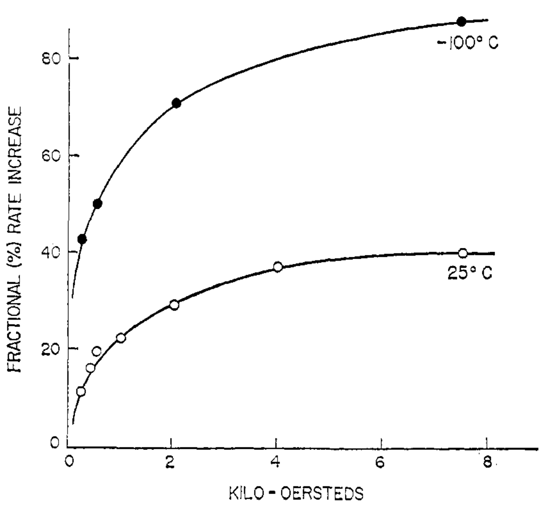

Figure 2. Fractional increase in parahydrogen conversion rate at 25 and −100° as a function of extrinsic field for 0.0028% chromia–alumina.

to be noted that a small fraction of the total chromium in the appropriate layer state would be sufficient to account for our observations. It is to be expected that, of the three samples investigated, that containing 0.0028% Cr_2O_3 would have the largest fraction of its chromia in this layer state.[5]

These observations of reaction acceleration caused by an extrinsic magnetic field, and the suggestion that the effect is due to some field-induced increase of effective magnetic moment in the catalyst, suggest that a reexamination of experimental data is called for in several areas. In particular, doubt is placed on the interpretation of previous magnetic susceptibility, epr, and nmr work on systems containing extremely thin layers of paramagnetic species in which exchange interaction may be present. This includes almost all transition metal oxides of interest in heterogeneous catalyst.

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(5) P. W. Selwood, forthcoming paper.

Makoto Misono, P. W. Selwood
Department of Chemistry, University of California
Santa Barbara, California 93106

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A Hexacoordinated Low-Spin Cobalt(II) Complex

Sir:

The interesting question as to the existence of the truly hexacoordinated complex molecule, $Co^{II}L_6$, with spin $S = {}^1/_2$ has not yet been answered.[1] In this paper we present evidence to show that the unstable paramagnetic species derived by allowing phenyl isocyanide to react with pentakis(phenylisocyano)cobalt(II) perchlorate[2,3] (I) is a hexacoordinated low-spin Co(II) complex. The solvent used was $CHCl_3 + CH_2Cl_2$ (1:1), and all experiments were carried out at Dry Ice–acetone temperature (∼−50°), unless otherwise specified.

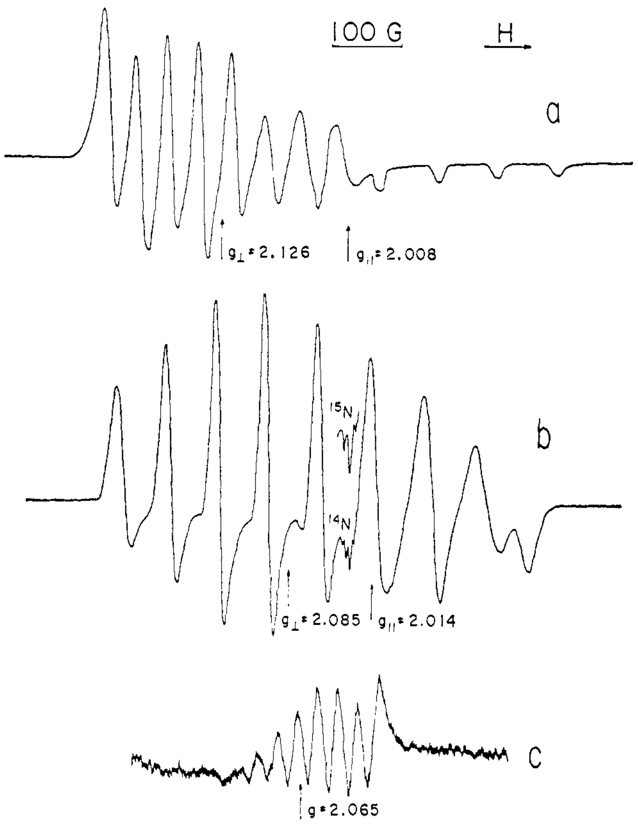

Figure 1. Esr spectra of cobalt(II) phenyl isocyanide (L) complexes, in solution: (a) $Co^{II}L_5$ at 77°K; (b) $Co^{II}L_6$ at 77°K; (c) $Co^{II}L_6$ at 248°K. The esr parameters of the frozen systems were determined by computer simulation.

