Inorganica Chimica Acta, 65 (1982) L193–L195

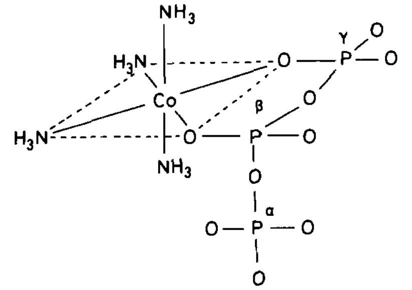
Phosphorus-31 NMR Study of Intermediates in Cobalt(III)-Assisted Triphosphate Hydrolysis

RICHARD D. CORNELIUS* and PAUL R. NORMAN

Department of Chemistry, Wichita State University, Wichita, Kans. 67208, U.S.A.

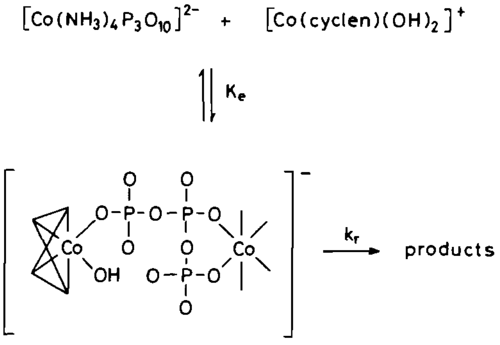
Received May 15, 1982

Hydrolysis reactions of coordinated polyphosphates have come under the scrutiny of several groups of workers [1–3] as a result of the important role which these and other phosphates play in biological systems. The hydrolysis reactions of the well characterized [4] complex $\beta\gamma$ $Co(NH_3)_4H_2P_3O_{10}$, *I*, have been studied in this laboratory as have the kinetics [5] of the interaction of this complex with the tetra-aza macrocyclic complex ion *cis*-$[Co(cyclen)(H_2O)_2]^{3+}$. These kinetic studies revealed a large rate acceleration (by a factor greater than 10^5) for the hydrolysis of coordinated triphosphate to ortho- and pyrophosphate in the presence of the macrocyclic complex ion. A dinuclear cobalt(III) species, *II*, appears to be the active moiety and an approximate equilibrium constant (K_e) of 3.0 ± 1.5 M^{-1} was calculated from the kinetic data for the formation of this intermediate, shown in equation 1.



(I)

^{31}P-NMR spectra taken during the reaction catalyzed by the cobalt(III)–cyclen complex [5] revealed a mutiplet which proved difficult to interpret in the absence of other evidence. Further experiments using a different added cobalt complex have afforded an explanation of this multiplet. The purpose of this communication is to provide ^{31}P-NMR data to support the kinetically obtained value for the equilibrium constant K_e to discuss the nature of the active species in solution.



(II)

Experimental

All ^{31}P-NMR spectra were run in aqueous solution on a Bruker WP-80 instrument using 30% D_2O as an internal lock and 85% H_3PO_4 as an external standard (0 ppm). A pulse width of 1.6 μs was used with a delay time of 2 seconds. All solutions were 0.1 *M* in Na_2H_2EDTA to prevent line broadening by traces of cobalt(II) species. Solutions were 0.1 *M* with respect to all cobalt(III) complexes.

Results and Discussion

Spectra of $\beta\gamma$-$Co(NH_3)_4H_2P_3O_{10}$ were taken in the absence (Fig. 1a) and presence of either *cis*-$[Co(cyclen)(H_2O)_2]^{3+}$ (Fig. 1b) or $[(Co(NH_3)_4(H_2O)_2]^{3+}$ (Fig. 1c). Any difference in the ^{31}P-NMR spectra of these three cases would be as a result of formation of new phosphate species in solution and would shed light on the identity of intermediates in the phosphate hydrolysis reaction. The most significant difference in the spectra is the occurrence of a new multiplet at 0 to +2.0 ppm when the cyclen species (Fig. 1b) is used to promote the reaction. In the presence of the tetraammine however, only a single peak occurs in this region of the spectrum (Fig. 1c). These peaks diminish with time and are therefore not due to hydrolysis products but to the reactive dinuclear cobalt(III) species, II.

