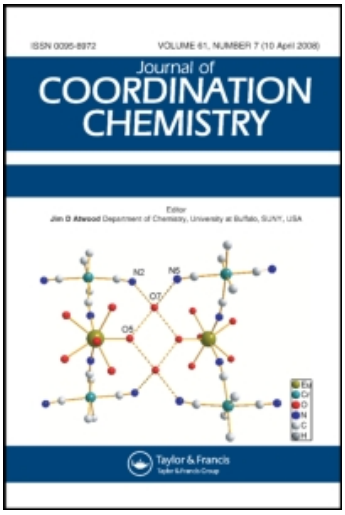

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE COORDINATION OF AMINOPHOSPHONATES TO CHROMIUM(III)

Christa R. A. Rajendram[a]; Patrick E. Hoggard[a]
[a] Department of Chemistry, North Dakota State University, Fargo, North Dakota

To cite this Article Rajendram, Christa R. A. and Hoggard, Patrick E.(1994) 'THE COORDINATION OF AMINOPHOSPHONATES TO CHROMIUM(III)', Journal of Coordination Chemistry, 33: 1, 15 — 32
To link to this Article: DOI: 10.1080/00958979408024258
URL: http://dx.doi.org/10.1080/00958979408024258

J. Coord. Chem., 1994, Vol 33, pp. 15–32
Reprints available directly from the publisher
Photocopying permitted by license only

THE COORDINATION OF AMINOPHOSPHONATES TO CHROMIUM(III)

CHRISTA R. A. RAJENDRAM and PATRICK E. HOGGARD*

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

(Received January 3, 1994; in final form February 2, 1994)

Attempts to induce coordination of the amine group in aminophosphonate complexes of chromium(III) were unsuccessful. However, N-phosphonomethylglycine forms a stable complex in which the amine, the carboxylate, and one phosphonate oxygen are coordinated. A similarly coordinated complex of N,N-diphosphonomethylglycine is unstable and reverts to an isomer in which the amine group is free. Several potential reasons for the failure of the amine group to coordinate in aminophosphonates in contrast to analogous aminocarboxylate complexes were explored. Steric factors appear unimportant. Contributing factors are (1) there is a driving force for the transfer of a proton from a phosphonate oxygen to the amine, establishing a preference for oxygen coordination; (2) coordination of the phosphonate end of an aminophosphonate appears to lower the basicity of the amine group much more than carboxylate coordination in an aminocarboxylate; (3) in an aminophosphonate the nitrogen lone pair orbitals lie lower in energy than they do in aminocarboxylates, decreasing the energy of the donor-acceptor interaction with metal orbitals.

KEYWORDS: chromium(III), aminophosphonates, N-phosphonomethylglycine, N,N-diphosphonomethylglycine

INTRODUCTION

Though aminophosphonates are similar to aminocarboxylates in basicity towards protons,[1] their metal complexation properties are quite dissimilar. The amino group is commonly coordinated in aminocarboxylate complexes,[2-5] but is rarely coordinated in aminophosphonate complexes.[6-10] The metal ion, rather than coordinate to the nitrogen, coordinates to a second phosphonate oxygen, or even to water.

There are a number of conceivable explanations for this phenomenon, and in this paper we explore several possibilities. One is that replacing an sp^2 carbon with an sp^3 phosphorus introduces a ring strain. Another is that in aminophosphonate complexes the four-membered ring in which two phosphonate oxygens bind to the metal is more favorable, sterically or otherwise, than the alternative five-membered ring in which one oxygen and the amino group are coordinated. Both of these are considered through molecular mechanics calculations.

The remaining hypotheses involve electronic properties. Coordination of an oxygen to a metal ion many reduce the basicity of an amino group on the same molecule, with a greater effect when the oxygen is from a phosphonate than when

* Author for correspondence.

it is from a carboxylate. Inductive effects may lead to a reduction in the electron density on the nitrogen atom because of withdrawal into the carboxylate or phosphonate group, an effect that would also have to be greater for phosphonates than for carboxylates. Finally, the energy of the nitrogen lone pair orbital may be lower in an aminophosphonate than in an aminocarboxylate, which would lead to a poorer energy match with the metal *d* orbitals and a weaker bond. We employ both semi-empirical and *ab initio* methods to try to evaluate these hypotheses.

We also report the synthesis and characterization of complexes of chromium(III) with ligands containing both carboxylate and phosphonate functionalities along with an amino group. This was done to test whether or not the amino group will coordinate in intermediate situations. In addition, there was some uncertainty that the aminophosphonates had been completely deprotonated during the reported syntheses of their metal complexes, and the possibility that amino group coordination did not occur only because it was present in solution as $R\text{-}NH_3^+$ needed to be excluded. We therefore attempted to synthesize aminophosphonate complexes of Cr(III) with sufficient base to completely deprotonate the ligands, looking for even a minor fraction containing an amine-coordinated complex. The ligands used are anions of aminomethylphosphonic acid (H_2amp), butyliminobis(methylenephosphonic acid) (H_4bidp), with two phosphonates, phosphonomethylglycine (H_3pgly), with one phosphonate and one carboxylate, and diphosphonomethylglycine (H_5dpgly), with two phosphonates and one carboxylate. The free acids are shown in Figure 1.

EXPERIMENTAL SECTION

Materials

Aminomethylphosphonic acid was obtained from Aldrich and N,N-bis(phosphonomethyl)glycine from Sigma Chemical Company. Phosphonomethylglycine (glyphosate) was provided by Monsanto. Butyliminobis(methylenephosphonic acid) (H_4bidp) was synthesized by the method of Moedritzer and Irani.[11]

Physical Measurements and Instrumentation

UV-visible absorption spectra were measured in aqueous solutions at room temperature with a Hewlett-Packard Model 8451A diode array spectrometer. Infrared spectra were recorded on a Mattson Galaxy-2020 FT-IR spectrometer with samples dispersed in KBr discs. Conductivity measurements were taken with a Cole-Parmer Model 1481-60 digital conductivity meter. Energy-dispersive X-ray fluorescence (EDXRF) spectra were measured with a Kevex Model 5100 spectrometer with Mo Kα radiation. ^{31}P NMR spectra were measured at room temperature in D_2O with a phosphoric acid reference on a Jeol GSX/CPF/GX 400 MHz spectrometer. Elemental analyses were performed by Desert Analytics Organic Microanalysis Laboratories and E + R Microanalytical Laboratory, Inc.

