[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Dihydrogen Ethylenediaminetetraacetatoaquonickel(II)[1]

BY GORDON S. SMITH AND J. L. HOARD

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The monoclinic cell of crystalline $Ni(OH_2)H_2Y$ ($H_2Y^= \equiv$ dihydrogen ethylenediaminetetraacetate) contains four molecules. The structure, based upon the space group $P2_1/c$, was determined by Patterson and Fourier analysis of spectrometrically measured X-ray data from the three principal zones, with refinement by difference synthesis. The quinquedentate octahedral molecule has H_2O bonded to Ni and one uncomplexed $\cdot CH_2 \cdot COOH$ arm; it displays also *quasi*-tetragonal distortion with two longer than normal axial bonds. The particularly long axial bond closes the strained G ring. (See preceding paper.) The strongly developed pattern of hydrogen bonding inferred from the packing relations suggests that the uncomplexed oxygen atom of G carries the second hydrogen of $H_2Y^=$.

Introduction

The crystalline compounds formed by Ni(II) and Cu(II) with ethylenediaminetetraacetic acid (abbreviated formula, H_4Y) were prepared by Brintzinger and Hesse,[2] who reported the anhydrous formula H_2MY. It has become evident that their partial analyses of these and related complexes generally left undetermined water molecules directly bound to the central atom. Kirschner's analysis[3] of the cupric compound yields the formula $H_2CuY \cdot H_2O$, perhaps better written as $H_2[Cu(OH_2)Y]$ or $Cu(OH_2)H_2Y$: our determination of structure for the isomorphous nickel compound, the subject of this paper, identifies the molecule as a quinquedentate octahedral complex with a water molecule bonded to nickel and one uncomplexed $\cdot CH_2 \cdot COOH$ constituting a free arm. The detailed structural comparison of $Ni(OH_2)H_2Y$ with the sexadentate CoY^- of the preceding paper (WH)[4] proves to be quite illuminating.

Experimental

The crystalline complex of Cu(II) was prepared readily by the procedure of Kirschner.[3] A similar procedure for the perhaps less stable Ni(II) compound gave a product visibly contaminated with starting materials. A slurry made up with equivalent amounts of H_4Y and nickel hydroxide (rather than a nickel salt) was warmed to give a solution from which a uniform product was obtained upon crystallization.

Photographic X-ray diffraction data from single crystals were used to determine the lattice parameters of Table I with an accuracy of, respectively, 0.2 and 0.3%, for the nickel and copper compounds. The observed X-ray symmetry 2/m and the systematic extinctions among the spectra supported the unique[5] selection of the monoclinic space group $P2_1/c$ for both compounds. Since the twofold ($\bar{1}$) positions of $P2_1/c$ were inadmissible for either the complex molecules or for water, it was concluded that all atoms must lie in fourfold general positions.[5] The assumption of four molecules of empirical formula $H_2MY \cdot H_2O$ per unit cell led to excellent agreement (Table I) between calculated and experimental (by flotation) densities and confirmation of Kirschner's chemical analysis.[3] The detailed similarity in the intensity distributions from the two compounds furnished additional evidence for isomorphism, and further X-ray studies were confined to the nickel complex.

TABLE I

UNIT CELL DATA

Compound	a, Å.	b, Å.	c, Å.	β°	d_c, g./cc.	d_X, g./cc.
$Ni(OH_2)H_2Y$	11.71	6.94	16.65	91.2	1.80	1.80
$Cu(OH_2)H_2Y$	11.61	7.00	16.50	92.0	1.84	1.82

Using essentially the technique described earlier[6] (but with substitution of a proportional for a Geiger counter), integrated intensities for the three principal zones of $Ni(OH_2)H_2Y$ were measured on a G.E. XRD-3 spectrometer modified for single crystal work. The small cross-sections, 0.09 × 0.09, 0.15 × 0.15, 0.13 × 0.15 mm., for specimens oriented, respectively, along a, b, c, together with the low value of the linear absorption coefficient, 27.2 cm.$^{-1}$, for Cu Kα radiation, made unnecessary any correction for variation of absorption with scattering angle. However, it was necessary to apply empirical corrections to the intensity data within the range of scattering angle in which partial resolution of the Kα doublet added complication to measurement by the convergent beam technique. While not fully satisfied with our procedure (a problem under current study), the internal consistency of the $Ni(OH_2)H_2Y$ data seems at least as good as for the $NH_4CoY \cdot 2H_2O$ data of WH taken wholly with MoKα radiation ($2\theta_{\max} < 60°$). The intensity data were converted to relative $[F]^2$ values in the usual manner.[7] Intensities were measurable for 466 forms, about 92.5% of the total permitted for $\sin \theta / \lambda \lesssim 0.645$.

Following virtual completion of the determination of structure, the infrared absorption spectra in the range 2–15 μ were taken for both crystalline materials on a Perkin–Elmer Model 21 Recording Spectrophotometer.

