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# Metal Complexes of α-Hydroxyimino Phosphonic Acid Derivatives. Separation of the *E* and *Z* Isomers by Metal Chelation and the Preparation and Characterization of Copper Bis[(*E*)-(α-(hydroxyimino)benzyl)phosphonate]-Water

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A new class of interesting ligands combining adjacent phosphoryl and oxime moieties has been recently prepared. Sodium methyl (α-(hydroxyimino)benzyl)phosphonate $\{Na[CH_3O(O)P(O)C(NOH)C_6H_5]\}$ is obtained as a mixture of *E* and *Z* isomers. The *E* isomer has been crystallized and characterized by a single-crystal X-ray diffraction study. It crystallized in the monoclinic system in the space group $P2_1/c$ with unit cell dimensions of $a$ = 6.496 (1) Å, $b$ = 31.998 (2) Å, $c$ = 10.087 (1) Å, $\beta$ = 92.82 (1)°, $V$ = 2094 (1) Å$^3$, and $Z$ = 8. When a mixture of the *E* and *Z* isomers was treated with $CoCl_2{\cdot}6H_2O$, the $Co^{2+}$ selectively precipitated the *E* isomer, allowing the purification and characterization of the *Z* isomer. The *E* isomer reacts readily with $CuCl_2{\cdot}2H_2O$, affording a pentacoordinate copper complex bound to two ligands and a water molecule. The X-ray crystal structure of the copper complex $Cu[(E)\text{-}CH_3O(O)P(O)C(NOH)C_6H_5]_2{\cdot}H_2O$ has revealed a mononuclear complex with a near-trigonal-bipyramidal geometry where each ligand acts solely as a bidentate ligand through the oxime nitrogen and the phosphoryl oxygen. The compound crystallized in the monoclinic system in the $C2/c$ space group with unit cell dimensions of $a$ = 17.774 (2) Å, $b$ = 16.986 (1) Å, $c$ = 7.279 (1) Å, $\beta$ = 113.44 (1)°, $V$ = 2016 (1) Å$^3$, and $Z$ = 4. The *Z* isomer did not react with the cupric ion under these conditions, presumably due to the formation of an intramolecular hydrogen bond between the oxime hydrogen and the phosphoryl oxygen. The existence of this bond is supported by semiempirical calculations (modified version of MNDO) that show that the hydrogen-bond formation stabilizes the molecule by 15 kcal. Also, IR data show a hydrogen bond only for the *Z* isomer.

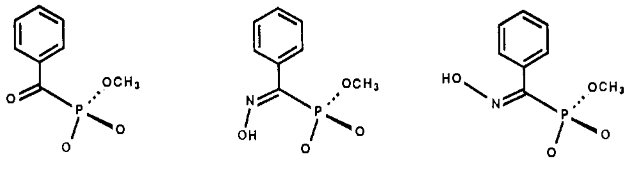
## Introduction

While acylphosphonates have been the focus of considerable attention, the chemistry of some of their derivatives has been overlooked. The recent synthesis and characterization of a novel class of compounds, α-hydroxyimino phosphonic acids and their derivatives, has led to new and interesting chemistry.$^{1-4}$ Dimethyl ((α-hydroxyimino)benzyl)phosphonate (**1**) is obtained as a mixture of *E* and *Z* isomers (55:45)$^{5,6}$ (see Chart I). In addition to thermal fragmentations and *Z* to *E* isomerizations, these compounds can be exploited for phosphorylation reactions. (*E*)-**2** undergoes a concerted, acid-catalyzed, stereoelectronically controlled cleavage of the C–P and N–O bonds to form benzonitrile and monomeric methyl metaphosphate, while the corresponding diacids serve as precursors for monomeric metaphosphate anion.$^{3,4}$

The combination of adjacent phosphonate and oxime moieties is expected to result in interesting metal-binding properties, since they can act as chelating bidentates, monodentates, bridging ligands, or any combination of these (see Chart II). Preliminary experiments have shown that some derivatives of acylphosphonates exhibit significant activity in inhibiting bioprosthetic heart valve calcification in rats, without adverse effects on somatic growth.$^7$ Their potential as drugs in the treatment of various metabolic bone diseases is currently being studied.

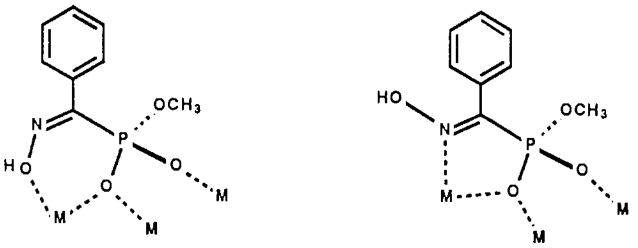
Obtaining further insights into and better understanding of the kinetics and mechanisms of the phosphorylation reactions, isomerizations, metal-binding properties, and biological activities of these potential ligands would be greatly facilitated by separation and purification of the (*E*)-**2** and (*Z*)-**2** isomers. This will allow the study of the effects of the metal ions (such as catalysis) on the phosphorylation reactions. In the event the C–P bond can be cleaved on the metal center, this could afford stereochemically controlled phosphorylation of adjacent ligands.

