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The Crystal and Molecular Structure of $[Co(NH_3)_5PO_4] \cdot 3H_2O$, a Na^+-K^+ ATPase Probe

GREG BREWER, STEPHEN DRUCKER, JAYMEE GIRARD, CHARLES GRISHAM and EKK SINN

Department of Chemistry, McCmorick Rd., University of Virginia, Charlottesville, Va. 22901, U.S.A.

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The title compound, $Co(NH_3)_5PO_4$, prepared by a modified literature procedure, was used to study the inhibition of Na^+-K^+ ATPase and to serve as a structural model for ML_4(nucleotide) complexes. The structure was determined by single crystal X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/n$, a = 8.638(3), b = 14.517(2), c = 9.145(2) Å, and β = 112.71(2)°. The structure, solved by the heavy atom method to an R value of 3.3% for 1924 reflections, consists of a slightly distorted octahedron with the cobalt bound to the five amines and a monodentate phosphate. Solution structural data is taken from ^{31}P NMR measurements. From comparison with other metal phosphate complexes it is concluded that multiple monodentate coordination of a di- or triphosphate closely resembles the coordination of a monophosphate. This is based on the similarity of the M–O–P bond angle which is 129.6° in the present example.

Introduction

The use of metal complexes of nucleotides as probes of the active sites of various ATP and GTP requiring enzymes has seen much activity in recent years [1]. Specifically the compounds which are used the most frequently are the beta, gamma complexes of a nucleotide with Cr^{+3} or Co^{+3}. These metal ions are used because they are kinetically inert. These complexes, ML_4(nucleotide) (where L = H_2O or NH_3 see Fig. 1), often bind to nucleotide requiring enzymes but do not react with them. Thus they are useful as probes for detailed stereochemical information of the active site areas [2]. The Co^{+3} complexes are ideally suited for NMR studies due to the fact that the d^6 electron configuration is diamagnetic.

NMR experiments using cobalt complexes of the nucleotides have aided in the estimation of M–P distances of the bound complexes and have also given a rough picture of the conformation of the triphosphate chain [3]. It is hoped that detailed structural information on these complexes will allow the further evaluation of the role of metal complexes in the activation or inhibition of ATPase systems. Unfortunately such structural information on the $M(L)_4$(nucleotide) (M^{+3}) complexes has not been available. The reason for this is the instability of these complexes, which on evaporation yield mixtures of metal phosphate and nucleoside monophosphate resulting from the non-enzymatic hydrolysis of the complexes [4]. It is hoped that structural information on simple metal phosphate compounds might shed some light on the $M(L)_4$(nucleotide) complexes since it is unlikely that solid state data will be available on these systems even in the future.

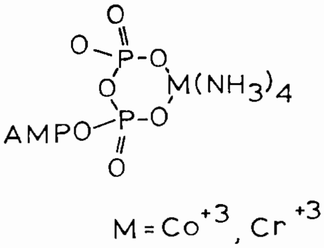

Fig. 1. Structure of a Metal Nucleotide Complex.

As part of this work, we undertook the X-ray diffraction study of $Co(NH_3)_5PO_4$, which may be viewed as the hydrolysis product of the $Co(NH_3)_5$(ADP) complex [5], and compared it with solution data. The structural data presented here will be useful in the interpretation of the competitive inhibition studies of this material and other simple complexes [6] conducted with Na^+-K^+ ATPase and in further evaluation of the structure of the many cobalt and chromium nucleotide complexes which to date have only been characterized in solution. Further this compound should be useful in the areas of metal phosphate binding [7] and the kinetics of metal phosphate hydrolysis reactions [8].

It is desired to supplement and compare solution structural information with solid state data available from single crystal X-ray diffraction. If a large number of systems can be investigated by both solid state and solution techniques, it may be possible to correlate the two types of information and to establish spectral-structural trends for these systems. This of course assumes that the solution and solid state structures do not differ significantly.

