haps the ribose–phosphate grouping of one nucleotide with the base of the other nucleotide.

The exact position of the binding site on the adenine base is as yet unknown. Nmr studies on the copper complexes of 3′- and 5′-AMP have indicated that copper binds to N-7 on the base,[3] but since the zinc complexes are formed under somewhat different conditions from those for the copper complexes, the binding sites may also be different. It can be demonstrated, through the use of CPK atomic models, that it is possible to obtain a parallel stacked structure maintaining the anti configuration of the base by linking the 5′ or 3′ phosphate to N_3, N_1, or N_7. CPK model studies also indicate that two types of stacked structures are possible. The two opposite sides of the base can be in contact, as in poly(A), or the same side of each base can be in contact, as has been proposed for the Cu–AMP complex,[3] for stacked nucleotides at high concentration,[34] and for 5′,5′-diadenosine.[9,37]

The continuous variation study shows that the complex contains the same number of zinc(II) atoms and AMP molecules. This 1:1 stoichiometry can be satisfied by a 2:2 complex of the type postulated for the Cu(II) reaction in which the face of one nucleotide is in contact with the same face of the other.[3] The CD bands which result from π interaction in the stacked bases of the dinucleotides linked through the 5′ phosphate are red shifted relative to the bands of the 3′–5′ dimer.[9,37] The conservative CD bands of the Zn–AMP complex are also shifted to the red, in line with the 2:2 binuclear structure.

The observed stoichiometry is also consistent with a face to back stacking that would be characteristic of a long polymeric structure in which each phosphate is linked by zinc(II) to the next base of the chain. Such a possibility is consistent with the precipitation of the nucleotide by Zn(II).

The role of the 2′-OH is particularly interesting because of the biological importance of the absence or presence of this group in a nucleotide. CPK models indicate that for the 3′ isomer it is possible for a Zn(II) ion which is coordinated to the phosphate and the base to bind also to the 2′-OH. Such additional coordination would increase the rigidity of the orientation of the bases relative to each other and thus help to contribute to the extremely high rotatory strength of the 3′ ribonucleotide complex. The removal of the 2′-OH would then weaken the structure and produce a drastic decrease in the rotatory strength.

On the other hand, with the 5′ isomer the 2′-OH cannot be directly involved in the complex unless N_3 is the base binding site. Furthermore, the titration behavior and uv spectra indicate that the 5′-dAMP complex is very similar to the 5′-AMP complex. The added possibility thus exists that the effect of the 2′-OH group is an indirect one on the configuration of the nucleotide, affecting the relative orientation of the bases in the complex. Such a possibility is consistent with the difference in the furanose ring conformation found for deoxyadenosine and riboadenosine.[38] A relative decrease in the rotatory strength is also found when the deoxy dimer and polymer are compared with the ribo dimer and polymer, and poly(dA), unlike poly(rA), does not exhibit conservative CD bands.[7]

The mechanism by which polypeptides or other polycations cause solubilization of the zinc nucleotide complex is not certain. Positive charges on the polypeptide may bind electrostatically to residual negative charges on the phosphates, or electron donor groups (such as amino groups) may bind to the zinc ions. The fact that the partly soluble Zn(II)–3′-AMP produces a similar conservative CD effect in the presence or absence of polypeptide indicates that the effect itself does not depend on the polypeptide.

Acknowledgment. The excellent technical assistance of Mrs. Joan Green, Mrs. William Heim, and Mr. Edward Tarien is gratefully acknowledged.

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Communications to the Editor

Oxidation of Cobalt(I) Carbonyl Complexes and Cobalt(I)-Catalyzed Oxidation of Carbon Monoxide

Sir:

In the context of the intense current interest in reactions of coordinated ligands and in the roles of such reactions in homogeneous catalysis, we wish to describe some novel reactions involving the oxidation of cobalt(I) carbonyl complexes and the catalysis by such complexes of the oxidation of carbon monoxide. Our results are also of some interest in connection with recent controversial accounts concerning the mechanisms of reduction of vitamin B_{12a} and related cobalt(III) complexes by CO.[1–4]