**Chart I**



acylphosphonate anion of (*Z*)-**2** anion of (*E*)-**2**

**Chart II**



Our interest in the chemistry of these novel compounds (α-hydroxyimino phosphonates) in conjunction with our ongoing interest in coordination chemistry$^{8-10}$ have prompted us to undertake this investigation of the coordination chemistry of these new ligands. We are interested in studying the effect of the metal centers on the isomerization and phosphorylation reactions of these ligands. Also, we are interested in investigating the metal-binding properties of these ligands and their effects on the redox and spectroscopic properties of the metal ions.

In this paper we describe the X-ray structure of (*E*)-**2**, the separation and purification of the (*Z*)-**2** isomer by metal chelation, and the spectroscopic characterization (IR, NMR) of both. Also, the reactivities of the two isomers toward metal ions were studied. The X-ray crystal structure and spectroscopic properties of the copper complex of the (*E*)-(α-(hydroxyimino)benzyl)phosphonate (**4**) are described as well.

## Experimental Section

All NMR spectra were recorded in $D_2O$ on a Bruker WH-300 spectrometer. The $^1H$ spectra were referenced internally to DSS, and the $^{31}P$

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**Table I.** $^1H$ and $^{31}P$ NMR Data for (*E*)-**1**, (*Z*)-**1**, (*E*)-**2**, and (*Z*)-**2**

| compd | $\delta(^1H)$, ppm | $J_{P-OCH_3}$, Hz | $\delta(^{31}P)$, ppm | solvent |
|---|---|---|---|---|
| (*E*)-**1** | $(CH_3)_2$ 3.77 d<br>$C_6H_5$ 7.55 m, 7.37 m | 10.93 | $11.60_{sep}$ | $CDCl_3$ |
| (*Z*)-**1** | $(CH_3)_2$ 3.75 d<br>$C_6H_5$ 7.45 m | 11.67 | $5.18_{sep}$ | $CDCl_3$ |
| (*E*)-**2** | $(CH_3)_2$ 3.59 d<br>$C_6H_5$ 7.46 m, 7.32 m | 10.94 | $6.43_q$ | $D_2O$ |
| (*Z*)-**2** | $(CH_3)_2$ 3.40 d<br>$C_6H_5$ 7.49 m | 11.24 | $1.83_q$ | $D_2O$ |

resonances were referenced to external 85% phosphoric acid.

The IR spectra were recorded on a Bruker IFS 113V spectrometer using a Ge-coated KBr beam splitter and an MCD detector. Typical spectra were recorded in the 400–4000-cm$^{-1}$ range with 0.5% KBr pellets by using 32 pulses and a 2-cm$^{-1}$ resolution.

**Preparation of [(*E*) + (*Z*)]-2 and Pure (*E*)-2.** The synthesis of the mixture of the (*E*)- and (*Z*)-methyl ($\alpha$-(hydroxyimino)benzyl)-phosphonate has been described previously[2] as has the preparation of the pure (*E*) isomer.[2,3] Slow evaporation from aqueous solution of the Na salt of the *E* isomer [(*E*)-**2**] yielded well-formed elongated colorless crystals. One crystal with approximate dimensions of 0.5 mm × 0.3 mm × 0.2 mm was selected for the X-ray diffraction study.

**Preparation of Pure (*Z*)-2.** A mixture of the *E* and *Z* isomers of the sodium salt of ($\alpha$-(hydroxyimino)benzyl)phosphonate (0.5 g, 2.1 mmol) was dissolved in 100 mL of deionized water and allowed to react overnight with 0.5 g (2.1 mmol) of aqueous $CoCl_2 \cdot 6H_2O$ at ambient temperature. The pink precipitate that formed (**3**) was filtered off, washed with cold water, ethanol, and ether, and then air-dried (Anal. Calcd for $C_{16}H_{18}N_2O_8P_2Co$: C, 39.42; H, 3.69; N, 5.75. Found: C, 39.36; H, 3.42, N, 5.39). The red solution that remained was passed through a cation-exchange resin (Dowex 50W-X8 200–400 mesh) in the sodium form. The colorless eluate was evaporated to dryness, the solid was extracted with cold methanol, and the methanolic solution was evaporated to dryness yielding predominantly the *Z* isomer (>80% by $^1H$ and $^{31}P$ NMR). Repeating the procedure on the same sample yielded the *Z* isomer (0.175 g, 78% yield) in high purity (>95%).

**Preparation of Copper Bis[($\alpha$-(hydroxyimino)benzyl)phosphonate]–Water (4).** The pure isomer (*E*)-**2** (0.1 g, 0.42 mmol) was added to an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.036 g, 0.21 mmol), and immediately the light blue color turned green. Slow evaporation of the aqueous solution afforded light blue-green well-formed X-ray-quality crystals. One crystal with approximate dimensions of 0.3 mm × 0.2 mm × 0.2 mm was used for the diffraction study. Anal. Calcd for $C_{16}H_{20}N_2O_9P_2Cu$: C, 37.69; H, 3.95;, N. 5.49. Found: C, 37.30; H, 3.98; N, 5.30.