$[Cr(Hamp)_2(H_2O)_2]Cl$

Aminomethylphosphonic acid (H_2amp, 0.46 g; 0.0040 mol) and $CrCl_3 \cdot 6H_2O$ (0.53

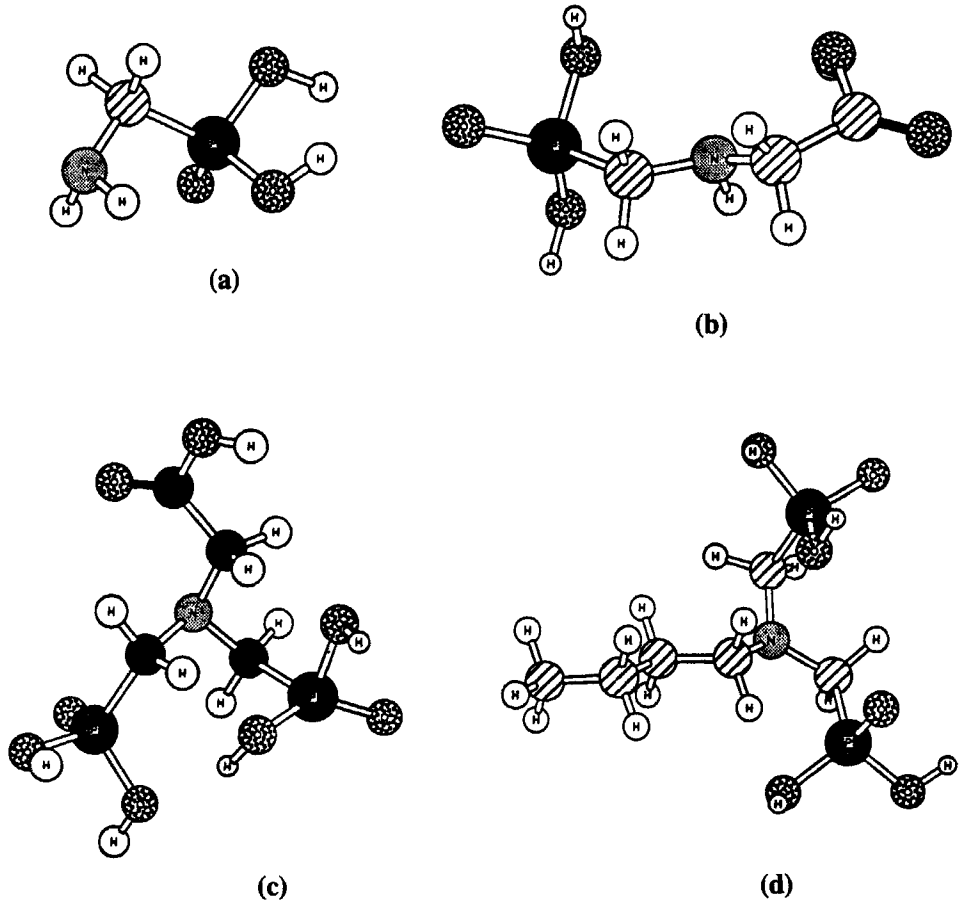

Figure 1 Phosphonic acids used in this work: (a) aminomethylphosphonic acid (H_2amp), (b) N-phosphonomethylglycine (H_3pgly), (c) N,N-diphosphonomethylglycine (H_5dpgly), (d) butyliminodimethylphosphonic acid (H_4bidp)

g; 0.00100 mol) were dissolved in water (10 mL). The solution was heated on a steam bath for 30 min. KOH (0.45 g; 0.008 mol) was added and the solution was heated for an additional 30 min. The resulting solution was concentrated, loaded onto a water-equilibrated Sephadex G-10 column, then eluted with water. The single, intense green band was collected and concentrated, and the complex was precipitated by the addition of methanol. *Anal.* Calcd. for $[Cr(CH_5NO_3P)_2(H_2O)_2]Cl$(%): C, 6.99; H, 4.11; N, 8.16. Found: C, 6.85; H, 4.03; N, 7.95.

$K[Cr(H_2bidp)_2(H_2O)_2]\cdot H_2O$

Butyliminodimethylphosphonic acid (H_4bidp, 2.61 g; 0.0100 mol) and $CrCl_3\cdot 6H_2O$ (1.33 g; 0.0050 mol) were dissolved in methanol (25 mL), and the solution was

heated on a steam bath for 30 min. KOH (1.12 g; 0.0200 mol) was then added and the solution heated further for 30 min. The solution was concentrated, filtered, and passed through a Sephadex G-10 column. It eluted as a single green band. The band was collected and concentrated, and the complex was precipitated by the addition of acetonitrile. The complex dissolves slowly in methanol and water. *Anal.* Calcd. for $KCr[C_6H_{15}NP_2O_6)_2(H_2O)_2]\cdot H_2O$(%): C, 21.72; H, 5.47; N, 4.22. Found: C, 21.82; H, 5.71; N, 4.15.

K[Cr(Hpgly)$_2$]

Phosphonomethylglycine (H_3pgly, 3.38 g; 0.0200 mol) and $CrCl_3\cdot 6H_2O$ (2.66 g; 0.0100 mol) were dissolved in water (50 mL). The solution was heated on a steam bath for 30 min. KOH (3.36 g; 0.060 mol) was added, bringing the pH of the solution to about 10, and the solution was heated for an additional 30 min. The solution was then evaporated to dryness. The residue was dissolved in methanol and eluted through a Sephadex LH-20 column, saturated in methanol. The first band eluted from the column was violet $[Cr(Hpgly)_2]^-$. Solid $K[Cr(Hpgly)_2]$ was obtained by quickly removing the methanol with a vacuum pump. The complex is soluble in water and in methanol. *Anal.* Calcd. for $K[Cr(C_3H_6NO_5P)_2]$(%): C, 16.95; H, 2.85; N, 6.59. Found: C, 17.12; H, 2.92; N, 6.55.

K[Cr(Hpgly)$_2$(H$_2$O)$_2$]

The second band eluted from the LH-20 column described above was blue-green $K[Cr(Hpgly)_2(H_2O)_2]$. This complex was precipitated by rapid removal of methanol with a vacuum pump. The complex is soluble in water and methanol. *Anal.* Calcd. for $K[Cr(C_3H_6NO_5P)_2(H_2O)_2]$(%): C, 15.62; H, 3.50; N, 6.07. Found: C, 15.51; H,3.32; N, 5.81.

K$_3$[Cr(H$_2$dpgly)$_2$]

Diphosphonomethylglycine (H_5dpgly, 2.63 g; 0.0100 mol) and $CrCl_3\cdot 6H_2O$ (1.33 g; 0.0050 mol) were dissolved in water (25 mL). The solution was heated on a steam bath for 30 min. KOH (3.36 g; 0.060 mol) was added and the solution was heated for an additional 30 min. The resulting solution was concentrated and passed through a Sephadex DEAE anion exchanger. With 0.8M KCl as the eluent, a minor violet band moved faster than an intense blue-green band. The blue-green band was collected and passed through a Sephadex G-10 column. A single band resulted, which was collected and concentrated. The complex was precipitated by the addition of methanol. *Anal.* Calcd. for $K_3[Cr(C_4H_8NO_8P_2)_2]$(%): C, 15.31; H, 2.57; N, 4.47. Found: C, 15.28; H, 2.46; N, 4.45.

