($f_{MM}$ = 0.82 mdyn/Å,[12] $d$ = 3.02 Å[13]), $Os_3(CO)_{12}$ ($f_{MM}$ = 0.91 mdyn/Å,[4] $d$ = 2.89 Å[14]), $Ir_4(CO)_{12}$ ($f_{MM}$ = 1.69 mdyn/Å,[4] $d$ = 2.68 Å[15]), and $Hg_2(OH_2)_2^{2+}$ ($f_{MM}$ = 1.93 mdyn/Å,[16] $d$ = 2.54 Å[17]). These force constants are not strictly comparable, because of differences in geometry and in required interaction constants. Nevertheless the trend is clear and the position of $L_3Pt_3(SnCl_3)_2$ is anomalous.

### Experimental Section

Orange-red crystals of $L_3Pt_3(SnCl_3)_2$ were kindly provided by Dr. L. J. Guggenberger, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co. Wilmington, Del. The compounds $LPtX_2$ (X = Cl, Br) were prepared by Chatt's method.[18] Infrared spectra were kindly recorded by Miss B. Prescott of Bell Telephone Laboratories, Murray Hill, N. J., with a Beckman IR 11 spectrometer using Nujol mulls. Raman spectra were obtained with microcrystalline samples of $LPtX_2$ and a single crystal as well as powder samples of $L_3Pt_3(SnCl_3)_2$, using a spectrometer[19] equipped with a He–Ne laser source.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KENTUCKY, LEXINGTON, KENTUCKY 40506

# Complexes with Sulfur and Selenium Donors. IV. Bis(*O,O'*-diisopropyldithiophosphato)nickel(II) and Its Pyridine and Picoline Adducts[1]

BY H. E. FRANCIS, G. L. TINCHER, W. F. WAGNER,
J. R. WASSON,* AND G. M. WOLTERMANN

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Planar, diamagnetic, four-coordinate compounds of nickel(II) are known readily to form paramagnetic five- and six-coordinate complexes upon addition of amines.[1-4] Purple bis (*O,O'*-diethyldithiophosphato)nickel(II), $Ni(C_2H_5dtp)_2$, and its green amine adducts have been the subject of several investigations.[4-6] The crystal structures of $Ni(C_2H_5dtp)_2$[5] and its trans pyridine diadduct have been determined.[6] The Ni–S distance increases from 2.21 Å in $Ni(C_2H_5dtp)_2$ to 2.49 Å in the pyridine diadduct. For both compounds is can be argued,[4] on the basis of P–S bond distances, that the Ni–S bond has appreciable ionic character. Similar proposals can be made for vanadium(III),[7] zinc(II), and cadmium(II)[8] substituted-dithiophosphate complexes. However, studies of the electronic spectra[1-4] of dithiophosphate complexes, particularly of the oscillator strengths of the transitions and nephelauxetic parameters,[9] have led to the conclusion that there is considerable covalency in the metal–ligand bonding.

It is well-known that the observation of proton magnetic resonance shifts in paramagnetic transition metal complexes can be used to obtain information about electronic structure.[10] Pmr studies of paramagnetic pyridine and other heterocyclic-amine complexes have demonstrated that unpaired electron density is delocalized into these amine ligands by a mechanism principally involving the ligand $\sigma$ molecular orbitals.[11] In order to obtain more definitive information regarding the electronic structure of dithiophosphate complexes, we have undertaken pmr studies of bis(*O,O'*-diisopropyldithiophosphato)nickel(II), $Ni(i\text{-}C_3H_7dtp)_2$, and its paramagnetic pyridine and picoline adducts. Additional characterization of the complexes was obtained by investigations of the thermal properties and electronic spectra of the compounds.

### Experimental Section

**Preparation of Complexes.**—Phosphorus(V) sulfide was obtained from Matheson Coleman and Bell, Norwood, Ohio. All other chemicals were of the best available commercial, reagent, or spectroscopic grades. Carbon and hydrogen analyses were obtained by Mr. D. G. Sharp of the departmental analytical services. Nickel was determined by the dimethyl glyoximate method. Carbon, hydrogen, and nickel analyses for the complexes are given below. *Anal.* Calcd for $C_{12}H_{28}O_4P_2S_4Ni$: C, 29.70; H, 5.83; Ni, 12.1. Found: C, 29.73; H, 5.78; Ni, 12.1. Calcd for $C_{22}H_{42}N_2O_4P_2S_4Ni$: C, 42.93; H, 6.30; Ni, 8.74. Found: C, 42.74; H, 7.33; Ni, 8.87.

