

^{14}N Nuclear Quadrupole Resonance Spectra of Coordinated Imidazole¹

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Abstract: The ^{14}N NQR spectra at 77 K have been measured for *N*-benzylimidazole, imidazolium iodide, imidazolium nitrate, and 1:1 zinc and cadmium complexes of imidazole. The changes in field gradient tensor at the imino nitrogen upon coordination have been related to the extent of electron donation to the Lewis acid center, using a modified Townes–Dailey model. Changes in field gradient tensor at the amino nitrogen are small, as expected. The NQR results suggest strongly that neutral ligands such as imidazole effectively transfer less electronic charge to the metal than most anionic ligands, e.g., than halides. However, anions such as nitrate, in which the charge is substantially delocalized, are less electron donating.

Introduction

As the side chain of the amino acid histidine, imidazole is an important component of many proteins. It has been assigned an important role in the functioning of many enzymes. For example, it plays an essential role in the “charge relay” mechanism that is thought to operate in the proteolytic enzyme chymotrypsin^{3,4} and in ribonuclease A.⁵ Imidazole also functions as the metal binding site in many metalloenzyme systems. Its involvements in the binding of zinc in carboxypeptidase,⁶ carbonic anhydrase,⁷ yeast alcohol dehydrogenase,⁸ and superoxide dismutase⁹ are of especial interest.

Because the imidazole nitrogens are not involved in the peptide bonds of the protein chain, they form readily available bonding sites for metal ions. In imidazole itself only the imino nitrogen is a likely binding site for a metal ion such as zinc, but in deprotonated imidazole, both nitrogens are strongly basic sites. The study of imidazole complexes forms a good starting point for evaluation of the interaction between metal ions and imidazole residues in proteins, because the electronic environment experienced at the nitrogens of imidazole should be little altered by incorporation of the imidazole residue into histidine, and the further incorporation of histidine into a protein. Of course, the steric requirements for imidazole coordination may differ substantially, but the simple imidazole complexes form a good benchmark for evaluation of electronic effects.¹⁰

Nuclear quadrupole resonance (NQR) spectroscopy can provide important insights into the nature of the charge distribution about quadrupolar nuclei such as ^{14}N , for which $I = 1$. Previous studies of the ^{14}N NQR spectra of L-histidine and imidazole¹¹ have revealed strong similarities, indicating that very similar electronic environments prevail. In this contribution we report the ^{14}N NQR spectra of a series of zinc and cadmium imidazole complexes. We also describe a model analogous to that applied to coordinated pyridine,¹² that accounts for the changes in electric field gradient (efg) at the nitrogen in terms of the extent of electron withdrawal upon coordination.

Experimental Section

Dihalobis(imidazole)zinc, $\text{Zn}(\text{Im})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), was prepared from aqueous solution of the zinc halide and imidazole in a 1:2 molar ratio. The ZnI_2 solution was prepared from I_2 and excess Zn metal, followed by filtration. The iodo and bromo imidazole complexes form initially as oils and crystallize upon addition of ethanol: mp $\text{Zn}(\text{Im})_2\text{Cl}_2$, 157–158 °C; $\text{Zn}(\text{Im})_2\text{Br}_2$, 128.5–130.5 °C; $\text{Zn}(\text{Im})_2\text{I}_2$, 162–163 °C. Anal. Calcd for $\text{Zn}(\text{Im})_2\text{Cl}_2$: C, 26.47; H, 2.94; N, 20.59; Zn, 23.90. Found: C, 26.16; H, 2.94; N, 20.27; Zn, 24.18. Calcd for $\text{Zn}(\text{Im})_2\text{Br}_2$: C, 19.94; H, 2.22; N, 15.51; Zn, 18.01. Found: C, 19.87; H, 2.13; N, 15.37; Zn, 18.57. Calcd for $\text{Zn}(\text{Im})_2\text{I}_2$: C, 15.82; H, 1.76; N, 12.31; Zn, 14.29. Found: C, 15.79; H, 1.94; N, 12.31; Zn, 14.50.

Alternative preparations have been reported.^{13,14}

Dinitratobis(imidazole)zinc, $\text{Zn}(\text{Im})_2(\text{NO}_3)_2$, was prepared from an aqueous solution in a 1:2 molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and imidazole. The solution was evaporated and the residue washed with cold H_2O . Anal. Calcd for $\text{Zn}(\text{Im})_2(\text{NO}_3)_2$: C, 22.15; N, 25.85; Zn, 20.00. Found: C, 22.02; N, 25.91; Zn, 20.10. A different preparation route has been reported by Goodgame et al.¹⁴

Catecholobis(imidazole)zinc, $\text{Zn}(\text{Im})(\text{C}_6\text{H}_4\text{O}_2)$. Several attempts were made to prepare a mixed catecholate–imidazole complex of zinc. Imidazole, catechol, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed in 2:1:1 mole ratios, with varying quantities of NaOH, in either water or ethanol solvent. The preparations were carried out in a nitrogen atmosphere. The solids obtained from the water and ethanol preparations exhibited low solubility in a wide range of solvents. In addition they yielded variable elemental analyses which differed from that expected. For example: Anal. Calcd for $\text{Zn}(\text{C}_6\text{H}_4\text{N}_2)_2(\text{C}_6\text{H}_4\text{O}_2)$: C, 46.54; H, 3.88; N, 18.10; Zn, 21.14. Found for water solvent preparation: C, 41.7; H, 3.31; N, 13.86; Zn, 23.19. For ethanol preparation (two analyses on same sample): C, 30.6, 35.7; H, 2.44, 2.82; N, 12.88, 12.64; Zn, 20.5, 21.0. The reported analyses showed poorly reproducibility for the same sample. The infrared spectra of these samples were essentially identical, and consistent with the presence of both coordinated imidazole and coordinated catecholate. The samples recovered from both water and ethanol yielded essentially identical ^{14}N NQR spectra, indicating the presence of a single type of coordinated imidazole. No evidence for nitrate was seen in the NQR spectra. The reasons for the poor agreement in the analytical results are not clear. Although catecholate complexes are generally air sensitive, care was taken to exclude air in the present work. There is likely to be a hydroxyzinc impurity in the sample because of the constraints placed on the pH range in which the compound can be formed.

