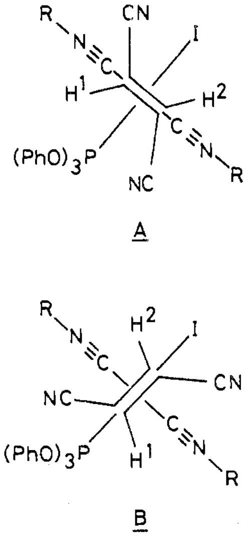

Figure 4. Isomeric forms of Rh(RNC)$_2$(P(OPh)$_3$)(FN)I (**10**) (viewed from the FN side). The rhodium atom is omitted for clarity.

temperature-dependent pmr spectra of FN of **10a** are shown in Figure 3. The broad singlet at 25° at δ 3.3 ppm is more broadened and shifted to the higher field as the temperature is lowered and apparently disappears at −5°. At −15° the FN signal appears as two broad components centered around δ 3.1 and 2.2 ppm. On further cooling the components become sharper without changing the chemical shift and the signal at −39° can be explained as a superposition of two AB type quartets with the coupling constants of 9.4 Hz (Figure 3). At −55° each component of the quartets is further split into a doublet; the lower field components have the coupling constants of 1.5 Hz and the higher field ones the values of 3.6 and 4.2 Hz. These pmr features may be interpreted as follows. In the temperature range between +25 and −5° a fast exchange between the free and coordinated FN is occuring. Below −15° the amount of free FN is negligible on the nmr time scale and the signal change will be due to the restricted rotation of FN in a time-averaged square pyramid. This topic has been discussed in detail in the compounds [Rh(RNC)$_4$(TCNE)]ClO$_4$, Rh(RNC)$_2$(PPh$_3$)(FN)I, and [Rh(RNC)$_2$(PPh$_3$)$_2$(FN)]ClO$_4$ in our previous paper.[2] When the rotation of FN is inhibited, there will be two isomeric forms of **10a** (A and B) as depicted in Figure 4. Each of them has a nonsuperimposable mirror image, resulting in four different isomers altogether. In each of A and B the H^1 and H^2 protons of FN are in different magnetic environments, resulting in an AB type quartet. Since there appears an overlap of two quartets, both of A and B will exist.

Registry No. **1a**, 53992-55-5; **1b**, 53992-57-7; **2a**, 53992-59-9; **2b**, 53992-61-3; **3a**, 53992-63-5; **3b**, 53992-65-7; **4a**, 53992-67-9; **4b**, 53992-69-1; **5a**, 53992-71-5; **5b**, 53992-73-7; **6a**, 53992-75-9; **6b**, 53992-77-1; **7a**, 53992-78-2; **7b**, 53992-79-3; **8**, 53992-81-7; **9a**, 54020-29-0; **9b**, 54020-31-4; **10a**, 53992-82-8; **10b**, 53992-83-9; [Rh(1,5-C$_8$H$_{12}$)(P(OPh)$_3$)$_2$]ClO$_4$, 32799-69-2; [Rh(1,5-C$_8$H$_{12}$)(PPh(OMe)$_2$)$_3$]ClO$_4$, 53992-85-1.

References and Notes

(1) W. H. Baddley, *Inorg. Chim. Acta, Rev.*, **2**, 7 (1968).
(2) (a) T. Kaneshima, K. Kawakami, and T. Tanaka, *Inorg. Chem.*, **13**, 2198 (1974); (b) K. Kawakami, T. Kaneshima, and T. Tanaka, *J. Organometal. Chem.*, **34**, C21 (1972).
(3) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, New York, N. Y., 1969, p 27.
(4) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, Wiley, New York, N.Y., 1967, p 538.
(5) I. Ugi and R. Meyr, *Org. Syn.*, **41**, 101 (1961).
(6) H. J. Harwood and D. W. Grisley, *J. Amer. Chem. Soc.*, **82**, 423 (1960).
(7) R. R. Shrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 2397 (1971).
(8) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).
(9) J. A. A. Ketelaar, C. van de Syolpe, A. Goudsmidt, and W. Dzeubas, *Recl. Trav. Chim. Pays-Bas*, **71**, 1104 (1952).
(10) L. Vallarino, *Gazz. Chim. Ital.*, **89**, 1632 (1959); *Chem. Abstr.*, **55**, 3485*f* (1961).
(11) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 3994 (1968).
(12) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 2705 (1970).
(13) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 774 (1968).
(14) C. W. Haigh, *J. Chem. Soc. A*, 1682 (1970).

Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19174

Properties of Ni(DPG)$_2$X (DPG = Diphenylglyoximato; X = Br, I) in the Presence of Donor Molecules and in the Solid

LARRY F. MEHNE and BRADFORD B. WAYLAND*

Received July 22, 1974 AIC40491A

Bis(diphenylglyoximato)nickel(II), Ni(DPG)$_2$, is oxidized by iodine and bromine in the presence of nitrogen donors to form nickel(III) complexes. Results from epr spectral studies of [Ni(DPG)$_2$(py)$_2$]I are compared with the results from the isoelectronic species Co(DPG)$_2$(py)$_2$. Both complexes have a $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Analysis of the nitrogen-14 hyperfine coupling from pyridine in the $g_\parallel$ and $g_\perp$ regions for these complexes indicates that the σ-donor orbital for coordinated pyridine is essentially an sp^2 hybrid. Electronic and epr spectra for samples of Ni(DPG)$_2$ X (X = Br, I) in the solid are reported. The observed epr signal is assigned to an imperfection in the metal chains, resulting in a [Ni^{II}(DPG)$_2$]$^+$ site.