***O,O*-Diisopropyldithiophosphoric Acid.**—A stoichiometric amount of absolute isopropyl alcohol was added to phosphorus(V) sulfide and the mixture was stirred magnetically until it became clear (about 3 hr). The acid obtained from the alcoholysis[12] of phosphorus(V) sulfide was used immediately for the preparation of the nickel complex. Before the acid can be stored, it is necessary to bubble nitrogen gas through it for several minutes.

**$Ni(i\text{-}C_3H_7dtp)_2$.**—Stoichiometric amounts of nickel(II) chloride and *O,O'*-diisopropyldithiophosphoric acid were stirred together for 1 hr and the mixture was extracted with chloroform. The chloroform extract was filtered and the solvent was allowed to evaporate. The purple crystals of $Ni(i\text{-}C_3H_7dtp)_2$ were then recrystallized several times from chloroform.

**Diadducts of $Ni(i\text{-}C_3H_7dtp)_2$.**—Pyridine and 3- and 4-methylpyridine diadducts were obtained as green crystals by evaporating amine solutions of $Ni(i\text{-}C_3H_7dtp)_2$. Attempts to prepare adducts with 2-picoline by this method were without success since the brown products rapidly lost amine at room temperature.

**Nmr Spectra.**—The nmr spectra were recorded on Varian T-60 (operating at 35°) and HA-60-IL (operating at 33°) spectrometers. Tetramethylsilane was employed as a internal calibrant. Assignments of the peaks were made on the basis of relative intensities, spin–spin splittings, and decoupling experiments.

The diamagnetic ligand resonances are as follows: for 12.41 *M*

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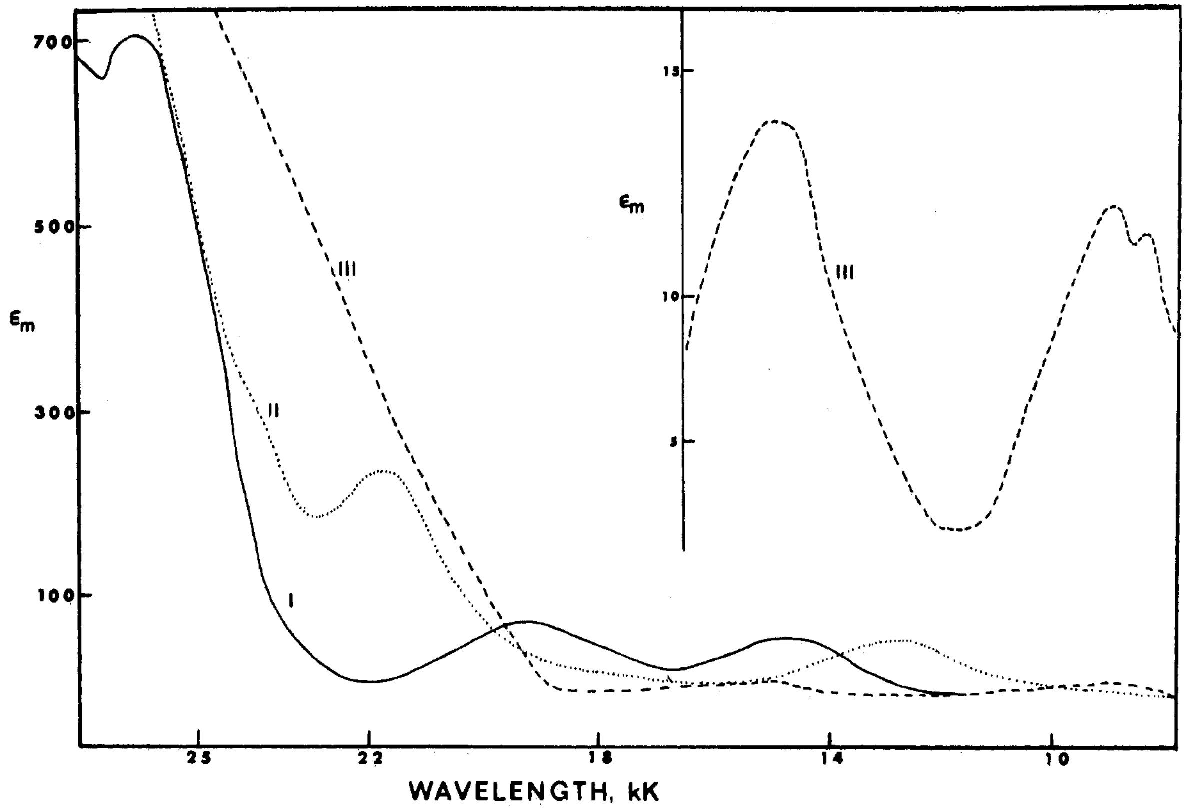

