correction for effects owing to the concomitant thermal formation of $[Cr(NH_3)_5H_2O]^{3+}$. Here the important effect is a reduction of the fraction of light absorbed by the iodo complex, and hence the measured quantum yield should be considered a reliable lower limit. The true value may well be closer to the value of 0.35 common to the chloro[2] and bromo[7] analogues.

Loss of iodide was considerably more difficult to follow for several reasons. First, we found it impossible to obtain either the perchlorate or the nitrate salts by reprecipitation techniques owing to the low solubility of the iodide salt and rapid decomposition of the complex ion. Photochemical iodide loss had therefore to be investigated in solutions from which the iodide ion had been removed by anion exchange through a 3 cm long column (perchlorate form of IRA 400 resin, 100 mesh) near 8 °C. This resulted in a solution of ill-defined composition containing the iodo pentaammine and aquo pentaammine ions. Were time now committed to a spectrophotometric determination of the composition, aquation was subsequently so advanced as to preclude useful photochemical measurements. It was best therefore to directly follow the time course of iodide formation at 7 °C before, during, and after irradiation by using a concentration cell with Ag/AgI electrodes. The resulting curves (Figure 1) show three phases: (1) thermal aquation of iodide prior to photolysis; the measured rate constant (7 °C) for our conditions was 1.23×10^{-4} s^{-1}, in good agreement with the value of 1.0×10^{-4} s^{-1} M calculated[18] from k_{298} and $E_{act} = 21.4$ kcal mol^{-1}; (2) release of additional iodide during the irradiation period, leading to upward curvature in the iodide/time plot; (3) thermal release of iodide at an increased but declining rate after photolysis.

These observations show that any photochemical iodide loss is obscured not only by the thermal loss of iodide from the iodo complex but also, and worse, by rapid thermal iodide aquation from the primary photoproduct of the ammonia loss mode, almost certainly *cis*-$[Cr(NH_3)_4H_2O(I)]^{2+}$. This phenomenon has been observed previously for the chloro compound.[3,19] To determine any photochemical quantum yield for iodide therefore, the starting concentrations, the absorbances at 546 nm of all species, the rate constants for the significant thermal reactions, and the light intensity and ammonia quantum yield are required. Five of these were unknowns, namely the exact initial concentrations of the iodo and aquo pentaammines, the iodide aquation rate constant and molar absorptivity at 546 nm of the major photoproduct, and the quantum yield for direct photoaquation of iodide.

The approach taken was to use the SIMPLEX method with a least-squares criterion for goodness of fit[20] to find the parameters in the differential equations for the main thermal and photochemical processes. These equations are

$$d[I^-]/dt = k_1[CI] + k_2[CWI] + \phi_2 I_a$$

$$-d[CI]/dt = k_1[CI] + I_a(\phi_1 + \phi_2)$$

$$d[CWI]/dt = \phi_1 I_a - k_2[CWI]$$

$$d[CW]/dt = k_1[CI] + \phi_2 I_a$$

where $[CI] = [[Cr(NH_3)_5I]^{2+}]$, $[CWI] = [[Cr(NH_3)_4H_2O(I)]^{2+}]$, $[CW] = [[Cr(NH_3)_5H_2O]^{3+}]$, and $I_a = I_0 f_{CI}(1 - 10^{-Abs})$ with Abs the total absorbance of all species at 546 nm, f_{CI} the fraction of absorbed light absorbed by the iodo compound, k_1 and k_2 the iodide aquation rate constants for CI and CWI, respectively, and ϕ_1 and ϕ_2 the ammonia and iodide quantum yields from CI.

Fortunately not all five unknown parameters had to be varied in an unconstrained way. Initial simulations showed that the results were fairly insensitive to the exact value of $\epsilon_{546}(CWI)$. Therefore, on the basis of comparison with the spectra of $[Cr(NH_3)_5Cl]^{2+}$ and *cis*-$[Cr(NH_3)_4H_2O(Cl)]^{2+}$, this unknown was set at 40 L mol^{-1} cm^{-1}. Simulations with the remaining four unknowns unconstrained led to negative quantum yields of iodide for all four data sets studied. Best fits with ϕ_2 constrained at 0.0 were superior to those where ϕ_2 was 0.1, consistent with this. Figure 1 shows the experimental points with fits (solid lines) for the best and worst data sets that we examined in detail.

