.02) and for N_2 flushing.[7] For the slow reaction at pH 1.0 the rate was also estimated by ion-exchange separation of $[Co(en)_2(glyO)]^{2+}$ from unreacted trans-OH_2 complex after 102 h (Dowex 50 W × 2, 2 mol dm^{-3} $NaClO_4$/0.2 mol dm^{-3} $HClO_4$).

After ca. 5 half-lives the products were adsorbed on Dowex 50 W × 2 resin and eluted with 1 mol dm^{-3} $NaClO_4$ at pH ~8 and then at pH ~4. Only one product was observed (other than in 0.1 mol dm^{-3} NaOH) and was identified as $[Co(en)_2(glyO)]^{2+}$ by comparisons of its visible spectrum (600–330 nm) and elution rate with authentic $[Co(en)_2(glyO)]I_2$. For the reaction in 1.0 mol dm^{-3} NaOH ~5% of an unidentified decomposition product was observed.

Co concentrations were determined by AA spectroscopy.

Competition Studies. One experiment was carried out at pH 8.0 in the presence of 1.0 mol dm^{-3} NaN_3. After 5 half-lives (9 h) the products were adsorbed on an ion-exchange column (Dowex 50 W × 2) and eluted at pH ≃6.0 with phosphate buffer (1.0 mol dm^{-3}).

Results and Discussion

The trans reactants were prepared via the base hydrolysis of *cis*-$[Co(en)_2Br(glyO)]^+$ at pH 9–10 (eq 3). This results in a 8–9% yield of *trans*-$[Co(en)_2(OH)(glyO)]^+$.[4]

$$cis\text{-}[Co(en)_2Br(glyOH)]^{2+} + OH^- \rightarrow [Co(en)_2(glyO)]^{2+} + cis\text{-}[Co(en)_2(OH)(glyO)]^+ + trans\text{-}[Co(en)_2(OH)(glyO)]^+ \quad (3)$$

(1) Boreham, C. J.; Buckingham, D. A.; Sargeson, A. M.; Warner, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 1975.
(2) Alexander, M. D.; Busch, D. *Inorg. Chem.* **1966**, *5*, 602.
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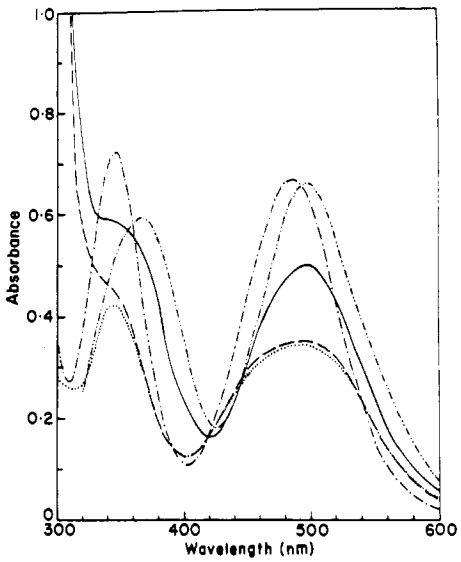

Figure 1. Visible absorption spectra for *trans*-$[Co(en)_2(OH)(glyO)]^+$ (3.47×10^{-3} mol dm^{-3}, pH 8, —), *trans*-$[Co(en)_2(OH_2)(glyO)]^{2+}$ (3.21×10^{-3} mol dm^{-3}, pH 3.7, - - -), *trans*-$[Co(en)_2(OH_2)(glyOH)]^{3+}$ (3.10×10^{-3} mol dm^{-3}, pH 0.5, ···), $[Co(en)_2(glyO)]^{2+}$ formed from *trans*-$[Co(en)_2(OH)(glyO)]^+$ alter 8 h (pH 8, - · -) and *cis*-$[Co(en)_2(OH)(glyO)]^+$ (3.47×10^{-3} mol dm^{-3}, pH 10, - · - ·),[1] all in 2-cm cells, in 0.2 mol dm^{-3} $NaClO_4$, and at 25.0 °C.

The two methods used for isolation of the trans reactant were very similar to those employed for the analogous glycinamide ions,[6] viz., (i) ion-exchange separation of the cis and trans hydroxo species[4] followed by treatment of the resulting solution to allow the cis-aqua ion to cyclize (pH ~4)[1] and subsequent ion-exchange recovery of the trans-hydroxo 1+ ion at pH 8 and (ii) cyclizing of the cis-aqua ion before ion-exchange separation of the trans-hydroxo ion at pH 8.

