Complexes of Iron(II) and Some 5-Substituted Tetrazoles[1]

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Three microcrystalline complexes of iron(II) have been prepared using the anions of 5-trifluoromethyltetrazole, 5-nitrotetrazole, and 5-chlorotetrazole. The complexes conform to the general formula $Fe(T)_2 \cdot 2H_2O$ where T represents the respective tetrazolate anion. Infrared and Mössbauer effect studies have made it possible to propose a structure for these compounds. The Mössbauer studies seem to indicate a partial localization of the π-cloud between two nitrogen atoms allowing bonding to occur at the corners of a tetrahedron. Quadrupole splitting is absent which indicates the electric field gradient tensor is zero at the iron atom lattice site. This arises in a field reducible to cubic symmetry (i.e., either tetrahedral or octahedral). Infrared data substantiate this finding by showing a loss of resonance character of the tetrazole ring and an increase in N=N bond character. To substantiate the bonding postulated, chemical evidence of the oxidation state of iron was utilized. A tentative structure is given along with infrared and Mössbauer data.

The complexes and properties of some 5-substituted tetrazole complexes of copper(II) have been recently reported[3,4] wherein the substituent was phenyl, a substituted phenyl, or an amino group. These publications dealt with complexes of tetrazole where the substituent on the tetrazole ring was an electron-rich source and could donate electrons to the delocalized π-cloud of the ring. These complexes were reported to be very insoluble in most solvents.

The present work was initiated to prepare the tetrazole analog of ferrocene by using tetrazoles with strongly electronegative groups on the carbon. The result was unexpected in that an iron(II) complex with tetrahedral configuration was formed. These compounds—similar to those of the copper(II) ion—are almost totally insoluble in the usual solvents.

Resonance absorption of low energy γ-radiation (Mössbauer effect)[5,6] has proved to be a powerful tool in the elucidation of molecular architecture and charge states in suitable target materials. Among the compounds of iron which have been studied using this technique are K_2FeO_4,[7] $Fe(acac)_3$,[8] ferrocene[9] and ferrocene related compounds,[10] iron carbonyls[11] and related compounds,[12] alloys and intermetallic systems, and a large number of metal–organic compounds. In the present investigation, three iron(II) tetrazole compounds have been studied in an attempt to relate the observable Mössbauer parameters to the structures of these novel substances. In addition, the infrared spectra for these compounds are here reported and interpreted in terms of a suggested bonding scheme.

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(3) N. A. Daugherty and C. H. Brubaker, Jr., J. Am. Chem. Soc., 83, 3779 (1961).

(4) C. H. Brubaker, Jr., ibid., 82, 82 (1960).

(5) For recent reviews, see "The Mössbauer Effect," H. Frauenfelder, W. A. Benjamin, Inc., New York, N. Y., 1962.

(6) (a) A. J. F. Boyle and H. E. Hall, Rept. Progr. Phys., 25, 441 (1962); (b) R. L. Mössbauer, Ann. Rev. Nucl. Sci., 12, 123 (1962).

(7) G. K. Wertheim and R. H. Herber, J. Chem. Phys., 36, 2497 (1962).

(8) G. K. Wertheim, W. R. Kingston, and R. H. Herber, ibid., 37, 687 (1962).

(9) L. M. Epstein, ibid., 36, 2731 (1962).

(10) R. H. Herber and G. K. Wertheim, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; to be submitted to J. Chem. Phys.

(11) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, Z. Naturforschung, 17a, 494 (1962); R. H. Herber, W. R. Kingston, and G. K. Wertheim, Inorg. Chem., 2, 153 (1963).

(12) G. K. Wertheim and R. H. Herber, J. Phys. Chem., in press.

Experimental

The chemicals used in this investigation were reagent grade. The tetrazoles used were obtained from Dr. Ronald Henry,[13] whose generosity in supplying these is gratefully acknowledged.

Analytical Methods.—The percentage iron was determined gravimetrically by igniting the hydroxide to Fe_2O_3. The samples for analyses were decomposed by heating gently with 6 N NH_4OH, digesting the precipitated iron oxides on a steam bath for 3 hr., redissolving in 2 N HCl, adding H_2O_2, and reprecipitating with base.