Figure 1.—Absorption spectra of Ni($i$-$C_3H_7$dtp)$_2$ and its pyridine and picoline adducts: I, pyridine; II, $\alpha$-picoline; III, $\gamma$-picoline.

TABLE I

ELECTRONIC SPECTRAL DATA

| Complex | Medium | $\nu_1$, cm$^{-1}$ | $\epsilon_1$[a] | $10^6 f_1$[b] | $\nu_2$, cm$^{-1}$ | $\epsilon_2$ | $10^6 f_2$ | $\nu_3$, cm$^{-1}$ | $\epsilon_3$ | $10^6 f_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Ni($i$-$C_3H_7$dtp)$_2$ | $CHCl_3$ | 14,650 | 62 | 616 | 19,230 | 79 | 981 | 25,970 | 697 | 9410 |
| Ni($i$-$C_3H_7$dtp)$_2$·2py | Pyridine | 8,550 | 14 | 115 | 9,010 | 14 | 186 | 14,930 | 15 | 183 |
| Ni($i$-$C_3H_7$dtp)$_2$·2$\beta$-pic | $\beta$-Picoline | 8,550 | 13 | 121 | 9,010 | 14 | 196 | 14,930 | 14 | 214 |
| Ni($i$-$C_3H_7$dtp)$_2$·2$\gamma$-pic | $\gamma$-Picoline | 8,550 | 12 | 111 | 9,010 | 13 | 185 | 14,930 | 16 | 262 |
| Ni($i$-$C_3H_7$dtp)$_2$·2$\alpha$-pic | $\alpha$-Picoline | 12,820 | 59 | 798 | . . . | . . . | . . . | 21,834 | 238 | 2848 |

[a] Molar absorption coefficient. [b] Oscillator strengths, $f$, were calculated using the expression $f = 4.60^{-9}\epsilon_{max}\nu_{1/2}$ where $\epsilon_{max}$ is the molar absorptivity of the band maximum and $\nu_{1/2}$ is the band width at half-height expressed in wave numbers: C. J. Ballhausen, *Progr. Inorg. Chem.*, **2,** 251 (1960).

pyridine ($\alpha$, $\beta$, $\gamma$), −518, −432, −456; for 10.19 *M* 2-picoline ($\alpha$, $\alpha$-$CH_3$, $\beta$, $\beta$, $\gamma$), −508, −150, −420, −426, −448; for 10.32 *M* 3-picoline ($\alpha$, $\beta$, $\beta$-$CH_3$, $\gamma$), −507, −424, −133, −443; for 10.06 *M* 4-picoline ($\alpha$, $\beta$, $\gamma$-$CH_3$), −508, −421, −133 (all in hertz from TMS).

Solution magnetic moments at 35° were determined by Evans' nmr method[13] for adducts in chloroform solution. The measured susceptibility was corrected for diamagnetism by the use of Pascal's constants.

**Electronic Spectra.**—Electronic absorption spectra were obtained with Cary Models 14 and 15 recording spectrophotometers using matched 1.0- and 2.0-cm quartz cells. Spectra of mulled solids were obtained using a technique described previously.[14]

**Thermal Analysis.**—A Perkin-Elmer DSC-1B calorimeter was used to obtain all calorimetric data. Instrument calibration constants were evaluated using pure (99.999%) indium metal (heat of fusion 6.79 cal/g) and the equations of Schwenker and Whitwell.[15] All areas were measured (in square inches) with a compensating polar planimeter.