Visible spectra for the trans-hydroxo and trans-aqua ions are given in Figure 1; these [$\epsilon_{498} = 74 \pm 2$ (pH 8), $\epsilon_{496} = 52 \pm 2$ (pH 4)] correspond closely with those for other *trans*-$[Co(en)_2(NH_2R)(OH_2/OH)]^{3+/2+}$ ions[6,10] and are significantly different (lower ϵ values) from the analogous cis ions. Also given in Figure 1 is the spectrum of the final product from the trans-hydroxo ion at pH 8. This corresponds to the $[Co(en)_2(glyO)]^{2+}$ chelate ($\epsilon_{498} = 92$). This result was substantiated by ion-exchange experiments. Similar results were obtained at pH 1 and 4. When optically pure Λ-*cis*-$[Co(en)_2Br(glyO)]^{2+}$ was employed, the trans reactant (pH 8) and the $[Co(en)_2(glyO)]^{2+}$ product resulting from it had no optical activity (600–300 nm, 5×10^{-4} mol dm^{-3} solution). For the reaction of the trans-hydroxo ion in 0.1 mol dm^{-3} NaOH some (~5%) decomposition product was observed on ion-exchange analysis; this could result either from the reactant or from base hydrolysis of the $[Co(en)_2(glyO)]^{2+}$ product.[9] The combined results showed that over the pH range 1–13 the trans-aqua and -hydroxo ions result in only the $[Co(en)_2(glyO)]^{2+}$ chelate (eq 4).

$$\textit{trans}\text{-}[Co(en)_2(OH_2/OH)(glyO/H)]^{3+/2+/+} \rightarrow [Co(en)_2(glyO)]^{2+} + H_3O^+/H_2O/OH^- \quad (4)$$

Rate data were obtained spectrophotometrically (560 nm), and first-order rate constants are given in Table I. These are plotted vs. pH in Figure 2. Clearly two regions of reactivity obtain corresponding to the slower reaction [$k_1 = (1.8 \pm 0.1) \times 10^{-6}$ s^{-1}] of the aqua ions and a faster reaction [$k_2 = (2.4 \pm 0.2) \times 10^{-4}$ s^{-1}] for the hydroxo ion; there does not seem to be any distinction in the reactivities of the protonated

Table I. Rate Data for Chelation of *trans*-$Co[(en)_2(OH_2/OH)(glyO/H)]^{3+/2+/+}$ Ions [25.0 °C, $\mu = 1.0$ ($NaClO_4$)]

pH	$10^6 k_{obsd}$, s^{-1}	pH	$10^6 k_{obsd}$, s^{-1}
1.0	1.8	7.0	32
1.0	1.7	8.0	103
2.0	1.9	8.1	115
4.0	2.2	10.0	228
4.1	2.5	12.77	259
6.0	8.7		

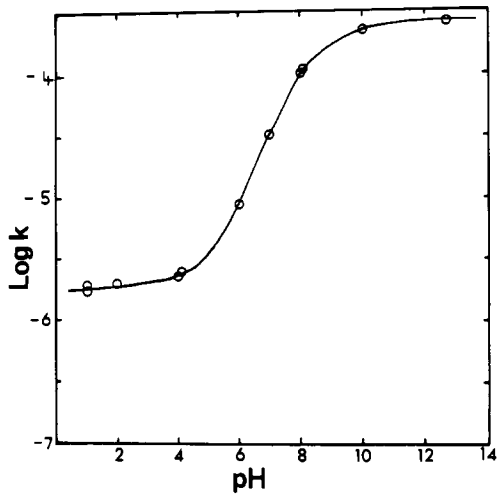

Figure 2. Plot of log k for formation of the $[Co(en)_2(glyO)]^{2+}$ chelate from *trans*-$[Co(en)_2(OH_2/OH)(glyO/H)]^{3+,2+,+}$ [25.0 °C, $\mu = 1.0$ ($NaClO_4$)] vs. pH. (The full line does not represent the theoretical curve for the aqua and hydroxo ions.)

carboxylate and ionic carboxylate complexes ($pK_a(est) \simeq 2$).[1] This latter result differs from that found for the cis species where the acid form was ca. 10× more reactive than its conjugate base.[1] Also for the cis ions, the aqua complexes are considerably more reactive than the hydroxo complex [($k_1 = 1.9 \times 10^{-2}$ s^{-1} (pH ~1) and 1.05×10^{-3} s^{-1} (pH ≃5), $k_2 = 1.74 \times 10^{-5}$ s^{-1} (pH >9)][1] whereas the reverse occurs here. That the trans-hydroxo species gave good linear log $(OD)_t - (OD)_\infty$ vs. time plots at pH >8 (Table I) eliminates any mechanism involving isomerization to the cis-hydroxo ion followed by cyclization in this species (Scheme I), since the latter is less reactive[1] [k_2(trans) = 2.4×10^{-4} s^{-1}, k_2(cis) = 1.74×10^{-5} s^{-1}]. However, unlike the *trans*-hydroxoglycinamide ion,[6] there is not a hydroxide-dependent path for the *trans*-hydroxoglycinate species, at least up to 0.1 mol dm^{-3} NaOH.

