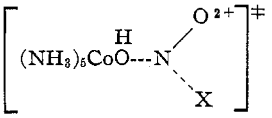
the range of thermodynamic discrimination, covers four orders of magnitude. This is in contrast with the reactivity patterns for the reactions of HONO where the rate constants for the formation of XNO are practically independent of the nature of X^-. In the case of HNO_2 it was concluded that no N–X bond making obtains in the transition state. Therefore, in the case of $Co(NH_3)_5ONO^{2+}$, there must be some N–X bond making in the transition state. A "quantitative" measure of the amount of bond breaking and bond making that obtains in the transition state



can be estimated from the log *k vs.* log *Q* plot presented in Figure 1. Assuming a linear free energy relationship, we obtain a slope of ~0.5, a value which suggests approximately "equal" contributions of bond making and bond breaking in the transition state for the reaction.

Finally, it is noteworthy that the catalysis of aquation of $Co(NH_3)_5ONO^{2+}$ by halides and thiocyanate ions, when combined with microscopic reversibility considerations, indicates that, provided the equilibrium is favorable, O-nitrosation on $Co(NH_3)_5OH^{2+}$ would be accomplished by XNO. Thus, the range of reagents involved in nitrosation in inorganic chemistry has been extended from the early studies with N_2O_3[3,5] to the more recent studies implicating NO^+[6–9] and to the present studies which show the importance of reaction paths involving nitrosyl halides and nitrosyl thiocyanate. We are planning to extend the studies of the effects of halides and pseudohalides to other metal complexes containing coordinated nitrite and coordinated nitrosyl.

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The Single-Crystal Electronic Spectrum of Bromotetrakis(2-methylimidazole)nickel(II) Bromide and an Interpretation of the Energy Levels of Some Tetragonally Distorted Nickel Complexes Using the Angular Overlap Model

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The single-crystal polarized electronic spectrum of the five-coordinate complex bromotetrakis(2-methylimidazole)nickel(II) bromide is reported. A general method for the analysis of the excited-state energies observed in the "d–d" electronic spectra of nickel halide complexes with D_{4h} or C_{4v} symmetry is described and used to derive the angular overlap σ- and π-bonding parameters of the ligands in several nickel halide complexes of known crystal structure.

Introduction

There has been considerable interest recently both in the electronic spectra of five-coordinate nickel complexes[1] and in the interpretation of the energy levels of tetragonally distorted compounds using ligand-field bonding parameters.[2] The single-crystal spectrum of bromotetrakis(2-methylimidazole)nickel(II) bromide, [Ni(2-meim)$_4$Br]Br, is therefore interesting both because it is a representative example of the spectrum of a square-pyramidal nickel complex and because it allows the ligand σ- and π-bonding parameters of a five-coordinate complex to be compared with those of similar six-coordinate compounds.

Single-Crystal Spectrum of [Ni(2-meim)$_4$Br]Br

The complex crystallizes in the tetragonal space group *P*4*nc*, $Z = 2$, with the faces (010), (100), etc. well developed. Although the refinement of the structure is not yet complete ($R \approx 9\%$) and the bond lengths are only approximate, the overall molecular geometry is quite clear.[3] The nickel ion is bonded to four imidazole nitrogen atoms, with a fifth bond to a bromide ion (Ni–Br ≈ 2.53 Å) and each NNiBr angle ~99°. The second bromide is trans to the first, but at the much longer distance of ~3.6 Å. The nickel ion is thus effectively five-coordinate and the molecular symmetry is C_{4v}. Each Ni–Br bond lies along the *c* crystal axis. The electronic spectra of three crystals were measured at room temperature with the electric vector parallel (||) and perpendicular (⊥) to the *c* axis (which is also the molecular *z* axis) using a microspectrophotometer[4] and a Glan–Thomson polarizing prism. A typical spectrum is shown in Figure 1A. The extinction coefficients of the bands were obtained by measuring the crystal thicknesses using a microscope with a graduated eyepiece.

Low-Temperature Mull Spectra of [Ni(2-meim)$_4$Br]Br and [Ni(2-meim)$_4$Cl]Cl.—As low-temperature spectra could not be obtained using the microspectrophotometer, the spectra of [Ni(2-meim)$_4$Br]Br and [Ni(2-meim)$_4$Cl]Cl, which is isomorphous with the bromide complex,[3] were measured as Nujol mulls at ~80°K (Figure 1B) using a Unicam SP 700 spectrophotometer.

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(1) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968), and references therein.

(2) A. B. P. Lever, *ibid.*, **3**, 119 (1968).

(3) D. M. L. Goodgame and A. Skapski, private communication.

(4) The microspectrophotometer and its method of use are described by P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

TABLE I

THE CALCULATED AND OBSERVED EXCITED-STATE TRANSITION ENERGIES OF SOME NICKEL COMPLEXES WITH D_{4h} OR C_{4v} SYMMETRY[a]