Introduction

Planar nickel(II) chelate complexes are known to frequently undergo one-electron oxidations at either the Ni(II) or chelate ligand sites.[1-3] Epr spectra are diagnostic for the presence of Ni(III) or oxidized ligand.[1,2] Bis(diphenylglyoximato)metal(II) (metal = nickel, palladium) react with I$_2$ and Br$_2$ to form species with the stoichiometry M(DPG)$_2$ X (X = Br, I).[4] The parent Ni(DPG)$_2$ complex occurs with a columnar structure involving a chain of M sites with M–M distances of 3.52 Å.[5] Reaction with halogens is thought to occur with retention of this general structural feature and a shortening of the average M–M distance to 3.27 Å[6] although the X-ray structure has not been completed.

Conductivity properties associated with pseudo one-dimensional systems have promoted a resurgence of interest in materials with structural features of this type.[7,8] This paper reports on the interaction of donor molecules such as pyridine with Ni(DPG)$_2$X to form nickel(III) species of the form [Ni(DPG)$_2$(py)$_2$]$^+$X$^-$ along with some properties of solid Ni(DPG)$_2$X. Spectroscopic and bonding properties of the nickel(III) complexes are compared with the isoelectronic $Co(DPG)_2(py)_2$ complexes.

Experimental Section

Materials. Diphenylglyoxime was prepared by refluxing α-benzil and excess hydroxylamine hydrochloride in absolute methanol.[9] The nickel(II) complex, $Ni(DPG)_2$, was obtained by adding a methanol solution of diphenylglyoxime to a warm aqueous solution of nickel(II) acetate buffered at pH 7.5 with an ammonium acetate–sodium acetate solution. The orange-red precipitate was washed with water and methanol and then recrystallized from hot *o*-dichlorobenzene as brick red needles. The palladium analog was prepared by the same method.

$M(DPG)_2X$ (M = Ni, Pd; X = Br, I) species were prepared by mixing solutions of the halogen (fivefold excess) with nearly saturated solutions of the $M(DPG)_2$ in *o*-dichlorobenzene[6] at 75° or in benzyl alcohol[4] at 100°. Slow cooling resulted in precipitation of the $M(DPG)_2X$ as small lustrous needles (80–90% yield). Materials with stoichiometry approaching $M(DPG)_2Br$ could also be obtained by the reaction of bromine vapor with powders of $M(DPG)_2$. High-quality crystals of the $Ni(DPG)_2X$ complexes were grown by diffusion of separate *o*-dichlorobenzene or benzyl alcohol solutions of halogen and $Ni(DPG)_2$ through a 4–8-μ sintered-glass disk.

The products resulting from dissolution of $Ni(DPG)_2I$ in aqueous hydrochloric acid were examined by titration with standard iodate solution.

$$IO_3^- + 2I^- + 6H^+ + 3Cl^- \rightarrow 3ICl + 3H_2O$$

$$IO_3^- + 2I_2 + 6H^+ + 5Cl^- \rightarrow 5ICl + 3H_2O$$

The results indicate that all of the iodine species in solution are in the form of I_2 molecules.

$$Ni(DPG)_2I \xrightarrow{HCl(aq)} Ni(DPG)_2 + {}^1/_2I_2$$

It should be noted that an experiment of this type does not necessarily reflect the oxidation state of iodine in the solid complex. The iodine in acid solution could be produced intramolecularly during dissolution (*i.e.*, $Ni^{III} + I^- \rightarrow Ni^{II} + {}^1/_2I_2$) or in solution as a result of reactions of the type

$$2Ni^{III} + 2H_2O \rightarrow 2Ni^{II} + H_2O_2 + 2H^+$$

$$2I^- + H_2O_2 + 2H^+ \rightarrow 2H_2O + I_2$$

The absorption spectrum of $Ni(DPG)_2I$ dissolved in chloroform also indicates the presence of I_2.[6]

$[Ni(DPG)_2(py)_2]X$ (X = Br, I) were obtained by dissolving $Ni(DPG)_2X$ in pyridine or by the direct reaction of iodine with $Ni(DPG)_2$ in pyridine followed by the removal of the solvent by vacuum distillation. When a weighed sample of $Ni(DPG)_2I$ is dissolved in pyridine and evaporated to constant weight, the sample shows a weight gain of 23.0%, which corresponds to the formulation $[Ni(DPG)_2(py)_2]I$ for the solid. The presence of this bis(pyridinate) complex in solution is demonstrated by ^{14}N hyperfine coupling from two equivalent pyridine nitrogens in the epr spectrum. $Co(DPG)_2(py)_2$ was synthesized by the method of Schrauzer.[10]

Instrumentation and Measurements. Bulk magnetic susceptibilities of powdered samples were measured on a Gouy balance using $Hg[Co(NCS)_4]$ and $CuSO_4 \cdot 5H_2O$ as calibrants. Magnetic moments in 10% v/v TMS–pyridine solution were determined by the nmr method of Evans.[11] The TMS resonance shift was measured on a Varian A-60A spectrometer and the susceptibility calculated using χ_v(solvent) = -0.610×10^{-6} cgsu/ml at 20°. Bis(diphenylglyoximato)nickel(II) in pyridine solvent was found to be diamagnetic by this method.

