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Crystal Structure and ¹⁴N Nuclear Quadrupole Resonance Spectrum of Catena- μ -imidazolato-bis(imidazole)zinc Nitrate. Donor Characteristics of Coordinated Imidazolate¹

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Abstract: The X-ray structure determination of catena- μ -imidazolato-bis(imidazole)zinc nitrate (**1**) reveals approximately tetrahedral coordination about each zinc. The structure consists of chains of bis(imidazole)zinc units bridged by imidazolate anions. Zn-N distances range from 1.986 (3) to 2.000 (3) Å, with no clear difference between the neutral and anionic ligand-metal distances. Pertinent crystallographic data: [Zn(C₃N₂H₄)₂C₃N₂H₃]_nNO₃, space group *P2₁/c*, *a* = 12.184 (3), *b* = 10.040 (2), *c* = 11.354 (2) Å; β = 91.00 (2)°; *Z* = 4; *R*₁ = 0.047 for 2043 observed reflections [with *I* > 2 σ (*I*)]. The ¹⁴N NQR spectra at 77 K were obtained for **1** and bis(imidazolato)cadmium. Application of the model previously developed for ¹⁴N NQR spectra of coordinated imidazole leads to the conclusion that the bridging imidazolato ligand is a slightly stronger donor than neutral imidazole.

The imidazole moiety is of great biochemical importance owing to its presence in the side chain of the amino acid histidine. In histidine, the p*K*_a of the imino nitrogen of imidazole is 6.09, which makes it possible for imidazole to function as either a proton donor or acceptor.² This ability is important in the proposed mechanisms of action of both chymotrypsin³ and ribonuclease A.⁴

The amino nitrogen of imidazole in histidine has a p*K*_a of 14.4,⁵ which is very similar to the p*K*_a of 14.2–14.5 observed for imidazole itself.⁶ However, upon coordination to Zn(II), the p*K*_a of imidazole is lowered to between 7.0 and 7.3,⁷ making possible the ready involvement of the amino nitrogen in proton transfer processes. A similar effect is seen in the Co(II) complex of cyclic-L-histidyl-L-histidine, which has a p*K*_a of 8.5.⁷ The p*K*_a of a water molecule bound to a zinc coordinated to four *N*-methylimidazole ligands is 9.12.⁷ The greater acidity of the amino nitrogen has led Appleton and Sarkar to propose that the nucleophilic hydroxide which attacks CO₂ in the active site of carbonic anhydrase may not be coordinated to zinc,⁸ but instead is generated by abstraction

of a proton from a water molecule by a zinc-bound imidazolate of one of the three metal-binding histidine residues.^{7,9}

A zinc-bound imidazolate ring is also of importance in the active site of superoxide dismutase, as revealed by a recent X-ray structure determination.¹⁰ The imidazole ring of HIS-61 is bound to both zinc and copper in the active site. It has been suggested that this interaction is responsible for the organization and maintenance of the active site structure.¹¹ The other zinc ligands are neutral histidines.

In light of these considerations, complexes involving the anionic imidazolato (Im⁻) ligand in which the metal ion environment is structurally similar to that expected in metalloenzymes are clearly of interest. Polymeric complexes of the form [M(Im⁻)₂]_∞ for M = Zn,^{12,13} Cd,¹³ Cu,^{14,15} Co,^{12,16,17} and Ni¹⁶ have been reported. (The symbol Im⁻ is employed to distinguish imidazolate anion from neutral imidazole, Im.) The structure of the Zn compound has been determined. Zinc is tetrahedrally coordinated to four bridging imidazolato ligands, resulting in a three-dimensional network.¹⁸ The only reported mixed imidazole-imidazolato complex, Cu-

Table II. ^{14}N NQR Data for Imidazolate-Containing Complexes at 77 K

Assignment	ν_+ ^a	ν_- ^a	ν_0 ^a	e^2Qq_{zz}/h ^a	η
[Zn(Im) ₂ (Im ⁻)](NO ₃) imino	1769	1061	708	1887	0.751
	1718	1033	685	1834	0.747
amino	1325	662	662	1325	1.00
	1387	722	615	1439	0.855
imidazolato	1926	1041	885	1978	0.895
	1906	1021	885	1951	0.907
nitrate Cd(Im ⁻) ₂	560				
	1838	1206	632	2029	0.623
	1733	1042	691	1850	0.746
	1653	968	685	1747	0.784

^a kHz.