The violet fraction was unstable. Within four hours it turned blue-green, with a spectrum identical to that of the complex described above. We were unable to precipitate the violet material.

Calculations

Molecular mechanics calculations were done with the program PCMODEL.[12] This calculation employs the MMX force field,[13] and does not ordinarily use any

bending constants for L_1-M-L_2 angles with transition metals, instead assuming that van der Waals forces are sufficient to keep coordinating atoms at the proper angular distance from each other. In some calculations we added force constants typical of those in other systems in order to check this assumption.[14] In most cases this did not change greatly either the geometry or the strain energy. Energies reported here were taken from calculations without the added bending constants. Two energy values were of interest: the strain energy (the sum of the bond-stretching, angle-bending, torsional, and van der Waals contributions) and the MMX energy, which is the strain energy plus the dipole-dipole energy from the interaction of internal charges. All geometry optimizations were performed from several different initial geometries, and the dihedral driver was applied exhaustively to find the global minimum.

Semi-empirical molecular orbital calculations were performed with the program MOPAC.[15] Because parameters for transition metal ions are lacking, Al^{3+} was used in place of Cr^{3+}. *Ab initio* calculations of the restricted Hartree-Fock type were performed with the program GAMESS,[16] with a 3-21G basis set.

STRUCTURES

X-ray powder diffraction spectra of all the solids obtained were featureless. None of our attempts to grow crystals for single crystal diffraction studies were successful.

The IR spectrum was the most important tool for determining which groups were coordinated. Nitrogen coordination can be inferred from shifts in the N-H and adjacent C-H frequencies. The N-H stretching frequency occurs at about 3335 cm^{-1} in the free amine. When nitrogen is coordinated the N-H stretching becomes weaker, hence ν(N-H) shifts to lower frequencies. When the nitrogen is protonated the N-H bond becomes still weaker than when it is coordinated.[17] Thus the expected order of N-H stretching frequencies is free amine > coordinated amine > protonated amine. All the ligands used in this work have a methylene group adjacent to the amino nitrogen. Grigoryev has proposed that the C-H stretching frequency from the methylene adjacent to a coordinated amine has a frequency higher than when the nitrogen is free and deprotonated, but lower than when the nitrogen is protonated.[18,19]

The asymmetric and symmetric stretching modes of the PO_3 group are usually well resolved and seen at 1000–1200 and 900–1000 cm^{-1}, respectively.[20] In complexes where a phosphonate is coordinated, these bands occur over a narrower range of frequencies and are fewer in number than the corresponding bands for the free acid.[21] Phosphonate coordination was inferred on this basis for all of the complexes for which IR spectra could be measured.

The asymmetric and symmetric CO_2 stretching bands of free carboxylate ions occur near 1578 and 1414 cm^{-1}, respectively.[22] When carboxylate is coordinated as a unidentate ligand, the asymmetric stretching frequency increases to around 1630 cm^{-1}, while the symmetric stretching frequency decreases to about 1320 cm^{-1}. By this criterion carboxylate was coordinated in each of the solid phosphonomethylglycine and diphosphonomethylglycine complexes.

Electronic spectra can be used to assess the coordination surroundings. For a Cr(III) complex with six nitrogen ligands the lowest energy band tends to fall between 430 and 465 nm.[23] With two nitrogen and four oxygen ligands, this band

occurs between 500 and 540 nm, and with six oxygens it is usually found from 585 to 680 nm.

$[Cr(Hamp)_2(H_2O)]^+$

A 4:1 ratio of aminomethylphosphonate to Cr(III) was used in the synthesis, with enough base to completely deprotonate the ligand, in an attempt to make $[Cr(Hamp)_3]$, the analog of $[Cr(gly_3)]$, gly = glycine, or, failing that, $[Cr(amp)_3]^{3-}$. The complex actually obtained had a molar conductance in water of 105 $Ohm^{-1} \cdot cm^2\ mol^{-1}$, which corresponds to a 1:1 salt. The complex was eluted from a Sephadex SP cation exchange column as a single band with 0.3M KCl, characteristic of a unipositive complex. The ligand thus took the form $Hamp^-$. EDXRF analysis showed the presence of Cr, P, and Cl, but not K, indicating the absence of impurities containing K^+.

Aminomethylphosphonate could act as a tridentate ligand, but the protonated atom in $Hamp^-$ would not ordinarily be expected to coordinate. This implies that the two water molecules in the formula are coordinated, since Cr(III) rarely departs from six-coordination. Aminophosphonate can act as a bidentate ligand through the amine and one phosphonate oxygen (the other would be protonated), or through two phosphonate oxygens with the amine group protonated. The electronic spectral data are given in Table 1 and IR data in Table 2. The 590 nm first band maximum in the absorption spectrum is characteristic of an environment with six oxygen ligands. The lack of a significant shift of the amine stretching and bending frequencies, or the stretching frequency of the adjacent methylene, from those of the free ligand implies that the amine is not coordinated (it is protonated in both the free acid and the complex). Therefore, the chromium must be coordinated by two oxygen atoms from each phosphonate group and the oxygen atoms from two water molecules.

The two water molecules could be either *cis* or *trans* to each other. PCMODEL calculations were done on both geometries to estimate the relative energies. The *trans* isomer yielded the lower MMX energy by 62 kJ/mol. The calculations showed the *trans* isomer to be stabilized by hydrogen bonds between the water oxygens and the amine hydrogens. The complex with this configuration is displayed in Figure 2.

$[Cr(H_2bidp)_2(H_2O)_2]^-$

It was hoped that butyliminobis(methylenephosphonic acid) (H_4bidp) would, when

Table 1 Electronic spectral data for Cr(III) aminophosphonic acid complexes in aqueous solution

Complex	λ, nm (ε_{max})	λ, nm(ε_{max})
$[Cr(Hamp)_2(H_2O)_2]^+$	438 (25)	590 (31) 656 (sh)
$[Cr(H_2bidp)_2(H_2O)_2]^-$	454 (20)	630 (28) 656 (sh) 686 (sh)
$[Cr(Hpgly)]^{2-}$	414 (28)	554 (25)
$[Cr(Hpgly)_2(H_2O)_2]$	420 (53)	584 (54)
$[Cr(H_2dpgly)_2]^-$ (green)	428 (28)	588 (27)
$[Cr(H_2dpgly)_2]^-$ (violet)	416	570

