Halogen Oxidation of Bis(diphenylglyoximato) Complexes of Nickel(II) and Palladium(II). Stoichiometry, Structure, and Thermal Stability

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Abstract: Oxidation of orthorhombic $M(HDPG)_2$ (H_2DPG = diphenylglyoxime) with I_2 and Br_2 results in the formation of an isomorphous tetragonal series of complexes of $M(HDPG)_2X_y$ [$M = Ni$, $X = I$, $y \leq 1.02$ (± 0.04), Br, $y \leq 1.14$ (± 0.03); $M = Pd$, $X = I$, $y \leq 1.02$ (± 0.04), Br, $y \leq 1.08$ (± 0.02)] stoichiometry. Oxidation of $M(HDPG)_2$ with an excess of IBr and 1:1 I_2/Br_2 yields complexes of $M(HDPG)_2(IBr)_z$ ($M = Ni$, $z = 0.54$; $M = Pd$, $z = 0.44$) and $M(HDPG)_2I_xBr_y$ ($M = Ni$, $x = 0.45$, $y = 0.67$; $M = Pd$; $x = 0.45$, $y = 0.44$) stoichiometries, respectively. Differential scanning calorimetry and thermal gravimetric analysis data show that halogen is lost from these halogen-containing complexes to regenerate the orthorhombic $M(HDPG)_2$ compound. The bromine-containing complexes lose ~80% of their halogen prior to the tetragonal–orthorhombic phase transition at ~200 °C and then lose the remaining ~20% immediately after the transition. The exotherm accompanying the phase transition is shown to be associated with a side reaction involving the formation of an impurity phase. Similarly iodine is lost from the iodine-containing complexes in two stages, but these are not obviously associated to the phase transition and there is no impurity-associated exotherm at the phase transition. The behavior of the mixed halogen complexes is more complex than that of the homogeneous materials.

In recent years there has been a renewed interest in mixed-valent and partially oxidized chain inorganic complexes due to the observation of a variety of anisotropic properties associated with the one-dimensionality of the system.[1-9] Most of the one-dimensional complexes studied to date have been stoichiometric and even for the well-established nonstoichiometric $K_2Pt(CN)_4X_{0.30}\cdot 3H_2O$ (X = Cl, Br) doping with the halogen over a range of stoichiometries has not been achieved.[1] Halogen oxidation of bis(diphenylglyoximato) complexes of nickel(II) and palladium(II), i.e., $M(HDPG)_2$ (M = Ni, Pd; H_2DPG = diphenylglyoxime), has been reported to yield dark dichroic complexes of $M(HDPG)_2X$ stoichiometry.[10-12] Preliminary single-crystal x-ray data suggested a parallel stacking of $M(HDPG)_2$ molecules such that the phenyl groups of the $M(HDPG)_2$ planes form a one-dimensional channel which is filled with halogen.[11] Uncertainty persisted, however, as to the form of the halogen and consequently the oxidation state of the metal.[10-13] Attempts to extend the series of complexes by oxidation of bis(diphenylglyoximato)platinum(II) with chlorine, bromine, iodine, and thiocyanogen have lead to the isolation of the diamagnetic hexacoordinate platinum(IV) complexes and no evidence supporting the formation of a partially oxidized phase.[14]

Recently the x-ray crystal structure determination of $Ni(HDPG)_2I$ clearly showed one-dimensional channels containing the iodine.[15,16] The root mean square amplitude of vibration parallel to the iodine channels was reported to be so large (0.75 Å), however, that the presence of I, I_2, or I_3^- could not be differentiated. Raman and ^{129}I Mössbauer data suggest that the channels are principally filled with I_3^-.[15]

Comparison of the divalent $M^{II}(HDPG)_2$ (M = Ni, Pd) and oxidized $M(HDPG)_2X$ complexes reveal significant differences in their properties. The divalent complexes are translucent,[14] possess metal-metal spacings ~3.5 Å,[14] and exhibit conductivities less than 10^{-12} ohm^{-1} cm^{-1}.[18] The oxidized complexes are black to gold and highly reflecting in appearance,[10-12] possess significantly shorter (0.19–0.27 Å) interplanar spacings; and exhibit conductivities approximately five orders of magnitude greater than those reported for the unoxidized complexes.[11,18]

These results suggest that the oxidized complexes can be described by a semiconductor model. Thus, the halogen oxidation appears to have profound effect on the electronic structure. Before the physical properties can be adequately interpreted, however, it is necessary to understand the chemical properties of the system. Herein we report that the previously described $M(HDPG)_2X$ tetragonal structure[11,15] can exist with a wide range of occupancy of the halogen sites and we discuss the thermal stability of this class of one-dimensional complexes.

Experimental Section

Bromine, chlorine, cyanogen bromide, diphenylglyoxime, iodine, iodine monobromide, iodine monochloride, nickel(II) chloride hexahydrate, silver thiocyanate, and sodium tetrachloropalladate were obtained commercially. Thiocyanogen was prepared in dichloromethane at −78 °C by a literature procedure.[19] Elemental analyses are reported as obtained from Galbraith Laboratories. Computer evaluation of the elemental analyses was carried out using both the COORDINATION COMPOUND ANALYSIS program[20] and CHEMICAL ANALYSIS program.[21]

X-ray powder diffraction data were obtained on a tungsten calibrated Philips diffractometer and/or Debye-Scherrer camera using monochromatic Cu Kα radiation. Based on the tetragonal structure[11,15] a least-squares refinement of the unit cell constants was made with the use of the REFINE program.[14] Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were recorded at 20°/min with a duPont 900 differential thermal analyzer and a duPont 951 thermal gravimetric analyzer. The crystal structures of the complexes were monitored during the DSC scans by quenching samples and obtaining x-ray scattering data in a Debye–Scherrer camera. Infrared spectra (KBr) were recorded on a Beckman IR-12 spectrometer. Proton NMR spectra were obtained with a Jeolco C-60H spectrometer utilizing $(CD_3)_2CO$ as solvent and Me_4Si as an internal reference.

