

Preparation and Characterization of a Chromium(III) Complex of an α -Aminophosphonic Acid Ligand

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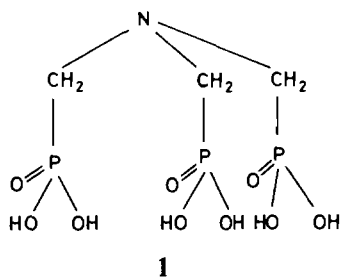
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Abstract

A new chromium(III) complex of nitrilotri(methylenephosphonic acid), $\text{Cr}[\text{N}(\text{CH}_2\text{P}(\text{O})_2\text{OH})_3]_2^{3-}$ has now been prepared and characterized by means of electronic, vibrational and NMR spectra. The tridentate character of the aminophosphonic acid was established on the basis of infrared and NMR spectra as well as paramolybdate titrations.

Introduction

Several chromium(III) complexes with amines, carboxylates, halides and thiols as ligands have already been reported [1–3]. On the other hand, the literature on the complexes of α -aminophosphonic acids has been scanty [4], although tripodal ligands such as **1** have now been synthesized [5].



In view of the current interest in the synthesis of cage complexes of metal ions [6–9], complexes of such tridentate ligands are also deriving importance. Considerable difficulties have been experienced in the preparation of clathrochelate complexes of chromium(III) [9].

It is of interest to investigate whether the bis-chelates of Cr(III) with nitrilotri(methylenephosphonic acid) can be prepared and whether such derivatives would form useful intermediates for the preparation of other cage and macrocyclic complexes of Cr(III).

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Experimental

Materials

The sample of nitrilotri(methylenephosphonic acid) was obtained as a gift from Aquapharm Chemical Company, Pune. Chromium acetate monohydrate (BDH, AnalaR) and anhydrous ethylenediamine (SD's Lab-Chem Industries, Bombay) were used in this study. Other materials used were of reagent grade or better.

Preparation of tri-sodium bis-nitrilotri(methylenephosphonato)chromium(III) derivative

To a solution containing nitrilotri(methylenephosphonic acid) (4.0 M, 30 ml at pH 3.0), chromium acetate monohydrate (2.5 g, 0.8 M) was added and then the mixture was refluxed for *ca.* 2 h. The reaction mixture was cooled and methanol (approximately 4 times the volume of reaction mixture) was added. A green precipitate obtained was filtered off and dried *in vacuo* after washing with methanol and ethyl ether. Since attempts to recrystallize the crude product from a variety of solvent media were not successful, it was purified by passing through a column of Biogel P-2 (10 × 1.2 cm) and reprecipitated by the addition of methanol. *Anal.* Calc. for $\text{Na}_3\text{Cr}[\text{N}(\text{CH}_2\text{POH}(\text{O})_2)_3]_2$; Na, 9.0; P, 26.0; N, 3.92; C, 10.1. Found: Na, 8.1; P, 28.7; N, 4.20; C, 10.5%; indicating the presence of some impurities.

Repurification of the complex in solution was made using Dowex 1-X8 or Sephadex QAE-25 (12 × 1.2 cm) columns in Cl^- forms at pH 3.0. An aliquot of a solution of the Cr(III) complex (50 ml, *ca.* 5×10^{-3} M) was loaded on the column. The complex was then eluted with 2.0 M NaCl adjusted to pH 3.0 from Dowex 1-X8 and 1.0 M NaCl adjusted to pH 3.0 from Sephadex QAE-25. The major part of the complex (>95% Cr) eluted as a single band. The concentration of the complex was higher when eluted from Sephadex QAE-25 columns. The complex was analysed for Cr:N and Cr:P ratios using standard methods [10–12].

Instrumental Techniques

The electronic spectra of the complex was recorded on a Varian Cary 219 spectrophotometer.

Infrared spectral measurements were made using the KBr mulling technique and a Perkin-Elmer model 983 instrument. The emission spectrum of the Cr(III) complex was recorded using a Hitachi 650-40 model self-correcting type of spectrofluorimeter. Room temperature ^1H , ^{13}C and ^{31}P NMR studies on the Cr(III) complex, as well as on the free ligand, were carried out in D_2O using a Bruker CXP FT NMR (90 MHz) spectrometer.

