containing $(RO)_3P$ and F_3P (and perhaps even CO) in place of $(NCC_2H_4)_3P$ might be stable enough to be isolated.

A final point requiring discussion is the observed paramagnetism of the compound in bulk as contrasted with the indication from the discussion of bonding that the compound should have no unpaired electrons. In view of the instability of the compound, the observation of visible traces of nickel metal in some preparations, field-strength dependence of the observed magnetism, and the lack of correspondence of the observed magnetism with any integral number of electrons, we believe it is safe to attribute the observed magnetism to the presence of nickel metal and perhaps also paramagnetic decomposition products.

Acknowledgments. We wish to thank Professor J. Lewis and Mr. Brian Bentley of the University of Manchester, England, for making the magnetic measurements. We also thank Dr. Martin Grayson of The American Cyanamid Co. for generous gifts of tris-(β-cyanoethyl)phosphine. B. H. C. Winquist is grateful to the Woodrow Wilson Fellowship Foundation for a fellowship award during 1964–1965 and to the National Institutes of Health for a fellowship from 1965 to 1967. The calculations were done at the Computation Center at MIT.

Chromatographic Resolution of the Antipodes of a Helical Complex of Nickel(II)

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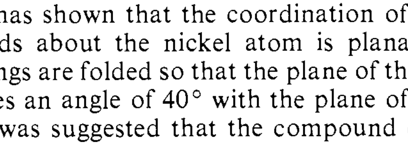
Abstract: Chromatographic resolution of the complex ion triaquotribenzo[*b,f,j*][1,5,9]triazacycloduodecinenickel(II), $Ni(TRI)(H_2O)_3^{2+}$, has been achieved on microcrystalline cellulose and on potato starch. Fractional crystallization of partially resolved samples reveals that the chromatographic resolutions are essentially complete. This first separation of enantiomeric complexes on cellulose shows this to be a very convenient and useful material for such procedures. (+)- or (−)-$Ni(TRI)(H_2O)_3^{2+}$ does not racemize at a measurable rate in acidic or neutral solutions; however, the complex is unstable in aqueous base. The chirality of the complex may be assigned on the basis of the natural helical form of the molecule with respect to the C_3 axis. Circular dichroism spectra and optical rotatory dispersions are reported.

Although early attempts were made to resolve $Ni_2(trien)_3^{4+}$ [2,3] and $Ni(en)_3^{2+}$ [4,5] into optical isomers, the first successful separation of a dissymmetric nickel(II) complex into antipodal forms involved tris-(2,2′-bipyridine)nickel(II).[6] The resolution of this material was initially accomplished by crystallizing the *d*- or *l*-tartrate salt. Racemization of $Ni(bipy)_3^{2+}$ proceeds with a half-life of 2.5 min in aqueous solution at 30°. The rate of racemization is accelerated by both acid and base.[7] Tris(1,10-phenanthroline)nickel(II) was resolved at a later date[8] and found to racemize much more slowly. Its racemization half-life is 2 hr in aqueous solution at 30° and the rate is almost independent of pH. In 1962 Broomhead and Dwyer prepared and resolved the related ions $[Ni(bipy)_2(phen)]^{2+}$ and $[Ni(bipy)(phen)_2]^{2+}$.[9] These enantiomers, like $[Ni(bipy)_3]^{2+}$, racemize rapidly in aqueous solution at rates that are accelerated by both acid and base. The diamagnetic complex shown in structure I has been partially resolved by preferential adsorption of one enantiomorph on (+)-quartz.[10,11] The asymmetry of this complex was attributed to distortion of the planar structure toward a "quasi-tetrahedral" arrangement. A recent X-ray determination of the structure of this complex has shown that the coordination of the nitrogen ligands about the nickel atom is planar, but the chelate rings are folded so that the plane of the formazyl ring makes an angle of 40° with the plane of coordination. It was suggested that the compound exists as a



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[1] National Institutes of Health Postdoctoral Fellow, 2-F2-GM-28, 091-02.