Determination of Structures

With all atoms in the general positions[5] of $P2_1/c$, the entire molecule constitutes the asymmetric unit, and there are (exclusive of hydrogen) 66 positional coördinates to be determined. The Patterson syntheses,[8] P(X,Z) and P(Y,Z) showed more large peaks than could be accounted for on the basis of Ni–Ni interactions alone. Knowing, however, that the short b translation must correspond to the molecular thickness, the Patterson projection P(X,Z) was expected and was found to show identifiable features characteristic also of $\rho(x,z)$. A partial interpretation along these lines provided positions for nickel and four lighter atoms bound to nickel which were consistent with both P(X,Z) and P(Y,Z). Using these parameters for phase determination, the first incomplete electron density maps were constructed and found to be consistent with the original interpretation. Vector separations, nickel peak to minor peaks, as read from $\rho(x,z)$ were compared with $P(X,Z)$ to check on the reality of the minor peaks. It was then possible to include contributions from more light atoms in the structure factor calculations,[9,10] to assign more phases and add more terms to $\rho(x,z)$. Thus was begun a process of successive approximation which en-

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[1] Supported by National Science Foundation.

[2] H. Brintzinger and G. Hesse, *Z. anorg. allgem. Chem.*, **249**, 113 (1942).

[3] S. Kirschner, THIS JOURNAL, **78**, 2372 (1956).

[4] H. A. Weakliem and J. H. Hoard, *ibid.*, **81**, 549 (1959).

[5] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 99.

[6] J. L. Hoard, R. E. Hughes and D. E. Sands, THIS JOURNAL, **80**, 4507 (1955).

[7] *Cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons, Ltd., London, 1953.

[8] All calculations of Fourier type were carried out on the IBM 650 computer using a program kindly supplied by Miss Dorothy Booth of the Bell Telephone Laboratories.

[9] Carried out on the IBM 650 calculator using a program written by Dr. H. A. Weakliem.

[10] The atomic form factors of J. Berghuis, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955), were used for light atoms. The form factor used for nickel was that of L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957), with the dispersion corrections of C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

abled us to build up $\rho(x,z)$ and $\rho(y,z)$ to the point that (1) the octahedral coördination of six atoms (N and O) about nickel was well defined, (2) the locations of the remaining oxygen atoms were less certainly indicated, but (3) the pattern of carbon linkages was obscured through severe overlap. In terms of a direct reading of the still incomplete maps, either a sexadentate complex similar to CoY^- of WH (plus a free water molecule) or a quinquedentate complex with one uncomplexed $\cdot CH_2 \cdot COOH$ arm and a water molecule bound to nickel was possible. However, carbon positions were predictable within reasonable limits for each interpretation, and the agreement between calculated and observed structure amplitudes proved to be clearly superior for the free arm model (shown in its final form in Fig. 1). This structure, moreover, lent itself to major refinement by means of difference syntheses,[7] $\rho - \rho_c$, ρ_c being the projected electron density as given by the Fourier synthesis of calculated amplitudes, which were carried through for all three zones of reflection.

Refinement through successive cycles of difference synthesis, with objective re-evaluation at the end of each cycle of scale factor and thermal parameter (treated as independent for each zone), proceeded until the values of $R = \Sigma||F| - |F_c||/\Sigma|F||$ for all zones lay in the range 0.12–0.13, and the concurrently obtained values of B in the range 2.1–2.3 Å.^{2}. Minor refinement of positional coördinates was still in prospect, but it had become feasible to include all Fourier coefficients in the syntheses of electron density maps. Two of these, $\rho(x,z)$ and $\rho(y,z)$ are reproduced in Fig. 2 and 3, with added indication of final atomic positions and the bonding pattern in the complex as aids to the Reader (see also Fig. 1) in following the Discussion.

The difference syntheses at this point displayed the following unsatisfactory characteristics: (1) negative densities at positions corresponding to the water molecule and to all oxygen atoms not bonded to nickel together with somewhat positive densities at the positions of nickel and the remaining five atoms bound to it, and (2) indications of contradictory and sometimes non-trivial parameter shifts for some atoms, particularly carbon overlapping in one or more projections with the non-chelated oxygen atoms. Both effects were seen to arise from inadequacy of the model using a single value of B. Some further refinement was achieved by allowing two distinct values of the thermal parameter (for each zone) assigned as follows: the larger, B'', to the six oxygen atoms judged to have larger than the average thermal motions, the smaller, B', to all other atoms. (Presumably the ring carbon atoms would have an intermediate value of B, but we were reluctant to introduce another disposable parameter.) With the aid of the following approximate analysis, applicable to well-resolved atoms of either class, the difference maps corresponding to the average B were used to estimate initial values of B' and B''.

