plex and methyl isocyanide. This intermediate then rearranges on heating to the inserted product. The structure of the intermediate is open to some consideration. A five-coordinate complex, such as proposed in the carbonylation reaction,[5] is possible, since the starting platinum complex is formally coordinately unsaturated. The solubility in chloroform and the molecular weight values (osmometric in chloroform) are in accord with this. On the other hand, there are few known five-coordinate platinum(II) complexes, if one excludes those well-known complexes of polydentate phosphines and arsines, and no analogous complexes of the general formula $(phos)_2Pt(L)RX$ with other ligands. Failure to observe an intermediate, $[(C_6H_5)_3P]_2PtR_2 \cdot CNCH_3$, in the reaction of $[(C_6H_5)_3P]_2PtR_2$ and methyl isocyanide lends indirect support also. We feel that a more likely structure is an ionic complex, *trans*-$(R_3P)_2Pt(CNCH_3)R'^+X^-$.[6] Conductivity data in dichloromethane indicate their formulation as 1:1 electrolytes.[7] It is possible, of course, that solid-state and solution structures will be different, the latter depending also on the nature of the solvent. Additional work, including possibly a crystal structure determination, is needed to clarify this situation.

Assuming an ionic structure for this intermediate, one can then visualize the resultant rearrangement to proceed by halide ion attack at the metal, displacing the alkyl or aryl group to the coordinated isocyanide; perhaps *via* a five-coordinated intermediate (Figure 1).

In this work no evidence was obtained which suggested that aggregation of isocyanides to oligomeric or polymeric structures occurred even if excess isocyanide was present. Such reactions appeared rather favorable in the nickel isocyanide work.[3] We did observe, however, that a second isocyanide did react with the insertion product $[(C_6H_5)_3P]_2Pt(CR{=}NCH_3)Br$ to give $[(C_6H_5)_3P]_2Pt(CR{=}NCH_3)Br \cdot CH_3NC$, which could presumably be an early precursor to such oligomers.

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(6) The methyl groups bound to phosphorus in the analogous compound $[(C_6H_5)_2(CH_3)P]_2(C_6H_5)I \cdot MeNC$ are split into a triplet in the nmr, indicating a trans arrangement of the phosphines.

(7) At ~5 × 10^{-4} *M* concentrations, Λ_M [cm^2/(ohm mol)] (25°) is 54, 57, and 56 for $[(C_6H_5)_3P]_2Pt(CNCH_3)C_6H_5{}^+I^-$, $[(C_6H_5)_3P]_2Pt(CNCH_3)C_6H_5{}^+Cl^-$, and $[(C_6H_5)_3P]_2Pt(CNCH_3)CH_3{}^+I^-$. The Λ_M value for 5 × 10^{-4} *M* concentrations of $(C_4H_9)_4N^+I^-$ and $(C_2H_5)_4N^+ClO_4^-$ in dichloromethane is ~72 cm^2/(ohm mol).

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Characterization of Pentaaquomonoamminecobalt(III)

Sir:

The enormous decrease in reactivity brought about by replacing H_2O in $Co(H_2O)_6{}^{3+}$ completely by NH_3 is a matter of interest. A systematic study of the reactions of the entire series of the aquoammine complexes can be expected to help in understanding this particular problem in chemical reactivity. Such a study has, until now, not been possible because the ions at the aquo end of the series are poorly characterized. We have been investigating these ions, and in the course of this work have characterized the species $CoNH_3(H_2O)_5{}^{3+}$, which has not hitherto been described. This report deals with the preparation of this new species and with some of its properties.

The species $CoNH_3(H_2O)_5{}^{3+}$ was first encountered in separating, by means of a cation-exchange resin, the products obtained from treating "$KCo(NH_3)_2(CO_3)_2$"[1] with 1 *M* $HClO_4$. However, the yields of the new species obtained by this method proved to be small and erratic. A slight change in the procedure has led to success in the three preparative attempts which have been made with the modified procedure.