Thermogravimetric data were obtained with a Perkin-Elmer TGS-1 thermobalance.

## Results

**Ni($i$-$C_3H_7$dtp)$_2$. Pmr and Ligand Field Spectra.**—The pmr spectrum of diamagnetic Ni($i$-$C_3H_7$dtp)$_2$ is one characteristic of an isopropoxy group interacting with a phosphorus-31 nucleus. The strong methyl resonance, split into a doublet by the neighboring CH proton, appears at $\delta$ 8.62 with $J_{CH_3} = 6.3$ Hz. The CH absorption appears as a 14-peak multiplet with $\delta$ 4.95 and $J_{CH} = 2.5$ Hz and $J_{POCH} = 6.5$ Hz.

The electronic absorption spectra of Ni($i$-$C_3H_7$dtp)$_2$ and its adduct complexes are shown in Figure 1 and the energies and oscillator strengths of the transitions are given in Table I. Assuming effective $D_{2h}$ geometry for Ni($i$-$C_3H_7$dtp)$_2$ leads to the assignments $^1B_{1g} \leftarrow {}^1A_g$ and $^1B_{3g} \leftarrow {}^1A_g$ for the bands at 14,650 and 19,230 cm$^{-1}$, respectively. The assignment of the third band at 25,970 cm$^{-1}$ to the $^1A_u \leftarrow {}^1A_g$ transition is consistent with the assignments for Ni(MNT)$_2^{2-}$ (MNT = $S_2C_2(CN)_2^{2-}$)[16] and the observed extinction coefficient and

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TABLE II

OBSERVED ISOTROPIC SHIFTS (Hz) FOR Ni($i$-$C_3H_7$dtp)$_2\cdot$2L

| Ligand | [Ni($i$-$C_3H_7$dtp)$_2$], mol/ml | $\mu_{eff}$,[a] BM | $\mu_{eff}$,[b] BM | $\alpha$-H | $\beta$-H | $\gamma$-H | $\alpha$-$CH_3$ | $\beta$-$CH_3$ | $\gamma$-$CH_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Pyridine | 0.010 | 3.34 | 2.31 | −534 | −438 | −457 | ... | ... | ... |
| $\alpha$-Picoline | 0.025 | 2.96 | ... | −521 | −424 | −450 | 148 | ... | ... |
| $\beta$-Picoline | 0.026 | 2.95 | 2.18 | −553 | −444 | −444 | ... | −135 | ... |
| $\gamma$-Picoline | 0.024 | 4.19 | 2.79 | −591 | −451 | ... | ... | ... | −123 |

[a] Solution of Ni($i$-$C_3H_7$dtp)$_2$. [b] Solution of Ni($i$-$C_3H_7$dtp)$_2\cdot$2L.

oscillator strength agree with the expected metal→ligand charge-transfer character of the transition. In view of the lesser extent of conjugation in $i$-$C_3H_7$dtp than in MNT it is not surprising that $i$-$C_3H_7$dtp is a comparatively weak ligand. Comparable results were obtained in a study[9] of chromium(III) complexes.

The electronic spectra of the $\gamma$-picoline and $\beta$-picoline adducts are consistent with the trans octahedral structure proposed for the complexes. Essentially identical spectra were recorded for the adducts in neat ligands and mulled solids. Similar spectra have been reported for the green bis-amine adducts of nickel dithiophosphates[1,4,17] and other complexes with sulfur ligands.[18] To a first approximation Ni($i$-$C_3H_7$dtp)$_2$ adducts with pyridine, $\gamma$-picoline, and $\beta$-picoline can be treated as having octahedral geometry. Employing the "rule of average environment" and the data of Drago and Rosenthal[19] for Ni(py)$_6^{2+}$, a value of $10Dq = 8.58$ kK for $i$-$C_3H_7$dtp is obtained. This value is close to that reported by Sgamellotti and coworkers[4] and places $i$-$C_3H_7$dtp close to water in the spectrochemical series. The slight splitting of the low-energy band at about 9 kK (absent in the mulled solids) arises from tetragonal symmetry components of the ligand field present in the bis-amine adducts. For a tetragonal nickel(II) complex with effective $D_{4h}$ symmetry the lowest energy transitions are $^3B_{2g} \leftarrow {}^3B_{1g}$ and $^3E_g \leftarrow {}^3B_{1g}$ with energies $10Dq_L$ and $10Dq_L - (35/4)Dt$, respectively.[20]