We conclude the following:

(1) For all data sets fits can be found having relative standard deviations of 1–5% and giving consistent and physically reasonable parameters. The deviations from experiment are clearly not random but can be partially explained by hysteresis in the iodide electrode response.

(2) The calculated initial concentrations correspond well to a slightly diluted and partially aquated (10–30%) version of the original solution placed on the ion-exchange column.

(3) The rate constant for iodide loss from the ammonia photoaquation product is $(3 \pm 1) \times 10^{-3}$ s^{-1} (four runs), about 30 times that for the iodo pentaammine. This factor compares with a factor of about 100 found for the analogous chloro pentakis(methylamino) compound.[19]

(4) The "best fit" quantum yield for iodide photolysis is close to zero.

Our results show that the iodo pentaammine, like the chloro and bromo pentaammines, loses ammonia efficiently on irradiation into the ligand field bands with at most a minor yield of iodide. Its photochemistry is therefore also antithermal, inconsistent with the predictions of the VC theory and consistent with Adamson's simpler rule. In terms of fundamental behavior, however, we do not make much of this last point.

It seems that the excited-state bond strength, assuming the VC calculated values may be relied upon, cannot be the only important factor operating. Many years ago, Manfrin et al. pointed out[4] that much of Cr(III) photochemistry was consistent with another simple rule, preferential aquation of an uncharged ligand. An enhanced escape rate of the neutral ammonia molecule probably accounts for the deviation of this molecule (and the bromo pentaammine) from the VC theoretical predictions.

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Department of Chemistry **A. D. Kirk***
University of Victoria **S. Arunachalam**
Victoria, BC, Canada V8W 2Y2 **D. Kneeland**

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Synthesis and Characterization of Substitution-Inert Cobalt(III) Complexes Containing an *N*-Glycoside Derived from Ethylenediamine and a Monosaccharide (D-Mannose, L-Rhamnose, or D-Ribose)

Sir:

We report the first successful synthesis, isolation, and characterization of substitution-inert cobalt(III) complexes containing an *N*-glycoside derived from ethylenediamine (en) and D-mannose (D-Man), L-rhamnose (L-Rha), and D-ribose (D-Rib), the results of which suggest a novel coordination behavior of sugars.

The interaction of carbohydrates with transition metals is of current interest in coordination chemistry and in bioinorganic chemistry. Despite a wide interest in complexes with sugars, very little is known about the structural details of the complexes.[1] Metal complexes are divided into two classes such as substitution inert and substitution labile on the basis of their chemical properties. Therefore, it is desirable to examine these two types of complexes in order to elucidate the interaction of sugars with metals. Recently, we have extensively investigated the synthesis

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Table I. Observed H-H Vicinal Coupling Constant Values[a] (^3J) in the Sugar Rings (Hz)

complex	$^3J_{1,2}$	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{4,5}$	$^3J_{5,6}$
1	4.3	3.5	2.1	7.8	3.4, 5.8
2	4.3	3.5	2.1	6.1	6.7
3	4.0	4.0	0.0	4.0, 5.3	

[a] Not simulated values.

and characterization of the novel type of nickel(II) complexes containing *N*-glycosides obtained from the reaction of a monosaccharide and $[Ni(diamine)_3]^{2+}$ as a class of substitution labile.[2] At this time, we could obtain the typically substitution-inert cobalt(III) complexes containing an *N*-glycoside derived from en and an aldose by the following procedure.

A 10-mmol quantity of a monosaccharide (D-Man, L-Rha, or D-Rib) and a 10-mmol sample of en were dissolved into 250 mL of methanol, and the solution was refluxed with stirring. To the solution was added a methanol solution (100 mL) of cobalt(II) chloride hexahydrate (5 mmol) with small portions over 40 min. As soon as each portion was added, the solution became brown[3] and gradually turned wine red. The refluxing was continued for another 20 min. After cooling, the solution was evaporated to dryness. The residue was dissolved into water, and the solution was subjected to SP-Sephadex C-25 cation-exchange column chromatography. Elution with 0.01 N NaCl produced a broad red band.[5] The red band for each sugar did not consist of a single species. Therefore, after being desalted, the red solution was subjected to Dowex 50W-X8 cation-exchange column chromatography. Elution with 0.1 N $NaClO_4$ gave a red major band and a trace one. Complete separation was achieved for the L-Rha and D-Rib complexes. The major fraction of the L-Rha or D-Rib complex was desalted by gel permeation chromatography, and the aqueous solution was concentrated followed by addition of excess ethanol to yield red crystalline solids,[6] which were recrystallized from a minimum amount of warm ethanol. While the separation for the D-Man complex was incomplete, however, the major fraction was desalted and evaporated to dryness. The residue was dissolved into a minimum amount of warm water–ethanol (1:2) and the solution cooled to give pure crystals.[7]