[2] tren is the abbreviation for tris(aminoethyl)amine $N(CH_2CH_2NH_2)_3$.

[3] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 486 (1926).

[4] W. R. Bucknall and W. Wardlaw, *ibid.*, 2739 (1928).

[5] C. H. Johnson, *Trans. Faraday Soc.*, **28**, 854 (1932).

[6] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931).

[7] G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, **56**, 195 (1952); N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **48**, 244 (1952); **49**, 180 (1953); **50** 24, 1325 (1954); F. Basolo, J. C. Hayers, and H. M. Neuman, *J. Am. Chem. Soc.*, **75**, 5102 (1953); R. G. Wilkins and M. J. G. Williams, *J. Chem. Soc.*, 1763 (1957).

[8] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1949).

[9] J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.*, **15**, 453 (1962).

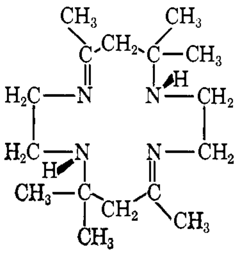
[10] H. Irving and J. B. Gill, *Proc. Chem. Soc.*, 168 (1958).

[11] H. Irving, J. B. Gill, and W. R. Cross, *J. Chem. Soc.*, 2087 (1960).

mixture of *cis* and *trans* isomers with respect to the aryl groups; however, only the *cis* isomer should be dissymmetric.[12]

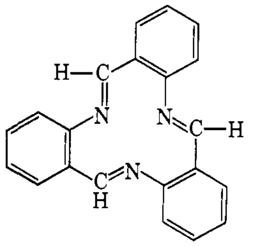
Optical activity has been observed in a number of nickel(II) complexes containing various optically active ligands, such as *d*- and *l*-propylenediamine,[13] *d*-glutamic acid,[13] *d*-tartrate,[14] *l*-1,2-cyclohexanediamine,[15] and certain optically active xanthates.[16] It is not certain whether the dissymmetric nickel(II) ions so produced exist preferentially in one of the two diastereoisomeric forms.

Rate studies on the racemization of the few known optically active nickel(II) compounds indicate that the rate of racemization is coincident with the rate of dissociation of a ligand.[7] The inability of early investigators to resolve $Ni(en)_3^{2+}$ and $Ni_2(trien)_3^{4+}$ into optical isomers is now well understood, for these compounds are much more labile toward substitution reactions than the compounds that have yielded enantiomorphs.[17] As a result of increased interest in the complexes of macrocyclic ligands it has been found that nickel(II) complexes of totally closed, macrocyclic ligands are exceptionally inert toward replacement by other ligands.[18–22] If racemization and dissociation proceed by the same mechanism, dissymmetric nickel compounds having macrocyclic ligands should be resolvable and their enantiomorphs should be quite inert to racemization. This suggestion is supported by the recent report[23] that the nickel(II) complex shown in structure II can be resolved into antipodes. The asymmetry in this case arises from the asymmetry of the coordinated secondary amine groups. Breaking of the N–Ni bond would be accompanied by racemization. In this and related cases[24] involving asymmetric nitrogen bound to metal ions, the actual racemization path involves previous dissociation of the proton from the secondary amine, rather than the breaking of the metal–nitrogen bond.



II

We have completed the resolution of a nickel(II) complex which contains a closed tridentate macrocyclic Schiff base ligand, tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecine (hereafter referred to as TRI), structure III. This compound has been resolved by column chromatography and yields both *d* and *l* isomers. These enantiomers have been shown to be very stable toward racemization.



III

Experimental Section

Materials. $Ni(TRI)(NO_3)_2H_2O$ was prepared as previously described.[18] Microcrystalline, nonionic cellulose was obtained from the Avicel Sales Division of American Viscose Division, FMC Corp., Marcus Hook, Pa. The commercial name for this material is Avirin or Avicel, Technical Grade. Potato starch was obtained from Fisher Scientific Co. (Fisher Catalog No. S-513).