Spin susceptibilities were measured by comparison of the area under the epr absorption curve of a weighed amount of complex with the areas produced by known amounts of polycrystalline DPPH under identical instrumental conditions and modulation amplitude and corrected for changes in signal amplification.

All electron paramagnetic resonance spectra were collected on a Varian Model V-4502 X-band spectrometer, equipped with a Fieldial Mark I, Hewlett-Packard Model 7001AM X-Y recorder, and a Hewlett-Packard frequency meter, Model X532B. Cooling was provided by cold nitrogen gas and the temperature was controlled to ±2° using a Varian V-4557 variable-temperature accessory. The field and frequency calibrations were made using polycrystalline DPPH (g = 2.0036), field dial, and an X532B frequency meter. Powdered samples were run under vacuum and solutions were degassed by the freeze–pump–thaw cycle method before recording their spectra. Single-crystal measurements were obtained by mounting the crystal on a quartz rod in conjunction with a Varian Model E-229 goniometer head.

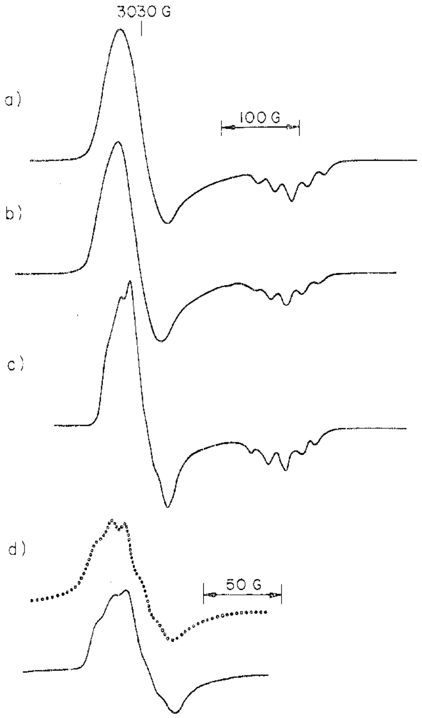

Figure 1. Epr spectra for $[Ni(DPG)_2(py)_2]X$ complexes in frozen solution (−140°): (a) $X^- = I^-$ ($g_\parallel = 2.034$, $g_\perp = 2.162$, $a_\parallel(^{14}N) =$ 20.1 G) in pyridine; (b) $X^- = Br^-$ ($g_\parallel = 2.039$, $g_\perp = 2.17$, $a_\parallel(^{14}N) =$ 20 G) in pyridine; (c) $[Ni(DPG)_2(py)_2]^+$ in a mixed pyridine–dichloromethane medium; (d) expanded $g_\perp$ region of (c) (———) and simulation using $g_\perp = 2.162$ and $a_\perp(^{14}N) = 15.5$ G (· · · · ·).

Electronic spectra were collected on a Cary Model 14 spectrophotometer. Absorbances were measured against air and then corrected for base line variations and solvent absorptions where appropriate.

Results and Discussion

$[Ni(DPG)_2(py)_2]X$ (X = Br, I). $Ni(DPG)_2X$ (X = Br, I) when dissolved in nitrogen donor solvents such as pyridine and piperidine result in formation of paramagnetic complexes. Solution magnetic susceptibility measurements for $Ni(DPG)_2I$ in pyridine by the nmr method demonstrate the presence of one unpaired electron per nickel ($\chi_g(24°) = 2.71 \times 10^{-6}$ cgsu/g; μ_{eff} = 2.07 BM). Epr spectra for frozen solutions of $Ni(DPG)_2X$ in pyridine are given in Figure 1. Epr spectra identical with those in Figure 1 can also be obtained by addition of I_2 to pyridine solutions of $Ni(DPG)_2$. A complex with the stoichiometry $[Ni(DPG)_2(py)_2]I$ can be isolated from these solutions. Presence of ^{14}N hyperfine lines with the intensity ratios of 1:2:3:2:1 in frozen pyridine also indicates the stoichiometry $[Ni(DPG)_2(py)_2]I$. Closely related observations are obtained in piperidine solution and glass media.