NMR Studies

The NMR studies on the complex used chloroform, tetramethylsilane and orthophosphoric acid as internal standards for ^1H , ^{13}C and ^{31}P spectra, respectively. The samples were kept in an inner tube (5 mm) and the reference chloroform or orthophosphoric acid was kept in the outer tube to minimize the bulk susceptibility effect of a paramagnetic sample. The concentrations of the complex were of the order of *ca.* 10^{-2} M. The sweep widths scanned were 1000 Hz (for ^1H and ^{31}P). The compound gave well resolved ^1H and ^{31}P NMR spectra with adequate information after 48 scans. Decoupling experiments were also carried out to examine ^1H - ^{31}P and ^{13}C - ^{31}P coupling. The typical pulse time was 1 μs for ^1H spectra and 10 μs for ^{31}P spectra. Appropriate cycle times were employed for ^1H , ^{31}P and ^{13}C spectra.

Conductivity and Paramolybdate Titrations

The molar conductance of the Cr(III) complex was measured in aqueous medium using a Systronics conductivity bridge and $[\text{Cr(III)}] = 1 \times 10^{-3}$ M. Paramolybdate titration for detecting the number of coordinated water ligands was carried out by standard methods [13] using a solution at $[\text{Cr(III)}] = 1 \times 10^{-2}$ M.

Results and Discussion

Although the procedures for the synthesis of $\text{Na}_3\text{Cr}[\text{N}(\text{CH}_2\text{POH}(\text{O})_2)_3]_2$ gave a methanol insoluble salt, elemental analysis data for C, N, P and Na contents were only in poor agreement with those

calculated for the formula. On the other hand, the ratios of C:P, C:N and N:P calculated for $\text{Na}_3\text{Cr}[\text{N}(\text{CH}_2\text{POH}(\text{O})_2)_3]_2$, 2.58, 0.389 and 6.66, are in reasonable agreement with the found values *viz.*, 2.63, 0.40 and 6.83. The poor agreement of the analytical values may be due to some impurities of the sodium salts of the free ligand being present in the Cr(III) complex.

High solubility in water and near insolubility in several non-aqueous solvents precluded further recrystallization to obtain pure solid samples. However, after ion-exchange separation, a major band with a trinegative charge was obtained in the pure form. The ratios of Cr:P (1.6 ± 0.1) and Cr:N ($1:1.9 \pm 0.1$) as analysed in the eluate from ion-exchange columns was reproducible and consistent with the formulation $\text{Cr}[\text{N}(\text{CH}_2\text{P}(\text{O})_2\text{OH})_3]_2^{3-}$. Therefore, for all spectroscopic measurements (except in the case of infrared spectra) the eluate obtained from Dowex 1-X8 or Sephadex QAE-25 was used. The conductance measurements showed that the complex has a molar conductivity of 460 mho/cm^2 , which is characteristic of a 3:1 electrolyte.

The electronic spectral data for the Cr(III) complex of nitrilotri(methylenephosphonic acid) in 1.0 M NaCl medium after the necessary purification on Sephadex QAE-25 column are listed in Table I. It is evident that the lowest energy d-d band for the species occurs at 610 nm which is lower than the lowest energy band obtained for $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Typically $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ exhibits the lowest energy spin allowed $^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ transition at 575 nm. A lower ligand field stabilization energy seems to be appropriate for nitrilotri(methylenephosphonate) under investigation. In case of complexes like $\text{Cr}(\text{en})_3^{3+}$, $\text{Cr}(\text{sar})^{3+}$ and $\text{Cr}(\text{sep})^{3+}$ with D_3 point group symmetry, generally only two d-d bands are observed [9, 14, 15], although in such symmetries $^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g}$ levels in Q_h point group are expected to be split into two of three individual components with small energy separations. Therefore, the observation that for the chromium complex of nitrilotri(methylenephosphonic acid) (2), there are only two well resolved d-d bands centred at 610 and 432 nm seems reasonable. It is also of interest that there is an un-

TABLE I. The Electronic Spectra Data on Cr(III) Nitrilotri(methylenephosphonic acid) and Related Complexes in Aqueous Media

Complex	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	Reference
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	408	15.5	575	13.7	28
$[\text{Cr}(\text{OX})_3]^{3-}$	420	87.5	573	68.9	29
$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)]^{2+}$	370	29.3	502	48.4	30
$\text{Cr}[\text{CH}_3\text{N}(\text{CH}_2\text{P}(\text{OH})(\text{O})_2)_2]_2^-$	445	29.8	640	33.1	31
$\text{Cr}[\text{N}(\text{CH}_2\text{P}(\text{OH})(\text{O})_2)_3]_2^{3-a}$	432 ± 2	45.0 ± 3	610 ± 2	50.0 ± 3	this work

^a A weak shoulder at ~ 470 nm ($34.0 \text{ M}^{-1} \text{cm}^{-1}$) was also observed.