The tetrazole content of the complexes was determined gravimetrically by precipitating the tetrazoles as their silver salts.[14] The silver salts of the tetrazoles used in this investigation must be handled with care since they detonate easily when dry.[15] Samples for analysis were decomposed by treating with 1 N aqueous NaOH. The hydrous iron oxides were filtered off and washed with distilled water. The filtrate and washings were combined and acidified with 0.1 N HNO_3 to a pH of 6.5. A 10% excess based on a calculated value of $AgNO_3$ was added to precipitate the tetrazole. The precipitates were dried in a vacuum oven at 65° to constant weight.

Determination of C, H, and N in the complexes was made by Alfred Bernhardt.[16] The waters of hydration were determined by initial loss of weight on thermal decomposition analysis.

A. Complex with 5-Trifluoromethyltetrazole, $Fe(C_2N_4F_3)_2 \cdot 2H_2O$.—To a solution prepared by diluting 2.5 ml. of 12 N HCl 1:1 with distilled water was added 1.0 g. of $FeCl_2 \cdot 4H_2O$. A second solution was prepared by dissolving 1.8 g. of sodium 5-trifluoromethyltetrazole in 5.0 ml. of distilled water. The solution of the ferrous chloride was added slowly to the solution of the tetrazole and a pink microcrystalline precipitate formed which was collected on a fine grade fritted glass crucible and dried in vacuo over P_2O_5.

Anal. Calcd. for $Fe(C_2N_4F_3)_2 \cdot 2H_2O$: Fe, 15.3; C, 13.1; N, 30.6; H, 1.1. Found: Fe, 15.0; C, 13.3; N, 31.2; H, 1.3.

When neutral aqueous solutions of $FeSO_4$ and $NaC_2N_4F_3$ were mixed in a 1:2 ratio, an intensely colored gel formed which thickened to a rubbery mass. No attempt was made to analyze the gel.

B. Complex with 5-Nitrotetrazole, $Fe(CN_5O_2)_2 \cdot 2H_2O$.—To a solution of 2.5 ml. of 12 N HCl diluted 1:1 with distilled water was added 1.0 g. of $FeCl_2 \cdot 4H_2O$. This solution was added slowly to one containing 2.5 g. of sodium 5-nitrotetrazole in 5.0 ml. of distilled water. A yellow microcrystalline precipitate formed which was collected on a fine grade fritted glass crucible and dried in vacuo over P_2O_5.

Anal. Calcd. for $Fe(CN_5O_2)_2 \cdot 2H_2O$: Fe, 17.5; C, 7.5; N, 43.8; H, 1.3. Found: Fe, 17.5; C, 6.9; N, 41.4; H, 1.8.

C. Complex with 5-Chlorotetrazole, $Fe(CN_4Cl)_2 \cdot 2H_2O$.—To a solution of 2.5 ml. of 12 N HCl diluted 1:1 with distilled water was added 1.0 g. of $FeCl_2 \cdot 4H_2O$. This was added slowly to one containing 1.8 g. of sodium 5-chlorotetrazole in distilled

(13) U. S. Naval Ordnance Test Station, China Lake, Calif.

(14) R. Herbst and J. Mihina, J. Org. Chem., 15, 1082 (1950).

(15) E. von Herz, U. S. Patent 2,066,954, Jan. 5, 1937.

(16) Micronalytisches Laboratorium im Max Planck Institute für Kohlenforschung, Mülheim, Germany.

water; a red microcrystalline precipitate formed which was collected on a fine grade fritted glass crucible and dried *in vacuo* over P_2O_5.

Anal. Calcd. for $Fe(CN_4Cl)_2\cdot2H_2O$: Fe, 18.7; C, 8.0; N, 37.5; H, 1.3. Found: Fe, 18.5; C, 8.2; N, 36.6; H, 1.1.

D. Oxidation State of Iron.—Since iron(II) is quite susceptible to oxidation, chemical evidence of the oxidation state of the iron was obtained to complement the physical data obtained from the Mössbauer studies. All attempts to prepare a similar complex with iron(III) chloride under the same conditions failed.