The presence of ^{14}N hyperfine from the axial pyridine ligands and the epr g values ($g_\parallel$ = 2.034, $g_\perp$ = 2.162) indicate that $[Ni(DPG)_2(py)_2]I$ is an authentic nickel(III) complex with the odd electron in the d_{z^2} mo. The g value expressions for the $(d_{z^2})^1$ configuration in effective axial symmetry are $g_\parallel$ = 2.002 and $g_\perp = 2.002 - 6\lambda/\Delta E_{xz,yz\rightarrow z^2}$.[12]

Electronic spectra for $Ni(DPG)_2$ and $Ni(DPG)_2I$ in pyridine are shown in Figure 2. Oxidation of $Ni(DPG)_2$ by iodine in pyridine results in the appearance of a new band as a shoulder on the charge-transfer and intraligand band region. Gaussian analysis of this region indicates that the new band is centered

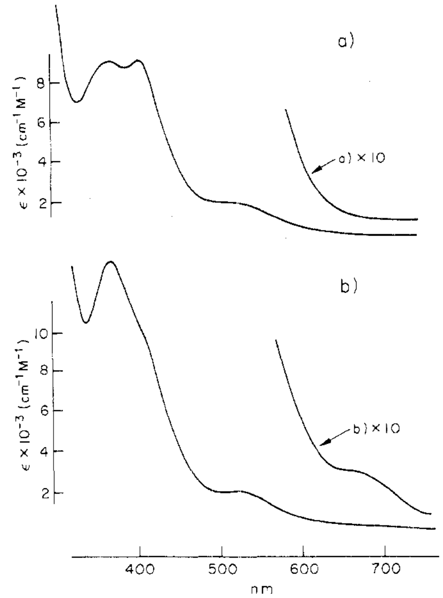

Figure 2. Electronic spectra for pyridine solutions of $Ni(DPG)_2$ in the presence and absence of iodine: (a) 0.837×10^{-3} *M* $Ni(DPG)_2$; (b) 0.8376×10^{-3} *M* $Ni(DPG)_2$ and 0.4188×10^{-3} *M* iodine.

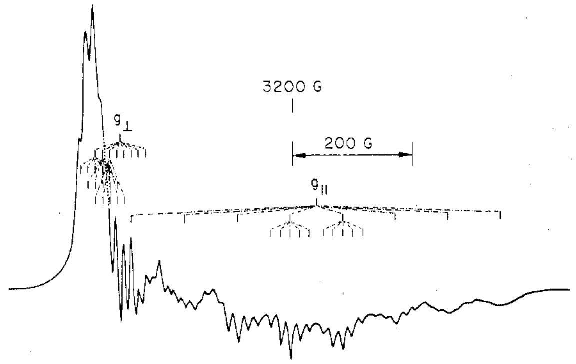

Figure 3. Frozen-solution epr spectrum for $Co^{II}(DPG)_2(py)_2$ in a mixed toluene–pyridine medium (−160°).

at 14,650 cm^{-1} (ϵ_{max} 100 M^{-1} cm^{-1}). This band is clearly associated with a d → d transition and is in the region appropriate for the $d_{xz,yz} \rightarrow d_{z^2}$. Using $\Delta E_{xz,yz \rightarrow z^2} = 14{,}650$ cm^{-1} and $g_\perp = 2.162$ results in $\lambda_{eff} = -391$ cm^{-1} which is 55% of the free-ion value (λ_0(Ni(III)) $\simeq -715$ cm^{-1}).[13] This result is similar to those reported by Gore and Busch in related Ni(III) complexes.[14] The large reduction in the effective spin–orbit coupling constant is associated with the axial ligands strongly interacting with nickel(III). The charge effects can be explored further by comparing this Ni(III) species with the isoelectronic $Co(DPG)_2(py)_2$.

$Co(DPG)_2(py)_2$. $Co(DPG)_2$ interacts with pyridine to form a bis(pyridinate), $Co(DPG)_2(py)_2$, and the epr spectrum has previously been reported in dichloromethane media.[10] We have reexamined the epr spectrum for $Co(DPG)_2(py)_2$ in frozen toluene in order to obtain more accurate epr parameters (Figure 3). The odd electron in $Co(DPG)_2(py)_2$, as in the nickel(III) complex, is placed in the d_{z^2} by the epr *g* values and the presence of pyridine ^{14}N hyperfine coupling (Figure 3). The appropriate relationships between electronic structure and metal nuclear hyperfine parameters for the $(d_{xz}\ d_{yz}, d_{xy})^6(d_{z^2})^1$ configuration are[12]

$$A_\parallel(^{59}Co) = P[-K + 4/7 - 1/7(g_\perp - 2.002)]$$

$$A_\perp(^{59}Co) = P[-K - 2/7 + 15/14(g_\perp - 2.002)]$$

$$\langle A\rangle(^{59}Co) = P[-K + 2/3(g_\perp - 2.002)]$$

The epr parameters for $Co(DPG)_2(py)_2$ are $g_\parallel = 2.016$, $g_\perp = 2.243$, $A_\parallel(^{59}Co) = 0.00834$ cm^{-1} (88.7 G), and $A_\perp(^{59}Co) = 0.00127$ cm^{-1} (12.1 G). Solving the coupling constant expressions results in $P = 0.0170$ and $K = 0.0460$. Signs for the cobalt-59 coupling constants ($A_\parallel > 0$, $A_\perp < 0$) are established from the condition that *P* must be positive. Reduction of the cobalt *P* value and effective spin–orbit coupling constant by ~25% from the free-ion value of $P_0 \approx 0.023$[15] is largely caused by redistribution of odd electron population from the cobalt d_{z^2} to the pyridine ligand σ-donor orbital.