	Transition energies, kK													
Excited state[b]	$[Ni(2\text{-meim})_4Br]Br$ Obsd[c]	$[Ni(2\text{-meim})_4Br]Br$ Calcd	$[Ni(2\text{-meim})_4Cl]Cl$ Obsd	$[Ni(2\text{-meim})_4Cl]Cl$ Calcd	$Ni(py)_4Br_2$ Obsd[d]	$Ni(py)_4Br_2$ Calcd	$Ni(py)_4Cl_2$ Obsd[d]	$Ni(py)_4Cl_2$ Calcd	$Ni(pyr)_4Br_2$ Obsd[e]	$Ni(pyr)_4Br_2$ Calcd	$Ni(pyr)_4Cl_2$ Obsd[e]	$Ni(pyr)_4Cl_2$ Calcd	$Ni(tu)_4Cl_2$ Obsd[g]	$Ni(tu)_4Cl_2$ Calcd
$^3E(1)$	5.15	5.57	5.50	5.58	8.43	8.43	9.04	9.04	7.24	7.24	8.00	8.00	7.50	7.27
$^1A(1)$		7.27		7.63		10.75		11.57		10.84		12.06		9.72
$^3B_2$	11.60	11.63	11.50	11.52	11.49	11.49	11.73	11.73	10.89	10.90	10.95	10.95	9.30	9.19
$^3A_2(1)$	10.30	10.32	10.55	10.54	14.08	14.08	14.93	14.93	12.00	12.00	13.10	13.10	12.30	12.38
$^1B_1(1)$	12.40	12.27	12.56	12.61	12.26	12.26	12.62	12.62		14.28	~13.5[f]	14.67	10.50	10.50
					12.45[f]		12.80[f]							
$^3E(2)$	15.30	15.19	15.15	15.13	16.39	16.39	16.82	16.81	15.90	15.90	16.40	16.40	13.50	13.67
$^1E(1)$	17.30	17.24	17.60	17.54	21.04[f]	20.25	21.77[f]	21.27		20.86		22.04		17.37
$^1A_2$		18.98		19.49		23.25		24.51		22.43		24.01		20.62
	~21.7[f]		~21.7[f]										~20.0[f]	
$^1B_2(1)$		23.31		23.46		23.32		23.95		24.69		25.14		19.25
$^3A_2(2)$	22.80	22.40	~23.0[f]	23.11		24.90		25.59		25.12		26.13	22.20	22.29
					26.03[f]		26.76[f]		25.80[f]		26.50[f]			
$^3E(3)$	24.80	25.01	~26.0[f]	26.05		25.96		26.47		27.11		27.77	23.30	23.19
$^1A_1(2)$		24.92		25.57		22.06		22.15		26.53		26.44		18.82
$^1E(2)$	27.70	27.89		28.50		27.08		27.46		30.57		31.01		23.13

[a] Abbreviations used are the following: py, pyridine; pyr, pyrazole; tu, thiourea. [b] The symmetry designations are those for the C_{4v} point group; these are converted to symbols appropriate to the D_{4h} point group by the addition of a g subscript. [c] The transition energies below 22 kK were estimated from the low-temperature mull spectrum, while those above 22 kK were obtained from the single-crystal spectrum. [d] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967). [e] C. W. Reimann, *J. Phys. Chem.*, **74**, 561 (1970). [f] As these transitions could not be unambiguously assigned, they were not included in the fitting of the spectral data. [g] M. Gerloch, J. Lewis, and W. R. Snail, *J. Chem. Soc. A*, 2686 (1963).

The band maxima obtained are listed in Table I and are quite similar to the values reported by Goodgame, *et al.*[5] The low-temperature mull spectrum of $[Ni(2\text{-meim})_4Br]Br$ differs from a superimposition of the $\|$ and $\perp$ spectra of the single crystal only in a slight shift to higher energy of most of the bands and in the resolution of the broad peak at ~10 kK into three components.

Band Intensities.—In an octahedral ligand field the three excited spin-triplet states of Ni(II) transform as $^3T_{2g}$, $^3T_{1g}(1)$, and $^3T_{1g}(2)$,[6] and in a C_{4v} ligand field the $^3T_{2g}$ state splits into ^3E and $^3B_2$, while the $^3T_{1g}$ levels go to ^3E and $^3A_2$. The ground state in C_{4v} transforms as $^3B_1$ and the only d–d transitions allowed by an electric dipole mechanism are $^3B_1 \rightarrow {}^3E$ in xy polarization. The only transition forbidden by vibronic selection rules is $^3B_1 \rightarrow {}^3B_2$ in z polarization. Thus, the three transitions $^3B_1 \rightarrow {}^3E$ are expected to be considerably more intense in xy than in z polarization, while the two bands $^3B_1 \rightarrow {}^3A_2$ should appear weakly both in xy and in z polarization and $^3B_1 \rightarrow {}^3B_2$ should appear weakly only in xy polarization. The bands at 4.8 and 15.0 kK are more intense in xy than in z polarization, implying their assignment as $^3B_1 \rightarrow {}^3E(1)$ and $^3E(2)$, respectively. The band at 10.0 kK (which is resolved into three components, one weaker than the other two, in the low-temperature mull spectrum; see Figure 1) is present weakly in xy polarization but absent in z, suggesting that it may contain $^3B_1 \rightarrow {}^3B_2$, and also possibly $^3B_1 \rightarrow {}^3A_2(1)$. The polarization properties of the bands above 15 kK provide no clues as to their probable origin. Assignments based upon the above suggestions were used as initial guesses to fit the observed transition energies to a set of ligand bonding parameters by the method described in a following section. It quickly became apparent that this choice was almost certainly correct, as assignments of the bands in any other way produced excited-state energies incompatible with the observed spectrum as well as chemically unacceptable ligand bonding parameters. Also, a reasonable fit to the observed transition energies could only be obtained if each of the other bands was assigned in a unique manner. The final band assignments are given in Table I. The sharp, weak bands at 4.22, 6.05, 6.95, and 8.18 kK in the mull spectra of both the chloride and bromide complex are too low in energy to be due to spin-forbidden transitions and are assigned as overtones of ligand infrared transitions.

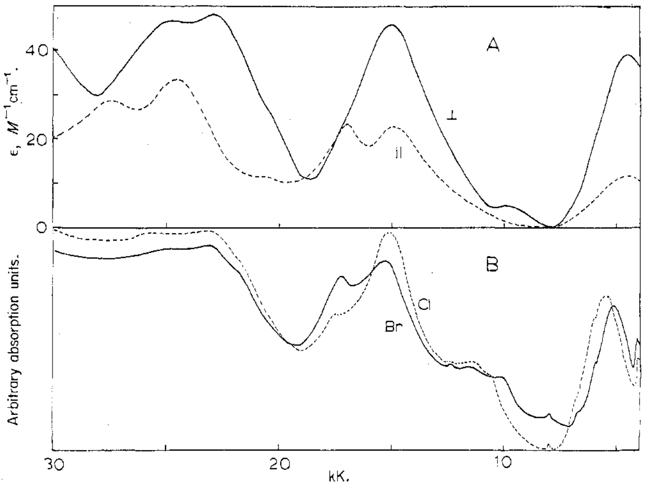

Figure 1.—(A) The spectrum of a single crystal of $[Ni(2\text{-meim})_4Br]Br$ at 293°K with the electric vector parallel ($\|$) and perpendicular ($\perp$) to the molecular z axis. (B) The mull spectra at 80°K of $[Ni(2\text{-meim})_4Br]Br$ (unbroken line) and $[Ni(2\text{-meim})_4Cl]Cl$ (broken line).