Our studies relate to the oxidation of the ion $[Co^{I}(CN)_2(PEt_3)_2(CO)]^-$ (**1**), whose preparation we have recently described,[5] by $Fe(CN)_6{}^{3-}$. In alkaline aqueous solutions containing excess $Fe(CN)_6{}^{3-}$, the overall oxidation of **1** proceeds quantitatively in accord with eq 1 to yield $[(NC)_5Fe^{II}CNCo^{III}(CN)_2(PEt_3)_2(H_2O)]^{3-}$ [**2**, λ_{max} 410 nm (ϵ_{max} 1.54×10^3)] which we have isolated in pure form as the potassium salt and fully characterized.[5] **2** is the analog of the ion, $[(NC)_5Fe^{II}CNCo^{III}$-

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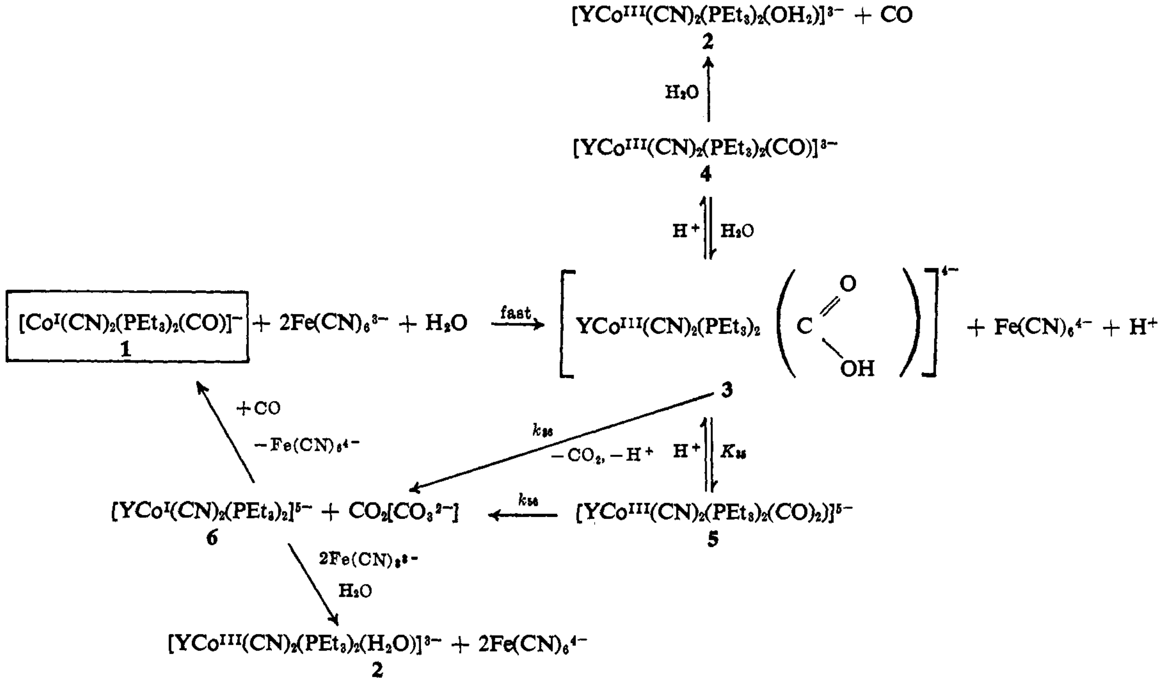
Scheme I



$[Y = (NC)_5Fe^{II}CN\text{-}]$

$(CN_5]^{6-}$, which has previously been prepared by the oxidation of $Co(CN)_5^{3-}$ or $HCo(CN)_5^{3-}$ with $Fe(CN)_6^{3-}$ [6,7]

$$[Co^I(CN)_2(PEt_3)_2(CO)]^- + 4Fe(CN)_6^{3-} + 4OH^- \longrightarrow \underset{2}{[(NC)_5Fe^{II}CNCo^{III}(CN)_2(PEt_3)_2(H_2O)]^{3-}} + CO_3^{2-} + 3Fe(CN)_6^{4-} + H_2O \quad (1)$$

The results of our detailed studies on this reaction, including kinetic measurements on some of the component steps and detection and characterization of some of the intermediates, provide support for Scheme I. Some of the significant features of this scheme and the evidence upon which it is based are as follows.