Elemental analyses[8] indicated that the complexes obtained from D-Man (**1**), L-Rha (**2**), and D-Rib (**3**) contain one sugar residue and two en moieties. The electrical conductivity data[9] indicated that the three complex ions behave as univalent cations in aqueous solution. The electronic absorption spectra[10] of these complexes closely resemble each other, and they have two main peaks in the d–d transition region. Each lowest energy peak shows a symmetrical curve without any shoulder in the first absorption region, which is characteristic for the *cis*(*O–O*)-$[CoN_4O_2]$ type.[11] The CD curves of **2** and **3** closely resemble each other and are nearly mirror images of that of **1**.[12] There are two negative peaks for **1** and two positive peaks for **2** or **3** in the first absorption region. From the empirical rule on the CD signs in this region and from comparison with the CD signs of optically active *cis*(O–O)-$[Co(O)_2(en)_2]^+$ type complexes in this region,[13] **1** can be assigned the Δ configuration and **2** and **3** the Λ configuration. In each ^{13}C NMR spectrum, one of the signals assigned to the en carbon atoms appears at 7–8 ppm downfield from the other three,[15] which is presumably corresponding to the carbon atom adjacent to the glycosidic nitrogen atom. Consequently, **1**, **2**, and **3** will be denoted $[Co(D\text{-}Man\text{-}en)(en)]ClO_4\cdot NaClO_4\cdot {}^3/_2H_2O$, $[Co(L\text{-}Rha\text{-}en)(en)]Br\cdot H_2O$, and $[Co(D\text{-}Rib\text{-}en)(en)]ClO_4\cdot 2H_2O$.

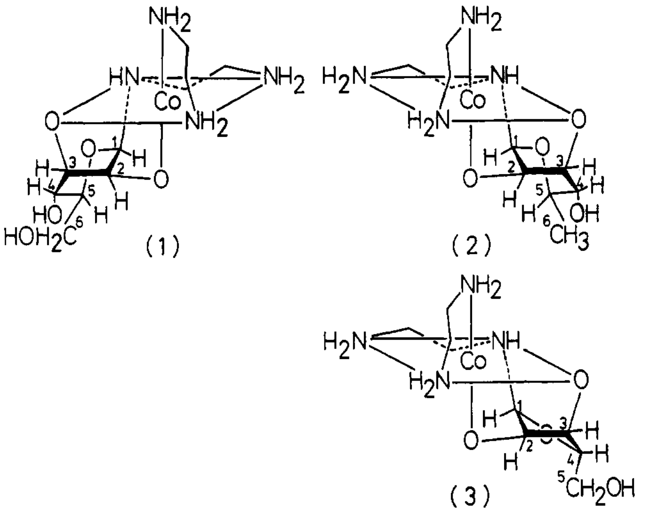

Figure 1. Proposed structures of Δ-$[Co(D\text{-}Man\text{-}en)(en)]^+$ (**1**), Λ-$[Co(L\text{-}Rha\text{-}en)(en)]^+$ (**2**), and Λ-$[Co(D\text{-}Rib\text{-}en)(en)]^+$ (**3**).

In the 400-MHz ^1H NMR spectra of the three complexes, all of the signals from the sugar units could be assigned completely by employing the double- and triple-resonance techniques. The conformations of the sugar rings were analyzed by the observed vicinal coupling constant values (Table I) on the basis of the Karplus relationship.[15,16] The coupling constant values of **1** and **2** are much the same except for the $^3J_{5,6}$ values. It is very important that the $^3J_{3,4}$ values are very small (2.1 Hz) in **1** and **2**.

