Ho_2O_3, with $a_0 = 10.606 \pm 0.001$ Å. This may be compared with the literature[2] value of $a_0 = 10.6065$ Å. A portion of yttria recovered from a projectile was also annealed (at 1055° for 2 days). A similar marked improvement in the line profile of the X-ray pattern for this (single phase) material was observed. The derived lattice constant was $a_0 = 10.604 \pm 0.001$ Å. (*cf.* literature[2] value, $a_0 = 10.6021$ Å.).

Although the ionic radii[4] of Ho^{3+} and Y^{3+} are approximately the same (0.91 Å.), no C → B conversion was observed in the case of Y_2O_3. However, the fact that the lattice parameter of C-type yttria is slightly smaller than that of holmia (10.6021 Å. as compared with 10.6065 Å.) suggests that $r_{Y^{3+}}$ is slightly less than $r_{Ho^{3+}}$ and that the pressure achieved during impact was insufficient to effect the conversion in the oxide with the smaller cation.

The absence of a B → A conversion in the case of Sm_2O_3 is presumably to be explained in the same way.

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Preparation and Spectral Properties of Some Alcohol Complexes of Nickel(II)

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We have in the past reported on the preparation, stoichiometry, and electronic spectra of several transition metal ion complexes of nonaqueous solvents.[2,3] It was of interest to extend these studies to alcohols and to locate these materials in the spectrochemical series.

Alcohols are fairly common solvents and although a large number of complexes of polyhydric alcohols are known[4] those of the simple alcohols with transition metals have not been well characterized. There is some evidence for the existence of complexes in solution[5] and Quagliano and his co-workers[6] report the separation of hexaethanolnickel(II) perchlorate but do not present an elemental analysis or characterize it further.

We have had considerable success in dehydrating aquo-metal complexes with 2,2-dimethoxypropane, which reacts with water according to eq. 1.

$$(CH_3O_2)_2C(CH_3)_2 + H_2O \longrightarrow (CH_3)_2C{=}O + 2CH_3OH \quad (1)$$

A whole series of complexes has been prepared by adding ligands to methanolic solutions of the dehydrated metal ion. It seemed that it should be possible to prepare a methanol complex from the solution which resulted after dehydration. This proved to be the case when the initial aquo complex was hexaaquonickel(II) perchlorate. By dehydrating with the ketal, 2,2-diethoxypropane, we were able to isolate the corresponding ethanol complex.

Experimental

The alcohol complexes are extremely hygroscopic. All manipulations, including the initial filtrations, were carried out in a dry atmosphere box in baked equipment. Microanalyses were accomplished with the use of closed pigs which were weighed, filled in the drybox, reweighed, and analyzed immediately.

Reagents.—2,2-Dimethoxypropane (Dow, technical grade) is contaminated with acetone, methanol, and 2-methoxy-1-propene. The vinyl ether must be removed because it polymerizes in the presence of the metal ion. The brown polymer precipitates with the alcohol complex and is difficult to remove because of the sensitivity of the complex. Purification can best be accomplished by fractionation at reduced pressure. The fraction boiling at 34° at 130 mm. was used here. 2,2-Diethoxypropane (Eastman, White Label) was used without further purification as was hexaaquonickel(II) perchlorate (G. F. Smith). The alcohols used as solvents were dried by stirring over 4A molecular sieve and distilling from Grignard grade magnesium.

Preparation of Hexamethanolnickel(II) Perchlorate.—One gram (2.73 mmoles) of hexaaquonickel(II) perchorate was dissolved in 5 ml. of methanol. To this solution 3.65 g. (32.8 mmoles) of dimethoxypropane (100% excess) was added. This solution was stirred under dry nitrogen for 10 hr. at 4°. Upon the addition of copious quantities of dry ether (about ten times the volume of the solution) the desired methanol complex separates as a pale yellow-green powder.

Anal. Calcd. for $[Ni(CH_3OH)_6][ClO_4]_2$: C, 16.01; H, 5.34; Ni, 13.06. Found: C, 15.96; H, 5.15; Ni, 13.44.

Preparation of Hexaethanolnickel(II) Perchlorate.—The preparation is identical with that of the methanol complex described above except that ethanol and diethoxypropane were substituted for methanol and dimethoxypropane.

Anal. Calcd. for $[Ni(CH_3CH_2OH)_6][ClO_4]_2$: C, 26.95; H, 6.74; Ni, 11.56. Found: C, 26.02; H, 6.91; Ni, 11.40.

Spectra.—Infrared spectra in the region 250 to 4000 cm.$^{-1}$ were obtained on a Perkin-Elmer Model 521 grating spectrophotometer. The spectra were obtained as Nujol mulls of the complexes between NaCl and CsBr plates. A stream of dry nitrogen was passed through the sample compartment during the scan time.

Spectra in the range 350 to 1400 mμ were obtained on a Cary Model 14M spectrophotometer. The complexes were examined as solutions in the appropriate alcohol in 1-cm. stoppered cells.

Results

Infrared Spectra.—The O–H stretching frequencies observed in the two alcohol complexes were compared with the free O–H frequencies of the appropriate alcohol in dilute solution in carbon tetrachloride (see Table I). The values for water in the aquo complex are included for reference. The spectra of the alcohol complexes show none of the characteristic absorptions of water and give no indication of perchlorate coordination. The metal–oxygen stretching frequencies appear to be in the range 600–700 cm.$^{-1}$ but the appearance of a perchlorate mode in that region makes identification difficult.