Preparation of Samples. Bis(diphenylglyoximato)nickel(II). A mixture of 1.88 g of $NiCl_2\cdot 6H_2O$ (7.92 mmol), 3.98 g of diphenylglyoxime (16.5 mmol), and 0.66 g of NaOH (16.56 mmol) was heated under reflux in ethanol for 24 h. The resulting product was recrystallized via Soxhlet extraction with dichloromethane: yield 3.20 g (5.96 mmol; 75%). Anal. Calcd:[21] C, 62.60; H, 4.13; N, 10.43. Found: C, 62.49; H, 4.26; N, 10.36.

Bis(diphenylglyoximato)palladium(II). The same procedure as described above was utilized except for the use of Na_2PdCl_4.

Reaction of $Ni^{II}(HDPG)_2$ with Thiocyanogen. To a solution of 311 mg of $Ni(HDPG)_2$ (0.579 mmol) in 600 ml of dichloromethane at ambient temperature was added the filtrate of the reaction of 540 mg of AgSCN (3.25 mmol) and 4.0 ml of 0.581 N bromine (in dichloromethane) at 0 °C. The resulting homogeneous gold solution was allowed to stand for 24 h at −8 °C with no precipitation of a complex. Upon reducing the volume of the solvent, crystals of the starting nickel(II) complex separated and were isolated. The reaction was repeated using a 46.9:1 SCN/Ni ratio without the isolation of an oxidation product even at −78 °C. Under similar conditions thiocyanogen oxidatively adds to Pt(HDPG)$_2$.[14]

Reaction of Ni(HDPG)$_2$ with Cyanogen Bromide. To a warm filtered solution of 340 mg of Ni^{II}(HDPG)$_2$ (0.63 mmol) in 300 ml of dichloromethane was added 410 mg of cyanogen bromide (38.8 mmol) in 100 ml of dichloromethane. After 24 h the deposited gold-black needle crystals were collected by filtration. After air drying 70 mg of product (0.116 mmol; 18.5%) was collected. The infrared spectrum of the product was similar to that of Ni^{II}(HDPG)$_2$ with no evidence for a ν_{CN} absorption in the 2000–2300 cm^{-1} region in Nujol or KBr. The observed chemical analysis is best fitted[20] by a Ni(HDPG)$_2$Br$_y$ ($0.78 < y < 0.81$) stoichiometry[2] (see Table I).

Reaction of Pd^{II}(HDPG)$_2$ and Iodine Monochloride. To 700 ml of a warm filtered dichloromethane solution containing 503 mg of Pd^{II}(HDPG)$_2$ (0.86 mmol) was added 1 ml of neat ICl. After standing at ambient temperature for 24 h the solution was concentrated to 50 ml. Upon cooling to −8 °C yellow prisms of Pd^{II}Cl$_2$(H$_2$DPG) were deposited. Recrystallization was effected from dichloromethane–*n*-hexane: yield 195 mg (0.468 mmol; 55%). Anal. Calcd:[20,21] C, 40.27; H, 2.90; N, 6.70; Cl, 16.98. Found: C, 39.85; H, 2.83; N, 6.62; Cl, 17.45.

Reaction of Ni^{II}(HDPG)$_2$ and Iodine Monochloride. The above reaction was repeated using the nickel(II) complex. Decomposition which caused the decoloration of the solution and formation of a white precipitate was observed. A similar decomposition is effected by chlorine oxidation of Ni^{II}(HDPG)$_2$.[10]

Synthesis of M(HDPG)$_2$X$_y$ (M = Ni, Pd; X = Br, I). These complexes were made by the general method of the addition of a warm dichloromethane solution of halogen to a hot filtered dichloromethane solution of M(HDPG)$_2$ [M = Ni(~10 mmol), Pd(~1 mmol)] and allowing the solution to stand for 24 h at ambient temperature. The black-gold crystals were separated by filtration and air dried. Yields of 20–200 mg were typically obtained with the larger yields found for reaction with the greater ratio of halogen to M(HDPG)$_2$. Upon the oxidation of the nickel(II) complexes a white residue frequently was formed in addition to the desired product. The product was collected via aqueous extraction of residue and filtration of the chlorocarbon phase.

In a typical synthesis, addition of 80 ml of 0.0433 N I$_2$ (in dichloromethane) to 306 mg of Ni(HDPG)$_2$ (0.572 mmol) in refluxing dichloromethane (350 ml) followed by cooling to ambient temperature for 24 h affords 60 mg of Ni(HDPG)$_2$I$_{0.38}$. Similarly the use of 100 or 20 ml of 0.0433 N I$_2$ affords crystals of Ni(HDPG)$_2$I$_y$ $0.58 < y < 0.62$ and $y = 0$, respectively. The reaction of 0.57 mmol of Ni(HDPG)$_2$ with 2.2 and 7.0 ml of 0.49 M bromine yields crystals of Ni(HDPG)$_2$Br$_y$ $0.1 < y < 0.18$ and $1.08 < y < 1.11$, respectively. Since an excess of halogen is required to prepare Ni(HDPG)$_2$X$_y$ (y = maximum value of ~1.15), a complex equilibria must be important in the preparation. The elemental analyses of a variety of M(HDPG)$_2$X$_y$ (M = Ni, Pd; X = Br, I) are listed in Tables I–III.

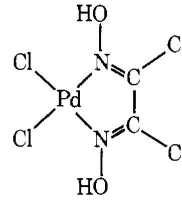
Reaction of M^{II}(HDPG)$_2$ (M = Ni, Pd) with Iodine Monobromine. The above reaction was repeated using 414 mg of Ni(HDPG)$_2$ (0.77 mmol) or 523 mg of Pd(HDPG)$_2$ (0.89 mmol) dissolved in 400 or 800 ml of warm dichloromethane. After addition of a 50-ml solution of 0.1 N IBr in dichloromethane and standing at ambient temperature for 18 h dark gold crystals of nominal Ni(HDPG)$_2$(IBr)$_{0.54}$ (471 mg; 95%) and Pd(HDPG)$_2$(IBr)$_{0.48}$ (347 mg; 57%) stoichiometries were obtained. Elemental analyses are listed in Table IV.