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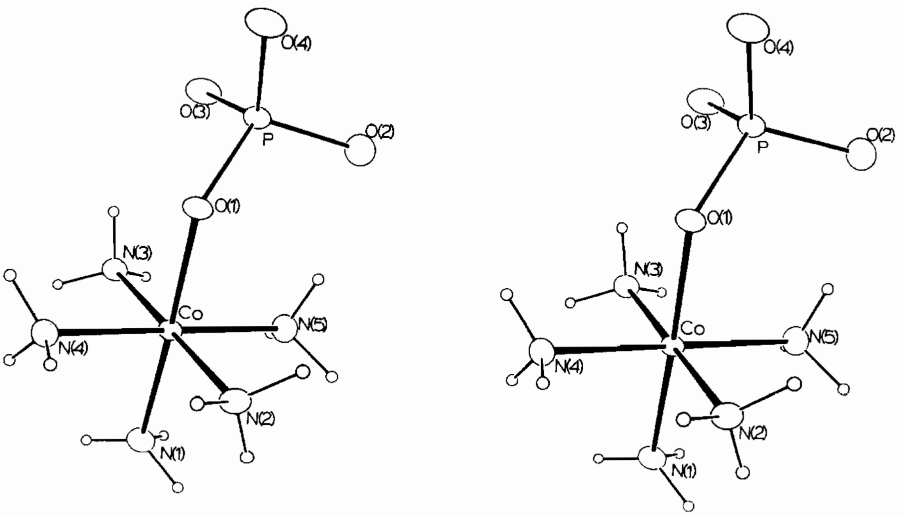

Fig. 2. ORTEP of $Co(NH_3)_5(PO_4)$.

Experimental

Preparation of [Co(NH₃)₅PO₄]·3H₂O

This compound was synthesized by a slight modification of the procedure given by Schmidt and Taube [9]. This earlier procedure used $[Co(NH_3)_5H_2O)](ClO_4)_3$ as the starting material and isolated the product as a dihydrate. The present procedure used $[Co(NH_3)_5H_2O]Cl_3$ as the starting reagent and isolated the product as a trihydrate. Other than this change, the procedure to prepare the complex is the same as reported earlier. The yield was 17%. Elemental analysis was conducted by Galbraith Laboratories. $[Co(NH_3)_5PO_4]\cdot 3H_2O$ requires 23.89% N, 7.22% H and 10.57% P. Found: 23.88% N, 6.79% H, and 10.67% P.

Suitable quality crystals for X-ray diffraction were grown by the vapor diffusion of ethanol into aqueous solutions of the complexes.

Crystal Data

$CoPO_7N_5H_{21}$, Formula weight = 293.0; monoclinic, $P2_1/n$; a = 8.638(3), b = 14.517(2), and c = 9.145(2) Å; β = 112.71(2)°; d(obs) = 1.83 (determined by flotation in $CHCl_3$ and$CHBr_3$), d(calc) = 1.84 g/cm^3; Z = 4.

Cell dimensions and space group were obtained by standard methods on an Enraf-Nonius four circle Cad-4 diffractometer. The $\theta-2\theta$ scan technique was used as described previously [10] to record the intensities for all non-equivalent reflections for which $1 < 2\theta < 60°$. Scan widths were calculated as (A + Btanθ), where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to $K\alpha_1-K\alpha_2$ splitting. The values of A and B are 0.6 and 0.35 respectively.

The intensities of three standard reflections showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 2637 independent intensities, there were 1924 with $F_o^2 > 3\sigma$, where $(F_o)^2$ was estimated from counting statistics [11]. These data were used in the final refinement of the structural parameters.

Structure Determination

A three dimensional Patterson synthesis was used to determine the heavy atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier synthesis. Full matrix least square refinement was carried out as previously described [10]. Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for four cycles of least squares refinement and then held fixed.

The model converged with R = 3.3% and R_w = 4.0%. A final Fourier difference map was featureless. Lists of the observed and calculated structure factors and anisotropic thermal parameters are available from the Editor. The principal programs used are as described previously [10].

³¹P NMR

The ^{31}P NMR spectra were recorded on a Nicolet Magnetics Corp. NT-360/Oxford NMR spectrometer at 145 MHz, 24 °C with a 10 mm broad-band probe and an internal ^2H lock (30% D_2O, total sample volume 2.5 ml). Proton-band (modulated) decoupling was used. Chemical shifts are referenced to 85% phosphoric acid.

