between the Co, Ni, and Cu atoms on the one hand and Re on the other. Treating the M–O–S group as a linear system without an interaction constant and taking k_{MO} to be as high as 2.0 mdynes/Å., it is found that at most about 18 cm.$^{-1}$ of the greater downshifts found in the Re_3X_9 complexes must be attributed to a pure mass effect. This gives a corrected downshift of ~77 cm.$^{-1}$ to be compared with the ranges of 40–73 cm.$^{-1}$ for the Co(II), Ni(II), and Cu(II) complexes. The downshift of the PO frequency in $Re_3Cl_9[(C_6H_5)_3PO]_3$, 68 cm.$^{-1}$, when lessened by 14 cm.$^{-1}$ to allow for metal atom mass differences, becomes 54 cm.$^{-1}$, which may be compared with downshifts[22] of 40–61 cm.$^{-1}$ for $(C_6H_5)_3PO$ complexes of the ions Co(II), Ni(II), Cu(II), and Zn(II). It therefore appears that ligands of the sulfoxide and phosphine oxide types are held at least as strongly by the Re_3X_9 groups as by the divalent metal ions toward the end of the first transition series.

In $[Re_3Cl_{12}]^{3-}$ and $Re_3Cl_9[(C_2H_5)_2(C_6H_5)P]_3$, it has been found that the bonds from the rhenium atoms to the three nonbridging in-plane chlorine atoms and to the phosphorus atoms were longer, by ~0.13 and ~0.3 Å., respectively, than the "normal" single bond distances.[6] It was suggested that steric effects were at least partly responsible for this, perhaps abetted by an inherently low ability of the centrifugally directed orbitals of rhenium to form bonds. For the O-bonded sulfoxides and the phosphine oxide, the steric effect is small. Therefore, the indication from the large downshifts in the SO and PO stretching frequencies is that there is not in fact any inherent inability of the centrifugally directed orbitals to form bonds with donor atoms and that the unusual lengths of the bonds which have been observed are entirely due to steric factors.

(22) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

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Polarized Spectra of Tetracyano Nickelate Crystals

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Polarized electronic absorption spectra of different crystals containing $Ni(CN)_4^{2-}$ have been obtained. The electronic spectrum consists of a very weak band at 20,000 cm.$^{-1}$, a broad parallel band at 23,000 cm.$^{-1}$, and a band seen both parallel and perpendicular at 27,000 cm.$^{-1}$. With Ba^{2+} as cation an additional band is seen at 22,000 cm.$^{-1}$. In addition, two peaks have been observed at ~5600 and ~7000 cm.$^{-1}$. However, these latter are associated with the vibrational properties of the complex. The ground state of the molecule possesses a square-planar configuration, but in order to interpret the electronic spectrum, it is proposed that the observed transitions terminate on potential surfaces where the stable conformation of the molecule is that of a distorted tetrahedron. This hypothesis is strongly supported by semiquantitative considerations.

Introduction

The electronic structure of the square-planar nickel(II) cyanide complex has been considered by many authors.[1–4] In order to try to settle some of the outstanding questions we have studied the absorption spectra of various crystals containing the $Ni(CN)_4^{2-}$ unit.

Experimental

We have in this investigation examined the following crystals: $K_2Ni(CN)_4 \cdot H_2O$, $Na_2Ni(CN)_4 \cdot 3H_2O$, $CaNi(CN)_4 \cdot 5H_2O$, $SrNi(CN)_4 \cdot 5H_2O$, and $BaNi(CN)_4 \cdot 4H_2O$.

The crystal spectra were obtained using a Cary Model 14 spectrophotometer. Two methods were used. The first utilized the Cary in its normal arrangement but with the crystal mounted on the cold finger of a liquid nitrogen cryostat that is constructed so that it fits into the sample compartment of the Cary. The light emergent from the Cary is polarized by a Glan–Thompson polarizer placed immediately before the crystal (a second polarizer is mounted in the reference beam and is rotated in phase with that in the sample beam).

