TABLE I

LINE BROADENING DATA FOR Fe(III)–8.5 *M* KNCS SOLUTION

Fe(III), *M*	*t*, °C.	Δ′, gauss	$T'_{2p} \times 10^5$ *M* sec.
0.05	2.0	0.46	11.2
0.05	15.0	1.38	3.74
0.05	28.0	2.44	2.12[a]
0.03	12.3	0.57	5.44
0.03	21.3	1.03	3.01
0.03	26.0	1.47	2.11[b]
0.03	31.0	1.96	1.58[c]
0.015	28.0	0.87	1.77[d]
0.015	38.5	1.41	1.10

[a] pH 1.02. [b] pH 1.28. [c] pH 2.42. [d] pH 1.24.

Treatment of Data and Results

We have followed the treatment given earlier.[3] We have defined T'_{2p} by $T'_{2p} \equiv 2[\mathrm{Fe(III)}]/\gamma\Delta'$ where [Fe(III)] refers to total iron molarity, γ is the magnetogyric ratio for N^{14} (1934 gauss^{-1} $\mathrm{sec.}^{-1}$), and Δ′ is the line broadening (in gauss) in free thiocyanate ion, measured from full widths at half-maximum absorption. The results obtained correspond to the case $T'_{2p} = [\mathrm{Fe(III)}]p_0\tau_{40}/p_4$, where p_0 and p_4 are the atom fractions of N^{14} in free and bound thiocyanate, respectively, and τ_{40} is the mean lifetime of a thiocyanate ion for change from the complex to free thiocyanate. No direct measurements on species in thiocyanate solutions at 8 *M* appear to have been made. Although much study has been given to the question of the species present in Fe(III)–thiocyanate solutions, no clear-cut results are available on the higher species. We have assumed the species $\mathrm{Fe(NCS)_4^-}$ to predominate and have calculated our data on this basis. Jørgensen[4] indicates that the iron is bound to sulfur in such species. Our results are not unambiguous on this point but suggest rather that it is the nitrogen atom which is bound to iron. If the thiocyanate ligand is bound to sulfur, then the paramagnetic electrons of iron(III) must be σ delocalized through the SCN linkages. We have found for the Ni(II)–$\mathrm{N_3^-}$ system that while the N^{14} line for the terminal atoms in $\mathrm{N_3^-}$ is readily broadened by Ni(II), the line for the central nitrogen atom requires about a tenfold greater nickel concentration to produce a broadening effect. This suggests that the σ delocalization in the electronically related azide ion is not very great.

TABLE II

RATE DATA FOR LABILE COMPLEXES AT 25°

	k_1, $\mathrm{sec.}^{-1}$	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.	Ref.
$\mathrm{Fe(NCS)_4^-} + \mathrm{NCS^-} \rightleftharpoons$	$1.0 \pm 0.1 \times 10^5$	10.3 ± 0.5	-1.5 ± 1.5	This work
$\mathrm{Fe(H_2O)_6^{3+}} + \mathrm{H_2O} \rightleftharpoons$	3×10^3	. . .	. . .	*a*
$\mathrm{Fe(H_2O)_6^{3+}} + \mathrm{NCS^-} \rightarrow \mathrm{FeNCS^{2+}}$	127 (M^{-1} $\mathrm{sec.}^{-1}$)	13	−5	*b*
$\mathrm{Fe(H_2O)_6^{3+}} + \mathrm{Cl^-} \rightarrow \mathrm{FeCl^{2+}}$	9 (M^{-1} $\mathrm{sec.}^{-1}$)	17	2	*c*
$\mathrm{Ni(NCS)_4^{2-}} + \mathrm{NCS^-} \rightleftharpoons$	7×10^5	9	−5	3

[a] Private communication from R. E. Connick. [b] J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958). [c] R. E. Connick and C. P. Coppel, *ibid.*, **81**, 6389 (1959).

We have arbitrarily used the rate law $R = 4k_1[\mathrm{Fe(III)}]$. The value of k_1 is then given by $k_1 = [\mathrm{NCS^-}]/4T'_{2p}$. Our results are presented in Table I. No large variation in pH was attempted. At low pH the decomposition of thiocyanate becomes a problem; at high pH hydrolysis of Fe(III) will occur. In the range studied (1–2.4) no effects were found. The rate is found to be first order in Fe(III) concentration. We have not varied the thiocyanate concentration in these studies because our experience has shown that it is very difficult to treat the results of such variations considering uncertainties in species and the effects of including several species in the n.m.r. theory. The following rate parameters were calculated: k_1 (25°) = $1.0 \pm 0.1 \times 10^5$ $\mathrm{sec.}^{-1}$, $\Delta H^* = 10.3 \pm 0.5$ kcal./mole, and ΔS^* (from k_1) = -1.5 ± 1.5 e.u.