Tetrakis(imidazole)zinc nitrate, $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$, was obtained as crystals from an ethanol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and imidazole in a 1:4 molar ratio, mp 147–148 °C. Anal. Calcd for $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$: C, 36.18; N, 32.84; Zn, 10.89. Found: C, 35.75; N, 32.42; Zn, 12.31. A different preparative procedure has been reported.¹⁴

Tetrakis(imidazole)zinc perchlorate, $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$, was prepared by the method of Bear and co-workers.¹⁵ The crystals formed as needles rather than as plates as reported. Anal. Calcd for $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$: C, 26.85; H, 2.98; N, 20.88; Zn, 12.19. Found: C, 26.62; H, 2.90; N, 20.99; Zn, 11.96.

Hexakis(imidazole)zinc chloride tetrahydrate, $[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, was prepared as previously reported.¹⁶

Hexakis(imidazole)zinc nitrate, $[\text{Zn}(\text{Im})_6](\text{NO}_3)_2$, formed as prismatic crystals from an ethanol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and imidazole in 1:6 molar ratio, mp 188–189 °C. Anal. Calcd for $[\text{Zn}(\text{Im})_6](\text{NO}_3)_2$: Zn, 10.89; C, 36.18; H, 4.02; N, 32.83. Found: Zn, 12.31; C, 35.73; H, 3.77; N, 32.42.

Dibromobis(imidazole)cadmium, $[\text{Cd}(\text{Im})_2\text{Br}_2]$, formed immediately as a white precipitate upon addition of 2 equiv of imidazole to an aqueous solution of $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$. Volume loss was observed at 202 °C. Anal. Calcd for $[\text{Cd}(\text{Im})_2\text{Br}_2]$: C, 17.68; N, 13.75; Cd, 27.45. Found: C, 14.99; N, 11.76; Cd, 30.01.

Catena- μ -dichloro-bis(imidazole)cadmium, $[\text{Cd}(\text{Im})_2\text{Cl}_2]_\infty$, was prepared by the method of Flook et al.¹⁷ Anal. Calcd for $[\text{Cd}(\text{Im})_2\text{Cl}_2]$:

Table I. ^{14}N Nuclear Quadrupole Resonance Spectra of Imidazole Complexes at 77 K

compd	imino nitrogen, $\text{N}_{(2)}$					amino nitrogen, $\text{N}_{(1)}$				
	ν_+	ν_-	ν_0	e^2Qq/h	η	ν_+	ν_-	ν_0	e^2Qq/h	η
<i>N</i> -benzylimidazole	2780	2729	(51)	3679	0.022	1776	1521	255	2198	0.784
1. imidazole (Im) ^a	2560		220	3270	0.135	1425		718	1430	0.995
2. L-histidine ^a	2631	2411	220	3362	0.131	1406	749	657	1437	0.915
3. $[\text{Cd}(\text{Im})_6](\text{NO}_3)_2$	2287	1938	349	2817	0.248	1406	910	496	1544	0.462
4. $[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	2286	1928	358	2809	0.255	1467	1035	432	1688	0.518
5. $[\text{Zn}(\text{Im})_6](\text{NO}_3)_2$	2296	1910	386	2804	0.275	1397	888	509	1523	0.668
6. $\text{Cd}(\text{Im})_2\text{Cl}_2$	2001		(450)	2368	0.380	1524	1084	440	1739	0.506
	1952		(400)	2336	0.342	1470	1024	454	1668	0.514
7. $\text{Cd}(\text{Im})_2\text{Br}_2$	1934	1430	504	2243	0.499	1474	1084	390	1705	0.457
8. $\text{Zn}(\text{Im})_2(\text{C}_6\text{H}_4\text{O}_2)$	1930	1365	565	2197	0.574	1280	855	425	1428	0.597
9. $\text{Zn}(\text{Im})_2\text{Cl}_2$	1896	1293	603	2126	0.567	1417	989	428	1604	0.534
10. $\text{Zn}(\text{Im})_2\text{Br}_2$	1872	1266	606	2092	0.579	1505	1170	335	1783	0.376
	1844	1223	621	2045	0.607					
11. $\text{Zn}(\text{Im})_2\text{I}_2$	1839	1234	605	2049	0.591	1492	1159	333	1767	0.377
	1832	1227	605	2039	0.593	1516	1226	290	1828	0.317
12. $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$	1857	1172	685	2019	0.678	1466	1105	361	1714	0.421
	1857	1236	621	2062	0.602	1416	924	492	1560	0.631
13. $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$	1844	1162	682	2004	0.681					
14. $\text{Zn}(\text{Im})_2(\text{NO}_3)_2$	1816	1128	688	1963	0.701	1394	911	483	1537	0.629
	1776	1113	663	1926	0.689					
15. $\text{ImH}^+\text{NO}_3^-$						1303	737	566	1360	0.832
16. ImH^+I^-						1348	828	520	1451	0.717

^a See ref 11.**Table II.** ^{14}N NQR Spectra Due to Nitrate Ion

compd	ν_+	ν_-	ν_0	e^2Qq_{zz}/h	η
$\text{Zn}(\text{Im})_2(\text{NO}_3)_2$	576	309	267	590	0.905
$[\text{Zn}(\text{Im})_6](\text{NO}_3)_2$	560				
$[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$	567	380	187	631	0.592
$[\text{Cd}(\text{Im})_6](\text{NO}_3)_2$	532	382 ^a		609	0.492
$\text{ImH}(\text{NO}_3)$	651	363 ^a	288	676	0.852

^a These resonances were either very weak or partially obscured by overlap with other bands.

C, 22.57; N, 17.55; Cd, 35.11. Found: C, 22.84; N, 17.84; Cd, 35.19.

Hexakis(imidazole)cadmium nitrate, $[\text{Cd}(\text{Im})_6](\text{NO}_3)_2$, was prepared by the method of Mighell and Santoro,¹⁸ mp 189.5–190.5 °C. Anal. Calcd for $\text{Cd}(\text{Im})_6(\text{NO}_3)_2$: C, 33.54; H, 3.73; N, 30.43; Cd, 17.39. Found: C, 33.39; H, 3.85; N, 30.66; Cd, 17.54.

The NQR spectra were obtained at 77 K, using the double resonance technique described previously.^{12,19}

Infrared spectra were obtained as Nujol mulls, using a Beckman Model 4240 spectrophotometer.

Results

The ^{14}N NQR spectra due to the nitrogen atoms of imidazole in several imidazole complexes are listed in Table I, along with the calculated quadrupole coupling constants e^2Qq_{zz}/h and asymmetry parameter η . The spectra due to NO_3^- in the nitrate complexes are listed in Table II.