Measurements. Rotations were measured in a 1-dm cell with a Rudolph Model 80 photoelectric polarimeter, fitted with a Beckman monochromator and a mercury light source. Optical rotatory dispersions were measured with a Cary Model 60 recording spectropolarimeter in a 1-cm cell. We are indebted to Dr. Fred L. Urbach, Western Reserve University, for this measurement. The circular dichroism spectra were determined in a 1-cm cell with a Durrum-Jasco ORD/UV-5 instrument, Durrum Instrument Corp., Palo Alto, Calif.

Chromatographic Resolution of $Ni(TRI)(NO_3)_2H_2O$. The chromatographic columns ranged in dimension between 2.0 and 7.0 cm in diameter and from 30.0 to 100.0 cm in height. Each column was packed by pouring an aqueous suspension of cellulose onto a glass wool pad located just above the stopcock. The solvent was permitted to filter through the pad at a rate of approximately 0.2 ml/min. The column was washed with distilled water for 24 to 36 hr by eluting at a flow rate of 1.0 ml/min. The sample was placed on the column as a saturated aqueous solution to which had been added three drops of 1.0 *N* nitric acid. It was eluted from the column with distilled water at a flow rate of 0.5 ml/min. Distilled water, which had passed through the column during the washing procedure, was used as the blank in the measurement of rotations. Best conditions for the resolution were found to involve columns 2.2 cm in diameter and 65 cm in height and 10-ml aliquots of a slightly acidic saturated solution of $Ni(TRI)(NO_3)_2H_2O$. The solubility of $Ni(TRI)(NO_3)_2H_2O$ is approximately 0.02 g/ml. The sample moves down the column as one broad band. The size of the fractions collected was determined by the dimensions of the column.

The column used for resolutions on potato starch is 2.2 cm in diameter and 60.0 cm in height. Before packing the column, the starch was washed at least five times by repeatedly stirring with an ample amount of 0.01 *M* HNO_3, then decanting or filtering to remove the dilute acid. This procedure was necessary in order to remove water-soluble impurities. The starch column was packed as described above but the starch was suspended in 0.01 *M* HNO_3 instead of distilled water. The starch was washed for another 48 hr, by allowing 0.01 *M* HNO_3 to flow through the column. To attain a suitable flow rate, 0.2 ml/min, it was necessary to apply air pressure to the 0.01 *M* HNO_3 head at the top of the column. A 10-ml portion of a saturated 0.01 *M* HNO_3 solution of $Ni(TRI)(NO_3)_2H_2O$ was placed on the column, and the sample was eluted with 0.01 *M* HNO_3. The sample moved down the column as one broad band. Fractions of 3 ml were taken and diluted with 0.01 *M* HNO_3 and their rotations were read in a 1-dm tube. Nitric acid (0.01 *M*)

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(12) D. Dale, *J. Chem. Soc.*, 2786 (197).

(13) F. Woldbye, "Technique of Inorganic Chemistry," Vol. IV, H. B. Joanassen and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 351.

(14) S. F. Mason, *Quart. Rev.* (London), 17, 59 (1963).

(15) R. S. Treptow, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1966.

(16) B. Sjoberg and R. Backstrom, *Acta Chem. Scand.*, **16**, 786 (1962).

(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 199–205; *Advan. Inorg. Chem. Radiochem.*, 3, 1 (1961); F. Basolo, *Surv. Progr. Chem.*, 2, 1 (1964); and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

(18) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966).

(19) G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

(20) D. A. House and N. F. Curtis, *ibid.*, **86**, 1331 (1964), and references therein.

(21) J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).

(22) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

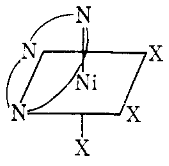
(23) L. G. Warner, N. J. Rose, and D. H. Busch, *ibid.*, **89**, 703 (1967).

(24) D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966); D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).