The second method employs a reflecting microscope mounted in place of the cell compartment (using the infrared optical path) and thus allows spectra of very small crystals to be obtained. A cryostat, similar to that described by Ferguson and Wignall,[5] has been used to cool the crystals to near the temperature of liquid nitrogen.

Spectra have been taken in the extinction directions parallel and perpendicular to the *c* axis of the crystals.

The Crystal Spectra

The crystal structures of the complexes have been reported by Brasseur and de Rassenfosse[6–7] and Lambot[8] in the early forties. However, the *R* values calculated from some of their data leave much to be

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(1) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(2) H. B. Gray and C. J. Ballhausen, *ibid.*, **85**, 260 (1963).

(3) M. Bán and E. Horváth, *Acta Phys. et Chem. Szeged*, **5**, 34 (1959).

(4) S. Kida, J. Fujita, K. Nakamoto, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **31**, 79 (1958).

(5) J. Ferguson and T. F. Wignall, *Spectrochim. Acta*, **15**, 1127 (1959).

(6) H. Brasseur and A. de Rassenfosse, *Bull. soc. franc. mineral.*, **61**, 129 (1938).

(7) H. Brasseur and A. de Rassenfosse, *Mem. soc. roy. sci. Liege*, **4**, 397 (1943).

(8) H. Lambot, *Bull. soc. roy. sci. Liege*, **12**, 533 (1943).

desired. In some cases they are so high that the entire structure determination becomes doubtful. In the case[6] of $BaNi(CN)_4 \cdot 4H_2O$, the CN group was treated as one atom in the structure factor calculations and thus precludes any conclusions about the planarity of the complex ion. A sketch of some of the structures is given in Figure 1.

The polarized spectra were measured with the electric vector parallel and perpendicular to the c axis of the crystals, this axis being nearly but not quite perpendicular to the planes of the stacked $Ni(CN)_4^{2-}$ groups. It is thus *nearly* but not quite coincident with the fourfold symmetry axis of the complex ion.

The over-all electronic spectrum for all but the barium salt (Figure 2) is: a very weak band at 20,000 cm.$^{-1}$, a broad parallel band at 23,000 cm.$^{-1}$, and a somewhat sharper band seen both parallel and perpendicular at 27,000 cm.$^{-1}$. In addition the Ba complex exhibits a rather narrow, temperature-dependent, perpendicular band at 22,000 cm.$^{-1}$. Above 30,000 cm.$^{-1}$ the absorption rises steeply and we could not get sufficient light through the crystals to measure the spectra accurately.

Since we are not dealing with a uniaxial crystal, the position of the bands depends upon the exact orientation of the crystals. Figure 3 shows the extreme positions of the "barium band" when the electric vector makes an angle of ~20° with the c axis. This shows that the c axis is not perpendicular to the plane of the molecule. A weak "triplet band" may be seen at ~20,000 cm.$^{-1}$. Most important, it is seen that the band at ~23,000 cm.$^{-1}$ is strongly parallel polarized.

Not shown are two very weak bands, the first located at 5600 cm.$^{-1}$ (three peaks with a separation of ~50 cm.$^{-1}$), the second at 7000 cm.$^{-1}$ (two peaks separated by ~300 cm.$^{-1}$). However, these two bands are *not* electronic transitions. With the O–H stretching frequency in water being ~3500 cm.$^{-1}$ and the C–N stretching frequency in cyanide being 2050 cm.$^{-1}$ we see that the first band is likely to be a combination band ($3500 + 2050 = 5550$) and the second one an overtone of the OH stretching frequency ($2 \times 3500 = 7000$). This prediction is completely substantiated by measurements on deuterated crystals.

Interpretation of the Spectra.—The first question which must be answered is: Are the observed bands "ligand field" bands or must we invoke the empty CN^- π orbitals?

Since the coulomb energy of the d electrons in Ni^{2+} is about −10 e.v. and the energy of the empty antibonding π CN orbitals is ~−5 e.v. we see that the energy difference is ~5 e.v. = 40,000 cm.$^{-1}$. We may thus conclude that the bands below 30,000 cm.$^{-1}$ certainly are "ligand field" bands.[2] With a molar extinction of 50–100 we may further conclude that they are spin-allowed transitions.