Reaction of M(HDPG)$_2$ (M = Ni, Pd) with 1:1 I$_2$/Br$_2$. The above reaction was repeated with either 348 mg of Ni(HDPG)$_2$ (0.54 mmol) or 401 mg of Pd(HDPG)$_2$ (0.69 mmol) dissolved in 400 and 700 ml of dichloromethane, respectively. Addition of 70 ml of dichloromethane containing 315 mg of Br$_2$ (0.056 M) and 500 mg of I$_2$ (0.056 M) leads to the formation of dark needle crystals of nominal Ni(HDPG)$_2$Br$_{0.67}$I$_{0.45}$ (232 mg; 55%) and Pd(HDPG)$_2$Br$_{0.44}$I$_{0.45}$ (309 mg; 66%) stoichiometries, respectively. Elemental analyses are listed in Table IV.

Results and Discussion

Stoichiometry. Careful evaluation of the elemental analysis data (Tables I–IV) by computer techniques[20,21] revealed that in addition to the previously described formally stoichiometric 1:1 M/X M(HDPG)$_2$X (M = Ni, Pd; X = Br, I) complexes a series of nonstoichiometric complexes could be isolated. A maximum M/X ratio of 1.14 (±0.03), 1.02 (±0.04), and 1.08 (±0.04) was observed for the Br$_2$, I$_2$, and IBr oxidation product of Ni(HDPG)$_2$ and 1.08 (±0.02), 1.02 (±0.04), and 0.96 (±0.04) for the Br$_2$, I$_2$, and IBr oxidation product of Pd(HDPG)$_2$. For example, the designation of the bromine stoichiometry of 1.13:1 Br/Ni is supported by deviations of 0.17, 0.03, 0.13, and 0.20% between the observed and theoretical values for the C, H, N, and Br analyses, respectively. A 1:1 Br/Ni ratio gives the larger deviations of 0.88, 0.10, 0.30, and 1.47%, respectively, for the C, H, N, and Br analyses. In addition to the maximum stoichiometries observed, various materials containing less than a 1:1 M/X ratio have been characterized. Samples of M(HDPG)$_2$X$_y$ ($0 < y < 1.15$) were characterized by x-ray powder diffraction to be homogeneous in nature and did not contain a mixture of M^{II}(HDPG)$_2$ and M^{II}(HDPG)$_2$X$_{max}$. Oxidation of M^{II}(HDPG)$_2$ (M = Ni, Pd) with IBr resulted in the isolation of complexes with a 1:1 I/Br ratio. Oxidation of Ni(HDPG)$_2$ with ICl led to decomposition into a white product which has also been reported for the Cl$_2$ oxidation of Ni(HDPG)$_2$.[10]

Oxidation of Pd(HDPG)$_2$ with ICl led to the formation of Pd(H$_2$DPG)Cl$_2$. This diamagnetic complex exhibits a phenyl proton at τ −2.77 in the ^{1}H NMR spectrum. The low solubility of Pd^{II}(H$_2$DPG)Cl$_2$ (**1**) in CDCl$_3$, CD$_3$CN, and (CD$_3$)$_2$CO has thwarted the observation of the hydroxyl protons. There is, however, a broad absorption at 3260 cm^{-1} assignable to a ν_{OH} stretch, which is in good agreement with the value of 3200 cm^{-1} reported for Co(HDMG)(H$_2$DMG)Cl$_2$[22] (H$_2$DMG = dimethylgloxime).



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In order to synthetically verify the existence of X$_3^-$ within the tetragonal M(HDPG)$_2$X structure, an attempt was made to oxidize Ni(HDPG)$_2$ with thiocyanogen,[23] thereby introducing a linear triatomic monoanionic pseudohalide into the tetragonal structure.[32] This synthesis was not successful, however, and only the starting nickel(II) complex was isolated. Likewise oxidation of Ni(HDPG)$_2$ with cyanogen bromide did not lead to the incorporation of cyanide into the structure, but gave a gold-black crystalline phase which did not exhibit a ν_{CN} absorption in the infrared. The best computer fit of elemental analysis[21] clarified the composition to be Ni(HDPG)$_2$Br$_{\sim 0.8}$. Thus, all attempts to oxidize Ni(HDPG)$_2$ with a pseudohalogen oxidant, thereby introducing a pseudohalide into the tetragonal structure, were unsuccessful.

Structure. The x-ray powder diffraction data and the refined unit cell constants shown in Table V clearly indicate that all of the complexes of M(HDPG)$_2$X$_y$ (M = Ni, Pd; X = Br, I; $y \lesssim 1.15$) stoichiometry are isomorphous with each other and with the previously reported tetragonal Ni(HDPG)$_2$I,[13,15] Ni(HDPG)$_2$Br,[13] Pd(HDPG)$_2$I,[13] and Pd(HDPG)$_2$Br[13] complexes. The intensities of the singlet x-ray diffraction lines in the diffractometer trace varied with halogen content, y, although the line positions did not change significantly. This indicates a common structure for the complex over a wide range of stoichiometry with varying degrees of occupation of the halogen sites. A typical variation of intensities of the 110, 020 (≡200), and 220 reflections for Ni(HDPG)$_2$Br$_y$, as a

Table V. Representative Least-Squares Refined Tetragonal Cell Constants for $M(HDPG)_2(X_xY_y)$

M	X,Y	$x+y$	a, Å	c, Å
Ni	Br	1	19.51[a]	6.72[a]
Ni	Br	0.79	19.66	6.57
Ni	Br	1.09	19.69	6.56
Ni	Br	1.14	19.69	6.56
Ni	IBr	1.08	19.65	6.66
Ni	I	1	19.92[a]	6.56[a]
Ni	I	1	19.887 (4)[b]	6.542 (2)[b]
Ni	I	0.58	19.84	6.54
Pd	Br	1	19.76[a]	6.57[a]
Pd	Br	0.10	19.85	6.58
Pd	Br	1.03	19.87	6.58
Pd	Br	1.07	19.86	6.58
Pd	I,Br	0.96	19.85	6.56
Pd	I	1	19.78[a]	6.52[a]