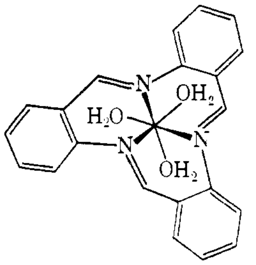
which had passed through the column was used as the blank during the reading of the rotations.

Results and Discussion

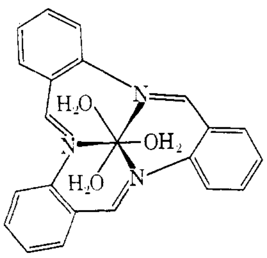
Two products are obtained from the self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) ion.[19,22] One is a complex containing a closed tridentate macrocyclic ligand, structure III, while the second complex contains an analogous tetradentate macrocyclic ligand. Recently, we have shown that the nickel complex of the trimeric ligand can be produced as the exclusive product by the metal ion induced rearrangement of the metal-free bisanhydro trimer of *o*-aminobenzaldehyde.[18] X-Ray structure studies have shown that this complex has a pseudo-octahedral geometry, structure IV.[25] The three nitrogen donor atoms of the organic ligand occupy one face of the octahedron, while the other three coordination sites are filled by uninegative donor atoms and/or solvent molecules. Spectral evidence has indicated that when Ni(TRI)(NO_3)$_2$$H_2O$ is dissolved in water, the other three positions are filled by water molecules.[22] Regardless of what fills the other three positions, the complex has no plane of symmetry, center of inversion, or alternating rotation–reflection axis. Therefore it is expected to exist in *d* and *l* forms. The asymmetry of the nickel(II) ion is easily seen if one considers the definite sequence of atoms in the macrocyclic ligand. From structure III, it may be seen that this macrocyclic ligand is composed of three nitrogen–carbon–benzene units. Looking down the principal threefold axis of rotation, we see that the sequence nitrogen–carbon–benzene may progress in either a clockwise or counterclockwise direction (structures Va and Vb). Further inspection reveals that these two arrangements are nonsuperimposable mirror images.



IV



Va



Vb

Attempts were made to prepare diastereoisomers with Ni(TRI)(H_2O)$_3^{2+}$ using *d*-tartaric acid, *d*-antimonyl tartrate, α-bromocamphor-π-sulfonate, Co(EDTA)$^-$, *d*-dibenzoyl tartrate, and bis(oxalato)ethylenediaminecobalt(III), but we were unable to obtain a product which exhibited a rotation other than that traceable to the resolving agent. Partial resolutions were achieved by passing saturated aqueous solutions of Ni(TRI)(NO_3)$_2$$H_2O$ through columns packed with microcrystalline nonionic cellulose and eluting with distilled water. Several columns were tried with a variety of dimensions, and in every instance partial resolution was obtained.

Table I contains examples of the data obtained for two typical resolution experiments. The $(+)_{546}$ isomer adsorbs preferential on the cellulose, as evidenced by the negative rotations of the initial fractions. The $(+)_{546}$ isomer can be removed from the cellulose by eluting with dilute HNO_3. Since the size of the sample exceeded the adsorbing capacity of the column in each of the resolutions reported in Table I, the same sample size was used with a larger column (2.0 × 150 cm) in the hope of attaining a more nearly ideal chromatographic separation of the isomers. In this case, all of the sample was strongly adsorbed and it was distributed over the entire column. Consequently, selective removal of the $(+)_{546}$ or $(-)_{546}$ isomer by eluting with distilled water or dilute acid was not achieved. Partial resolution could also be accomplished by packing, washing, and eluting the cellulose with methanol, but the maximum specific rotation obtained was approximately −120°. This resolution procedure would appear to be specific for *nonionic* cellulose. Attempted resolution of Ni(TRI)(H_2O)$_3^{2+}$ on cationic exchange cellulose under the same conditions gave no separation of the optical isomers.