Using the observed $g_\perp$ and an effective spin–orbit coupling constant (λ_{eff}) reduced from the free-ion value ((λ_0(Co(II)) $\simeq -515$ cm^{-1})[13] by the same fraction as the *P* value permits the estimation of the $d_{xz,yz} \rightarrow d_{z^2}$ energy separation as ~9500 cm^{-1}.

Cobalt spin densities ($\rho_{3d} = 0.74$, $\rho_{4s} = 0.044$, $\rho_{Co} = 0.78$) are estimated from the ^{59}Co hyperfine coupling constants. Cobalt $3d_{z^2}$ spin densities (ρ_{3d}) are evaluated from comparison of the observed *A* dipolar value ($^4/_7P = 0.00971$ cm^{-1}) with the theoretical value ($^4/_7P_0 = 0.013$ cm^{-1}) for a cobalt 3d electron. Cobalt 4s spin densities are estimated from the relationship $A(\text{contact}) = \rho_{4s}A(Co_{4s}) + \rho_{3d}A(Co_{3d})$, where $A(Co_{4s}) = 0.1234$ cm^{-1} (1320 G) and $A(Co_{3d}) = -0.00841$ cm^{-1} (−90 G).[16]

Nitrogen-14 Hyperfine Splitting and Donor Atom Spin Densities. Pyridine ^{14}N hyperfine coupling is resolved in both the $g_\parallel$ and $g_\perp$ regions for $Co(DPG)_2(py)_2$ and $[Ni(DPG)_2(py)_2]^+X^-$ (Figures 1 and 3). Analysis of the ^{14}N coupling constant data for these complexes provides a means of evaluating the coordinated pyridine N_{2s} and N_{2p} spin densities. Isotropic ^{14}N coupling constants yield the N_{2s} spin densities ($\rho_{2s} = \langle a\rangle/a(N_{2s})$; $a(N_{2s}) = 0.0516$ cm^{-1} (552 G)), and the anisotropic data yield the 2p spin densities ($\rho_{2p} = (a_\parallel - \langle a\rangle)/a(N_{2p})$; $a(N_{2p}) = 0.00318$ cm^{-1} (34 G)).[17]

The observed pyridine ^{14}N coupling constants for $Co(DPG)_2(py)_2$ are $a_\parallel(^{14}N) = 16.4 \pm 0.2$G (0.00154 cm^{-1}) and $a_\perp(^{14}N) = 12.1 \pm 0.5$ G (0.00127 cm^{-1}). Analysis of these data gives $\rho_{2s} = 0.0264$, $\rho_{2p} = 0.0566$, and $\rho_{2s}/\rho_{2p} = 0.47 \pm 0.05$, which corresponds closely to an sp^2 hybrid. The total spin density on each pyridine is ~0.083. Summing the cobalt and pyridine spin densities accounts for 95% of the odd electron ($\rho_{Co} = 0.78$, $2\rho_{py} = 0.17$). This result suggests that the donor orbital for coordinated pyridine may be essentially a localized sp^2 hybrid. A large series of tetraphenylporphyrin–cobalt(II) complexes with phosphorus donors have been similarly analyzed and 92–98% of the spin density is accounted for by summing the cobalt and phosphorus atoms.[18–20] The relatively small atomic hyperfine parameters for ^{14}N made the estimated spin densities subject to larger fractional uncertainties than those of the phosphorus donors we have recently reported.

The ^{14}N coupling constants for $[Ni(DPG)_2(py)_2]I$ are $a_\parallel(^{14}N) = 20.1 \pm 0.5$ G (0.00191 cm^{-1}) and $a_\perp(^{14}N) = 15.5 \pm 0.5$G (0.00156 cm^{-1}) which transcribe into 2s and 2p spin densities of 0.033 and 0.072, respectively. The ratio $\rho_{2s}/\rho_{2p} = 0.45$ is close to an sp^2 hybrid and virtually the same as in the Co(II) complex. The total spin density on each pyridine in $[Ni(DPG)_2(py)_2]I$ of 0.105 is about 27% larger than in the isoelectronic cobalt(II) complex.

The results from analysis of the epr parameters for the isoelectronic species $[Ni(DPG)_2(py)_2]^+$ and $Co(DPG)_2(py)_2$ clearly show the metal center charge effects. The nickel(III) species has smaller (λ_{eff}/λ_0), larger $\Delta E_{xz,yz \rightarrow z^2}$, and larger pyridine spin density, properties which are associated with the substantially more effective interaction of pyridine with nickel(III) compared with the isoelectronic cobalt(II).