The multiplet that appears in the ^{31}P-NMR spectrum when $Co(NH_3)_4H_2P_3O_{10}$ is hydrolyzed in the presence of the cyclen complex can be interpreted in terms of the stereochemistry of the coordinated secondary amine nitrogen atoms of the macrocyclic

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

TABLE I. Relative Intensities of α, β and γ Phosphorus Resonances for the Complex βγ-[$Co(NH_3)_4H_2P_3O_{10}$] in the Presence of Cobalt(III)–Amine Complexes.[a]

Species	Relative Intensity		
	α	β	γ
βγ[$Co(NH_3)_4H_2P_3O_{10}$] (βγ)	1.0	1.0	1.0
(βγ) + [$Co(cyclen)(H_2O)(OH)$]$^{2+}$ (pH 6.0; time, 30 min)	0.6	0.6	1.0
(βγ) + [$Co(cyclen)(OH)_2$]$^+$ (pH 8.0; time, 30 min)	0.4	0.4	1.0
(βγ) + [$Co(NH_3)_4(H_2O)(OH)$]$^{2+}$ (pH 6.0; time, 0)	0.9	1.0	1.0
(βγ) + [$Co(NH_3)_4(H_2O)(OH)$]$^{2+}$ (pH 6.0; time, 60 min)	0.9	0.9	1.0

[a] Solutions were 0.1 *M* in both phosphate and amine complex.

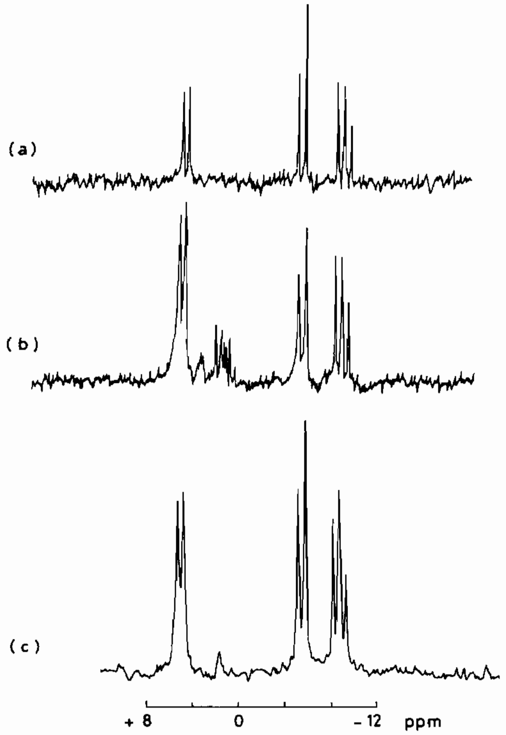


Fig. 1. 32.4 MHz ^{31}P-NMR spectra of 0.1 *M* βγ-[$Co(NH_3)_4H_2P_3O_{10}$] at pH 6.0 a) in the absence of additional cobalt(III) species, b) in the presence of 0.1 *M* [$Co(cyclen)(H_2O)OH$]$^{2+}$, and c) in the presence of 0.1 *M* [$Co(NH_3)_4(H_2O)OH$]$^{2+}$.

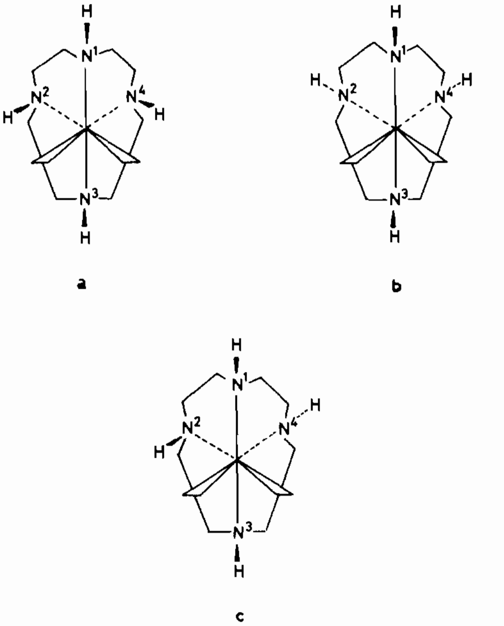


Fig. 2. Possible configurations of the secondary amine nitrogen atoms in the complex *cis*-[$Co(cyclen)(H_2O)_2$]$^{3+}$.

