found earlier for the chromium(II) reduction of other pentaamminecobalt(III) complexes. The results of our rate measurements are summarized in Table I.

TABLE I
RATE CONSTANTS FOR THE REDUCTION OF HALOPENTAAMMINECOBALT(III) COMPLEXES BY CHROMIUM(II) AT 25°

Oxidant	k, M^{-1} sec.$^{-1}$	
	$\mu = 0.1^a$	$\mu = 1.0^b$
$(NH_3)_5CoF^{2+}$	$(2.5 \pm 0.5) \times 10^5$	$(9 \pm 1) \times 10^5$
$(NH_3)_5CoCl^{2+}$	$(6 \pm 1) \times 10^5$	$(2.6 \pm 0.5) \times 10^6$
$(NH_3)_5CoBr^{2+}$	$(1.4 \pm 0.4) \times 10^6$	c
$(NH_3)_5CoI^{2+}$	$(3 \pm 1) \times 10^6$	c

[a] 0.1 M $HClO_4$. [b] 0.1 M $HClO_4$–0.9 M $NaClO_4$. [c] Too fast for measurement.

These electron-transfer reactions have previously been shown[2] to proceed by inner-sphere mechanisms, through bridged intermediates of the type $[(NH_3)_5Co\text{-}X\text{-}Cr(H_2O)_5]^{4+}$, resulting in transfer of the halide from cobalt to chromium. The electron-transfer step is thus presumably preceded by a substitutional step of the type

$$(NH_3)_5CoX^{2+} + Cr(H_2O)_6^{2+} \longrightarrow [(NH_3)_5Co\text{-}X\text{-}Cr(H_2O)_5]^{4+} + H_2O$$

leading to the formation of the bridged intermediate. In view of the very high rate constants reported above, the possibility that the rates of these electron-transfer reactions are determined by this substitutional step cannot be overlooked. In this connection it is of interest that the sequence of rates reported here with Cr^{2+} as reductant, *i.e.*, $(NH_3)_5CoI^{2+} > (NH_3)_5CoBr^{2+} > (NH_3)_5CoCl^{2+} > (NH_3)_5CoF^{2+}$, is the reverse of that found earlier for the much slower reductions of these complexes by Fe^{2+},[3] and Eu^{2+},[1] which are also believed to proceed through inner-sphere mechanisms. In the latter two cases, it seems likely that the order of rates is determined by the increasing stability of the product halide complex, *i.e.*, FeX^{2+} or EuX^{2+}, in going along the sequence X = I to X = F.

Acknowledgment.—Support of this work through a grant from the National Science Foundation is gratefully acknowledged.

(2) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(3) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

Correspondence

Infrared Spectra of, and Protonation Sites in, Solid Ethylenediaminetetraacetic Acid

Sir:

There is a controversy regarding the protonation sites in ethylenediaminetetraacetic acid (H_4Y) and its derivatives.[1-8] The interpretation of the infrared spectra which seems to be at the origin of much of the controversy has been limited mainly to the 1800–1500 cm.$^{-1}$ region.[1-7] We want to report some spectral data concerning solid H_4Y which support the assumption that the nitrogen atoms are protonated in the H_4Y crystal.

We have investigated the infrared spectra of the solid acid H_4Y, of its disilver salts, Ag_2H_2Y, and of its hydrochloride, $H_4Y{\cdot}2HCl$, between 4000 and 250 cm.$^{-1}$. The spectra are shown on Figure 1 together with the spectrum of potassium hydrogen ditrichloroacetate, $KH(CCl_3COO)_2$, which has been recorded for comparison.

The disilver salt exhibits two very strong absorption bands at 1620 and 1392 cm.$^{-1}$, which are assigned to the antisymmetrical and symmetrical COO^- stretching vibrations, respectively. There is no C═O stretching band attributable to the COOH group. The structure of the H_2Y^{2-} ion of Ag_2H_2Y may then be represented just as in the case of the disodium salt,[3] by $(^-OOCCH_2)_2NH^+\text{-}CH_2CH_2\text{-}NH^+(CH_2COO^-)_2$.[9] The broad bands appearing in the 3000–2600 cm.$^{-1}$ region of the Ag_2H_2Y spectrum which are deuteration sensitive may then be assigned to the NH^+ groups. The sharp bands near 3000 cm.$^{-1}$, which are superimposed on the large ones, are not deuteration sensitive and are then due to the CH_2 groups.

