two small ethanol rinses. This solution was evaporated overnight to half its original volume and the yellow precipitate was collected on a sintered-glass funnel by suction filtration. The solid was washed five times with 2–3-ml portions of water and then dried by exposure to a stream of air for 15 min. Its melting point was 189–191°.

A portion of this product was immediately sublimed at 10^{-6} Torr at a bath temperature of 130–140° for 1 hr. The X-ray powder patter and melting point (193–194°) were taken within 1 hr of the termination of sublimation. Another portion of the crude product was kept in a screw-cap vial for 8 days longer; it then melted at 168–174° and decomposed on attempted sublimation.

Several lanthanide chelates of the basic formula CsM(hfa)$_4$ were prepared by the method of Lippard;[2] however, in some cases the yield of product was raised from 45 to 80% by doubling the concentration of Cs(hfa) added to the reagent solution. The products were purified either by recrystallization from 50% ethanol or by sublimation. Monohydrates for the rare earth ions La$^+$ through Nd^{3+} resulted both from the original preparation and on crystallization from 50% aqueous–ethanol solutions. Anhydrous forms were usually obtained by recrystallization from 1-butanol and washing with toluene.

The lanthanum monohydrate, CsLa(hfa)$_4 \cdot H_2O$, was dissolved in butanol and part of the solvent was evaporated. The compound that separated, Cs$_2$La(hfa)$_5$, melted at 226–227° and the melting point was unchanged by sublimation at 135°, 10^{-2} Torr. *Anal.* Calcd for $C_{22}H_5F_{30}Cs_2LaO_{10}$: C, 20.9; H, 0.35; H$_2$O, 0; Cs, 18.5; La, 9.7; equiv wt 720. Found: C, 20.7; H, 0.4; H$_2$O, 0.3; Cs, 17.6; La, 9.4; equiv wt 732.

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Magnetic Circular Dichroism and Electronic Structure of Square-Planar Nickel(II) Complexes

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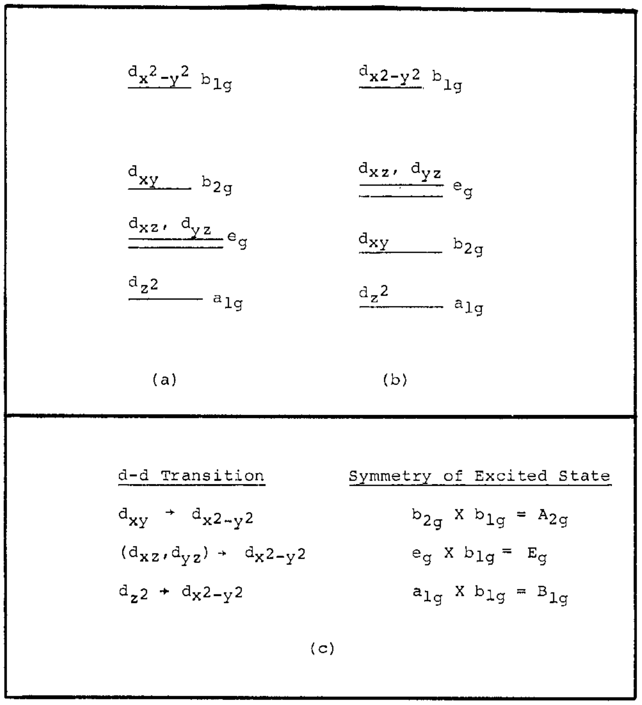
Although it has been established that the splitting of the d orbitals by a square-planar ligand field results in one high-energy ($d_{x^2-y^2}$) and four lower energy [(d_{z^2}, d_{xy}, and the degenerate pair, d_{xz} and d_{yz})] orbitals, the exact ordering of these lower energy orbitals is not certain.[1-3] The work of Martin, *et al.*,[4] and McCaffery, Schatz, and Stephens[5,6] has demonstrated the usefulness of magnetic circular dichroism (MCD) studies in obtaining spectroscopic information about d^8 square-planar complexes. This communication reports the MCD spectra of three complexes of Ni(II) (two with sulfur and one with nitrogen as the donor atoms) having square-planar microsymmetry.