As the transitions $^3B_1 \rightarrow {}^3E$ in xy polarization are formally allowed in C_{4v} symmetry they are expected to have a greater intensity than the corresponding transitions in analogous centrosymmetric complexes. The electronic spectrum of a single crystal of $Ni(pyr)_4Br_2$

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(5) D. M. L. Goodgame, M. Goodgame, and G. W. Rayner Canham, *Inorg. Chim. Acta*, **3**, 399 (1969).

(6) The numbers in parentheses indicate the order of increasing energy of the states. The Russell–Saunders term origins are not indicated, as the states coming from the two $^3T_1$ levels of an octahedral nickel complex generally have an approximately equal admixture of ^3P and ^3F wave functions.

(pyr = pyrazole) has been measured by Reimann.[7] This complex approximates closely to D_{4h} symmetry[8] and has molar extinction coefficients of $\epsilon \sim 3$ for each spin-allowed band between 6 and 20 kK and $\epsilon \sim 16$ for the band at ~26 kK. Similar band intensities were observed[9] for a chloroform–pyridine solution of $Ni(py)_4Br_2$ (py = pyridine), which also has approximate D_{4h} symmetry in the solid state.[10] As expected, the transitions to the three ^3E levels in $[Ni(2\text{-meim})_4Br]Br$ are considerably more intense ($\epsilon \sim 40$–50) than the corresponding bands in the two centrosymmetric complexes, while the vibronically allowed transitions $^3B_1 \rightarrow {}^3B_2$ and $^3A_2(1)$ in the xy spectrum of $[Ni(2\text{-meim})_4]Br$ are similar in intensity to these bands in the pyrazole and pyridine complexes. However, the transition $^3B_1 \rightarrow {}^3A_2(2)$ at 22.8 kK in $[Ni(2\text{-meim})_4Br]Br$ is considerably more intense than might be expected for a vibronically allowed transition, being apparently about equal in intensity to the statically allowed $^3B_1 \rightarrow {}^3E$ transitions. The vibronically allowed transitions $^3B_1 \rightarrow {}^3E(1)$ and $^3E(2)$ in z polarization are also significantly more intense than the corresponding bands in the centrosymmetric complexes. The high intensities of the spin-forbidden transitions $^3B_1 \rightarrow {}^1E(1)$ and $^1E(2)$ at 17.0 and 27.7 kK in z polarization are also most surprising, being in fact comparable to those of the spin-allowed $^3B_1 \rightarrow {}^3E$ transitions. The intensity of the spin-forbidden bands cannot be borrowed from neighboring spin-allowed bands *via* spin–orbit coupling in the generally accepted way, as the polarization properties of the spin-forbidden bands should then mirror those of the spin-allowed ones, which is not the case. Moreover, the intensities seem to be too large to be explained in this manner. Conceivably, the high spin–orbit coupling constant of the bromide ion may be contributing to the breakdown of the normal spin-selection rules. This hypothesis gains some support from the fact that the $^3B_1 \rightarrow {}^1E(1)$ transition in the chloride complex seems to be considerably weaker than that in the bromide compound (Figure 1B; the spin–orbit coupling constant of the bromide ion is about 4 times that of the chloride ion).

It thus appears that the selection rules are not obeyed in a straightforward manner in $[Ni(2\text{-meim})_4Br]Br$, implying that caution must be exercised in utilizing relative band intensities to assign transitions in complexes of this kind.

Interpretation of the Energy Levels Using an Angular Overlap Model

There has been much discussion on the best way to parametrize the d-orbital splittings in metal complexes with tetragonal symmetry.[2] Ballhausen and coworkers pioneered the interpretation of tetragonal distortions using the radial integrals Dq, Ds, and Dt of the electrostatic crystal-field theory.[11] The electronic spectral transition energies of many complexes have been interpreted using these parameters, but most workers have preferred to convert Ds and Dt into the perhaps chemically more meaningful semiempirical molecular orbital parameters $\delta\sigma$ and $\delta\pi$ introduced by Yamatera[12] and McClure[13] ($\delta\sigma$ and $\delta\pi$ represent the difference in σ- and π-antibonding effects between the axial and in-plane ligands of a tetragonal complex). Recently Schäffer and Jørgensen introduced the angular overlap model (AOM) as a means of rationalizing the energies of the d orbitals in metal complexes.[14–16] This uses the Wolfsberg–Helmholz approximation[17] to estimate the energy e by which a metal orbital is raised upon interaction with a ligand orbital as

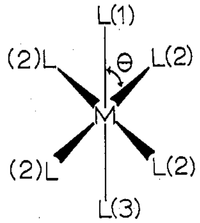

Figure 2.—Schematic diagram of a complex with C_{4v} symmetry.

$$e_\sigma = KS_\sigma^2, \quad e_\pi = KS_\pi^2 \tag{1a}$$

where

$$K \approx H_L^2/(H_M - H_L) \tag{1b}$$

Here H_L and H_M are the diagonal matrix elements of the ligand and metal orbitals, S is the diatomic overlap integral, and the σ and π subscripts designate the symmetry about the metal–ligand bond. The total energy of each d orbital in a complex is then obtained by summing the effects of all the ligands using the angular overlap matrix derived from the geometry of the molecule.[16] The AOM or closely related models have successfully been used to interpret the electronic spectra[18,19] and g values[20] of a variety of copper complexes. If the metal–ligand orbital overlaps can be estimated, the AOM has the following two advantages over the simpler Yamatera–McClure approach. (1) When the ligand orbitals are degenerate in the absence of metal–ligand bonding, as is the case with a halide ion, then the energy of interaction with ligand orbitals of σ and π symmetry can be expressed in terms of only one parameter (K in eq 1). In practice, this means that the *absolute* values of the σ- and π-bonding parameters of the ligands in a tetragonal complex can be estimated, rather than merely their *relative* values. (2) The σ- and π-donor powers of ligands are obtained in a form which is essentially independent of the metal–ligand distance. Thus if e_σ and e_π are obtained at one bond length, eq 1a allows them to be calculated at any other bond length, provided that the variation of S_σ and S_π with distance is known.