Table I. Chromatographic Resolution of Ni(TRI)(NO_3)$_2$$H_2O$ on Cellulose[a]

Fraction	α_{obsd}, deg[b]	Concn, $M \times 10^3$ [c]	$[\alpha]_{546}$, deg
1[d]	-0.351 ± 0.006	6.35	−212.7
2	-0.336 ± 0.007	5.45	−120.9
5	$+0.111 \pm 0.007$	5.25	+41.4
1[e]	-0.161 ± 0.008	1.29	−244.7
2	-0.221 ± 0.008	2.84	+152.4
3	-0.115 ± 0.009	2.90	−77.7
4	-0.094 ± 0.006	3.82	−48.2
8	No rotation	...	...
9	No rotation	...	...

[a] Sample was 10 ml of a saturated aqueous solution, ~0.2 g. [b] Measured at 546 mμ, room temperature. 1-dm cell. [c] Determined from the optical density measured at 275 mμ. [d] Column dimension: 2.2 × 60 cm. [e] Column dimension: 2.0 × 100 cm.

Columns packed with potato starch gave a chromatographic behavior that is more satisfactory in certain superficial ways. Table II summarizes typical data. Dilute HNO_3 was required for the procedure in

Table II. Chromatographic Resolution of Ni(TRI)(NO_3)$_2$$H_2O$ on Starch[a,b]

Fraction	α_{obsd}, deg[c]	Concn, $M \times 10^3$ [d]	$[\alpha]_{546}$, deg
1	-0.052 ± 0.006	4.80	−212.0
4	-0.068 ± 0.006	6.82	−195.4
9	-0.027 ± 0.006	2.90	−182.4
10	No rotation	...	...
12	$+0.035 \pm 0.005$	3.29	+208.3

[a] Sample was 8 ml of a saturated 0.01 *M* HNO_3 solution, approximately 0.16 g. [b] Column dimension: 2.2 × 60 cm. [c] Measured at 546 mμ, room temperature. 1-dm cell. [d] Determined from the optical density measured at 275 mμ.

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(25) E. B. Fleischer and E. Klem, *Inorg. Chem.*, 4, 637 (1965).

order to achieve useful packing of the column. When water was used, the potato starch packed so tightly that no eluent could be forced through the column. The highest specific rotations of the plus and minus fractions, during the resolutions using starch, were of about the same magnitude. These values compare very well with the highest specific rotations observed on samples obtained from cellulose columns. In practice, the cellulose column was more convenient to use because of ease of packing, shorter eluting times, and the fact that the cellulose could be used as it came from the manufacturer, without extensive prewashing.

Samples isolated *via* the cellulose column procedure were recrystallized by allowing the very slightly acidic solution to evaporate slowly under a stream of air. Under these conditions the racemic form is less soluble than the active form, *i.e.*, the least soluble fraction of the recrystallized $Ni(TRI)(NO_3)_2H_2O$ has a lower specific rotation than the solid $Ni(TRI)(NO_3)_2H_2O$ obtained by evaporating the eluent directly from the column, while the specific rotation of the filtrate shows a higher $[\alpha]_{546}$ than the "crude" or first recrystallized fraction. This behavior has been observed with both plus and minus rotating fractions. After separation of some five fractions, the specific rotation of the filtrate appears to level off at *ca.* 230°. This corresponds closely to the highest specific rotations obtained chromatographically on either the starch or cellulose columns. From these observations, we feel that the chromatographic resolution of $Ni(TRI)(H_2O)_3^{2+}$ is essentially complete.