In order to make assignments, we now notice that the "first" band at 23,000 cm.$^{-1}$ (disregarding for the moment the barium salt) is seen only parallel. If the complex has a regular square-planar configuration in

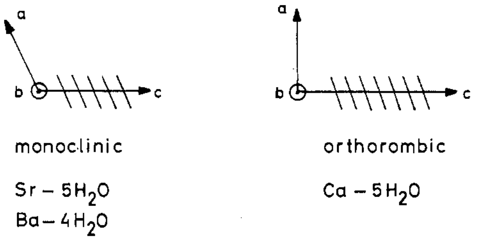

Figure 1.—Stylized crystal structures of $BaNi(CN)_4 \cdot 4H_2O$, $SrNi(CN)_4 \cdot 5H_2O$, and $CaNi(CN)_4 \cdot 5H_2O$. The $Ni(CN)_4^{2-}$ planes are seen edge on.

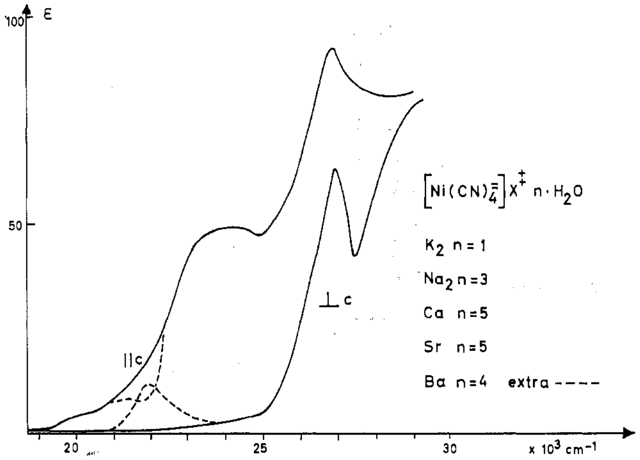

Figure 2.—Crystal spectrum of the nickel cyanide crystals. ε is the molar extinction coefficient.

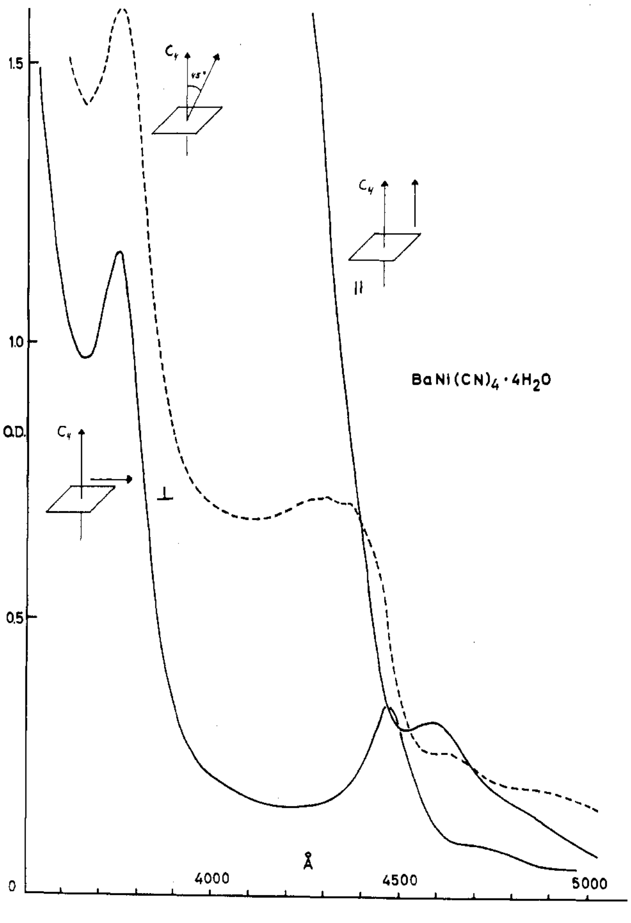

Figure 3.—Crystal spectrum of $BaNi(CN)_4 \cdot 4H_2O$.