A schematic diagram of a complex with C_{4v} symmetry is shown in Figure 2. In this, the numbers in

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[7] C. W. Reimann, *J. Phys. Chem.*, **74**, 561 (1970).

[8] A. D. Mighell, C. W. Reimann, and A. Santoro, *Acta Crystallogr., Sect. B*, **25**, 595 (1969).

[9] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

[10] A. S. Antsishk and M. A. Porai-Koshits, *Kristallografiya*, **3**, 676 (1958).

[11] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 5; C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 790 (1964).

[12] H. Yamatera, *Bull. Chem. Soc. Jap.*, **31**, 95 (1958).

[13] D. S. McClure, "Advances in the Chemistry of Co-ordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.

[14] C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).

[15] C. E. Schäffer and C. K. Jørgensen, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **34**, 2 (1965).

[16] C. E. Schäffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968).

[17] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[18] P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

[19] D. Smith, *J. Chem. Soc. A*, 1209 (1971), and references therein.

[20] K. Dawson, M. A. Hitchman, J. F. C. Rossotti, and K. Prout, *J. Chem. Soc. A*, in press.

parentheses indicate different ligands (different either in nature or in bond length). The method of obtaining the energies of the d orbitals by summing the effects of the ligands in a complex using the angular overlap matrix has been given by Schäffer.[16] Assuming that the π-bonding effect of each ligand is isotropic about the M–L bond (which is true where L is a halide ion but not necessarily so where it is a ligand such as imidazole) the energies E of the d orbitals are given by

$$E(x^2 - y^2) = 0.75(1 - \cos 2\theta)^2 e_\sigma(2) + \sin^2 2\theta e_\pi(2) \qquad (2a)$$

$$E(z^2) = e_\sigma(1) + e_\sigma(3) + 4\{(0.25 + 0.75 \cos 2\theta)^2 e_\sigma(2) + 0.75 \sin^2 2\theta e_\pi(2)\} \qquad (2b)$$

$$E(xy) = 4 \sin^2 \theta e_\pi(2) \qquad (2c)$$

$$E(xz) = E(yz) = e_\pi(1) + e_\pi(3) + 2\{(\cos^2 \theta + \cos^2 2\theta) e_\pi(2) + 0.75 \sin^2 2\theta e_\sigma(2)\} \qquad (2d)$$

Here $e_j(i)$ represents the energy (relative to the free ion) by which the d orbital is raised upon interaction with the orbital of symmetry j belonging to ligand i. If $\theta = 90°$ and L(1) = L(3) the expressions reduce to those[14] of a tetragonal complex of D_{4h} symmetry.

The matrix elements of the excited states of a tetragonally distorted nickel complex are given in Table II. These matrix elements are readily calculated from the wave functions listed by Golding[21] and the electrostatic matrix elements given by Griffith.[22] When used in conjunction with eq 2a–d these matrix elements allow the excited-state energies of a nickel complex of C_{4v} (or D_{4h}) symmetry to be estimated from the ligand bonding parameters, the effective Racah parameters B and C, and the angle θ between the in-plane and axial metal–ligand bond directions.

Method of Deducing Ligand-Field Parameters from the Excited-State Energies.—Within the present model, the excited-state energies of $[Ni(2\text{-meim})_4Br]Br$ depend upon the six parameters e_σ(Br), e_π(Br), e_σ(2-meim), e_π(2-meim), B, and C. Unfortunately, these cannot all be allowed to vary until a best fit to the observed excited-state energies is obtained. This is because only three observables in a C_{4v} complex are related to the ligand–metal interaction, namely, the energy *separations* between the four nonequivalent d orbitals (see Figure 3). However, the AOM fixes the ratio between the σ- and π-bonding parameters of the halide ion as

$$e_\sigma(\mathrm{Br})/e_\pi(\mathrm{Br}) = \{S_\sigma/S_\pi\}^2$$

The above ratio was estimated by calculating the σ and π diatomic overlaps between nickel (3d) and bromine (4p) functions at the appropriate bond distances. The 3d functions of Richardson, *et al.*,[23] were used, while the halide functions were those of Clementi and Raimondi.[24] The "best" set of ligand-field and Racah parameters were estimated by fitting the excited-state energies calculated using the matrix elements in Table II and eq 2a–d to the nine band maxima observed for $[Ni(2\text{-meim})_4Br]Br$ using a least-squares technique. In order to determine the sensitivity of the calculated parameters to the magnitudes of the overlap integrals this procedure was carried out with the ratio $e_\sigma(\mathrm{Br})/e_\pi(\mathrm{Br})$ fixed using overlaps corresponding to the nuclear charge distributions $(Ni^{2+})(Br^-)$, $(Ni^+)(Br^-)$, and $(Ni^0)(Br)$. The quality of the spectral fit was found to be quite insensitive to the choice of nuclear charge distribution, while the bonding parameters altered by no more than a few per cent. The parameter K of eq 1, however, which depends directly on the overlap, rather than upon a ratio of overlaps, was found to depend quite significantly on the nuclear charge distribution used to estimate the overlaps. The calculated

TABLE II

THE MATRIX ELEMENTS OF THE EXCITED STATES OF A NICKEL COMPLEX WITH TETRAGONAL SYMMETRY

Diagonal elements[a]	Triplet states[b]
$^3B_2$	$= E(x^2 - y^2) - E(z^2)$
$^3A_2(F)$	$= E(z^2) - E(xy) + 12B$
$^3A_2(P)$	$= E(z^2) + E(x^2 - y^2) - 2E(xz) + 3B$
$^3E(F,T_2)$	$= 0.75E(z^2) + 0.25E(x^2 - y^2) - E(xz)$
$^3E(F,T_1)$	$= 0.25E(z^2) + 0.75E(x^2 - y^2) - E(xz) + 12B$
$^3E(P)$	$= E(x^2 - y^2) - E(xy) - E(xz) + 3B + E(z^2)$

Off-diagonal elements	Triplet states
$\langle ^3A_2(F) \vert ^3A_2(P) \rangle$	$= 6B$
$\langle ^3E(F,T_2) \vert ^3E(F,T_1) \rangle$	$= \sqrt{3}(E(x^2 - y^2) - E(z^2))/4$
$\langle ^3E(F,T_1) \vert ^3E(P) \rangle$	$= 6B$