The complex ion $Ni(TRI)(H_2O)_3^{2+}$ establishes only the second class of dissymmetric six-coordinate nickel(II) complexes to be resolved into enantiomers. All the other six-coordinate compounds are of the tris(bidentate) class. They are further restricted to ligands that contain the N=C—C=N linkage ($Ni(bipy)_3^{2+}$ and $Ni(phen)_3^{2+}$ are prime examples). Whereas these compounds are of the classic type involving D_3 symmetry, and having six strong azomethine donors about the nickel(II) ion, the $Ni(TRI)(H_2O)_3^{2+}$ ion has a C_3 axis as its only symmetry element and involves only three azomethine donors with three water molecules, of relatively weak donor strength, occupying the remaining positions in the coordination sphere. One cannot assign an absolute handedness to the asymmetry of $Ni(TRI)(H_2O)_3^{2+}$ on the basis of the chirality rules that have recently been designed for the common helical asymmetric structures.[26] Nevertheless, a definite chirality is imposed on the $Ni(TRI)(H_2O)_3^{2+}$ ion by the macrocyclic tridentate ligand. The helical nature of this structure can be defined with reference to the C_3 axis by the relative tilt of the benzene rings. The rings of the chelated ligand are so arrayed that the structure resembles a three-bladed propeller.[25] Consequently, the chirality of $Ni(TRI)(H_2O)_3^{2+}$ may be either right-handed or left-handed, and the corresponding isomers are designated delta (Δ) or lambda (λ) using Piper's convention.[27]

The $Ni(TRI)(H_2O)_3^{2+}$ ion is inert toward racemization in neutral and acidic aqueous solution, in contrast to the racemization behavior of $Ni(bipy)_3^{2+}$ and $Ni(phen)_3^{2+}$. We find no evidence that solutions containing resolved $Ni(TRI)(H_2O)_3^{2+}$ racemize (measurements taken over a period of 3 months). Complexes containing TRI are unstable in aqueous solution above pH 7, where it has been suggested that the azomethine linkage undergoes hydrolysis.[19] This configurational stability is not surprising in light of the extreme inertness toward dissociation of $Ni(TRI)(H_2O)_3^{2+}$.

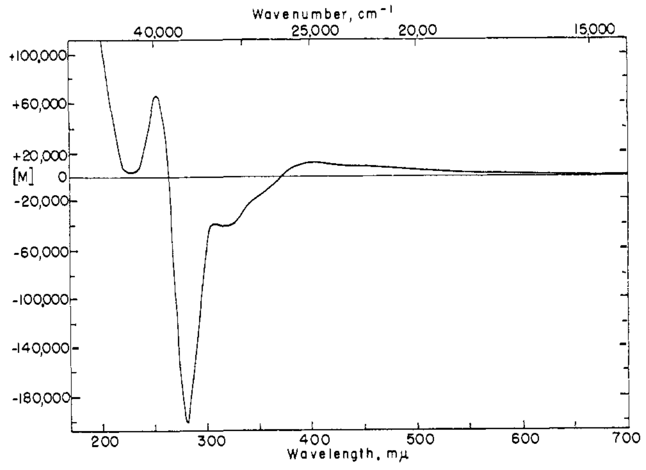

Figure 1. ORD of $(+)_{546}$-$Ni(TRI)(H_2O)_3^{2+}$.

Resolutions performed by preferentially adsorbing one enantiomer on cellulose are very rare, whereas resolutions with starch and quartz adsorbents are quite common.[28] The use of cellulose for resolving metal complexes has been discussed, but no well-defined procedures have been reported.[29] Dwyer and co-workers have chromatographically separated mixed $[Co(en)_n(l\text{-}pn)_{3-n}]^{3+}$ complexes on cellulose powder into D and L forms.[30] Close inspection reveals that these D and L forms (*e.g.*, $[DL\text{-}Co(l\text{-}pn)_3]Cl_3$) are diastereoisomers rather than enantiomorphs, as was indicated recently.[31] The total chromatographic resolution of a trinuclear complex cation of cobalt(III) has recently been reported, but the adsorbent was a cationic exchange cellulose.[31]

The optical rotatory dispersions of both enantiomorphs were measured from 700 to 230 mμ.

Measurements at frequencies lower than 230 mμ were generally unreliable because of intense light absorption. The ORD curve of the $(-)_{546}$ isomer appears to be the mirror image of that for the $(+)_{546}$ isomer (Figure 1) within experimental error. Some of the data obtained from the ORD curve for the $(+)_{546}$ isomer are tabulated in Table III.