It may be noted here that addition of 0.01 *M* Fe(II) to 8.5 *M* KNCS produced no observable line broadening at 27 and 40°.

Discussion

Some data for related systems are given in Table II. As has been noted before, the exchange rate for higher complexes is greater than for the mono complex. The exchange of thiocyanate ion in our case is much more rapid at 25° than water exchange in the aquo Fe(III) ion. The Fe(III) and Ni(II) thiocyanate exchanges have fairly similar apparent rate parameters. Uncertainty as to species makes it difficult to try to understand this result.

It will be of interest to compare the water exchange rate with that for thiocyanate ion in solutions containing the thiocyanate complexes as was done for the nickel system.[3]

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(4) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p. 79.

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The Evaluation of Group Overlap Integrals

BY S. F. A. KETTLE

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The semi-empirical molecular orbital theory of inorganic molecules,[1] in which there has recently been

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

renewed interest,[2] requires the evaluation of group overlap integrals (G) in terms of atomic overlap integrals (S).[3] The general method for this has been described by Ballhausen[4] and a simplification, applicable when all ligands lie on the cartesian coordinate axes, by Bedon, Horner, and Tyree.[5]

Group overlap integrals have been evaluated for the more common geometries, but as the semi-empirical molecular orbital method is currently being applied to fairly complex molecules[6] it is evident that other group overlap integrals will be needed.

Consider the example discussed by Bedon, Horner, and Tyree[5] that of the evaluation of $G_\sigma\ (\mathrm{E_g}) = \int \mathrm{d}_{z^2}\psi_{\mathrm{e_g}}\,\mathrm{d}\tau$, where $\psi_{\mathrm{e_g}}$ is a ligand group orbital of $\mathrm{e_g}$ symmetry.

$$G_\sigma\ (\mathrm{E_g}) = \int \frac{(2z^2 - x^2 - y^2)}{\sqrt{3}}\ \frac{1}{\sqrt{12}} \times (2\sigma_5 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_6)\,\mathrm{d}\tau$$

(where we have used the same labels for the ligand orbitals as Bedon, *et al.*[5])

$$G_\sigma = \frac{2}{\sqrt{3}} \int \left(\frac{2z^2 - x^2 - y^2}{\sqrt{3}}\right) \sigma_5\,\mathrm{d}\tau - \frac{2}{\sqrt{3}} \int \left(\frac{2z^2 - x^2 - y^2}{\sqrt{3}}\right) \sigma_1\,\mathrm{d}\tau$$

$$= \frac{2}{\sqrt{3}} S_\sigma - \frac{2}{\sqrt{3}} S'_\sigma$$

Now

$$2z^2 - x^2 - y^2 = -[(2x^2 - y^2 - z^2) + (2y^2 - x^2 - z^2)]$$

so

$$S' = -\int \frac{(2x^2 - y^2 - z^2)}{\sqrt{3}}\,\sigma_1\,\mathrm{d}\tau - \int \frac{(2y^2 - x^2 - z^2)}{\sqrt{3}}\,\sigma_1\,\mathrm{d}\tau$$

Because of the cubic symmetry of the system the integrals on the right-hand side of the above expression are equal to S_σ and S'_σ, respectively. Hence $S'_\sigma = -{}^1/_2 S_\sigma$ so that $G_\sigma(\mathrm{E_g}) = \sqrt{3}S_\sigma$. Here we have used the fact that σ_1 lies on the x axis. This is not generally true for other atomic arrangements, but for some of these the relationship between S_σ and S'_σ can be determined from the orthogonality conditions. In the above example we could, for instance, have used the fact that

$$\int \mathrm{d}_{z^2}\psi_{\mathrm{a_{1g}}}\,\mathrm{d}\tau = 0$$

As an example of this we consider the σ group overlap integral between a d_{z^2} orbital and the appropriate linear combination of ligand σ orbitals in an icosahedral complexion.

$$G_\sigma\ (\mathrm{H_g}) = \int \mathrm{d}_{z^2}\psi_{\mathrm{H_g}}\,\mathrm{d}\tau$$

where

$$\psi_{\mathrm{H_g}} = \frac{1}{2\sqrt{15}} (5\sigma_{11} - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6 - \sigma_7 - \sigma_8 - \sigma_9 - \sigma_{10} + 5\sigma_{12})$$

