noticeable color changes were observed when absolute ethanol solutions containing these chelates were converted to glasses by cooling to liquid nitrogen temperatures.

Upon excitation to a charge-transfer excited state (π^*,d) there will be considerable redistribution of the electron density in the chelate because of transfer of the excited electron from an orbital centered at the metal ion to one largely delocalized on the ligands. Thus, it is anticipated that there are large and important increases in the metal ion–ligand bond distances when these chelates are excited to charge-transfer states; in consequence the ligand field splitting will be lower in this excited state of the chelate.

If the ligand field splitting is lowered sufficiently upon excitation and is then near the magnetic crossover point at room temperature, an excited-state equilibrium will be established between the diamagnetic (t_{2g}^5, π^*) and the paramagnetic (t_{2g}^3, e_g^2, π^*) configurations. The luminescence intensity will be decreased accordingly—approximately in proportion to the extent of crossover to the high-spin state. In this case not only is the intersystem crossing rate constant greatly enhanced by the formation of the high-spin paramagnetic species, a group of closely spaced energy levels, *e.g.*, ligand field states of the high-spin species, are also created; these are available to the excited species and their presence would enhance further the probability of nonradiative decay of the excitation energy.[1,9]

The extent of crossover will be governed by a Boltzmann-like distribution, and a very marked temperature dependence is anticipated. The smaller excited state ligand fields, Dq^*, that exist with the Fe(II)–imines and with the most hindered Ru(II) and Ir(III) chelates could result in nearly complete crossover to the high-spin forms at room temperature. Thus, luminescence would not be observed. Reducing the sample solution temperature to form a rigid glass might permit observation of the characteristic charge-transfer luminescence. The experimental facts are consistent with these explanations: the imine chelates of Fe(II), the metal ion which would show the smallest ligand field splittings, show no luminescence even at the lowest temperatures. The most hindered ligands, 2-Me-phen and ter, form chelates with Ru(II) that do not luminesce at room temperature but do emit the characteristic red-orange luminescence at the temperatures of liquid nitrogen. With Ir(III), the metal ion that would be subject to the largest ligand field splittings, only the most hindered ligand, 2-Me-phen, forms a chelate that fails to show charge-transfer luminescence in fluid solution although this chelate too emits in rigid media.

These considerations can account for the observed phenomena under discussion regardless of the kind of luminescence (fluorescence or phosphorescence) and the multiplicity (singlet or triplet) of the emitting excited state in the low-spin cases. Two alternatives should also be considered, particularly for the Fe(II)–imines. The existence of triplet ligand field excited state(s) ($^3T_{1g}$, $^3T_{2g}$) at energies below the lowest energy charge-transfer excited state (emission from such states might be in the near-infrared and not detectable in the present work) has been discussed by Palmer and Piper;[13] no firm conclusions were reached. Distortion of the excited chelate species from octahedral microsymmetry might cause a triplet ($^3T_{1g}$) to assume lowest energy among the ligand field states;[20] paramagnetic quenching of the luminescence would probably result in this event.

Acknowledgment. This work was supported by the National Science Foundation (Grant GP-8585).

Electron Transfer through Organic Structural Units. VI. Steric Assistance in the Outer-Sphere Reduction of Pyridinepentaamminecobalt(III) Derivatives[1]

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Received March 8, 1969

Abstract: Pentaamminecobalt(III) complexes of pyridine, five alkyl-substituted pyridines, and quinoline have been prepared as their perchlorates, and their rates of reduction with Cr(II) at 25° have been measured. Reductions proceed *via* an outer-sphere mechanism with formation of $Cr(H_2O)_6^{3+}$ and release of the heterocyclic ligand. Specific rates for the 3- and 4-substituted pyridine complexes are comparable to that for the unsubstituted pyridine derivative, but the complexes of 2-methylpyridine and quinoline are reduced about 100 times as rapidly as are the other members of the series. These two complexes, for which molecular models show serious interference between the organic ligand and *cis* ammonias, also undergo aquation with loss of the heterocyclic base much more rapidly than do the 3- and 4-substituted complexes. This work reinforces an earlier suggestion, arising from the study of the reduction of carboxamidopentaamminecobalt(III) derivatives, that, for outer-sphere reductions of complexes of this sort, a major requirement for activation is the stretching of the Co(III)–N bonds.