If the difference map near the j^{th} atomic position be taken as the difference between two Gaussian distributions, each of the form $\exp(-pr^2)$, if the slope be zero at the atomic site and if the error in scale factor be negligible, then in two dimensions (Z_j = at. no.)

$$\Delta p_j = (p - p_o)_j = (\pi/Z_j)(\rho - \rho_c) = (\pi/Z_j)\Delta\rho_j$$

Using the approximation for a Gaussian electron density given by Hamilton[11]

$4\pi^2/p_j = B_j + K_j$, K_j a constant, we obtain

$$\Delta B_j = -(4\pi^2/p_j^2)\Delta p_j = -(4\pi^3/p_j^2 Z_j)\Delta\rho_j$$

Following introduction of the new thermal parameters into the difference syntheses, refinement for each zone was carried through several cycles with periodic adjustment of parameters. R-values, with missing reflections included, of 0.091, 0.094, 0.100 for, respectively, $h0l$, $hk0$ and $0kl$ zones were then obtained. Average values of B', B'' and B from the earlier analysis, with mean deviations to indicate the variations among the three zones, were, respectively, 1.99 ± 0.01, 2.94 ± 0.06 and 2.19 ± 0.04 Å.^{2}. The last figure is very near to the analogous B = 2.14 ± 0.03 Å.^{2} obtained for $NH_4CoY \cdot 2H_2O$ in WH. There were, to be sure, residual features on our final difference maps to suggest that a further generalization of thermal parameters and the inclusion of contributions from hydrogen atoms could lead to a further modest refinement of the structure. However, indications from different zones of contradictory shifts in atomic positions were small and mostly confined to carbon atoms. It was seen also that small shifts in carbon positions alone could be introduced so as to constrain all C–C and all C–N (save one) bond distances to the respective ranges 1.52–1.54 Å. and 1.48–1.49 Å., with only a nominal (0.5%) increase in R values. This result perhaps indicates the modest improvement which might be attained by introducing further B's as disposable parameters with, however, the attendant danger of giving the final analysis an unduly subjective flavor. Consequently, we accept as final the positional coördinates (Table II) given by the last difference syntheses with B' and B'' as thermal parameters. We note that there remain no outstanding discrepancies between observed and calculated amplitudes.[12] Extinction in the crystals is apparently small.

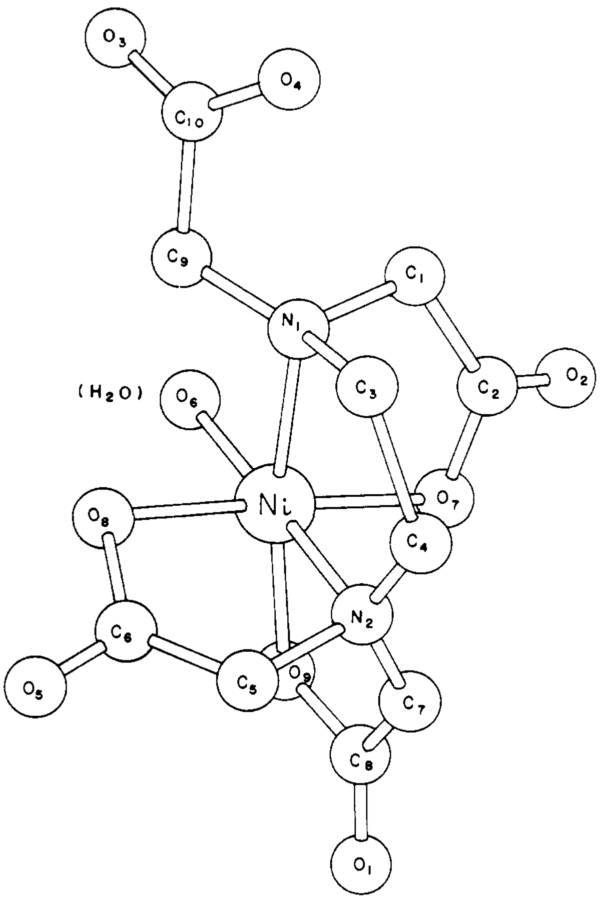

Fig. 1.—Model in true perspective of $Ni(OH_2)H_2Y$.

The assessment of accuracy of atomic positions is completely straightforward only for those few atoms which are reasonably well resolved upon two of the three electron density maps; *e.g.*, for the nickel atom standard deviations of $\sigma(x) = \sigma(z)$ = 0.002 Å., $\sigma(y)$ = 0.003 Å. are obtained by Cruickshank's method.[13] Insofar as they can be estimated by approximating to this procedure,[13] the corresponding σ values for lighter atoms lie in the range 0.01–0.025 Å. We list below standard deviations expected to apply on the average to the corresponding class of bond distance or bond angle.

Lengths: Ni–O or Ni–N, 0.014 Å.; N–C or O–C in ring, 0.022 Å.; others, 0.025–0.030 Å.

Angles: At. Ni, 0.85°; NiNC or NiOC, 1.1°; others 1.5–1.8°

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[11] W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

[12] Following submission with the manuscript for inspection by referees, amplitude data for $Ni(OH_2)H_2Y$ have been deposited as Document number 5746 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[13] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949); F. R. Ahmed and D. W. J. Cruickshank, *ibid.*, **6**, 385 (1953).