When the iron(II) complexes were placed in oxygen-free water and strong base previously prepared from oxygen-free water was added, the complexes decomposed easily, forming ferrous hydroxide as indicated by its green color. Subsequent solution in hydrochloric acid and oxidation with sodium peroxide gave ferric hydroxide on reprecipitation with base.

One major experimental problem associated with purifying these compounds was that, once formed and isolated, they were insoluble in all solvents available. Some typical solvents tried were: water, ethanol, N-methylformamide, dimethylsulfolane, fluoroboric acid, concd. H_2SO_4, dioxane, perfluoroethanol, carbon disulfide, and ethyl acetate. The solids decompose on heating, all detonating above 250°; thus purification by sublimation or distillation was not possible.

Infrared Spectra of the Complexes.—The infrared spectra of $NaCN_4Cl\cdot1.5H_2O$, $Fe(CN_4Cl)_2\cdot2H_2O$, $NaCN_4NO_2\cdot4H_2O$, $Fe(CN_5O_2)_2\cdot2H_2O$, $NaC_2N_4F_3\cdot H_2O$, and $Fe(C_2N_4F_3)_2\cdot2H_2O$ were obtained by use of the KBr disk technique on a Beckman IR5 instrument. As can be seen in Table I, several bands are shifted or missing in the spectrum of the complex when compared to the sodium salt of the starting material. These are attributed to the loss of resonance character in the ring when it becomes coordinated to the iron.

Mössbauer Study of Molecular Structure.—The experimental details of the Mössbauer technique have been discussed in detail in the literature,[5,6,17] and are essentially those employed in the previously reported studies of Wertheim, *et al.*[7,8] Measurements were made both at room temperature and at 78°K. using a source consisting of Co⁵⁷ diffused into a metallic chromium matrix. The parabolic drive used to impart a Doppler velocity to the source was calibrated from the six-line hyperfine spectrum[18] of metallic iron used as a stationary absorber.

The sample thickness was approximately 0.025 cm. Since the density of the material has not yet been determined accurately,

the amount of iron per unit thickness can only be estimated. If a density of ≈ 1.0 g. cm.⁻³ is assumed, the weight of sample is 0.025 g. cm.⁻² and the weight of Fe calculated is

$$0.025 \text{ g. cm.}^{-2} \times 0.15 \text{ for } Fe(C_2N_4F_3)_2\cdot2H_2O = 0.00375 \text{ g. cm.}^{-2}$$

The weight of Fe⁵⁷ is $0.00375 \times 0.022 = 8.3 \times 10^{-5}$ g. In contrast, a "thin" iron foil absorber (0.5 mil) has 2.2×10^{-4} g. cm.⁻² of Fe⁵⁷ so that there can be no question that the Mössbauer data reported pertain to a "thin" absorber.

In a typical spectrum the calibration constant was 0.0432 mm. sec.⁻¹ chan.⁻¹ and we swept ± 100 channels on each side of the mid-point. From this the velocity range covered is approximately from −4.3 to +4.3 mm. sec.⁻¹.

Results and Discussion

Three microcrystalline complexes of iron(II) have been prepared using the anions of 5-trifluoromethyltetrazole, 5-nitrotetrazole, and 5-chlorotetrazole as ligands. The complexes conform to the general formula $Fe(T)_2\cdot2H_2O$ where T represents the respective tetrazolate anion. In all the complexes the tetrazole anion coordinates to the metal ion in a tetrahedral configuration where the partially localized π-cloud between the N=N bond takes up one corner of the tetrahedron.

A. Mössbauer Effect.—The results of the resonant γ-ray absorption measurements on the three iron(II) tetrazole absorbers are summarized in Table II. There are two rather surprising features evident from these data, related to (a) the absence of quadrupole splitting and (b) the small isomer shift which is observed in these compounds. Since the maximum quadrupole splitting which has so far been observed is on the order of ≈ 2.5 mm. sec.⁻¹, there is little chance that the second half of a quadrupole split pattern could have gone unnoticed. Moreover, the isomer shift for a spectrum with an undetected peak would be very much outside the range of any iron compound yet observed.