The method described by Mori, *et al.*, is followed up to the point at which ammonium carbonate is to be added to convert the carbonatocobalt(III) complex to a carbonatodiammine. Our modification consists in adding solid ammonium chloride instead of ammonium carbonate, 1 mol for each mole of cobalt. The product from this step is obtained in solid form by following the Mori procedure, and this solid is the starting material for the operations which are to be described.

The solid material (10 g) is dissolved in 100 ml of cold 1 *M* $HClO_4$. A solution of $Hg(ClO_4)_2$ is added until the color of the cobalt species changes from blue to violet (this step removes Cl^- from the Co(III) complex). The resulting solution is charged onto a column of Dowex 50X2 100–200 mesh cation-exchange resin, kept at 0°. The column is first eluted with cold 0.5 *M* $HClO_4$ to remove Hg(II) and Co(II) and then with cold 2 *M* $HClO_4$. At this stage a broad violet band moves down the column. From its ion-exchange behavior, and the chemistry of the treatment needed to convert it, we take the band to be comprised of a condensed form of the monoammine complex. The corresponding diammine species is eluted less rapidly and it would tend to concentrate in the trailing part of the band. Thus only the leading 80% or so of the violet band was collected.

Analyses for Co(III), Co(T) (total cobalt), and NH_3 were made on the violet solution eluted, with the results for three separate preparations being as follows: (1) 2.52×10^{-3}, 2.47×10^{-3}, 2.51×10^{-3} (2) 1.10×10^{-3}, 1.09×10^{-3}, 1.10×10^{-3} *M;* (3) 1.00×10^{-3}, 9.91×10^{-4}, 1.04×10^{-3} *M*.

The methods of analysis applied to the violet material and to the monoammine were as follows. For Co(III), the solution was added to excess Fe^{2+} and Fe^{2+} was titrated with $Cr_2O_7{}^{2-}$, using sodium diphenylaminesulfonate as indicator[2] (the monoammine, its precursor, and the diammine and its precursor all react rapidly enough with Fe^{2+} to make this method of analysis feasible). For Co(T), thiocyanate[3] was used to develop the color of Co^{2+} after decomposing the Co(III) with NaOH and then acidifying with HCl. For NH_3, am-

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(1) M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *Bull. Chem. Soc. Jap.*, **29**, 883 (1956).

(2) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1963, p 457.

(3) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

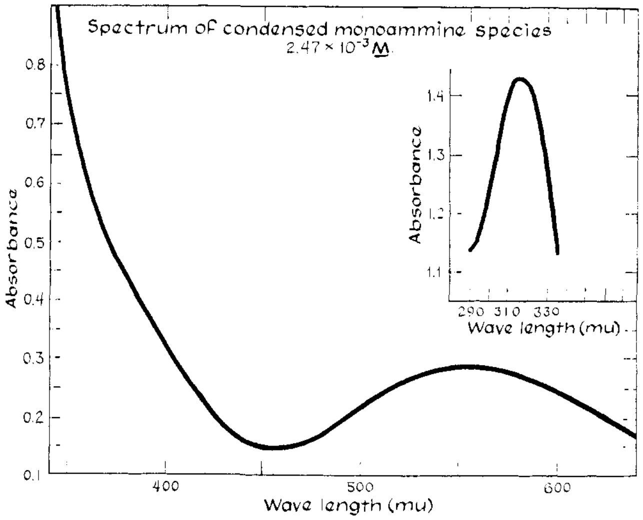

Figure 1. The absorption spectrum of the precursor for $Co(NH_3)(H_2O)_5^{3+}$.

monia was distilled from reduced solutions which had been made alkaline.

To prepare the monoammine, a solution of the violet species was condensed using a rotary evaporator without supplying heat. After the solution was reduced to small volume—at this stage it contains also perchloric acid at high concentration—the solution was concentrated further on a vacuum line until a solid precipitated. A total analysis on the solid was not made, the solid being difficult to weigh, as it is very hygroscopic, but cobalt and ammonia were determined in solutions made from the solid.