(Im)₂(Im⁻)Cl, consists of pentacoordinate copper linked by bridging imidazolato groups to form chains.²⁰ We report here the synthesis and structure of [Zn(Im)₂(Im⁻)](NO₃), and the ^{14}N NQR spectra of this new substance and polymeric Cd(Im⁻)₂.

Experimental Section

Catena- μ -imidazolato-bis(imidazole)zinc(II) Nitrate. [Zn(Im)₂(Im⁻)](NO₃) was prepared from an aqueous solution of Zn(NO₃)₂ and imidazole in a 1:6 molar ratio. Crystals form in 1–2 days. The substance exhibits low solubility in water, ethanol, and acetone; the crystals obtained from the initial preparations were not recrystallized. Anal. Calcd for Zn(Im)₂(Im⁻)(NO₃): Zn, 19.70; C, 32.73; H, 3.33; N, 29.70. Found: Zn, 19.65; C, 32.17; H, 3.10; N, 29.37. The complex was also obtained as the second product in an attempted preparation of a mixed imidazole-oxalato complex. To an aqueous solution of Zn(NO₃)₂ and imidazole in 1:2 molar ratio was added 1 equiv of sodium oxalate. An initial precipitate was removed by filtration; crystals of [Zn(Im)₂(Im⁻)](NO₃) appeared in the filtrate in approximately 4 days. Found: Zn, 19.63; C, 32.43; H, 3.12; N, 29.84. A crystal from the oxalate-containing solution was employed in the X-ray study.

The polymers, [Zn(Im⁻)₂] and [Cd(Im⁻)₂], were prepared by the method of Bauman and Wang¹³ using metal nitrate salts. Satisfactory elemental analyses were obtained for both substances.

Tetrakis(imidazole)zinc(II) nitrate, [Zn(Im)₄](NO₃)₂, was prepared as previously reported.²¹

Infrared spectra were obtained as Nujol mulls using a Beckman Model 4240 spectrophotometer. The NQR spectra were obtained at 77 K, using the double resonance technique described previously.²²

Results

The infrared spectrum of [Zn(Im)₂(Im⁻)](NO₃) is a composite of the spectra of Zn(Im⁻)₂ and [Zn(Im)₄](NO₃)₂ (Table I).²³ Bands which may be assigned to N–H stretching and bending modes^{24a} are observed, indicating the presence of coordinated imidazole. Similarly, bands which correspond to those observed in the spectrum of Zn(Im⁻)₂, but absent in the spectrum of [Zn(Im)₄](NO₃)₂, indicate the presence of imidazolato anion.

The ^{14}N NQR spectrum indicates the presence of seven distinct nitrogen environments (Table II). Six are assigned to the imidazole and imidazolato ligands; the seventh is assigned to the nitrate ion.

Crystal Data. ZnO₃N₇C₉H₁₁, mol wt 330.7 amu, monoclinic, $a = 12.184$ (3) Å, $b = 10.040$ (2) Å, $c = 11.354$ (2) Å, $\beta = 91.00$ (2)°, $V = 1388.8$ Å³, $Z = 4$, $\rho_c = 1.58$ g/cm³, $\mu(\text{Cu K}\alpha) = 27.4$ cm⁻¹, $F(000) = 672$, systematic absences for $0k0$ when $k = 2n + 1$ and $h0l$ when $l = 2n + 1$ establish the space group as $P2_1/c$. The cell dimensions were obtained from a least-squares fit to the automatically centered settings for 15 reflections on a Syntex P2₁ diffractometer equipped with a graphite monochromator, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å.