Circular dichroism spectra of $(+)_{546}$- and $(-)_{546}$-$Ni(TRI)(H_2O)_3^{2+}$ also were measured from 700 to 230 mμ. Again light absorption prevented measurements at lower frequencies. The spectrum (Figure 2) of the $(+)_{546}$ isomer has three positive peaks located at 360, 336, and 296 mμ and one very intense negative peak at 268 mμ. The absorption spectrum of Ni(TRI)-

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[26] J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

[27] T. S. Piper, *ibid.*, **83**, 3908 (1961).

[28] R. G. Wilkins and M. J. G. Williams, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 206; A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 196; S. Kirschner, "Preparative Inorganic Reactions," Vol. I, W. L. Jolly, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 41.

[29] H. Krebs, J. Diewald, H. Arlitt, and J. A. Wagner, *Z. Anorg. Allgem. Chem.*, **287**, 98 (1956); H. Krebs, J. Diewald, and J. A. Wagner, *Angew. Chem.*, **67**, 705 (1958).

[30] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963).

[31] G. R. Brubaker, J. I. Legg, and B. E. Douglas, *ibid.*, **88**, 3446 (1966).

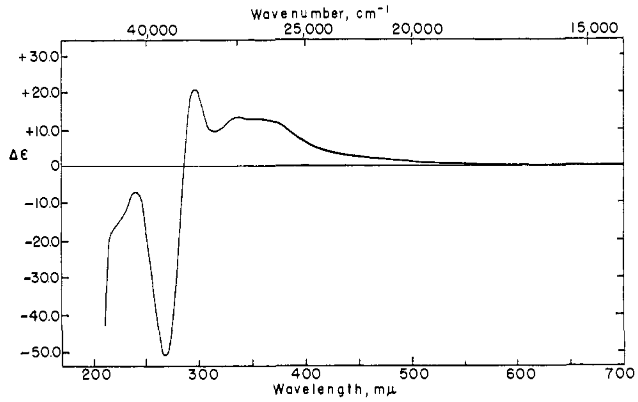

Figure 2. CD spectrum of $(+)_{546}$-Ni(TRI)$(H_2O)_3^{2+}$.

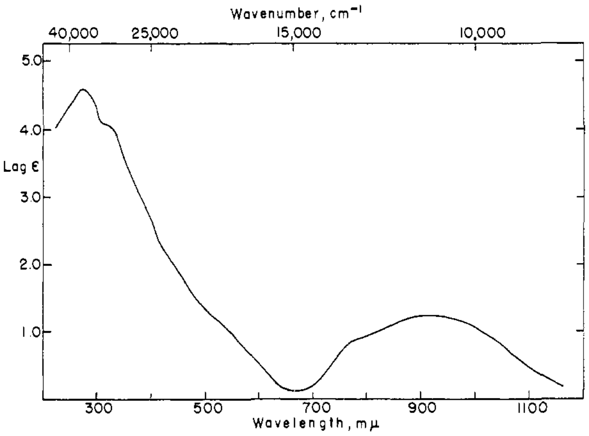

Figure 3. Absorption spectrum of Ni(TRI)$(NO_3)_2H_2O$ dissolved in distilled water.