## X-ray Crystallography

**Collection and Reduction of X-ray Data.** The crystals were mounted on glass fibers by using epoxy. Data were collected on a PW 1100 Philips four-circle computer-controlled diffractometer. Mo K$\alpha$ ($\lambda$ = 0.71069 Å) radiation with a graphite crystal in the incident beam was used. Unit cell parameters were obtained by a least-squares fit of 25 high-angle reflections (13° < $\theta$ < 16°). Both data sets were collected in the $\omega$–2$\theta$ scan mode. The scan width, $\omega$, for each reflection was 1° with a scan time of 20 s. Background measurements were made at both limits of each scan. For each data set Lorentz and polarization corrections were applied. None of the data sets displayed any decay in the intensities of the three standard reflections, and no correction was applied. No absorption correction was applied. Other information pertinent to data collection and processing is given in Table II. The space group of (*E*)-**2** was uniquely determined as $P2_1/c$ by the systematic absences.[11] Similarly, the space group of **4** was determined to be $C2/c$.

**Solution and Refinement of the Structure.** The atomic coordinates for the non-hydrogen atoms of (*E*)-**2** were obtained by the direct-methods program SHELX-86. The coordinates of the Cu atom in **4** were obtained from a three-dimensional Patterson synthesis. In both cases, the heavy atoms were placed in their positions and the remaining non-hydrogen atoms were found in a series of subsequent difference Fourier maps. Neutral-atom scattering factors and anomalous dispersion corrections were obtained from ref 12. Anisotropic thermal parameters were used for all the non-hydrogen atoms in both structures. The aromatic hydrogens were placed in their calculated positions ($d$(C–H) = 0.95 Å), were constrained to "ride" on the carbon atoms, and were refined with a common thermal parameter for each aromatic ring.

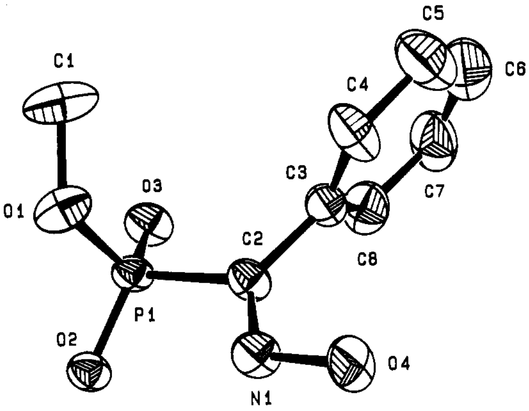

**Figure 1.** Structure of molecule 1 of the (*E*)-**2** anion, showing 50% probability thermal ellipsoids and atom-labeling scheme.

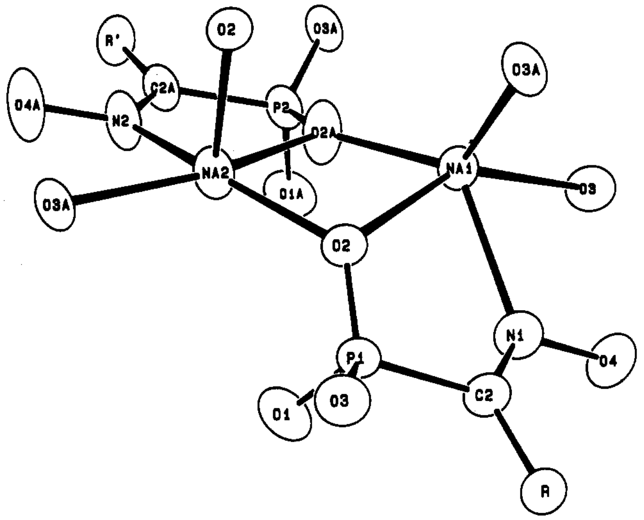

**Figure 2.** ORTEP diagram showing the interaction of the (*E*)-**2** anions with the sodium cations. For clarity's sake, the phenyl rings are represented by R and R′ and the methyl groups were omitted.

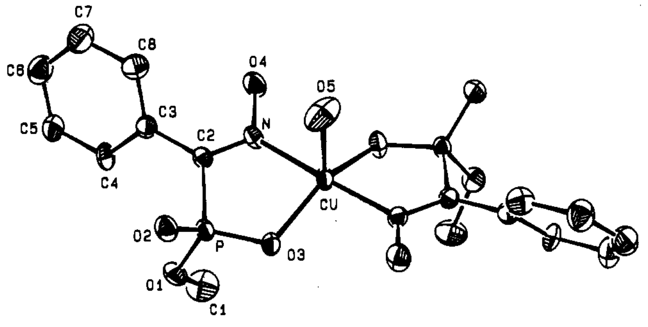

**Figure 3.** Structure and labeling scheme of the Cu complex of (*E*)-**2** (**4**), showing 50% probability ellipsoids. A 2-fold axis runs through O(5) and Cu.

