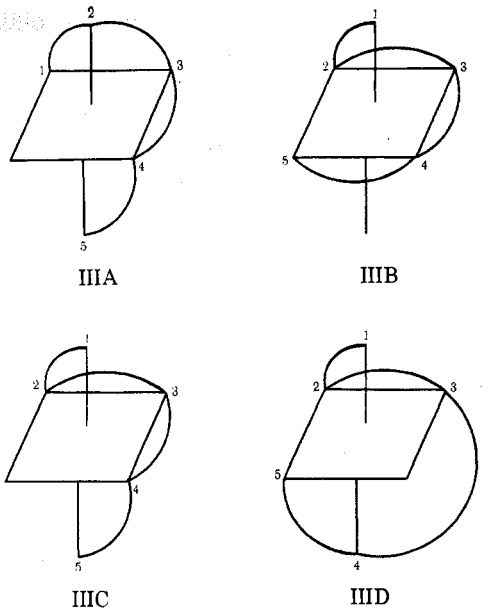
As noted previously the lowest energy band is extremely broad with from zero to three relatively sharp bands superimposed on it. These bands usually appear as shoulders rather than as isolated bands. This so-called "fine structure" is especially noticeable in methanol solution, less so in nitromethane, and practically undetectable in Nujol. The splitting of this band may arise *via* one or some combination of the following rationalizations. The broad band may contain a number of component vibrational transitions which are sufficiently widely spaced so that they may be observed as poorly resolved shoulders.[16] Since these spectral features appear to be solvent dependent, this argument seems quite tenable. Alternatively, some splitting of the lowest energy band could arise from tetragonal distortion of the formally octahedral complex. The symmetry of these complexes is, at best, C_{4v} and some of the splitting of the first octahedral band may be attributed to the effects of lower symmetry.[17]

Finally, it may be interesting to speculate how the pyDPT ligand attaches itself to the octahedral nickel(II) ion. A linear pentadentate ligand in which the donor atoms are members of a continuous chain of atoms as pyDPT may attach itself to an octahedral metal ion in one or several manners, structures IIIA–IIID. In order for any of these structures to be adopted, a twist must occur at one or more donor atoms in the coordinating molecule, for example at the 2 and 4 positions in IIIA. Therefore, if the molecule is not flexible enough to allow for this stereochemical twist, it may not function as a pentadentate ligand but rather as a quadridentate or tridentate ligand.[4]

The greatest amount of twist must occur at the azomethine linkages (*i.e.*, the 2 and 4 positions) in the py-



DPT ligand in order for it to function as a pentadentate ligand. A study of Dreiding stereomodels shows that of the four arrangements IIIB and IIIC are the least favored sterically. It is possible to construct a model of IIIA although some strain is apparent. Perhaps the most favored arrangement is IIID which is quite easy to achieve using the stereomodels and presents the least strain on the ligand.

Acknowledgment.—This investigation was supported by VPISU–NASA Multidisciplinary Grant 47-004-006. Much of the instrumentation used to carry out this study was obtained by NSF Departmental Equipment Grants GP 8617 and GP 9530.

(16) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
(17) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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Circular Dichroic Spectral Studies of Mixed Amino Acid–Acetylacetone Complexes of Nickel(II) and Observations on the Proline–Nickel(II) Complexes[1]

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Circular dichroic spectra demonstrate formation of mixed amino acid–acetylacetone complexes of Ni(II), containing one moiety each of the chelants. Group theoretical arguments are used to deduce from the CD spectra that the arrangement of the chelants is trans, or equatorial. Amino acids used are valine, serine, arginine, ornithine, proline, aspartic acid, and asparagine. CD spectra of prolinatonickel(II) may differ from those of the normal amino acid complexes due to the dissymmetric nitrogen of the complex. Spectra of *trans*-bis(prolinato)bis(aquo)nickel(II) and *cis*-bis(prolinato)nickel(II) are identified through group theoretical arguments. A possible mechanism for change from the trans bis-prolinato complex to the cis form is suggested.