Diagonal elements	Singlet states[b]
$^1B_1(D)$	$= 8B + 2C$
$^1B_1(G)$	$= E(z^2) + E(x^2 - y^2) - 2E(xz) + 9B + 2C$
$^1A_1(D)$	$= 8B + 2C$
$^1A_1(G,A_1)$	$= 16B + 4C$
$^1A_1(G,E)$	$= E(z^2) + E(x^2 - y^2) - 2(E(xz) + 2E(xy))/3 + 9B + 2C$
$^1A_1(S)$	$= E(z^2) + E(x^2 - y^2) - 2(E(xy) + 2E(xz))/3 + 18B + 5C$
$^1B_2(G)$	$= E(x^2 - y^2) - E(xy) + 8B + 2C$
$^1B_2(D)$	$= E(z^2) + E(x^2 - y^2) - 2E(xz) + 9B + 2C$
$^1A_2$	$= E(z^2) - E(xy) + 12B + 2C$
$^1E(G,T_1)$	$= 0.75E(z^2) + 0.25E(x^2 - y^2) - E(xz) + 8B + 2C$
$^1E(G,T_2)$	$= 0.25E(z^2) + 0.75E(x^2 - y^2) - E(xz) + 12B + 2C$
$^1E(D)$	$= E(z^2) + E(x^2 - y^2) - E(xy) - E(xz) + 9B + 2C$

Off-diagonal elements	Singlet states
$\langle ^1B_1(D) \vert ^1B_1(G) \rangle$	$= -2\sqrt{3}B$
$\langle ^1A_1(D) \vert ^1A_1(G,A_1) \rangle$	$= E(z^2) - E(x^2 - y^2)$
$\langle ^1A_1(D) \vert ^1A_1(G,E) \rangle$	$= -2\sqrt{3}B$
$\langle ^1A_1(G,E) \vert ^1A_1(S) \rangle$	$= 2\sqrt{2}(E(xy) - E(xz))/3$
$\langle ^1B_2(G) \vert ^1B_2(D) \rangle$	$= 2\sqrt{3}B$
$\langle ^1E(G,T_1) \vert ^1E(G,T_2) \rangle$	$= \sqrt{3}(E(x^2 - y^2) - E(z^2))/4$
$\langle ^1E(G,T) \vert ^1E(D) \rangle$	$= 2\sqrt{3}B$

[a] The symmetry designation is that for a C_{4v} complex; the corresponding symbols for a D_{4h} complex merely require the addition of a g subscript. If the nature of a state is ambiguous, its origin is designated in parentheses by the Russell–Saunders free-ion term followed, if necessary, by the symmetry of the state in a parent octahedral complex. [b] The matrix elements are given in terms of the oribital energies E and the effective Racah parameters B and C, relative to the ground state.

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(21) R. M. Golding, "Applied Wave Mechanics," Van Nostrand, London, 1969, p 207. There is a sign error in two of the wave functions given in this reference. The correct wave functions are

$$|^1T_1x0\rangle = (-\sqrt{3}/2\sqrt{2})\{(\theta^+\xi^-) - (\theta^-\xi^+)\} - (1/2\sqrt{2})\{(\epsilon^+\xi^-) - (\epsilon^-\xi^+)\}$$

$$|^1T_1y0\rangle = (+\sqrt{3}/2\sqrt{2})\{(\theta^+\eta^-) - (\theta^-\eta^+)\} - (1/2\sqrt{2})\{(\epsilon^+\eta^-) - (\epsilon^-\eta^+)\}$$

(22) J. S. Griffith, "Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 410.

(23) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(24) E. Clementi and D. L. Raimondi, *ibid.*, **38**, 2686 (1963).

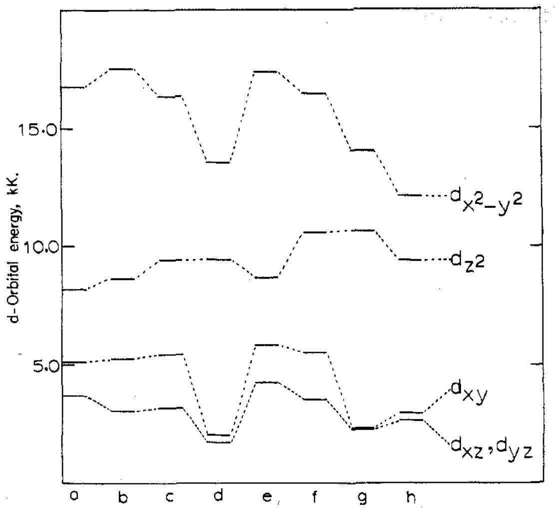

Figure 3.—d-Orbital energies of the complexes: a, [Ni(2-meim)$_4$Br]Br with $\theta = 99°$; b, [Ni(2-meim)$_4$Br]Br with $\theta = 90°$; c, Ni(pyr)$_4$Br$_2$; d, Ni(py)$_4$Br$_2$; e, [Ni(2-meim)$_4$Cl]Cl with $\theta = 99°$; f, Ni(pyr)$_4$Cl$_2$; g, Ni(py)$_4$Cl$_2$; h, Ni(tu)$_4$Cl$_2$ with $\theta = 96.7°$.

and observed frequencies below 30 kK are given in Table I, and the diatomic overlap integrals, ligand bonding parameters, and Racah parameters are listed in Table III, in each case estimated using overlaps corresponding to a nuclear charge distribution of (Ni$^+$)(Br$^-$) except for the parameter K, for which the value corresponding to all three of the nuclear charge distributions is given. The fitting process in effect neglects the contribution of the absorption of vibrational quanta to the energies of the band maxima. At ~80°K this contribution should be no more than 200–300 cm^{-1} which would have a negligible effect on the estimated bonding parameters.