TABLE I. Positional and Thermal Parameters for $Co(NH_3)_5(PO_4)\cdot 3H_2O$.

Atom	*X*	*Y*	*Z*	B11 or B
Co	0.07978(5)	0.15597(3)	−0.22440(5)	0.92(1)
P	0.1342(1)	0.37261(6)	−0.2275(1)	1.14(3)
O(1)	0.1683(3)	0.2768(2)	−0.1420(3)	1.46(8)
O(2)	0.1863(4)	0.3669(2)	−0.3700(3)	4.24(11)
O(3)	−0.0535(3)	0.3963(2)	−0.2823(3)	1.20(9)
O(4)	0.2414(3)	0.4442(2)	−0.1078(3)	1.91(9)
O(W1)	0.2319(3)	0.4449(2)	0.3863(3)	2.50(9)
O(W2)	0.9640(4)	0.2488(2)	0.1780(4)	2.89(11)
O(W3)	0.3542(4)	0.0962(2)	0.4811(4)	4.77(12)
N(1)	−0.0033(4)	0.0322(2)	−0.2960(4)	1.69(11)
N(2)	0.3138(3)	0.1140(2)	−0.1593(3)	1.22(9)
N(3)	−0.1524(4)	0.1992(2)	−0.2872(3)	1.22(9)
N(4)	0.0830(4)	0.1284(2)	−0.0139(3)	2.07(10)
N(5)	0.0690(4)	0.1820(2)	−0.4394(3)	1.53(10)
H(11)	−0.059(5)	0.017(3)	−0.242(5)	2.6(10)
H(12)	0.073(5)	−0.005(3)	−0.322(5)	2.8(11)
H(13)	−0.069(7)	0.035(4)	−0.392(7)	6.2(16)
H(21)	0.371(5)	0.156(3)	−0.202(5)	2.5(10)
H(22)	0.318(6)	0.065(4)	−0.202(5)	3.4(12)
H(23)	0.356(6)	0.108(4)	−0.063(6)	4.5(13)
H(31)	−0.197(5)	0.169(3)	−0.223(5)	2.9(10)
H(32)	−0.203(6)	0.198(4)	−0.389(6)	4.2(13)
H(33)	−0.144(6)	0.258(4)	−0.251(6)	4.6(13)
H(41)	0.040(6)	0.175(4)	0.033(6)	4.4(13)
H(42)	0.164(8)	0.105(5)	0.026(7)	6.8(17)
H(43)	0.002(8)	0.091(4)	−0.027(7)	6.6(17)
H(51)	0.152(5)	0.147(3)	−0.473(5)	2.4(9)
H(52)	0.106(6)	0.240(4)	−0.441(5)	3.8(12)
H(53)	−0.020(8)	0.171(4)	−0.499(7)	5.7(15)
H(W11)	0.199(7)	0.422(4)	−0.540(6)	4.1(14)
H(W12)	0.171(7)	0.480(4)	−0.645(7)	5.2(15)
H(W21)	0.931(6)	0.289(4)	0.106(6)	4.8(13)
H(W22)	0.866(6)	0.212(4)	0.163(6)	3.5(13)
H(W31)	−0.093(7)	0.410(4)	−0.085(7)	4.9(15)
H(W32)	−0.153(7)	0.459(4)	0.020(7)	5.4(16)

TABLE II. Interatomic Distances (A) for $[CO(NH_3)_5(PO_4)]\cdot 3H_2O$.

Co	O(1)	1.945(1)	O(2)	N(5)	2.853(2) S
Co	N(1)	1.952(2)	O(3)	O(W1)	2.733(2) D
Co	N(2)	1.971(2)	O(3)	O(W3)	2.817(3) C
Co	N(3)	1.964(2)	O(3)	N(23)	2.981(2) S
Co	N(4)	1.956(2)	O(4)	O(W3)	2.763(2) E
Co	N(5)	1.969(2)	O(4)	N(1)	2.874(2) A
P	O(1)	1.567(1)	O(4)	N(1)	3.010(3) F
P	O(2)	1.536(2)	O(W1)	N(3)	3.019(2) A
P	O(3)	1.540(1)	O(W1)	N(4)	3.004(2) A
P	O(4)	1.534(1)	O(W2)	O(W3)	2.807(3) G
O(1)	N(3)	3.028(2) A	O(W2)	N(2)	3.058(3) A
O(2)	O(W1)	2.661(2) B	O(W2)	N(4)	2.930(3) I
O(2)	O(W2)	2.820(3) C	O(W3)	N(5)	3.088(3) K