The characteristics of MCD spectra have been described elsewhere.[7-9] Since the ground state of a Ni(II) complex in a square-planar ligand field is orbitally nondegenerate, only A and B terms are expected to be present in the MCD spectrum. A B term peaks near the corresponding absorption maximum and is brought about through the mixing of different states by the magnetic field, whereas an A term changes sign near the absorption maximum and is observed only when either the ground or excited state is degenerate. Thus, in the case of a square-planar, d^8 complex an A term indicates that the excited state is degenerate.

Of all the square-planar, d^8 complexes, PtCl$_4^{2-}$ is probably the most extensively studied. Chatt, *et al.*,[10] proposed that the d orbitals increase in energy as shown in Figure 1a. Thus the excited-state symmetries of



d-d Transition	Symmetry of Excited State
$d_{xy} \rightarrow d_{x2-y2}$	$b_{2g} \times b_{1g} = A_{2g}$
$(d_{xz}, d_{yz}) \rightarrow d_{x2-y2}$	$e_g \times b_{1g} = E_g$
$d_{z2} \rightarrow d_{x2-y2}$	$a_{1g} \times b_{1g} = B_{1g}$

Figure 1.—Alternative orderings of the d-orbital energy levels: (a) after Chatt, *et al.*,[10] and (b) after Leussing.[11] Representations are given for the various excited states arising from d–d transitions, assuming D_{4h} symmetry.

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the three d → d transitions were $A_{2g} < E_g < B_{1g}$. This ordering was supported by Gray, *et al.*,[12,13] and also by two groups of investigators,[4,5] who measured the MCD spectrum of $PtCl_4^{2-}$ and determined that the E_g state was of higher energy than the A_{2g}. Jørgensen,[11] in reporting the absorption spectra of some sulfur-containing complexes, chose this order in assigning the d → d bands for bis(diethyldithiophosphato)nickel(II), $Ni(S_2P(OC_2H_5)_2)_2$, or $Ni(dtp)_2$, and for bis(diethyldithiocarbamato)nickel(II), $Ni(S_2CN(C_2H_5)_2)_2$ or $Ni(dtc)_2$, both of which are coordinated through four sulfur atoms in a square-planar arrangement. He pointed out Leussing's[3,11] warning, however, that the ordering of levels found for the tetrahalides may not be observed in a complex in which the coordinated atoms are attached to form chelate ligands.

According to Leussing the effect of chelate ligands would be to change the order of the transitions from $A_{2g} < E_g < B_{1g}$ to $E_g < A_{2g} < B_{1g}$. This change could result from interchange of the order of the b_{2g} and e_g orbitals as shown in Figure 1b. The MCD spectra of $Ni(dtp)_2$ and $Ni(dtc)_2$ (Figures 2 and 3) indicate that the lowest energy transition is degenerate and thus support the order $E_g < A_{2g} < B_{1g}$.

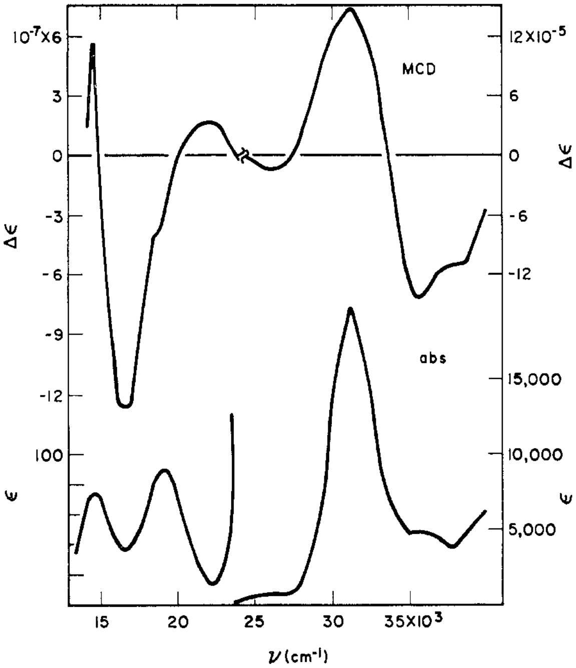


Figure 2.—MCD and absorption spectra of $Ni(dtp)_2$ in chloroform.