Solid $M(DPG)_2X$. Crystals and powders of $M(DPG)_2X$ (M = Ni, Pd; X = Br, I) have a green to bronze lustrous appearance. Magnetic susceptibility studies demonstrate that

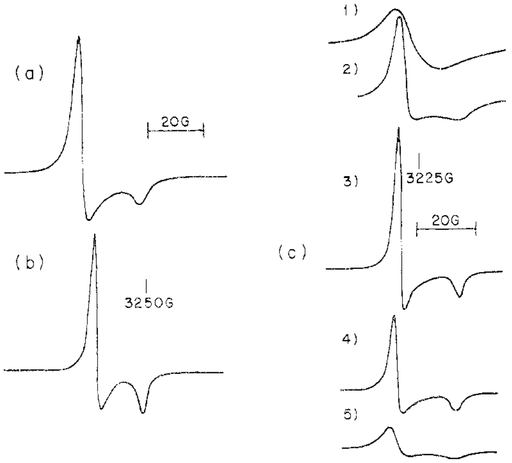

Figure 4. Epr spectra from powders of $M(DPG)_2X$: (a) $Ni(DPG)_2I$ (25°), $g_\perp = 2.022$, $g_\parallel = 2.009$; (b) $Pd(DPG)_2I$ (25°), $g_\perp = 2.018$, $g_\parallel = 2.008$; (c) temperature dependence of $Ni(DPG)_2Br$ resonance, at (1) −140°, (2) −85°, (3) −40°, (4) 30°, (5) 100°. (The g values at 30° are $g_\perp = 2.022$ and $g_\parallel = 2.009$.)

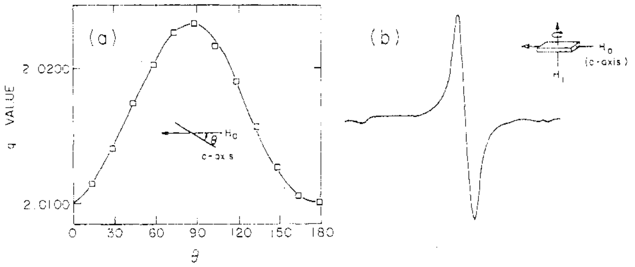

Figure 5. Angular dependence for the epr spectrum from a crystal of $Ni(DPG)_2Br$: (a) data collected with *a* axis perpendicular to the external magnetic field, H_0; (b) observed epr signal with the *c* axis and H_0 coincident.

the solids are essentially diamagnetic when pure.[6,21,22] We find a molar susceptibility for $Ni(DPG)_2I$ of -152×10^{-6} cgsu/mol at 297°K which can be factored into diamagnetic ($\chi_d = -383 \times 10^{-6}$ cgsu/mol)[21] and paramagnetic ($\chi_p = +231 \times 10^{-6}$ cgsu/mol) contributions. The observed χ_p is associated with temperature-independent paramagnetism.

Characteristic epr spectra, which are only slightly dependent on the choice of metal,[6] are frequently observed for samples of these complexes (Figure 4). Spin susceptibility measurements on samples of $Ni(DPG)_2I$ prepared from dichlorobenzene indicated the presence of 0.3–0.5% paramagnetic centers, while similarly prepared samples of $Ni(DPG)_2Br$ contained 1–3% of these centers. The direct reaction of solid $Ni(DPG)_2$ with bromine frequently resulted in much higher fractions (>10%) of paramagnetic sites. Slowly diffusing separate benzyl alcohol solutions of iodine and $Ni(DPG)_2$ through a 4–8-μ sintered-glass disk produced crystals of $Ni(DPG)_2I$ which showed no epr transitions.[21] $Pd(DPG)_2I$ crystals can also be obtained without epr-detectable paramagnetic centers.[23] The frequently observed epr spectrum is most probably caused by a defect in the crystal resulting in a paramagnetic impurity center. Single-crystal studies for $Ni(DPG)_2Br$ (Figure 5) show that the g_{zz} value for this paramagnetic center is aligned with the crystal c axis which is the axis along which the "$Ni(DPG)_2$" units stack. The paramagnetic sites are thus oriented in the crystal in the same manner as the bulk $Ni(DPG)_2$ units. This alignment has also been demonstrated in $Ni(DPG)_2I$.[6]

Epr g values slightly in excess of the free-electron value (*e.g.*, for $Ni(DPG)_2I$; $g_\parallel = 2.009$ and $g_\perp = 2.022$) and only a small metal dependency are indicative of a coordination-stabilized ligand cation radical.[3] There is no evidence for impurity centers corresponding to Ni(III) or Pd(III) species which would produce distinctive epr spectra with substantially larger g value anisotropy.[1] Solid $Ni(DPG)_2X$ contains $Ni(DPG)_2$ units stacked in columns.[6] Occurrence of nickel(III) requires the presence of axial donors such as pyridine or M–M interactions which shift the d_{z^2} above the filled ligand π orbitals. In the absence of these axial interactions, oxidation will most probably result in loss of an electron from the ligand based π orbitals. A $Ni(DPG)_2^+$ unit which does not fit properly into the column could then be expected to be formulated as $[Ni^{II}(DPG)_2]^+$. This type of species is undoubtedly responsible for the observed paramagnetic center in samples of $M(DPG)_2X$.