The reductions, with Cr(II), of carboxylatopentaaminecobalt(III) complexes proceed with transfer of the carboxylate group from cobalt to chromium and are subject to steric retardation. The formato derivative (I, R = H) is reduced about 10,000 times as

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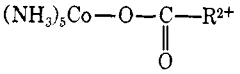
[1] From the M.Sc. thesis of Y. W. This work was supported in part by the Petroleum Research Fund of the American Chemical Society under Grant 2868-A3.

Table I. Pentaamminecobalt(III) Perchlorates, $RCo(NH_3)_5(ClO_4)_3$[d]

R	Method	Heating time, min (temp, °C)	% Co		λ_{max}, mμ	ε
			Calcd	Found[a]		
2-Methylpyridine	TEP	5 (95)	11.0	10.7	460	90
3-Methylpyridine	DMF	5 (100) 15 (70)	11.0	10.5	475[b]	60
4-Methylpyridine	DMF	15 (70)	11.0	11.3	476	68
4-Ethylpyridine	DMF	20 (70)	10.8	10.7	475[c]	73
Quinoline (IV)	TEP	10 (70)	10.3	9.9	476	70
3,5-Lutidine (III, X = 3,5-$(CH_3)_2$)	DMF	5 (100) 15 (70)	10.8	10.5	475	62
4-Cyanopyridine	TEP	15 (65)	10.7	10.6	468	78

[a] See ref 5. [b] Shoulder at 330 mμ in addition to λ_{max} listed. [c] Additional maximum at 332 mμ (ε 98). [d] For preparations of the parent pyridine complex, see ref 7 and 9.

rapidly as the triethylacetato (I, R = CEt_3), and the specific rates of reduction of a number of aliphatic complexes of this type correlate well with Taft's steric substituent parameters.[2] On the other hand, Cr(II) reductions of carboxamido complexes (II) have been found to be fastest when groups R and R′ are sterically most demanding. This contrasting trend, taken in conjunction with the isolation of $Cr(H_2O)_6^{3+}$ as the sole Cr(III) product from the reactions of the amide derivatives,[3] indicates that such reductions employing an outer-sphere path are subject to steric acceleration and suggests an activation process for which a major requirement is stretching of the Co(III)–N bonds.

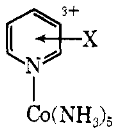


$(NH_3)_5Co{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R^{2+}$

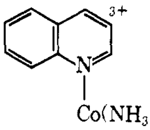
I

$(NH_3)_5Co{-}O{=}\underset{\displaystyle NR_2}{\underset{|}{C}}{-}R'^{3+}$

II



III



IV

The range of specific rates in the carboxamido series is narrow (only a single power of ten), and the picture may well be clouded by electronic effects which for these systems are, at present, of unknown magnitude and direction. Another, perhaps less serious, doubt pertains to the proposed mechanism, for in some cases where $Cr(H_2O)_6^{3+}$ is isolated as a product there is the possibility that it may be formed during the isolation procedure by aquation of a less stable inner-sphere oxidation product in which Cr(III) is bound to the organic ligand.[3,4] These points prompted the present further study of steric effects in outer-sphere reductions of Co(III), dealing with the $Co(NH_3)_5$ complexes of quinoline (IV) and substituted pyridines (III). Here, the absence of localized unshared electron pairs rules out the inner-sphere path for reduction, and the oxidants chosen allow less variation in electronic effects than was the case with the amide complexes. We find the reductions of these heterocyclic derivatives to be subject to steric acceleration similar to, but more striking than, that observed for the amide derivatives.