1. Addition of **1** to a *neutral* aqueous solution of $Fe(CN)_6^{3-}$ resulted in an initial rapid reaction, with an end point corresponding to a $Fe(CN)_6^{3-}$:**1** ratio of 2.0:1. The formulation of the relatively unstable product of this reaction [λ_{max} 500 nm (ϵ_{max} 5.0 × 10^2)], which decomposed in a pH-dependent manner within a few minutes (see below), as $[(NC)_5Fe^{II}CNCo^{III}(CN)_2(PEt_3)_2(COOH)]^{4-}$ (**3**) is supported apart from considerations of chemical plausibility (i) by its strong retention on an anion-exchange resin (which favors the proposed $Fe(CN)_6^{4-}$-containing formulation rather than the neutral solvated alternative $[(H_2O)Co^{III}(CN)_2(PEt_3)_2(COOH)]$, (ii) by the spectral similarity to the more stable corresponding alkoxycarbonyl products, *i.e.*, ($[(NC)_5Fe^{II}CNCo^{III}(CN)_2(PEt_3)_2(COOR)]^{4-}$), of the 2:1 reaction of $Fe(CN)_6^{3-}$ with **1** in anhydrous methanol or ethanol (ROH), and, most convincingly, (iii) by the observation that the spectrum of the product of rapid decomposition of an aqueous solution of **3**, following acidification (pH <2) and loss of CO, corresponds to that of the known[5] species **2** in accord with Scheme I. Also in accord with our formulation of **3** is the fact that this species could not be generated through the oxidation of **1** by nonbridging outer-sphere oxidants such as $Co^{III}(EDTA)^-$. The reaction of **1** with $Co^{III}(EDTA)^-$ did not proceed beyond the 1:1 stage, *i.e.*, the formation of $[Co^{II}(CN)_2(PEt_3)_2(CO)]$ [λ_{max} 403 nm (ϵ_{max} 5.1 × 10^2)] which, however, underwent the further expected reaction (analogous to that of $Co^{II}(CN)_5^{3-}$)[6] with 1 equiv of $Fe(CN)_6^{3-}$ to form **3**.

2. Over the pH range 6–12.5 the species **3** undergoes decomposition at a measurable rate to yield products which are identifiable as characteristic derivatives of the common intermediate **6**, in accord with Scheme I, *e.g.*, **2** in the presence of excess $Fe(CN)_6^{3-}$ (corresponding to the overall reaction of eq 1) and **1** in the presence of excess CO. At constant pH, this decomposition (followed spectrally at 420 nm) exhibited pseudo-first-order kinetics according to eq 2. The pH dependence of the rate was quantitatively fitted by eq 3 and 4 (which are derived for Scheme I) using the values $K_{35} = 3.4 \times 10^{-12}$ M (pK_a = 11.5), $k_{36} = 1.0 \times 10^{-3}$ sec^{-1}, and $k_{56} = 3.4$ sec^{-1}.

$$-d[\mathbf{3}]_{total}/dt = -(d[\mathbf{3}]/dt + d[\mathbf{5}]/dt) = k_{obsd}[\mathbf{3}]_{total} \quad (2)$$

$$= k_{36}[\mathbf{3}] + k_{56}[\mathbf{5}] \quad (3)$$

$$k_{obsd} = (k_{36}[H^+] + k_{56}K_{35})/([H^+] + K_{35}) \quad (4)$$

3. The intermediate **6** could also be trapped by adding other ligands which are effective in coordinating to cobalt(I) and, therefore, displace $Fe(CN)_6^{4-}$ from **6** to form stable adducts. Thus, the oxidation of **1** by 2 equiv of $Fe(CN)_6^{3-}$ in the presence of acrylonitrile yielded the stable adduct $[Co^I(CN)_2(PEt_3)_2(CH_2{=}CHCN)]^-$ which was isolated in pure form as the potassium salt. In the presence of allyl alcohol, the neutral π-allyl cobalt(III) adduct **7** (which was isolated in pure form and fully characterized analytically and by nmr[8]) was obtained, presumably through

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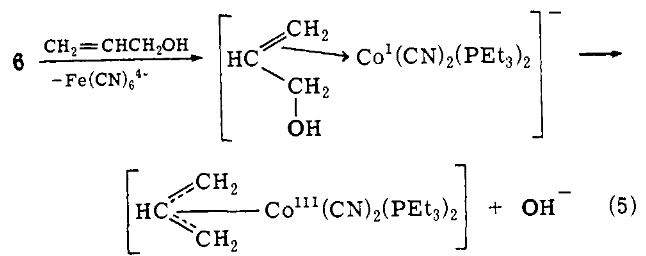
(8) Nmr ($CDCl_3$): attributable to $P(CH_2CH_3)_3$, δ 1.2 (18 H, m, CH_3), 2.1 (12 H, m, CH_2); attributable to π-C_3H_5, δ 2.85 (2 H, d, J =

the reaction sequence



7 (5)