The ligand field strength of the ligands along the $z$ axis is given by $Dq_z = 0.1E(^3B_{2g} \leftarrow {}^3B_{1g}) - 1.75Dt$ when configuration interaction between $E_g$ states is not taken into account. The value of $10Dq_z - 10Dq_L$ is expected to be positive since pyridine lies above $i$-$C_3H_7$dtp in the spectrochemical series; hence, $Dt$ is expected to be a negative number. Assigning the 8.55-kK band to the $^3B_{2g} \leftarrow {}^3B_{1g}$ transition gives a value of $10Dq$ for $i$-$C_3H_7$dtp in excellent agreement with the "rule of average environment" treatment of the complex given above. Taking the experimental value of $Dt$ to be $-54$ cm$^{-1}$ gives a value of $Dq = 0.996$ kK in reasonable agreement with a $Dq$ value for pyridine equal to 0.986 kK.[19] In the absence of low-temperature spectral data for the picoline adducts of Ni($i$-$C_3H_7$dtp)$_2$ the ligand field analysis cannot be taken further.

The electronic spectrum of Ni($i$-$C_3H_7$dtp)$_2$ in neat $\alpha$-picoline is consistent with a five-coordinate geometry[21] for the adduct formed in solution. Comparable spectra have been found[1,4,17] for the paramagnetic adducts of Ni($i$-$C_3H_7$dtp)$_2$ and related complexes with secondary amines. The steric crowding of the methyl group is responsible for five-coordination on the $\alpha$-picoline adduct. Molecular models indicate that this form would be preferred. Furlani[21] has also noted that a high-spin trigonal bipyramid with sulfur ligands would be unusual. The extent of out-of-plane distortion of the dithiophosphate ligands is very difficult to assess from the available data. The only structural study of a five-coordinate nickel dithiophosphate complex is that for 2,9-dimethyl-1,10-phenanthrolinebis($O,O'$-dimethyldithiophosphato)nickel(II) which was found[22] to contain the highly distorted $NiS_3N_2$ chromophore.

The magnetic moment of Ni($i$-$C_3H_7$dtp)$_2\cdot$2($\gamma$-pic) in chloroform given in Table II is anomalously high. This is probably a consequence of employing the Evans method to measure the magnetic susceptibility. The Evans method frequently yields anomalously high values of $\mu_{eff}$ presumably because of various solvation and dissociation phenomena.

**Nmr Spectra of Paramagnetic Adducts.**—The observed isotropic shifts for the pyridine and picoline adducts are collected in Table II. These shifts are in agreement with other reports in which a pyridine type ligand is attached to nickel.[23] The contact shift for the protons of the adducts were observed to be a linear function of the molar concentration of complex. Upfield methyl shifts at the $\gamma$ position in pyridine type ligands of octahedral Ni(II) complexes have long been attributed to anomalous $\pi$-spin density in these systems. Since octahedral Ni(II) does not possess unpaired $t_{2g}$ $\pi$-bonding d electrons, the mechanism of this d$\pi$ delocalization has been rationalized in terms of indirect polarization mechanisms, the most appealing of these mechanisms being that in which the unpaired spin density in the nitrogen 2s orbital could cause unpairing of a filled $\pi$ MO by exchange polarization. This is in accord with the $\sigma$-bonding scheme for these types of adducts since this mechansim does not postulate metal–ligand $\pi$ bonding.