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(3) It is presumed that this brown material is $[(en)_2Co(O_2)(OH)Co(en)_2]^{3+}$, which is the reactive species in this reaction. The same major product was also obtained from the reaction of $[(en)_2Co(O_2)(OH)Co(en)_2](ClO_4)_3\cdot H_2O$[4] with a monosaccharide.

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(5) A large amount of brownish species adsorbed to the resin.

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(7) The yields were 0.9% for D-Man, 2.1% for L-Rha, and 1.9% for D-Rib per the amount of starting cobalt.

(8) Anal. Calcd for $[Co(D\text{-}Man\text{-}en)(en)]ClO_4\cdot NaClO_4\cdot {}^3/_2H_2O$ ($C_{10}H_{27}N_4O_{14.5}NaCl_2Co$): C, 20.42; H, 4.63; N, 9.53; Na, 3.91; Cl, 12.06. Found: C, 20.11; H, 4.21; N, 9.38; Na, 3.32; Cl, 12.07. Calcd for $[Co(L\text{-}Rha\text{-}en)(en)]Br\cdot H_2O$ ($C_{10}H_{26}N_4O_5BrCo$): C, 28.52; H, 6.22; N, 13.30; Br, 18.97. Found: C, 28.86; H, 6.23; N, 13.01; Br, 19.67. Calcd for $[Co(D\text{-}Rib\text{-}en)(en)]ClO_4\cdot 2H_2O$ ($C_9H_{26}N_4O_{10}ClCo$): C, 24.31; H, 5.89; N, 12.60; Cl, 7.97. Found: C, 24.12; H, 5.54; N, 12.47; Cl, 8.06.

(9) Electrical conductivity data (H_2O, 25 °C) for **1**: $\Lambda_0/2$ 102 Ω^{-1} cm^2 mol^{-1}. For **2**: Λ_0 106 Ω^{-1} cm^2 mol^{-1}. For **3**: Λ_0 93 Ω^{-1} cm^2 mol^{-1}.

(10) Electronic absorption spectral data in H_2O for **1**: $\tilde{\nu}_{max}$ 19 500 (log ϵ 1.89), 26 900 (2.12), 44 800 (4.19) cm^{-1}. For **2**: $\tilde{\nu}_{max}$ 19 400 (log ϵ 2.01), 26 900 (2.26), 44 800 (4.13) cm^{-1}. For **3**: $\tilde{\nu}_{max}$ 19 400 (log ϵ 2.00), 26 800 (2.23), 44 800 (4.15) cm^{-1}.

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(12) CD spectral data in H_2O for **1**: $\tilde{\nu}_{max}$ 17 500 ($\Delta\epsilon$ −0.34), 20 400 (−1.12), 22 800 (sh, −0.14), 25 200 (+0.54), 28 200 (sh, −0.42), 31 500 (−0.77), 37 200 (+2.92), 46 000 (+12.39) cm^{-1}. For **2**: $\tilde{\nu}_{max}$ 17 300 ($\Delta\epsilon$ +0.71), 20 400 (+1.65), 22 900 (sh, +0.34), 25 100 (−0.52), 27 900 (+0.65), 31 300 (+0.57), 36 900 (−3.46), 45 900 (−12.85) cm^{-1}. For **3**: $\tilde{\nu}_{max}$ 17 400 ($\Delta\epsilon$ +1.09), 20 500 (+0.68), 23 000 (sh, +0.36), 25 100 (−0.25), 27 600 (+0.68), 30 000 (sh, +0.17), 37 600 (−3.79), 45 500 (−10.85) cm^{-1}.

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(16) The conformations were qualitatively analyzed on the basis of criteria as follows obtained from reported ^3J values of monosaccharides with the chair conformations.[17] $^3J_{1,2}$: 1–2 (for the dihedral angle 60 or 120°), ≃8 (180 or 0°), 0 (90°) Hz. $^3J_{4,5}$ in six-membered rings and $^3J_{3,4}$ in five-membered rings: ≃1 (for the dihedral angle 60 or 120°, ≃10 (180 or 0°), 0 (90°) Hz. Others: 3–4 (for the dihedral angle 60 or 120°), 9–10 (180 or 0°), 0 (90°) Hz.