Solid H_4Y shows only one broad band near 1690 cm.$^{-1}$ in the 1800–1500 cm.$^{-1}$ region. Chapman[1,5] has concluded that H_4Y must then be a normal carboxylic acid containing four COOH groups and therefore there is no protonation on the nitrogen atom. Langer[6] supports this view, saying that the single band near 1700 cm.$^{-1}$ observed for solid H_4Y is due to dimeric COOH groups attached to neutral nitrogen. If H_4Y is a normal acid it should show a normal acid spectrum over the entire infrared region. However, this is not the case.

In the 4000–2000 cm.$^{-1}$ region, for instance, the absorption pattern of H_4Y is much more similar to that of Ag_2H_2Y than to a normal carboxylic acid spectrum.[10] The broad bands which appear between 3000 and 2600

(1) D. Chapman, *J. Chem. Soc.*, 1766 (1955).

(2) R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962).

(3) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

(4) D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963).

(5) D. Chapman, D. R. Lloyd, and R. U. Prince, *J. Chem. Soc.*, 3645 (1963).

(6) H. G. Langer, *Inorg. Chem.*, **2**, 1080 (1963).

(7) J. E. Tackett and D. T. Sawyer, *ibid.*, **3**, 304 (1964).

(8) R. J. Kula and D. T. Sawyer, *ibid.*, **3**, 458 (1964).

(9) Incidentally this interpretation implies that the Ag^+ ions are not bound to the nitrogen atoms.

(10) S. Bratož, D. Hadži, and N. Sheppard, *Spectrochim. Acta*, **8**, 249 (1956).

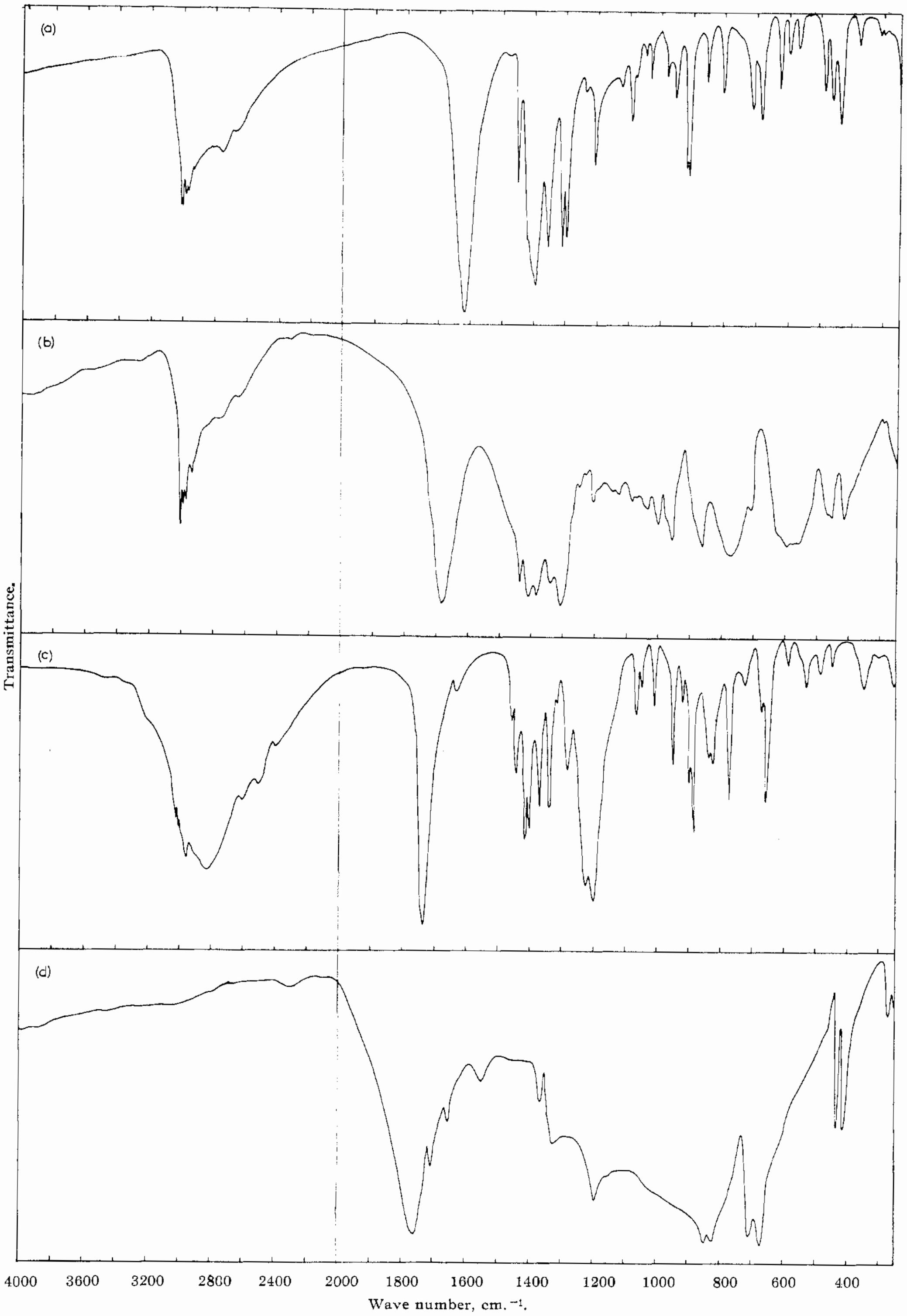
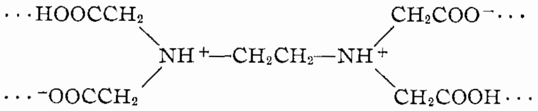