Introduction

We have shown earlier[2] that 1:1 complexes between Ni(II) and the normal amino acids have a characteristic circular dichroism in the visible Ni(II) absorption bands. Potentially tridentate aspartic acid and asparagine induce a markedly different CD spectrum. Group theoretical arguments could be invoked to deduce from the splitting pattern of the $T_{1g}(O_h)$ upper state in the red region of the spectrum that these last complexes show cis tridentate chelation. When L-lactic acid, with the same spatial geometry as L-alanine, complexes with

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.
(2) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **91**, 6940 (1969).

Ni(II), significant differences are seen[3] in the signs of similar components of the CD spectrum from those in the spectrum of the amino acid complex. This indicates that the nature of the chemical bonding, as well as the geometrical structure of the ligand, plays a significant role in determining the CD spectrum.

The present report carries these points further by exploring the role of a second ligand, not itself asymmetric, in the dichroism response of the metal ion transitions to the optically active amino acid ligand. In the prior work, it was seen that substitution of the unidentate ligand ammonia for water, in the Ni(II) coordination sphere, shifted absorption wavelengths and altered intensity relations of absorption peaks, without qualitatively changing the CD spectrum. Investigation of the chelant, acetylacetone, shows changes of a different sort, which are to be described in what follows.

Experimental Section

Solid $Ni(acac)_2 \cdot 2H_2O$ was prepared by the method of Gach[4] and maintained over Drierite. Stock solutions in water, about 0.032 *F*, were prepared periodically and showed pH 8.9–9. Aliquots of these stocks were used to make up solutions for observation. The L-amino acids used were obtained from Nutritional Biochemicals Co. Measurements of pH were performed with a Radiometer 4 instrument. Spectral observations were recorded with a Jasco ORD/CD-5 spectropolarimeter.

The solutions studied generally had final Ni(II) concentrations of 0.019 *M*. Certain ones had twice this concentration. Solutions were prepared by mixing aliquots of amino acid solution, $Ni(acac)_2$ solution, and occasionally also 1:1 nickel(II)–amino acid complex solution and making to volume. Adjustment of pH was accomplished by adding NaOH.

Results

A solution of $Ni(acac)_2$ in water has a very intense ligand-based absorption which hides the 400-nm region peak of Ni(II) (aq) and of its complexes. The absorption peak in the red has its maximum at 630 nm (0.0192 *M*, pH 9.06), very like the absorption for the 1:1 amino acid complex of Ni(II) (*e.g.*, 0.0385 *M* valine, 0.0192 *M* $NiCl_2$, pH 7.50) but shifted from Ni(II) (aq), which has its peak at 656 nm. The absorption extends from below 500 nm to above 700 nm. CD measurements were primarily limited to this red peak, with some penetration of the edge of the 400-nm region peak. It is of course ambiguous as to which transitions might be observed in this latter region, but the CD can be used in fingerprint fashion.

Mixed Complexes with Normal or Basic Amino Acids.—The typical 1:1 amino acid–nickel(II) complex, as illustrated by valine, shows two CD components in the red absorption region:[2] a positive one at longer wavelength and a negative one at shorter wavelength (Figure 1C). When increasing concentrations of valine are added to 0.019 *M* $Ni(acac)_2$ solution, a CD spectrum appears (Figure 1A) which contains only one (negative) extremum, at shorter wavelength than the absorption maximum. The positive dichroism at longer wavelength present in the simple 1:1 complex is totally absent. In the 400-nm region there is seen the long wavelength end of a strong negative CD, whereas in the simple amino acid complex there is a small positive peak here. Serine with $Ni(acac)_2$ shows a similar pattern of CD, though the intensity is less. With the amino acid arginine, the CD of the mixed complex may be stronger than in the case of valine. Ornithine with the $Ni(acac)_2$ has a weaker CD spectrum and at elevated pH shows a tendency for the CD spectrum of the simple amino acid complex to dominate. In all cases, the spectral intensity tends to increase as pH is elevated from 7 toward 9, and occasionally a variation of the spectrum intrudes at the highest pH levels (*e.g.*, pH 10–11).