A crystal of dimensions ca. $0.3 \times 0.3 \times 0.3$ mm was used for data collection. The data collection was performed in the $2\theta:\theta$

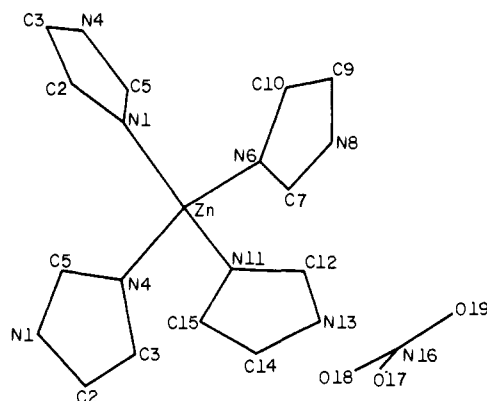


Figure 1. Coordination about the zinc center in the solid state structure of [Zn(Im)₂(Im⁻)](NO₃).

scan mode. The variable scan option was used (2.0–10.0°/min) with the total background/scan time set at 0.25. Three standards from different parts of the reciprocal space were monitored every 50 reflections. Examination of these standards revealed no crystal deterioration. The $\bar{h}k\bar{l}$ and $\bar{h}kl$ octants were collected out to $2\theta = 126^\circ$ ($\sin \theta/\lambda = 0.578$). A total of 2372 unique reflections were collected with 2043 observed reflections (using a $2\sigma(I)$ criterion based on counting statistics). The data were corrected for Lorentz and polarization effects but not absorption.

The structure was solved by direct methods using the programs supplied by Syntex.²⁵ An E map clearly showed the Zn and one imidazole ring. A weighted Fourier map revealed the missing nonhydrogen atoms. The nonhydrogen atoms were refined with anisotropic thermal parameters to a value of $R = 0.06$ and $R_w = 0.106$ ($R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w |F_o| - |F_c|]^2 / \sum w |F_o|^2]^{1/2}$).²⁶ Six of the 11 hydrogen atoms were located in a difference map and were included in the refinements with isotropic thermal parameters. The positions of the remaining hydrogen atoms were calculated and allowed to vary. The hydrogen atoms, H5 and H8, would refine to positions too close (~ 0.3 – 0.5 Å) to the atoms they are bonded to. A difference map showed two separate areas of residual electron density about the area of H13. For these reasons, the positions of the 3 hydrogen atoms were fixed in subsequent refinements.

The final refinement with 216 parameters and 2043 reflections gives agreement factors $R_1 = 0.047$, $R_2 = 0.068$ with $[(\sum w (F_o - F_c)^2) / (m - n)]^{1/2} = 1.45$ where m is the number of observations and n is the number of parameters. A final difference map shows no electron density above 40% of a hydrogen atom.

Description of the Structure. The structure is depicted in Figures 1 and 2. Each zinc cation is tetrahedrally coordinated

Table III. Bond Lengths in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$

Zn-N ₁	1.986 (3)	N ₈ -C ₉	1.351 (9)	H ₂ -C ₂	1.10 (7)
Zn-N _{4'}	1.994 (3)	C ₉ -C ₁₀	1.370 (7)	H ₃ -C ₃	1.06 (6)
Zn-N ₆	2.000 (3)	N ₆ -C ₁₀	1.373 (6)	H ₅ -C ₅	1.01 (4)
Zn-N ₁₁	1.991 (3)	N ₁₁ -C ₁₂	1.316 (6)	H ₇ -C ₇	1.05 (6)
N ₁ -C ₂	1.342 (7)	C ₁₂ -N ₁₃	1.333 (7)	H ₈ -N ₈	1.01 (5)
C ₂ -C ₃	1.354 (8)	N ₁₃ -C ₁₄	1.347 (8)	H ₉ -C ₉	0.77 (5)
C ₃ -N ₄	1.352 (6)	C ₁₄ -C ₁₅	1.349 (8)	H ₁₀ -C ₁₀	1.06 (5)
N ₄ -C ₅	1.328 (5)	N ₁₁ -C ₁₅	1.381 (6)	H ₁₂ -C ₁₂	0.88 (5)
N ₁ -C ₅	1.318 (5)	N ₁₆ -O ₁₇	1.267 (5)	H ₁₃ -N ₁₃	0.99 (4)
N ₆ -C ₇	1.313 (5)	N ₁₆ -O ₁₈	1.215 (5)	H ₁₄ -C ₁₄	1.01 (6)
C ₇ -N ₈	1.320 (6)	N ₁₆ -O ₁₉	1.216 (6)	H ₁₅ -C ₁₅	0.80 (8)