With the use of SHELX-76,[13] full-matrix, least-squares refinement was carried out on 142 variables for structure **4**. Structure (*E*)-**2** was refined in two blocks, each containing one of the two independent molecules and both the sodium ions, by using 147 variables per block. Both refinements used unit weights and converged to reasonable discrepancy indices, which are listed in Table II.

Final non-hydrogen positional parameters, together with their estimated standard deviations, for both structures, appear in Table III. Important interatomic distances and bond angles, together with their standard deviations, are given in Table IV. Listings of the anisotropic thermal parameters, final observed and calculated structure factors, positional and thermal parameters of the hydrogen atoms, and bond

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**Table II.** Experimental Details of the X-ray Diffraction Studies of (*E*)-**2** and **4**

| | (*E*)-**2** | **4** |
|---|---|---|
| | (A) Crystal Parameters[a] | |
| formula | $NaPNO_4C_8H_9$ | $CuP_2N_2O_9C_{16}H_{20}$ |
| *a*, Å | 6.496 (1) | 17.774 (2) |
| *b*, Å | 31.998 (2) | 16.986 (1) |
| *c*, Å | 10.087 (1) | 7.279 (1) |
| β, deg | 92.82 (1) | 113.44 (1) |
| *V*, Å$^3$ | 2094 (1) | 2016 (1) |
| space group | $P2_1/c$ | *C*2/*c* |
| *Z* | 8 | 4 |
| *d*(calcd), g cm$^{-3}$ | 1.503 | 1.680 |
| *d*(obsd),[b] g cm$^{-3}$ | 1.48 | 1.65 |
| mol wt | 474.11 | 509.83 |
| | (B) Measurement of Intensity Data | |
| instrument | Philips PW 1100 | Philips PW 1100 |
| radiation | Mo Kα | Mo Kα |
| temp, °C | 23 | 23 |
| 2θ range, deg | 4–45 (±*h*,*k*,*l*) | 4–45 (±*h*,*k*,*l*) |
| | (C) Treatment of Intensity Data[c] | |
| μ, cm$^{-1}$ [d] | 2.42 | 12.16 |
| no. of unique data | 2834 | 1409 |
| no. of obsd unique data ($F_o > 6\sigma(F_o)$) | 2010 | 1136 |
| no. of params refined | 147 | 142 |
| max param shift in final refinement cycle | 0.01 | 0.01 |
| max electron dens on final refinement cycle, e Å$^{-3}$ | 0.399 | 0.48 |
| $R_1$[e] | 0.049 | 0.037 |
| $R_2$[f] | 0.057 | 0.041 |

[a] From a least-squares fit to the setting angles of 20 reflections with $2\theta > 25°$. [b] By suspension in $CHBr_3$/hexane. [c] $F_o$ and $\sigma(F_o)$ were corrected for background, attenuation, and Lorentz–polarization effects of X-radiation. [d] No absorption corrections were performed. [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

lengths and bond angles of the phenyl rings are available in Tables S1–S6, supplied as supplementary material. Figure 1 depicts the molecular structure and labeling scheme of the anion of (*E*)-**2** (molecule 1), and Figure 2 displays the coordination of the sodium ions. Figure 3 depicts the structure and labeling scheme of the copper complex (**4**).

## Quantum-Mechanical Calculations

Semiempirical calculations were carried out on sodium (*Z*)-methyl (α-(hydroxyimino)benzyl)phosphonate with a modified version of MNDO,[14] which has recently been corrected for its failure to describe hydrogen bonding appropriately.[15] Total geometry optimizations were done with estimations of second derivatives (Hessian matrix) for each of the 3*n*–6 parameters in each compound. The optimizations started from a few conformations in order to verify global minima.

## Results

**Preparation of Compounds.** The purification of the *Z* isomer of (α-(hydroxyimino)benzyl)phosphonate from a mixture (55:45) of the *E* and *Z* isomers was effected by the selective precipitation of the $Co^{2+}$ complex of the *E* isomer from aqueous solution. This procedure seemed most effective when the metal used was divalent cobalt and where the stoichiometric ratio between metal and the mixture of isomers was 1:1. The chemical analysis of the Co complex demonstrated that the complex contained two ligands per metal atom, and the IR spectra of the complex clearly indicated that the ligand bound to the metal was indeed the *E* isomer (vide supra). The excess $Co^{2+}$ was completely removed by cation exchange, and the remaining NaCl was removed by precipitating it with cold methanol. The two isomers can easily be distinguished either by $^1H$ or $^{31}P$ NMR spectroscopy, as is evident from resonances and multiplicities given in Table I.

The direct reaction in water between $CuCl_2{\cdot}2H_2O$ and (*E*)-**2** yielded the 2:1 complex, which is somewhat water soluble. In addition, some small quantities of a dark green compound were observed and as yet have not been characterized.

**X-ray Crystallography.** Figure 1 displays the structure of molecule 1 of the free ligand [anion of (*E*)-**2**], and the important metrical parameters appear in Table IV. The *E* configuration is clearly evident from Figure 1. We have considered the possibility that the two isomers might cocrystallize, resulting in disorder around the oxime moiety. The clean difference map around the nitrogen atoms in conjunction with the reasonable thermal parameters of O(4) and O(4A) seem to indicate that this is not the case. Moreover, the Na ions seem to interact with the nonbonding pairs of electrons on the nitrogen atoms, thus rendering the disorder impossible.