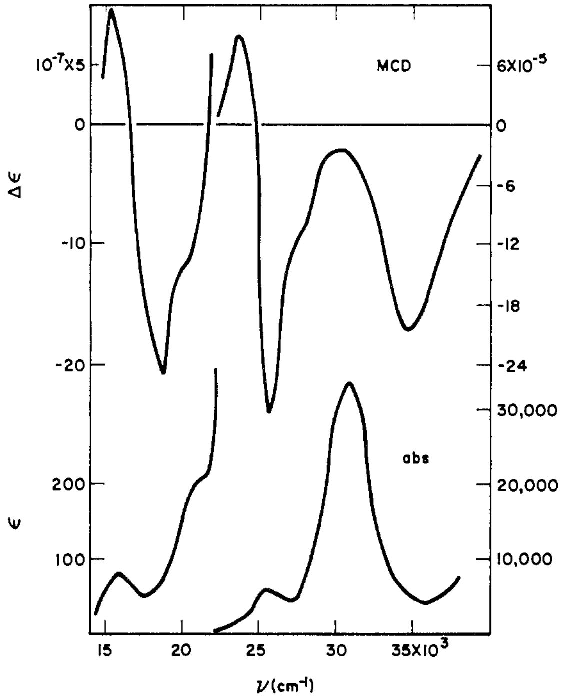
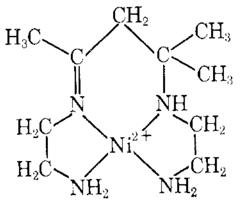


Figure 3.—MCD and absorption spectra of $Ni(dtc)_2$ in chloroform.

The absorption spectrum of $Ni(dtp)_2$ (Figure 2) clearly shows the two lowest energy d → d bands at about 14,700 and 19,100 cm^{-1}. The MCD in the region of the lower band contains an A term and indicates that this transition is degenerate. The shoulder at about 19,000 cm^{-1} on the MCD curve is consistent with a positive B term at the higher energy transition. In Figure 3, a similar situation is observed for $Ni(dtc)_2$ except that the transitions are displaced toward higher energy so that the higher energy visible absorption band appears as a shoulder on the first charge-transfer band. Figure 4 shows the MCD in the range of the lowest energy band for $[Ni(C_{10}H_{24}N_4)][ZnCl_4]$, a complex of a macrocyclic, tetradentate ligand having nitrogen as the donor atoms (I). Once again the lowest energy transition appears to be degenerate. Thus for each of these three nickel complexes containing multidentate ligands, MCD studies have shown that the E_g state is lower in energy than the A_{2g} or B_{1g} states.



I

1,9-diamino-4,6,6-trimethyl-3,7-diazanona-3-enenickel(II) cation

Experimental Section

The MCD spectra were obtained from a JASCO recording ORD–CD spectrophotometer used in conjunction with a superconducting magnet. The measurements were made at room temperature and at a constant magnetic field of 65,000 G. The MCD units ($\Delta\epsilon = \epsilon_l - \epsilon_r$) are l. cm^{-1} G^{-1} mol^{-1} and the absorption units (ϵ) are l. cm^{-1} mol^{-1}. All absorption spectra were obtained from a Cary 14 recording spectrophotometer. The $Ni(dtp)_2$ was prepared by a standard method,[14] and the $Ni(dtc)_2$ was precipitated from aqueous $NiCl_2 \cdot 6H_2O$ and Na(dtc). All spectra of these two compounds were obtained using chloroform solutions. In addition, a complex containing nitrogens as the four donor atoms was prepared and absorption and MCD spectra were obtained over the lowest d → d band. This compound, the macrocyclic $[Ni(C_{10}H_{24}N_4)][ZnCl_4]$, was pre-

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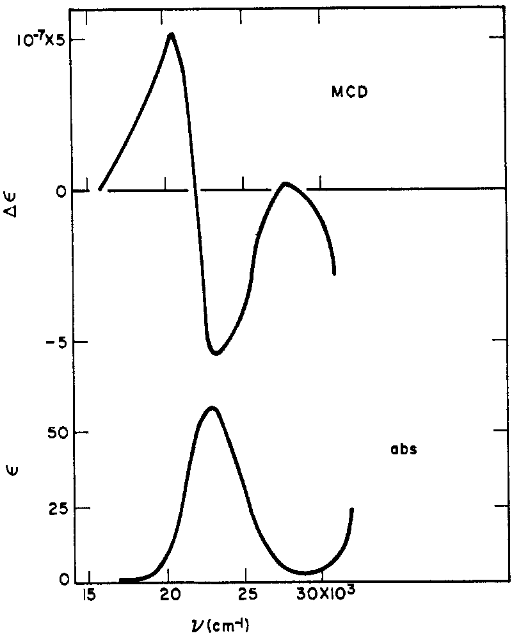

Figure 4.—MCD and absorption spectra of $[Ni(C_{10}H_{24}N_4)]$-$[ZnCl_4]$ in water.

pared as described by MacDermott and Busch[15] and the spectra were obtained from a water solution.

