with 20 ml of tetrachloroethylene in the same fashion as the WCl_6 reduction. After 60 hr the organic material was removed by distillation *in vacuo* and the excess $WOCl_4$ sublimed away at 175°. A 0.3-g amount of an olive green powder was obtained which represents 18% of theory for $WOCl_3$. An infrared spectrum of this material showed a single broad band centered at 784 cm^{-1} and an analysis of the X-ray powder diffraction data yielded lattic constants of $a = 10.706$ and $c = 3.853$ Å for a tetragonal unit cell. These results compare well with the data reported by Fowles and Frost[23] for $WOCl_3$. Gas chromatographic analysis of the organic material verified the presence of C_2Cl_6.

Niobium Pentachloride and Tantalum Pentachloride in Tetrachloroethylene.—A 1.00-g sample of $NbCl_5$ was treated with tetrachloroethylene in the same fashion discussed above. After 1 week the organic material was distilled away and the solid product was heated to 130° in a sealed tube, whereupon much $NbCl_5$ sublimed away leaving behind only 0.12 g of a brown powder (14% of theory for $NbCl_4$). Its X-ray powder diffraction pattern was identical with that of $NbCl_4$.[18] Gas chromatographic analysis of the organic material verified the presence of C_2Cl_6.

A 1.00-g sample of $TaCl_5$ did not react after 2 weeks.

Acknowledgments.—We wish to thank Miss Sally DeLong for her helpful suggestions, Mr. Gary Weber for some of the X-ray calculations, and the National Science Foundation for financial support for part of this research.

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The Circular Dichroism of Tris(*l*-cyclohexanediamine)nickel(II) Chloride[1a]

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A discussion of the optical activity of coordination compounds in terms of the electronic structure of the metal ion was first presented by Moffitt in 1956.[2] Subsequent theoretical treatments by Piper and Karipides[3] and by Liehr[4] suggested specific crystal field or molecular orbital models for determining electric and magnetic transition moments. McCaffery and Mason performed empirical calculations of these quantities[5] and proposed a criterion for determining the absolute configuration of certain complexes based on a correlation of their circular dichroism behavior.[6]

The metal ions most extensively studed by these and later workers have been of the d^3 or d^6 configuration. The d^8 configuration of Ni(II) is of potential theoretical interest because it has three, rather than two, spin-allowed d–d bands in an octahedral field. Unfortunately, only a limited number of Ni(II) complexes have been found to be capable of resolution. They have been listed in a recent review.[7] A further problem encountered with Ni(II) is that its d–d bands do not all fall within the region of the spectrum commonly accessible to ORD and CD instruments.[8]

The complex ion, $Ni(l\text{-chn})_3^{2+}$, is not subject to racemization because its optical activity is inherent in the ligands.[9] This note reports its CD spectrum from 1200 to 300 mμ and endeavors to show that the rotational strengths of the three d–d transitions, as well as some other features of the CD spectrum, can be explained by present theory.

Experimental Section

Resolution of the ligand has been described previously.[10] To prepare the complex, nickel chloride (0.022 mol) was added to a solution of *l*-chn (0.074 mol) in 250 ml of water. The volume was reduced to 175 ml by boiling. Orchid crystals appeared upon cooling. Recrystallization from hot water gave the final product $[Ni(l\text{-chn})_3]Cl_2 \cdot 3H_2O$. *Anal.* Calcd for $NiC_{12}H_{48}N_6Cl_2O_3$: C, 41.08; H, 9.19; N, 15.97. Found: C, 41.20; H, 9.07; N, 15.99.

The absorption spectrum was determined on a Cary Model 14 RI spectrophotometer. Circular dichroism was measured on an instrument constructed in this laboratory by Professor Denning.[11]

Results and Discussion

The ligands of $Ni(l\text{-chn})_3^{2+}$ are bound as bidentate chelates in the manner of ethylenediamine. The absorption spectrum of the complex (Figure 1) has the three d–d bands typical of octahedrally coordinated Ni(II) indicating approximate O_h symmetry. As a result of the chelate rings, the actual symmetry is D_3. The CD spectrum reveals optical activity in all three absorption bands, but not to the same degree. This behavior can be explained on the basis of magnetic-dipole selection rules.[2] Thus, the low-energy band ($^3A_{2g} \rightarrow {}^3T_{2g}$) is the only one of the three transitions which is magnetically allowed in the O_h approximation. Correspondingly, it has the most intense circular dichroism. On the other hand, the moderately dichroic second band ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) becomes allowed only through mixing with $^3A_{2g} \rightarrow {}^3T_{2g}$ under the actual, D_3, field. Finally, the third band ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) is only weakly dichroic since it is magnetically forbidden unless configuration interaction is considered.[4] It is a two-electron transition in the strong-field limit and a transition between different terms ($^3F \rightarrow {}^3P$) in the weak-field limit.

A further interesting feature of the CD spectrum is revealed if the disposition of the ligands around the

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[1] (a) Taken from the Ph.D. thesis of Richard S. Treptow, University of Illinois, 1966; (b) Miami Valley Laboratories, The Procter & Gamble Co., Cincinnati, Ohio 45239.

[2] W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

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[5] A. J. McCaffery and S. F. Mason, *Trans. Faraday Soc.*, **59**, 1 (1963); *Mol. Phys.*, **6**, 359 (1963).

[6] (a) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962); (b) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[7] F. Woldbye in "Technique of Inorganic Chemistry," Vol. IV, H. B. Jonassen and A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp 249–368.