Table 2 *Infrared spectral data for chromium(III)-aminophosphonate complexes.*

H_2amp	$[Cr(Hamp)_2(H_2O)_2]Cl$	H_4bidp	$K[Cr(bidp)_2(H_2O)_2]$	H_3pgly	$K[Cr(Hpgly)_2$	$K[Cr(Hpgly)_2(H_2O)_2$	H_5dpgly	$K_3[Cr(H_2dpgly)_2]$	Assignment
3142	3139	2960	2961	3230	3152	3150	3118	3118	υ(N–H)
1528	1530			1561		1563			$\delta(NH_2)$
1217	1132	1175	1113	1160	1135	1118	1244	1178	$\upsilon_{as}(PO_3)$
930	942	941	930	917	960	947	936	941	$\upsilon_s(OP_3)$
1078	1050	1152	1079	1094	1052	1060	1137	1086	δ(O–P–O)
2950	2945	2960	2961	3014	2922	3014	2956	2952	$\upsilon(CH_2)$
1440	1442	1425	1438				1430	1400	$\delta(CH_2)$
				1734	1636	1636	1752	1640	$\xi_{as}(CO_2)$
				1485	1386	1400	1390	1323	$\upsilon_s(CO_2^-)$
		2574	2600						υ(O–H)
			519		505	500			υ(Cr–O)

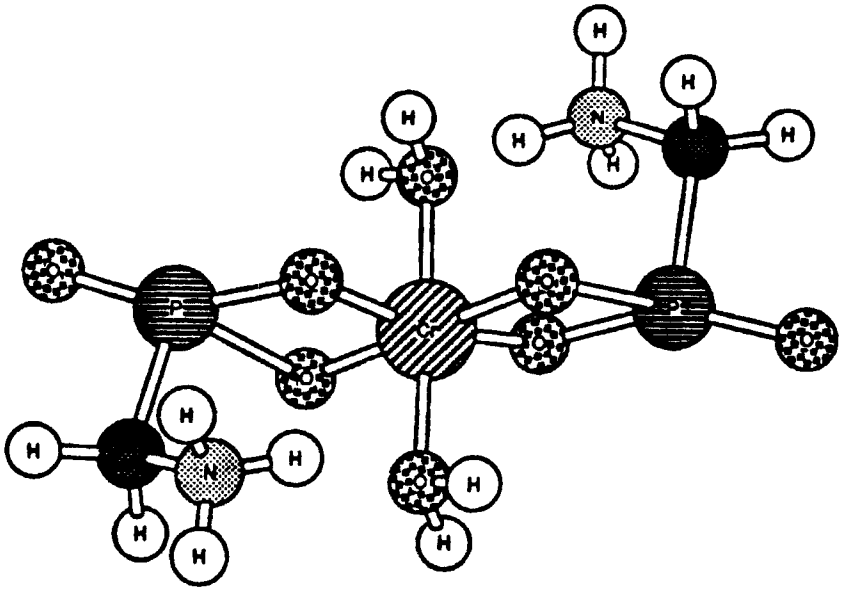

Figure 2 $[Cr(Hamp)_2(H_2O)_2]^+$ (O,O coordination mode).

deprotonated to H_2bidp^{2-}, act as a tridentate ligand through the amino group and one oxygen from each phosphonate, as does iminodiacetic acid, which has large formation constants with most metal ions. In the synthesis reported above, two equivalents of base were used, but in other experiments four equivalents were used, in order to insure deprotonation of the amine, with like results. Elemental analysis confirmed the presence of two butyliminodimethylphosphonates per chromium. The complex had a molar conductivity in water of 107 $Ohm^{-1} \cdot cm^2\ mol^{-1}$, characteristic of a 1:1 electrolyte. It was eluted from a Dowex 1 × 8 anion exchange column as a single band with 0.3M KCl, implying a uninegative charge. EDXRF analysis showed the presence of Cr, K, and P, but not Cl. We conclude that the ligand coordinates as H_2bidp^{2-}.

It is again evident from the electronic absorption and IR spectral data that the nitrogen atoms are not coordinated. The lowest energy band in the visible spectrum occurs at 630 nm, indicating a lower ligand field stabilization energy for butyliminodimethylphosphonate than for water, since the first band maximum of $[Cr(H_2O)_6]^{3+}$ occurs at 575 nm.[24] The infrared spectral data for $K[Cr(H_2bidp)_2]$ and H_4bidp are listed in Table 2. Since both the free ligand and the Cr(III) complex showed bands due to stretching and in-plane deformation of a phosphonic acid OH group, not all P-OH groups in the complex are deprotonated or coordinated. The two remaining protons in H_2bidp^{2-} may both reside on phosphonates, or one phosphonate may be deprotonated in favor of the amine.

At least four positions in the octahedron must be occupied by phosphonate oxygens, and possibly a fifth if the amine is protonated. Only one peak at −1.21 ppm (width 0.4 ppm) was observed in the ^{31}P NMR spectrum in aqueous solution,

with H_3PO_4 as the reference. If the two phosphorus atoms are equivalent, the most likely structure is that in which the H_2bidp^{2-} ligand is coordinated by one oxygen from each of the four phosphonates, plus two water molecules in *trans* geometry. The relative energies of the *cis* and *trans* isomers were estimated with PCMODEL calculations. The *trans* isomer had the lower energy by 92 kJ/mol, supporting the *trans* assignment. This is illustrated in Figure 3. With respect to the water molecules this complex is similar to $[Cr(Hamp)_2(H_2O)_2]^+$, and the PCMODEL calculations indicated that the coordinated water molecules in $[Cr(H_2bidp)_2(H_2O)_2]^-$ are also stabilized by hydrogen bonding interactions. However, $Hamp^-$ appears to coordinate through two phosphonate oxygens (because the proton is on the amine), which, from the NMR evidence, appears not to occur for any of the H_2bidp^{2-} phosphonate ligands.

K[Cr(Hpgly)$_2$] and K[Cr(Hpgly)$_2$(H$_2$O)$_2$]

Phosphonomethylglycine was expected to act as a tridentate ligand, coordinating through the amino, phosphonate, and carboxylate groups, and to yield a *bis* complex with chromium(III). The elemental analyses showed that both of the complexes (violet and blue-green) isolated have two ligands per chromium.

The molar conductance values in aqueous solution of these complexes were 98 and 102 Ohm^{-1} cm^2 mol^{-1} for the violet and the blue-green complexes, respectively, corresponding to 1:1 electrolytes. Both complexes were eluted through a Dowex 1 × 8 anion exchange column with 0.3 M KCl, consistent with a uninegative charge. The violet fraction moved faster than the blue-green, from which we conclude that the blue-green complex is more polar than the violet. EDXRF analysis showed the presence of Cr, K, and P, but not Cl for both complexes.