Table IV. Bond Angles in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ (See Figure 1)

N ₁ -Zn-N _{4'}	111.5 (1)	H ₃ -C ₃ -N ₄	112 (3)	C ₁₄ -C ₁₅ -N ₁₁	108.8 (5)
N ₁ -Zn-N ₆	106.5 (1)	H ₅ -C ₅ -N ₁	122.5 (4)	C ₁₅ -N ₁₁ -C ₁₂	105.5 (4)
N ₁ -Zn-N ₁₁	112.7 (1)	H ₅ -C ₅ -N ₄	123.5 (4)	C ₁₅ -N ₁₁ -Zn	128.0 (3)
N _{4'} -Zn-N ₆	110.6 (1)	H ₇ -C ₇ -N ₆	120 (3)	H ₉ -C ₉ -N ₈	125 (4)
N _{4'} -Zn-N ₁₁	105.9 (1)	H ₇ -C ₇ -N ₈	129 (3)	H ₉ -C ₉ -C ₁₀	128 (4)
N ₆ -Zn-N ₁₁	109.7 (1)	H ₈ -N ₈ -C ₇	124.4 (5)	H ₁₀ -C ₁₀ -N ₆	123 (3)
Zn-N ₁ -C ₂	125.4 (3)	H ₈ -N ₈ -C ₉	127.6 (5)	H ₁₀ -C ₁₀ -C ₉	129 (3)
N ₁ -C ₂ -C ₃	108.6 (5)	Zn-N ₆ -C ₇	126.6 (3)	H ₁₂ -C ₁₂ -N ₁₁	127 (3)
C ₂ -C ₃ -N ₄	108.8 (5)	N ₆ -C ₇ -N ₈	111.1 (4)	H ₁₂ -C ₁₂ -N ₁₃	122 (3)
C ₃ -N ₄ -C ₅	103.8 (4)	C ₇ -N ₈ -C ₉	108.0 (5)	H ₁₃ -N ₁₃ -C ₁₂	125.5 (4)
N ₄ -C ₅ -N ₁	114.0 (3)	N ₈ -C ₉ -C ₁₀	106.8 (5)	H ₁₃ -N ₁₃ -C ₁₄	126.5 (5)
C ₅ -N ₁ -C ₂	104.7 (4)	C ₉ -C ₁₀ -N ₆	107.4 (4)	H ₁₄ -C ₁₄ -N ₁₃	125 (3)
C ₅ -N ₁ -Zn	129.8 (3)	C ₁₀ -N ₆ -C ₇	106.7 (4)	H ₁₄ -C ₁₄ -C ₁₅	128 (3)
Zn-N ₄ -C ₃	123.5 (3)	C ₁₀ -N ₆ -Zn	126.4 (3)	O ₁₇ -N ₁₆ -O ₁₈	119.1 (4)
Zn-N ₄ -C ₅	132.7 (3)	Zn-N ₁₁ -C ₁₂	126.3 (3)	O ₁₇ -N ₁₆ -O ₁₉	118.9 (4)
H ₂ -C ₂ -N ₁	122 (4)	N ₁₁ -C ₁₂ -N ₁₃	110.9 (4)	O ₁₈ -N ₁₆ -O ₁₉	122.0 (4)
H ₂ -C ₂ -C ₃	130 (4)	C ₁₂ -N ₁₃ -C ₁₄	108.1 (4)	N ₈ -H ₈ -O ₁₇	165 ^a
H ₃ -C ₃ -C ₂	139 (3)	N ₁₃ -C ₁₄ -C ₁₅	106.7 (5)	N ₁₃ -H ₁₃ -O ₁₇	157 ^a
				H ₁₅ -C ₁₅ -C ₁₄	140 (6)
				H ₁₅ -C ₁₅ -N ₁₁	110 (6)

^a Hydrogen bond angles.

