

TABLE I
EQUILIBRIUM CONSTANT FOR THE FORMATION OF THE
NITRATOPENTAQUOCHROMIUM(III)
COMPLEX AT IONIC STRENGTH 1.0 M^a

Temp, °C	(NO ₃ ⁻) ₆ , M	10 ³ (CrNO ₃ ²⁺) ₆ q, M	10 ³ K, M^{-1}
34.9	0.70	6.95	0.99
34.9	0.50	5.16	1.03
34.9	0.30	3.29	1.09
25.1	0.70	5.48	0.78
25.1	0.50	4.19	0.84
25.1	0.30	2.57	0.85
10.2	0.70	3.85	0.55
10.2	0.50	2.82	0.56
10.2	0.30	1.76	0.59

^a (H⁺) = 0.40 M and [Cr(III)] = 0.10 M . Ionic strength maintained with HClO₄.

$\Delta H^\circ = 4.5 \pm 0.2$ kcal mole⁻¹ and $\Delta S^\circ = 5.9 \pm 0.6$ cal mole⁻¹ deg⁻¹ at 25.0°. If no correction is applied and ΔH is calculated at each nitrate concentration, then the mean values are $\Delta H_m^\circ = 4.2 \pm 0.2$ kcal mole⁻¹ and $\Delta S_m^\circ = 4.6 \pm 0.6$ cal mole⁻¹ deg⁻¹ at 25.0°.

The entropies of formation of various chromium(III) complexes are compared in Table II. The entropies

TABLE II
ENTROPIES OF FORMATION OF CHROMIUM(III) COMPLEXES
Cr³⁺ + X⁻ \rightleftharpoons CrX²⁺

X ⁻	Ionic strength, M	ΔS° , eu	$S^\circ_{X^-}$, eu ^a	Ref
F ⁻	0.5	28.2	-3.6	<i>b</i>
Cl ⁻	1.0	15.7	13.2	<i>c</i>
Br ⁻	2.0	4.9	19.3	<i>d</i>
NCS ⁻	0.5	~2	20.2	<i>e</i>
NO ₃ ⁻	1.0	5.9	15.6	<i>f</i>

^a The entropies of the polyatomic anions have been corrected for the loss of rotational entropy upon complex formation. For purposes of comparison with the earlier work the corrected entropies are those reported in ref 3. ^b T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). ^c C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). ^d Reference 9. ^e C. Postmus and E. L. King, *ibid.*, **59**, 1208, 1216 (1955). ^f This work.

of the anions presented in this table have been corrected for the loss of rotational entropy upon complex formation.^{3,5} It will be seen that there is a good correlation between ΔS° and the corrected entropies of the anions. The slope of the plot of ΔS° against $S^\circ_{X^-}$ is close to the theoretical value of -1.5.⁶ The fact that the nitrate complex satisfies this relation between ΔS° and $S^\circ_{X^-}$ indicates that, in common with the other chromium(III) complexes, only one water molecule is lost upon formation of the nitrate complex and thus that the nitrate ligand is not chelated.⁷

The Aquation Reaction.—The first-order rate constants for the aquation of the nitrate complex are presented in Table III. In the range (H⁺) = 0.076–0.99

(5) J. H. B. George, *J. Am. Chem. Soc.*, **81**, 5530 (1959).

(6) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

(7) If the nitrate group were chelated in the chromium(III) complex, then 16.7 cal mole⁻¹ deg⁻¹, the entropy of a water molecule, would have to be subtracted from ΔS° for the nitrate complex in order to make the value of ΔS° for the nitrate complex comparable with those for the other chromium(III) complexes. This corrected value of ΔS° does not lie on the plot of ΔS° against $S^\circ_{X^-}$.

TABLE III
FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF THE
NITRATOPENTAQUOCHROMIUM(III) ION
AT IONIC STRENGTH 1.0 M^a

Temp, °C	(H ⁺), M	10 ⁵ k, sec ⁻¹
34.9	0.990	23.3
34.9	0.401	24.8
34.9	0.201	26.3
34.9	0.081	29.9
25.1	0.990	7.19
25.1	0.201	7.94
25.1	0.081	9.14
15.6	0.990	2.17
15.6	0.201	2.58
15.6	0.076	2.72

^a Ionic strength maintained with LiClO₄.