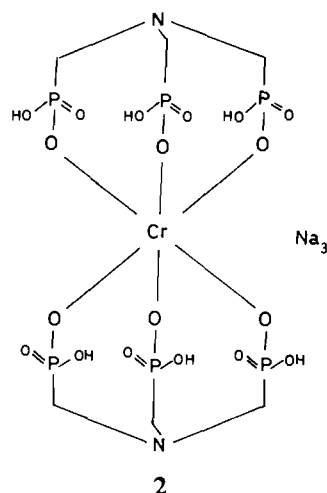


TABLE II. Infrared Spectral Data on Sodium Salt on Nitrilotri(methylenephosphonic acid) Ligand and its Complex with Cr(III)

IR bands		
Free ligand (cm^{-1})	Cr(III) complex (cm^{-1})	Assignment
1427	1434	$\rho(\text{CH}_2)$
1324	1320	$\rho_w(\text{CH}_2)$
1095 ^a	1173	$\nu_{\text{as}}(\text{P}=\text{O})$
1050 ^a	1094, 1052	$\delta(\text{O}-\text{P}-\text{O})$
968	939	$\nu_s(\text{P}-\text{O})$
769	840, 761	$\rho_t(\text{P}-\text{O})$

^aThe band observed was broad and unresolved and $\nu_{\text{as}}(\text{P}=\text{O})$ and $\delta(\text{O}-\text{P}-\text{O})$ seem to occur at similar frequencies.

resolved and weak shoulder at 470 nm in the spectrum of 2. Although this band may well arise from the split components of the spin allowed d-d transition, the weakness of the band is more suggestive of the band arising from a spin forbidden doublet-quartet transition. It has been reported that such doublet-quartet transitions are possible in the case of related complexes [16, 17] and this possibility was further confirmed by fluorescent studies. The luminescence spectrum after excitation at 650, 580 and 403 nm gave emission spectra with maxima at 720, 649 and 468 nm, respectively. The intense emission band was centred at 468 nm which may well be related to that observed at 470 nm in the electronic spectra.

The infrared spectral data on the sodium salt of nitrilotri(methylenephosphonic acid) and its Cr(III) complex in the region 1600–600 cm^{-1} are listed in Table II. The free ligand as well as the Cr(III) complex exhibited bands due to $\nu(\text{OH})$, $\nu(\text{CH})$ and in plane $\nu(\text{OH})$ deformation in phosphonic acid in the spectral region 3500–1600 cm^{-1} . However, the

$\nu_{\text{as}}(\text{P}=\text{O})$ and $\nu_s(\text{P}-\text{O})$ bands give more definitive clues regarding the complexation behavior of the phosphonic acid ligand.

It has been reported already that $\delta(\text{OPO})$ bands appear in the region of 950–1100 cm^{-1} [18], whereas $\nu(\text{P}=\text{O})$ bands appear at 1100–1300 cm^{-1} [19, 20]. The complexation of the phosphonic acid ligand has to occur with oxygen as the donor atom. This may lead to the depletion of electron density at the phosphorus centres owing to the electron withdrawing nature of metal ions and the bond order of ($\text{P}=\text{O}$) may increase. Therefore, an increase in the frequency of $\nu_{\text{as}}(\text{P}=\text{O})$ and a decrease in the frequency of $\nu_s(\text{P}-\text{O})$ are expected when Cr(III) is coordinated to the ligand. In the case of $\delta(\text{O}-\text{P}-\text{O})$, the coordination of the ligand to Cr(III) will render ($\text{O}-\text{P}-\text{O}$) linkage asymmetric and further splitting up of ($\text{O}-\text{P}-\text{O}$) is predicted. Whereas in the case of the sodium salt of the free ligand a broad band centering at 1095 cm^{-1} was observed, in the case of the Cr(III) complex peaks were observed at 1173, 1094 and 1052 cm^{-1} . The transition due to $\nu_s(\text{P}-\text{O})$ is attributable to the peak at 968 cm^{-1} in the case of the free ligand, whereas the corresponding peak occurred at 939 cm^{-1} in the case of the Cr(III) complex. This decrease in $\nu_s(\text{P}-\text{O})$ frequency is as expected. It seems reasonable to assign the doublet at 1094 and 1052 cm^{-1} to the bending motion of the ($\text{O}-\text{P}-\text{C}$) linkage in the complex. The bands in the region 1320–1430 cm^{-1} may be assigned to the wagging and deformation motions of CH_2 [21]. A sharp band was observed at 840 cm^{-1} in the case of the IR spectrum of the Cr(III) complex. Although aquo derivatives of Cr(III) are known to exhibit broad $\rho(\text{H}_2\text{O})$ bands at 780–850 cm^{-1} [22], the sharp features of the band seem more characteristic of skeletal vibration of CH_2 rather than $\rho(\text{H}_2\text{O})$. Further, paramolybdate titrations also revealed that there is no coordinated water molecule in the complex, ruling out the possibility of bidentate binding of the α -aminophosphonic acid.