[a] Reference 11. [b] Reference 15.

function of y, is depicted in Figure 1. The refined unit cell data also show that the metal atom spacings ($c/2$) are 3.26–3.36 Å, which is significantly shorter than the metal-metal spacings (~3.50 Å) reported for the unoxidized $M^{II}(HDPG)_2$.[14] Thus $M(HDPG)_2X_y$ possesses a one-dimensional structure with the metal atoms colinear with the c axis and the halogens in channels formed by four phenyl rings also parallel with the c axis.[15,24] The adjacent $M(HDPG)_2$ molecular planes are rotated by 90° with respect to each other.[15]

The form of the halogen in the channels (i.e., X^-, X_2, or X_3^-) is of considerable interest. The oxidation state is extremely important in the understanding of the physical properties of the system as it describes the number of electrons in the conduction band. Thus if the channels were filled with X^-, X_2, and X_3^- the oxidation state of the metal would be 3+,[29] 2+, and 2.33+,[29] respectively and only the former or latter case would result in a nonfilled band. Possible 1-D structures are schematically illustrated in Figure 2. In order to account for the presence of X_3^- via Raman and Mössbauer spectroscopy[15] and the facile loss of X_2[11] (vide infra) it is likely that the halogen is in a dynamic redox equilibrium

$$\begin{gathered} X_2 + X^- = X_3^- \\ X_3^- + X_2 = X_5^- \end{gathered} \tag{1}$$

such that the halogen chain may in fact account for the observed conductivity[11,18] of the order of ~10^{-5} ohm^{-1} cm^{-1} and thus the metal would be in an oxidation state between 2+ and ~3+.

For a $M(HDPG)_2X_y$ complex the M–M spacings are invariant with y. This suggests that the oxidation state of the metal remains constant with halogen loss and different halogen equilibria, eq 1, are established to maintain the constant oxidation state. This model has to be ruled out because more halogen is liberated than that would be required to maintain a constant oxidation state. More precise single-crystal x-ray data would be required to rigorously verify the absence of change in the M–M spacings as a function of halogen content. Since the halides fill a channel parallel to the c axis, the maximum halogen content, X/M = y, that can be accommodated by the tetragonal $M(HDPG)_2X$ structure[13,16] can be calculated from the effective length per halogen atom, r_{X_n},

$$r_{X_n} = \frac{1}{n} \sum r_X^{vdW} + r_X^{cov} + r_X^{ion} \tag{2}$$

of the halogen containing species, X_n, and the length of the unit cell c axis per metal atom, $c/2$, by

$$y = r_X/r_M = 2r_{X_n}/c = X/M \tag{3}$$

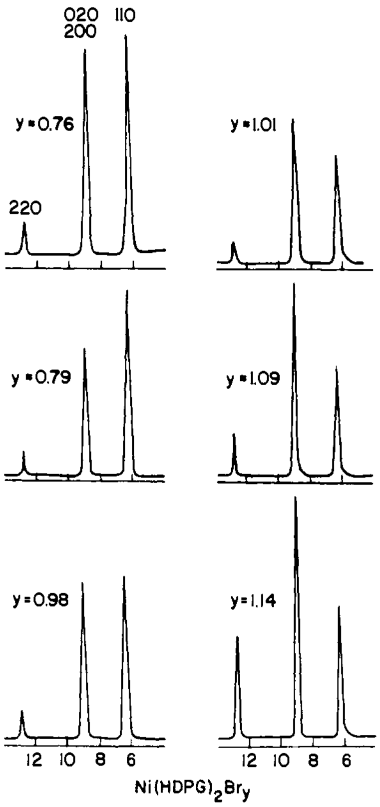


Figure 1. Relative x-ray diffractometer intensities for $Ni(HDPG)_2Br_y$ as a function of y for the 110, 020 (≡200), and 220 reflections.

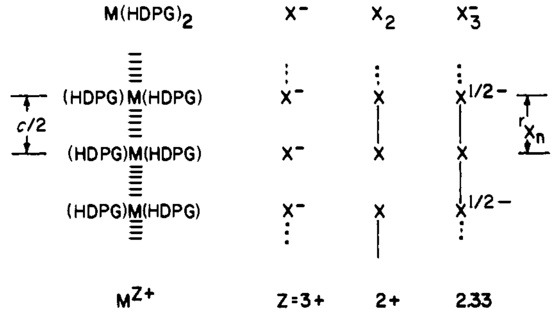


Figure 2. Schematic structures of $M(HDPG)_2X$ (M = Ni, Pd; X = Br, I), where the halogen resides in a one-dimensional channel surrounded by four phenyl rings.

Table VI lists the effective length per halogen atom r_{X_n} for various halogen-containing complexes calculated from the sum of covalent, r_X^{cov}, van der Waals, r_X^{vdW}, and ionic radii, r_X^{ion}. Thus, the ratio of the effective halogen length to the c-axis length, eq 3, reflects the maximum halogen content anticipated for the structures proposed in Figure 2, containing X^-, X_2, and X_3^- in the 1-D channel. The observed X/M ratios, Table VII, are in good agreement with the ratios calculated for X_3^-, marginal agreement for X_2, but are significantly larger than the ratio calculated for X^-. This is in accord with the ^{127}I Mössbauer and Raman data, which also support the presence of an asymmetric X_3^- in the solid-state structure of $Ni(HDPG)_2I$.[15] In complexes containing less than the maximum halogen ratio, however, the extra space available per halogen atom may allow a different distribution of halogen oxidation states in the solid.