Table I

INFRARED ABSORPTION OF IRON(II) TETRAZOLE COMPLEXES IN KBr DISKS. HYDRATE PEAKS ARE OMITTED

s, strong; m, medium; w, weak absorption

NaCN₄-Cl·1.5-H₂O	Fe(CN₄-Cl)₂·2H₂O	NaCN₄-NO₂·4-H₂O	Fe(CN₄-NO₂)₂·2H₂O	NaC₂N₄F₃·H₂O	Fe(C₂N₄-F₃)₂·2H₂O
722m	717w		660w		
				748s	757s
				773m	770w
		840	842s		
995w				973w	
1010w	1034w	1041	1068ms	1038s	1038s
1044s	1054m	1065		1073w	1065s
1063m				1083w	
1089w					
1124m	1169w	1172		1131s	
1156m		1192		1190–1157 broad	1190–1157 broad
1193m					
1295w			1229w	1230s	1239s
1351s	1374s	1314	1328s	1324w	
1370m					
1447w		1408	1431ms	1410m	1420w
		1438	1449ms	1497s	1508m
		1527	1563s		
1621s		1636		1637s	
1661m					

Table II

MÖSSBAUER PARAMETERS FOR THREE Fe(II) TETRAZOLE COMPOUNDS

Compound	T, °K.	E, mm. sec.⁻¹	I.S., mm. sec.⁻¹	$\Gamma_{1/2}$, mm. sec.⁻¹	ϵ, %
$(CF_3CN_4)_2Fe(II)\cdot2H_2O$	298	0	0.475	0.475	4.3
	78	0	.580	.533	6.8
$(O_2NCN_4)_2Fe(II)\cdot2H_2O$	78	0	.604	.523	5.5
$(ClCN_4)_2Fe(II)\cdot2H_2O$	78	0	.579	.440	11.4

The $3d^6 4s^0$ configuration for an Fe(II) atom, corresponding to a ^5D state for the free atom, is readily distorted in an asymmetric electric field arising from chemical bonding in such a way that the degeneracy of the $^3/_2^-$ level from which the M1 transition in Fe⁵⁷ originates is removed. The resultant quadrupole splitting is manifested in the Mössbauer spectrum as a doubly peaked resonance maximum, and has been observed in a large number of compounds including ferrocene and related metal organics,[9,10,12] in FeF_2,[19] $FeCl_2\cdot4H_2O$,[20] $FeSO_4\cdot7H_2O$,[20] $Fe(NH_4)_2(SO_4)_2\cdot6H_2O$,[20] and in $FeSiF_6$,[21] among others.

The absence of observable quadrupole splitting in an Fe(II) compound can only be ascribed to a molecular structure in which the electric field gradient tensor is zero at the iron atom lattice site. In the present case such a situation can obtain if the postulate is made that

(17) G. K. Wertheim, *J. Appl. Phys.*, **S32**, 110 (1961).

(18) J. G. Dash, R. D. Taylor, D. W. Nagle, P. P. Craig, and W. M. Visscher, *Phys. Rev.*, **122**, 1116 (1961); S. S. Hanna, T. Heberle, C. Littlejohn, G. T. Perlow, R. S. Preston, and D. H. Vincent, *Phys. Rev. Letters*, **4**, 28 (1960); see also R. S. Preston, S. S. Hanna, and T. Heberle, *Phys. Rev.*, **128**, 2207 (1962).

(19) G. K. Wertheim, *Phys. Rev.*, **121**, 63 (1961).

(20) S. De Benedetti, G. Lang, and R. Ingalls, *Phys. Rev. Letters*, **6**, 60 (1961).

(21) C. E. Johnson, W. Marshall, and G. T. Perlow, *Phys. Rev.*, **126**, 1503 (1962).

the bonding between the tetrazole ring and the iron atom arises from an overlap of the π-electron density associated with two nitrogen–nitrogen double bonds and the vacant d-orbitals on the iron atom in such a way that the four π-electron distributions occupy tetrahedral bonding sites with respect to the iron atom. A representation of this structure is given in Fig. 1.