4. The trapping of **6** by CO results in the regeneration of **1** and thus provides the basis for a *catalytic cycle*, *i.e.*, **1** → **3** (**5**) → **6** → **1**, in which the oxidation of CO by Fe(CN)$_6^{3-}$ proceeds readily under the catalytic influence of **1**, *i.e.*

$$CO + 2Fe(CN)_6^{3-} + 4OH^- \xrightarrow{1} CO_3^{2-} + 2Fe(CN)_6^{4-} + 2H_2O \quad (6)$$

This was confirmed in an experiment in which the (incremental) addition of 9.4 × 10^{-3} *M* Fe(CN)$_6^{3-}$ to a CO-saturated solution (pH 12) containing a catalytic amount (3.0 × 10^{-4} *M*) of **1** resulted in the formation of 4.6 × 10^{-3} *M* CO$_3^{2-}$ (determined gravimetrically as BaCO$_3$).

The reaction scheme that we have described possesses several features in common with certain other systems, notably (1) the reactions of water or alcohols with other carbonyl complexes such as $[IrCl_2(PR_3)_2(CO)_2]^+$ and $[PtCl(PR_3)_2(CO)]^+$ to yield the corresponding stable hydroxycarbonyl and alkoxycarbonyl derivatives, *i.e.*, $[IrCl_2(PR_3)_2(CO)(COOH)]$[10] and $[PtCl(PR_3)_2(CO\text{-}OR)]$,[11,12] and (2) the reductions of various other metal complexes, notably of Rh(III),[13] by CO, many of which probably proceed through related mechanisms involving the loss of CO$_2$ from intermediates of the type MCOOH which were first proposed for the oxidation of CO by Hg(II)[14] and Ag(I).[15] Of particular interest in this context are some recent studies on the reduction of vitamin B$_{12a}$ and certain related cobalt(III) complexes by CO, the mechanisms of which have been the subjects of considerable uncertainty and controversy.[1-4] It is not unlikely that at least some of these reactions, including the reported aquocobalamin-catalyzed oxidation of CO by O$_2$,[1] proceed through mechanistic schemes similar to that which we have described.

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13 Hz, CHH′), 3.72 (2 H, d, *J* = 7 Hz, CHH′), 5.4 (1 H, m, CH). The π-allyl region of the nmr spectrum resembles that of other π-allyl complexes.[9]

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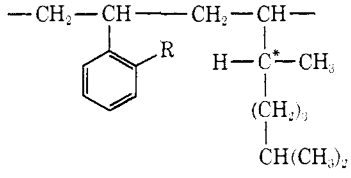
Circular Dichroism between 230 and 185 nm of the Aromatic Chromophore in High Molecular Weight Hydrocarbons[1]

Sir:

The main disadvantage in investigating chiroptical properties of the aromatic chromophore in low molecular weight alkyl aryl hydrocarbons is, in general, the very low ellipticity of its π → π* electronic transitions with respect to the absorption. As a consequence, the investigation[2,3] has been until now limited to the ^1L_b transition[4] and in one case only[5] the first extremum of the Cotton effect, related to the ^1L_a transition, has been reached.

In a previous paper, it was reported[6] that the absorption band between 275 and 245 nm of coisotactic copolymers of (*R*)-3,7-dimethyl-1-octene (I) with styrene (II) is optically active and its ellipticity is much larger than in low molecular weight models, when less than 20–25% units of II are present.[6,7] Considering that contour and vibrational spacing were similar in the copolymer and in the models, the larger ellipticity of the former was attributed to the smaller conformational mobility[8] of the aromatic rings in the dissymmetric environment of the one screw sense helical macromolecules.



I-II copolymer, R = H
I-III copolymer, R = CH$_3$

Taking into account the larger dissymmetry factor of the copolymers, we have now investigated the 230–185-nm spectral region, where the ^1L_a and ^1B transitions[4] of the benzene chromophore are located.

Figure 1 reports the CD spectrum (Roussell Jouan Dichrograph II) in the region of a coisotactic random copolymer[6,7] of I with II containing 20 mol % of the latter. At least four optically active bands can be observed: a rather weak positive band ($[\theta]_{max}$ per

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[1] III. Optically Active Hydrocarbon Polymers with Aromatic Side Chains. For paper II see F. Ciardelli, O. Pieroni, C. Carlini, and C. Menicagli, *J. Polym. Sci., Part A-1*, **10**, 809 (1972).

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