It has been known that paramagnetic ions such as Cr(III) influence the line widths and positions of the resonance peaks in NMR spectra, because of electron spin-nuclear interaction [23, 24]. The phosphonic acid investigated in this study has three different NMR active nuclei namely ^{31}P , ^{13}C and ^1H located at different distances from a paramagnetic metal ion like Cr(III).

The Cr(III) complex of nitrilotri(methylenephosphonic acid) gave rise to sharp resonance lines not only in ^1H but also in ^{31}P and ^{13}C spectra. The ^1H and ^{31}P spectra of the free ligand as well as of the Cr(III) complex are shown in Fig. 1. It is evident from Fig. 1 that the ^{31}P signal is contact shifted due to complexation with a paramagnetic ion like Cr(III) and that ^{31}P and ^1H signals exhibit spin-spin coupling. Coupling constants were of the order of

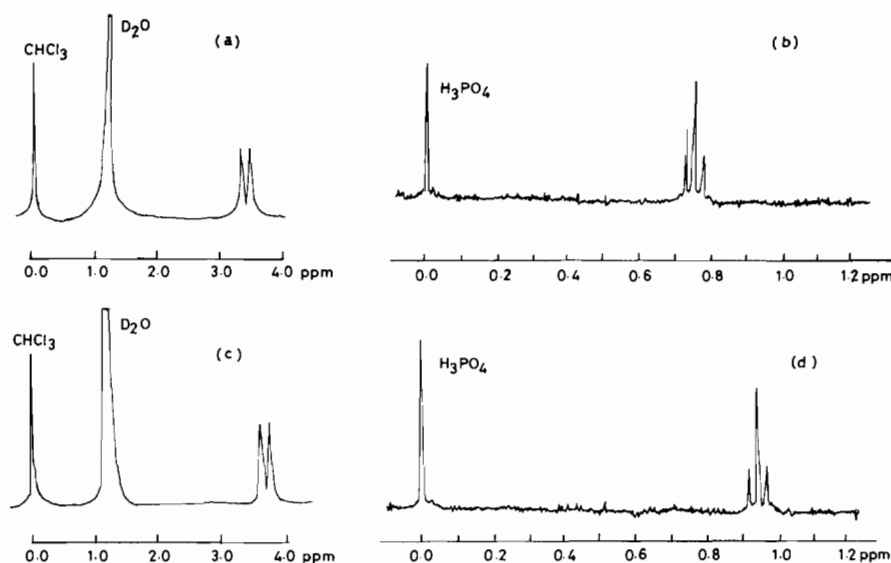


Fig. 1. NMR spectra of nitrilotri(methylenephosphonic acid) (a) ^1H ; (b) ^{31}P ; and its Cr(III) complex (c) ^1H ; (d) ^{31}P . CHCl_3 and H_3PO_4 were the internal standards for ^1H and ^{31}P spectra.