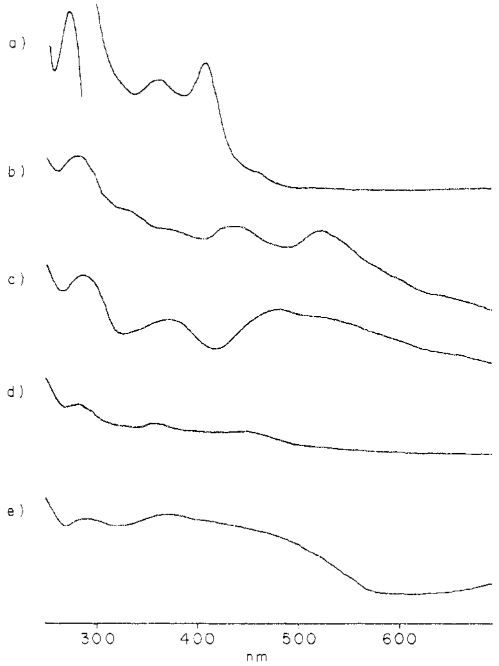

Figure 6. Electronic spectra of $M(DPG)_2$ species: (a) $Ni(DPG)_2$ (chloroform solution); (b) $Ni(DPG)_2$; (c) $Ni(DPG)_2I$; (d) $Pd(DPG)_2$; (e) $Pd(DPG)_2I$ ((b)–(e) are Nujol mulls).

The temperature dependence of the epr spectra in the crystal or powder is very unusual. Lowering the temperature results in broadening and eventual merger of the $g_\parallel$ and $g_\perp$ transitions (Figure 4). Although the general spectral changes are reversible with temperature, the transition intensities tend to decrease on cycling to low temperatures, suggesting a low-temperature annealing process. The temperature effects on the epr could possibly be associated with formation of dimer units.

The nature of the metal chelate and halogen species in the bulk solid $M(DPG)_2X$ is the more important issue and despite several attempts is not yet properly understood.[6,21,23] A preliminary X-ray structure determination for $Ni(DPG)_2I$ provided data which failed to refine in three dimensions;[6] however, presence of $Ni(DPG)_2$ units stacked along the c axis was shown. The species in the solid can be formulated in the most general form as $[M(DPG)_2{}^{r+}]_n$, $(n/m)(I^{r-})_m$, where r is the average net positive charge on the $M(DPG)_2$ unit, n is the column length of the metal chelate fragments, and m is the length of any I^{r-} polymer units which could be present. Several of the more plausible formulations for the electron distribution consistent with the limited structural and magnetic data in the solid are as follows: (I) $[M(DPG)_2]_n{}^{n/3+}$,$(n/3)(I_3^-)$, where chains of both oxidized metallo chelates $M(DPG)_2{}^{1/3+}$ units and partially reduced iodine ($I^{1/3-}$) units occur; (II) $[M(DPG)_2]_n{}^{n+}$,$n(I^-)$, where either the metal or DPG ligand in each $M(DPG)_2$ unit loses one electron to each iodine atom. Formulation (I) is attractive in that the effective oxidation states for the metallo and halogen units correspond to values observed in the partially oxidized platinum chain salts ($M^{2.33+}$) and starch–iodine chain-type species (I_3^-), respectively.[7,24] Partially occupied electronic bands occurring in species of this type can produce metallic conduction.[7] Formulation (II) consists of stacked $M(DPG)_2^+$ units with I^- as the counteranion. Either metal d_{z^2} or ligand π bands will be half-filled in this model. Electronic spectra for $M(DPG)_2I$ (M = Ni, Pd) mulls (Figure 6) do not show the electronic spectral bands in the 6250-Å region characteristic of starch–iodine type materials,[24] which prompts us to favor formulation (II). However resolution of this problem must await complete X-ray structural characterization of these materials.

Acknowledgment. The authors acknowledge support of the National Science Foundation through Grant DMR72-03025 and Advanced Research Projects Agency Order 2380, Grant DAHC15-73-G14.

Registry No. $[Ni(DPG)_2(py)_2]I$, 53965-99-4; $[Ni(DPG)_2(py)_2]Br$, 53966-00-0; $Ni(DPG)_2$, 14286-61-4; $Co(DPG)_2(py)_2$, 42957-80-2; $Ni(DPG)_2I$, 53966-02-2; $Pd(DPG)_2I$, 53966-03-3; $Ni(DPG)_2Br$, 53966-01-1; $Pd(DPG)_2$, 16049-94-8.

References and Notes

(1) F. V. Levecchio, E. S. Gore, and D. H. Busch, *J. Amer. Chem. Soc.*, **96**, 3109 (1974).

(2) R. S. Drago and E. I. Baucom, *Inorg. Chem.*, **11**, 2064 (1972).

(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 40 (1968).

(4) L. E. Edelman, *J. Amer. Chem. Soc.*, **72**, 5765 (1950).

(5) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).