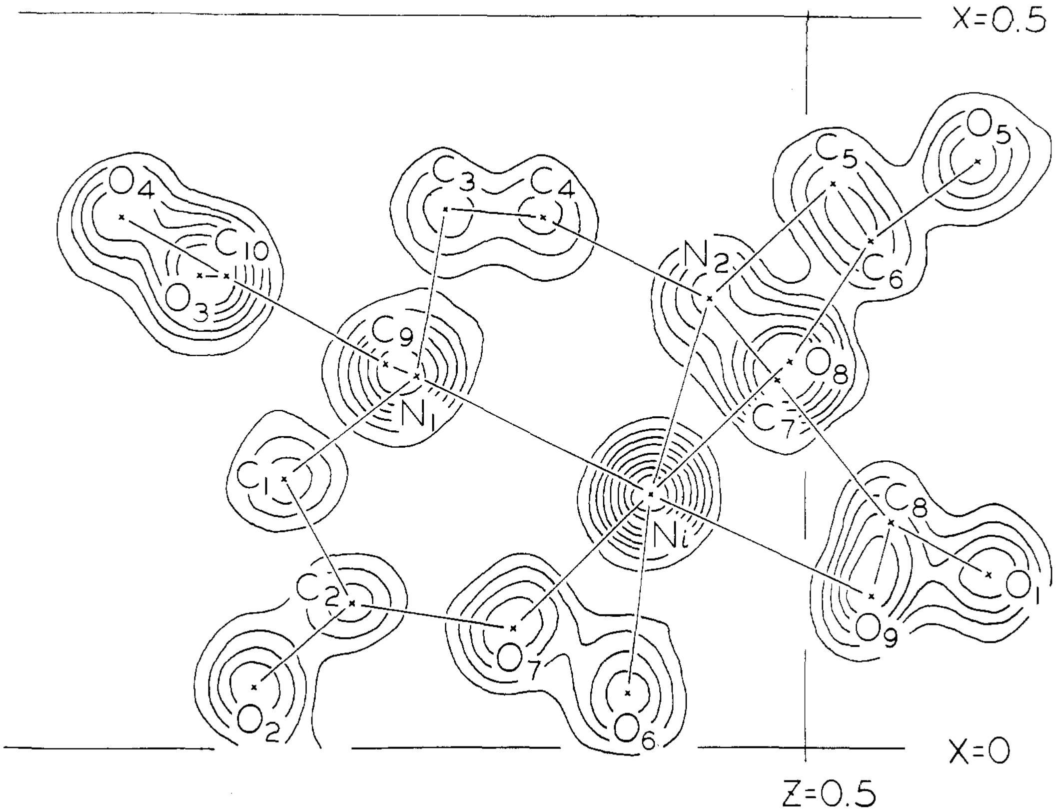

Fig. 2.—Electron density projected onto (010). Contours at intervals of 2e/Å.^{2} starting with 4e/Å.^{2} contour except around Ni where the interval is 5e/Å.^{2} starting with 5e/Å.^{2} contour. The skeleton of one molecule is indicated.

Discussion of the Structure

The geometry of the quinquedentate octahedral $Ni(OH_2)H_2Y$ (Fig. 1) is in several fundamental respects so similar to that of the sexadentate CoY^- of the preceding paper (*WH*) that we shall use a similar terminology. NNM is the plane defined by the two nitrogen atoms and the central atom (Ni, Co). E is the ethylenediamine ring ($Ni–N_1–C_3–C_4–N_2–Ni$ in Fig. 1) with NNM as median plane. G is a glycinic ring ($Ni–N_2–C_7–C_8–O_9–Ni$) with the closing M–O bond lying nearly in NNM. (There are two G rings in CoY^-.) R is also a glycinic type of ring, of which there are two ($Ni–N_1–C_1–C_2–O_7–Ni$ and $Ni–N_2–C_5–C_6–O_8–Ni$) in $Ni(OH_2)H_2Y$ (and two in CoY^-). The R rings (unlike E and G) are virtually flat, lie nearly at right angles to one another and to NNM, and the closing M–O bonds are approximately along the normal to NNM. By eliminating the water molecule (Fig. 1) and swinging the free arm around to form a second G ring we obtain (the mirror image of) the sexadentate configuration of WH, Fig. 2.

TABLE II

POSITIONAL COÖRDINATES WITHIN THE CELL[a]

Atom	10^4x	10^3y	10^4z	Atom	10^4x	10^3y	10^4z
Ni	1712	321	4242	C_9	2617	579	2968
N_1	2518	364	3122	C_{10}	3192	634	2203
N_2	3048	135	4523	O_1	1192	−115	5863
C_1	1832	267	2485	O_2	422	22	2357
C_2	980	120	2822	O_3	3217	820	2085
C_3	3777	279	3252	O_4	3635	521	1710
C_4	3597	93	3732	O_5	4040	524	5818
C_5	3857	232	5093	O_6	390	519	4123
C_6	3462	443	5297	O_7	820	123	3585
C_7	2493	−35	4858	O_8	2633	511	4928
C_8	1520	18	5377	O_9	1037	179	5283

[a] Rounding off to the nearest 0.0005 of x and z for light atoms is in order. For Ni y is more accurately 0.3212.