The chelating moiety, which is comprised of four atoms [O(2)–P–C–N], is not quite planar, with the torsion angles for the two molecules being 22.6 (5) and 17.2 (5)°. The dihedral angles between the phenyl rings and the chelating moieties are 70.0 (3) and 66.2 (4)°. The bond lengths and angles do not display any unusual features and are in agreement with literature values.[16] The geometry of the chelating moiety describes bite lengths of 2.839 (4) and 2.836 (4) Å. The sodium ions, which are the counterions for the ligand, do interact with the ligand itself. The sodium ion Na(1) is chelated by (*E*)-(α-(hydroxyimino)benzyl)phosphonate through the phosphonate oxygen O(2) and the oxyimino nitrogen (see Figure 2). The remaining coordination sphere is occupied with oxygen atoms from adjacent ligand molecules each acting as a monodentate ligand. The $PO_2^-$ unit acts as a bridging moiety between the two sodium atoms, and the remaining oxygen acts as a monodentate ligand. The coordination number of both sodium ions is five, and each is surrounded by four oxygen atoms and one nitrogen atom. The distances between the sodium ions and the first coordination sphere (see Table III) are in agreement with other such compounds.[16]

Figure 3 depicts the structure and labeling scheme of the copper complex of (*E*)-**2**. The five-coordinate copper is bound to two (*E*)-(α-(hydroxyimino)benzyl)phosphonates and one water molecule. The *E* isomer chelates the metal ion, with the oxime nitrogen and the phosphonate oxygen generating a five-membered planar chelate ring [the torsion angle O(3)–P–C(2)–N is –1.2 (4)°]. A crystallographic 2-fold axis passing through the water ligand O(5) and the copper atom generates a nearly trigonal-bipyramidal geometry around the copper atom, with the two nitrogen atoms occupying the axial positions and the oxygen atoms the equatorial ones. The bond angles describing this geometry are listed in Table IV. The nitrogen atoms of the two ligands are oriented trans to each other, as is required by the crystallographic 2-fold axis. This could be due to the greater steric crowding expected for the cis orientation.

Comparison of the geometry to that of the free ligand reveals that no significant changes have taken place as a result of complexation. The rotation of the C–P bond by approximately 20° results in the increased planarity of the chelating moiety and a reduced bite length of 2.714 (4) Å. Other bonds and angles and torsion angles are generally unchanged. The metal to ligand bond distances are in accordance with literature values for these types of compounds.[17]

**IR Spectroscopy.** Parts of the IR data are listed in Table V. The data allow a clear distinction between the two isomers. The most conspicuous characteristics of the *Z* isomer are a strong and sharp absorption at 3411 cm$^{-1}$, which is characteristic of hydrogen bonding, and absorptions at 895 and 621 cm$^{-1}$, which are absent in the *E* isomer. The assignment of the P=O, P—O—$CH_3$, and P—$O^-$ absorptions has been based on previous studies.[18-20] As

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**Table III.** Positional Parameters and Estimated Standard Deviations for (*E*)-**2** and **4**[a]