In comparing the NQR data in the light of crystal structure studies, it must be kept in mind that the NQR data are obtained at 77 K, whereas the X-ray structural studies are usually carried out at or near room temperature. There may be one or more phase changes in the temperature interval between room temperature and 77 K, resulting in different numbers of crystallographically distinct nitrogen sites at the two temperatures. Based on the X-ray crystal structure,²⁰ the environment around Zn in $\text{Zn}(\text{Im})_2\text{Cl}_2$ is approximately tetrahedral, with Zn–N distances of 1.995 and 2.020 Å. Since only one set of NQR signals ascribable to imino nitrogens is observed, it would appear that the slight differences in environment occasioned by the crystallographic nonequivalence have only a small effect on the NQR frequencies. On the other hand, two distinct im-

imidazole signals are observed in the spectra of $\text{Zn}(\text{Im})_2\text{Br}_2$ and $\text{Zn}(\text{Im})_2\text{I}_2$. In $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$, Zn is tetrahedrally coordinated by four imidazole molecules, with Zn distances of 2.001 and 1.997 Å.¹⁵ Two sets of imino nitrogen signals are seen for $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$, in agreement with the X-ray results. On the other hand, for $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$, only one set of signals is observed. Both $[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ¹⁶ and $[\text{Cd}(\text{Im})_6](\text{NO}_3)_2$ ¹⁸ exhibit relatively undistorted octahedral geometry. In the structure of the latter compound there is only one crystallographically distinct imidazole; correspondingly, only one set of imino nitrogen signals is seen in the NQR spectrum. However, in $[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ all six imidazole molecules are nonequivalent, whereas only one set of imidazole NQR signals is seen. The quadrupole coupling constants of 2809 and 2817 kHz for the imino nitrogens in $[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Cd}(\text{Im})_6](\text{NO}_3)_2$, respectively, are very little different. It appears that the coordinated nitrogen in the six-coordinated complexes is not very sensitive to bond length variations of up to 0.2 Å. Thus, it is not surprising that crystallographically nonequivalent ligands do not produce distinguishable signals in these compounds.

The compound $\text{Cd}(\text{Im})_2\text{Cl}_2$ poses special problems. On the basis of the crystal structure for this substance at (presumably) near room temperature, the environment about the Cd is six coordinate.¹⁷ Bridging chloride ions lead to a linear chain structure, with trans-axially coordinated imidazole groups. There is but one crystallographically distinct imidazole molecule per unit cell. However, the ^{14}N NQR spectrum of this compound at 77 K cannot reasonably be interpreted without assuming two distinct sets of imino and amino nitrogen resonances, which requires that there be at least two crystallographically distinct imidazole environments. Since the complex gives a very good elemental analysis, it seems unlikely that an impurity is responsible for additional lines. The crystals on which the X-ray work was carried out were grown from a solution containing alanine, reported to improve the quality of the crystals. Since we did not employ alanine, the crystals we have studied may have a different structure. There is the further possibility of a phase change in the temperature interval from room temperature to 77 K.

The assignment of resonances to the imino nitrogens in $\text{Cd}(\text{Im})_2\text{Cl}_2$ is complicated by the fact that in this compound

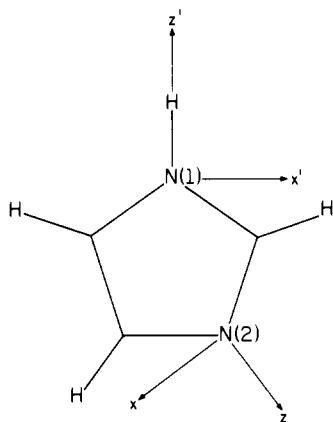


Figure 1. Orientation of geometric axis system at the nitrogens of imidazole. The z and z' axes are chosen to lie along the bisectors of the CNC angles. The y and y' axes are normal to the molecular plane.

the ν_- and ν_0 transitions of the imino nitrogens are obscured by the much more intense signals due to the amino nitrogens. The estimated values of ν_0 are listed in Table I in parentheses. The field gradient parameters for the imino nitrogens can therefore not be determined with as high precision as for the other complexes.

Discussion

Interpretation of Imino Nitrogen Data. To account for the change in field gradient at the imino nitrogen upon coordination, we have employed the Townes–Dailey approximations²¹ in a development similar to that employed previously in connection with pyridine complexes.¹² In the Townes–Dailey model, the electric field gradient at a quadrupolar nucleus is attributed solely to electrons in the valence shell p orbitals of the atom of interest. Since the lone pair electrons reside in an orbital of predominantly p character, localized on the nitrogen atom, one would expect them to make a large contribution to the efg experienced by the nitrogen nucleus. Therefore, the Z axis, along the direction of the largest component of the field gradient tensor, would be expected to lie close to the axis of the lone pair orbital. As illustrated in Figure 1, we define the geometric z axis to contain the bisector of the imino CNC angle. The orientation of the field gradient axes in gas-phase imidazole has been determined by a microwave study; the Z axis has been found to lie in the plane, and to form an angle of only 4° with z , the CNC angle bisector.²² Therefore, little error would be expected to result if the Z axis and the z axis are taken to be coincident in the derivation of the equations presented below. In all subsequent discussions, x , y , and z refer to the geometric axes defined in Figure 1, whereas X , Y , and Z refer to the axes of the diagonalized field gradient tensor.

We define b as the nitrogen N–C σ orbital population and a as the p_π orbital population on the imino nitrogen. It is assumed that both imino N–C σ orbitals have equivalent populations. For the axis system defined in Figure 1 and for a CNC bond angle of 2θ , the following expressions for the diagonal components of the efg tensor for gas-phase imidazole may be derived:

$$q_{zz} = q_0 \left[\sigma(1 - \cot^2 \theta) - \frac{a_0}{2} + b_0(\cot^2 \theta - 1/2) \right] \quad (1)$$

$$q_{yy} = q_0 \left[-\frac{\sigma}{2}(1 - \cot^2 \theta) + a_0 - \frac{b_0}{2}(1 + \cot^2 \theta) \right] \quad (2)$$

$$q_{xx} = q_0 \left[-\frac{\sigma}{2}(1 - \cot^2 \theta) - \frac{a_0}{2} + \frac{b_0}{2}(2 - \cot^2 \theta) \right] \quad (3)$$

The quantity σ , representing the population of the lone pair orbital of the imino nitrogen, is assigned a value of 2 in free

imidazole. The angle 2θ has been determined to be 104.5° . On the basis of crystal structure determinations for several imidazole complexes,^{16–18,20,23} it is safe to assume that 2θ is unchanged upon coordination. For free imidazole, e^2Qq_{zz}/h and η are given by

$$e^2Qq_{zz}/h = (e^2Qq_0/h)\alpha, \quad \alpha = 2(1 - \cot^2 \theta) - \frac{a_0}{2} + b_0(\cot^2 \theta - 1/2) \quad (4)$$

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \quad (5)$$

The value for e^2Qq_0/h , which refers to the quadrupole coupling constant generated by a single 2p electron in atomic nitrogen, has not been determined. We will employ the value 9.0 MHz used previously;¹² this value is intermediate among those employed by various workers. For an assigned value of e^2Qq_0/h , a_0 and b_0 can be calculated from the experimentally determined values for e^2Qq_{zz}/h and η .