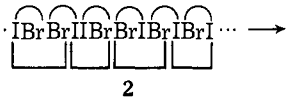
The structures of the mixed halogen complexes presumably reflect the mode of oxidation. If the oxidation with IBr occurs during crystal formation, then the one-dimensional channels

Table VI. Length of Various Halogen and Halogen Anions

Ion	Length, Å	Effective length, r_{X_n}, Å
Br^-	3.86[a,b]	3.86
$Br^- + I^-$		4.09
I^-	4.32[a,b]	4.32
Br_2	6.18[c]	3.09
BrI	6.58[c]	3.29
I_2	6.97[c]	3.49
Br_3^-	8.99[a,c,d]	3.00
Br_2I^-	9.30[a,c,e]	3.10
BrI_2^-	9.77[a,c,f]	3.26
I_3^-	10.12[a,c,g]	3.37

[a] Average of the Goldschmidt, Pauling, and Ladd ionic radii. [b] F. A. Cotton, and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley-Interscience, New York, N.Y., 1972, p 52. [c] F. A. Cotton and G. Wilkinson, *ibid.*, pp 117, 120. [d] Average taken from $(Me_3NH)_2Br_4$ [C. Romers and E. W. M. Keulemans, *Proc. Natl. Acad. Sci. U.S.A.*, **B61**, 345 (1958)], $CsBr_3$ [G. L. Breneman and R. D. Willett, *Acta Crystallogr.*, **25**, 1073 (1969)], and Ph_4AsBr_3 [J. Ollis, V. J. James, D. Ollis, and M. P. Bogaard, *Cryst. Struct. Commun.*, **5**, 39 (1976)]. [e] S. Soled and G. B. Carpenter, *Acta Crystallogr., Sect. B*, **29**, 2556 (1973). [f] G. B. Carpenter, *Acta Crystallogr.*, **20**, 330 (1966). [g] Average taken from Ph_4AsI_3 [R. C. L. Mooney and J. C. Slater, *ibid.*, **12**, 187 (1959)], NH_4I_3 [R. C. L. Mooney, *Z. Krist.*, **90**, 143 (1935)], NMe_4I_3 [R. C. L. Mooney, *Phys. Rev.*, **53**, 851 (1938)], CsI_3 [H. A. Tasman and K. H. Boswizk, *Acta Crystallogr.*, **8**, 857 (1955)], NEt_4I_3 [T. Migchelsen and A. Vos, *ibid.*, **23**, 796 (1967); T. M. Reddy, K. Knox, and M. B. Robin, *J. Chem. Phys.*, **40**, 1082 (1964)], $MoOCl(CNCH_3)_4I_3$ [C. T. Lam, D. L. Lewis, and S. J. Lippard, *Inorg. Chem.*, **15**, 989 (1976)].

should be filled in a random fashion such that only IBr_2^-, I_2Br^-, $IBrI^-$, and $BrIBr^-$ could be formed in the channel (**2**)



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and X_3^- species could not be present. Preliminary Raman data confirm the absence of X_3^- (X = Br, I).[30a] Similarly, oxidation with a 1:1 mixture of I_2 and Br_2 leads to a more complicated situation, since IBr is in equilibria with Br_2 and I_2.[31] Thus a random filling of the one-dimensional halogen channel with IBr, I_2, and Br_2 should result in the inclusion of X_3^-, X_2Y^-, and XYX^- into the one-dimensional structure. This problem is currently being focused on in detail using infrared and Raman spectroscopy.[30a]

Halogen oxidation of other inorganic and organic materials has lead to the isolation of phases containing various nonstoichiometric X/donor ratios. Iodine oxidation of bis(benzoquinonedioximato)nickel(II), $Ni(BQDG)_2$, yields a complex which contains 0.5 iodine atoms per Ni atom.[26-28] The characterization of a variable halogen ratio for this complex has not been reported. Recently halogen oxidation of Fe, Co, Ni, Cu, and Zn phthalocyanine complexes has been reported to yield an isomorphous series of complexes with variable halogen content; however, the poor solubility characteristics of these complexes have thwarted detailed characterization of the stoichiometry and structure.[30]

Halogen oxidation of tetrathiofulvalene, TTF, has lead to the formation of phases containing various stoichiometries,[32-36] including a highly conducting complex containing a nominal 0.7:1 X/TTF ratio, i.e., $TTFX_{0.7}$ (X = Br,[35,36] I[35]). These complexes are similar to the bromine and iodine oxidation product of $M(HDPG)_2$ in that the halogen resides in channels parallel to the *c* axis,[15] they are dark in appearance, and exhibit significantly higher conductivity than the unoxidized species. There are, however, significant differences with respect to the isolation of multiple phases, interpretation of the structure in terms of two interpenetrating monoclinic sublattices which describe the TTF and halogens, respectively, and significantly larger interhalogen spacings. In contrast to the short space allotted for each halogen in $M(HDPG)_2X$, strongly suggesting that X_3^- is the only species that would comfortably fit in the channel, the larger spacings of 4.99[37,38] and 4.538 Å[36] for the iodine and bromine oxidation product of TTF indicate that the X^- ion could fit in the channels of $TTFX_{0.7}$ without any steric interaction. This is consistent with the interpretation previously ascribed to the oxidation state of TTF in $TTFX_{\sim 0.7}$.[38] It is not necessary, however, that the halogen must be in the form of X^- in the structure and the existence of a dynamic equilibrium of the type outlined in eq 1 would not be surprising. This is consistent with the interpretation of the complex structure of $TTFI_{0.7}$ as containing TTF monomers, dimers, trimers, and I_3^- ions.[38]

Thermal Properties. Although the detailed behavior of the tetragonal $M(HDPG)_2X_y$ did vary considerably they all lost halogen and reverted to the parent divalent orthorhombic compound[14] prior to melting and complete thermal decomposition. The basic thermal properties and detailed differences can be illustrated by reference to the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data for $Ni^{II}(HDPG)_2$ and its bromine oxidation product, $Ni(HDPG)_2Br_{1.14}$, illustrated in Figure 3. The $Ni(HDPG)_2$ starting material gave a thermogram which was relatively featureless up to 325 °C, but then exhibited a sharp primary decomposition exotherm at 348 °C followed by a series of secondary decomposition peaks. Almost buried in the leading edge of the primary decomposition peak was the melting endotherm of $Ni(HDPG)_2$ at 341 °C. The decomposition was evidenced by sample weight loss (TGA) and increasing deviation from the orthorhombic $Ni(HDPG)_2$ x-ray diffraction pattern. The melting point was evidenced by a change in the appearance of the quenched sample from the needle crystal morphology to a fused mass.