Symmetry Transformations:

A. ½ + *X*, ½ − *Y*, ½ + *Z*
B. *X*, *Y*, *Z* − 1
C. *X* − ½, ½ − *Y*, *Z* − ½
D. −*X*, 1 − *Y*, −*Z*
E. ½ − *X*, ½ + *Y*, ½ − *Z*
F. ½ − *X*, ½ + *Y*, −½ − *Z*

(continued overleaf)

TABLE II. *(continued)*

G.	½ + X,	½ − Y,	Z − ½	H.	1.5 + X,	½ − Y,	½ + Z	I.	X + 1,	Y,	Z
J.	X + 1,	Y,	Z + 1	K.	X,	Y,	Z + 1	L.	X − ½,	½ − Y,	½ + Z
S.	X,	Y,	Z								

Bond Angles (deg) for [CO$(NH_3)_5(PO_4)$]·$3H_2O$

O(1)	Co	N(1)	177.02(7)	N(2)	Co	N(5)	90.51(7)
O(1)	Co	N(2)	87.57(6)	N(3)	Co	N(4)	88.74(7)
O(1)	Co	N(3)	91.68(6)	N(3)	Co	N(5)	89.85(7)
O(1)	Co	N(4)	87.09(7)	N(4)	Co	N(5)	178.10(7)
O(1)	Co	N(5)	94.23(7)	O(1)	P	O(2)	108.38(9)
N(1)	Co	N(2)	91.06(7)	O(1)	P	O(3)	109.37(8)
N(1)	Co	N(3)	89.69(7)	O(1)	P	O(4)	107.47(8)
N(1)	Co	N(4)	90.30(8)	O(2)	P	O(3)	110.65(10)
N(1)	Co	N(5)	88.42(8)	O(2)	P	O(4)	110.36(10)
N(2)	Co	N(3)	179.19(7)	O(3)	P	O(4)	110.52(9)
N(2)	Co	N(4)	90.92(7)	Co	O(1)	P	129.56(8)

TABLE III. Equations of the Principal Planes in [Co$(NH_3)_5PO_4$]·$3H_2O$ and the Distances (A) of Selected Atoms from the Plane.

(I) Plane Through O(1), N(1), N(2), N(3)

$(0.3549)X + (0.2369)Y + (-0.9044)Z - (2.7492) = 0$

O(1) −0.020; N(1) −0.0200; N(2) 0.020; N(3) 0.020; Co 0.025; P 0.965

(II) Plane Through O(1), N(1), N(4), N(5)

$(-0.9007)X + (0.3382)Y + (-0.2728)Z - (-0.0521) = 0$

O(1) −0.024; N(1) −0.024; N(4) 0.024; N(5) 0.023; Co 0.000; P 0.637

(III) Plane Through N(2), N(3), N(4), N(5)

$(-0.2331)X + (-0.9279)Y + (-0.2909)Z - (-1.8911) = 0$

N(2) −0.017; N(3) −0.017; N(4) 0.017; N(5) 0.017; Co −0.005; P −3.027

Results and Discussion

Structure

A stereoview of the Co$(NH_3)_5PO_4$ molecule is shown in Fig. 2. The final positional and thermal parameters for the atoms are given in Table I. Table II contains the interatomic distances and bond angles. The digits in parentheses are the estimated standard deviations in the least significant figure and are derived from the inverse matrix in the course of least squares refinement calculations.

The molecule consists of a slightly distorted octahedron. The six donor atoms are the five amine nitrogens and O(1) of the monodentate phosphate group. The equations of the three principal planes of the molecule passing through O(1)N(1)-N(2) & N(3), O(1)N(1)N(4) & N(5), and N(2)N(3)-N(4) & N(5) are given in Table III. The interplanar angles are 89.59°, 87.24°, and 88.60° not deviating greatly from the expected value of 90° for a regular octahedron.