The electronic spectral data for both complexes are shown in Table 1. Evidence for nitrogen coordination in the violet complex derives from the first band

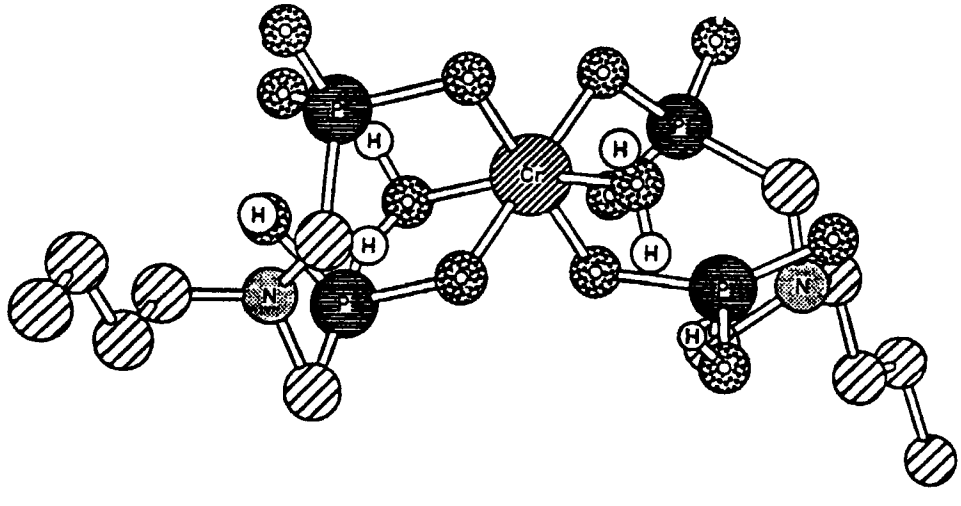

Figure 3 $[Cr(H_2bidp)_2(H_2O)_2]^-$.

maximum at 554 nm, while the blue-green complex had a maximum at 584 nm, and evidently has six oxygens in the coordination environment.

The IR spectral data are listed in Table 2. Additional evidence for nitrogen coordination in the violet complex comes from the N-H stretching frequencies, which are 3150 cm^{-1} for the free ligand H_3pgly, in which nitrogen is protonated, 3152 cm^{-1} for the blue-green complex, in which nitrogen is inferred to be protonated, and 3230 cm^{-1} for the violet complex, in which nitrogen is coordinated. The adjacent methylene stretching frequencies are 3014 cm^{-1} for free H_3pgly and 2922 cm^{-1} for the violet complex.

We conclude that in the violet complex $Hpgly^{2-}$ does indeed coordinate through the amine, the carboxylate, and one phosphonate oxygen. There are several possible isomers for $[Cr(Hpgly)_2]^-$: one meridional and five facial (all *trans*; *trans*-N,N; *trans*-$O(CO_2)$,$O(CO_2)$; *trans*-$O(OP_3)$,$O(OP_3)$; or all *cis*). The PCMODEL calculations yielded similar energies for the five facial isomers, but the MMX energy for the meridional isomer (Figure 4) was 39 kJ/mol below that of the most stable facial isomer.

In the blue-green complex the $Hpgly^{2-}$ ligands may coordinate through one phosphonate and one carboxylate oxygen, with two additional water molecules

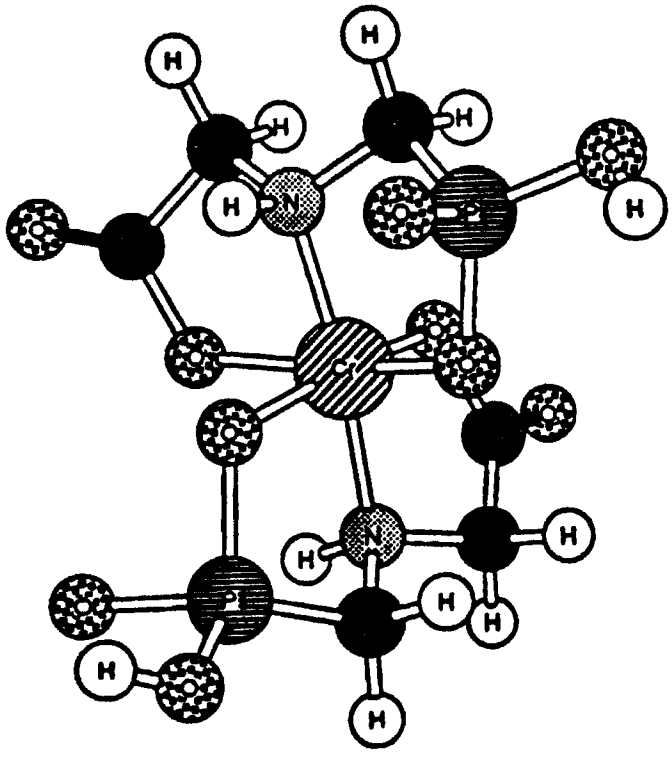

Figure 4 *mer*-$[Cr(Hpgly)_2]^-$ (O,O,N coordination mode).

coordinated, as in the $Hamp^-$ and H_2bidp^{2-} complexes, or they may coordinate through two phosphonate oxygens and one carboxylate oxygen. The chromatographic behavior implied that the blue-green complex is more polar than the violet complex. If the coordination sites are occupied by four phosphonates and two carboxylates the polarity would be more or less the same as that of the violet complex (assuming it to be the meridional isomer), or possibly even smaller, if the carboxylates are *trans* to each other. If two water molecules are coordinated *trans* to each other the polarity would also be expected to be small. Two water molecules *cis* to each other would seem to be required to achieve a sufficiently polar molecule.

PCMODEL calculations confirmed these qualitative arguments, except that slightly higher dipole moments were computed for both isomers without coordinated water (5.5 D for *cis* carboxylates, 5.2 D for *trans*) than for meridional $[Cr(Hpgly)_2]^-$ with nitrogen coordinated (3.6 D). Higher dipole moments resulted for either of the structures with two *cis* coordinated water molecules: 19 D for the *cis*-carboxylate, *trans*-phosphonate isomer, and 13 D for the *cis*-phosphonate, *cis*-carboxylate isomer. We conclude that water coordination is necessary to achieve a polarity sufficiently high to lead to the observed chromatographic behavior, and the blue-green complex should be represented as $[Cr(Hpgly)_2(H_2O)_2]^-$. This is also consistent with the elution order on Sephadex G-10. The larger size of the diaquo complex, primarily from the dangling amine chains, causes it to elute faster. The complex with this geometry is shown in Figure 5.

$K_3[Cr(H_2dpgly)_2]$

The N,N-diphosphonomethylglycine (H_5dpgly) complex was synthesized with the expectation that the nitrogen would behave towards a metal ion as in the analogous

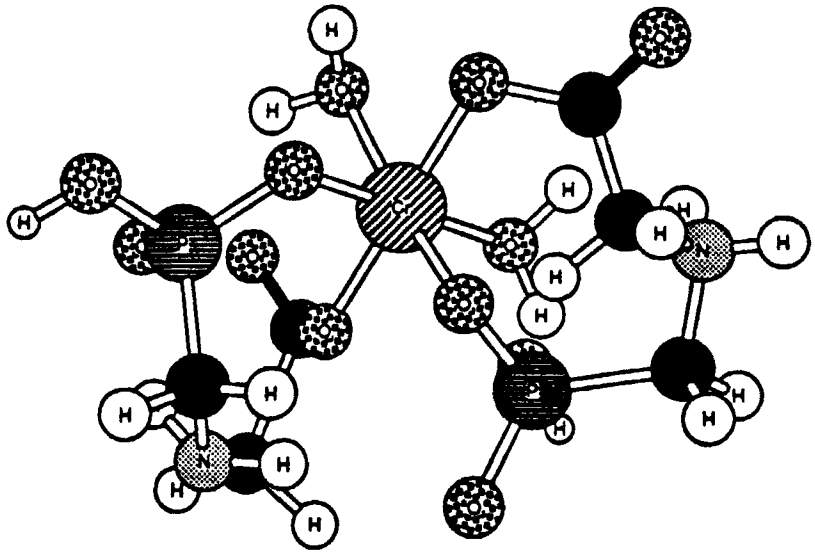

Figure 5 $[Cr(Hpgly)_2(H_2O)_2]^-$ (O,O coordination mode).