both the ground and excited states, we would have to invoke a "vibronic" intensity-giving mechanism. The $Ni(CN)_4^{2-}$ unit has sixteen different normal vibrations: $2\alpha_{1g}$, α_{2g}, $2\beta_{1g}$, $2\beta_{2g}$, ϵ_g, $2\alpha_{2u}$, $2\beta_{1u}$, $4\epsilon_u$. The electronic ground state of the complex is, in all proposed level schemes, $^1A_{1g}$. A closer analysis then shows that, with a "vibronic" mechanism, some transitions are forbidden parallel but all possible bands should be seen perpendicular. However, the band at 23,000 cm.$^{-1}$ is seen parallel but not perpendicular.

The absence of this band in the perpendicular polarization indicates that the D_{4h} vibronic selection rules may not be appropriate. In the following paragraphs it will be shown that a reasonable explanation of the properties of the 23,000 cm.$^{-1}$ band emerges if we assume that the transition terminates on a state having a D_{2d} equilibrium geometry. This choice of geometry is suggested by the fact that the tetrahedral molecule $Ni(CO)_4$ possesses two more electrons than $Ni(CN)_4^{2-}$, the extra electrons being located in the antibonding (*xy*) orbital. Evidently the occupancy of this orbital is responsible for the stereochemistry of the system. It is therefore reasonable to suppose that a change in the equilibrium configuration of the complex ion $Ni(CN)_4^{2-}$ occurs by the excitation of an electron to the empty (*xy*) orbital (Figure 4).

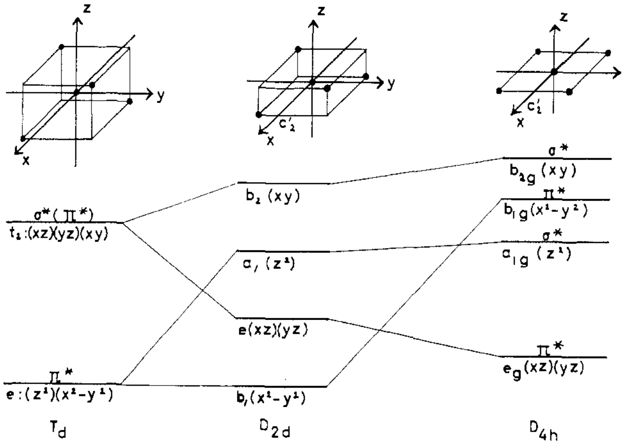

Figure 4.—Correlation of the antibonding molecular orbitals in T_d and D_{4h}.

Substituting one CN^- with one NO^- we get two electrons more into the system. Experimentally it is found that $[Ni(NO)(CN)_3]^{2-}$ is a permanganate-colored ion, presumably having a tetrahedral configuration.[9] It should indeed also be possible by careful oxidation to make $[Ni(NO)(CN)_3]^-$ and $[Ni(NO)(CN)_3]$ with presumably D_{2d} and D_{4h} structures.

The balancing forces which determine whether we shall have a paramagnetic, tetrahedral structure or a square-planar, diamagnetic structure for a Ni^{2+} complex are delicate. In Figure 5 we have tried *quantitatively* to indicate the correlation diagram between the orbitals in T_d and D_{4h}.

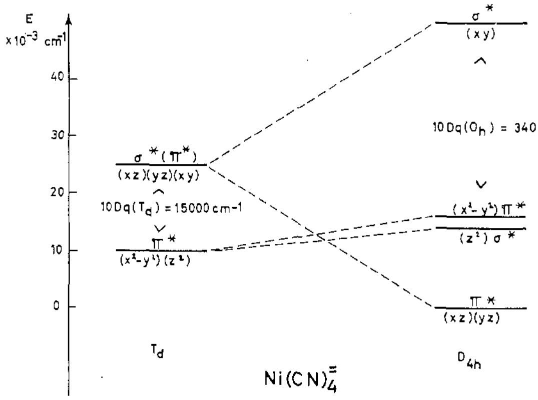

Figure 5.—Quantitative correlation diagram of orbitals in T_d and D_{4h}.