Experimental Section

Materials. Aquopentaamminecobalt(III) perchlorate,[5] azidopentaamminecobalt(III) perchlorate,[6,7] and nitrosyl perchlorate[8] were prepared as described. Sodium perchlorate, dimethylformamide (DMF), absolute methanol, and anhydrous ether were used as received. Triethyl phosphate was dried over Linde activated molecular sieves (Type 4A or 5A); heterocyclic ligands (Aldrich) were distilled if discolored and then dried over molecular sieves. Cr(II) solutions were prepared by reduction of a 1 *M* $Cr(ClO_4)_3$ solution in 1 *M* $HClO_4$ using zinc amalgam;[4,5] these solutions were protected from air by serum caps.

Preparation of Complexes. Complexes were prepared from the aquo derivative in DMF[4,9] or from the azido derivative in triethyl phosphate.[7] Heating times and temperatures are given in Table I. The DMF method is the more convenient, but it failed for the 2-methylpyridine and quinoline complexes and gave a very impure product with 4-cyanopyridine.[4] For preparations in triethyl phosphate, both the solvent and ligands were kept rigorously dry, and the operations were protected from atmospheric moisture until the heterocyclic derivative had formed (when this was not done, the desired organic complexes, which were yellow when pure, were seriously contaminated with the aquopentaammine complex, coloring them red or brown). Typically, a 0.5-g sample of the azidopentaammine complex was dissolved in 5 ml of TEP, and dry nitrosyl perchlorate was added. The mixture was allowed to stand at room temperature until bubbling ceased and the color changed from violet to rose-red (about 10 min). Unreacted $NOClO_4$ was filtered off, and 5 ml of heterocyclic base was added. The mixture was then heated (times and temperatures are listed in Table I), and the rose color of the solution changed to brown. A saturated methanolic solution of sodium iodide was then added to precipitate the desired complex as its iodide.[10] The yellow iodide was filtered off, washed with ethanol and then with ether, and recrystallized from a minimum volume of water. The recrystallized iodide was converted to the perchlorate by dissolving in water and then saturating with $NaClO_4$. The saturated solution was filtered rapidly and cooled slowly to −10°. The precipitated complex was then filtered off and dried *in vacuo* at 40°. This method, as well as the DMF preparation, failed with 3-cyanopyridine and 2,6-dimethylpyridine.

Kinetic Experiments. Rates were evaluated by following the decrease in absorbance at the visible absorption maxima of the cobalt(III) complexes. Reductions were carried out in a 1-cm cylindrical cell covered by a syringe cap through which Cr(II) was injected. Ionic strengths were kept near 1.3 by addition of $HClO_4$. Complexes weighing 7–15 mg were used. Rates were run under pseudo-first-order conditions with the ratio Cr(II)/Co(III) about 10. Temperatures were kept constant at 25.0 ± 0.2° during the entire series of experiments. Rate constants taken from several points in a single run agreed to 5% and from different runs to better than 10%. The solutions of the complexes of quinoline, 2-methylpyridine, and 4-cyanopyridine were prepared immediately before the kinetic runs; these complexes hydrolyze perceptibly to the aquo

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(2) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966).

(3) E. S. Gould, *ibid.*, **90**, 1740 (1968).

(4) E. S. Gould, *ibid.*, **89**, 5792 (1967).

(5) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

(6) M. Linhard and H. Flygare, *Z. Anorg. Allgem. Chem.*, **262**, 328 (1950).

(7) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

(8) G. Brauer, "Handbook of Preparative Inorganic Chemistry," English ed, Vol. 1, Academic Press, New York, N. Y., 1965, p 320.

(9) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965).

(10) The heterocyclic iodides prepared here are photosensitive; dry samples darken when exposed to light. In recrystallizing these iodides, care should be taken to minimize thermal decomposition; preparations should not remain above 60° for more than a few minutes. The perchlorates, in contrast to the iodides, appear to be stable at room temperature in the light.

complex on standing at room temperature, but such hydrolyses are negligibly slow compared to the Cr(II) reductions under our conditions.

Cation-Exchange Separations. Bio-Rad 50W-X2 resin (200–400 mesh) was washed successively with water, 4 *N* NaOH, water, 30% H_2O, water, 60% $HClO_4$, water, and finally with 0.02 *M* $HClO_4$. The spectrum of a dilute $HClO_4$ solution eluted from the resin which had been so treated showed no absorption peaks in the visible or ultraviolet. The resin was stored in contact with 0.02 *M* $HClO_4$.