The overall structure consists of a three dimensional hydrogen-bonded network which involves all of the oxygen and nitrogen atoms. The metal bonded oxygen atom is three coordinate being bonded to cobalt and phosphorus and hydrogen bonded to the N(3) amine nitrogen of a neighboring complex molecule. Each of the other oxygens is four coordinate: O(2), O(3), and O(4) are bound to the phosphorus, and O(2) is H-bonded to O(W1), O(W2), and N(5); O(3) is H-bonded to O(W1), O(W3), and N(3); O(4) is H-bonded to O(W3) and to N(1) amines of two different molecules. Of the water molecules: O(W1) is H-bonded to O(2), O(3), N(3), and N(4); O(W2) to O(W3), N(2), O(2), and N(4); O(W3) to N(5), O(W2), O(3), and O(4). The hydrogen-bond distances are given in Table IV.

Several structural parameters for this compound are compared with data taken from the literature for related compounds in Table V. This table includes compounds in which the phosphate acts as a bidentate ligand in Co$(en)_2PO_4$ [12] and Co$(NH_3)_4$-PO_4 [13], monodentate as part of a triphosphate chain in Co$(NH_3)_4(H_2P_3O_{10})$ [14] and [Zn(bipy)-(HATP)$]_2$ [15], and monodentate as a single phosphate in the present example. For compounds which contain more than one phosphate or multiple M–O(P) bonds etc., each value is given rather than

TABLE IV. Hydrogen Bond Distances (A) for [Co(NH$_3$)$_5$(PO$_4$)]·3H$_2$O.

O(1)	H(32)	2.18(1) A
O(2)	H(52)	1.99(1) S
O(2)	H(W11)	1.78(1) S
O(2)	H(W22)	1.85(1) C
O(3)	H(33)	2.21(1) S
O(3)	H(W12)	2.04(1) D
O(3)	H(W31)	1.97(1) S
O(4)	H(12)	2.08(1) E
O(4)	H(13)	2.04(1) A
O(4)	H(W32)	1.92(1) E
O(W1)	H(31)	2.15(1) A
O(W1)	H(43)	2.22(1) A
O(W1)	H(W11)	0.89(1) S
O(W1)	H(W12)	0.71(1) S
O(W2)	H(21)	2.11(1) A
O(W2)	H(41)	2.00(1) I
O(W2)	H(W21)	0.85(1) S
O(W2)	H(W22)	0.97(1) S
O(W3)	H(51)	2.08(1) K
O(W3)	H(W21)	1.98(1) L
O(W3)	H(W31)	0.89(1) A
O(W3)	H(W32)	0.89(1) A
N(1)	H(11)	0.85(1) S
N(1)	H(12)	0.95(1) S
N(1)	H(13)	0.84(1) S
N(2)	H(21)	0.96(1) S
N(2)	H(22)	0.83(1) S
N(2)	H(23)	0.82(1) S
N(3)	H(31)	0.92(1) S
N(3)	H(32)	0.86(1) S
N(3)	H(33)	0.92(1) S
N(4)	H(41)	0.95(1) S
N(4)	H(42)	0.74(1) S
N(4)	H(43)	0.86(1) S
N(5)	H(51)	1.02(1) S
N(5)	H(52)	0.90(1) S
N(5)	H(53)	0.77(1) S

Symmetry Transformations:

A. ½ + *X*, ½ − *Y*, ½ + *Z*
B. *X*, *Y*, *Z* − 1
C. *X* − ½, ½ − *Y*, *Z* − ½
D. −*X*, 1 − *Y*, −*Z*
E. ½ − *X*, ½ + *Y*, ½ − *Z*
F. ½ − *X*, ½ + *Y*, −½ − *Z*
G. ½ + *X*, ½ − *Y*, *Z* − ½
H. 1.5 + *X*, ½ − *Y*, ½ + *Z*
I. *X* + 1, *Y*, *Z*
J. *X* + 1, *Y*, *Z* + 1
K. *X*, *Y*, *Z* + 1
L. *X* − ½, ½ − *Y*, ½ + *Z*
S. *X*, *Y*, *Z*

TABLE V. Selected Structural Parameters for Metal Phosphate Complexes. Bond Distances are in Angstroms and Angles are in Degrees.