Table III

Ligand Bonding Parameters, Nickel–Halide Bond Lengths, and Diatomic Overlap Integrals of Some Nickel Complexes with Tetragonal Symmetry

Complex	Nickel–halide bond length Å	Ref	Diatomic overlap^a (×10^2) S_σ	S_π	Racah parameters,^{b} kK B	C	Ligand bonding parameters, kK: In-plane ligand e_σ^b	e_π^b	Halide e_σ^b	e_π^b	K^b	K^c	K^d
[Ni(2-meim)$_4$Br]Br	2.53	3	7.97	3.11	0.809	3.11	5.82	1.31	2.71^e	0.43^e	430.0	280.0	700.0
	3.57		1.39	0.00					0.08^e	0.00^e			
Ni(py)$_4$Br$_2$	2.58	10	7.45	2.79	0.804	3.10	4.50	0.50	2.45	0.34	440.0	280.0	740.0
Ni(pyr)$_4$Br$_2$	2.682	8	6.44	2.23	0.919		5.44	1.35	1.98	0.24	480.0	300.0	830.0
[Ni(2-meim)$_4$Cl]Cl^f		3			0.884	3.01	6.02	1.49	2.97^e	0.60^e			
									0.09^e	0.00^e			
Ni(py)$_4$Cl$_2$	2.387	*g*	8.40	3.56	0.798	3.30	4.67	0.57	2.98	0.54	420.0	290.0	670.0
Ni(pyr)$_4$Cl$_2$	2.507	8	7.14	2.75	0.944		5.48	1.37	2.54	0.38	500.0	340.0	830.0
Ni(tu)$_4$Cl$_2$	2.52	*h*	7.01	2.67	0.799	2.28	4.13	0.74	2.29^e	0.33^e	470.0	320.0	760.0
	2.40		8.26	3.47					3.18^e	0.56^e			

[a] Estimated using wave functions corresponding to a nuclear charge distribution of (Ni$^+$)(halide$^-$); see text. [b] Calculated using diatomic overlaps corresponding to (Ni$^+$)(halide$^-$). [c] Calculated using diatomic overlaps corresponding to (Ni^0)(halide). [d] Calculated using diatomic overlaps corresponding to (Ni^{2+})(halide$^-$). [e] Individual values for each halide were obtained by assuming that the perturbation it produced was proportional to the square of the metal–ligand overlap. [f] Estimated assuming bond lengths analogous to those in the isomorphous bromide complex. [g] M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **10,** 117 (1954). [h] A. Lope-Castra and M. Truter, *J. Chem. Soc. A*, 2686 (1963).

Discussion and Comparison with Other Tetragonally Distorted Nickel Complexes

The bonding parameters of [Ni(2-meim)$_4$Br]Br suggest that, in agreement with chemical intuition, the σ- and π-antibonding effects of the bromide ion are considerably less than those of the amine group. The d-orbital energies estimated for the complex are shown in Figure 3a. As expected, these depart drastically from the degeneracies found in an octahedral complex. Indeed, the d_{z^2} orbital is closer in energy to d_{xy} and d_{xz}, d_{yz} than to $d_{x^2-y^2}$, and the complex is in effect nearer to square planar than to octahedral symmetry. Figure 3b shows the d-orbital energies calculated using the ligand bonding parameters found for [Ni(2-meim)$_4$Br]Br but with a depression angle $\theta = 90°$ instead of 99°. The main effect of the 9° depression is to raise d_{xz}, d_{yz} by 0.65 kK, while lowering the d_{z^2} and $d_{x^2-y^2}$ orbitals by 0.45 and 0.72 kK, respectively.

As one of the main advantages of the AOM is that it should produce a self-consistent set of bonding parameters when applied to a range of complexes with similar ligands, it is of interest to analyze the electronic spectra reported for other nickel halide complexes with tetragonal symmetry. The electronic spectra of single crystals of Ni(pyr)$_4$Cl$_2$ and Ni(pyr)$_4$Br$_2$ have been measured by Reimann,[7] and the four lowest energy spin-allowed transitions could be unambiguously assigned. No spin-forbidden bands were observed for Ni(pyr)$_4$Br$_2$, while several weak, sharp peaks between 13 and 14 kK occurred for Ni(pyr)$_4$Cl$_2$, presumably being due to a vibronic progression originating on $^3B_{1g} \rightarrow {}^1B_{1g}$ (several sharp peaks were also seen in this region for the octahedral complex Ni(pyr)$_6$(NO$_3$)$_2$[7]). As no spin-forbidden bands could be assigned with certainty, the Racah parameter C could not be determined in these two complexes. The low-temperature mull spectra of Ni(py)$_4$Cl$_2$ and Ni(py)$_4$Br$_2$ were reported by Rowley and Drago[9] and again the four lowest energy spin-allowed transitions could be assigned. Two additional weak, sharp bands were observed at 12.26 and 12.45 kK in Ni(py)$_4$Br$_2$ and 12.62 and 12.80 kK in Ni(py)$_4$Cl$_2$, and Rowley and Drago assigned these to the spin-forbidden transitions $^3B_{1g} \rightarrow {}^1A_{1g}$ and $^3B_{1g} \rightarrow {}^1B_{1g}$, respectively. However, it seems more likely that in each case both transitions are associated with a vibronic progression originating on $^2B_{1g} \rightarrow {}^1B_{1g}$ with the transition $^3B_{1g} \rightarrow {}^1A_{1g}$ being considerably lower in energy. The splitting between the $^1B_{1g}$ and $^1A_{1g}$ states derived from the ^1E_g level of an octahedral complex is expected to be quite large in compounds such as these, being caused by the off-diagonal element coupling $^1A_{1g}(1)$ with $^1A_{1g}(2)$ (see Table II). The magnitude of this off-diagonal element depends upon the difference in σ-bonding strength between the axial and in-plane ligands (eq 2a and b) and is large enough in a planar complex to make $^1A_{1g}$ the ground state. The transition $^3B_{1g} \rightarrow {}^1B_{1g}$, however, is independent of the ligand field to first order, which probably explains its comparative sharpness and tendency to show fine structure. In the present calculations, $^3B_{1g} \rightarrow {}^1B_{1g}$ was assigned at 12.26 kK in $Ni(py)_4Br_2$ and 12.62 kK in $Ni(py)_4Cl_2$. In each of the above four complexes only one band was observed between 24.5 and 27 kK, and as the two transitions $^3B_{1g} \rightarrow {}^3A_{2g}(2)$ and $^3B_{1g} \rightarrow {}^2E_g(3)$ are expected in this region, these bands could not be assigned with certainty and so were not used in the estimation of the bonding parameters. The electronic spectrum of a single crystal of $Ni(tu)_4Cl_2$ (tu = thiourea) has been measured by Gerloch, *et al.*[25] This molecule has C_{4v} symmetry, with trans Ni–Cl bonds of 2.40 and 2.52 Å and a depression angle ClNiS of $\theta = 96.7°$.[26] Seven bands could be assigned in the spectrum. Parameters were also estimated for [Ni(2-meim)$_4$Cl]Cl. As the bond lengths of this complex are not known, the ratio e_σ(chloride)/e_π(chloride) was calculated assuming a slightly shorter bond than that in $Ni(py)_4Cl_2$. The calculated and observed excited-state energies of each of the above complexes are shown in Table I, and the ligand-field bonding parameters are given in Table III, together with the nickel–halide bond lengths and diatomic overlaps.[27] Figure 3 shows the d-orbital energies in the complexes.