| | (*E*)-**2** molecule 1 | | | (*E*)-**2** molecule 2 | | | **4** | | |
|---|---|---|---|---|---|---|---|---|---|
| atom | *x* | *y* | *z* | *x* | *y* | *z* | *x* | *y* | *z* |
| M | 0.6177 (3) | 0.54515 (7) | 0.9168 (2) | 0.9588 (3) | 0.46816 (7) | 0.8706 (2) | 0.00000 (0) | 0.86234 (5) | 0.25000 (0) |
| P | 0.1084 (2) | 0.56859 (5) | 0.8165 (2) | 0.4666 (2) | 0.44377 (5) | 0.7864 (2) | 0.10628 (8) | 0.84267 (8) | 0.0275 (2) |
| O(1) | 0.1161 (6) | 0.5461 (1) | 0.6753 (4) | 0.4180 (6) | 0.4546 (2) | 0.6348 (4) | 0.1423 (2) | 0.7625 (2) | −0.0125 (5) |
| O(2) | −0.0012 (5) | 0.5384 (1) | 0.9005 (4) | 0.5969 (6) | 0.4776 (1) | 0.8446 (5) | 0.1219 (2) | 0.9028 (2) | −0.0998 (5) |
| O(3) | 0.3176 (5) | 0.5842 (1) | 0.8606 (4) | 0.2738 (5) | 0.4336 (1) | 0.8532 (4) | 0.0197 (2) | 0.8313 (2) | 0.0142 (5) |
| O(4) | −0.3869 (6) | 0.6381 (1) | 0.7716 (5) | 0.9372 (7) | 0.3668 (2) | 0.7897 (6) | 0.1641 (2) | 0.8824 (2) | 0.5956 (5) |
| N | −0.2509 (7) | 0.6048 (2) | 0.7968 (5) | 0.8148 (7) | 0.4030 (2) | 0.7924 (5) | 0.1227 (2) | 0.8660 (2) | 0.3958 (5) |
| C(1) | 0.269 (1) | 0.5583 (3) | 0.5817 (7) | 0.238 (1) | 0.4395 (3) | 0.5601 (7) | 0.1333 (4) | 0.6902 (3) | 0.083 (1) |
| C(2) | −0.0610 (8) | 0.6134 (2) | 0.7844 (6) | 0.6216 (8) | 0.3961 (2) | 0.7802 (6) | 0.1667 (3) | 0.8643 (3) | 0.2922 (6) |
| C(3) | 0.0244 (8) | 0.6548 (2) | 0.7467 (6) | 0.5202 (8) | 0.3551 (2) | 0.7616 (7) | 0.2556 (3) | 0.8812 (3) | 0.3693 (6) |
| C(4) | −0.006 (1) | 0.6702 (2) | 0.6201 (7) | 0.419 (1) | 0.3367 (2) | 0.8636 (8) | 0.3090 (3) | 0.8269 (3) | 0.3441 (8) |
| C(5) | 0.079 (1) | 0.7084 (2) | 0.5868 (9) | 0.317 (1) | 0.2983 (2) | 0.843 (1) | 0.3928 (3) | 0.8426 (4) | 0.4158 (8) |
| C(6) | 0.189 (1) | 0.7312 (2) | 0.680 (1) | 0.315 (1) | 0.2794 (3) | 0.722 (1) | 0.4225 (3) | 0.9134 (4) | 0.5097 (8) |
| C(7) | 0.225 (1) | 0.7159 (2) | 0.8065 (9) | 0.413 (1) | 0.2976 (2) | 0.620 (1) | 0.3697 (4) | 0.9676 (4) | 0.5356 (9) |
| C(8) | 0.140 (1) | 0.6776 (2) | 0.8398 (7) | 0.516 (1) | 0.3350 (2) | 0.6397 (8) | 0.2863 (3) | 0.9524 (3) | 0.4665 (8) |
| O(5) | | | | | | | 0.00000 (0) | 0.9880 (3) | 0.25000 (0) |

[a] M = Na for (*E*)-**2** and M = Cu for **4**. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

**Table IV.** Geometry (Å and deg) of Compounds (*E*)-**2** and **4**

| | (*E*)-**2** | (*E*)-**2** | **4** |
|---|---|---|---|
| | Bond Lengths for the Ligands | | |
| P(1)–O(1) | 1.599 (4) | 1.584 (4) | 1.581 (3) |
| P(1)–O(2) | 1.489 (4) | 1.477 (4) | 1.478 (4) |
| P(1)–O(3) | 1.495 (4) | 1.487 (4) | 1.514 (3) |
| P(1)–C(2) | 1.825 (6) | 1.830 (6) | 1.831 (4) |
| O(1)–C(1) | 1.455 (9) | 1.441 (9) | 1.452 (7) |
| O(4)–N(1) | 1.401 (6) | 1.407 (7) | 1.373 (4) |
| N(1)–C(2) | 1.276 (7) | 1.274 (7) | 1.285 (7) |
| C(2)–C(3) | 1.493 (8) | 1.475 (8) | 1.481 (6) |
| C(3)–C(4) | 1.37 (1) | 1.38 (1) | 1.388 (8) |
| C(3)–C(8) | 1.382 (9) | 1.39 (1) | 1.400 (7) |
| | Bond Angles for the Ligands | | |
| O(1)–P(1)–O(2) | 104.6 (2) | 107.9 (3) | 106.8 (2) |
| O(1)–P(1)–O(3) | 110.4 (2) | 110.7 (2) | 110.7 (2) |
| O(1)–P(1)–C(2) | 103.9 (2) | 103.5 (2) | 104.8 (2) |
| O(2)–P(1)–O(3) | 120.0 (2) | 117.3 (2) | 119.2 (2) |
| O(2)–P(1)–C(2) | 108.0 (2) | 108.6 (3) | 110.1 (2) |
| O(3)–P(1)–C(2) | 108.8 (2) | 108.1 (2) | 104.4 (2) |
| P(1)–O(1)–C(1) | 120.7 (4) | 123.4 (4) | 120.8 (3) |
| O(4)–N(1)–C(2) | 115.0 (5) | 114.2 (5) | 115.6 (5) |
| P(1)–C(2)–N(1) | 113.0 (4) | 113.1 (4) | 112.5 (4) |
| P(1)–C(2)–C(3) | 120.9 (4) | 120.1 (4) | 121.9 (3) |
| N(1)–C(2)–C(3) | 126.1 (5) | 126.7 (5) | 125.5 (5) |
| C(2)–C(3)–C(4) | 121.1 (5) | 120.8 (6) | 120.3 (5) |
| C(2)–C(3)–C(8) | 119.5 (6) | 121.0 (6) | 120.2 (5) |
| C(4)–C(3)–C(8) | 119.3 (6) | 118.2 (6) | 119.5 (5) |