Figure 1.—Infrared spectra of (a) disilver salt, Ag_2H_2Y; (b) ethylenediaminetetraacetic acid, H_4Y; (c) hydrochloride, $H_4Y \cdot 2HCl$; (d) potassium hydrogen ditrichloroacetate, $KH(CCl_3COO)_2$. Combined spectra of the respective mulls in Nujol and Fluorolube.

cm.$^{-1}$ (Figure 1b) seem too weak to be assigned to the OH stretching vibration of a COOH group, and we assign them by analogy with the Ag_2H_2Y spectrum to the NH^+ groups. The infrared spectrum of the hydrochloride, $H_4Y \cdot 2HCl$ (Figure 1c), on the other hand, shows a normal νOH band near 2860 cm.$^{-1}$ comparable to those of carboxylic acids.

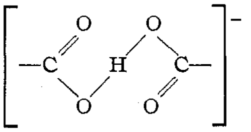
The structure of H_4Y should then be represented diagrammatically by



$$\begin{matrix} \cdots \mathrm{HOOCCH_2} & & \mathrm{CH_2COO^-}\cdots \\ & \mathrm{NH^+{-}CH_2CH_2{-}NH^+} & \\ \cdots {}^-\mathrm{OOCCH_2} & & \mathrm{CH_2COOH}\cdots \end{matrix}$$

This structure implies the presence of COO^- and COOH groups, and the corresponding spectrum is expected to be a superposition of the spectra of H_2Y^{2-} and H_6Y^{2+} ions; in particular, there should be a strong $\nu_a COO^-$ band near 1620 cm.$^{-1}$ and a strong

$\nu C{=}O$ band near 1740 cm.$^{-1}$. This has not been observed; the most important features of the H_4Y spectrum are the presence of a single $\nu C{=}O$ band near 1690 cm.$^{-1}$, the absence of any νOH band above 2000 cm.$^{-1}$, and the presence of an almost continuous absorption between 1600 and 300 cm.$^{-1}$ on which sharper bands are superimposed. A probable explanation of these features is that there is a symmetrical hydrogen bond of the type



in the H_4Y crystal. This centered bond would make the carboxylic and carboxylate groups equivalent, giving rise to a single $\nu C{=}O$ band, and it would lower the νOH frequency below 2000 cm.$^{-1}$.[11,12] Similar spectra have been observed[11] for acid salts of carboxylic acids of the general formula $MH(RCOO)_2$ containing symmetrical hydrogen bonds, $(COOH\text{-}OOC)^-$. The spectrum of $KH(CCl_3COO)_2$ shown in Figure 1d is a typical example of a symmetrically hydrogen-bonded acid salt; its most important features are the same as those of H_4Y, *i.e.*, a single $\nu C{=}O$ band, no νOH band above 2000 cm.$^{-1}$, and the broad 1600–400 cm.$^{-1}$ absorption due to symmetrically hydrogen-bonded OH groups.