Table VII. Calculated Halogen–Metal Ratios That Can Be Accommodated by the Tetragonal $M(HDPG)_2X$ Structure for X^-, X_3, and X_3^-

Complex[a]	*c*, Å[b], calcd	X^-/M, calcd	$\frac{1}{2}X_2$/M, calcd	$\frac{1}{3}X_3^-$/M, calcd	X/M = *y*, obsd
$Ni(HDPG)_2I$	6.56	0.76	0.94	0.97	1.02 ± 0.04
$Ni(HDPG)_2I_{1/2}Br_{1/2}$	6.68	0.82	1.02	1.05	1.08 ± 0.04
$Ni(HDPG)_2Br$	6.72	0.87	1.09	1.12	1.14 ± 0.03
$Pd(HDPG)_2I$	6.52	0.75	0.94	0.97	1.02 ± 0.04
$Pd(HDPG)_2I_{1/2}Br_{1/2}$	6.55	0.80	1.00	1.03	0.96 ± 0.05
$Pd(HDPG)_2Br$	6.52	0.85	1.06	1.09	1.08 ± 0.02

[a] Nominal stoichiometry. [b] From Table V.

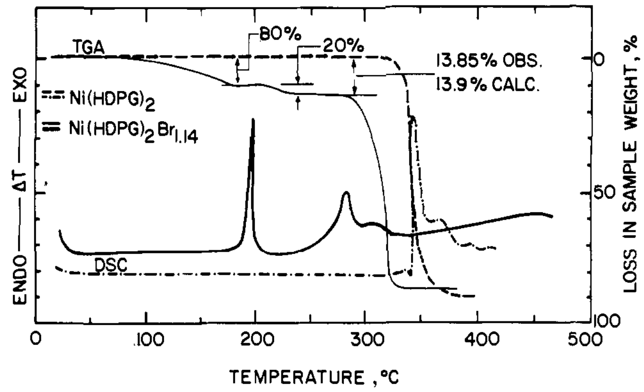

Figure 3. DSC and TGA traces (20 °C/min) for $Ni(HDPG)_2$ and $Ni(HDPG)_2Br_{1.14}$ showing the two-stage bromine loss, melting point depression, and impurity related exotherm.

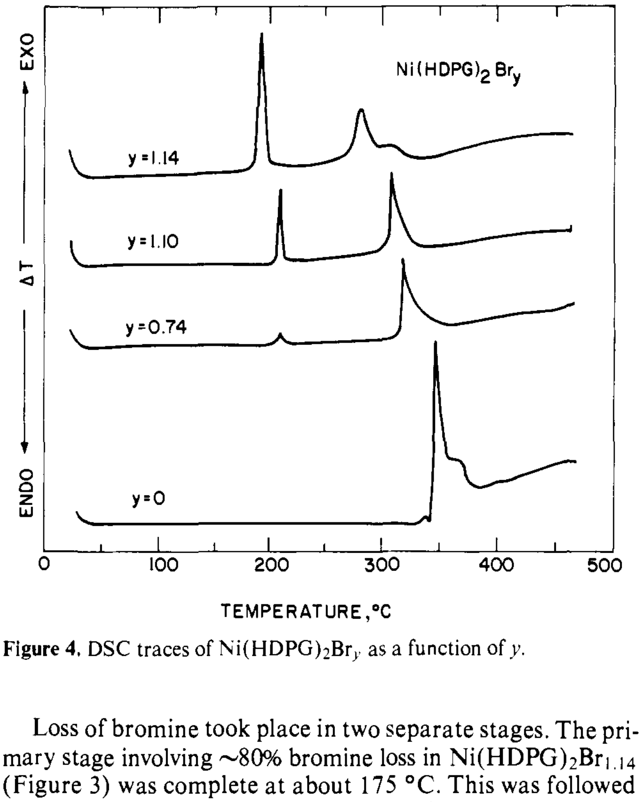

Figure 4. DSC traces of $Ni(HDPG)_2Br_y$ as a function of y.

Loss of bromine took place in two separate stages. The primary stage involving ~80% bromine loss in $Ni(HDPG)_2Br_{1.14}$ (Figure 3) was complete at about 175 °C. This was followed by an exothermic reaction (ΔH = 24 kcal/g-mol $Ni(HDPG)_2$) peaking at ~200 °C as the tetragonal $Ni(HDPG)_2Br$ lattice reverted to the orthorhombic $Ni(HDPG)_2$ lattice. The remaining bromine was then lost from the orthorhombic lattice. This was followed by melting (265 °C) and decomposition of the $Ni(HDPG)_2$ compound. The x-ray diffraction pattern from the $Ni(HDPG)_2$ left after bromine loss contained some diffraction lines which could not be indexed on the basis of either this compound or the starting material and were probably due to a secondary reaction product (possibly halogenation of the ligand) present as an impurity.

The details of the thermal behavior of $Ni(HDPG)_2Br_y$ changed significantly with decreasing bromine content. The melting temperature and the subsequent decomposition temperature increased and the magnitude of the ~200 °C exotherm decreased as the value of y was decreased (Figure 4). It seems reasonable to conclude that the impurity detected by x-ray diffraction accounts for the depression of both the melting temperature and the ensuing decomposition temperature of the $Ni(HDPG)_2Br_y$. The memory of initial bromine content would then be due to the impurity concentration being proportional to the initial bromine content. The efficiency of the impurity producing side reaction should, however, be a function of the temperature at which the bromine loss from the $Ni(HDPG)_2Br_y$ occurred. Bromine loss was therefore induced isothermally from $Ni(HDPG)_2Br_{1.14}$ in the DSC cell and the samples cooled to room temperature and then run through a normal DSC heating cycle.