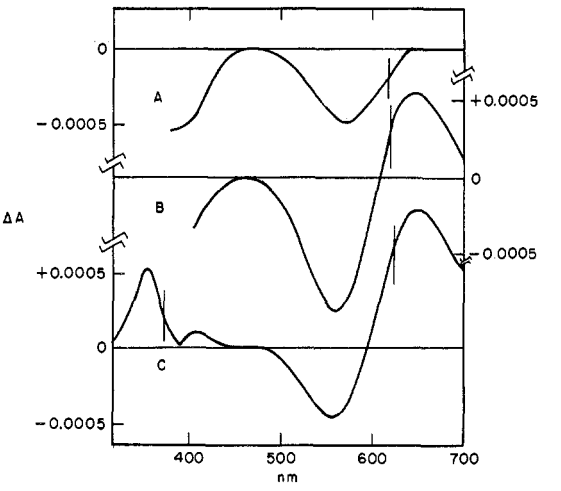

Figure 1.—CD spectra for Ni(II) complexes involving valine (50-nm path length). Vertical bars locate absorption peak maxima. The absorption of the peak in the red extends from below 500 nm to above 700 nm: A, valine–$Ni(acac)_2$, 2:1, pH 8.70; B, valine–$Ni(acac)_2$–(valine–Ni(II)), 2:1:1, pH 8.01; C, valine–$NiCl_2$, 2:1, pH 7.50.

If an equal concentration of 1:1 amino acid–nickel(II) complex is added to a mixture of amino acid and $Ni(acac)_2$ as above, the resultant CD spectrum is a composite of that of the simple amino acid complex and that of the mixed complex (Figure 1B). Quantitatively, the positive CD at 650 nm, characteristic of the amino acid complex, is considerably less intense than it would have been in the absence of the acetylacetonate, and the negative CD at about 565 nm is more intense than the expected sum of the negative CD equivalent to the intensity of the 650-nm CD of the amino acid complex and that for the mixed complex without added amino acid complex. Some of the added Ni(II), therefore, must have been converted to mixed complex. With more excess amino acid, and higher pH, the amount of additional mixed complex apparently increases, in general.

Proline Systems.—As with the normal amino acids, the CD of the proline–nickel(II) complex becomes visible in mixtures of the components near pH 4, and the intensity of the CD increases with increasing pH, toward pH 6. The CD spectrum of the complex, however, is not similar to those for the complexes with the normal amino acids (Figure 2C) but tends to resemble more that for the aspartic acid complex. There is a negative extremum at about 370 nm and a positive one at about 410 nm. In the red, there is a positive CD at about 600 nm and a negative one at about 675 nm. With increased pH, say pH 6–8, the last (negative) component tends to disappear, while the other components (particularly the two positive ones) intensify (Figure 2D). The result is that a 400–405-nm component dominates the one at shorter wavelength, and a positive component at about 585 nm is left with *no* CD to longer wavelength where a negative CD exists at lower pH (absorption maximum, 620 nm). With 2:1 ratio of amino acid to Ni(II), the minimum in the curve at about 670 nm is

(3) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **92**, 1211 (1970).
(4) F. Gach, *Monatsh. Chem.*, **21**, 98 (1900).

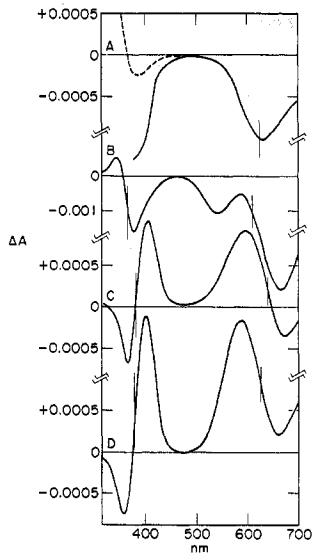

Figure 2—CD spectra for Ni(II) complexes involving proline: A, proline–Ni(acac)$_2$, 1:1, pH 8.33 (solid curve, 50-mm path, dotted, 10 mm); B, proline–NiCl$_2$, 5:1, pH 9 (5-mm path); C, proline–NiCl$_2$, 1:1, pH 6 (10-mm path); D, proline–NiCl$_2$, 1:1, pH 7.5 (10-mm path).

still quite positive above pH 8. With ratios of 3:1 and 5:1, in alkaline solution, a second CD spectrum replaces this. It is characterized by sign inversion at the 365-nm absorption peak (positive peak at 345 nm, stronger negative extremum at 375 nm) and two resolved negative dichroisms in the 615-nm absorption—at 545 and 665 nm, respectively (Figure 2B). At all these ratios from 1:1 to 5:1, essentially the same CD spectrum is seen below pH 6, and the same one is seen between pH 6 and 8. It is only from about pH 8 up that any influences of the higher stoichiometric ratios are to be seen.