The lengths of the six bonds formed by nickel show significant variations. Using O_R and O_G for oxygen atoms in R and G rings, we find: $Ni–O_R$ = 2.03, 204 Å.; $Ni–OH_2$ = 2.08 Å.; $Ni–O_G$ = 2.16 Å.; $Ni–N_2$ = 2.08 Å.; $Ni–N_1$ = 2.13 Å. Bond lengths predicted from Pauling's Tables[14] are Ni–O = 2.05 Å., Ni–N = 2.09 Å., in close agreement with our values $Ni–O_R$ = 2.035 Å., $Ni–N_2$ = 2.08 Å. With these values as norms the indicated increases in bond lengths for $Ni–OH_2$ and $Ni–N_1$ are probably significant, for $Ni–O_G$ definitely significant. On the reasonable basis that a slightly longer bond to oxygen of a water molecule is normal, we can interpret the bonding pattern as displaying four shorter equatorial bonds ($Ni–O_7$, $Ni–O_8$, $Ni–O_6$, $Ni–N_2$ in Fig. 1) and two longer axial bonds ($Ni–N_1$, $Ni–O_9$). Pronounced *quasi*-tetragonal distortion of Cu(II) in octahedral coördination is well established and, judging from our results for $Ni(OH_2)H_2Y$, is presumed to be present in the isomorphous $Cu(OH_2)H_2Y$.

The conclusion of WH that G rings are definitely less stable than R rings, although based mainly upon the analysis of cumulative bond angle strain in forming a G ring, also received support

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(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

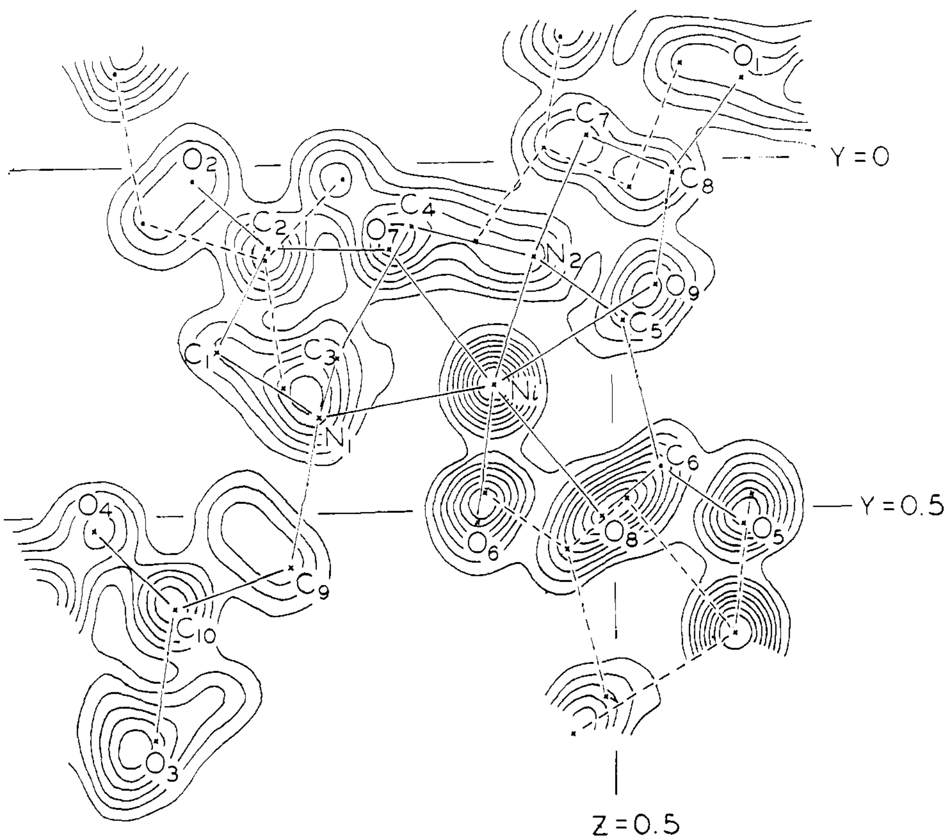

Fig. 3.—Electron density projected along *a*. Contours at intervals of 2.5e/Å.^{2} except around Ni where the interval is 5e/Å.^{2}; 5e/Å.^{2} is the lowest contour. The skeleton of one complete molecule is indicated by solid lines, bits of others by dashed lines.