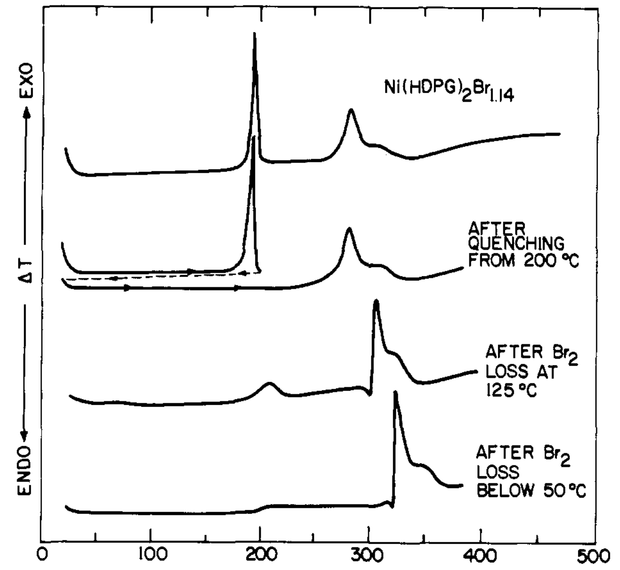

Figure 5. DSC trace from $Ni(HDPG)_2Br_{1.14}$ as a function of thermal treatment.

It was found that as the temperature at which bromine was expelled from the lattice was reduced, the area under the ~200 °C exotherm was also reduced and the melting and primary decomposition temperatures increased. The thermogram given after heating at 125 °C is shown in Figure 5. After heating at temperatures closer to room temperature the ~200 °C exotherm was eliminated entirely and the tetragonal-orthorhombic phase change was evidenced simply by a small change in baseline indicative of a decrease in heat capacity (Figure 5).

It is apparent therefore that the melting and decomposition temperature depression was due to an impurity and that this impurity was formed during the primary bromine loss reaction. Also the ~200 °C exotherm was not due directly to the tetragonal-orthorhombic phase transition, but was also associated with the temperature of bromine loss and therefore in some way with the impurity. Samples heated normally at 20 °C/min, quenched back to room temperature directly after the ~200 °C exotherm, and cycled again at 20 °C/min did not show any change in melting and decomposition temperatures from those run through without quenching. Only the ~200 °C exotherm was eliminated. For samples containing $y < y_{max}$ the ~80% bromine loss plateau was attained at lower temperatures, but the ~4:1 ratio in bromine loss in the two separate loss reactions was maintained.

Although the iodine oxidation product of $Ni(HDPG)_2$ also decayed back to the parent compound, the pattern of events was not as obvious. The thermal data presented in Figure 6 show that the halogen is again lost in two separate steps, albeit at higher temperatures, but there is no sign of an exotherm corresponding to that observed at the ~200 °C tetragonal-orthorhombic transition in Figure 3. There was in fact a tetragonal-orthorhombic lattice transformation indicated at ~300 °C by x-ray diffraction just prior to the melting temperature of the material (312 °C), but no obvious associated exotherm or endotherm. The melting temperature and tem-

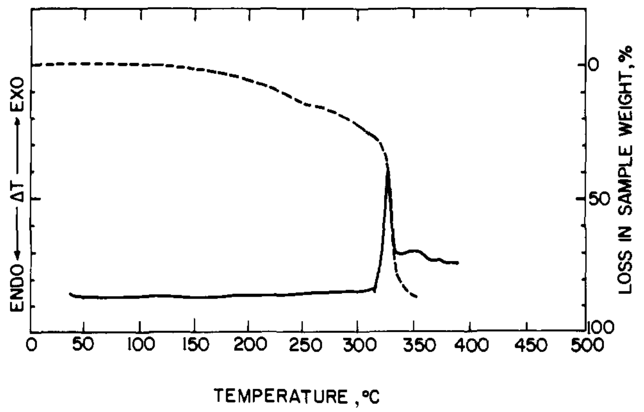

Figure 6. DSC (solid line) and TGA (dashed line) traces for Ni(HDPG)$_2$I.

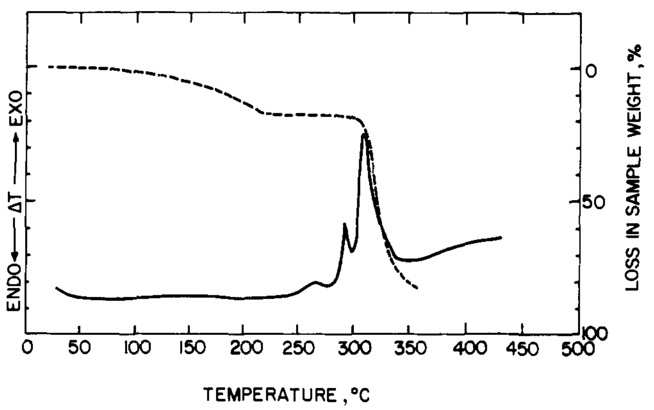

Figure 7. DSC (solid line) and TGA (dashed line) traces for Ni(HDPG)$_2$(IBr)$_{0.54}$.

perature of the ensuing decomposition was again a function of initial halide concentration, but the melting point depression was much less than was the case with the bromine-containing complexes. It seems probable that this effect was again due to the presence of impurities produced as a secondary product of the halogen loss.

Mixed iodine-bromine oxidation products of Ni(HDPG)$_2$ were prepared from mixed $I_2 + Br_2$ (1:1) and from IBr. The thermal properties of the products of these two syntheses were essentially identical and are illustrated in the DSC and TGA traces of Ni(HDPG)$_2$(IBr)$_{0.54}$ shown in Figure 7. Halogen loss was essentially complete at 225 °C, but changes in crystal structure did not begin until the 250–275 °C region and then took place in two separate processes. X-ray powder analysis of quenched samples indicated that the first exotherm corresponded to a partial transformation to the orthorhombic Ni(HDPG)$_2$ lattice and the second exotherm corresponded to the completion of this process. The third exotherm peaking at about 310 °C was the usual Ni(HDPG)$_2$ decomposition.