Ethylenediaminetetraacetic acid is then not a normal acid containing four COOH groups but it should have both nitrogen atoms protonated while the remaining acidic protons should form very strong, probably symmetrical, hydrogen bonds of the type $(COOHOOC)^-$. The NH^+ groups are also hydrogen-bonded, as indicated by the frequency and the breadth of the NH^+ stretching bands; however, it does not seem possible at present to specify this interaction.

Similar conclusions about protonation sites on nitrogen atoms are reached also for solid iminodiacetic and nitrilotriacetic acids. The details of this study will be published.

[11] D. Hadzi and A. Novak, *Spectrochim. Acta*, **18**, 1059 (1962).

[12] R. Blinc, D. Hadzi, and A. Novak, *Z. Elektrochem.*, **64**, 567 (1960).

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Stereochemically Nonrigid Structures

Sir:

Chemists portray molecules in a rigid, point group formalism that ignores dynamics. Neglect of the effects of dynamics on stereochemistry can lead to serious misconceptions and, at the very least, is a step removed from reality. The dynamic processes critical to stereochemistry are those which permute identical nuclei. Should the time scale of such processes for a given molecule be comparable to or shorter than that of a laboratory observation, then the molecule must be considered as a nonrigid structure for the purposes of the experiment. The consequences of the rigid approach can be rather serious, *e.g.*, incorrect spectroscopic assignments and failure to recognize intramolecular rearrangements.[1] Liehr[2] has previously presented elegant arguments against the rigid stereochemical approach, but a casual perusal of current literature shows that his admonitions unfortunately have been overlooked or ignored.

The question of conformation in isolated eight-coordinate species illustrates the inherent problems of point group formalism. As a specific example, consider the octacyanomolybdate ion, $Mo(CN)_8^{4-}$. In a crystalline potassium salt,[3] the anion has near D_{2d} (dodecahedral) symmetry[4] with two equally-populated cyanide environments. The most plausible structural alternative is the D_{4d} square antiprism with all cyanide groups equivalent, and some investigators[5] have concluded that the anion has this symmetry in the solution state although the data have also been interpreted[6] in terms of a dodecahedral configuration. Recently, we have found that the C^{13} n.m.r. absorption mode of $Mo(CN)_8^{4-}$ enriched[7] in C^{13} consists of a single sharp resonance (1.2 c.p.s. line width). The single absorption peak is literally without structural significance, but we believe that in the context of this note the stereochemical aspect is worthy of discussion. Our n.m.r. data are consistent with the following possibilities, (1) D_{4d} point group symmetry, (2) D_{2d} point group symmetry with very small chemical shift between nonequivalent sites, and (3) D_{2d} or D_{4d} symmetry with rapid intramolecular[8] exchange of cyanide groups. The last alternative is the only realistic one for the n.m.r. time scale because the energy difference between the two idealized geometries presumably is small and the distortion required to interconvert these structures is also small.[9] Point group symmetries should not be used to describe eight-coordinate structures if in the context of the description or the observa-

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[1] Certainly, the static approach has led to an unreasoning and invalid reliance upon crystallographic data for characterization of solution, liquid, and vapor states of molecules.

[2] A. D. Liehr, *J. Phys. Chem.*, **67**, 471 (1963).

[3] It is conceivable that square antiprismatic (D_{4d}) geometry may prevail in other salts.

[4] J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).

[5] H. S. Stammreich and O. Sala, *Z. Elektrochem.*, **65**, 149 (1961).

[6] R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962).

[7] This enriched complex was prepared by the procedure outlined in *Inorg. Syn.*, **3**, 160 (1950), from a commercial sample of KCN enriched in C^{13} to about 50%. Intensities of the $C^{12}N$ and $C^{13}N$ infrared stretching frequencies were approximately equal in the enriched cyanomolybdate sample. Measurements were made on a saturated aqueous solution of $K_4Mo(CN)_8 \cdot 2H_2O$ in a 5-mm. tube at 15 Mc. by Mr. H. Retcofsky of the U. S. Bureau of Mines, Pittsburgh, Pa. The chemical shift is +40.3 p.p.m. from carbon disulfide.

[8] Intermolecular cyanide exchange has been shown to be very slow; exchange is less than 2% in 7 days in the dark: A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950). Exchange between $Mo(CN)_8^{4-}$ and CN^- is photocatalyzed. The C^{13} n.m.r. spectrum of $Mo(CN)_8^{4-}$(aq) in the dark was identical with the spectrum obtained in the light.

[9] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).