from a possibly significant difference in bond lengths; the data gave virtually identical values for Co–O_G and Co–N with Co–O_R shorter by 0.03 Å. We note that the quinquedentate complex has but one G ring. The extensions beyond normal values in the two axial bonds of the complex, *ca.* 0.05 Å. for Ni–N_I and *ca.* 0.12 Å. for Ni–O_G strongly suggest an additional instability in the latter not accounted for by natural distortion of the bonding orbitals of the central atom. The three possible *a priori* choices for the equatorial band of four shorter bond distances are the observed band, (A) Ni–N_I 2(Ni–O_R),Ni–OH_2 and the rejected possibilities, (B) 2(Ni–N),Ni–O_G, Ni–OH_2, (C) Ni–N, 2(Ni–O_R),Ni–O_G. Comparison of A and C shows that the monodentate ligand H_2O is preferred to O_G for a short bond; however, the preference seems clearly reversed for the weak axial bond else we should expect to find replacement of O_G by an additional molecule of water to give a quadridentate complex. Comparison of A and B indicates that 2(Ni–O_G) bonds contribute greater stability, *i.e.*, lesser free energy, than the pair Ni–N and Ni–O_G. The comparison of Ni–N with Ni–O_R could still be in favor of the former, although overridden by an even stronger preference for Ni–O_R over Ni–O_G.

Noting first that carbon–oxygen distances of 1.26 and 1.31 Å. are obtained for the ·COOH group of the uncomplexed arm, we then group all remaining bond distances into classes. Within each class we list the averaged distance with mean deviation and (in parentheses) maximum deviation from the mean; in no case does this last attain more than possible significance in the statistical sense. C–N, 1.49 ± 0.02 (0.03) Å.; C–C, 1.52 ±0.02 (0.05)Å.; C–O (in ring), 1.26 ±0.03 Å. for *R*, 1.26 Å. for G; C–O (external), 1.22 ±0.01 Å. for R, 1.29 Å. for G. Analysis of the pattern of hydrogen bonding (*vide infra*) indicates (1) that the external oxygen atom O_1 of G carries a proton, and (2) that the hydrogen bonding of external oxygen atoms is very much stronger in $Ni(OH_2)H_2Y$ than in CoY^-. A less pronounced differentiation in the R rings of $Ni(OH_2)H_2Y$ between ring and external C–O distances as compared with CoY^- (1.30 and 1.22 Å., respectively) appears reasonable and is formally but inconclusively supported by our data. Our averaged bond lengths may also be compared with typical data from recent structural studies of amino acids, *e.g.*, for glycine[15] values of C–N = 1.474, C–C = 1.523, C–O = 1.255, 1.252 Å. are reported.

Bond angle data are grouped below into natural classes. For the pair of R rings and for chemically similar bond angles in E the averaged values with mean deviations are listed. The sum of all bond angles within the ring ($\lesssim$540°) also is given for each ring type.

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(15) R. E. Marsh, *Acta Cryst.*, **10**, 814 (1957).

R: NiNC, 108.8 ± 0.2°; NCC, 112.4 ± 0.4°; CCO, 117.9 ± 0.9°; CONi, 116.6 ± 0.8°; ONiN, 82.7 ± 0.9°; sum, 538.4 ± 0.7°

G: NiNC, 104.5°; NCC, 111.7°; CCO, 119.8°; CONi, 109.5°; ONiN, 79.4°; sum, 524.9°

E: NiNC, 104.3 ± 0.4°; NCC, 109.7 ± 0.4°; NNiN, 86.5°; sum, 514.5°

>CO of rings: CCO, 116.3 ± 1.8°; OCO, 125.0 ± 1.0°

Arm: NiN_1C_9, 108.7°; $N_1C_9C_{10}$, 115.6°; $C_9C_{10}O_3$, 113.2°; $C_9C_{10}O_4$, 126.1°; $O_3C_{10}O_4$, 120.6°

Between rings: O_8NiO_9, 92.5°; O_9NiO_7, 86.0°; O_8NiN_1, 99.3°; O_9NiO_6, 95.4°; O_6NiN_1, 99.7°; N_2NiO_7, 94.4°; O_7NiO_6, 91.3°; O_6NiO_8, 90.6°; $C_4N_2C_5$, 111.5°; $C_4N_2C_7$, 112.4°; $C_5N_2C_7$, 113.9°; $C_3N_1C_1$, 113.9°; $C_3N_1C_9$, 110.2°; $C_1N_1C_9$, 111.6°

The accuracy of our bond angle determinations, especially for several data involving carbon atoms, does not justify detailed comparisons of the kind given in WH for CoY^-. However, conclusions based upon the ring sums and the more accurately defined angles, *e.g.*, those at nickel and perhaps at nitrogen, are still of interest. Substitution of Ni(II) for Co(III) requires an increase of 0.16-0.25 Å. in the lengths of the bonds formed by the central atom. If the angles at the light atoms are to be maintained unchanged, then the bond angle at the central atom must be further decreased by the substitution. To a first approximation, this is what is observed: The sums of the ring bond angles for both G and R rings are virtually the same in $Ni(OH_2)H_2Y$ as in CoY^-. The R rings are nearly flat, the G ring is constrained by the orientation of the tetrahedral nitrogen atom to be folded in the same way and roughly to the same degree as in CoY^-. The bond angle at nitrogen in the G ring also is closed from the tetrahedral value by about the same amount in both complexes. Most significant is the decrease in bond angle at the central atom for both R and G rings.