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On the Stoichiometry of Trisodium Orthophosphate Dodecahydrate

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Excess sodium hydroxide in trisodium orthophosphate dodecahydrate, $Na_3PO_4 \cdot 12H_2O$, and the isomorphous arsenate, vanadate, and manganate compounds has been reported repeatedly. Menzel and his collaborators[1-3] showed that pure $Na_3XO_4 \cdot 12H_2O$ (X = P, As, V) cannot be crystallized from a solution containing the stoichiometric ratio $Na_2O:X_2O_5 = 3:1$. Solutions with $Na_2O:X_2O_5$ ratios from about 2.6:1 up to 9:1 yielded crystals with $Na_2O:X_2O_5$ ratios between 3.01:1 and 3.25:1. A ratio higher than 3.25:1 was never observed by these workers and they assumed this to be a limiting composition. Their analytical results did not allow them to distinguish between water contents of 11.75 mol of H_2O or 12 mol of H_2O. In the first case NaOH would be substituted for water molecules; in the second case it would be included in the dodecahydrate structure. Menzel, *et al.*, called these compounds ψ-12-hydrates (ψ for pseudo) to distinguish them from the stoichiometric compositions, which could be obtained only from the hydration of lower hydrates, but never were found to be in equilibrium with their solutions. Serebrennikova[4] claimed that the limiting ratio for these compounds is $Na_2O:X_2O_5 = 3.33:1$ and drew an analogy to the structure of hydroxide apatite. Lux, *et al.*,[5] investigated the corresponding sodium manganate ψ-12-hydrate and suggested $Na_3MnO_4(NaOH)_{0.25}(H_2O)_{12}$ as the limiting composition. However, they stated that their analyses are not sufficiently accurate to exclude beyond all doubt the composition $Na_3MnO_4(NaOH)_{0.25}(H_2O)_{11.75}$. Bell[6] described the compound as a complex with the formula $n(Na_3PO_4 \cdot xH_2O) \cdot NaY$ where $n = 4$ or 7, $x = 11$ or 12, and Y^- is a monovalent anion such as OH^-, MnO_4^-, OCl^-, or NO_3^-. Quimby[7] reported the formula $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$ with x varying between 0.1 and 0.25. Chrétien and Lelong[8] claimed that the compound $Na_3VO_4 \cdot 0.25NaOH \cdot 12H_2O$ is a complex formed by trisodium orthovanadate and sodium hydroxide tetrahydrate.

A recent determination of the crystal structure of trisodium orthophosphate dodecahydrate undertaken during a study of the crystal chemistry of hydrated sodium phosphates, arsenates, and vanadates[9] has clarified the manner in which the sodium hydroxide is built into the crystal structure of the $Na_3XO_4 \cdot 12H_2O$ salts.

Experimental Section

Crystal data are in close agreement with those of Clark and Gross:[10] $a = 11.890$ (6) Å, $c = 12.671$ (7) Å, $V = 1551$ (3) Å^3, space group $P\bar{3}c1$, $Z = 4$, $d_x = 1.65$ g/cm^3, $d_m = 1.64$ g/cm^3. The unit cell constants are based on the refinement of 20 reflections which had been centered on an automatic four-angle X-ray diffractometer. Systematic extinctions ($h\bar{h}0l$ only with $l = 2n$) are consistent with space groups $P\bar{3}c1$ and $P3c1$; the centric space group was confirmed by the successful refinement of the structure. The crystal used for the structure determination was commercial sodium phosphate (tribasic crystal, Baker 3836) which contained an excess of 0.155 mol of NaOH per formula unit $Na_3PO_4 \cdot 12H_2O$ according to a company analysis. The crystal structure was determined by three-dimensional Patterson and Fourier methods and refined to $R = 0.056$ for 556 observed F_{hkl}.

Results and Discussion

The prominent structural unit is a two-dimensionally infinite sheet of $Na(OH_2)_6$ coordination octahedra with a composition $Na(OH_2)_4$. Within one sheet the $Na(OH_2)_6$ octahedra share corners to form rings of six octahedra, with each ring connected to six other ones

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