Compound*	M–O(P)	M–N(av)	P–O(M)	P–Oav	M–O–P	O–M–O
Co(NH$_3$)$_4$(triph)	1.953(7)	1.945	1.505(7)	1.537	129.0	92.8
	1.936(6)		1.496(6)	1.541	130.1	
				1.535		
Co(NH$_3$)$_4$PO$_4$	1.925(5)	1.938	1.584(5)	1.547	93.1(4)	76.1(4)
	1.932(5)		1.574(6)		93.1(4)	
[Zn(bipy)ATP]$_2$	2.21(4)	2.14	1.47(3)	1.51	124(2)	76(1)
	2.09(3)		1.48(5)	1.56	127(2)	93(1)
	2.02(3)		1.48(5)	1.57	134(5)	99(1)
	2.00(3)		1.54(4)		124(2)	
	2.39(3)	2.15	1.45(3)	1.53	129(2)	81(1)
	2.05(4)		1.51(4)	1.53	127(2)	93(1)
	2.00(3)		1.52(3)	1.56	135(2)	95(1)
	2.01(4)		1.57(3)		127(2)	
Co(NH$_3$)$_5$PO$_4$	1.945(1)	1.962	1.567(1)	1.544	129.56	–
Co(en)$_2$PO$_4$	1.948(4)	1.944	1.560(5)	1.539	92.5(2)	75.8(2)
	1.927(4)		1.574(4)		92.9(2)	

*Co(NH$_3$)$_4$(triph), ref. [14]; Co(NH$_3$)$_4$PO$_4$, ref. [13]; [Zn(bipy)ATP]$_2$, ref. [15]; Co(NH$_3$)$_5$PO$_4$, present work; Co(en)$_2$PO$_4$, ref. [12].

TABLE VI. Bond Angles and ^{31}P NMR Chemical Shifts for Metal Phosphate Complexes.

Compound	Coordination	Chemical shift	P–O–M°
ATP*	–	6.0	–
PO_4^{-3}	–	–5.0	–
$Co(NH_3)_4(ATP)$*	mono	–4.0	–
$Co(NH_3)_4$(triphos)*	mono	–4.2	129.0
$Co(NH_3)_5PO_4$	mono	–14	129.6
$Co(NH_3)_5(HPO_4)^+$	mono	–11	–
$Co(NH_3)_5(H_2PO_4)^{+2}$	mono	–8	–
$Co(NH_3)_4(H_2O)(HPO_4)^+$	mono	–14	–
$Co(en)_2(H_2O)(H_2PO_4)^{+2}$	mono	–9	–
$Co(en)_2(H_2O)(HPO_4)^+$	mono	–12	–
$Co(en)_2(OH)(PO_4)^{-1}$	mono	–14	–
$Co(NH_3)_4PO_4$	bi	–24	93.1
$Co(en)_2PO_4$	bi	–23	92.7

*For compounds with a triphosphate the chemical shift value is for the terminal phosphate.

an average of the particular parameter. All of the compounds have similar P–O and P–O(M) distances as expected. The zinc complex has an elongated M–N distance reflecting the difference in binding character of aliphatic and aromatic nitrogen and the change of metal from Co^{+3} to Zn^{+2}. A smaller elongation is also observed in the M–O(P) distance in the zinc compound.

One conclusion which can be drawn from these results is that simple monodentate phosphate coordinates in a similar arrangement to that exhibited by the triphosphate compounds. This is based on the M–O–P bond angle of ~129° in the two compounds which exhibit multiple monodentate phosphate binding and in the present example. This means that multiple monodentate coordination of a di- or triphosphate causes very little strain since the M–O–P angles in these compounds deviate only slightly from the totally unconstrained angle of 129.56° in $Co(NH_3)_5PO_4$. It may be concluded that the flexibility of the di- and tri-phosphate chains is great enough to allow each phosphate to coordinate independently of each other in a manner which resembles the truly monodentate situation afforded by $Co(NH_3)_5PO_4$.