Reaction mixtures for the ion-exchange chromatographic experiments with the complexes of 3-methyl- and 2-methylpyridine were 0.02 *M* in Co(III) and 0.06 *M* in Cr(II); reaction was allowed to proceed for four half-life periods in a small vial sealed with a rubber serum cap. Air was then bubbled through the mixture to oxidize unreacted Cr(II), and the solution was added to the resin column. Elution with 2 *M* $NaClO_4$ (50 sec/ml) removed, in succession, Co(II), the unreacted Co(III) in very small amount, and then $Cr(H_2O)_6^{3+}$. Dimeric and polymeric forms of Cr(III) remained on the column and were not eluted. The extinction coefficients for the Cr(III) band were 13.4 at 574 mμ (very broad) and 15.4 at 408 mμ (lit.[11] 13.6 and 15.6). These experiments confirm that, except for the dimeric and polymeric materials, the only Cr(III) substance obtained was the aquo complex. This was obtained in 94% yield from the 2-methyl complex and in 92% yield from the 3-methyl complex.

Results and Discussion

Rate data are summarized in Table II. Reactions were carried out in 1.0 *N* $HClO_4$; in view of the behavior of other pyridine derivatives,[4] rates were assumed to be independent of acidity. The absence of localized unshared electron pairs on the oxidant would appear to rule out an inner-sphere path for these reactions; moreover, Nordmeyer and Taube[12] have experimentally established an outer-sphere path for reduction of the parent pyridine derivative, and we have confirmed this for reductions of the 2- and 3-methylpyridine complexes.

Table II. Specific Rates for Chromous Reduction of Pentaamminecobalt(III) Complexes[a]

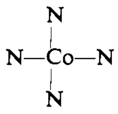
Ligand	10^3k
Pyridine	4.1[b]
2-Methylpyridine	190
3-Methylpyridine	4.5
4-Methylpyridine	1.6
4-Ethylpyridine	2.6
3,5-Lutidine	2.2
Quinoline	250

[a] Specific rates in M^{-1} sec^{-1} at 25.0°; $(H^+) = 1.0$ *M*; $\mu = 1.3$; $(Cr^{2+}) = 0.1$ *M*; $(Co^{III}) = 0.005$–0.009 *M*. [b] Recent literature values for this complex[12] are 0.00384 at $(H^+) = 0.1$ and 0.00402 at $(H^+) = 0.63$ *M*. Both values are at $\mu = 1.0$.

The rate differences here noted among the 3- and 4-alkylpyridine complexes are too slight to warrant rationalization on a structural basis; of greater interest are the values for the 2-methylpyridine (III, R = 2-CH_3) and quinoline (IV) derivatives. Note that the specific rate for the 2-methylpyridine complex is over 100 times that for the 4-methyl isomer (although electronic effects in the two complexes should be very similar), and the quinoline complex is found to be reduced still more rapidly. These are almost certainly steric effects, for molecular models show that two of the five Co-bound ammonia ligands seriously interfere with the methyl group of the 2-pyridine complex and with the *peri*-H of the quinoline derivative; such interference occurs in none of the other complexes in the series. The trend here is thus in the same direction as that reported in reduction of carboxamido $Co(NH_3)_5$ derivatives,[3] but the magnitudes are more convincing.

Steric assistance to outer-sphere reduction brings to mind that described for aquation of Co(III) complexes,[13] especially since the 2-methylpyridine and quinoline complexes undergo perceptible aquation when their aqueous solutions stand for several hours at room temperature, in contrast to solutions of the 3- and 4-alkylated pyridine complexes, which remain unchanged for weeks. However, the similarities are little more than formalistic. Whereas the trend in aquation implies a dissociative transition state, *i.e.*, one in which progress toward bond-breaking overshadows any beginnings of bond-making, such a discription is obviously inapplicable to outer-sphere redox reactions, in which bonds are neither made nor broken. It is suggested instead that such assistance in the redox series is related to the necessity for reorganization of the inner sphere of ligands about Co(III) preceding the electron transfer. In accordance with Marcus's picture,[14] outer-sphere reduction of a Co(III) complex occurs most readily when such a complex closely resembles the corresponding Co(II) complex. Hence, it seems likely that an important requirement for activation is the stretching of the Co(III)–N bonds so that they more nearly approach the length of Co(II)–N bonds, under which circumstances Co(III) can accept the incoming electron while undergoing a minimum of atomic motion.[15] Severe steric crowding would be expected to favor stretching.