| (*E*)-**2** | | (*E*)-**2** | | **4** | |
|---|---|---|---|---|---|
| | | Coordination Sphere of the Metals | | | |
| Na(1)–O(2) | 2.498 (4) | Na(2)–O(2) | 2.281 (4) | Cu–N | 2.011 (3) |
| Na(1)–O(3) | 2.361 (4) | Na(2)–O(2) | 2.322 (4) | Cu–O(3) | 1.955 (3) |
| Na(1)–N(1) | 2.435 (4) | Na(2)–N(2) | 2.401 (4) | Cu–O(5) | 2.135 (5) |
| Na(1)–O(2A) | 2.284 (4) | Na(2)–O(2A) | 2.372 (4) | | |
| Na(1)–O(3A) | 2.485 (4) | Na(2)–O(3A) | 2.340 (4) | | |
| | | Bond Angles for the Cu Complex (**4**) | | | |
| N–Cu–N′ | 176.5 (2) | O(3)–Cu–O(3′) | 148.7 (2) | | |
| N–Cu–O(3) | 86.3 (2) | O(3)–Cu–O(5) | 105.6 (1) | | |
| N–Cu–O(3′) | 94.6 (2) | Cu–N–O(4) | 125.2 (3) | | |
| N–Cu–O(5) | 88.3 (1) | Cu–N–C(2) | 118.4 (4) | | |

**Table V.** 1R Absorption Spectra (cm$^{-1}$) for (*Z*)-**2**, (*E*)-**2**, **3**, and **4**

| (*E*)-**2** | (*Z*)-**2** | **3** | **4** | assgnt |
|---|---|---|---|---|
| 3383 b | 3411 vs | 3211 | 3281 | O–H |
| | | | 1776 m | Cu–$H_2O$ |
| 1221 | 1241 | 1187 | 1206 | P–O |
| 1087 | 1111 | 1051 | 1060 | P–O–$CH_3$ |
| 1075 | 1028 | 1038 | | P–O–$CH_3$ |
| 1007 | | 1016 | 1003 | |
| 970 | | 986 | | |
| | 895 | | | |
| 726 | | 731 | | |
| | 621 | | | |
| 587 | | | | |

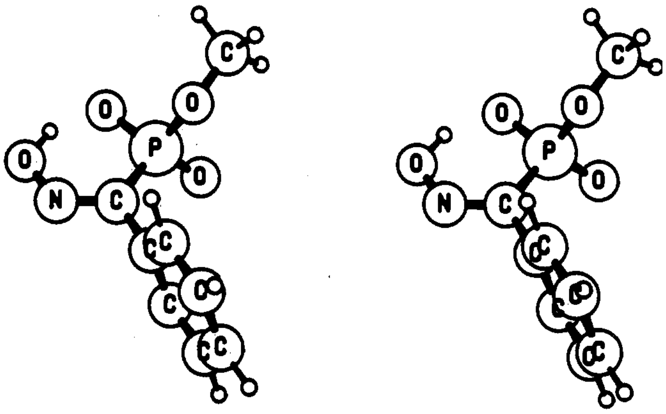

**Figure 4.** Stereoview of the "gas-phase" hydrogen-bonded optimal structure of (*Z*)-**2**.

a consequence of the metal binding, the complexes clearly display a red shift in the $P{=}O$ stretching frequency. The $P{=}O$ frequency of the $Co^{2+}$ complex is lower by 34 cm$^{-1}$ than that of the free ligand, while the corresponding shift for the copper complex is 15 cm$^{-1}$.

**Theoretical Calculations.** Calculation of the structure of sodium (*Z*)-methyl (α-(hydroxyimino)benzyl)phosphonate has revealed two optimized structures. One having an intramolecular hydrogen bond that stabilizes the structure and its global minima is depicted in Figure 4. It has a hydrogen bond between the oxime oxygen and the phosphoryl function. The existence of such a bond is evident from the atom–atom bond density matrix. The density between the acceptor phosphoryl oxygen and the donor hydroxyl proton is 0.0850 (distance of 1.432 Å), while the antibonding density among the two oxygens involved is −0.0088 ($R$ = 2.396 Å). These are values that were previously found to be characteristic of H-bonding. The stabilization carried by the H-bond becomes evident when the proton's position is "forced" to rotate from its optimal H-bonding arrangement. Some 15 kcal is lost when it is rotated to an "anti" direction with respect to the phosphoryl oxygen.

## Discussion

While it has been possible to obtain the pure *E* isomer of **2**, the *Z* isomer remained inaccessible, and previous studies probing the chemistry of the isomers had to be performed on isomeric mixtures. We were able to come up with a facile method for obtaining the *Z* isomer in good yield and high purity by capi-

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(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley and Sons: New York, 1977; pp 226–230.

(20) (a) Mikulski, C. M.; Henry, W.; Pytlewski, L. L.; Karayannis, N. M. *J. Inorg. Nucl. Chem.* **1978**, *40*, 769. (b) Mikulski, C. M.; Henry, W.; Pytlewski, L. L.; Karayannis, N. M. *Transition Met. Chem.* (*Weinheim, Ger.*) **1977**, *2*, 135.

talizing on the different metal-binding properties of the two isomers.

