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The Complexes of Bromine and Iodine with Bis(diphenylglyoximato)nickel(II) and Bis(diphenylglyoximato)palladium(II)

Sir:

Several years ago Simek[1] reported magnetic studies of Ni(dpg)$_2$Br and Ni(dpg)$_2$I [dpg = $(C_6H_5)_2C_2N_2O_2H^-$, the anion of diphenylglyoxime] from which he concluded that these are not simple nickel(III) complexes. We have prepared the two palladium members of this series, and we wish to summarize evidence that the four compounds are inclusion-like molecular complexes stabilized by charge-transfer interaction.

Mixing warm *o*-dichlorobenzene solutions of bis(diphenylglyoximato)nickel(II), Ni(dpg)$_2$, or bis(diphenylglyoximato)palladium(II), Pd(dpg)$_2$, and the elemental halogen gave upon standing analytically pure samples of Ni(dpg)$_2$Br, Ni(dpg)$_2$I, and Pd(dpg)$_2$I. Pd(dpg)$_2$Br was formed as a mechanical mixture with Pd(dpg)$_2$, from which individual crystals could be separated and then identified by appearance, X-ray diffraction patterns, and epr spectra. The four M(dpg)$_2$X compounds occur as black needles and are easily distinguished from the two parent compounds, dark red Ni(dpg)$_2$ and yellow Pd(dpg)$_2$.

The needle-like crystals of the four M(dpg)$_2$X compounds are isomorphous. Dimensions of the tetragonal unit cells, measured from sodium chloride calibrated (a = 5.628 A) single-crystal precession photographs made with Mo Kα radiation, are given in Table I. Density measurements show that there are four M(dpg)$_2$X formula units per primitive unit cell. Systematic extinctions give P4/ncc (D_{4h}^8) as the common space group.[2]

Table I. Crystal Data for M(dpg)$_2$X Complexes

	Ni(dpg)$_2$Br	Ni(dpg)$_2$I	Pd(dpg)$_2$Br	Pd(dpg)$_2$I
Unit cell				
a, ± 0.06, A	19.51	19.92	19.78	20.17
c, ± 0.02, A	6.72	6.56	6.57	6.52
Density				
Calcd, g/cm^3	1.60	1.69	1.72	1.78
Found, g/cm^3	1.64	1.72	1.70	1.78
Epr data				
$g_\perp$ ± 0.0002	2.0221	2.0222	2.0177	2.0166
$g_\parallel$ ± 0.0004	2.0118	2.0121	2.0097	2.0088
Δg ± 0.0006	0.0103	0.0101	0.0080	0.0078

The unit cell dimensions together with a consideration of the distribution of the metal and halogen atoms among the equipoints of rank four[3] of space group P4/ncc strongly suggest that the structures are derived from those of Ni(dpg)$_2$ and Pd(dpg)$_2$[4] and consist of M(dpg)$_2$ molecules (with square-planar coordination) arranged like interlocking blocks in stacks parallel to the c direction with a metal–metal distance of $c/2$ in each stack. Both the equipoint analysis and the three-dimensional Patterson function (calculated with the intensity data collected from Ni(dpg)$_2$I) indicate that the halogens lie in channels which are surrounded by phenyl groups and are parallel to the M(dpg)$_2$ stacks. These halogen chains are thought to be the source of the strong, broad visible absorption which is more intense for light polarized parallel to the c direction. The 001 projection of this structural model can be refined with the $hk0$ data for Ni(dpg)$_2$I to a residual parameter $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$. The complete three-dimensional solution of the structure has not yet been achieved.

Elemental iodine is evolved slowly when Ni(dpg)$_2$I is left standing at room temperature and more rapidly when it is warmed in an oven. The loss of iodine is eventually quantitative. The iodine-free solid residue is initially rust colored and has an X-ray powder pattern and a visible absorption spectrum (mull) which are different from those of either solid Ni(dpg)$_2$I or solid Ni(dpg)$_2$. We believe this initial residue to be a metastable empty "host" form of Ni(dpg)$_2$. Either recrystallization from chloroform or baking at 140° for 24 hr converts it to a more reddish solid which has been shown to be "normal" Ni(dpg)$_2$ by comparison of X-ray powder patterns and visible absorption spectra.

Single crystals of Ni(dpg)$_2$I were examined with a polarizing microscope from time to time while being baked at 50°. The loss of iodine was marked by a substantial reduction in visible absorption which progressed along the needle-like crystals. Single crystal precession X-ray photographs taken before and after this mild heating show that the unit cell constants remain about the same even though a good deal of mechanical damage occurs during the loss of iodine.

The density of Ni(dpg)$_2$I falls to 1.42 ± 0.02 g/cm^3 (flotation method) when the iodine is removed by mild heating.[5] After standing for 24 hr at 145° the density is found to be 1.47 ± 0.01 g/cm^3, the same value obtained for normal Ni(dpg)$_2$.

The visible absorption spectrum of a mulled powdered sample of Ni(dpg)$_2$ shows two bands with λ_{max} 427 and 514 mμ, respectively. The empty host form has a similar spectrum except with λ_{max} 447 and 567 mμ. The shift of the two visible bands to longer wavelength in the metastable host form of Ni(dpg)$_2$ probably results from the shorter Ni–Ni distance (approximately 3.27 A compared to 3.52 A in normal Ni(dpg)$_2$[4]) and is consistent with Drickamer's report[6] of a shift to longer

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(1) M. Simek, *Collection Czech. Chem. Commun.*, 27, 337 (1962).