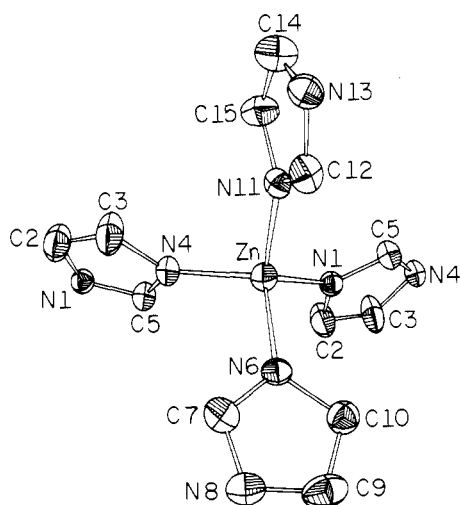


Figure 2. Thermal ellipsoids at 30% probability for zinc and coordinated ligands in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$.

to two imidazole rings and to two bridging imidazolate anions which are related to each other by the 2_1 symmetry element x, y, z and $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ (see Tables III and IV, bond lengths and bond angles). The imidazole and imidazolate rings are planar to within 2 standard deviations (Table V).²³ The rings are twisted slightly out of the plane of the bond to the Zn^{2+} .

The crystal lattice can be described as stacks of infinite $([\text{Zn}(\text{Im})_2(\text{Im}^-)]^+)_n$ chains with interleaving layers of NO_3^- anions (Figure 3). The nitrate anion is involved in hydrogen bonding with the imidazole rings (intermolecular contacts), through O₁₇ with nitrogens N₈ and N₁₃.

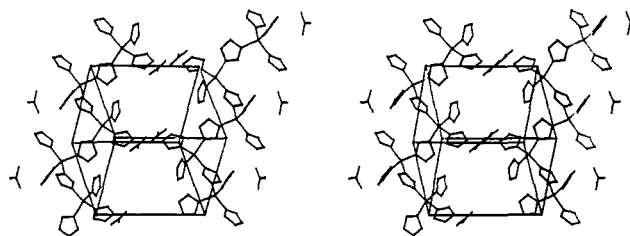


Figure 3. Stereoview of the lattice packing in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$.

The O₁₇-N₈ and O₁₇-N₁₃ intermolecular distances are within the reported range of NH—O hydrogen bonds²⁷ and account for a lengthening of the N₁₆-O₁₇ bond within the nitrate ion.

Discussion

The X-ray structural results for $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ reveal that zinc is coordinated in the expected tetrahedral arrangement by two imidazole and two bridging imidazolato ligands. The space group symmetry requirements dictate that there is one unique formula unit per unit cell. Thus there should be six distinct nitrogen signals characteristic of the imidazole moieties, two each for the amino and imino nitrogens of the imidazole rings and two for the nitrogens of the bridging imidazolato ligand. The ¹⁴N NQR spectrum for the solid at 77 K is in agreement with these expectations.

It is relatively easy to identify the transitions due to the amino nitrogens by analogy with the data discussed in the previous paper. However, the distinction between the imino nitrogens of the neutral and anionic ligands is not so obvious. Figure 4 shows the previously established relationship²¹ between $h/e^2 Qq_{zz}$ and η for the coordinated imino nitrogen of imidazole, along with the seven points representing the data

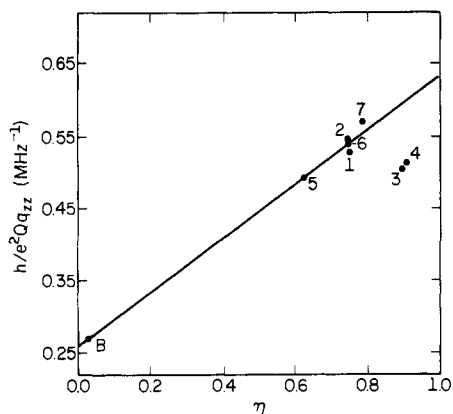


Figure 4. Relationship between h/e^2Qq_{zz} and η for coordinated imino nitrogens of imidazole.²¹ Data sets 1, 2, 3, and 4 correspond to $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$; sets 5, 6, and 7 correspond to $\text{Cd}(\text{Im}^-)_2$.