It should be noted that the π-bonding effect of the amines would be more properly represented by two parameters $e_\pi(\|)$ and $e_\pi(\perp)$, these being parallel and perpendicular to the plane of the ligand. However, it is unfortunately impossible to measure these quantities separately in complexes of this kind. In the two pyridine compounds the amine rings are inclined at ~45° to the *xy* plane[10,28] so that the measured value of e_π will be an average of $e_\pi(\|)$ and $e_\pi(\perp)$. In the 2-methylimidazole and pyrazole complexes, however, the aromatic rings are parallel to the *z* axis[3,8] and if $e_\pi(\|) > e_\pi(\perp)$, then the true values of e_π ($e_\pi = 0.5[e_\pi(\|) + e_\pi(\perp)]$) should be somewhat smaller than those given in Table III.

Dependence of the Ligand Bonding Parameters on Bond Length.—It is apparent (Figure 3) that on going from two comparatively strongly bound halide ions in $Ni(py)_4(halide)_2$ to two weakly bonded halide ions in $Ni(pyr)_4(halide)_2$ to one strongly coordinated anion in [Ni(2-meim)$_4$(halide)](halide) there is a fairly regular increase in the separation between the $d_{x^2-y^2}$ and d_{z^2} orbitals. Remembering that e_σ and e_π represent the σ- and π-antibonding effect of *one* ligand at the bond distance indicated (Table III), the perturbing effect of the bromide ion follows the sequence [Ni(2-meim)$_4$Br]Br > $Ni(py)_4Br_2$ > $Ni(pyr)_4Br_2$. As expected, this is the order in which the Ni–Br bond lengths increase. The trend for the chloride complexes is similar. The variation in the perturbation produced by a chloride or bromide ion among the complexes is quite large, increasing by ~40% on going from $Ni(pyr)_4Br_2$ to [Ni(2-meim)$_4$Br]Br. Indeed, although chloride has a stronger ligand field strength than bromide when averaged over all the complexes, the perturbation produced by the bromide group in [Ni(2-meim)$_4$Br]Br is significantly greater than that produced by a chloride ion in $Ni(pyr)_4Cl_2$.

While the effect of a ligand on the d orbitals depends upon its distance from the metal ion, the AOM predicts that the parameter *K* of eq 1 should be essentially independent of the metal–ligand bond length (provided that H_M and H_L remain effectively constant). The values of *K* obtained for the three bromide complexes are indeed approximately equal when the possible error (~5%) introduced by the uncertainty in bond length, and hence overlap, is taken into account. The three chloride complexes with known bond lengths also have similar *K* values, though that of $Ni(py)_4Cl_2$ does seem to be significantly lower than those of the other two complexes. Better agreement between the *K* values is obtained using overlaps estimated from wave functions derived from the more covalent nuclear charge distribution $(Ni^0)(Br)$ than the ionic distribution $(Ni^{2+})(Br^-)$.

Magnitude of the Ligand Bonding Parameters.—It is interesting to see whether the AOM predicts d-orbital splittings of the same order of magnitude as those observed experimentally. Approximate values for *K* can be estimated from the diagonal matrix elements $H_M = -53.5$, $H_L = -65.8$ kK for $NiBr_4^{2-}$ and $H_M = -56.7$, $H_L = -70.7$ kK for $NiCl_4^{2-}$ calculated by Day and Jørgensen.[18] Substitution of these in eq 1b gives $K = 350$ kK for the nickel–bromide interaction and $K = 360$ kK for the nickel–chloride interaction, which fall within the range of values estimated for the present series of complexes. The AOM thus does predict a metal–ligand interaction of the correct order of magnitude, and in this respect it is superior to the simple electrostatic model, which predicts d-orbital splittings much smaller than those actually observed.[8,29] It is interesting to note that *K*(chloride) is not much larger than *K*(bromide) so that the AOM ascribes the greater ligand perturbation generally produced by chloride largely to the better orbital overlap which occurs with this ion.

Some support for the assumption that e_σ(halide)/e_π(halide) $\approx (S_\sigma/S_\pi)^2$ is provided by the near equality of the bonding parameters obtained for pyrazole and 2-methylimidazole. These ligands are very similar and it seems reasonable that they should have comparable bonding parameters. In going from $Ni(pyr)_4Br_2$ to [Ni(2-meim)$_4$Br]Br two weakly bound bromide ions are replaced by one quite strongly bonded one. If the bromide π interaction were greatly different from that assumed here, the change in the energies of d_{xy} and d_{xz}, d_{yz} would not be properly represented, and it seems likely that different π-bonding parameters would be obtained for pyrazole and 2-methylimidazole.

The general self-consistency of the model is further supported by the close similarity between the parameters obtained for each amine when different halide

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(25) M. Gerloch, J. Lewis, and W. R. Snail, *J. Chem. Soc. A*, 2686 (1963).

(26) A. Lope-Castro and M. Truter, *J. Chem. Soc.*, 1309 (1963).

(27) The calculations were performed with the ratio e_σ(halide)/e_π(halide) fixed by overlaps estimated using nuclear charges corresponding to (Ni^0)-(halide), $(Ni^+)(halide^-)$, and $(Ni^{2+})(halide^-)$. As with [Ni(2-meim)$_4$Br]Br, the spectral fit and e_σ and e_π values were quite insensitive to the nuclear charges used and only the results obtained using the ratio from $(Ni^-)(halide^-)$ are given in the tables. The parameter *K*, however, does depend on which charge distribution is used in the overlap calculations, and the values obtained using all three charge distributions are given.