On adding slightly more than 1 equiv of isocyanide to the solution of blue hydrated form of I, a reversible color change from blue-green to orange was seen on freezing at 77°K. With a large excess of isocyanide, the orange color remained on thawing, but at room temperature the color quickly turned brownish. Thus there appears to be an equilibrium between I and some unstable orange species II.

The conversion from I to II can be followed better by observing esr absorption at 77°K. Progressive addition of isocyanide to the solution of I causes a monotonic decrease in the spectrum (Figure 1a) of I, with a concomitant rise of the new peaks shown in Figure 1b, presumably of the orange species II. The spectrum of I was completely replaced by that of II when 1.3 ± 0.1 mole equiv of isocyanide was added to a 10^{-2} *M* solution of I. The latter spectrum can be interpreted as the superimposed parallel and perpendicular absorptions, each split into eight lines by ^{59}Co nuclear interaction with coupling constants 64.0 and 75.0 G, respectively. The liquid solution shows an eight-line spectrum (28-G splitting) with unsymmetrical intensity distributions (Figure 1c). The *g* values and the hyperfine (hf) constant in frozen and liquid solution, respectively, are consistent with each other, indicating that the two spectra do represent the same species.

The same spectrum of II, but less intense, was obtained when varying amounts of H_2O, NH_3, or $NH_2CH_2CH_2NH_2$ were added to the solution of I. These reagents, which decompose I in solution at room tem-

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

(2) A. Sacco, *Gazz. Chim. Ital.*, 84, 370 (1954); J. M. Pratt and P. R. Silverman, *Chem. Commun.*, 117 (1967).

(3) J. M. Pratt and P. R. Silverman, *J. Chem. Soc., A*, 1286 (1967).

perature, probably liberate the isocyanide from part of I, which then adds to the rest of I to form II at low temperatures.

The possibility that the unstable species II is the hexacoordinated low-spin complex is supported by the esr spectrum: the five-line super-hf structure (5.5-G splitting) in one of the parallel peaks with intensity ratio of approximately 1:2:3:2:1 was proved by ^{15}N labeling to be caused by two nitrogen nuclei. Consequently, there must be two isocyanide groups in the axial positions. This fact, combined with the above observations, immediately points to the hexacoordinated structure. Furthermore, the observed $g_{\parallel}$ of II is considerably larger than any of the known tetra- and pentacoordinated phenyl isocyanide low-spin complexes of Co(II),[4] in which $g_{\parallel}$ (2.003–2.008) is closer to the free-spin value, 2.0023.

From all these observations, we conclude that the species II is in fact the complex ion, Co^{II} (phenyl isocyanide)$_6$. Recently Pratt and Silverman[3] reported visual observation of similar color change ("mauve" instead of "orange") with the corresponding methyl isocyanide complex. These authors presumed that the mauve species may be a hexa(isocyanide) complex, but no evidence was given. Several Co(II) complexes were reported by Stoufer and others,[5] in which the high- and low-spin states are apparently in equilibrium. The integrated intensity of the spectrum at 77°K of II represents all the Co(II) in the system within ±10%. Also II does not show the line broadening even at 248°K in significant contrast to the systems of Stoufer and others.

Since narrow esr absorption is obtained even near 0°, the geometrical structure of II must be axially distorted from the ideal octahedral symmetry so as to lift the degeneracy of e_g orbital levels, as, indeed, is indicated in the frozen spectrum. The axial distortion may be effected by interaction with surrounding molecules, especially with the counterions (ClO_4^-). It could also be due to the static Jahn–Teller effect, in which case the unpaired electron orbital would be the vibronic mixture[6] $\psi = \cos^2(\phi/2)\,(d_{3z^2-r^2}) + \sin^2(\phi/2)\,(d_{x^2-y^2})$. This is, indeed, consistent with the comparatively large positive deviation of $g_{\parallel}$, since $d_{x^2-y^2}$ will contribute to the positive shift through coupling with the lower t_{2g} orbitals. In this connection it is worth pointing out that similar positive shifts were also found with the low-spin cobalt(II) phthalocyanine with its axial site occupied by heterocyclic amines,[7] where the ligand field is expected to be near octahedral.