Here a fivefold rotation axis of the icosahedron is taken as the z axis, ligands 11 and 12 lying on this axis, the nomenclature being an obvious extension of that of Bedon, *et al.*[5] It follows that

$$G_\sigma\ (\mathrm{H_g}) = \sqrt{\frac{5}{3}}\left[S_\sigma - S'_\sigma\right]$$

Now, from the condition

$$\int \mathrm{d}_{z^2}\psi_{\mathrm{A_g}}\,\mathrm{d}\tau = 0$$

where

$$\psi_{\mathrm{A_g}} = \frac{1}{\sqrt{12}} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7 + \sigma_8 + \sigma_9 + \sigma_{10} + \sigma_{11} + \sigma_{12})$$

we deduce that

$$S'_\sigma = -\frac{1}{5}S_\sigma$$

and

$$G_\sigma\ (\mathrm{H_g}) = 2\sqrt{\frac{3}{5}}S_\sigma$$

An important, but limited, class of group overlap integrals may thus be evaluated very simply—namely, those between the orbitals of a central atom and a set of surrounding ligand orbitals, each ligand lying on a rotation axis of the complex ion.

In the more general case group overlap integrals are required between the orbitals of an atom and those of N surrounding atoms, a symmetry axis passing through the first atom which relates the surrounding atoms one to another. The z direction is then taken along the symmetry axis and the problem closely resembles that discussed by Dunitz and Orgel.[7] We give in the table below expressions which enable group overlap integrals to be determined between sets of s, p, and d orbitals in this more complex case. The coordinate system is shown in Figure 1; each set of equivalent atoms is characterized by a particular value of θ, each member of the set by a value of ϕ. The expressions given by Dunitz and Orgel and which are closely related to those in the first section of the table are confined to overlap between orbitals on a central atom and surrounding orbitals which are symmetric with respect to reflection in a vertical mirror plane. We therefore include in Table I overlap with orbitals antisymmetric with respect to such a reflection. Atomic overlap integrals

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(2) See R. F. Fenske, *Inorg. Chem.*, **4**, 33 (1965), and references therein.

(3) B. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(4) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 174.

(5) H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *Inorg. Chem.*, **3**, 647 (1964).

(6) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

(7) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

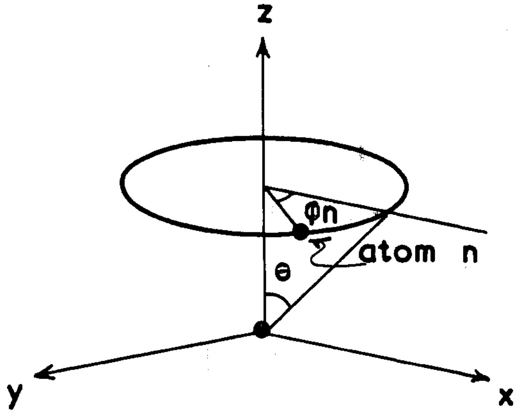

Figure 1.

TABLE I

GENERAL EXPRESSIONS FOR GROUP OVERLAP INTEGRALS[a]

σ_v—Symmetric Overlaps

$$G\ (\mathrm{s}) = \sqrt{N}S_\sigma(\mathrm{s})$$

$$G\ (\mathrm{p}_z) = \sqrt{N}\,[\cos\theta S_\sigma(\mathrm{p}) - \sin\theta S_\pi(\mathrm{p})]$$

$$G\ (\mathrm{p}_x) = [\sin\theta S_\sigma(\mathrm{p}) - \cos\theta S_\pi(\mathrm{p})]\sum_N c_n\cos\phi_n$$

$$G\ (\mathrm{p}_y) = [\sin\theta S_\sigma(\mathrm{p}) - \cos\theta S_\pi(\mathrm{p})]\sum_N c_n\sin\phi_n$$

$$G\ (\mathrm{d}_{z^2}) = \sqrt{N}\left[(\cos^2\theta - \frac{1}{2}\sin^2\theta)S_\sigma\ (\mathrm{d}) - \frac{\sqrt{3}}{2}\sin 2\theta S_\pi\ (\mathrm{d}) + \frac{\sqrt{3}}{2}\sin^2\theta S_\delta(\mathrm{d})\right]$$

$$G\ (\mathrm{d}_{xz}) = \left[\frac{\sqrt{3}}{2}\sin 2\theta S_\sigma(\mathrm{d}) + \cos 2\theta S_\pi(\mathrm{d}) - \frac{1}{2}\sin 2\theta S_\delta(\mathrm{d})\right]\sum_N c_n\cos\phi_n$$