When proline is added to Ni(acac)$_2$, a CD spectrum completely different from any of the above appears (Figure 2A). In the 400-nm region there is the strong negative dichroism described for valine and its analogs. In the region of the 625-nm absorption peak, there is a single, strong negative dichroism, with its extremum varying from 665 nm for 0.5:1 proline–Ni(acac)$_2$ at pH 7.9 to 640 nm at pH 8.7 and 635 nm for a ratio of 2:1 at pH 8.1. With a shorter path length observation it is seen that there is a negative minimum in the CD at 380 nm, rising sharply to a much greater positive dichroism at some shorter wavelength. When a proline–nickel(II) complex is also added, the CD shows a mixture of the two dichroisms, at lower pH (*e.g.*, pH 6.77). At higher pH, and with excess proline, the spectrum of the simple complex disappears, so that (for example) with 0.038 *M* proline, 0.019 *M* Ni(acac)$_2$, and 0.019 *M* 1:1 proline–nickel(II), at pH 8.5, only a very intense mixed-complex spectrum is to be seen. The intensity is greater than that of the proline–Ni(acac)$_2$ without addition of proline–nickel(II) by a factor close to 2—*i.e.*, essentially by the ratio of the increased Ni(II) content.

Aspartic Acid and Asparagine Systems.—Addition of aspartic acid to Ni(acac)$_2$ gives a simple CD spectrum which is essentially independent qualitatively of amino acid proportion (0.5–2 times the Ni(II) concentration) and pH (8.3–9.6), where other systems show significant alterations. The CD in the 400-nm region (Figure 3) is positive, rather than negative as seen with the previously mentioned amino acids, and the absorption peaking at about 615 nm is accompanied by a broad positive dichroism peaking at about 605 nm. In the presence of additional aspartic acid–Ni(II) complex, the intensity of the CD increases, with no qualitative alteration.

Addition of asparagine to Ni(acac)$_2$ gives qualitatively the same findings as for the aspartic acid systems (Figure 3), though there is a small change with pH,

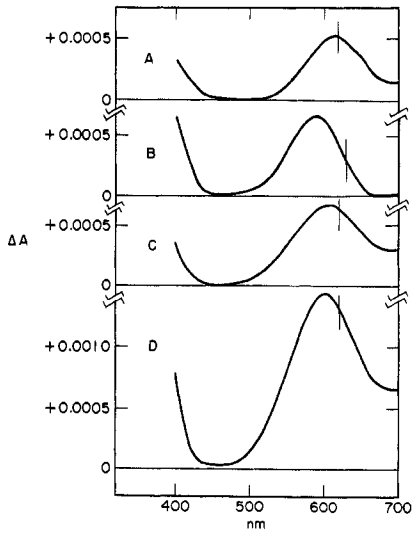

Figure 3.—CD spectra for Ni(II) complexes involving asparagine and aspartic acid (50-mm path length): A, asparagine–Ni(acac)$_2$, 1:1, pH 8.36; B, asparagine–Ni(acac)$_2$–(asparagine–Ni(II)), 1:1:1, pH 6.29; C, aspartic acid–Ni(acac)$_2$, 1:1, pH 8.97; D, aspartic acid–Ni(acac)$_2$–(aspartate–Ni(II)), 1:1:1, pH 8.66.

and similarly when an asparagine–nickel(II) complex is added directly to the system.

Discussion

From the published constants,[5] 0.02 *M* Ni(acac)$_2$ would be about half-dissociated at pH 6.24, 20% at pH 7.24, 7% at pH 8.24, and still over 2% dissociated at pH 9.24. It is thus possible that the mixed complex which is identified by its CD spectrum might contain either one or two acetylacetone groups. If the complex with the characteristic CD did require two acetylacetone groups, then addition of an amino acid–nickel(II) complex to the solution would be expected to diminish the formation of the complex containing two acetylacetone groups, as this ligand becomes distributed over more Ni(II) ions. If, however, the mixed complex requires only a single acetylacetone group, the total amount of complex characterized by the CD spectrum should be increased, by the same redistribution. The approximate doubling of the CD intensity on doubling of the Ni(II) content leads to the conclusion that the mixed complex seen in our experiments contains one each of acetylacetone and amino acid residues. There is no indication in our spectra of a second CD spectrum to be identified with a mixed complex containing two acetylacetones.