On the other hand, it is worth noting that the $3d^5 4s^0$ configuration of Fe(III) representing a half-filled d-electron shell, (i.e., corresponding to a ^6S state for a free Fe(III) atom) is much less readily deformed by an external inhomogeneous electric field, and large departures from cubic symmetry are required to result in observable quadrupole splitting. Thus, the splitting in Fe-(cpd)$_2^+$ is less[9,10,22] than 4 Mc. sec.$^{-1}$, and the definitive conclusion regarding the relationship between molecular structure and the absence of quadrupole splitting must be made in the light of the known oxidation state of the iron atom.[23]

The isomer shifts which are noted for the absorbers listed in Table II are reminiscent of the shifts which have been observed for ferrocene and related Fe(II) compounds, and imply[24] a strong-field interaction in the case of the iron–tetrazole bond. The quantitative evaluation of 4s-electron density is complicated by the presence of 3d-electrons both from the Fe(II) atom itself as well as from the d-orbital occupancy due to bonding. If each partially localized N=N bond contributes effectively a pair of electrons to the iron atom—resulting in d^2sp hybridization—the double occupancy of the hybridized 4s-orbital is effectively reduced by the presence of a completely filled 3d-shell.

This is to say, the observed isomer shift $\approx 0.59 \pm 0.01$ mm. sec.$^{-1}$ is relatively small for an ionic Fe(II) compound (see the correlations in ref. 24) for which typical values are ≈ 1.1 to 1.3 mm. sec.$^{-1}$. The conclusion to be drawn from this is that covalency reduces the 4s-electron density at the nucleus since such covalency increases the 3d-electron density which acts as partial shielding. This reduced 4s-electron density is experimentally observed as a *smaller* isomer shift than that expected for a completely ionic Fe(II) compound but larger than that expected for the addition of an unshielded 4s-electron.

As has been reported, the isomer shift parameter is insensitive to nonnearest neighbor atoms. This fact is borne out by the relative constancy of the isomer shift at 78°K. for the trifluoromethyl-, nitro- and chlorotetrazole, independent of the nature—and electronegativity— of the side-chain group.

Finally it is worth noting that the ratio of the resonance effect (ϵ, Table II) at 78°K. to that at 298°K. is much smaller in the case of the trifluoromethyltetrazole than has previously been observed for metal organic Fe(II) compounds such as those having a ferrocene-like structure. The fraction of recoil free (nonphonon) transitions which occur in the absorber is governed by the Debye–Waller factor[25] which involves, among other parameters, the effective Debye temperature of the

(22) U. Zahn, P. Kienle, and H. Eicher, Z. Physik., **166**, 220 (1962).

(23) In view of the solubility data discussed earlier, a second proposed structure was included in one referee's comments, "The experimental facts may also be explained if the iron is tetrahedrally surrounded by four rings, each σ-bonded to the iron, and have this go on (in silica-like fashion) in three-dimensional array with each ring bonded to two iron atoms and each iron to four rings. Such a scheme would give low solubility and low volatility."

There is nothing in the Mössbauer or infrared data which would argue *against* a polymeric structure. The fact that $\epsilon^{298}/\epsilon^{18} \approx 0.63$ indicates a Debye temperature well above room temperature. This may indicate either strong ionic interactions or infinite (polymeric) networks or both.