nitrilotriacetic acid, which can coordinate as a tetradentate ligand, though it does not invariably do so. The synthesis was carried out with Cr:ligand ratios of 1:1 and 1:2. In both instances two fractions resulted, blue-green and violet, on a Sephadex G-10 column. The blue-green fraction eluted more slowly than the violet. The violet fraction was too unstable to isolate as a solid.

The blue-green complex had a molar conductivity of 458 $Ohm^{-1} \cdot cm^2 \cdot mol^{-1}$, consistent with a 1:3 electrolyte. It was eluted from a Dowex 1 × 8 anion exchange column with 0.6 M KCl as the eluent, well-separated from the violet fraction, which preceded it. Though this suggests a divalent charge (we usually find 1.0 M necessary for −3 ions), we conclude that diphosphonomethylglycine coordinates as H_2dpgly^{3-}, and the chromatographic behavior may be due to the protonation of a free phosphonate or amine group on the column. EDXRF analysis showed the presence of K, Cr, and P, but not Cl.

The electronic spectral data for the blue-green complex in Table 1 show a first band maximum at 598 nm, indicating a coordination environment of six oxygens. The IR spectral data are shown in Table 2. The N-H and adjacent CH_2 stretching frequencies are essentially unchanged from those of the free acid, confirming the failure of the amino groups to coordinate and their presence in protonated form. The implied coordination mode for H_2dpgly^{3-} is through one oxygen from each phosphonate and the carboxylate oxygen. If the amine is protonated, one uncoordinated phosphonate oxygen on each ligand must be deprotonated.

The first band maximum in the electronic spectrum of the violet fraction was at 570 nm, consistent with a coordination environment of two nitrogens and four oxygens (though also with one nitrogen and five oxygens). The violet fraction converted over time to a blue solution with the spectrum of $[Cr(H_2dpgly)_2]^{3-}$ described above. Which group is displaced by the amine in the violet complex is not clear.

The blue-green complex could have a facial (*cis*- or *trans*-carboxylate) or meridional (*cis*-or *trans*-carboxylate) configuration. The facial *trans*-carboxylate geometry is shown in Figure 6. PCMODEL calculations assigned the lowest energy and the highest dipole moment to the meridional, *cis*-carboxylate isomer, but the calculated energy differences (16 to 27 kJ/mol) are not sufficient to make a firm assignment. If the violet complex has a −3 charge, a higher polarity for the blue-green complex is required to explain the ion-exchange behavior.

COMPUTATIONAL RESULTS AND DISCUSSION

The synthetic experiments lead to the conclusion that phosphonate groups inhibit coordination by an amino group on the same ligand, while carboxylate groups may promote amino group coordination, or at least do not hinder it. We were unable to find even a minor product with amino group coordination in the syntheses of chromium(III) complexes with aminomethylphosphonic acid or N-butyliminodiphosphonic acid. In both of these we have inferred coordination by water molecules in preference to the amine. In N-phosphonomethylglycine, a carboxylic acid function is added to aminomethylphosphonic acid. Two stable complexes were isolated from reaction mixtures with H_3pgly, one of which has an amino group coordinated. The addition of a second phosphonic acid function in N,N′-diphosphonomethylglycine also led to the isolation of two complexes, one

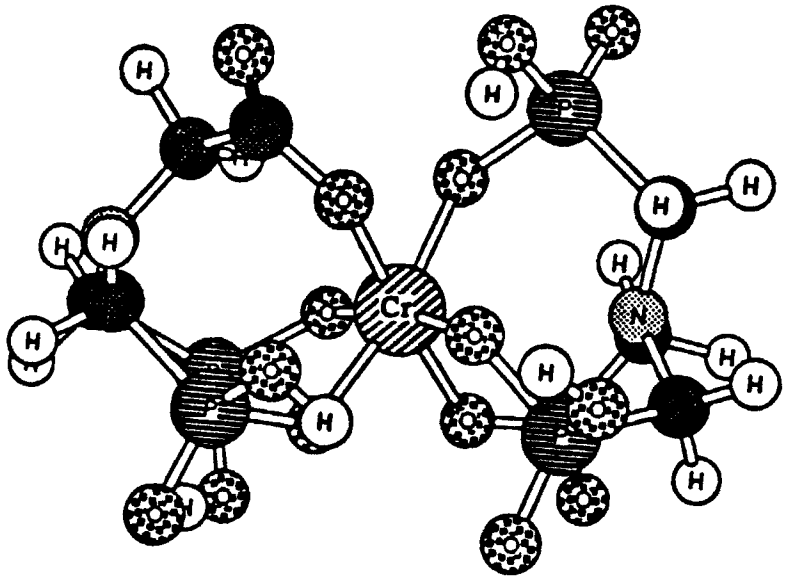

Figure 6 $[Cr(H_2dpgly)_2]^{3-}$ (O,O,O coordination mode), facial, *trans*-carboxylate isomer.

with a coordinated amine. However, this complex was obtained in smaller yield and isomerized within hours to the stable form, coordinated only by carboxylate and phosphonate oxygens.

Something about the phosphonate group is clearly sufficiently different from the carboxylate that it radically alters the coordination behavior of the amino group. It is not the proton basicity of the nitrogen, which is similar for phosphonates and carboxylates (see Table 3). Phosphonate oxygens are more basic than carboxylate oxygens, however, which may have consequences for coordination behavior. Both aminocarboxylates and aminophosphonates are zwitterions in solution, and the ammonium nitrogen is the last group to be deprotonated. Tests were devised for each of the hypotheses mentioned in the introduction, and the results are discussed below.

Table 3 Basicities in water of aminophosphonates and aminocarboxylates.[a]

Ligand	$pK(-NH_3^+)$	$pK_1(O_c)$[a]	$pK_1(O_p)$	$pK_2(O_p)$
Glycine[b]	9.8	2.4		
Aminomethylphosphonic acid[b]	10.0		5.4	
Phosphonomethylglycine[c]	10.1		2.2	2.5

[a]O_c = carboxylate oxygen; O_p = phosphonate oxygen
[b]A.E. Martell, R.M. Smith, *Critical Stability Constants, Vols I,II* (Plenum Press New York). 1974 [c]R.J. Motekaitis, A.E. Martell, *J. Coord. Chem. 14*, 139 (1985).