The ^{18}O-tracer results are given in Table II. The experimental R value ($R = [46]/([44] + [46])$) is expressed in terms of percent enrichment per oxygen of the carboxyl group, and the percent retention relates to the enrichment in *cis*-$[Co(en)_2Br(glyOH)]Br_2$ used to prepare the trans reactants. It is clear from experiments 1 and 2 that some label is lost during preparation of *cis*-$[Co(en)_2Br(glyOMe)]^{2+}$ or in its subsequent acid hydrolysis. It is likely that the latter process is largely responsible for this loss since earlier studies[5] showed little loss on coordination of glyOMe and the conditions of acid hydrolysis (24 h, 35 °C, ca. 3.5 mol dm^{-3} HBr)[4] will undoubtedly lead to some exchange in the monodentate glycinate ligand.[8] Experiment 3 relates to the chelate formed directly during preparation of the cis- and trans-hydroxo species, and its high enrichment is in accord with direct entry of the carboxyl group during base hydrolysis.[4] Experiments 4–7 relate to the $[Co(en)_2(glyO)]^{2+}$ chelate recovered from reactions of the trans-aqua and -hydroxo species. These are to be compared with experiment 8 which relates to glycine recovered from unenriched complex. The slow reaction of the trans-aqua

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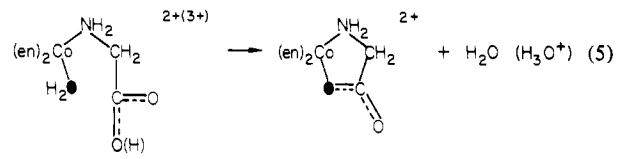
Table II. ^{18}O-Tracer Results for the Chelation of Glycine in the *trans*-$[Co(en)_2(OH_2/OH)(glyO/H)]^{3+/2+/+}$ Ions (25.0 °C, variable μ)

expt	complex (conditions)	R^a	atom % enrichment[b]	% retention[c]
1	glyOMe	0.01713	0.627	
2	*cis*-$[Co(en)_2Br(glyOH)]Br_2$	0.01546	0.545	100
3	$[Co(en)_2(glyO)]^{2+}$	0.01532	0.538	98.7
4	$[Co(en)_2(glyO)]^{2+}$ (0.01 $HClO_4$)	0.01471	0.508	93.2
5	$[Co(en)_2(glyO)]^{2+}$ (pH 3.7)	0.01507	0.527	96.7
6	$[Co(en)_2(glyO)]^{2+}$ (pH 8.0)	0.01493	0.519	95.2
7	$[Co(en)_2(glyO)]^{2+}$ (pH 10.0)	0.01485	0.515	94.5
8	$[Co(en)_2(glyO)]^{2+}$	0.00448	0.002	0.4
9	CO_2 (blank)	0.00444		

[a] Observed R values; $R = [46]/([44] + [46])$ (for CO_2). [b] Atom % enrichment $= 100R/(2 + R) - 100R'(2 + R')$ where R is as given and R' is for the CO_2 blank (experiment 9). [c] Percent retention per O atom on comparison with experiment 2.

complex in 10^{-2} mol dm^{-3} $HClO_4$ (experiment 4, 10 days) appears to result in some exchange into the reactant and/or product, but this is minor and is in agreement with results obtained previously on the chelate.[9] Clearly close to complete retention of the oxygens of the carboxylate group occurs under all conditions. Thus loss of bound water or hydroxide ion is required in forming the chelate.

The results clearly eliminate any prior isomerization to, or equilibration with, the cis-aqua ions (Scheme I). For these species tracer results[1] require subsequent cyclization to occur intramolecularly with incorporation of the coordinated water oxygen into the chelate (eq 5). This would halve the retention



(5)

results found here. For the trans-hydroxo ion the result is not as clear since the corresponding tracer experiment was not done for the cis species. However the kinetic analysis given above appears to eliminate involvement of the cis ion as an intermediate.