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[1] Abstracted from a thesis submitted by V. Imhof to the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

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TABLE I
HYDROXYL INFRARED STRETCHING FREQUENCIES (CM.$^{-1}$)

	$[Ni(CH_3OH)_6]$-$[ClO_4]_2$	$[Ni(C_2H_5OH)_6]$-$[ClO_4]_2$	$[Ni(H_2O)_6]$-$[ClO_4]$
$\nu_{\text{free O—H}}$	3622	3610	3760
$\nu_{\text{complex O—H}}$	3360	3380	3470

TABLE II
SPECTRAL DATA FOR THE OCTAHEDRAL NICKEL(II) COMPLEXES OF ETHANOL AND METHANOL
(ν IN UNITS OF CM.$^{-1}$ × 10^3)

	$[Ni(CH_3OH)_6]$-$[ClO_4]_2$	$[Ni(C_2H_5OH)_6]$-$[ClO_4]_2$
ν_1 (${}^3A_{2g} \rightarrow {}^3T_{2g}$)	8.431	8.18
$\epsilon_1{}^a$	2.4	2.7
ν_2 (${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$)	14.226	13.404
ϵ_2	4	3
ν_3 (${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$)	25.000	24.795
ϵ_3	6.3	7.1
ν_2 calcd.	14.017	13.656
% difference in ν_2	1.5	1.8
$15B$	13.936	13.650
β	0.88	0.86

[a] Calculated from $\epsilon = A/bc$ where b, the cell thickness, is 1 cm., c, the concentration, is in moles/l., and A is the absorbance.

Electronic Spectra.—The spectra of the two alcohol complexes in this region are quite similar to that of the octahedral water complex, showing three transitions with some doublet character to the middle band. The values listed in Table II for ν_2 are the weighted averages of the doublet maxima.

The transitions in question are all Laporte-forbidden d–d transitions and hence weak in pure octahedral symmetry. The band frequencies and intensities indicate that the complexes have essentially octahedral symmetry.

The ground-state term of the gaseous divalent nickel ion is a ${}^3F$ which splits in the influence of the ligand field into a ${}^3A_{2g}$, ${}^3T_{2g}$, and ${}^3T_{1g}$ in order of increasing energy. The first excited triplet state in the gaseous ion is a ${}^3P$ which becomes a ${}^3T_{1g}$ in the ligand field. Energies are measured from the ${}^3A_{2g}$ as ground The secular determinants involved are (for a general review see ref. 6)

$$ {}^3A_{2g}[-12Dq];\ {}^3T_{2g}[-2Dq];\ {}^3T_{1g}\begin{bmatrix} 6Dq & 4Dq \\ 4Dq & 15B \end{bmatrix}\begin{matrix} {}^3F \\ {}^3P \end{matrix} $$

where B is a Racah parameter. The distances between terms of maximum S are simple multiples of B. In this case $15B$ represents the ${}^3P$–${}^3F$ term splitting.

The energy of the ${}^3T_{1g}(P)$ level above the ground ${}^3A_{2g}$ can be found simply by subtracting the energy of the ${}^3A_{2g}$ ($12Dq$) from the observed band maximum for ν_3. If this energy is substituted into the expanded ${}^3T_{1g}$ determinant (quadratic in E) a value for $15B$ for the complex can be obtained. This value can then be used to calculate the other eigenvalue which is the energy of the ${}^3T_{1g}(F)$ above the ground state. The value of the band maximum for ν_2 calculated in this way gives a check on the accuracy of the band assignments; see Table II.

The lowest energy transition in these complexes is from ground to ${}^3T_{2g}$. It follows directly from the secular determinants that the energy of this transition gives $10Dq$ immediately. Thus from Table II it can be seen that the Dq values for methanol and ethanol toward nickel(II) are 843 and 818 cm.$^{-1}$, respectively.

The calculations of $15B$ described above give a value somewhat lower than the value of the free gaseous ion,[7] 15,840 cm.$^{-1}$. This is the nephelauxetic effect caused by the lowering of interelectronic repulsions through some form of covalency. The nephelauxetic parameter is simply the ratio of a gas phase parameter to the value of the same parameter in a complex. In this case it is the ratio of B for the free and complexed nickel ion.

Discussion

The Dq values for the methanol and ethanol complexes are very close to that for water. For purposes of comparison these values and those for some common solvents are[2,3]: NH_3 (1060); H_2O (860); $HC(O)N(CH_3)_2$ (850); CH_3OH (843); C_2H_5OH (818); $(CH_3)_2SO$ (773); $CH_3C(O)N(CH_3)_2$ (769).

It is interesting that the spectrochemical order $H_2O > CH_3OH > C_2H_5OH$ parallels the magnitude of the O–H infrared frequency shift of the solvent on complexation ($\Delta\nu_{O-H}$ of Table I). The spectrochemical order does not parallel the inductive order of the substituent, $C_2H_5 > CH_3 > H$, nor does it parallel the dipole moments of these three molecules (H_2O = 1.82, CH_3OH = 1.71, C_2H_5OH = 1.73).

The positions of water and methanol in the nephelauxetic series are very close (H_2O, β = 0.89; CH_3OH, β = 0.88) while a slightly lower value, β = 0.86, is found for ethanol.

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Preparation and Properties of Dichlorobis(1-octene)platinum(II)

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Complexes of platinum in which more than one monoolefin is bound to the same metal atom have been