M the observed rate constant is given by

$$k = k_0 + k_{-1}/(H^+)$$

where $k_0 = (7.2 \pm 0.2) \times 10^{-5}$ sec⁻¹ and $k_{-1} = (1.4 \pm 0.7) \times 10^{-7}$ M sec⁻¹ at 25°. The enthalpy and entropy of activation for the acid-independent path are $\Delta H_d^\ddagger = 21.4 \pm 0.2$ kcal mole⁻¹ and $\Delta S_d^\ddagger = -5.7 \pm 0.6$ cal mole⁻¹ deg⁻¹. These values are in very good agreement with those obtained by Swaddle.³ The contribution of the acid-dependent path is small and accurate activation parameters for this reaction were not obtained. The rate constant for the acid-independent formation reaction, calculated from the equilibrium constant and the aquation rate, is approximately 7×10^{-7} M^{-1} sec⁻¹ at 25.0°. ΔH_f^\ddagger and ΔS_f^\ddagger are calculated to be about 28.8 kcal mole⁻¹ and 0.2 cal mole⁻¹ deg⁻¹, respectively. The values of the various activation parameters are similar to those calculated for the corresponding reactions of the bromopentaquo-chromium(III) ion^{8,9} and are consistent with the view that the nitrate ligand is monodentate in the nitrate chromium(III) complex.

(8) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(9) J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

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Absorption Spectra of Square-Planar Complexes of Ethylenebisbiguanide with Nickel(II) and Palladium(II)

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It has been proposed by Gray¹ and by Gray and Ballhausen² that the energy levels of the antibonding molecular orbitals derived from atomic d orbitals in square-planar transition metal complexes most often occur in the order $x^2 - y^2 \gg xy > z^2 > xz, yz$. More recently, elegant use of molecular orbital theory has led to simi-

(1) H. B. Gray, *Transition Metal Chem.*, **1**, 240 (1965).

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

lar conclusions concerning the relative energy levels of these d_{z^2} and d_{xy} orbitals, as is described in papers by Basch and Gray,³ by Martin and co-workers,⁴ and by others.⁴

Gray's proposal was based on the spectral properties of square-planar complexes in which the donor atoms are carbon (in cyanide), sulfur, chlorine, and bromine. Until now, absorption spectra have not been available for square-planar complexes involving donor atoms other than those. This note reports the absorption spectra of square-planar complexes of nickel(II) and palladium(II) with a tetradentate nitrogen-donor ligand, *viz.*, ethylenebisbiguanide (enbbg, $C_6H_{16}N_{10}$).

Preparation of these compounds has been described by Ray.⁵ The chloride salt of $Ni^{II}(\text{enbbg})^{2+}$ is a typical square-planar d^8 complex, orange and diamagnetic.

The absorption spectrum of $Ni(\text{enbbg})Cl_2$ in 0.0100 *M* solution (observed in 1-cm cells with a Cary Model 14 spectrophotometer over a range of 300–1600 $m\mu$, *i.e.*, *ca.* 33,000–6200 cm^{-1}) consists of only a single detectable peak, with maximum absorbance at a wavelength of 478 $m\mu$ (20,900 cm^{-1}) (see Figure 1). A similar peak