$(H_2O)_3^{2+}$ is also reproduced in Figure 3. As a first approximation, the absorption maxima have been assigned to the following transitions in (pseudo) O_h symmetry:[22] ν_1, 10,890 cm^{-1} (920 mμ), $^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2, 12,900 cm^{-1} (775 mμ), $^3A_{2g} \rightarrow {}^1E_g$; ν_3, 18,500 cm^{-1} (540 mμ), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F). The bands at 30,800 cm^{-1} (325 mμ) and 36,400 cm^{-1} (275 mμ) are attributed to parity-allowed transitions and almost certainly involve the ligands. A band has been observed in the Nujol spectrum of Ni(TRI)$(H_2O)_3[B(C_6H_5)_4]_2$ at 25,000 cm^{-1} (400 mμ) which may be assigned to ν_4, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P).[22] Since the effective symmetry of the Ni(TRI)-$(H_2O)_3^{2+}$ ion can be no higher than C_{3v}, the CD spectrum should be more correctly interpreted using this point group. A correlation diagram of ligand field states of nickel(II) in O_h and C_{3v} symmetry appears in Figure 4. All transitions between term states of the same multiplicity are vibronically allowed in both O_h and C_{3v} symmetry. Magnetic selection rules for these transitions are indicated by arrows in the figure along with their corresponding polarizations. The transitions $^3A_2 \rightarrow {}^3E$, $^3A_1$ (from $^3T_{2g}$ in O_h) should be magnetically allowed, but unfortunately the CD spectrum could not be measured in the region where this transition occurs. Upon descending in symmetry to C_{3v}, transitions to the ^3E component of $^3T_{1g}$ (P) and $^3T_{1g}$ (F) become magnetically allowed. Although the transition $^3A_2 \rightarrow {}^3A_2$, ^3E (P) appears in the spectral region of interest, no band could be detected in the CD spectrum from 400 to 700 mμ. The absence of a band in this region is probably due to the very weak rotatory power of this transition. The band at 360 mμ in the CD spectrum is very difficult to assign since the solution absorption spectrum shows no hint of a band in that region. Although the band might be attributed to a relatively low-intensity charge-transfer band (not seen in the spectra), it seems most likely that it is associated with the $^3A_2 \rightarrow {}^3E$ (P) transition. The latter is a common characteristic of magnetically allowed transitions with the intense optical activity but low absorption. In either case, the absorption band due to the transition must be obscured by the intense band at 325 mμ (ε 11,500). It is also reasonable to suppose that the band could be due to a transition which is forbidden in the electric dipole sense but magnetically allowed. The relatively high Δε value of 12.6 might indicate that the band is due to charge transfer; however, a large Δε for d–d transition may be accounted for by mixing the $^3A_2 \rightarrow {}^3E$ (P) with the parity-permitted transition at 325 mμ. The latter hypothesis appears plausible in that ν_4 occurs at about 400 mμ. The bands in the CD at 336 and 268 mμ can be assigned to the parity-allowed bands in the absorption spectrum at 325 and 275 mμ. The band at 296 mμ in the CD may be either a component of the absorption maximum at 275 mμ or a third charge-transfer band of relatively low molar absorptivity (since this band is flanked by two other bands of high extinction coefficient: 325 mμ (ε 11,500) and 275 mμ (ε 41,700).

Table III. Optical Rotatory Dispersion Data (mμ) for $(+)_{546}$-Ni(TRI)$(H_2O)_3^{2+}$

λ_{max}	$\lambda_{[m]=0}$	λ_{min}
470 sh	. . .	. . .
390	375	320
308	. . .	. . .
254	265	282

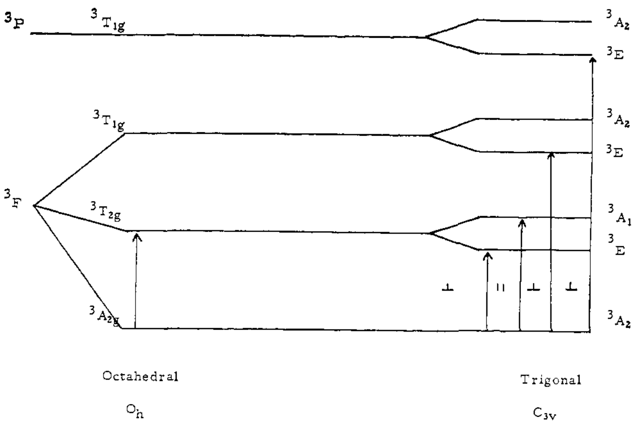

Figure 4. Correlation diagram of ligand field states of nickel(II) in octahedral and trigonal fields.

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