While we do not know the binding mode of the $Co^{2+}$ complex, the copper complex resulted in a mononuclear species where each ligand acts solely as a bidentate ligand and the two ligands are disposed trans to one another. The capability of divalent copper to display coordination numbers of 4, 5, and 6 and to adopt various coordination geometries (square planar, tbp, square pyramidal, distorted octahedral)[21] in conjunction with the versatility of these ligands give rise to a number of possible interactions ranging from monomers through dimers to polymers. Under these specific conditions we have obtained the compound that has been described. It is entirely possible that other structures will be found in the future.

Both the $^1H$ and $^{31}P$ NMR spectra are affected in a similar way by the shielding of the oxime oxygen. The close proximity to the methyl group in the *Z* isomer and to the aromatic H(4) and H(8) protons in the *E* isomer causes an upfield shift in both cases. The same trend is observed in the $^{31}P$ spectra. This trend is in agreement with our previous measurements of the dimethyl ($\alpha$-(hydroxyimino)benzyl)phosphonates, where each isomer has been characterized crystallographically, and thus the NMR spectra were unambiguously assigned.[2]

The infrared spectra allow for easy identification of the isomers and detection of metal binding and demonstrate the existence of a hydrogen bond in the *Z* isomer.

It is interesting that both the cobalt and copper ions reacted preferentially with the *E* isomer of ($\alpha$-(hydroxyimino)benzyl)-phosphonate. Chart I and CPK models demonstrate that at least in principle both isomers are capable of chelating metal ions. The *E* isomer can do so through the phosphonate oxygen and the oxime nitrogen, forming a five-membered chelate ring, while the *Z* isomer could bind the metal atom through the phosphonate oxygen and the oxime oxygen, forming a six-membered chelate ring. When a mixture of the *E* and *Z* isomers of the closely related compounds, where the oxime hydrogen had been replaced by a methyl group, was allowed to react with cupric chloride dihydrate, we have isolated a complex where the metal ion was bound to the *Z* isomer displaying the latter mode of chelation.[22] These results could be due to two main effects: the formation of an intramolecular hydrogen bond between the oxime and phosphonate moieties in the *Z* isomer of ($\alpha$-(hydroxyimino)benzyl)phosphonate and the increased basicity of the oxime oxygen upon methylation. While we do not have direct experimental evidence to prove the existence of such an intramolecular hydrogen bond in solution, we do have semiempirical calculations that predict the existence of such a bond. Our IR results clearly show the existence of a hydrogen bond (a sharp peak at 3411 $cm^{-1}$ for the *Z* isomer only) though we have not been able to determine whether it is inter- or intramolecular. Moreover, the studies of Berlin et al. on a series of dialkyl $\alpha$-hydroxyimino phosphonates have demonstrated the existence of such an intramolecular hydrogen bond in chloroform solutions,[6] and Breuer et al. suggested this hydrogen-bond formation in an attempt to explain the mechanism of the thermal fragmentation of dimethyl ($\alpha$-(hydroxyimino)benzyl)phosphonate.[2] If such a hydrogen bond were formed by a solvent molecule rather than by the oxime hydrogen, than it is to be expected that the methyl ether would form a hydrogen bond stronger than that of the corresponding free oxime. Thus, it would seem reasonable to suggest that the intramolecular hydrogen bond does exist in solution and prevents the chelation of metal ions by (*Z*)-**2**.

## Conclusions

The existence of an intramolecular hydrogen bond in the *Z* isomer of sodium methyl ($\alpha$-(hydroxyimino)benzyl)phosphonate prevents the *Z* isomer from readily interacting with cupric ion in aqueous solution. On the other hand, the *E* isomer is very reactive toward divalent metal ions in aqueous solutions and this reactivity provided the basis for the successful separation of the *E* and *Z* isomers. Although we have demonstrated only one mode of interaction between these novel ligands and metal ions, there undoubtedly are many possibilities, which we are currently investigating.

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**Registry No.** (*E*)-**1**, 114142-43-7; (*Z*)-**1**, 114142-46-0; **2**·Na, 119878-70-5; (*Z*)-**2**·Na, 119878-71-6; (*E*)-**2**·Na, 119878-72-7; **4**, 119878-73-8.

**Supplementary Material Available:** Tables S1, S3, S5, and S6, listing thermal parameters, positional and thermal parameters of hydrogen atoms, and nonessential bond lengths and angles (3 pages); Tables S2 and S4, listing structure factors (18 pages). Ordering information is given on any current masthead page.

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(21) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 800–821.

(22) Gibson, D. Unpublished results. The compound copper bis[(*Z*)-methyl ($\alpha$-(methoxyimino)benzyl)phosphonate]-2-water crystallized in the space group $P2_1/c$ with unit cell dimensions of $a = 12.728$ (2) Å, $b = 8.775$ (1) Å, $c = 11.236$ (1) Å, $\beta = 91.73$ (1)°, $V = 1254$ (1) Å$^3$, and $Z = 2$. The structure was refined to discrepancy factors of $R_1 = 0.044$ and $R_2 = 0.053$.