The 600–700-nm region absorption of Ni(II) involves a transition in O_h symmetry between the A_{2g} ground

(5) R. M. Izatt, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **59**, 235 (1955).

state and a $T_{1g}(\Gamma_4)$ upper state. Under lowered symmetry the latter splits into an A (or B) state and an E state and, with still lower symmetry, into three states. The CD spectrum may be expected to show transitions for as many of these derivative states as satisfy the magnetic transition moment representation selection criterion. Thus the aspartic acid–nickel(II) complex in ammonia has been seen clearly to have three CD components,[2] in accord with C_s symmetry. The alanine or valine complexes show two components. In the case of the hydroxy acid complexes in general, the components are not resolved, and the envelope approximates that of the absorption peak itself.[3]

The valine–acetylacetone–nickel(II) complex shows a single CD component in this absorption peak (Figure 1A). The dichroism is symmetrical, but its extremum is at such short wavelength relative to the absorption maximum that essentially all the dichroism falls to wavelengths shorter than the absorption maximum. At longer wavelength no dichroism is seen. Comparing this with the CD spectrum of the simple amino acid–nickel(II) complex (Figure 1C), say, a reasonable interpretation is that in the mixed complex the T_{1g} level has been split into A + E components, only one of which shows circular dichroism. Such selection would be expected, according to the rules, for a D_{4h} symmetry (or C_{4v} or C_4 derivable from it) or for D_{3d} (and C_{3v}). Dealing with a bis chelate, we cannot readily visualize a relevant structure with a virtual threefold axis, so we restrict our attention to the suggestion that the system behaves as if it has a fourfold axis.

Four bonds to Ni(II) are distinguished by being to chelant ligands, and if the two chelant ligands are trans to each other, *i.e.*, arranged equatorially, a virtual fourfold axis may be visualized. Monodentate axial bonds to water give a resultant D_{4h} equivalence. This implies that it is not the detailed differences between the two ends of one chelant, nor yet the differences between two differing chelants, nor even the detailed differences in bonding between the three different types of oxygen and the amino group, that are symmetry determining in this context but the grouping and arrangement around the central atom taken as a whole. In analogy with crystal field arguments for ordering d-orbital energies in going from O_h to D_{4h} symmetry, effective bond length considerations may be dominant, but this is open to some speculation. In prior discussion of the amino acid–nickel(II) systems,[2] it appeared, similarly, that the primary distinction was between monodentate and chelate bonding. In a later survey of the Co(III) geometric complexes,[6] the point has been made that bonding-electron distribution at the metal ion was more significant than the distribution of chelant skeletal nuclei in space. The observations here on the mixed complexes appear to reinforce this view.

We may therefore assume that the equatorial bonding charge distribution acts effectively uniformly at the four chelant bonding positions and differently from those to the axial water groups that complete the coordination sphere to present effective D_{4h} local symmetry to the Ni(II). The position of the single CD component in the mixed complex relative to the absorption wavelength indicates that the daughter E_g state which gives rise to it lies higher than its sibling A_{2g}. The trans geometry thus deduced for the mixed complex is consistent with that reported for crystalline diaquobis(glycinato)-nickel(II)[7] and that of diaquobis(acetylacetonato)-nickel(II),[8,9] even though the tris-acetylacetonato complex and the trimeric anhydrous $Ni(acac)_2$ must have cis chelant groups.[10] It may be noted also that in the bis-aquo complexes above,[7-9] the Ni–O bonds to the axial water are the longest of the six bonds of nickel.

In the case of the mixed complex with acetylacetone and proline, it is possible to interpret the CD spectrum (*e.g.*, Figure 2A) as showing the order of the daughter levels to be inverted, with the E_g now lying lower, to give a single CD at longer wavelength than the absorption maximum. The experimental data are not as clear-cut here, however, and it is not possible definitely to eliminate the chance that we are seeing a CD envelope with its maximum displaced in wavelength because of a weak component of opposite sign at shorter wavelength than the absorption maximum. The sign of the CD, if it is indeed a single component, is the same as that for the valine double complex, though in the 1:1 amino acid–nickel(II) complexes the signs of corresponding components are inverted between the valine and proline complexes.