(24) L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters, **6**, 98 (1961).
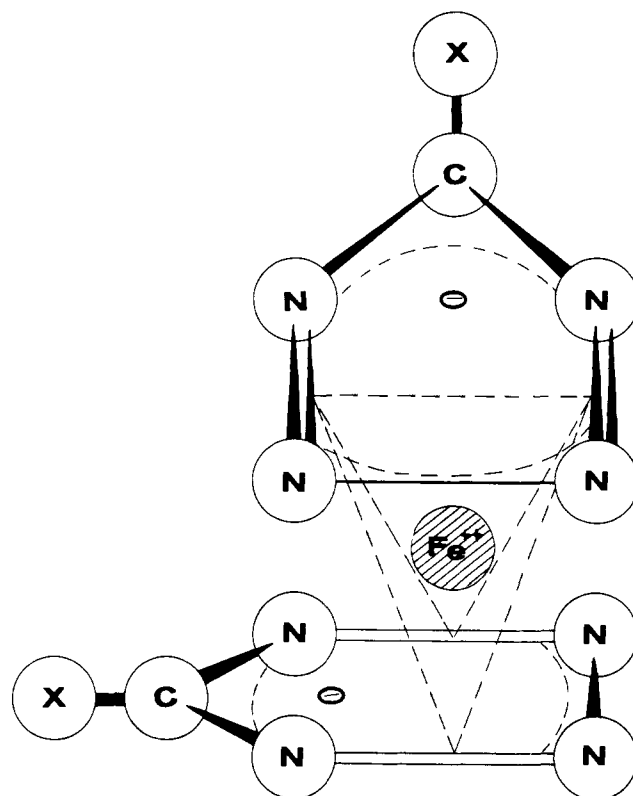
(25) See, for example, ref. 6a, pp. 475-479.

Fig. 1.—A tentative bonding scheme for Fe(II) tetrazole; X = CF$_3$, NO$_2$, Cl, etc.

solid. The present results on the trifluoromethyltetrazole compound suggest that, at least for this absorber, the effective Debye temperature lies well above room temperature.

B. Magnetic Susceptibility Measurement.—Since the largest amount of starting material available was sodium 5-trifluoromethyltetrazole, it was possible to prepare the iron complex with this single ligand in sufficient quantity to obtain magnetic susceptibility data. The measurement was obtained by standard Gouy procedure using a semimicro analytical balance and a permanent magnet having a field strength of 4500 gauss. The resulting magnetic susceptibility for the complex was 1.1 B.M. at 25°. This value is low for an Fe(II) compound, indicating perhaps a super exchange phenomenon. Further measurements are being made on this as well as related compounds.

C. Infrared Studies.—Comparison of the infrared spectra of the sodium salts of the tetrazoles and the complexes supports the bonding demonstrated by the Mössbauer studies. The spectrum of the nitro derivative gives the most pertinent information. Not only does the sodium salt contain peaks absent in the spectrum of the complex but also appreciable shifts in peaks are observed which are readily explained on the basis of bonding indicated by the Mössbauer study.

In the sodium salt the C–NO$_2$ group stretches occur at 1314 and 1527 cm.$^{-1}$, corresponding to symmetric and asymmetric, respectively.[26] In the complex these peaks have been shifted to 1328 and 1563 cm.$^{-1}$, respectively. This shift is in line with a loss of the ability of the nitro group π-cloud to overlap with the π-cloud of the ring because of the localization of the π-electrons in the N=N bonds.

(26) (a) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, pp. 300–301; (b) see also K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden–Day, Inc., San Francisco, Calif., 1962, p. 50.

This is also in line with the color change during complexation. The sodium salt is colorless while the complex is bright yellow, which is typical of nitro compounds where the NO_2 group cannot resonate with a ring. The complex contains appreciable covalent character as shown in the Mössbauer study and the partially localized π-cloud between the nitrogen atoms as shown in Fig 1 will not allow resonance of the nitro group; thus a color change is observed.

The 1431-cm.$^{-1}$ band in the nitro complex and at 1438 cm.$^{-1}$ in the sodium salt is a combination band of the 660 cm.$^{-1}$ nitro group deformation band[27] and the 840 cm.$^{-1}$ C–NO_2 stretching band.[27]

The 1408-cm.$^{-1}$ band in the sodium salt of the nitrotetrazole is shifted to the 1449 cm.$^{-1}$ region and is the band associated with the partially localized N=N bond.[28]

The trifluoromethyltetrazole system shows a shift from 1410 cm.$^{-1}$ in the salt to 1420 cm.$^{-1}$ in the complex with a slight change in intensity. This too can be attributed to the N=N bond.