(6) A. S. Foust and R. H. Soderberg, *J. Amer. Chem. Soc.*, **89**, 5507 (1967).

(7) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).

(8) A. Garito and A. Heeger, *Accounts Chem. Res.*, **7**, 232 (1974).

(9) H. Grossman and J. Mannheim, *J. Chem. Soc.*, **112**, ii, 391 (1917).

(10) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, **92**, 1551 (1970).

(11) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(12) A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

(13) B. A. Goodman and J. B. Raynor, *Advan. Inorg. Chem. Radiochem.*, **13**, 135 (1970).

(14) E. S. Gore and D. H. Busch, *Inorg. Chem.*, **12**, 1 (1973).

(15) A. Abragram and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **206**, 173 (1951).

(16) M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc. A*, 2069 (1971).

(17) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967.

(18) B. B. Wayland and M. E. Abd-Elmageed, *J. Chem. Soc., Chem. Commun.*, 61 (1974).

(19) B. B. Wayland and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, **96**, 4809 (1974).

(20) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, **96**, 2795 (1974).

(21) J. Simek, *Collect. Czech. Chem. Comm.*, **27**, 337 (1962).

(22) I. B. Barnaovskii and V. I. Belova, *Zh. Neorg. Khim.*, **10**, 306 (1965).

(23) H. J. Keller and K. Seibold, *J. Amer. Chem. Soc.*, **93**, 1309 (1971).

(24) R. Bersohn and I. Isenberg, *J. Chem. Phys.*, **35**, 1640 (1961).

Contribution from the Research School of Chemistry,
Australian National University, Canberra, A.C.T., Australia

Thio Derivatives of 1,3-Diketones and Their Metal Complexes. Dithiomalonamide and Its Nickel(II), Palladium(II), and Platinum(II) Derivatives

R. L. MARTIN* and A. F. MASTERS

Received May 29, 1974 AIC40348H

The complexes $[M(NH_2SacNH_2Sac)_2]$ (M = Ni, Pd, Pt; $NH_2SacNH_2Sac^-$ = dithiomalonamidate anion) have been synthesized and characterized. Comparative (ir, visible, uv, pmr, and mass) spectral studies on the divalent metal complexes and the related species dithiomalonamide and 3,5-diamino-1,2-dithiolium iodide have established their structural characteristics. The electrochemical behavior of the above compounds in acetone–0.1 *M* Et_4NClO_4 at both a dme and a platinum electrode is also reported. Polarography (dc and ac), coulometry, and linear sweep and cyclic voltammetry have been employed to investigate the electrode processes. The mass spectrometric behavior of a number of substituted 1,2-dithiolium cations is correlated in terms of pyrolytic decomposition as the precursor to ionization. It is concluded that NH_2SacNH_2Sac preferentially coordinates the group VIII metals *via* SS rather than SN or NN donation. The substitution of the CH_3 groups in dithioacetylacetone by NH_2 has been shown to have a marked effect on the redox and ion fragmentation behavior of these chelates.

Introduction

Dithiomalonamide[1] and N,N′-disubstituted dithiomalonamides[2] can function as either neutral or anionic ligands with nitrogen and sulfur available as potential donor atoms. The small amount of data available on such complexes[2–5] is conflicting and their interpretation is often speculative. Thus, bis(dithiomalonamidato)nickel is claimed to be dimeric in one report[3] and monomeric in another.[5] It has been inferred[4] that bis(dithiomalonamide)cobalt(II) dichloride coordinates *via* both sulfur atoms, while the coordination in the nickel analog is assigned[5] as being through sulfur and nitrogen. On the other hand, bis(dithiobiureto)nickel has been shown by X-ray analysis[6] to involve coordination *via* both sulfur atoms. Unfortunately, the interpretation of the infrared data obtained for some bis(dithiobiuret)metal(II) dichlorides is not compelling.[7,8] However, coordination *via* both sulfur atoms appears to be probable in these cases.

By contrast, complexes of dithioacetylacetone and related ligands have been more extensively studied.[9–15] Such studies have been hampered, to some extent, by the tendency of the free ligands to polymerize in the absence of a coordinating site. Oxidation of dithio-β-diketonate complexes frequently yields the corresponding 1,2-dithiolium ion.[10,16,17] Dithiomalonamide offers advantages over many dithio-β-diketones in that it is stable in the form of free dithiomalonamide and will complex metal centers as such. Alternatively, it can lose a proton and coordinate metal ions as an anionic ligand, or it can readily be oxidized to the "3,5-diamino-1,2-dithiolium" ion.[18] Hordvik[19] has suggested that this species would be better formulated as an imine-type moiety, and this is reflected in some of its chemistry (*vide infra*). However for purposes of reference and comparison, we will refer to it as a dithiolium ion.

The electrochemical behavior of tris(β-diketonato)ruthenium complexes has been shown to depend upon the nature of the chelate ring substituents,[20] and a similar effect has been observed with dithio-β-diketonates. In particular, the replacement of both CH_3 groups by NH_2 groups should facilitate oxidation of the derived metal complexes.

Accordingly, we have prepared complexes of both dithio-