The aspartic acid and asparagine mixed complexes show a CD only slightly displaced to shorter wavelength from the absorption itself and no evidence for a missing component (see Figure 3B). The appearance is rather like that for some of the hydroxy acid complexes.[3] It could be interpreted as the result of three unresolved components of the same sign in very low symmetry, consequent to retention of tridentate chelation by the amino acid.

One may describe the effect of a dissymmetric environment on a central metal ion as a pseudoscalar field, which combines a polar vector field that produces ligand field effects with an axial vector field which yields circular dichroism in the resultant absorption transitions. Superposition on this of a second dissymmetry gives a new (resultant) polar field and a new (resultant) axial field. If the two polar fields are essentially identical ("crystal field" conditions), the resultant change in CD spectrum is ascribable to the resultant axial field and conceivably may even be reproduced by scalar addition of the CD spectra of the component dissymmetric fields taken separately. Under "crystal field" assumptions, chemical alterations which produce only polar vector field changes should not alter the axial vector field and even more so if chemical alterations give no polar field changes. Chelation of an α-amino acid would be presumed to have a polar vector field influence determined primarily by the bonding and an axial vector field determined by the ligand geometry, for which the positioning of the "asymmetric carbon" is a marker.

Thus, as would be predicted, the CD spectrum of the mono(amino acid) chelate was found to be unaffected by substitution of monodentate ammonia for monodentate water.[2] The changes on introducing chelating acetylacetone, to give the mixed bis chelate, seen in the $T_{1g}(O_h)$ upper state in the 600-nm region, are complicated by the potentially changed symmetry splittings,

(6) L. I. Katzin and I. Eliezer, *Coord. Chem. Rev.*, in press.

(7) H. C. Freeman, J. M. Guss, and R. L. Sinclair, *Chem. Commun.*, 485 (1968).

(8) H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1481 (1964).

(9) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

(10) G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).

reflecting change in the polar vector field. The Ni(II) transitions in the 400-nm region are unfortunately overlain by the acetylacetonate band. The nickel(II)–L-proline chelate differs from that for the normal amino acids (*e.g.*, L-valine) in that binding of the secondary amino group now introduces a second dissymmetry field, based on the asymmetry around the nitrogen atom. *A priori*, on the above considerations, one might expect the CD spectra of the two complexes to be the same, as statistically equal numbers of molecules with *R* and with *S* configuration around the nitrogen should form, giving neutralization of the axial vector effects for its field.

The experimental results, however, show a wide difference between the CD spectra of the proline complex and that for the normal amino acids, and for this there are at least three possible explanations. The first is that there are not equal numbers of *R* and *S* isomers as postulated, *i.e.*, that there is selective coordination of one of the isomers due to some geometrical factor. Such a selectivity has been indicated, for example, for the Co(III) complexes with sarcosine, which similarly introduces a dissymmetric nitrogen.[11,12] A second possibility is that there is not simple scalar additivity of CD spectra, as might be hoped, but something more complicated. A third possibility is that the difference in binding between proline and valine is sufficient (*e.g.*, $pK_2 = 10.64$ *vs.* 9.62 for valine[13]) that assumption of equivalent polar vector fields is not valid, so that the axial field signaled by the asymmetry around the carbon is operating on a different electronic substrate, producing a different CD spectrum. The implied difference in bond lengths corresponding to the energy level inversion suggested for the mixed complexes might be a symptom for this. Considerations such as discussed here would also perhaps delineate the area of applicability of attempts to resolve "additive" dichroic effects in other systems.[14,15]

In our earlier discussion of the amino acid–nickel(II) CD spectrum,[2] the assumption was made that the effective symmetry was C_{2v}, with only two of the three spectral components derived from the $T_{1g}(O_h)$ band showing a CD, in accord with the selection rules. Particularly with the newer spectra available (the mixed complexes and the proline complexes) and more detailed comparison with the three-component CD of the aspartic acid complex, we have become more inclined to believe that the amino acid–nickel(II) complex CD is in fact what it seems—a two-component dichroism. This implies a splitting to A (or B) and E, rather than to three one-dimensional components, which requires that the effective symmetry must be at least C_3 or C_4, rather than the C_{2v} implied from the stoichiometric structure. However, any of the reasonable symmetries derivable from O_h which give such a pair of components will predict only the E component to show dichroism, as with the D_{4h} case discussed above. A possible explanation, in terms of the findings on the mixed complexes, might be the following.