The peak near 1508 cm.$^{-1}$ in the trifluoromethyltetrazole salt and complex is the C–CF_3 stretching frequency while the peak near 757 cm.$^{-1}$ is the C–CF_3 deformation frequency.[29] The peak at 1038 cm.$^{-1}$ seems to be a combination peak involving the C–CF_3. The area from 8 to 9 μ has previously been assigned[30] to the CF_3 group and shows the typical broad diffuse bands.

The stretching frequency of the C=N delocalized part of the ring appears in all free salts at about 1635 cm.$^{-1}$; it disappears in all the complexes where a partially localized N=N bond is formed giving an *endo-* C–N single bond.[31]

In the sodium salt of the nitro and chloro complexes where the electrons from the group substituted in the 5-position can be delocalized into the ring system, we find a doublet occurring in the 9 to 10 μ region which has

been previously assigned[32] to the skeletal vibrations of the tetrazole ring. In the complexes where delocalization has been decreased, only a single appears. In the trifluoromethyl compound where no delocalization of the substituent group can occur, only a singlet appears in the sodium salt. However, in the complex, a doublet appears. The peak in the region 1055–1065 cm.$^{-1}$ of the three complexes is intensified. This band can then be tentatively assigned to the ring skeletal N=N bond vibration. The second peak of this doublet is at 1038 cm.$^{-1}$ and has been assigned previously to a C–CF_3 combination peak.

Even though these complexes are formed in very strongly acidic media, no protonation of the free electron pairs on any of the nitrogen atoms seems to occur as shown by the absence of C–H and N–H stretching bands.

Finally, the peaks in the water region of the spectrum are very unusual. These peaks are usually quite broad; in the spectra of the dihydrates of these complexes, however, they are narrow and quite sharp. This seems to indicate that the waters of hydration in these compounds are quite unusual. It is possible that the two molecules of water of hydration are bound to the complex through the hydrogens in a manner that restricts their vibrational ability; this should narrow and sharpen their infrared absorption bands.

The X-ray powder diffractograms have been obtained, but no correlations have as yet been made. Further work is now in progress on these and similar compounds.

(27) A. Weissberger, Editor, "Techniques of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 540.

(28) R. J. W. Le Febre and R. L. Werner, *Australian J. Chem.*, **10**, 26 (1957).

(29) L. J. Bellamy, ref. 26a, p. 332.

(30) L. J. Bellamy, ref. 26a, p. 330.

(31) L. J. Bellamy, ref. 26a, p. 272.

(32) E. Lieber, D. Levering, and L. Patterson, *Anal. Chem.*, **23**, 2594 (1951).

Nuclear Magnetic Resonance Studies of Metal–Ethylenediaminetetraacetic Acid Complexes[1]

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The proton n.m.r. spectra for the ethylenediaminetetraacetic acid complexes of Li(I), Na(I), K(I), Cs(I), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Pb(II), Hg(II), and Al(III) have been measured in aqueous solutions as a function of solution pH. Chemical shift data for the methylenic and ethylenic protons indicate that the nitrogen sites of the ligand rather than the carboxylate groups are protonated as the pH is lowered in solutions of the Li, Na, K, Cs, Sr, and Ba complexes. Similar evidence, however, is lacking over the accessible pH range for the chelates of Mg, Pb, Zn, Hg, and Al. The relative ease of protonation for the various metal chelates has been used to establish the extent of coordination of the metal ions with the ligand nitrogen sites. Additional evidence for the relative stabilities of the various chelates is provided by pH studies for solutions with a metal-to-ligand ratio of 1:3. A strong metal ion and pH dependence is observed for the exchange rates of the metal ions between ligands. The exact nature of the bonding of the four carboxylate groups in the metal chelate is not completely evident, but the simplicity of the spectra seems to indicate that the metal–oxygen bonds are relatively labile.

Because of the extensive applications of ethylenediaminetetraacetic acid (EDTA) and its metal–chelate analogs in chemistry, many papers have appeared concerning their properties and structures. A number of these papers have been summarized in the monographs on metal chelate chemistry.[2,3] Several structures

(2) (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952; (b) S.