The fact that the experimentally determined Z axis lies only 4° off the CNC angle bisector in gaseous imidazole²² supports the assumption that the two N–C σ orbital populations are approximately equal. With this assumption, the sole difference in the treatment of imidazole and pyridine is the value of the angle 2θ . This angular difference is reflected in a difference in the mixing of p orbitals in the molecular plane. The net effect is to reduce the magnitude of the parameters a_0 and b_0 for imidazole relative to those of pyridine (vide infra).

Upon coordination to a Lewis acid such as zinc or cadmium, the lone pair orbital becomes the donor orbital. We assign an occupation, σ , which is less than 2. As the donor orbital population decreases upon coordination, corresponding population increases should occur in the nitrogen N–C σ and π orbitals due to inductive effects. Following the arguments advanced in connection with an analogous model for coordinated pyridine, the populations, a and b , become

$$a = a_0 + A(2 - \sigma) \quad b = b_0 + B(2 - \sigma) \quad (6)$$

where a_0 and b_0 refer to the free imidazole populations and A and B are linearly related constants which are positive and whose sum $2B + A < 1$.

In the pyridine study, where $|q_{zz}| > |q_{yy}| > |q_{xx}|$ for the complexes studied, the following linear relationship between $1/\alpha$ and η was derived:

$$\frac{1}{\alpha} = \frac{1}{K} + \frac{L}{K} \eta \quad (7)$$

$$K = \frac{1}{(B - A)} \{2(B - A) + (b_0 - a_0) + (b_0A - Ba_0)\} \quad (8)$$

$$L = \frac{2}{3(A - B)} [(1 - \cot^2 \theta) + A/2 - B(\cot^2 \theta - 1/2)] \quad (9)$$

Since $1/\alpha = e^2Qq_0/e^2Qq_{zz}$, a plot of h/e^2Qq_{zz} vs. η yields values for K and L , and consequently the relationship between A and B , merely by multiplying the slope and intercept by an appropriate value of e^2Qq_0/h . However, the slope of a graph of h/e^2Qq_{zz} vs. η for the imidazole complexes reveals that the changes in 2p orbital populations on the nitrogen as compared with pyridine have caused a shift in the field gradient at $N_{(2)}$ into a region in which $|q_{zz}| > |q_{xx}| > |q_{yy}|$. In this region, the appropriate equations are

$$\alpha = (1 - \cot^2 \theta)\sigma - 1/2[a_0 + A(2 - \sigma)] + [b_0 + B(2 - \sigma)][\cot^2 \theta - 1/2] \quad (10)$$

$$a\eta = 3/2\{[a_0 + A(2 - \sigma)] - [b_0 + B(2 - \sigma)]\} \quad (11)$$

Elimination of σ from these expressions yields

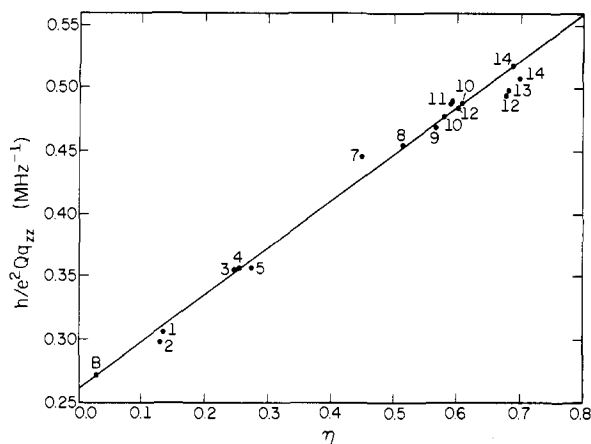


Figure 2. Graph of h/e^2Qq_{zz} vs. η for the imino nitrogen NQR data of zinc and cadmium imidazole complexes. Point B represent *N*-benzylimidazole, employed as reference compound. The remaining numbered points correspond to the compounds numbered in Table I.

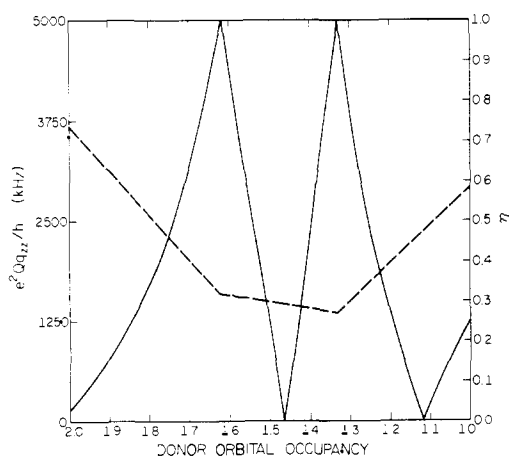


Figure 3. Graph of e^2Qq_{zz}/h (dashed line) and η vs. donor orbital occupancy, σ , for imino nitrogen in imidazole.

$$\frac{1}{\alpha} = \frac{1}{K} - \frac{L}{K} \eta \quad (12)$$

where K and L are defined by eq 8 and 9. This expression predicts that for a series of coordinated imidazole compounds there should be a linear relationship between $(e^2Qq_0)/\alpha$ (e^2Qq_{zz}), the reciprocal of the reduced quadrupole coupling constant, and the asymmetry parameter η .

Application of these relationships to coordinated imidazole requires choice of a suitable reference substance. Solid imidazole itself is not suitable, because strong hydrogen bonding perturbs the environment at both nitrogens, but most especially at the imino nitrogen.²⁴ The data for gas-phase imidazole are free of this complication, but there is ordinarily a substantial shift in efg parameters associated with the transition from the gas to solid phase, aside from shifts due to specific interactions. We have chosen to use 1-benzylimidazole as reference; replacement of the amino hydrogen by the benzyl group should leave the electron distribution in the ring essentially unperturbed, while at the same time eliminating hydrogen bonding effects.