The analogous M–O–P bond angle of the bidentate compounds, ~93°, is highly constrained (~36°) relative to the monodentate compounds. The bidentate complexes must exhibit considerable bond strain in comparison to the monodentate examples. The structural parameters and stereochemistry of the structurally unknown $M(NH_3)_4$ (nucleotide) materials must lie closer to the present monodentate example than to either bidentate complex. Further attempts at predicting the structure of these important nucleotide complexes or evaluating enzyme binding site distances using these complexes from solution data should use the structural parameters afforded by the monodentate complexes as a starting point.

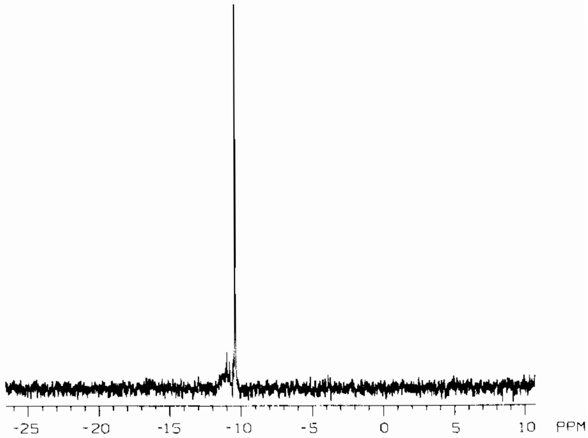

Fig. 3. ^{31}P NMR spectra of $Co(NH_3)_5(PO_4)$.

^{31}P NMR

The ^{31}P NMR of the compound was investigated to verify that the phosphate was coordinated in solution rather than being replaced by some solvent species such as H_2O or OH^-. The spectrum shown at pH = 7.1 in Fig. 3 reveals a single resonance at –11 ppm relative to phosphoric acid. This signal exhibits the normal dependency on pH as shown previously [16]. At low pH, the molecule exists largely as the protonated $Co(NH_3)_5PO_4H_2^{+2}$ and at high pH, as the neutral $Co(NH_3)_5PO_4$. This is the form of which the structure was determined. The solution behavior of this molecule is in sharp contrast to that observed for $Co(NH_3)_4(PO_4)$ and $Co(en)_2PO_4$. The latter exhibits a monodentate phosphate at low and high pH, $Co(en)_2(H_2O)(H_2PO_4)^{+2}$ and $Co(en)_2$-

(OH)(PO$_4$)$^-$, respectively, and a bidentate phosphate at intermediate values [16]. Co(NH$_3$)$_4$PO$_4$ has been shown to undergo a similar hydrolysis reaction [13b)]. Presumably, the monodentate forms of Co(NH$_3$)$_4$PO$_4$ and Co(en)$_2$PO$_4$ which exist at either pH extreme structurally resemble the present compound, which is always monodentate. Structural investigation of this possibility is being carried out.

It is interesting to note that the ^{31}P NMR signals for the bidentate complexes are well separated from the monodentate materials. The chemical shift values for a variety of phosphate complexes are given in Table VI. The bidentate materials have a chemical shift of less than −20 ppm and the various monodentate compounds have values greater than −15 ppm. This significant drop in chemical shift may be in accordance with the general trend that large chemical shifts are expected on phosphate coordination [17]. Chemical shift may be a good indication of the mode of phosphate coordination. In addition to distinguishing monodentate from bidentate coordination, ^{31}P NMR may be able to be used to predict the P–O–M bond angle of monodentate materials. The present data are insufficient to allow any firm statement to be made on this possibility, but merely suggest that such a relationship may exist. In a complete analysis many factors would have to be considered, such as charge on the complex and other groups bonded to the phosphate.

More structural examples are needed before any detailed analysis could be made. If a wide variety of compounds are studied it may be possible to ascertain the dependence of the ^{31}P NMR chemical shift on the P–O–M bond angle for these complexes. This could lead to a clearer estimation of the structure of the many CoL$_4$ nucleotide complexes which to date are uncharacterized in the solid state.

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