ligand. The cyclen complex can only exist in the *cis* configuration because of the small 'hole' size of the macrocycle [6]. Dreiding models of the *cis*-[$Co(cyclen)(H_2O)_2$]$^{3+}$ show that three configurations of the cobalt complex have the preferred gauche arrangement for the methylene groups in each chelate ring [7]. These three configurations are shown in Fig. 2. In Figs. 2a and b, the molecule posseses a C_2 axis of symmetry through nitrogen atoms 1 and 3, and as a result the nitrogen atoms in these two structures are achiral. In Fig. 2c, however, this C_2 axis is lost and nitrogen atoms 1 and 3 become chiral, opening several possibilities for the stereochemistry about the phosphate groups upon coordination to the cyclen species. Given the chirality of the β-phosphorus atom of the phosphato complex, at least six diastereomers for the active complex *II* can be postulated. Since the spectrum in the presence of added [$Co(NH_3)_4(H_2O)_2$]$^{3+}$ shows only a single peak attributable to an intermediate, the ^{31}P-NMR spectra provided indirect evidence for the existence of several isomers of the cobalt(III) complex of cyclen which have been overlooked in kinetic studies of cyclen species [8, 9].

Inspection of the intensities of the various phosphorus resonances yields some insight into the processes occurring in solution. Table I shows that the relative intensities for the α, β and γ phosphorus atom resonances in the $Co(NH_3)_4H_2P_3O_{10}$ compound are in the expected 1.0:1.0:1.0 ratio. In the presence of either of the additional cobalt(III) amine complexes the intensities of the α and β resonances are reduced compared to those of the γ-phosphorus atom. This decrease would be expected if the α and

β phosphates were complexed, resulting in new phosphorus resonances which would reduce the relative intensities from the normal 1:1:1 ratio.

The intensities of the spectra for samples with the added tetraammine complex indicate that initial coordination (time = 0, Table I) is through the uncoordinated α-phosphate group. The subsequent decrease in intensity of the β-phosphorus atom resonance (time = 30 or 60 min in Table I) may indicate internal nucleophilic attack of the coordinated hydroxide ion on the triphosphato complex, resulting in displacement of one of the O–P–O bonds and consequent cleavage of the triphosphate chain.

In addition to giving evidence as to the nature of species present in solution, the NMR spectra also support a non-kinetic estimate of the equilibrium constant K_e for reaction 1. From the data in Table I the relative concentrations of dinuclear species and free triphosphato complex can be determined in the presence of the cobalt(III) complex of the macrocyclic ligand. These calculated concentrations give a value for the constant K_e of 3.7 M^{-1} at pH 8.0, in good agreement with the kinetically determined figure (3.0 ± 1.5 M^{-1}) at pH 10.05. This agreement lends weight to the assignment of a rate constant of 0.010 $\sec^{-1}$ for the formation of hydrolysis products from the dinuclear species [5], since the uncertainty in this rate constant was due largely to errors in calculating K_e. Thus, the available NMR data supports the previously suggested mechanism [5] for the cobalt(III) amine promoted hydrolysis of $\beta\gamma$-$Co(NH_3)_4H_2P_3O_{10}$ and furthermore supports the numerical value of the equilibrium constant determined for reaction 1.

Acknowledgement

We wish to thank the University of Kansas for access to NMR facilities. This research was supported by NSF Grant CHE-8024042.

References

1 a) R. D. Cornelius, *Inorg. Chem., 19,* 1288 (1980);
b) *Inorg. Chim. Acta, 46,* L108 (1980).
2 P. W. A. Hubner and R. M. Milburn, *Inorg Chem., 19,* 1267 (1980).
3 B. Anderson, R. M. Milburn, J. Harrowfield, G. Robertson and A. M. Sargeson, *J. Am. Chem. Soc., 99,* 2652 (1977).
4 R. D. Cornelius, P. A. Hart and W. W. Cleland, *Inorg Chem., 16,* 2799 (1977).
5 R. D. Cornelius and P. R. Norman, *J. Am. Chem. Soc.,* in press.
6 J. P. Collman and P. W. Schneider, *Inorg. Chem., 5,* 1380 (1966).
7 M. Kobayashi, *J. Chem. Soc. Jpn., 64,* 648 (1943).
8 Y. Hung and D. H. Busch, *J. Am. Chem. Soc., 99,* 4977 (1977).
9 R. W. Hay and P. R. Norman, *J. Chem. Soc. Chem. Comm.,* 734 (1980).