were found to be monomeric and both exhibited normal magnetic moments. The visible spectrum of the anhydrous material in carbon tetrachloride, Figure 1, shows a well-separated shoulder on the high-energy side of the visible band; the spectrum of the dihydrate in the same solvent shows a less pronounced shoulder much closer to the main band. Since a well-separated shoulder is present on the high-energy side of the main band in the spectra of all other β-dicarbonyl complexes of copper(II), this shoulder probably results from further splitting of the d orbitals as the symmetry is decreased from octahedral to square-planar; such an assignment has been discussed for bis(acetylacetonato)-copper(II).[7] The position of this band, nearer the main band, in the dihydrate spectrum is probably due to a less pronounced tetragonal distortion and, thus, suggests that the waters are coordinated to the copper to give a distorted octahedron.

(7) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

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Magnetic Circular Dichroism for Tetrachloroplatinate(II) Ion[1]

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Magnetic circular dichroism (MCD) has been observed for solutions of K_2PtCl_4 in dilute HCl which provides information relevant to the assignment of energy levels of the square-planar $PtCl_4^{-2}$ ion. The energy level scheme of this ion has recently been discussed on the basis of polarized single-crystal spectra recorded at 15°K.[2] The experimental arrangement for the determination of circular dichroism was described earlier.[3] Modifications have included: (1) a 30-fold electrical expansion of the recorder scale which does not appreciably alter the signal-to-noise ratio, (2) the replacement of the Jouan monochromator by an Applied Physics Corp. Model 15 monochromator, (3) the use of a 500-w xenon arc light source, (4) a change of the crystal modulation frequency in the dichrograph from 60 to 82 cps, (5) the use of an electromagnet to provide a magnetic field of 12,000 gauss in which the light beam travels from the south toward the north pole. A clockwise rotation for an observation toward the light source is called positive. Under these experimental conditions the MCD near 500 mμ for an aqueous cobalt(II) chloride solution is positive, in agreement with the normal convention and contrary to that employed by Schooley, *et al.*[4]

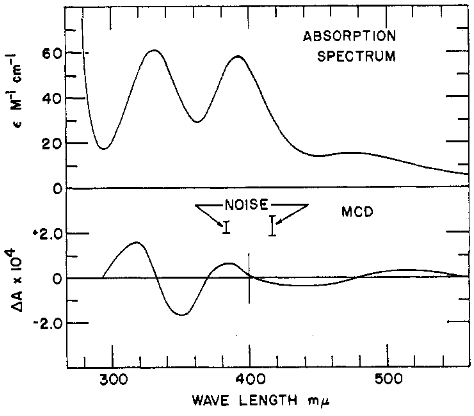

Figure 1.—Absorption spectrum and magnetic circular dichroism for a solution of K_2PtCl_4 in dilute aqueous HCl. Cell length = 1.00 cm; concentration of K_2PtCl_4 0.015 *M*.

The MCD for a solution of K_2PtCl_4 in dilute HCl is shown in Figure 1 together with a plot of its absorption spectrum. A reference trace was obtained with the light passing through the solution in the absence of a magnetic field. An MCD appears clearly to be associated with the absorption band having a maximum at 330 mμ. There is a distinct positive lobe at shorter wavelengths. The MCD trace crossed the reference at 332 mμ to give a negative lobe at longer wavelengths. The small positive lobe from 370 to 400 mμ is at most only slightly greater than the noise. Beyond 400 mμ, there was no deviation of the MCD from the reference line greater than the noise level. The MCD peaks correspond to a $\Delta A/A_{\max}$ of 1.5×10^{-4} where ΔA is the difference in absorbance between right- and left-handed light and $A_{\max}$ is the absorbance at the band maximum.

The MCD may arise from the Zeeman splitting of two transitions which possess different absorptions for the right- and left-handed light. If the transitions may each be represented by a Gaussian function whose central frequencies differ by the Zeeman splitting, 2δ, the amplitudes of the MCD lobes will be proportional to δ and inversely proportional to the width of the band.[3]

The two transitions may, in general, proceed from separate states differing by an energy $2\delta_g$ and initially filled according to a Boltzmann distribution and terminate in separate excited states differing by an energy, $2\delta_m$. Thus $\delta = \delta_m \pm \delta_g$. A least-squares method was utilized to fit the experimental MCD to separate values of δ_g and δ_m, based on the assumption that each of the two transitions is circularly polarized completely.[5] From the curve in Figure 1, the least-squares program gave splittings of 0.00 and 0.45 cm^{-1} for the ground and excited states, respectively.

The result, $\delta_g = 0$, is gratifyingly consistent with the

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(1) Work was performed in part in the Ames Laboratory of the Atomic Energy Commission and in part under support by a grant from the United States Public Health Service, Contribution No. 1801.

(2) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, (1965).

(3) J. G. Foss and M. E. McCarville, *J. Am. Chem. Soc.*, **87**, 228 (1965).

(4) D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci.*, **53**, 579 (1965).