For a hypothetical $Ni(CN)_6^{4-}$ the separation $(xy)\sigma^*$ and $(x^2 - y^2)\pi^*$ is equal to $10Dq$ (octahedron). Removing the axial cyanides to get the square-planar configuration is not expected to influence the orbitals (*xy*) and $(x^2 - y^2)$ much. Therefore their separation must be approximately $10Dq$ in D_{4h}. A reasonable order of magnitude for the separation is about 34,000 cm.$^{-1}$, since this is the value[10] of $10Dq$ in $Fe(CN)_6^{4-}$. The tetrahedral splitting is then taken as four-ninths of this value, or $10Dq$ (tetrahedron) = 15,000 cm.$^{-1}$. Explicit calculations[2] using an sp hybrid for the σ ligand orbital and a $p_z\pi$ carbon orbital show that the group overlap integrals $G(x^2 - y^2, \pi)$ and $G(z^2, \sigma)$ are nearly identical in $Ni(CN)_4^{2-}$ assuming a square-planar configuration. We have therefore taken these two orbitals to be approximately degenerate. From Table I we can see that the group overlap properties indicate that $(x^2 - y^2)\pi^*$ in T_d is placed in between $(x^2 - y^2)\pi^*$ D_{4h} and (*xz*), $(yz)\pi^*$ in D_{4h}. Rough calculations then indicate that $(x^2 - y^2)^*$ D_{4h} is placed about 5000 cm.$^{-1}$ above $(x^2 - y^2)^*$ T_d and that we have a separation of 15,000 cm.$^{-1}$ between $(x^2 - y^2)^*$ and $(xz)^*(yz)^*$ in D_{4h}.

Table I

Group Overlap Integrals *G* in T_d and D_{4h}

D_{4h}	$G(a_{1g}d,p\sigma)$	$= S(d\sigma,p\sigma)$
	$G(b_{2g}d,p\sigma)$	$= \sqrt{3}S(d\sigma,p\sigma)$
	$G(b_{1g}d,p\pi)$	$= 2S(d\pi,p\pi)$
	$G(e_gd,p\pi)$	$= \sqrt{2}S(d\pi,p\pi)$
T_d	$G(t_2d,p\sigma)$	$= -(2\sqrt{3}/3)S(d\sigma,p\sigma)$
	$G(t_2d,p\pi)$	$= (2\sqrt{2}/3)S(d\pi,p\pi)$
	$G(ed,p\pi)$	$= (2\sqrt{6}/3)S(d\pi,p\pi)$

Comparing the electronic ground states $^3T_{1g}$ in T_d with $^1A_{1g}$ in D_{4h} we find that due to the exchange interactions between the d electrons the $^3T_{1g}$ (T_d) is $9F_2 + 60F_4$ more stable than $^1A_{1g}$ (D_{4h}). Assuming[10] $F_2 \approx 10F_4 = 1000$ cm.$^{-1}$ this is some 15,000 cm.$^{-1}$. However, each of the eight electrons in D_{4h} has a single electronic energy *less* than those in T_d and consequently a D_{4h} structure can be expected to be stable after all.

The transformation properties of the orbitals in D_{4h} are (*xz*) (*yz*): e_g, (z^2): a_{1g}, $(x^2 - y^2)$: b_{1g}, and (*xy*): b_{2g}. The ground state is thus $(e_g)^4(a_{1g})^2(b_{1g})^2$, $^1A_{1g}$. Now we

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(9) C. C. Addison and J. Lewis, *Quart. Rev.* (London), **9**, 149 (1955).

(10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co, New York, N. Y., 1962, p. 253.