$$G\ (\mathrm{d}_{yz}) = \left[\frac{\sqrt{3}}{2}\sin 2\theta S_\sigma(\mathrm{d}) + \cos 2\theta S_\pi(\mathrm{d}) - \frac{1}{2}\sin 2\theta S_\delta(\mathrm{d})\right]\sum_N c_n\cos\phi_n$$

$$G\ (\mathrm{d}_{xy}) = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(\mathrm{d}) + \frac{1}{2}\sin 2\theta S_\pi(\mathrm{d}) + \frac{1}{2}(1+\cos^2\theta)S_\delta(\mathrm{d})\right]\sum_N c_n\sin 2\phi_n$$

$$G\ (\mathrm{d}_{x^2-y^2}) = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(\mathrm{d}) + \frac{1}{2}\sin 2\theta S_\pi(\mathrm{d}) + \frac{1}{2}(1+\cos^2\theta)S_\delta(\mathrm{d})\right]\sum_N c_n\cos 2\phi_n$$

σ_v—Antisymmetric Overlaps

$$G'\ (\mathrm{p}_x) = S_\pi(\mathrm{p})\sum_N c_n\sin\phi_n$$

$$G'\ (\mathrm{p}_y) = S_\pi(\mathrm{p})\sum_N c_n\cos\phi_n$$

$$G'\ (\mathrm{d}_{xz}) = [\cos\theta S_\pi(\mathrm{d}) - \sin\theta S_\delta(\mathrm{d})]\sum_N c_n\sin\phi_n$$

$$G'\ (\mathrm{d}_{yz}) = [\cos\theta S_\pi(\mathrm{d}) - \sin\theta S_\delta(\mathrm{d})]\sum_N c_n\cos\phi_n$$

$$G'\ (\mathrm{d}_{xy}) = [\sin\theta S_\pi(\mathrm{d}) - \cos\theta S_\delta(\mathrm{d})]\sum_N c_n\cos 2\phi_n$$

$$G'\ (\mathrm{d}_{x^2-y^2}) = [\sin\theta S_\pi(\mathrm{d}) - \cos\theta S_\delta(\mathrm{d})]\sum_N c_n\sin 2\phi_n$$

[a] c_n is the coefficient associated with the *n*th orbital in the combination of surrounding-atom orbitals of correct symmetry to interact with the central atom orbital indicated.

are given as $S\rho(t)$ where ρ is the symmetry of the diatomic overlap and t the atomic orbital species on the central atom. It should be noted that only the symmetries of the orbitals on the surrounding atoms are specified. The formulas in the table will usually have to be applied to these orbitals as well.[8] For polyhedral molecules[6,9] it is best to obtain group overlap integrals within suitable fragments of the molecule using the expressions given in the table. The group overlap integrals appropriate to the whole molecule are then simply related to those of the fragments.

As an example in the use of this table we evaluate the group overlap integral between the ligand σ orbitals and the metal $\mathrm{d}_{x^2-y^2}$ orbital in a ML_4 complex of S_4 symmetry. The ligand group orbital of B symmetry is

$$\psi(\mathrm{B}) = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

the ligand orbitals being labeled cyclically viewed down the S_4 axis. The group overlap integral is then

$$\int \mathrm{d}_{x^2-y^2}\psi(\mathrm{B})\,\mathrm{d}\tau = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(\mathrm{d})\right]\left[\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}\right] = 3\sin^2\theta S_\sigma(\mathrm{d})$$

In the limiting cases of square-planar complexes and tetrahedral complexes this expression reduces to $\sqrt{3}S_\sigma(\mathrm{d})$ and $(2/\sqrt{3})S_\sigma(\mathrm{d})$, respectively.

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[8] For an example see D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).

[9] J. D. Corbett and R. E. Rundle, *Inorg. Chem.*, **3**, 1408 (1964).

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The Characterization of the Dimethylammoniate of Diborane

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The literature contains many conflicting reports for the chemical and physical properties of a material called methylamine borane. One compound, a crystalline, volatile solid prepared from sodium borohydride and methylammonium chloride,[1] has been identified as $H_3B\text{-}NH_2CH_3$. Another material,[2] a nonvolatile liquid prepared from diborane and methylamine, has not been characterized completely. The n.m.r. spectrum[3] of this nonvolatile liquid is consistent with the ionic structure, $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$. The following chemical and physical data provide more evidence that this compound is the dimethylammoniate of diborane, $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$.

Experimental

Reaction of Diborane and Methylamine.—Diborane (1.10 mmoles) and methylamine (2.84 mmoles) were condensed on the

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[1] H. Noth and H. Beyer, *Ber.*, **93**, 928 (1960).

[2] E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

[3] S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87** 2755 (1965).