From the experimentally determined values of e^2Qq_{zz}/h and η for 1-benzylimidazole, values of 1.026 and 1.018 are calculated for a_0 and b_0 , respectively, using eq 1-5. These values are surprisingly small, considering the electronegativity difference between N and C. The lower values as compared with pyridine, in which a_0 and b_0 were 1.203 and 1.337, respectively, probably arise from the altered hybridization of orbitals in the five-

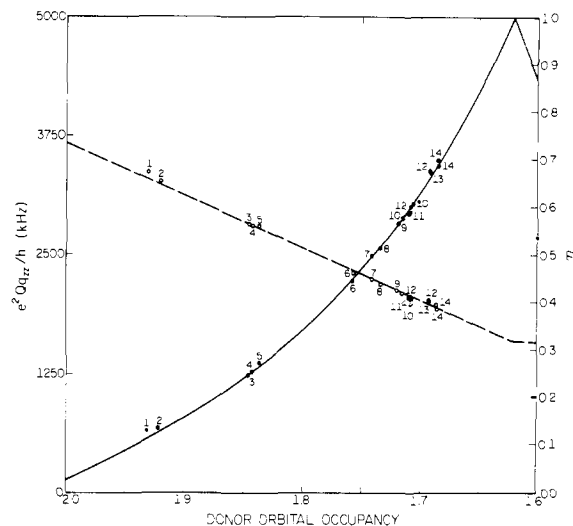


Figure 4. Graph of e^2Qq_{zz}/h and η vs. donor orbital occupancy in the range $2.0 > \sigma > 1.6$. The numbered points correspond to the compounds numbered in Table I.

membered ring. Furthermore, since 2θ is rather small, the centroids of charge in the σ orbitals may not lie precisely along the internuclear axes as assumed. In any event, interpretation of the values of these parameters is not of importance for our present purposes. We are concerned only with the changes that occur upon coordination to an acid center.

The line defined by eq 12 is constrained to pass through the point representing 1-benzylimidazole. Figure 2 shows the data for the imino nitrogens of all the zinc and cadmium imidazole complexes listed in Table I, except for $\text{Cd}(\text{Im})_2\text{Cl}_2$. This compound was omitted because of the uncertainties alluded to earlier. A very good linear relationship is obtained for a wide range of imidazole coordination environments. The values of A and B are determined from this line to be $A = 0.261 + 1.261 \cdot B$. Employing the physically reasonable constraints that both A and B must be positive, and that $2B + A < 1$, we obtain $0 < B < 0.227$ and $0.267 < A < 0.546$. In keeping with our assumption in treating the data for coordinated pyridine, we assume that $2B + A = 0.62$. The physical meaning of this, rather crudely, is that 62% of the charge withdrawn from the nitrogen by donation to the Lewis acid is restored via inductive electron flow in the σ and π bonds. The resulting values for A and B are 0.400 and 0.110, respectively.

Having chosen values for A and B it is possible to relate the observed quantities e^2Qq_{zz}/h and η to the donor orbital occupancy, as shown in Figure 3. An expanded display of the range $\sigma = 2.0$ to $\sigma = 1.6$ is shown in Figure 4. All of the observed imino nitrogen data are shown on the figure. It is evident that the experimental data fit the predicted relationship very well. From this graph it is possible to estimate values of σ for coordinated imidazole compounds; these are listed in Table III.

The data displayed in Figure 3 and the σ values listed in Table III provide several interesting comparisons. There has been some uncertainty regarding the correct assignment of the two sets of ^{14}N NQR resonances to the two nitrogens in solid imidazole.^{11,25-27} The assignment of the transitions listed in Table I to the imino nitrogen is supported by the fact that the fit of the data to the calculated curve is very good. The presence of extensive hydrogen bonding interactions in solid imidazole is evident from solid-state IR spectra.²⁸ It would appear that ^{14}N NQR spectroscopy has the potential for serving as a sensitive probe of hydrogen bonding interactions in solids.

The datum for histidine fits the calculated relationship very well, as expected. The derived value of $\sigma = 1.931$ reflects the effects of hydrogen bonding to the imino nitrogen in the solid-state structure of L-histidine.²⁹

Table III. Donor Orbital Occupancies of the Imino Nitrogen Atoms of Coordinated Imidazole

compd	σ^a	compd	σ^a
L-histidine	1.931 ± 0.01	$\text{Zn}(\text{Im})_2\text{Br}_2$	1.714 ± 0.001
imidazole (s)	1.921 ± 0.005		1.706 ± 0.002
$[\text{Cd}(\text{Im})_6]-(\text{NO}_3)_2$	1.846 ± 0.001	$\text{Zn}(\text{Im})_2\text{I}_2$	1.708 ± 0.004
$[\text{Zn}(\text{Im})_6]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	1.843 ± 0.001		1.706 ± 0.005
$[\text{Zn}(\text{Im})_6]-(\text{NO}_3)_2$	1.837 ± 0.003	$[\text{Zn}(\text{Im})_4]-(\text{ClO}_4)_2$	1.707 ± 0.001
$\text{Cd}(\text{Im})_2\text{Cl}_2$	1.758 ± 0.01		1.692 ± 0.006
	1.756 ± 0.005	$[\text{Zn}(\text{Im})_4]-(\text{NO}_3)_2$	1.691 ± 0.005
$\text{Cd}(\text{Im})_2\text{Br}_2$	1.739 ± 0.001		
$\text{Zn}(\text{Im})_2-(\text{C}_6\text{H}_4\text{O}_2)$	1.732 ± 0.003	$\text{Zn}(\text{Im})_2-(\text{NO}_3)_2$	1.684 ± 0.005
$\text{Zn}(\text{Im})_2\text{Cl}_2$	1.718 ± 0.001		1.684 ± 0.001

^a The listed uncertainties are an estimate of the precision with which σ is determined by the fit of the data to the calculated curves in Figure 4.

When six imidazoles are coordinated to the metal, the population of the donor orbital is nearly independent of both the metal and counterion. The extent of donation by each imidazole is less in the hexakis(imidazole)zinc complexes than in tetrakis(imidazole)zinc nitrate, in which the metal ion has a four-coordinate, tetrahedral environment. This result is consistent with the greater number of coordinated ligands and the observed Zn–N bond distances, 2.2 and 2.0 Å in the hexakis¹⁶ and tetrakis¹⁵ complexes, respectively.