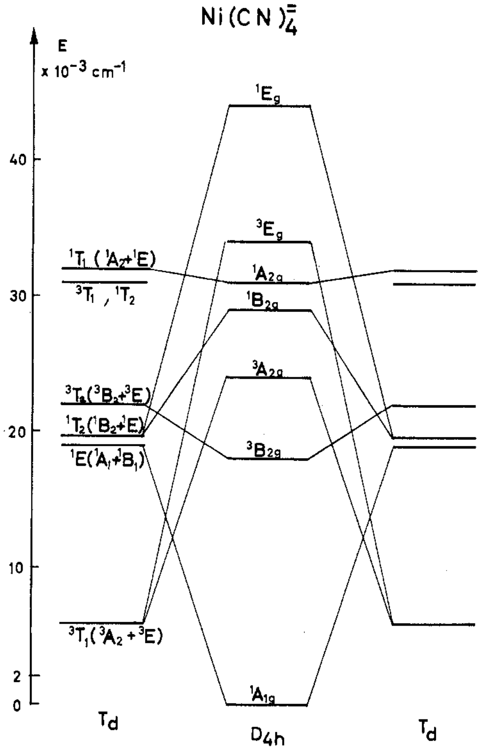

Figure 6.—Energy level diagram for $Ni(CN)_4^{2-}$ in D_{4h} and T_d. The diagram does not imply anything about the amount of distortion, and the connecting lines between the D_{4h} and T_d configurations are only drawn as straight lines for convenience.

would expect that exciting an electron to $(xy)\sigma^*$ would *unbalance* the square-planar configuration and make the structure move toward a tetrahedral structure. The low-lying excited states will be

$$(e_g)^4(a_{1g})^2(b_{1g})(b_{2g}) \qquad {}^{1,3}A_{2g};\ {}^{1,3}A_2$$
$$(e_g)^4(a_{1g})(b_{1g})^2(b_{2g}) \qquad {}^{1,3}B_{2g};\ {}^{1,3}B_2$$
$$(e_g)^3(a_{1g})^2(b_{1g})^2(b_{2g}) \qquad {}^{1,3}E_g;\ {}^{1,3}E$$

in D_{4h} and D_{2d} symmetry, respectively.

In making the band assignments we now make use of the Franck–Condon principle. The transitions start out from a potential surface, which in its equilibrium is characterized by the symmetry D_{4h}. However, we assume that the electronic structure of the excited states does not have a D_{4h} stable configuration, but a D_{2d} structure. The vertical transition from the ground state terminates in a highly excited vibrational state of the D_{2d} surface and under suitable conditions one should see progressions in the distorting vibrations. However, within the Born–Oppenheimer approximation the excited electronic states must be characterized in D_{2d} symmetry, and the symmetry elements which are relevant in the discussion of the electronic transition[11] are those common to D_{4h} and D_{2d}.

A transition of, *e.g.*, $^1A_{1g}$ (D_{4h}) to $^1B_{2g}$ (D_{4h}) is allowed vibronically, both parallel and perpendicular. However, if the equilibrium configuration of the excited state is D_{2d} it is orbitally allowed only in parallel polarization. Experimentally the difference would be that in the first case we would see in the vibrational structure a false origin followed by progressions of the totally symmetric α_{1g} vibrations, but in the second case there would be no false origin and we would see progressions in the β_{1u} vibrations.

The energies of the excited states assuming D_{4h} symmetry are given in Table III of ref. 2. Assuming $(x^2 - y^2)^*$ and $(z^2)^*$ degenerate, and that $\Delta_1 = 34{,}000$ cm.$^{-1}$, $\Delta_2 = 0$ with $\Delta_3 = 15{,}000$ cm.$^{-1}$, we get, taking $F_2 = 10F_4 = 1000$ cm.$^{-1}$, a level diagram as in Figure 6. On both sides are pictured the states as they should be in T_d with[12] $10Dq = 15{,}000$ cm.$^{-1}$. Arbitrarily we have placed the $^1A_{1g}$ in D_{4h} some 6000 cm.$^{-1}$ below $^3T_1$ in T_d. This last number is, however, not critical.