(5) J. G. Foss and M. E. McCarville, submitted for publication.

generally accepted assignment of the ground state to a nondegenerate Γ_1 wave function.[2] The Γ_i designations pertain to the representations of the total wave function containing both the spin and the orbital parts ($\Gamma_1 = a_{1g}$). In the two-hole formalism for the d^8 configuration the major component of the ground state is $^1(b_{1g}^*)^2 = {}^1A_{1g}$. (The x and y axes have been chosen to pass through the ligands.) On the basis of low-temperature polarized spectra of single crystals the peak at 30,300 cm^{-1} in solution was attributed to transitions to degenerate Γ_5 states ($\Gamma_5 = e_g$) whose principal components were $^1(b_{1g}^*e_g)^1E_g$ states. The MCD, which indicates a Zeeman splitting of excited states, therefore strongly supports this assignment since transitions to nondegenerate states would be incapable of such Zeeman splitting. The value of δ_m of 0.45 corresponds to an effective magnetic moment of 0.8 BM. For the $(b_{1g}^*e_g)^1E_g$ state the magnetic moment is just the magnitude of the off-diagonal angular momentum matrix element $\langle\psi_a L \psi_b\rangle$ (where ψ_a, ψ_b are the degenerate wave functions[6]) which is 1 BM. The MCD corresponds, therefore, in order of magnitude with the expected splitting of the degenerate ^1E_g states.

Although weaker Γ_5 transitions are predicted to lie at lower energies, calculated at 21,100 and 18,700 cm^{-1} for the crystalline K_2PtCl_4 together with several close lying transitions to nondegenerate states, it has not been possible to observe an appreciable MCD in these regions with the present equipment as has been indicated in Figure 1.

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(6) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

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Chloroform Solvates of Tetrapyridinenickel(II) Perchlorate and Tetrafluoroborate

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In a previous study of pyridine complexes of nickel(II), the complexes $Ni(C_5H_5N)_4(ClO_4)_2$ and $Ni(C_5H_5N)_4(BF_4)_2$ were prepared and characterized as six-coordinate spin-free tetragonal complexes.[2] In this article we report a novel chemical reaction that these materials undergo. When these complexes are suspended in acidic solvents, solvent molecules are taken up by the solid and a stereochemical change occurs to produce a four-coordinate, spin-paired nickel(II) cation. This reaction occurs apparently without dissolution of the complex.

Experimental Section

The blue tetragonal complexes were prepared by previously reported syntheses.[2] Chloroform was shaken with calcium chloride, allowed to stand overnight, and distilled. Dichloromethane was used after being stored for 2 weeks over molecular sieves. Infrared Spectra were obtained with a Perkin-Elmer Model 521 recording spectrometer, equipped with a N_2 purge to exclude moisture. X-Ray diffraction powder patterns were obtained using a copper $K\alpha_1$ target (λ 1.54050 A) and a powder camera with a rotating sample holder. Samples for analysis were weighed in closed "pigs," which were loaded in a dry atmosphere box to exclude moisture. The magnetic susceptibility was measured by the Gouy method.

Anal. Calcd for $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$: C, 36.4; H, 3.03. Found: C, 35.0; H, 3.03. Calcd for $Ni(C_5H_5N)_4(BF_4)_2 \cdot CHCl_3$: C, 37.1; H, 3.12. Found: C, 37.3; H, 3.49.

These analyses can be compared to those obtained after the chloroform has been removed in a dry atmosphere. *Anal.* Calcd for $Ni(C_5H_5N)_4(ClO_4)_2$: C, 41.8; H, 3.48. Found: C, 41.8; H, 3.59. Calcd for $Ni(C_5H_5N)_4(BF_4)_2$: C, 43.7; H, 3.74. Found: C, 42.4; H, 3.94.

Results and Discussion

The complexes $Ni(C_5H_5N)_4(ClO_4)_2$ and $Ni(C_5H_5N)_4(BF_4)_2$ have been reported and characterized[2] as having six-coordinate, tetragonal structures containing monodentate coordinated anions. The perchlorate complex is soluble in dichloromethane, and the solution has an electronic spectrum identical with that of the Nujol mull. However, when either of those complexes is suspended in chloroform or the tetrafluoroborate complex is suspended in dichloromethane, the complexes do not dissolve, but change in color from pale blue to yellow. This color change is rapid for the tetrafluoroborate complex in chloroform.[3] These yellow compounds are extremely hygroscopic, changing to blue almost immediately upon contact with moist air. When these yellow compounds are removed from their "solution" by filtration in a dry atmosphere box, they may be stored in a moisture-free environment several months before changing back to a pale blue color, but when placed under vacuum, away from moist air, they return to a blue color much more rapidly. This color change may be accomplished in the case of the methylene chloride solvate on a vacuum filter apparatus in the dry atmosphere box. For $Ni(C_5H_5N)_4(ClO_4)_2 \cdot CHCl_3$ 12 hr pumping in a vacuum desiccator is required, while 24 hr pumping in a vacuum desiccator is needed for $Ni(C_5H_5N)_4(BF_4) \cdot CHCl_3$. Once the yellow compounds have been converted back to the blue color in the absence of moisture, they are reactive to the solvent, whereas the blue compound formed in moist air is impervious to attack by the solvents.

Infrared spectra and X-ray powder patterns (Table I) indicate that the original compounds and the blue materials obtained from desolvation of yellow compounds under anhydrous conditions are identical. The yellow compounds show structured infrared bands indicating C_{3v} coordinated anions. On the other hand, the blue compounds obtained from the yellow compounds through exposure to moist air analyze well for

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(1) Abstracted in part from the Ph.D. Thesis of M. R. Rosenthal, University of Illinois, Urbana, 1965.

(2) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

(3) Similar behavior is noted for a methylene chloride solvate of $Ni(C_5H_5N)_4(BF_4)_2$.