Suitable reference planes from which to measure the departures from planarity of R and G rings are provided by the observation that the sum of the three bond angles at carboxylate carbon is in every case $\gtrsim 359.6°$, thus (despite the rather large probable error) establishing essential planarity for all C·COO groups. Observed departures of nickel and nitrogen atoms from the reference plane of the appropriate C·COO group are, respectively, 0.17 and 0.22 Å. (averaged values) in the *same* sense for R rings, 0.23 and 0.53 Å. in the *opposite* sense for the G ring.

The principal part of the distortion from planarity of the E ring is describable as a twist about a line through nickel bisecting the C–C bond so that carbon atoms lie on opposite sides though not quite equidistant (0.34, 0.39 Å.) from NNM. The E ring differs from the R and G rings in that the increased strain associated with substitution of Ni(II) for Co(III) apparently has resulted in approximately equal decreases in the bond angles at nitrogen and at the central atom.

All atoms (except hydrogen) of the free arm and its extension (N_1–Ni) back to the central atom come out within 0.05 Å. of planarity. No atom of the five comprising the equatorial band of four shorter bonds departs from the median plane by more than 0.09 Å. The exigencies of forming the girdle of an E and two G rings in CoY^- require the large value (104.0°) for the open O_GCoO_G angle between rings. Were a similar girdle formed about Ni(II), with ring bond angles as found in $Ni(OH_2)H_2Y$, the open O_GNiO_G angle would need to be about 115°. In $Ni(OH_2)H_2Y$, despite the smoothing effect arising from the presence of a monodentate ligand, the mean deviation from a right angle of the bond angles at the central atom is 5.5°; in CoY^-, it is 4.2° or, omitting the extraordinary 104° angle, 3.3°.

Four theoretical stereoisomers, all optically active, of a quinquedentate octahedral complex MYX, with X as monodentate ligand (or void), must be considered (Fig. 4). (We ignore configurations which require spanning of octahedral *trans* positions by a single ring.) The spatial distribution of bond directions at nitrogen is implied for each stereoisomer in Fig. 4 by indicating the bond geometry of the E ring. I and II are derivable from the sexadentate configuration of Fig. 2 in WH by opening, respectively, a G or an R ring, with I the preferred form. III, like II, may be said to have a single R and two G rings, whereas in IV the rings are neither R nor G, but approach more nearly to the latter type. In both III and IV, however, interference between the methylene group of the free arm and a part of the ring closed on the same (in Fig. 4 the lower) side of NNM is so serious as to imply further large distortion of the ring systems. We conclude that III and IV are certainly less stable than II which, in turn, has been shown to be less stable than I. Indeed, this analysis promises maximum simplification to the practical stereochemistry of quinquedentate octahedral complexes wherein H_4Y or one of its anions in the complexing agent.

With those atoms, *e.g.*, Pd(II) and Pt(II), which may be thought to demand planar four-coördination, H_4Y (or one of its anions) as *sole* complexing agent should form a *relatively* weak complex. On the assumption that axial bonds are non-existent, *i.e.*, the net force is repulsive out to distances well beyond reasonable covalent bond lengths, there remains no alternative to closure of E and, perforce, two G rings to achieve a pattern of four planar bonds. The relative instability of the complex is not merely the result of using G instead of the more stable R rings: our earlier analysis strongly suggests that G rings carry additional strain in the absence of R rings. The enthalpy change on formation of this species must compare unfavorably with that for the related complex formed with two molecules of methylamine-diacetic acid. We judge that the experimental data reported for the Pd(II) and Pt(II) complexes by Busch and Bailar[16] are consistent with our analysis, though the configurations of interest are inferred rather than proved.

Careful study of the packing relations betweeen molecules strongly indicates that hydrogen bonding contributes largely to the stability of the crystal. This conclusion is inferred from the number and closeness of O–O contacts between molecules. The complete structure is too complex for clear illustration in perspective, and the essential re-

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(16) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 716 (1956).

lations are best described (with some help from Figs. 2 and 3) in a more formal way. If M represents the molecule of Figs. 2 and 3 (and Table II), neighboring molecules of primary interest are derived from M through symmetry operations as follows. The glide plane at $y = 3/4$ with glide of $-c/2$ yields M^a; the screw axis through $x = 0$, $z = 1/4$ with translation $b/2$ yields M^b; the inversion centers 0 0 1/2, 0 1/2 1/2 yield, respectively, M^c,M^d. Then, for example, O_9^c identifies the oxygen atom in M^c structurally equivalent to O_9 (Figs. 1-3) in M.