The thermal properties of the palladium compounds paralleled those of their nickel analogues and differed only slightly in such details as reaction temperature and peak shape. The unoxidized Pd(HDPG)$_2$ melted at 362 °C and had a primary decomposition peak at 375 °C. Bromine loss from P(HDPG)$_2$Br took place in a single process complete at 175 °C and was followed at 185 °C by the tetragonal → orthorhombic transformation and the accompanying impurity-related exotherm. Iodine loss from Pd(HDPG)$_2$I took place in two processes as described for the nickel compounds with no exotherm obviously associated with the lattice transformation. As in the nickel compounds the mixed halogen oxidation products showed no differences in behavior with synthetic procedure (IBr or I_2 plus Br_2). Halogen loss was complete at 275 °C and was followed by a two-stage lattice transformation and then decomposition similar to the analogous nickel compound.

The results presented above clearly indicate the similarities in the thermal behavior of the M(HDPG)$_2$X$_x$Y$_y$ (M = Ni, Pd; X, Y = Br, I; $x + y < 1.15$) complexes. Such similarities are not surprising considering their structural isomorphism. The detailed behavior and the differences in behavior of the basic M(HDPG)$_2$X$_y$ tetragonal lattice containing different halogen species are somewhat more subtle. The bromine-containing compounds are the only ones which show a significant exotherm associated with the collapse of the tetragonal lattice with halogen-filled channels to form the orthorhombic M(HDPG)$_2$ lattice. This exotherm, however, becomes less pronounced at lower values of y even though the tetragonal lattice is preserved. In the iodine compound there is no significant exotherm associated with the same tetragonal → orthorhombic transformation and in the mixed halogen (I, Br) compound the situation was more complex with two separate lattice transformations. It is highly probable that the exotherm associated with the tetragonal-orthorhombic transition is not a function of the differences in free energy of the two structures, but is of chemical origin. The memory of the melting and decomposition temperatures for the initial bromine concentration in the M(HDPG)$_2$Br complexes and the bromine expulsion temperature indicate a chemical reaction to produce an unknown impurity phase. This reaction apparently becomes less significant when bromine expulsion occurs at lower temperatures. The melting and subsequent decomposition temperatures are in each case, however, significantly lower than those of the pure parent metal diphenylglyoximes.

The two-stage bromine loss from the Ni(HDPG)$_2$Br lattice can be explained on the basis of the difference in stability of bromine in the tetragonal and the orthorhombic lattices. The two-stage loss of iodine is apparently due to two separate reaction mechanisms, the second of which may result in the presence of decomposition products other than the M(HDPG)$_2$. The lack of any exotherm in the region of 200 °C suggests that there is no significant reordering of iodine and bromine in the case of the mixed iodine–bromine compounds and supports the Raman evidence.[30a]

A study of the kinetics of halogen loss from the M(HDPG)X$_y$ complexes has been initiated. Preliminary isothermal ($T \leqslant 125$ °C) time dependence data for the loss of bromine from the polycrystalline Ni(HDPG)$_2$Br$_{1.1}$ indicate an initial square root dependence and a logarithmic dependence at longer times, consistent with a one-dimensional diffusion model.[39] At extended times the bromine loss reaches an asymptotic value which is ~80% of the total halogen content. The recovered crystals containing the residual halogen are dark red in color and have a tetragonal unit cell. These observations are consistent with the DSC data presented in Figure 3, which indicate that the tetragonal structure is maintained below the ~200 °C exotherm.

Conclusions

Halogen oxidation of the orthorhombic divalent M(HDPG)$_2$ (M = Ni, Pd) complexes in dichloromethane results in the formation of an isomorphous tetragonal series of complexes containing a variable amount of halogen, which is present in channels parallel to the c axis. The halogen size relative to the unit cell dimensions indicate the presence of X_3^- in the complexes with the maximum halogen content and a possible redox equilibrium between X_2, X^-, X_3^-, and possibly X_5^- for complexes with lower halogen contents. The oxidation of I_2 and Br_2 or IBr yields a tetragonal complex containing both iodine and bromine. The bromine-containing complexes lose halogen in two stages, whereby ~80% of the halogen is easily lost from the tetragonal structure below 200 °C and the remaining halogen is lost immediately after the tetragonal–orthorhombic phase change. This leaves $M(HDPG)_2$ and an impurity phase which causes a depression of the melting point. The iodine-containing complexes also lost halogen in two separate processes; however, in contrast to the bromine-containing complexes, there was no obvious correlation with the phase change. The loss of halogen from the mixed halogen-containing species is more complex than that observed for the $M(HDPG)_2X$, (M = N, Pd; X = Br, I). Preliminary kinetic data is consistent with a one-dimensional diffusion model for the halogen loss from these complexes.

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Supplementary Material Available: Tables of elemental analyses (Tables I–IV) (4 pages). Ordering information is given on any current masthead page.

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Electronic Structure of Three-Coordinate Nickel(I): Electron Paramagnetic Resonance of Nickel-Doped Halobis(triphenylphosphine)copper(I)

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Abstract: Successful preparation and electron paramagnetic resonance of single crystals of Ni-doped $(Ph_3P)_2CuX{\cdot}0.5C_6H_6$ (X = Cl, Br) are described. For both the chloro and bromo complexes the isotropic and anisotropic parts of the ^{31}P superhyperfine tensors of the two inequivalent phosphorus ligands are markedly different. Additional superhyperfine structure observed in the spectra of the bromo complex is attributed to $^{79,81}Br$ superhyperfine and nuclear quadrupole coupling. Anisotropic line widths in the chloro complex are attributed to unresolved $^{35,37}Cl$ superhyperfine and quadrupole structure. The orientations and magnitudes of the various EPR tensors, including the Br quadrupole coupling, suggest that the metal–halogen bond is fairly ionic (~80%), and that the unpaired spin is rather strongly localized on the Ni atom yet is involved in a halogen–metal $p_\pi \rightarrow d_{xy}$ bond.

Although complexes containing nickel in the +1 oxidation state are still rather uncommon, the number of examples is steadily increasing.[2] There is also clear evidence that certain of these complexes represent thermodynamically stable species; i.e., there are no kinetic barriers to disproportionation to the more normal 0 and +2 oxidation states. Halotris(triphenyl-