TABLE III. ^1H , ^{31}P and ^{13}C NMR Data on Nitrilotri(methylenephosphonic acid) and its Complex with Cr(III)

Spectra	Nucleus	Ligand $\text{N}(\text{CH}_2\text{P}(\text{OH})_2\text{O})_3$	Complex $\text{Na}_3\text{Cr}[\text{N}(\text{CH}_2\text{P}(\text{OH})(\text{O})_2)_3]_2$
^1H NMR ^a	$\text{CH}_2\text{-P}$	3.28 ^d	3.60 ^d
^{31}P NMR ^b	$\text{CH}_2\text{-P}$	9.40 ^e	7.20 ^e
^{13}C NMR ^c	$\text{CH}_2\text{-P}$	53.50 ^f	53.00 ^f

Temperature 27 °C, solvent D_2O , data in ppm. ^a CHCl_3 internal standard. ^b H_3PO_4 internal standard. ^c $\text{Si}(\text{CH}_3)_4$ internal standard. ^dAppears as a doublet due to $^1\text{H}\text{-}^{31}\text{P}$ coupling with J value of 12 Hz. ^eAppears as a triplet due to $^1\text{H}\text{-}^{31}\text{P}$ coupling. ^fAppears as a doublet due to $^{13}\text{C}\text{-}^{31}\text{P}$ coupling.

12 Hz in the free ligand as well as in the complex and are typical of a related H-C-P structure [25]. The chemical shifts of the peaks observed in the NMR spectra of the free ligand and its Cr(III) complex are listed in Table III. In the structure of the ligand, there are three sets of equivalent methylene protons, carbons and phosphorus centres. On coordination to Cr(III), however, if one of the arms of the tridentate were not coordinated, the chemical shifts and the interaction of the spin of nuclei in the uncoordinated arm of the nitrilotri(methylenephosphonic acid) ligand with the electron spin of the Cr(III) centre are expected to be different.

It is evident from the ^{31}P spectra that in the complex as well as the free ligand there is only one type of phosphorus which is coupled to a proton. The singlet character of the broad band (proton) decoupled ^{31}P signal of the complex shown in Fig. 2 gives compelling evidence that all the three phosphonic acid groups in the ligand are coordinated to the metal ion.

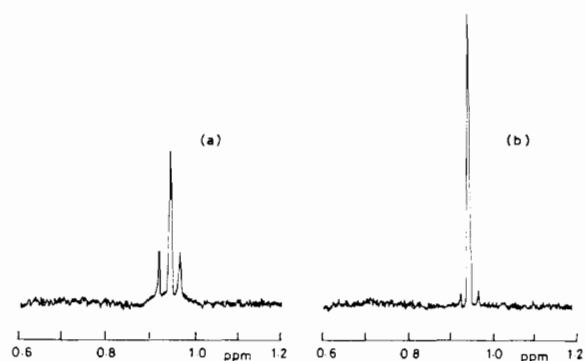


Fig. 2. Normal (a) and broad band ^1H decoupled (b) ^{31}P NMR spectra of the Cr(III) complex of nitrilotri(methylenephosphonic acid).

Similarly in the case of the ^1H spectra, the magnetic equivalence of the methylene protons (appearing at 3.28 ppm with respect to chloroform in the free ligand) seems to be retained on complexation

to Cr(III). The proton signal, however, undergoes a marginal contact shift (to 3.60 ppm). Since protons are four bonds away from the paramagnetic centre in the complex and there is no extended conjugation in the ligand structure, the marginal influence of Cr(III) on the chemical shifts of methylene protons is not entirely surprising. The methylene carbons in the ligand are also only marginally shifted due to the paramagnetism of Cr(III) in the complex as seen from the data given in Table III.

It is true that in a number of studies information concerning the molecular geometry of the paramagnetic complexes has been obtained [26, 27] from measurement of pseudo contact coupling, especially when the axial symmetry is known and g_{\parallel} and g_{\perp} components of the g tensors parallel and perpendicular to the principal axis could be estimated. Similarly the spin delocalizations on the ligand structure could also be assessed from the analysis of line width before and after complexation with Cr(III). The line widths of the methylene proton signal varied from 6.4 to 7.3 Hz in the free ligand whereas the same proton exhibited signal widths of 2.68 to 4.03 Hz in the complex. A detailed analysis of NMR results will be attempted by different workers.

Preliminary investigations to react the Cr(III) complex of the phosphonic acid ligand with ethylenediamine with a view to prepare cage complexes were made. Although the replacement of the phosphonate group by ligands having nitrogen donor atoms, as judged from the electronic and infrared spectra occurred, the products obtained were intractable. However, the present study led to the preparation, purification and characterization of a new complex $\text{Na}_3\text{Cr}[\text{N}(\text{CH}_2\text{P}(\text{O})_2\text{OH})_3]_2$.

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