The donor orbital populations in the tetrahedral complexes exhibit a strong dependence on both the metal ion and counterion. Since the smaller zinc ion is more acidic than the cadmium ion, one would expect a greater degree of electron withdrawal from the coordinated nitrogen in the zinc complexes, as observed.

One would expect that in tetrahedral complexes of the form $\text{M}(\text{Im})_2\text{L}_2$, those complexes of a given metal containing the most strongly donating ligands L will require the least electron withdrawal from the imidazole donor orbitals. We observe the σ values to vary in the order $\text{L} = \text{catecholato} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{Im} > \text{NO}_3^-$. Although the order of the anions is not unusual, the position of imidazole seems anomalous in terms of its expected position in the spectrochemical series.³⁰ We have considered the possibility that this apparent discrepancy is due to the fact that imidazole is the sole neutral ligand in the series, and that the charged ligands exert a significant direct effect on the field gradient at the imino nitrogen. From the geometry of $\text{Zn}(\text{Im})_2\text{Cl}_2$,²⁰ one can calculate the contribution to the major component of the field gradient tensor at the imino nitrogen due to negative point charges located at each of the two chloride atomic positions, using the expression

$$V_{zz} = eq_{zz} = \frac{-e(3 \cos^2 \theta - 1)}{r^3} \quad (13)$$

The calculated values of eq_{zz} are -9.90×10^{12} and -8.49×10^{12} esu cm^{-3} . These can be converted to values of e^2Qq_{zz}/h by choice of an appropriate value for Q . Using the Clementi SCF functions for the nitrogen 2p orbital,³¹ and neglecting Sternheimer shielding effects,³² a value of 1.66×10^{25} cm^{-3} can be calculated for q_0 . In order that $e^2Qq_0/h = 9.0$ MHz, Q must have a value of 0.0156 b. The calculated contributions to e^2Qq_{zz}/h from point charges then become -11.2 and -9.5 kHz. This contribution is of the same sign as the contribution from the electrons of the donor orbital. Thus, to compare the donor orbital occupancies of imidazole in $\text{Zn}(\text{Im})_2\text{Cl}_2$ and $\text{Zn}(\text{Im})_4^{2+}$, the point charge contributions to the field gradient

Table IV. Comparative Donor Orbital Occupancies for Imidazole and Pyridine Complexes

complex	σ for L =	
	pyridine	imidazole
CdL_2Cl_2	1.87 ± 0.02	1.758 ± 0.01
		1.756 ± 0.005
$\text{ZnL}_2(\text{NO}_3)_2$	1.767 ± 0.007	1.684 ± 0.005
	1.761 ± 0.004	1.684 ± 0.001
ZnL_2I_2	1.793 ± 0.001	1.708 ± 0.004
	1.788 ± 0.001	1.706 ± 0.005
ZnL_2Br_2	1.792 ± 0.001	1.714 ± 0.001
	1.781 ± 0.002	1.706 ± 0.002
ZnL_2Cl_2	1.795 ± 0.003	1.718 ± 0.001
	1.789 ± 0.001	
$[\text{ZnL}_4](\text{ClO}_4)_2$	1.747 ± 0.005	1.707 ± 0.001
		1.692 ± 0.006

components should be subtracted. However, the effective charge at each chloride is less than 1.0, because of electron donation to the central metal. Assuming a net charge at each chloride of -0.8 , as estimated from the ^{35}Cl NQR spectrum of $\text{Zn}(\text{py})_2\text{Cl}_2$,³³ the corrected value of e^2Qq_{zz} in $\text{Zn}(\text{Im})_2\text{Cl}_2$ is about 2110 kHz. The correction due to charge is clearly much too small to change the relative position of $[\text{Zn}(\text{Im})_4]-(\text{NO}_3)_2$. This treatment, which takes account of only the closest and most important charges, is only approximate, but it does suggest that the electrostatic effect can be neglected in comparing donor orbital occupancies in cases where the charges of the other ligands vary.

It is also of interest to compare the values of σ obtained for the imidazole complexes with those found for analogous pyridine complexes, Table IV. The same trends in relative donor orbital occupancies are seen. Note that σ for $[\text{Zn}(\text{py})_4](\text{ClO}_4)_2$ shows the same decrease relative to the $\text{Zn}(\text{py})_2\text{X}_2$ complexes as seen for $[\text{Zn}(\text{Im})_4](\text{NO}_3)_2$ and $[\text{Zn}(\text{Im})_4](\text{ClO}_4)_2$. A lower than expected donor orbital occupancy of the nitrogen orbitals is observed also in $\text{Pd}(o\text{-phen})_2^{2+}$ as compared with $\text{Pd}(o\text{-phen})\text{X}_2$, where X are anionic ligands.³⁴

From the fact that the relative ordering of σ values is so systematically carried from one set of complexes to another, we conclude that the relative values of σ deduced from the NQR data do indeed reflect relative effective charges at the central metal. This in turn means that neutral ligands such as imidazole or pyridine are less donating toward the metal ion than most ionic ligands. Because the field gradient is a one-electron operator, the NQR data are a direct reflection of the charge distribution in the ground electronic state. In this respect they differ from electronic spectral data, which relate to properties of both ground and excited states. The NQR data suggest that the extent of electron donation to the metal increases with the energy of the donor orbital. Thus, in general, anionic ligands are stronger donors than neutral ligands; however, in most cases where charge is delocalized, as in NO_3^- , the ligand may be more weakly donating. Secondly, the NQR data indicate that among ligands for which the donor orbital energies are comparable (Cl^- , Br^- , I^-), the extent of charge donation is greatest for the ligands of smallest radii.

Interpretation of Amino Nitrogen Data. The amino nitrogen of imidazole experiences a structural environment similar to that found in pyrrole. From microwave studies of both pyrrole³⁵ and imidazole²² it has been determined that the major component of the efg tensor is along the direction y' in Figure 1, normal to the plane of the ring. To treat the NQR data for the amino nitrogen using the model described above for the imino nitrogen, we designate the population of the nitrogen orbital in the N–H bond as σ . The condition that q_{zz} lies normal to the plane of the ring corresponds to the region on the graph of Figure 3 of $1.00 < \sigma < 1.33$. This range of nitrogen

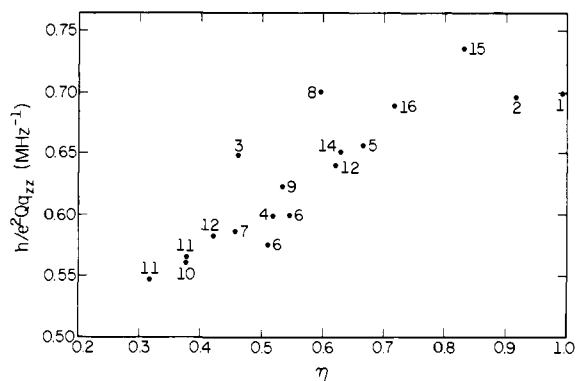


Figure 5. Graph of h/e^2Qq_{zz} vs. η for the amino nitrogen NQR data of zinc and cadmium imidazole complexes.