Attachment of a single amino acid chelant to Ni(II) defines a plane through the central ion. Let us assume for the moment that this affects the two trans bonding positions in the plane differently from the cis axial positions (*e.g.*, repels the cis axial water ligands more than the ones in the plane) so that effective D_{4h} microsymmetry ensues. This should give a one-component CD like that of the mixed complex. However, vibration of the central metal ion against the chelant in the equatorial plane could, in one phase, give a D_{4h} structure in which the bonds in the plane are *longer* than the axial bonds. The A and E energy levels would now invert (see Figure 4) so that the single CD would now be at

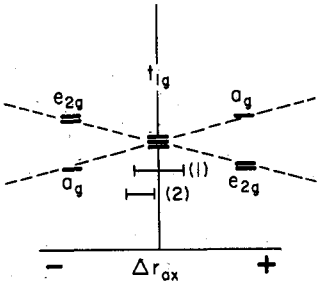

Figure 4.—Diagram of relations of the $t_{1g}(O_h)$ state as a function of the difference in axial and equatorial bond lengths; Δr_{ax} is the axial ligand distance minus the equatorial ligand distance: (1) hypothetical relation for mono(amino acid) chelate, giving two-component CD as a function of vibrational amplitude; (2) relation for mixed bis chelate, giving one-component CD as a function of vibrational amplitude (see text).

shorter wavelength than the absorption maximum (and inverted in sign, according to the experimental spectrum). The average through the solution population would result in the two-component spectrum observed. On such an hypothesis it would be presumed that in the mixed complex the second chelant group limits the vibrational excursions so that the conditions for inversion of the levels are not achieved.

Hidaka and Shimura[16] have prepared K[Ni(L-pro)$_3$], its hydroxyproline analog, and also [Ni(L-pro)$_2$(H$_2$O)$_2$]. They have published CD curves which are presumably obtained from simple solutions of the solids in water, but no indication of the relevant solution parameters (concentration, pH) are given. These are of particular interest, since the CD spectrum given for Ni(L-pro)$_2$·(H$_2$O)$_2$ is close to that which we have found for 1:1 complex in the 400-nm region but in the 550–700-nm region shows indication of three components, whereas even at 2:1 ligand–nickel(II) and pH 8.12 we see only a single peak. No comparable CD has been seen under other conditions either. The CD we have found in alkaline solutions (pH 8–11), with ligand ratios 3–5:1, has the same two-component structure in the 550–700-nm region as does the CD attributed[16] to K[Ni(L-pro)$_3$], but we have never seen anything like the apparent five components of the CD for the 400-nm region absorption. (The CD given for the tris-hydroxyproline compound[16] resembles, in the 550–700-nm region, spectra we have seen for 3:1 proline–nickel(II) systems in the pH region of incomplete transition between the intermediate- and high-pH CD spectra.)

If the two negative CD components at about 540 and 665 nm, respectively, in our high-ratio, high-pH

(11) D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966).

(12) S. Larson, K. J. Watson, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 847 (1968).

(13) H. A. Sober, Ed., "Handbook of Biochemistry," 2nd ed, The Chemical Rubber Co., Cleveland, Ohio, 1970, pp J-142 166.

(14) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965).

(15) N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **42**, 1779 (1969).

(16) J. Hidaka and Y. Shimura, *ibid.*, **43**, 2999 (1970).

spectra (Figure 2B), which seem symmetrical, are taken to represent widely split A + E offspring of the T_{1g} (O_h) upper level, only one derivative point group will furnish the correct selection rule, namely, C_3. This would be consistent with expectation for the tris(amino acid) complex of the β or cis configuration.[17] However, one might consider the spectrum to represent a three-component spectrum with one component forbidden, which would match C_{2v} symmetry, which might correspond to one form of cis bis complex. There is an obvious difficulty, looking at the peaks, of matching the two components of the CD to yield the observed absorption curve. Synthesis of the absorption peak from Gaussian components in fact shows the major absorption component to be a third one at about 603 nm, which has no CD associated, and is about as intense as the 540- and 665-nm absorption components taken together.