A comparison with the states in T_d then shows that identifying the observed parallel transition at 23,000 cm.$^{-1}$ with $^1A_{1g} \rightarrow {}^1B_2$ we get the ordering of the states as shown in Figure 6. $^1A_{2g}$ is seen to be stable in a square-planar configuration and the transition $^1A_{1g} \rightarrow {}^1A_{2g}$ is expected to occur at 30,500 cm.$^{-1}$. However, it is probably covered by the charge-transfer bands.

The intense allowed $^1A_{1g} \rightarrow {}^1B_2$ transition is rather broad since several quanta of the β_{1u} are excited. This is the vibration which takes $D_{4h} \rightarrow T_d$; in D_{2d} it transforms as α_1.

From the level diagram given in Figure 6 we see that ^1E_g is expected to have a very distorted equilibrium configuration. The transition $^1A_{1g} \rightarrow {}^1E$ is perpendicularly allowed in D_{2d}. The doubly degenerate E state is further expected to undergo a distortion of the Jahn–Teller type. A transition from the ground state to the split components of ^1E may then be observed both parallel and perpendicular. It is thus possible that the sharp peak at 26,000 cm.$^{-1}$ is a vibrational level of ^1E.

The weak absorptions, found at $\sim$20,000 cm.$^{-1}$, have previously[1] been assigned as spin-forbidden transitions. A glance at Figure 6 shows that this idea is compatible with our level scheme, but that our assignments must differ from those given in ref. 1. However, the available data do not permit a closer analysis.

The Barium Nickel Cyanide Band.—For the crystal $BaNi(CN)_4 \cdot 4H_2O$ the "specific" band at 22,000 cm.$^{-1}$ appears sharp perpendicular, and as a weak shoulder parallel. It does not show up axially. In $BaNi(CN)_4 \cdot 4D_2O$ it is very sharp parallel (a half-width of 800 cm.$^{-1}$) and perpendicular it is seen at almost the same position and with almost the same intensity as in parallel, but with a shoulder toward the red. No trace of it is observed axially.

No satisfactory explanation of these experimental facts has so far been proposed. Two possibilities seem worthwhile persuing: (1) It is a spin-forbidden band blown up in intensity due to the presence of the heavy barium nucleus. However, the band has never been seen in aqueous solution, regardless of which heavy cations were present, nor is there any trace of it in the $SrNi(CN)_4 \cdot 5H_2O$ crystal spectrum. (2) It is not a band associated with a *single* nickel cyanide chromophore, but arises from some property of the crystal lattice. The fact that the deuterated crystals behave

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(11) C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2708 (1953).

(12) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

differently from the nondeuterated crystals seems to point in this direction.

Even though we do not claim to know all the answers to the electronic structures of Ni(CN)$_4^{2-}$ we do think that the basic idea, namely a change in geometry for some of the excited states, is correct. Measurements at liquid helium temperature are planned and should be of great help in order to settle the outstanding questions.

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CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
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The Hydrolysis of Thorium(IV) at 0 and 95°[1]

BY C. F. BAES, JR., NORMAN J. MEYER,[2] AND C. E. ROBERTS

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The hydrolysis of thorium(IV) in 1 *m* (Na)ClO$_4$ was measured at 0 and 95° to establish better the reactions which occur and their temperature coefficients. Potentiometric measurements were made primarily with the quinhydrone electrode at 0° and with the glass electrode at 95°. Measurements of the solubility of ThO$_2$ as a function of acidity together with the potentiometric results at low hydrolysis were consistent with formation of ThOH^{3+}, Th(OH)$_2^{2+}$, and Th$_2$(OH)$_2^{6+}$, initial hydrolysis products proposed at 25° by previous investigators. Their results along with the present measurements were compared with numerous possible schemes of hydrolysis products, Th$_x$(OH)$_y^{(4x-y)+}$, by means of a general least-squares computer program. Two schemes of four species—(I) x,y: 1,1; 1,2; 2,2; 5,12 and (II) x,y: 1,1; 1,2; 2,3; 6,15—approximate the data, but yield systematic deviations which are similar at all three temperatures. Two schemes of five species—(III) x,y: 1,1; 1,2; 2,2; 3,6; 6,15 and (IV) x,y: 1,1; 1,2; 2,2; 4,8; 6,15—fit the data within the expected experimental error, scheme IV being the better. The assumption of six or more hydrolysis products is not justified by the accuracy of the measurements. The equilibrium quotients found for the formation of the five species in scheme IV from Th^{4+} and H$_2$O were: log $Q_{x,y}$ = (0°) −4.32, −8.48, −5.60, −22.79, and −43.84; (25°) −4.12, −7.81, −4.61, −19.01, and −36.76; (95°) −2.29, −4.50, −2.55, −10.49, and −20.63. The indicated average enthalpy and entropy changes per OH$^-$ bound in the polymeric species were nearly constant at ~7.3 kcal. and ~13.6 cal./°K., respectively.