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In the usual chair conformation, the value of $^3J_{3,4}$ should be large (9-10 Hz), in agreement with the trans coupling. These consideration led to the conclusion that each sugar ring in **1** and **2** is not in the usual chair conformation but adopts the β-$^3S_5$ skew-boat conformation. It is interesting that the value of $^3J_{3,4}$ is 0 Hz in **3**, which suggested that the dihedral angle between the planes of H-C3-C4 and C3-C4-H is ca. 90°. And it shows that the sugar ring in **3** takes the five-membered α-$^2T_3$ twist conformation.

From all of the results obtained coupled with the inspection of the scale models, it was concluded that the sugar unit of each tetradentate *N*-glycoside ligand facially coordinates to the cobalt atom through the N atom on C1 and through the two O atoms on C2 and C3 (Figure 1).

It is very interesting that the three-point metal bindings induce the conformational changes from the chair conformation that the free sugars usually take.[18] This coordination geometry would be generally possible for sugars containing the cis arrangement between two hydroxyl groups on C2 and C3 such as D-mannose, L-rhamnose, and D-ribose. On the other hand, it seems to be impossible for sugars containing the trans arrangement between two hydroxyl groups such as D-glucose and D-galactose. The results of this work suggest the novel aspect of selective complexation for aldoses.

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Department of Synthetic Chemistry
Faculty of Engineering
The University of Tokyo
Hongo Bunkyo-ku, Tokyo 113, Japan

Katsuaki Ishida
Shigenobu Yano*
Sadao Yoshikawa*

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Articles

Contribution from the Department of Inorganic Chemistry,
Guindy Campus, University of Madras, Madras 600 025, India

Photochemical Reactions of Cobalt(III)-Amine Complexes in Nonaqueous Solvents: Mechanistic Details of the Oxygenation Reactions of Cobalt(II) Systems

P. Ramamurthy and P. Natarajan*

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Flash photolysis of a series of cobalt(III)-amine complexes dissolved in air-equilibrated neat acetonitrile and methanol produces transients due to the oxygenation of the photoproduced cobalt(II) amines. The kinetics of the oxygenation reaction has been investigated by observing the transients in a time-resolved manner at different wavelengths. The study reveals that the cobalt(II)-amine complex forms a 1:1 adduct with oxygen to give a superoxo complex that dimerizes, reacting with the starting complex to give a μ-superoxo dinuclear cobalt(III) complex. The μ-superoxo dinuclear complex is reduced to give the final product, the μ-peroxo dimer. The first step is found to depend upon the concentration of dissolved oxygen and the second step on the concentration of the cobalt(III) amine. Time-resolved absorption spectra of the transient species have been obtained, and the spectra are compared with those of well-characterized dioxygen complexes of cobalt(III). Steady photolysis studies of the cobalt(III) amines have been carried out, and the spectra for the oxygenation products have been obtained.

Introduction

The reactions of dioxygen complexes of transition metals have been of considerable interest, centered primarily on studies of cobalt-dioxygen bonding as a model for biological processes.[1-10] Cobalt(II) complexes normally form μ-peroxo-bridged complexes in aqueous solution. Whenever the chelating agent has an insufficient number of coordinating groups or is present in insufficient concentration to completely saturate the coordination sites available on the cobalt ion, a second bridge may form.[5] It was suggested that μ-peroxo-bridged complexes of cobalt are formed via an intermediate mononuclear superoxo complex.[5] It has been possible to limit the oxygenation reaction to a 1:1 (cobalt:oxygen) superoxo complex formation by using solvents of low dielectric constant or complexes in which steric hindrance prevents the bridge formation.[11] There is evidence for the formation of dinuclear μ-superoxo or μ-peroxo complexes from the mononuclear superoxo precursors.[2] A general reaction mechanism for the formation of the μ-peroxo dinuclear complex proposed by Wilkins[12] involves the reactions

$$\mathrm{CoL^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLO_2{}^{2+}}$$

$$\mathrm{CoLO_2{}^{2+} + CoL^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{peroxo complex}}{LCo\text{-}O_2\text{-}CoL^{4+}}}$$

Earlier investigations reveal that the photochemistry of transition-metal coordination complexes has been affected significantly by the solvent medium.[13] Earlier, we have investigated[14,15] the photochemistry of *cis*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$ in acetonitrile, which undergoes charge-transfer photolysis to produce the corresponding cobalt(II) complex, which in turn reacts with dissolved oxygen.

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