The parent pyridine complex, the quinoline complex, and the 3- and 4-alkylated derivatives show the visible d–d absorption maximum at 475–476 mμ, typical of $N\text{-}Co(NH_3)_5$ complexes, but the 2-methylpyridine derivative exhibits a maximum at 460 mμ. There is little that can be said at this time about this very surprising value (which has been checked with three separate preparations of this derivative), except that steric interactions almost certainly keep the pyridine ring well out of the



$$\begin{array}{c} N \\ | \\ N\text{—}Co\text{—}N \\ | \\ N \end{array}$$

planes in the coordination octahedron and thus diminish overlap between the π orbitals of the ring and the $d_{x^2-y^2}$ orbitals of the metal. The difficulty is that, as has been noted by a number of authors,[16] ligands such as

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[11] J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

[12] F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

[13] R. G. Pearson, C. R. Boston, and F. Basolo, *ibid.*, **75**, 3089 (1953).

[14] See, for example, R. A. Marcus, *J. Chem. Phys.*, **24**, 970 (1956).

[15] A second barrier to reduction is the change in multiplicity which occurs when Co(III), with no unpaired electrons, is converted to Co(II), which has three. Activation probably requires excitation of a t_{2g} electron in Co(III) to an e_g orbital (for a recent summary of this view, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1968, p 511). It might then be argued that steric crowding, which would be expected to weaken the ligand field about Co^{3+}, should facilitate excitation, hence accelerate reduction. However, the visible spectrum of the 2-methyl compound indicates a ligand field splitting slightly *greater* than that for the uncrowded complexes. It appears, then, that this effect is of secondary importance.

[16] See, for example, B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 193.

pyridines, which have both bonding and antibonding π orbitals, may, depending on other circumstances, lead either to a larger or smaller crystal field splitting than would be observed with a (hypothetical) ligand which is otherwise similar but incapable of π bonding. Since the direction of the spectral effects resulting from π interaction cannot be simply predicted, the effect of removing such interaction is likewise in doubt.

For the 4-cyanopyridine derivative, the reduction path is not simple. Disappearance of Co(III) is not clearly first order in Co(III), as is observed with the other complexes. This system, in which reduction of the ligand may compete with reduction of Co(III),[2,9] is the subject of investigation now in progress.

Water Exchange between Solvent and Aquoethylenediaminenickel(II) Complexes

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Abstract: Water exchange rates with $Ni(H_2O)_6^{2+}$ (pH 6), $Ni(H_2O)_4(en)^{2+}$, and $Ni(H_2O)_2(en)_2^{2+}$ are reported. The k_1 (25°, sec^{-1}) values for a particular water molecule are $4.4\ (\pm 0.2) \times 10^4$, $4.4\ (\pm 0.2) \times 10^5$, and $5.4\ (\pm 0.3) \times 10^6$, respectively. The corresponding ΔH^* values are 10.3 ± 0.5, 10.0 ± 0.5, and 9.1 ± 0.5 kcal mole^{-1}. Scalar coupling constants (A/h) in the same order are $2.2\ (\pm 0.4) \times 10^7$, $2.2\ (\pm 0.2) \times 10^7$, and $2.3\ (\pm 0.2) \times 10^7$ cps. T_{1e} for $Ni(H_2O)_2(en)_2^{2+}$ is *ca.* 2.5×10^{-12} sec. Some discussion of the effects of water substitution on lability of the remaining water is given.