Thorium(IV) ion, when compared to other tetravalent cations, is unusually resistant to hydrolysis at 25°. At moderate concentrations, its hydrolysis is first detectable at a pH below 3. The hydroxyl number, $\bar{n}$ (*i.e.*, the average number of OH$^-$ ions bound per Th^{4+} ion present) rises rapidly with pH until hydrolytic precipitation occurs at $\bar{n} \sim 2.5$ and pH ~4. Thorium hydrolysis thus is accessible to study over a fairly wide range in $\bar{n}$ and over a convenient range in pH.

The hydrolytic behavior of Th^{4+} has been widely investigated at room temperature.[3] Potentiometric studies of Kraus and Holmberg,[4] Hietanen,[5] and Hietanen and Sillén[6] are perhaps the most extensive. At present, however, no generally accepted scheme of hydrolysis products has appeared to account for the observed behavior of this ion. The previous potentiometric studies have made it clear that highly polymerized hydrolysis products Th$_x$(OH)$_y^{(4x-y)+}$ are involved, and this is also shown by the preliminary ultracentrifuge results of Johnson and Kraus,[7] as well as by cryoscopic measurements of Souchay.[8]

From their results in 1 *M* NaClO$_4$ at 25°, Kraus and Holmberg[4] concluded that Th(OH)$_2^{2+}$ and Th$_2$(OH)$_2^{6+}$ definitely were formed. The species ThOH^{3+} was found to be surprisingly unstable compared to UOH^{3+} and PuOH^{3+}. While additional, more polymeric hydrolysis products were evident, Kraus and Holmberg felt that insufficient data were available to establish them reliably.

Hietanen[5] chose to interpret her results in terms of the following "core-link" mechanism of continuous polymerization

$$\mathrm{Th_2(OH)_3}^{5+},\ \mathrm{Th_3(OH)_6}^{6+},\ \mathrm{Th_4(OH)_9}^{7+}\ \ldots\ldots\ \mathrm{Th}_x(\mathrm{OH})_{3x-3}{}^{(n+3)+}$$

This scheme, however, fails to account properly for the careful measurements of Kraus and Holmberg at low $\bar{n}$ values.

Lefebvre[9] later re-examined these two sets of data and concluded that the following simpler scheme described the hydrolysis process

$$\mathrm{Th(OH)_2}^{2+},\ \mathrm{Th_2(OH)_2}^{6+},\ \mathrm{Th_5(OH)_{12}}^{8+}$$

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] Summer research participant with the Oak Ridge National Laboratory, 1961–1962, sponsored by the Oak Ridge Institute of Nuclear Studies.

[3] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants; Part II, Inorganic Ligands," The Chemical Society, London, 1958, p. 6.

[4] K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[5] S. Hietanen, *Acta Chem. Scand.*, **8**, 1626 (1954).

[6] S. Hietanen and L. G. Sillén, *ibid.*, **13**, 533 (1959).

[7] Described in ref. 4, pp. 329, 330.

[8] P. Souchay, *Bull. soc. chim. France*, **15**, 227 (1958).

[9] J. Lefebvre, *J. chim. phys.*, **55**, 227 (1958).