The following short oxygen–oxygen contacts between M and neighboring molecules are obtained: $O_3..O_5^a$, 2.58 Å.; $O_1..O_7^c$, 2.55 Å.; $O_6..O_2^b$, 2.63 Å.; $O_6..O_9^d$, 2.87 Å., with estimated standard deviations of 0.02-0.03 Å. All four hydrogens of each asymmetric unit, *i.e.*, of each $Ni(OH_2)H_2Y$ molecule deemed capable of forming hydrogen bonds are indeed used to bridge 7/9 of all oxygen atoms to give a structure layered parallel to (100). No hydrogen bonded atoms are centered within the layer $0.39 < x < 0.61$, and no hydrogen bond crosses this region. Across $x = 1/2$ there is a maze of contacts involving methylene carbon and carboxylate atoms coming variously from the free arm E and one of the R rings; when carefully sorted out, these contacts prove to have normal van der Waals values.

Of the two hydrogen bonds formed by the water molecule (O_6), the shorter (2.63 Å.) bond is to an external oxygen O_2 of an R ring (Fig. 1); the longer (2.87 Å.) bond is to a ring oxygen O_9 of G. The computed bond angle $O_2^bO_6O_9^d$ is 96.3°. In considering the bond formed between O_3 of the free arm and O_5, the external oxygen of the second R ring, we assign the proton to O_3: (1) The bond data, C_{10}–O_3 = 1.31 Å., C_{10}–O_4 = 1.26 Å., $C_9C_{10}O_3$ = 113.2°, $C_9C_{10}O_4$ = 126.1°, are indicative of carboxyl with the proton attached to O_3; (2) the infrared absorption spectrum of crystalline $Ni(OH_2)H_2Y$ shows the two well defined bands at about 1216 and 1729 cm.$^{-1}$ which seems unambiguously to be associated with uncomplexed[17] ·COOH. Certainly this assignment is not unexpected on a chemical basis. The bond angle of interest is then $C_{10}O_3O_5^a$ = 123°.

Assignment of the proton to a particular oxygen atom is least certain for the final class of hydrogen bond, that formed between the external oxygen O_1 of G and a ring oxygen O_7 of R (Fig. 1). On the basis of bond angle at the central protonated oxygen atom either assignment is equally probable (120–122°). However, it is difficult to see how the Ni–O_7 bond (2.03 Å.) could sustain its apparent role of substantial equivalence to Ni–O_8 (2.04 Å.) if O_7 had really to be regarded as OH. Assignment of the proton to O_1 seems reasonable and probable by contrast. The long Ni–O_9 bond may even be largely electrostatic in character, and the existence of the G ring in the crystalline complex may actually depend upon the additional stabilization arising from the hydrogen bonding of both O_1 (as OH) and O_9 of G to other molecules.

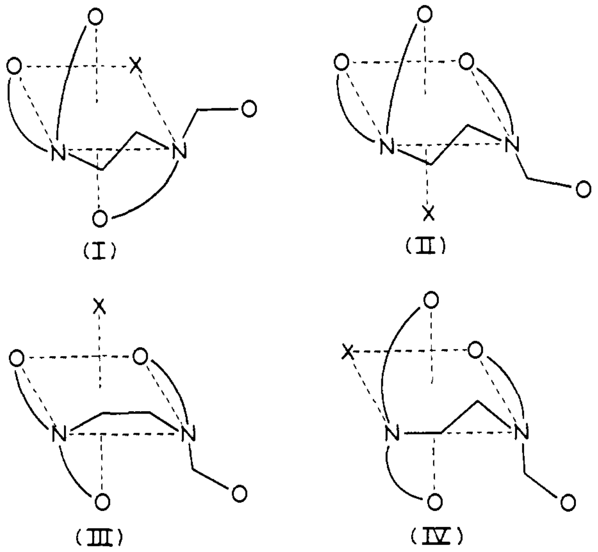

Fig. 4.—The stereoisomers of a quinquedentate octahedral complex MYX. Note particularly the indicated geometry of the E ring.

Our infrared absorption spectrum from crystalline $Cu(OH_2)H_2Y$ shows somewhat stronger development of the bands ascribed to free ·COOH than does the nickel complex. However, we cannot agree that the stronger of these at about 1720 cm.$^{-1}$ has attained "... approximately equal[3]..." intensity with the very strong band at about 1615 cm.$^{-1}$ associated with carboxylate groups bound to the central atom. Neither can we subscribe to the apparently *a priori* assumption that in the crystalline Cu(II) complex "... two carboxyl groups of the ligand are protected from coördination by being bound to protons." The *quasi*-tetragonal distortion of the bond orbitals may well be more pronounced for Cu(II) than for Ni(II), but the evidence for isomorphism of the crystalline pair is too detailed to admit of more than small variations within the isostructural pair, $M(OH_2)H_2Y$.

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ITHACA, NEW YORK

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[17] *Cf.* M. L. Morris and D. H. Busch, THIS JOURNAL, **78**, 5178 (1956).