If this spectrum actually is that of the cis complex and if the spectrum seen in the pH 4–6 region, independent of ligand ratios from 0.5–5:1, is reasonably to be attributed to the 1:1 complex, what represents the trans 2:1 complex, expected from the analogous crystalline material[7] already discussed? This would need be the variant seen between pH 6 and 8, for both 1:1 and 2:1 ligand–Ni(II) systems, which has a single, positive component in the red, at 595 nm (Figure 2D). In the 400-nm region it differs from the 1:1 spectrum only in small relative intensity alterations between the components. An awkwardness for this assignment is the fact that near pH 6 the intensity of the 595-nm peak is almost precisely the same for a solution with a 1:1 ligand–nickel(II) ratio, for which at most half the Ni(II) can appear as 2:1 complex, as for the solution with a 5:1 ligand ratio. Potential support for the assignment is the single CD peak, as for the mixed trans complex, and that the spectrum as a whole is closely the sign inverse of the CD spectrum assigned to a 2:1 species for the complexes with the aliphatic amino acids (see Figure 1f–1h, ref 2).

Whether the high-pH complex is the cis bis chelate, which seems most probable, or possibly tris chelate (which would be derived from such a precursor), the factors that may influence the formation of cis rather than trans bis chelate are obviously of interest. The best clue may be the fact that even with 5:1 ligand–nickel(II) solutions, alkaline pH seems to be required to transform the intermediate spectrum (with a single peak in the red), which seems to characterize trans bis chelate, into the form which is probably cis bis chelate. One hypothetical scenario might start with the bis-aquo trans bis chelate, in which action of the elevated pH transforms an axial water group into an hydroxyl. One of the amino acid moieties, or merely its amino group, now dissociates in kinetic equilibrium. At pH 7–8, say, well below its pK_H, the amino group protonates. Let us assume that now RNH_3^+ attacks NiOH (with formation of product H_2O) in preference to $NiOH_2$ (with formation of H_3O^+). Since the position thus attacked is axial to the original plane, the chelation is now cis, and the change is made. Possibly also involved may be a difference in the electrostatics of RNH_3^+ at the lower pH and RNH_2 at pH sufficiently elevated to partially dissociate the former, but both mechanisms could operate, in proportion appropriate to the pH.

(17) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965), and references cited therein.

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Chelative Addition of Hydrazine to Coordinated Isocyanides. The Structure of 1,1′-Dichloropallado-2,5-di(methylamino)-3,4-diazacyclopentadiene, $[(CH_3)_2C_2N_4H_4]PdCl_2$

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The structure of the addition product of hydrazine with *cis*-dichlorobis(methyl isocyanide)palladium has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the space group D_{2h}^{17}-*Cmcm* with four molecules in a cell of dimensions $a = 18.043$ (4), $b = 7.326$ (1), and $c = 6.839$ (1) Å. The observed and calculated densities are 2.141 (7) and 2.141 g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure has resulted in $R = 0.030$ for the 599 data having $F_o^2 > 3\sigma(F_o^2)$. The Pd atom is four-coordinate and bonded to two Cl atoms and to the two C atoms of the novel –C–N–N–C– chelate skeleton resulting from the addition of a hydrazine molecule to two coordinated isocyanide molecules. The complex is rigorously planar and is required to have *mm*-C_{2v} symmetry. The Pd–Cl distance is 2.387 (1) Å and the Pd–C distance is 1.948 (5) Å. The distances within the chelate ring are C–N = 1.309 (6) and N–N = 1.395 (8) Å. The molecular plane of the complex is normal to the *c* axis of the crystal, and the molecules are stacked to form chains parallel to *c*.

Introduction

Reactions between tetrakis(methyl isocyanide)platinum(II) and hydrazine were first reported by Chugaev and coworkers[1] in 1925. They isolated a red compound which they formulated as **1** on the basis of conductivity and analytical data. Treatment of **1** with hydrochloric acid resulted in the evolution of methyl isocyanide and

(1) L. Chugaev, M. Skanavy-Grigorieva, and A. Posniak, *Z. Anorg. Allg. Chem.*, **148**, 37 (1925).