[8] L. T. Taylor and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 5372 (1967).

[9] The abbreviation chn is used for *trans*-1,2-diaminocyclohexane (cyclohexanediamine).

[10] R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

[11] R. G. Denning, *J. Chem. Phys.*, **45**, 1307 (1966).

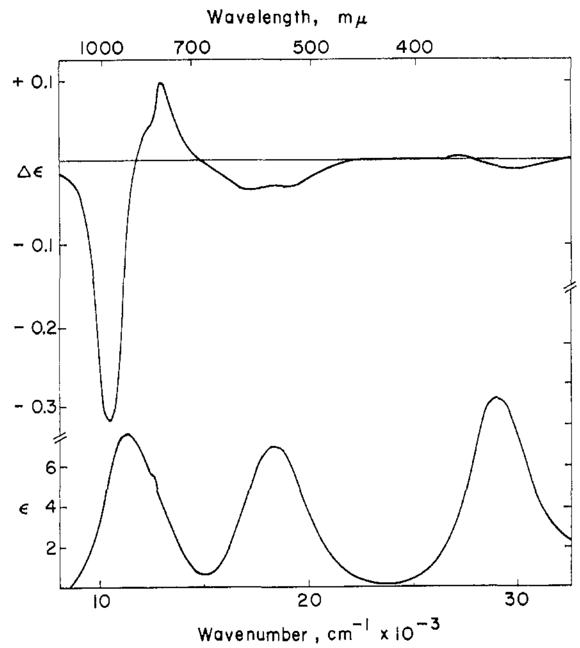

Figure 1.—CD and absorption spectra of $[Ni(l\text{-chn})_3]Cl_2 \cdot 3H_2O$ in anhydrous methanol.

metal ion is considered in greater detail. $Ni(l\text{-chn})_3^{2+}$ can exist in either the Δ or Λ configuration.[12] With a knowledge of the absolute configuration of the ligand these configurations are known to have the *lel* and *ob* conformations, respectively.[13] The former is thermodynamically more stable. Thus, it can be assumed that the CD spectrum is predominantly that of the Δ, *lel* diastereoisomer. The ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition has first a large, negative and then a smaller, positive CD component. The very same characteristic is found for the magnetically allowed, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $(-)_{T_{1g}}$-$[Co(l\text{-chn})_3]Cl_3$, which is known to have the Δ, *lel* configuration.[14] Thus, an example of the correlation of circular dichroism and absolute configuration has been found which spans d^6 and d^8 metal ions. This implies that the criterion of McCaffery, Mason, and Ballard[6] may extend beyond d^3 and d^6 cases. Indeed, a theoretical basis for this proposal is contained in the expressions of Liehr for the rotational strengths of trigonal complexes.[4]

Assignments of the various CD band components can be made by reference to the D_3 point group. The negative and positive components of the first band are assigned ${}^3A_2 \rightarrow {}^3E$ and ${}^3A_1$, respectively, in keeping with the pattern established by d^3 and d^6 tris-1,2-diamine complexes.[6b] The spike appearing on the positive component is attributed to the singlet state, ${}^1E$, which is strongly mixed with the near-lying triplet states. The second and third absorption bands each have ${}^3E$ and ${}^3A_2$ components in D_3. Since transitions to ${}^3A_2$ are electrically and magnetically forbidden, each of the bands is expected to have only a single CD component, ${}^3E$. In both cases, however, two CD bands are evident indicating a removal of the degeneracy of the ${}^3E$ state. This is possibly the result of spin–orbit coupling or a loss of D_3 symmetry through ion pairing.

Acknowledgment.—The author is indebted to the late Professor T. S. Piper, under whose direction this research was begun.

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New Analogs of Spodiosite, Ca_2VO_4Cl and Ca_2AsO_4Cl

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Recently the crystal structures of Ca_2PO_4Cl and Ca_2CrO_4Cl, analogs of the mineral spodiosite, Ca_2PO_4F, have been determined.[1] These crystals are orthorhombic, space group Pbcm, with four molecules per unit cell. The structure contains distinct oxygen tetrahedra, MO_4^{3-}, which appear to be held together by the calcium ions. The crystal structures indicate that these tetrahedra are distorted, this distortion being greater for the chromate(V) than for the phosphate. This has been attributed to an electronic ordering of the single d electron in the e orbitals of the CrO_4^{3-} complex.[2]

It was also noted that the infrared vibrational spectrum of these two species showed splitting of the band associated with the asymmetric stretch.[2] This splitting is greater for the chromate(V) and is attributed to the greater distortion of the CrO_4^{3-} tetrahedra.

This paper reports the results of an attempt to prepare new phases with the spodiosite structure and to determine if the extra distortion in the CrO_4^{3-} ion is indeed attributable to electronic ordering. Attempts were made to prepare such compounds using V, As, Sb, Mo, and W as possible central atoms.

Experimental Section

All samples were prepared from a $CaCl_2$ flux. The metallic oxide, $CaCO_3$, and the flux were mixed in a 30-ml Pt crucible and in mole ratios of 1:3:12. The crucibles were covered and placed in a furnace. The samples were soaked for 16 hr at 900° under an oxygen atmosphere and then cooled to about 200° at a rate of 14.5°/hr.

After cooling to room temperature the crucibles and product were boiled in distilled water. The product was washed on a Büchner funnel until no sign of Cl^- could be detected with silver nitrate solution. This indicated that all of the flux had been washed away. The product was obtained in both crystal and powder form. Separation of the powder was accomplished by placing the product in a beaker with distilled water and after

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