Table V. Infrared Absorptions Due to N-H Stretching and Out of Plane Bending Modes in Imidazole Complexes

compd	ν_{N-H} , cm^{-1}	γ_{N-H} , cm^{-1}
Zn(Im) ₂ (NO ₃) ₂	3265	736, 708
[Zn(Im) ₆](NO ₃) ₂	3180	748, 712
Zn(Im) ₂ Cl ₂	3307	740, 706
Zn(Im) ₂ Br ₂	3347	708, 685
Zn(Im) ₂ I ₂	3337	695, 682
Cd(Im) ₂ Br ₂	3343	708
[Cd(Im) ₆](NO ₃) ₂	3320 (sh)	750, 712
Cd(Im) ₂ Cl ₂	3300 (sh)	730

orbital populations in N-H bonds is consistent with previous experience.

Coordination of the imino nitrogen to an acid site should result, via inductive effects, in slight changes in populations of the orbitals of the amino nitrogen, N₍₁₎. However, intermolecular interactions, particularly those involving hydrogen bonding, might be expected to obscure the variations in intramolecular effects. Figure 5 shows a graph of h/e^2Qq_{zz} vs. η for the amino nitrogen data of Table I. A considerable scatter is evident. Furthermore, there is no evident correlation between the trend observed in the field gradient parameters for the imino nitrogen and the data for the corresponding amino nitrogens. On the other hand, the IR spectra of the solid complexes furnish an indication that hydrogen bonding effects are largely responsible for the variations seen. The frequencies of the N-H stretching, ν_{N-H} , and out of plane N-H bending modes, γ_{N-H} , are listed in Table V for several of the complexes studied. The band assignments were made by analogy with previous work.^{36,37} The values of ν are highest for weakly hydrogen-bonding anions such as I⁻ or Br⁻, lower for Cl⁻, and lowest for the more strongly hydrogen-bonding nitrates. The opposite trend is observed in the N-H bending mode, as expected. It is noteworthy that the nature of the counterion has a greater effect on the observed IR frequencies than the nature of the metal ion, or its coordination number. Similarly, the lowest ¹⁴N coupling constants correspond to the complexes containing the more strongly hydrogen-bonding species such as nitrate. Presumably a hydrogen-bonding interaction of the hydrogen with a base site results in a shift in electron density toward nitrogen, i.e., in an increase in the value of σ . From the slope of the curve of e^2Qq_{zz}/h vs. σ in the region $1.00 < \sigma < 1.33$, Figure 3, hydrogen bonding is thus expected to cause a decrease in coupling constant, as observed. These considerations are illustrated by the data for [Zn(Im)₄](ClO₄)₂. The crystal structure data for this compound¹⁵ reveal two non-equivalent coordinated imidazole molecules. For one, the angle made by the CNC bisector and the nitrogen-oxygen vector to the nearest oxygen of an adjacent ClO₄⁻ is 21.3°. The corre-

sponding N-O distance is 2.95 Å. For the other imidazole, the angle and N-O distance are 36.8° and 3.06 Å, respectively. The nitrogen in this latter environment is clearly involved in a weaker hydrogen bonding arrangement than the former.

Two distinctly different field gradient parameters are observed for amino nitrogens in this compound. The lower value of e^2Qq/h , 1560 kHz, can be assigned to the amino nitrogen involved in stronger hydrogen bonding. From the values of e^2Qq/h and η observed, this nitrogen appears to experience an environment similar to that for the amino nitrogens of [Zn(Im)₄](NO₃)₂.

The values of η of the amino nitrogen vary over a wide range in an unpredictable manner. The lack of a regular behavior for this parameter is probably related to the fact that the lattice anions responsible for the variations in efg parameters occupy a variety of positions relative to the coordinated imidazole.

For imidazolium nitrate and imidazolium iodide, a single quadrupole coupling constant is observed in each case. This suggests, as expected, that the two nitrogens are equivalent. The efg parameters for the nitrate do not fit well on the calculated curve, no doubt for the reasons suggested above: hydrogen-bonding effects are important, and the environment about the nitrogens is distorted from that assumed in the model. The fit is much more satisfactory for imidazolium iodide.

On the basis of this study of imidazole complexes it should be possible to delineate some of the details of the metal ion environment in more complex metal-peptide complexes involving metal-imidazole interactions, using the ¹⁴N NQR spectra. In addition, analysis of the NQR data in terms of a model for coordinated imidazole provides useful insights. It is evident, for example, that charge withdrawal from the imino nitrogen is lower in six-coordinate than in four-coordinate metal complexes, and less in cadmium complexes than in analogous zinc species. Furthermore, the extent of charge withdrawal from the coordinated imino nitrogen in four-coordinate complexes is shown to vary with the nature of the other ligands present on the metal. The implications of this conclusion for the nature of the environment in zinc-containing metalloenzymes is explored in the paper which follows.