In four separate preparations, the ratios of Co(III) to NH_3 were 1.02, 1.00, 0.99, and 1.00. In the third preparation, Co(T) was also determined, and the ratio Co(T)/Co(III) was found to be 1.01. Three of the preparations were obtained following the procedure outlined above. In the fourth, the unmodified Mori procedure was used to obtain the solid. It was treated with acid and separated into components by cation exchange, thereby yielding a species which, from its behavior, we take to be $CoNH_3(H_2O)_4Cl^{2+}$. This was treated wth Hg^{2+} to remove Cl^-, to form a species undistinguishable from that prepared by the alternative procedure.

In Figures 1 and 2 the absorption spectra[4] of the diammine (Figure 2), the precursor to the monoammine (Figure 1), and the product (Figure 2) resulting from the evaporation procedure are compared. It is clear that the evaporation step, which entails prolonged contact of the Co(III) complex with concentrated acid at reduced temperatures, has caused a marked change in the absorption spectrum. This fact, the added one that the diammine and the monoammine have rather similar spectra, and the cation-exchange behavior (the monoammine is elutable readily by 1 M $HClO_4$) and the analytical results taken together would seem to constitute proof that the monoammine is $CoNH_3(H_2O)_5^{3+}$.

The monoammine undergoes a remarkable reaction when it is heated. At 60° in 1 M $HClO_4$, after 12 hr, analysis of the product solution shows that the monoammine has been transformed quantitatively to Co^{2+} and to the diammine

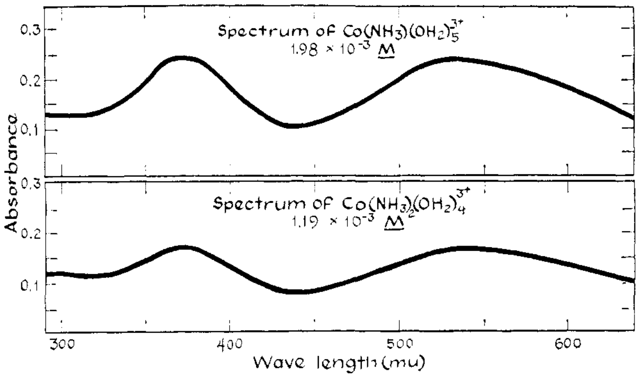

Figure 2. Comparison of the absorption spectra of the monoammine and diammine cobalt(III) species. Maxima and extinction coefficients for the monoammine are 536 (41.5) and 370 (40.0); and for the diammine, 540 (40.8) and 375 (40.4).

$$2CoNH_3(H_2O)_5^{3+} + \tfrac{1}{2}H_2O \longrightarrow Co(NH_3)_2(H_2O)_4^{3+} + Co(H_2O)_6^{2+} + H^+ + \tfrac{1}{4}O_2$$

(Analysis for O_2 was not made, but it should be noted that when Cl^- is present, the reaction is more rapid and chlorine is formed.) Support for the conclusion expressed in the equation is provided in the analytical results to be described.

Solution 1. $[CoNH_3(H_2O)_5]_0 = 1.92 \times 10^{-3}$ M in 1 M $HClO_4$. After heating for 12 hr at 60°, the mixture was separated on a cation-exchange resin, and the following were found: Co(II), 0.094, Co(III), 0.093, in the Co(III) fraction, NH_3, 0.188 mmol; to be compared to Co(T), 0.191 mmol, and $(NH_3)_0$ = 0.191 mmol.

Solution 2. $[CoNH_3(H_2O)_5^{3+}]_0 = 3.74 \times 10^{-4}$ M in 1 M $HClO_4$. After heating for 30 hr at 58°, the following were found: Co(II), 0.0150, Co(III), 0.0156, and NH_3, again in the Co(III) fraction, 0.0302 mmol. In this experiment Co(T) = 0.0296 mmol.

Solution 3. $[CoNH_3(H_2O)_5^{3+}]_0 = 8.63 \times 10^{-4}$ M in 1 M $HClO_4$ with NaCl added. After heating for 10 hr, the following were found: Co(II), 0.041, Co(III), 0.041, NH_3, 0.0752, Cl^-, 0.1013 mmol (0.042 mmol of Cl^- missing); to be expected, Co(T), 0.082, Cl^-, 0.1437, NH_3, 0.081 mmol.