[4] N. Kataoka and H. Kon, to be published.

[5] J. G. Schmidt, W. Brey, Jr., and R. C. Stoufer, *Inorg. Chem.*, 6, 268 (1967).

[6] M C. M. O'Brien, *Proc. Roy. Soc.* (London), A281, 323 (1964).

[7] J. M. Assour, *J. Am. Chem. Soc.*, 87, 4701 (1965).

Nobuko Kataoka, Hideo Kon
Laboratory of Physical Biology,
National Institute of Arthritis and Metabolic Diseases
National Institutes of Health, Bethesda, Maryland 20014

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The Photochemical Addition of Alcohols to Purine[1]

Sir:

We report here a new photoreaction of purine in deoxygenated alcohol solution which results in efficient addition of α-hydroxyalkyl groups to the purine 6 position. Figure 1 shows typical absorption spectrum changes resulting from irradiation of purine in methanol. The new peak near 292 nm and clean isosbestic points are also found after irradiation in deoxygenated ethanol, 2-propanol, and 1-butanol. Photolysis of purine in oxygen-saturated ethanol leads to different products, with bands near 280 and 310 nm.

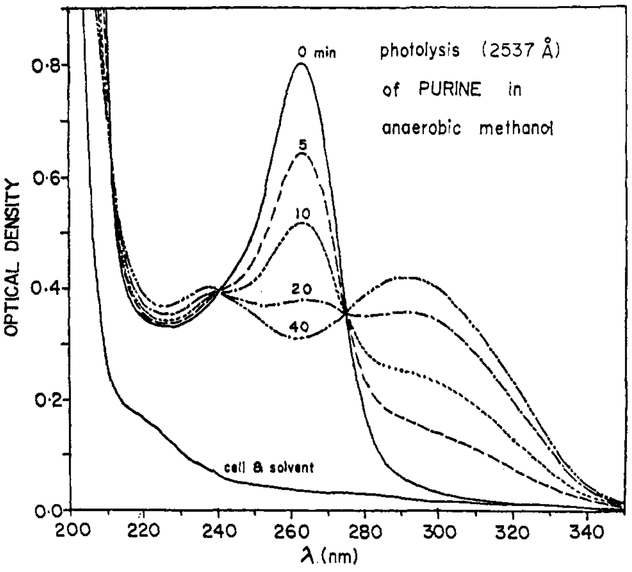

Figure 1. Spectral changes during photolysis (2537 Å) of purine in degassed methanol. Initial purine concentration 7.0×10^{-5} *M*; $I_0 = 6 \times 10^{-8}$ einstein/(cm^2 min); cell path = 14.7 mm; time in minutes.

Photoproducts of the anaerobic reaction with methanol, ethanol, and 2-propanol were recovered by evaporation, followed by recrystallization from dry ethylene chloride–methanol. The ethanol reaction yields two isomeric products in about equal amounts which were separated by fractional crystallization from ethylene chloride–methanol and chloroform–ethanol. Elemental analyses and mass spectrometer molecular weights correspond to 1:1 purine–alcohol adducts. Group analyses showed negligible alkoxyl or N-alkyl content. The nmr spectra of the four adducts in DMSO-d_6 solution all show a band at δ 4.6–4.9 ppm (one proton) relative to TMS and two sharp singlets at 6.9 and 7.2 ppm, above a broad absorption in the 6–8-ppm region. Addition of excess D_2O eliminates the broad absorption, producing a three-proton HOD peak and leaving one proton each for the 6.9- and 7.2-ppm singlets. We assign the three exchangeable protons to one OH and two NH groups and the two downfield protons (6.9 and 7.2 ppm) to ring CH groups associated with residual conjugation. The isopropyl adduct (Figure 2) shows sharp singlets at 0.97 and 1.18 ppm (three protons each) which can arise only from two *nonequivalent* methyl groups on the alcohol moiety. The remaining proton at 4.62 ppm must therefore be the purine CH at the site of addition. The nmr spectra for the other adducts are assignable in a similar manner by successively replacing the methyls of 2-propanol with hydrogens and retaining the nonequivalence of the a,b positions. In all cases, the spectra (further studied

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