Structural Differences

Does the replacement of an sp^2 carbon by and sp^3 phosphorus create extensive strain in the ring formed by coordination of an amino group and a phosphonate or carboxylate to a metal? We used PCMODEL calculations to compare $[CrCl_4(Hamp)]^{2-}$ with $[CrCl_4(gly)]^{2-}$, both coordinating through oxygen and nitrogen. Table 4 shows the bond angles in the optimized geometries, and also contributions to the total strain energies. The bond lengths and angles were generally similar in the two complexes, and only small contributions to the strain energy arose from deviations from the "strain-free" values in the force field. The van der Waals contributions were almost identical for the two complexes. We conclude that steric effects from the substitution of C by P are unimportant.

Competing Coordination Modes

One reason that the amino group may not coordinate in aminophosphonates is that coordination through a second phosphonate oxygen may be preferred. Even if true, it is not clear that this is a sufficient reason by itself, since the amino group can still coordinate even when a phosphonate already coordinates through two oxygens. In the butyliminodiphosphonate complex two waters are also coordinated and the phosphonates are coordinated through just one oxygen, but the amine still does not displace water. In $[Cr(Hamp)_2(H_2O)_2]^+$ both aminomethylphosphonates are coordinated through two phosphonate oxygens, but the amine is protonated and it participates in hydrogen bonding interactions with the waters that must be broken for the amine to lose a proton (even to hydroxide) and displace a water.

PCMODEL calculations were again used to compare the strain energies in the four-membered ring in which phosphonate coordinates through two oxygens, compared with the five-membered ring from coordination by the amino group and one phosphonate oxygen. The strain energy change was evaluated for the reaction

$$[Cr(Hamp\text{-}N,O)_2(H_2O)_2]^+ \rightarrow [Cr(Hamp\text{-}O,O')_2(H_2O)_2]^+ \qquad (1)$$

after optimizing the geometries of both complexes. This was found to be +26 kJ/mol, with the additional strain in the (O, O) mode about equally divided between

Table 4 Calculated bond lengths (Å) and bond angles (degrees) in $[Cr(Hamp)Cl_4]^{2-}$ and $[Cr(gly)Cl_4]^{2-}$.[a]

	Strain-free[b]	$[Cr(Hamp)Cl_4]^{2-}$	$[Cr(glycine)Cl_4]^{2-}$
Bond lengths			
Cr–Cl	2.30	2.34 (0.2)	2.33 (0.12)
Cr–N	1.98	2.02 (0.21)	2.00 (0.05)
Cr–O	1.80	1.84 (0.21)	1.83 (0.12)
Bond angles			
O–Cr–N	90	87.17	80.95
Cr–N–CH_2	107.7	110	111
Cr–N–CH_2	107.7	112	112
CH_2P–O	106	108 (0.07)	
CH_2–C–O	107		108 (0.01)
Cr–O–C(P)	106.8	117	122

[a]PCMODEL[12]calculation, energy contributions (kJ/mol) in parentheses. [b] in the PCMODEL force field

bond stretching and angle bending. However, the total MMX energy change for the rearrangement was −62 kJ/mol because of a very favorable change in the dipole-dipole energy. This arises primarily because of the change from a protonated phosphonate in the (N,O) mode to a protonated amine in the (O,O) mode. There is some question whether the PCMODEL force field overestimates this change. However, the difference in pK values (Table 3) between phosphonate and amine corresponds to 26 kJ/mol, so at the very least this cancels the increase in strain energy upon (O, O) coordination.

Effect of Coordination on the Nitrogen Basicity

If coordination of a nearby oxygen lowers the proton basicity of the nitrogen, is the effect greater for a phosphonate than for a carboxylate? To test this, MOPAC calculations (with geometry optimization) were used to evaluate the enthalpy changes for the following reactions from the calculated heats of formation of the constituents.[25]

$$NH_2CH_2PO_3H^- + H^+ \rightarrow NH_3^+CH_2PO_3H^- \qquad \Delta H = -1054 \text{ kJ/mol} \quad (2)$$

$$NH_2CH_2CO_2^- + H^+ \rightarrow NH_3^+CH_2CO_2^- \qquad \Delta H = -1062 \text{ kJ/mol} \quad (3)$$

$$(NH_3)_5Al(HO_3PCH_2NH_2)^{2+} + H^+ \rightarrow (NH_3)_5Al(HO_3PCH_3NH_3)^{3+} \qquad \Delta H = -134 \text{ kJ/mol} \quad (4)$$

$$(NH_3)_5Al(O_2CCH_2NH_2)^{2+} + H^+ \rightarrow (NH_3)_5Al(O_2CCH_2NH_3)^{3+} \qquad \Delta H = -192 \text{ kJ/mol} \quad (5)$$

Thus it is predicted that a gas-phase glycinate anion is slightly more basic than an aminomethylphosphonate anion. However, upon coordination to an aluminum ion the basicities decrease (in this case, largely because of the positive charge of the aluminum), but much more so for the phosphonate. The net difference was 50 kJ/mol.

It is very difficult to model the aqueous environment in MO calculations, but in an effort to anticipate the trend upon hydration of the ligands and their complexes, the MOPAC calculations were repeated with two water molecules hydrogen-bonded to the amine ends of the ligands. After this change, aminomethylphosphonate was calculated to be more basic than glycinate by 8 kJ/mol, and the phosphonate basicity was reduced by 53 kJ/mol more than the carboxylate basicity, an insignificant difference from the calculations on isolated molecules.

These figures do support the hypothesis that the substitution of coordinated phosphonate for coordinated carboxylate lowers the basicity towards protons of the amine group. Implicit in the hypothesis is the premise that this reduction would be accompanied by a similar decrease in the coordinating ability of the amine group towards the metal ion. This seems likely, at least for hard metals, but certainly need not be true.

Inductive Effects

A common argument in many systems involving nucleophilic behavior is that the nucleophilicity varies with the electron-withdrawing ability of nearby substituents. The coordination behavior of the amino group might be due to a greater degree of electron withdrawal by the phosphonate in aminophosphonates than by the carboxylate in aminocarboxylates. To test this, *ab initio* calculations were per-

formed on several of the ligands used in this study, and a Mullikan population analysis[26,27] was performed in the optimized geometry to estimate the electron density on the nitrogen and the oxygens(s). The results in Table 5 show little variation in electron density on the nitrogen with the total or relative numbers of phosphonate and carboxylate groups. Though population analyses are often considered crude, these calculations lend no support to inductive effects as an explanation for the coordination behavior of the amino group.