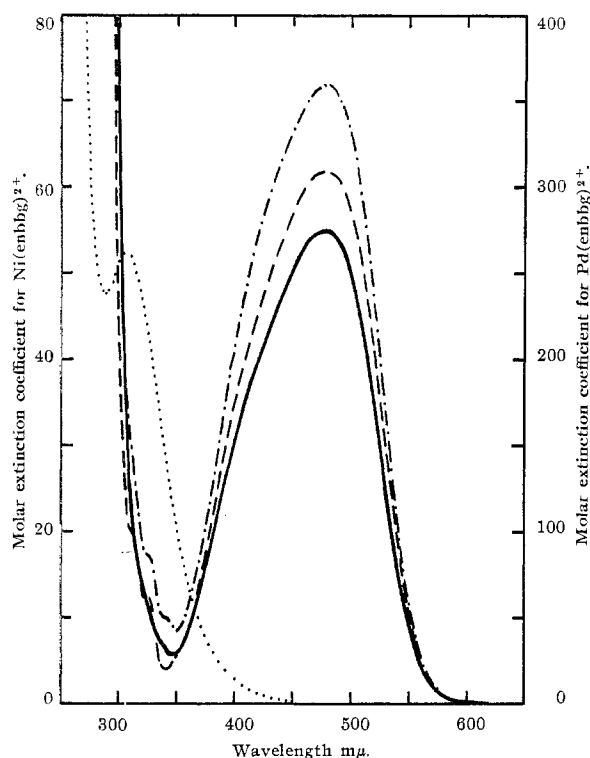


Figure 1.—Absorption spectra (25°): —, $Ni(\text{enbbg})^{2+}$ in H_2O ; ----, $Ni(\text{enbbg})^{2+}$ in formamide; - · -, $Ni(\text{enbbg})^{2+}$ in DMSO; · · · ·, $Pd(\text{enbbg})^{2+}$ in H_2O . Note use of different scale for $Pd(\text{enbbg})^{2+}$.

for $Pd(\text{enbbg})Cl_2$ in aqueous solution occurs at 307 $m\mu$ (32,500 cm^{-1}), which is consistent with the expectation of a substantial increase in the magnitude of ligand field splitting on going from the first transition series to the second. Finding peaks at these wavelengths is also consistent with the expected location of ethylene-

bisbiguanide in the spectrochemical series, *i.e.*, $Cl^- < \text{enbbg} < CN^-$.

Because no other peaks are found at longer wavelengths (even out to more than 1600 $m\mu$ in the case of $Ni(\text{enbbg})Cl_2$ in dimethyl sulfoxide solution) it must be assumed that the one observed peak corresponds to that $d-d$ transition which has the smallest energy. Peaks for two other such $d-d$ transitions, expected to occur at shorter wavelengths, are not observed, presumably because they are obscured by the very intense charge-transfer absorption occurring at wavelengths below about 300 $m\mu$.

Identification of the transition responsible for that lowest energy peak depends on the fact that its wavelength is not shifted by a change of solvent. The only significant difference between the spectra of $Ni(\text{enbbg})Cl_2$ in water and in dimethyl sulfoxide (DMSO) is a difference in molar extinction coefficient; *i.e.*, ϵ_{max} is 55 in H_2O and 72 in DMSO. In formamide solution, ϵ_{max} is 62. There does not seem to be any obvious correlation between absorbance and solvent dielectric constant.

The $d-d$ transition of lowest energy in a square-planar d^8 complex must be either $d_{xy} \rightarrow d_{x^2-y^2}$ (${}^1A_{1g} \rightarrow {}^1A_{2g}$) or $d_{z^2} \rightarrow d_{x^2-y^2}$ (${}^1A_{1g} \rightarrow {}^1B_{1g}$). If it were the latter, involving the d_{z^2} orbital, that orbital being the one which is most exposed and therefore most strongly influenced by the solvent, a change of solvent should change the wavelength of the peak. Because the wavelength of the observed peak is found to be independent of the choice of solvent, the transition producing that lowest energy peak must be $d_{xy} \rightarrow d_{x^2-y^2}$ (${}^1A_{1g} \rightarrow {}^1A_{2g}$), a conclusion which supports the proposal that the order of energy levels is $d_{xy} > d_{z^2}$.

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Ammonia Proton Contact Shift Studies. π Interaction of Ammonia with Metal Ions

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Proton contact shifts for many first transition series hexaaquometal ion complexes have recently been reported.^{1,2} These studies suggest that a π -donation

(3) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

(4) See footnotes in ref 3.

(5) P. Ray, *Chem. Rev.*, **61**, 313 (1961).

(1) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 54 (1966).

(2) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).