The studies reported here are in continuation of investigations of the effects on water exchange rates caused by substitution in the aquonickel(II) ion.[2–4] Using ^{17}O nmr, direct measurements of these effects can be made. In addition to interest in the effects themselves, comparisons with substitution rates in these ions may shed further light on the substitution mechanisms. The ethylenediamine complexes of nickel(II) are reasonably well characterized and lend themselves well to such studies.

Experimental Section

The nmr equipment previously described[5] was used with the important modification that a Varian 24.6-kG magnet with a field inhomogeneity of *ca.* 0.05 G was employed. The ^{17}O resonance was ordinarily observed at 14.19 MHz. Sample temperatures were controlled to ±0.10° using an ethanol circulation system below 50° and to ±0.3° above 50° using a thermostated air flow. Signal enhancement was obtained using a Fabri-Tek LSH 1024 point signal averager.

The water used was enriched to 7 atom % ^{17}O (56.3% ^{18}O and normal H content) and made by YEDA R & D Co. Ltd., Rehovoth, Israel. It was distilled *in vacuo* for reuse. Other reagents used were Mallinckrodt AR $Ni(NO_3)_2 \cdot 6H_2O$, Baker Analyzed ethylenediamine (en) (99.6%), and B & A reagent HNO_3.

Solutions were prepared from measured amounts of all reagents. The ionic strength was fixed by the nickel salt, and nitric acid concentrations and varied from 0.51 to 0.53 *M*. Measurements of pH were made using a Beckman Research Model meter. Solution composition calculations were done using the known starting amounts of all reagents. The measured pH's were only used to obtain estimates of species concentrations for use in the computer program based on SECANT 1620.[6] Values used for acid dissociation constants of enH^+, enH_2^{2+}, and the nickel(II)–en complex constants were those of Basolo and Murmann[7] at $\mu = 0.5$. Effects of temperature change on the various K_{eq} values were calculated from the calorimetric enthalpy values (assumed independent of temperature) of Holmes and Williams[8] at $\mu = 0.3$. Results of the computations indicated that solution compositions were essentially constant (±1%) over the temperature range used. The relative amounts of the various nickel species are given in Table I for the solutions used.

Treatment of Data and Results

The complexities of the solutions and the nmr phenomena involved required a moderately involved treatment of the data. Detailed basic considerations have been given previously.[5,9,10] The observed line-broadening data were treated in terms of the quantity $T_{2p}' \equiv 2M(\mathrm{Ni})/\gamma\Delta'$ where M(Ni) refers to total nickel concentration, γ is the magnetogyric ratio for ^{17}O (3628 G^{-1} sec^{-1}), and $\Delta' = W_{obsd} - W_0$, where W_{obsd} is the full nmr line width at half-maximum absorption (absorption curve) for solutions containing Ni(II) and W_0 is the same quantity for the appropriate blank not containing Ni(II). The observed width of the blank varied from 0.16 to 0.26 G as a function of temperature. The data are listed in Table II and plotted as $\log T_{2p}'$ *vs.* $10^3/T$ in Figure 1. Measured chemical shifts are treated in terms of the quantity $Q(\mathrm{obsd}) = TSM(H_2O)/M(\mathrm{Ni})$, where T is the absolute temperature, S is the chemical shift in parts per million relative to the $H_2{}^{17}O$ blank, and the molarities refer to total concentrations. Values

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[1] To whom inquiries should be addressed. This work supported by U.S.A.E.C., Contract No. AT(54-1)-2040, and is Report No. RLO-2040-9.

[2] S. Marks, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 7, 836 (1968).

[3] S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *ibid.*, 7, 929 (1968).

[4] R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *ibid.*, 5, 1906 (1966).

[5] R. Murray, H. W. Dodgen, and J. P. Hunt, *ibid.*, 3, 1576 (1964).

[6] Written by J. T. Godfrey, Advanced Technology Laboratories, General Electric Co.

[7] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, 74, 5243 (1952).

[8] F. Holmes and D. R. Williams, *J. Chem. Soc., A*, 1256, 1702 (1967).

[9] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

[10] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 4, 1061 (1965).