Nitrogen Lone Pair Orbital Energy

More significant than electron density in donor-acceptor bonding are the relative energies of the donor lone pair and the acceptor orbital. Given a constant orbital overlap, the bond strength varies inversely with the energy gap between the donor and acceptor orbitals.[28] The metal *d* (acceptor) orbitals are higher in energy than the ligand donor orbitals, so the lower the energy of the nitrogen lone pair, the weaker the metal-nitrogen bond (again assuming that the overlap integral is constant). A reasonable hypothesis, then, is that the nitrogen lone pair energy is depressed in aminophosphonates, relative to aminocarboxylates.

To test this a Foster-Boys orbital localization[29] was performed on the eigenfuctions obtained from the *ab initio* calculations described above. Table 5 presents the resulting energies for the orbital that was associated with the nitrogen lone pair. These results are in strong agreement with the hypothesis. Replacement of carboxylate in glycine with a phosphonate lowers the nitrogen lone pair energy by 99 kJ/mol. Replacement of carboxylates in iminodiacetate lowers the nitrogen lone pair energy by 41 kJ/mol for the first phosphonate and 308 kJ/mol for the second, according to the calculations. In addition, the calculations identified the nitrogen lone pair orbital as the HOMO in iminodiacetate and phosphonomethylglycine, but it dropped to the ninth HOMO in butyliminodimethylphosphonate. The intervening orbitals were localized on oxygens. In glycine the nitrogen lone pair orbital was found to be the third HOMO, dropping to the fifth in aminomethylphosphonic acid.

CONCLUSIONS

The synthetic attempts reported here confirm the reluctance of the amino group in aminophosphonate/carboxylate complexes to coordinate when the ligand has more

Table 5 Calculated[a] Mulliken populations and nitrogen lone pair energies for aminophosphonates.

Compound	Mulliken Population O	N	Lone Pair Energy kJ/mol
$NH_2CH_2CO_2^-$	-0.79	-0.81	-596
$NH_2CH_2PO_3H^-$	-0.94	-0.79	-695
$NH(CH_2CO_2^-)_2$	-0.83	-0.77	-48
$\begin{matrix}NHCH_2CO_2\\ \vert\\ CH_2PO_3H^-\end{matrix}$	-0.81 -0.98	-0.77	-89
$NH_2(CH_2PO_3H^-)_2$	-0.94	-0.77	-397

[a]with GAMESS[16]

phosphonate than carboxylate groups. Several of the hypotheses explored here have some merit in explaining this phenomenon. There appears to be some driving force for the replacement of a coordinated amine by a second oxygen from an already coordinated phosphonate, which derives in part from the change in the location of a proton from the phosphonate to the amine. PCMODEL calculations placed the preference energy at 62 kJ/mol, but possible deficiencies in the PCMODEL treatment of the dipole-dipole interaction, which is a general problem in molecular mechanics calculations,[30] mean that this may be an overestimate. It also appears that the coordination of the phosphonate lowers the proton basicity of the nitrogen more than carboxylate coordination does. We estimated this difference at approximately 50 kJ/mol, though it is difficult to extend this figure directly to metal-nitrogen coordination. The largest effect energetically, and perhaps the best single explanation for the failure of the amine to coordinate, was the drop in the nitrogen lone pair orbital energy upon replacement of a carboxylate by a phosphonate. This was accompanied by a change in the nature of the highest occupied ligand molecular orbitals to those centered on phosphonate oxygens.

These three hypotheses overlap considerably in that electronic effects in the oxygen part of the molecule affect what happens at the nitrogen. However there are two distinct points of view represented: (1) coordination of an oxygen lowers the coordinating ability of the nitrogen or (2) the loss of donor ability by the nitrogen is already present in the uncoordinated ligand.

References

1. A.E. Martell and R.M. Smith *Critical Stability Constants* (Plenum Press, New York, 1974 and 1976), vol. I and vol IV.
2. R. Tauler, B.M. Rode, *Inorg. Chim. Acta* **173**, 93 (1990).
3. S.J.R. Chaberk, A.E. Martell, *J. Am Chem. Soc.* **74**, 5052 (1952).
4. H.M.N.H. Irving, R.H. Al-Jarrah, *Anal. Chim. Acta* **60**, 345 (1971).
5. C.M. Gramaccioli, R.E. Marsh, *Acta Crystallogr.* **21**, 594 (1966).
6. T. Glowiak, W. Sawka-Dobrowolska, B. Jesowska-Trzebiatowska, A.J. Antonow, *Cryst. Molec. Struct.* **10**, 1 (1980).
7. I. Lukes, Z. Kvaca, I. Dominak, *Collect. Czech. Chem. Commun.* **53**, 987 (1988).
8. I. Lukes, D. Rejskova, Z. Kvaca, *Proc. Conf. Coord. Chem.* **11**, 197 (1987).
9. K. Govindaraju, T. Ramasami, D. Ramaswamy, *Inorg. Chim. Acta* **133**, 71 (1987).
10. I. Lukes, D. Rejskova, R. Odvarko, P. Vojtisek, *Polyhedron* **5**, 2063 (1986).
11. K. Mocdritzer, R.R. Irani, *J. Org. Chem.*, **31**, 1603 (1966).
12. K.E. Gilbert, *PCMODEL, Molecular Modeling Software*, Serena Software, Inc. 1987.
13. U. Burkert and N.L. Allinger *Molecular Mechanics*, ACS Monograph 177, Amer. Chem. Soc., Washington, D.C., 1982, p. 286.
14. K.R. Adam, M. Antolovich, C.G. Brigden, L.F. Lindoy, *J. Am. Chem. Soc.* **113**, 3346 (1991).
15. J.J.P. Stewart, QCPE Bulletin No. 455 1983
16. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
17. J.J.P. Stewart, *J. Comp. Chem.* **10**, 209 (1989).
18. M.W. Schmidt, J.A. Boatz, K.K. Baldridge, S. Koseki, M.S. Gordon, S.T. Elbert, B. Lam, *QCPE Bulletin* **7**, 115 (1987).
19. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, (Wiley Interscience, New York 1970).
20. A.I. Grigoryev, L.V. Nikitina, N.M. Dyatlova, *Russian J. Inorg. Chem.* **19**, 1079 (1974).
21. N.I. Voronezheva, A.I. Grigoryev, N.M. Dyatlova, *Russian J. Inorg. Chem.* **21**, 1129 (1976).
22. A.G. Menke, F. Walmsley, *Inorg. Chim. Acta* **17**, 193 (1976).
23. G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
24. C.S. Garner, D.A. House, *Transition Metal Chem. (Dekker)* **6**, 59 (1970).

25. C.R.A. Rajendram, Ph. D. Dissertation, North Dakota State University (1993).
26. R.S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).
27. C.E. Dykstra, *Ab Initio Calculation of the Structures and Properties of Molecules,* (Elsevier, New York, 1988).
28. K.F. Purcell, J.C. Kotz, *Inorganic Chemistry,* (W.B. Saunders Co., Philadelphia, 1977).
29. J.M. Foster, S.F. Boys, *Rev, Mod. Phys.* **32**, 300 (1960).
30. P. Comba, *Coord. Chem. Rev.* **123**, 1 (1993).