A distinction between paths a and b in Scheme II is not clear-cut. However, two independent pieces of information seem to support a concerted process. First, no N_3^- was incorporated during the cyclization process at pH 8. It is known that this anion competes favorably with solvent and the glycinate moiety in the corresponding base hydrolysis reaction of *cis*-$[Co(en)_2Br(glyO)]^+$[4] and that the *cis*- and *trans*-$[Co(en)_2N_3(glyO)]^+$ ions are stable under the reaction conditions.[4] We feel that if an intermediate of reduced coordination number were formed (Scheme II, path b), it would compete favorably for N_3^- as well as for the carboxylate moiety. Second, the rates found here are appreciably faster than those for isomerization in the closely related *trans*-$[Co(en)_2(H_2O/OH)(NH_3)]^{3+/2+}$ ions [$k_{H_2O} \simeq 10^{-8}$ s^{-1} (extrapolated data), $k_{OH} \simeq 1 \times 10^{-5}$ s^{-1}].[10] In these latter species there is no additional involvement of an attached ligand, and for the hydroxo complex at least the isomerization appears to occur without hydroxide exchange.[10] Thus we support a process involving the synergic displacement of coordinated water, or hydroxide, by the trans carboxylic acid or carboxylate anion (Scheme II, path a).

Registry No. *trans*-$[Co(en)_2(OH)(gly\text{-}O)]^+$, 70050-74-7; *trans*-$[Co(en)_2(OH_2)(gly\text{-}O)]^{2+}$, 77881-59-5; *trans*-$[Co(en)_2(OH_2)(gly\text{-}OH)]^{3+}$, 77881-60-8; $[Co(en)_2(gly\text{-}O)]^{2+}$, 16070-98-7.

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Molybdenum(IV) Compounds for Mediation of Electron Transfer. 1. Synthesis, Characterization, and Reactions of Compounds Containing Molybdenum(IV) Coordinated to Trihalostannate(II) Ions

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The presence of molybdenum in various enzymes such as nitrogenase, nitrate reductase, and sulfite oxidase, which catalyze the oxidation or reduction of small molecules, has stimulated interest in interactions of molybdenum and small molecules in general. The evidence[1] indicates that for nitrate reductase and sulfite oxidase, at least, the substrate binds directly to molybdenum atoms.

Molybdenum has been shown to catalyze the reduction of nitrate at mercury electrodes,[2] by Zn metal,[2] and by tin(II).[3,4] The latter system was also used to reduce nitrous acid, although nitrite is more labile to reduction than nitrate and can be reduced by Sn(II) alone. The perchlorate ion, although potentially a strong oxidant, is very inert in dilute aqueous acid at room temperature. However, its reduction, both at mercury electrodes[2] and by Sn(II)[5] is catalyzed by molybdenum. The chlorate ion in aqueous acid is so activated by molybdenum that it may be titrated to Cl^- by Sn(II) solutions in the presence of low concentrations of molybdenum.[6] Mechanisms derived from kinetic studies[5] indicate that the catalytically active species of molybdenum is Mo(IV).

In view of the importance of molybdenum in the biological reduction of oxyanions and the results that implicate Mo(IV) as the catalytically active species in the Sn(II) reductions, synthesis of a Mo(IV) complex compound containing $SnCl_3^-$ ligands has been attempted. Such a complex should allow Mo(IV), bound to a source of electrons in the form of Sn(II) ligands, also to bind to substrates such as NO_3^-, ClO_4^-, ClO_3^-, and N_2. Molybdenum would then act as a template and a pathway for electrons to effect rapid reduction of substrate.

Complexes containing Sn(II) as a ligand in the form of the $SnCl_3^-$ ion are well-known,[7] including the trigonal-bipyramidal $[Pt(SnCl_3)_5]^{3-}$, characterized by X-ray crystallography.[8] However, all compounds previously isolated have been of group 8 or 1B metals; this is, to our knowledge, the first report of a molybdenum compound containing a trihalostannate ligand.

Experimental Section

All manipulations were performed under nitrogen with use of standard Schlenk-type glassware. Solvents were dried with use of standard techniques and stored under nitrogen. Aqueous solutions were degassed by bubbling with nitrogen. Microanalyses were performed by the microanalytical laboratory at the University of Illinois. Infrared spectra were recorded as Nujol mulls with use of NaCl or CsBr windows on a Perkin Elmer 467 or 599B spectrometer. Electronic spectra were recorded on a Cary 14 spectrophotometer. Cuvettes were fitted with serum caps and preflushed with N_2, and the spectrum was recorded immediately after the solution was injected. Magnetic susceptibility measurements were made with use of the Guoy method.

NMe_4SnCl_3. The preparation of this salt has been previously reported,[9] and the method used here is similar except that it was

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