(2) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952, p 225.

(3) M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, pp 242–258.

(4) Although the crystal structures of the nickel and palladium complexes of diphenylglyoxime are not known in detail, they are reported to be essentially the same as the structure of bis(dimethylglyoximato)nickel(II); see C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958); and D. E. Williams, G. Wohlauer, and R. E. Rundle, *ibid.*, **81**, 755 (1959).

(5) One calculates a density of 1.37 g/cm^3 for the metastable form of Ni(dpg)$_2$, assuming unit cell constants identical with those of Ni(dpg)$_2$I.

(6) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960).

wavelength with increasing pressure for an analogous band in bis(dimethylglyoximato)nickel(II).

When $Ni(dpg)_2I$ is stirred in chloroform at 25°, one obtains a solution which has an absorption spectrum (240–700 mμ) which is simply a superposition of those of $Ni(dpg)_2$ and I_2. There is no spectroscopic evidence for the presence of another species in solution.

An interesting feature common to the four compounds is a prominent epr absorption which disappears when the halogen is driven out. For powdered samples this consists of a double peak, about 20 gauss wide, with the stronger component at lower field. Studies of oriented single crystals of $Ni(dpg)_2I$ show that the doubling arises from magnetic anisotropy. Table I lists $g_\parallel$ and $g_\perp$ (23°), corresponding to parallel and perpendicular orientations of the *c* axes with the magnetic field. We note that the epr spectrum changes more with a change in metal than with a change in halogen. Qualitative observations show that the signal strengths increase with decreasing temperature.

A Gouy bulk magnetic susceptibility measurement for $Ni(dpg)_2I$ gives an uncorrected molar susceptibility of -216×10^{-6} cgs unit at 28°. This diamagnetic susceptibility is in approximate agreement with the results of Simek.[1]

$Ni(dpg)_2I$ is an electrical semiconductor. Its specific conductivity increases with increasing temperature and exceeds that of $Ni(dpg)_2$ by a factor of at least 10^5 at room temperature.

We conclude that the four $M(dpg)_2X$ compounds contain halogen molecules surrounded by and interacting with phenyl groups in a $M(dpg)_2$ host. The characteristic but poorly understood epr spectra apparently result from this charge-transfer interaction. We suspect that these compounds are related to the weakly paramagnetic, semiconducting complexes of iodine with polycyclic aromatic hydrocarbons,[7] but a detailed study of the temperature dependence of the spin concentration will be needed to decide this.

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One Electron Transfer Oxidation of 7,12-Dimethylbenz[*a*]anthracene, a Model for the Metabolic Activation of Carcinogenic Hydrocarbons[1]

Sir:

In spite of a wealth of significant work concerned with the problem of relating the carcinogenicity of certain polycyclic aromatic hydrocarbons to their molecular structure,[2–5] there remains today great uncertainty regarding the basic question of whether it is the hydrocarbon itself or some metabolite produced *in vivo* that is the primary trigger for biological activity. Metabolites of several of the hydrocarbons, mostly phenolic or quinoid in nature, have been isolated, but these have proved to be either inactive or less active than the parent hydrocarbons.[6] We wish to describe a chemical model system capable of converting the potent 7,12-dimethylbenz[*a*]anthracene (DMBA) into biologically more active products.

Polycyclic hydrocarbons possess low ionization potentials and readily form radical cations under oxidizing conditions.[7,8] One electron transfer oxidants should therefore produce such species[9] as reactive intermediates; these could become stabilized either by addition of a nucleophile or loss of a proton, followed by dimerization[10] of the resulting radical or further oxidation of the latter to a cation and subsequent reaction with a medium constituent. The potential biochemical significance of such processes derives from the fact that one electron transfer agents such as manganese dioxide, ferricyanide, and Ce^{IV} have been shown to effect oxidative coupling reactions of phenols *via* radical intermediates[11] to produce from appropriate precursors a wide variety of natural products by pathways paralleling those occurring in plant cells.[12]

We have therefore investigated the action of the above reagents on DMBA, with the results summarized in Table I. With MnO_2[13] 25–35% conversion was achieved in 4 days, whereas almost complete utilization of DMBA within 24 hr was observed with $Fe^{III}Fe^{III}(CN)_6$[14] and $(NH_4)_2Ce^{IV}(NO_3)_6$. $K_3Fe^{III}(CN)_6$ yielded the same products but at a much slower rate. $FeCl_3$ showed no reaction. Fractionation of the MnO_2-oxidation products by preparative tlc on silica gel furnished in addition to DMBA five compounds, identified as DMBA-7,12-peroxide (I),[15] 7,12-benz[*a*]anthraquinone (II), 12-methyl-12-hydroxybenz[*a*]anthrone (III), 7-methyl-12-formyl-BA (IV), and 7-formyl-12-methyl-BA (V).[16] 7-Methyl-12-hydroxymethyl-BA (VI)[17] and 7-methyl-7-hydroxybenz[*a*] anthrone (VII) were isolated in addition to I, II, and III by tlc of the mixture derived by oxidation with $(NH_4)_2Ce^{IV}(NO_3)_6$. I, II, V, and VI were identified by melting point, infrared, nmr, and glpc com-

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[1] This investigation was supported by Public Health Service Research Grant CA 07445 and by Research Career Program Award 5-K6-AM-21846 from the National Institute of Arthritis and Metabolic Diseases.

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