Some experiments have been done on the kinetics of the disproportionation reaction. In a series of experiments at 59°, with the ionic strength fixed by the reactants, values of the specific rate of 1.6, 1.8, 1.6, and 1.6, M^{-1} sec^{-1} were measured. The initial concentrations of $HClO_4$ were 2.24, 0.83, 3.31, and 1.16 M and of $CoNH_3(H_2O)_5^{3+}$ were 1.98, 2.30, 0.97, and 3.7×10^{-3} M, respectively.

The reactions appear to be second order. This conclusion is not firm, as it is based on following the decline in monoammine only through two half-lives. It is supported to some extent by the constancy of the values of k, but is not fully substantiated by this evidence because the ionic strength varies in the series. The rate is rather insensitive to the concentration of acid, but a quantitative relation between rate and $[H^+]$ cannot be drawn, again because ionic strength also changes.

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[4] On the basis of the ion exchange and spectral evidence for the aquoamminecobalt(III) isomers, we believe this is *cis*-tetraaquodiamminecobalt(III). This matter will be discussed further in a later publication.

Further work on this reaction needs to be done before the mechanism is understood. The chemistry taking place here may have some relation to that supporting the remarkable conclusion reported by Williams and Hunt,[5] namely, that more than one NH_3 is transferred from Co(III) for each act of electron transfer between Co(II) and Co(III) ammines.

Acknowledgment. Financial support for this research by the Atomic Energy Commission, Grant No. AT 04 3 326, is gratefully acknowledged.

[5] T. J. Williams and J. P. Hunt, *J. Amer. Chem. Soc.*, **90**, 7213 (1968).

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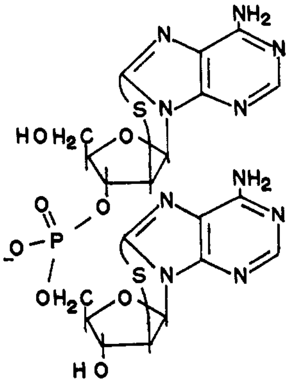
A Highly Stacked Dinucleoside Monophosphate Derived from Adenine 8-Cyclonucleosides

Sir:

Many purine 8-cyclonucleosides have been synthesized[1] and some of their physical properties were investigated.[2] In contrast to the ordinary purine nucleoside, all β-cyclonucleosides of this series have large positive Cotton curves in ORD and CD measurements around major absorption bands due presumably to an unusual interaction between transition moments of the base and the sugar, which were fixed together with anhydro linkages.

We now synthesized a dinucleoside monophosphate (I) (A^spA^s) from 8,2′-anhydro-8-mercapto-9-β-D-arabinofuranosyladenine[3] (A^s) linked with 3′-5′-phosphodiester linkage and an unusual strong stacking of two adenine rings in A^spA^s was found. Moreover, A^spA^s forms a left-handed helical structure opposite to the right-handed one in adenylyl-(3′-5′)-adenosine (ApA).

Compound I was synthesized from 5′-*O*-trityl-N^6-dimethylaminomethylene-8,2′-anhydro-9-β-D-arabinofuranosyladenine 3′-phosphate and N^6,O^2-dibenzoyl-8,2′-anhydro-8-mercapto-9-β-D-arabinofuranosyladenine using DCC as condensing agent, followed by removal of protecting groups, in a yield of 70%.[4]



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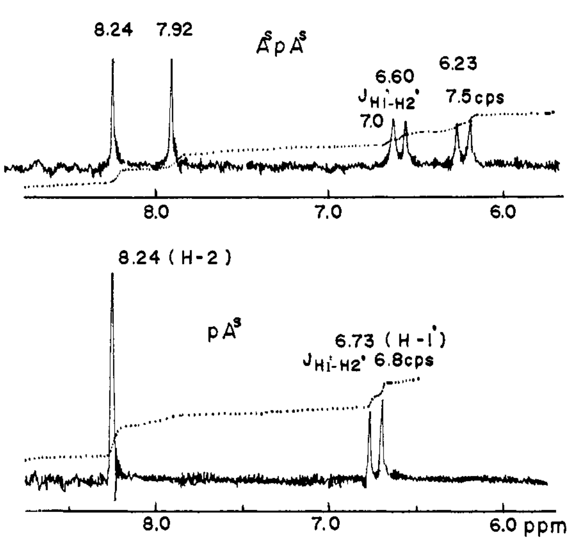

Figure 1. Nmr spectra of A^spA^s and pA^s.