References and Notes

- (1) This research has been supported in part by the National Institutes of Health, through Research Grant GM-23395, and by the National Science Foundation.
- (2) National Science Foundation Fellow, 1975-1978.
- (3) (a) G. Robillard and R. G. Shulman, *J. Mol. Biol.*, **71**, 507 (1972); (b) D. M. Blow, J. J. Birkløft, and B. S. Hartley, *Nature (London)*, **221**, 337 (1969).
- (4) D. M. Blow, *Acc. Chem. Res.*, **9**, 145 (1976).
- (5) J. H. Wang, *Science*, **161**, 328 (1968).
- (6) (a) J. A. Hartsuck and W. N. Lipscomb in "The Enzymes", Vol. III, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971, p 1; (b) W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3797 (1973); (c) F. A. Quiocho and W. N. Lipscomb, *Adv. Protein Chem.*, **25**, 1 (1971); (d) W. N. Lipscomb, *Chem. Soc. Rev.*, **1**, 319 (1972); (e) R. Breslow and D. L. Wernick, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 1303 (1977); (f) P. M. Hayes and P. A. Kollman, *J. Am. Chem. Soc.*, **98**, 3335 (1976).
- (7) (a) S. Lindskog, L. E. Henderson, K. K. Kannan, A. Liljas, P. O. Hyman, and B. Strandberg in "The Enzymes", Vol. V, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971, p 587; (b) K. K. Kannan, B. Notstrand, K. Fridborg, S. Lövgren, A. Ohlsson, and M. Petef, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 51 (1975); (c) J. M. Resando, *Biochemistry*, **14**, 675, 689 (1975); (d) R. K. Gupta and J. M. Resando, *J. Biol. Chem.*, **250**, 2630 (1975); (e) J. MacB. Harrowfield, V. Norris, and A. M. Sargeson, *J. Am. Chem. Soc.*, **98**, 7282 (1976).
- (8) (a) C.-I. Brändén, H. Jörnvall, H. Eklund, and B. Furugren in "The Enzymes", Vol. XI, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1975, p 104; (b) R. H. Prince and M. Huges, *Chem. Ind. (London)*, 648 (1975); (c) E. Zeppenzauer, H. Jörnall, and I. Ohlsson, *Eur. J. Biochem.*, **58**, 95 (1975); (d) M. F. Dunn, J.-F. Biellmann, and G. Branzant, *Biochemistry*, **14**, 1998, 3176 (1975); (e) J. P. Klingman and K. Welsh, *Biochem. Biophys. Res. Commun.*, **70**, 878 (1976).
- (9) (a) J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1349 (1975); (b) G. Rotilio, L. Calabrese, B. Mondovì, and W. E. Blumberg, *J. Biol. Chem.*, **249**, 3157 (1974); (c) J. A. Fee, *Biochim. Biophys. Acta*, **295**, 107 (1973); (d) I. Fridovich, *Annu. Rev. Biochem.*, **44**, 147 (1975); (e) S. J. Lippard, A. R. Burger, K. Ugurbil, M. W. Pantoliano, and J. S. Valentine, *Biochemistry*, **16**, 1137 (1977); (f) I. Fridovich, *Acc. Chem. Res.*, **5**, 321 (1972); (g) B. G. Malmstrom, L.-E. An-

- dreasson, and B. R. Einhammar, "The Enzymes", Vol. XII, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1975, p 507.
- (10) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).
- (11) (a) D. T. Edmonds and C. P. Summers, *J. Magn. Reson.*, **12**, 134 (1973); (b) M. J. Hunt, A. L. Mackay, and D. T. Edmonds, *Chem. Phys. Lett.*, **34**, 473 (1975); (c) M. J. Hunt and A. L. Mackay, *J. Magn. Reson.*, **22**, 295 (1976).
- (12) Y. N. Hsieh, G. V. Rubenacker, C. P. Cheng, and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 1384 (1977).
- (13) J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).
- (14) D. M. Goodgame, M. Goodgame, P. J. Hayward, and G. W. Rayner-Ganham, *Inorg. Chem.*, **7**, 2447 (1968).
- (15) C. A. Bear, K. A. Duggan, and H. C. Freeman, *Acta Crystallogr., Sect. B*, **31**, 2713 (1975).
- (16) C. Sandmark and C.-I. Brändén, *Acta Chem. Scand.*, **21**, 993 (1967).
- (17) R. J. Flook, H. C. Freeman, H. Huq, and J. M. Rosalky, *Acta Crystallogr., Sect. B*, **29**, 903 (1973).
- (18) A. D. Mighell and A. Santoro, *Acta Crystallogr., Sect. B*, **27**, 2089 (1971).
- (19) D. T. Edmonds, *Phys. Rep.*, **29**, 233 (1977).
- (20) B. K. S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1968).
- (21) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).
- (22) G. L. Blackman, R. D. Brown, F. R. Burden, and I. R. Elsum, *J. Mol. Spectrosc.*, **60**, 63 (1976).
- (23) (a) A. Santoro, A. D. Mighell, M. Zocchi, and C. W. Reimann, *Acta Crystallogr., Sect. B*, **25**, 842 (1969); (b) G. Fransson and B. K. S. Lundberg, *Acta Chem. Scand.*, **26**, 3977 (1972); (c) B. K. S. Lundberg, *ibid.*, **26**, 3977 (1972); (d) A. Gadet, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 1299 (1971); (e) C.-J. Antti and B. K. S. Lundberg, *Acta Chem. Scand.*, **25**, 1758 (1971); (f) C. B. Acland and H. C. Freeman, *Chem. Commun.*, 1016 (1971).
- (24) (a) S. Martinez-Carrera, *Acta Crystallogr.*, **20**, 783 (1966); (b) B. M. Craven, R. K. McMullan, J. D. Bell, and H. C. Freeman, *Acta Crystallogr., Sect. B*, **33**, 2585 (1977).
- (25) J. Koo and Y. N. Hsleh, *Chem. Phys. Lett.*, **9**, 238 (1971).
- (26) E. Schempp and P. J. Bray, *Phys. Lett. A*, **25**, 414 (1967).
- (27) D. T. Edmonds and P. A. Speight, *J. Magn. Reson.*, **12**, 134 (1973).
- (28) (a) C. Perchard, A. M. Bellocq, and A. Novak, *J. Chim. Phys. Phys.-Chim. Biol.*, **62**, 1344 (1965); (b) C. Perchard and A. Novak, *J. Chem. Phys.*, **48**, 3079 (1968).
- (29) (a) J. C. Madden, E. L. McGandy, and N. C. Seeman, *Acta Crystallogr., Sect. B*, **28**, 2377 (1972); (b) J. L. Madden, E. L. McGandy, N. C. Seeman, M. M. Harding, and H. Hoy, *ibid.*, 2382 (1972).
- (30) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", Harper and Row, New York, N.Y., 1972.
- (31) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177-478 (1974).
- (32) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants", Academic Press, New York, N.Y., 1969, Chapter 5.
- (33) Measurement by R. Farlee, using a super-regenerative oscillator-detector system, 27 °C; ³⁵Cl resonances at 10.14 and 10.29 MHz.
- (34) B. Plankey, C. P. Cheng, J. V. Rund, and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 8413 (1977).
- (35) L. Nygaard, J. T. Nielson, J. Kirchheinek, G. Mattesen, J. Rastrup-Anderson, and G. O. Sørensen, *J. Mol. Struct.*, **3**, 491 (1969).
- (36) C. Perchard and A. Novak, *J. Chim. Phys. Phys.-Chim. Biol.*, **65**, 1964 (1968).
- (37) J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **88**, 1451 (1969).

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-