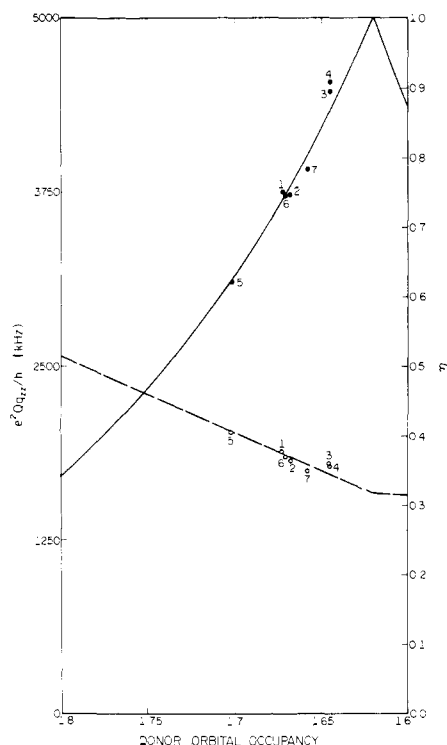


Figure 5. Relationship between e^2Qq_{zz}/h (dashed line) and η and nitrogen donor orbital occupancy σ for coordinated imidazole.²¹ The data points shown correspond to the observed ¹⁴N resonances for $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ (1,2, coordinated neutral imidazole; 3,4, bridging imidazolate); 5,6,7, $\text{Cd}(\text{Im}^-)_2$.

for $\text{Cd}(\text{Im}^-)_2$ and $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$, Table II. The data for the cadmium complex and two of the data sets for the zinc complex fit the observed relationship very well. The remaining two data sets for the zinc complex are clearly a much poorer fit.

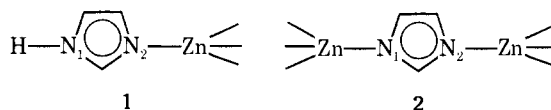
Figure 5 shows a portion of the previously established relationships²¹ between e^2Qq_{zz}/h or η and the donor orbital occupancy σ for coordinated imidazole, along with the data points for imino type nitrogens from Table II. The two data sets for the zinc complex that do not fit well are placed along the σ axis so as to minimize the total discrepancy in the fits to the e^2Qq_{zz}/h and η relationships.^{22b} The resulting σ values are listed in Table VI.

A comparison of the donor characteristics of neutral and bridging anionic ligands can conveniently be made with reference to **1** and **2**. Bridging Im^- , as in **2**, should be a stronger

Table VI. Donor Orbital Occupancies of Coordinated Imidazole

compd	σ
$[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$	1.672 ± 0.003
imidazole	1.667 ± 0.004
imidazolato	1.64 ± 0.01
$[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2^a$	1.707 ± 0.001
	1.692 ± 0.006
$[\text{Zn}(\text{Im})_4](\text{NO}_3)_2^a$	1.691 ± 0.005
$[\text{Zn}(\text{Im})_2(\text{NO}_3)_2]^a$	1.684 ± 0.005
$\text{Cd}(\text{Im}^-)_2$	1.701 ± 0.001
	1.670 ± 0.001
	1.657 ± 0.008

^a Reference 21.



donor toward the metal ion, because N1 in the bridging anion is bound to a more weakly acidic center than in the neutral ligand, in which N1 is bound to a proton. The NQR data suggest that in **1** the donor orbital occupancy, σ , of N1 is in the vicinity of 1.4, whereas in **2**, σ is in the range of 1.7. Thus, via inductive effects, N2 should be a stronger donor in bridging Im^- than in neutral imidazole. On these grounds the pair of points that fit well to the line at $\sigma = 1.672$ and 1.667 can be assigned to the imino nitrogens of neutral imidazole, and the two points corresponding to $\sigma = 1.64$ to the nitrogens of the bridging imidazolate.