(28) M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **10**, 117 (1954).

(29) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Oxford University Press, London, 1966, p 399.

complexes are compared. Thus, while e_σ and e_π of pyridine are significantly different from those of pyrazole and 2-methylimidazole, the parameters obtained for the chloride and bromide complex of each amine are very similar, and what differences do occur can probably be ascribed to slight changes in the Ni–N bond lengths.

The order of σ-antibonding power of the ligands (assuming average values for the halide ions) is 2-methylimidazole $\sim$ pyrazole $>$ pyridine $>$ thiourea $>$ chloride $>$ bromide, while the π-antibonding order is 2-methylimidazole $\sim$ pyrazole $>$ thiourea $>$ pyridine $\sim$ chloride $>$ bromide. These series represent the σ- and π-donor properties of the ligands toward nickel(II) at what are probably their usual bond distances. It is interesting that pyridine behaves as a comparatively weak π donor. For pyridine $e_\pi/e_\sigma \approx 0.125$, while for the other in-plane ligands this ratio is 0.2–0.25. The magnitude of e_π depends upon interactions with empty antibonding ligand orbitals as well as with filled bonding orbitals.[14] The former interactions produce a negative contribution to e_π, so that it is possible that the small value of e_π for pyridine is due to the presence of comparatively low-lying π-antibonding orbitals in this ligand. However, as has been mentioned, if the π-bonding effect of the amine groups is not symmetrical about the Ni–N bond directions, it is possible that e_π has been somewhat overestimated for 2-methylimidazole and pyrazole.

The separation between the e_g and t_{2g} orbitals in an octahedral complex is given[14] by $\Delta = 3e_\sigma - 4e_\pi$. The metal ion in $N(CH_3)_4NiBr_3$ is surrounded by a distorted octahedral array of bridging bromide ions at a mean Ni–Br distance of 2.56 Å.[30] The relevant overlaps using the $(Ni^+)(Br^-)$ wave functions[27] are $S_\sigma = 0.0766$ and $S_\pi = 0.0291$, and using eq 2 with the mean value of $K = 448$ kK found for the three bromide complexes a value of $\Delta = 6.4$ kK is estimated for $N(CH_3)_4NiBr_3$, which compares well with the value of $\Delta = 6.3$ kK observed experimentally.[30] The bonding parameters found for the terminal bromide groups in the complexes studied here are therefore in good agreement with the Δ value in the octahedral nickel bromide chromophore containing bridging halide ions.

Conclusions

The angular overlap model apparently provides a useful framework within which to interpret the excited-state energies of tetragonally distorted nickel halide complexes. It will be interesting to see whether this model can be extended to similar complexes with other metal ions and also to compounds with ligands such as $-NO_2$ and $-CN$ which are expected to have quite different bonding properties from those discussed here.

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[30] G. Stucky, S. D'Agostino, and G. McPherson, *J. Amer. Chem. Soc.*, **88**, 4828 (1966).

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Trivalent Nickel. I. A Pulse Radiolytic Study of the Formation and Decomposition of the Ammoniacal Complex in Aqueous Solution

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The oxidation of the $Ni^{II}(NH_3)_n$ complex by NH_2 radicals in aqueous solutions yields an unstable trivalent nickel complex. The specific rate of this reaction is $1 \times 10^7\ M^{-1}\ sec^{-1}$. The absorption spectrum of the trivalent complex was measured. The mechanism of disappearance of the trivalent complex is *via* a second-order reaction with $2k \leq 3.5 \times 10^7\ M^{-1}\ sec^{-1}$. The specific rate of the reaction $OH + NH_3 \rightarrow NH_2 + H_2O$ at pH 11.3 is $2.4 \times 10^7\ M^{-1}\ sec^{-1}$. The specific rate of oxidation of hydrazine by the trivalent nickel complex is $4 \times 10^6\ M^{-1}\ sec^{-1}$.

The preparation of different trivalent nickel complexes, both in the solid state and in solutions in organic solvents has been recently described.[1–14] On the other hand it has been argued that in many of these complexes the oxidation site is on the ligands and not on the central nickel ion.[15,16] It seems to us that enough evidence

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[1] A. V. Babaeva, V. I. Belova, Ya. K. Syrkin, and G. G. Afanas'eva, *Russ. J. Inorg. Chem.*, **13**, 610 (1968).

[2] A. V. Babaeva, I. B. Baranovskii, and G. G. Afanas'eva, *ibid.*, **10**, 686 (1965).

[3] I. B. Baranovskii and V. I. Belova, *ibid.*, **10**, 306 (1965).

[4] W. M. Vogel, *Electrochim. Acta*, **13**, 1815 (1968).

[5] L. Stein, J. M. Neil, and G. R. Alms, *Inorg. Chem.*, **8**, 2472 (1969).

[6] N. A. Matmijoff, L. B. Asprey, W. F. Wagennon, M. J. Reisfield, and E. Fukishima, *ibid.*, **8**, 750 (1969).

[7] D. C. Olson and J. Vasilenkis, *Inorg. Chem.*, **8**, 1611 (1969).

[8] N. F. Curtis and D. F. Cook, *Chem. Commun.*, 962 (1967).

[9] E. K. Barefield and D. H. Bush, *ibid.*, 522 (1970).

[10] B. M. Higgson and E. D. McKenzie, *Inorg. Nucl. Chem. Lett.*, **6**, 209 (1970).

[11] A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970); *Inorg. Chem.*, **9**, 2364 (1970).

[12] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

[13] K. A. Jensen, B. Nygaard, and C. Pederson, *ibid.*, **17**, 1126 (1963).

[14] R. S. Nyholm, *J. Chem. Soc.*, 2061 (1950); R. S. Nyholm, *ibid.*, 2602 (1951); R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

[15] P. Kreisman, R. Marsh, J. R. Preer, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 1067 (1968).

[16] E. I. Stiefel, J. H. Waters, E. Billing, and H. B. Gray, *ibid.*, **87**, 3016 (1965).