The structure of this compound was confirmed by elemental analyses, optical properties, and desulfurization with Raney nickel to afford 2′-deoxyadenylyl-(3′-5′)-2′-deoxyadenosine, which was identified with an authentic sample.[5]

Ultraviolet absorption properties of A^spA^s [$\lambda_{max}^{pH\,1}$ 276.5 nm (ϵ 42,000), $\lambda_{max}^{pH\,7}$ 271 nm (ϵ 38,000), $\lambda_{max}^{pH\,13}$ 271.5 nm (ϵ 35,800)] showed a large hypsochromic shift of maxima (5 nm) compared to those of the monomer and had a hypochromicity of 15% calculated from ϵ at λ_{max}. A small shift of absorption maxima (1 nm) was reported in the case of ApA and hypochromicity was 10%.[6]

As shown in Figure 1, nmr[7] of this compound in D_2O solution (sodium salt, 0.05 *M*) showed signals of H_2 (8.24 and 7.92 ppm) and $H_{1'}$ (6.60 ppm, $J_{1'-2'}$ = 7.0 cps; 6.23 ppm, $J_{1'-2'}$ = 7.5 cps). Ts'o, *et al.*,[8] reported that ApA (in D_2O, 0.02 *M*) gives also two groups of signals due to H_2 and H_8 (8.50, 8.36 and 8.64, 8.60, respectively), as well as signals of $H_{1'}$ (6.38 and 6.25). They could assign each signal to 3′-linked and 5′-linked nucleosides according to a general rule that the shielding effect of the ring current caused shift of the signal toward high magnetic field. We have examined CPK molecular models of A^spA^s and found that 5′-linked H_2 must be shielded by the ring current of the 3′-linked adenine. Therefore, a signal of 8.24 ppm is assigned to H_2 of the 3′-linked nucleoside and 7.92 ppm to the 5′-linked one. The shift of the H_2 signal compared to that of the monomer (disodium salt, 0.1 *M* in D_2O) was 32 cps toward high magnetic field and this was far greater than that observed in ApA. Although intermolecular interaction of the monomer at the observed concentration is highly probable, the difference in the chemical shift between the A^spA^s and the unassociated monomer can be substantially higher than that shown here.

[1] M. Ikehara, *Accounts Chem. Res.*, **2**, 47 (1969), and references cited therein.

[2] M. Ikehara, M. Kaneko, K. Muneyama, and H. Tanaka, *Tetrahedron Lett.*, 3977 (1967); M. Ikehara and M. Kaneko, *Chem. Pharm. Bull.*, **15**, 1261 (1967); M. Ikehara and M. Kaneko, *J. Amer. Chem. Soc.*, **90**, 497 (1968).

[3] M. Ikehara and H. Tada, *Chem. Pharm. Bull.*, **15**, 94 (1967).

[4] Unpublished experiments by M. Yasumoto.

[5] S. A. Narang, T. M. Jacob, and H. G. Khorana, *J. Amer. Chem. Soc.*, **87**, 2988 (1965).

[6] M. M. Warshaw and I. Tinoco, Jr., *J. Mol. Biol.*, **13**, 54 (1965).

[7] Nmr spectra were taken in D_2O solution at the concentration indicated in the text. The chemical shift was presented in δ using tetramethylsilane as external standard.

[8] P. O. P. Ts'o, N. S. Kondo, M. P. Schweizer, and D. P. Hollis, *Biochemistry*, **8**, 997 (1969).