The data for $\text{Cd}(\text{Im}^-)_2$ provide support for this assignment. The three sets of data for this compound all fit very close to the e^2Qq_{zz}/h and η relationships for coordinated imino nitrogen, as shown in Figure 4. The values of σ derived from the graph, Table VI, are all substantially below the value for neutral imidazole coordinated to four-coordinate Cd^{2+} ,²¹ as expected for the more strongly basic anionic ligand.

However, this assignment of imidazolate resonances presents us with a difficulty in accounting for the relative values of σ for neutral imidazole in the series of complexes listed in Table VI. If imidazolate is a more strongly donating ligand than neutral imidazole, then the zinc in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ should have a lower effective nuclear charge toward the two neutral imidazoles than the zinc in $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$ or $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$. Yet σ is *higher* for the $\text{Zn}(\text{Im})_4^{2+}$ species. Furthermore, the fit of the data assigned to imidazolate in $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ to the derived relationship displayed in Figure 5 is decidedly poorer than for other coordinated imidazole or imidazolate.

Since ¹⁴N NQR data for $\text{Cd}(\text{Im}^-)_2$ fit the graphical relationship shown in Figure 3 so well, it is of some interest to know why the bridging Im^- ligand of $[\text{Zn}(\text{Im})_2(\text{Im}^-)](\text{NO}_3)$ fits relatively poorly. The X-ray structural results do not reveal an exceptional distortion of the bridging ligand itself. However, the metal-nitrogen bond axes are 2.2 and 4.6° off the bisectors of the C-N-C ring bond angles. Calculations of the effects of such distortions for a proton coordinated to the imino nitrogen of imidazole do not reveal a very large dependence of the field gradient parameters on a distortion of this magnitude.²⁸ However, the change in η predicted by the calculations is in the observed direction. Because the charge distribution is different in the bridging anionic ligand, such a structural perturbation might effect a change of the observed magnitude in field gradient parameters. In any case, while the derived value for σ is less precise than we would like, the conclusion that σ is indeed lower in bridging Im^- than in neutral Im seems soundly based for both the cadmium and zinc complexes. It should be kept

in mind that in a metalloenzyme, a deprotonated, coordinated imidazole will in some cases possess an N1 nitrogen with an unshared electron pair that is free except for hydrogen bonding interactions with the surroundings. Such an imidazolate ligand should be more strongly donating toward the metal than the bridged imidazolate ligands observed here.

Two fairly obvious conclusions are supported by the present NQR results. On the one hand, replacement of a neutral ligand in the zinc coordination sphere by an anionic ligand will in general cause a decrease in the effective charge on the metal, and result in a lower extent of charge transfer from imidazole.²¹ Such a result would occur, for example, upon replacement of coordinated water by a carboxylate group. Obversely, the acidity of the proton bound to the amino nitrogen of coordinated imidazole varies in proportion to the extent of charge transfer from coordinated nitrogen. It has been suggested that in carbonic anhydrase the protonation-deprotonation equilibrium involving a coordinated imidazole might be involved in CO₂ hydration-dehydration.⁷ In this connection it is interesting that imidazole acts as a competitive inhibitor of human carbonic anhydrase B.²⁹ The action of imidazole could be accounted for in terms of a mechanism involving imidazole ionization as suggested; replacement of the coordinated water by the more strongly basic imidazole should increase pK_a for the already coordinated imidazoles of the protein, and thus turn off a key step in the enzymatic reaction.

Supplementary Material Available: Infrared spectra of [Zn(Im)₂(Im⁻)](NO₃), Zn(Im⁻)₂ and [Zn(Im)₄](NO₃)₂, Table I; selected best planes and deviations from selected planes for [Zn(Im)₂(Im⁻)](NO₃), Table V; structure factor amplitudes, atomic coordinates, and thermal ellipsoid parameters (15 pages). Ordering information is given on any current masthead page.

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