Hückel–McLachlan spin density calculations on these complexes show that the negative spin density in the $\gamma$ position could be interpreted by direct delocalization either in the highest bonding or the lowest antibonding orbitals. The $\sigma$–$\pi$ delocalization mechanism is considered the most likely for the following reasons. (a) Octahedral nickel complexes do not possess any $\pi$-bonding unpaired electrons. (b) The pyridine protons experience only $\alpha$-spin density. (c) The observed hyperfine coupling constants from the esr spectrum of

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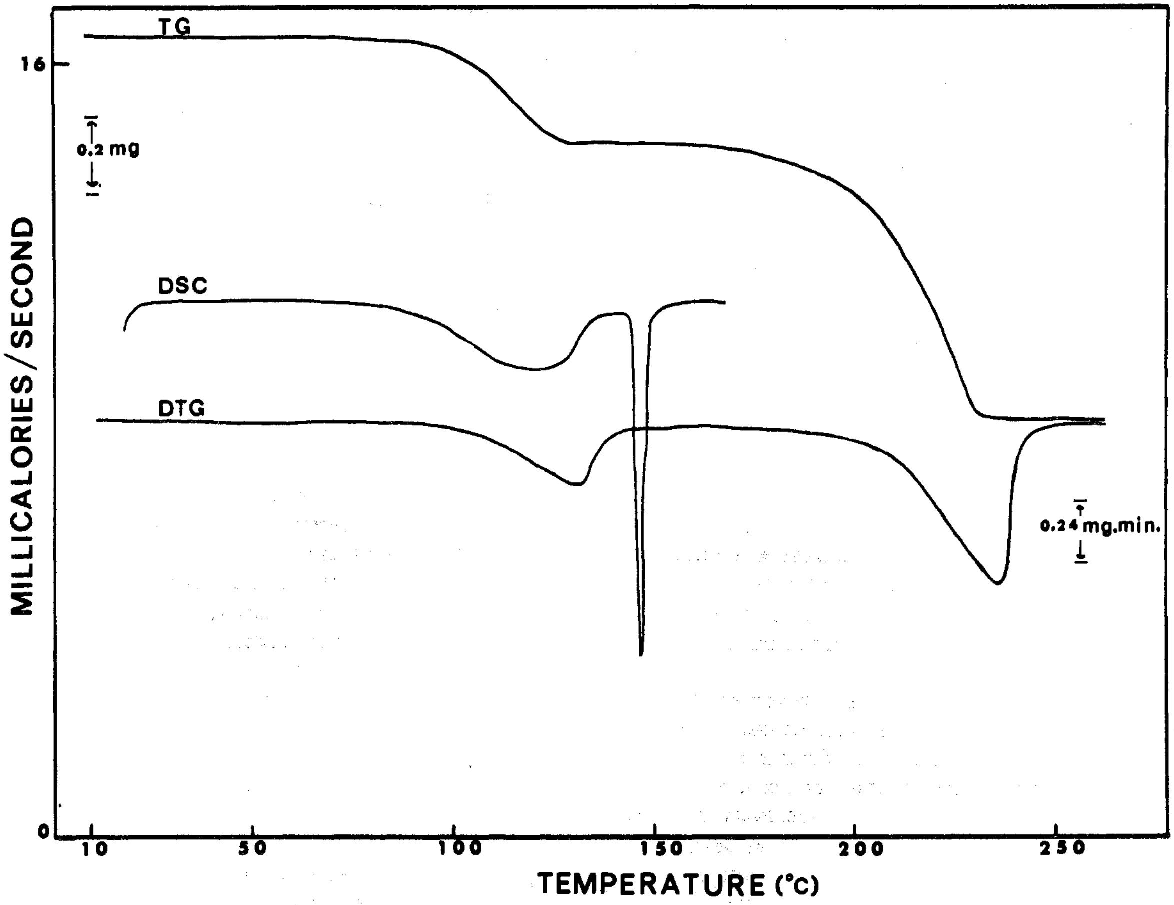

Figure 2.—Combined dsc–tg–dtg curves for $Ni(i\text{-}C_3H_7dtp)_2 \cdot 2py$ showing characteristics of decomposition.

the phenyl radical[24,25] are in good agreement with the nmr results. Open-shell INDO/2 calculations[26] on coordinated pyridine type ligands indicate that the observed shifts in these systems may be accounted for by a $\sigma$-spin delocalization model and that the upfield methyl shift is not indicative of $\pi$-spin delocalization.

Scarlett, *et al.*,[27] using an INDO calculation of spin densities in pyridine, found that all the spin densities are positive, in agreement with experiment; hence, the observed contact shifts are due to transfer of $\beta$ spin from the ligand to the metal atom leaving $\alpha$ spin on the ligand. Scarlett concluded that the operative mechanism is $\sigma$–$\pi$ delocalization. Although the unpaired electron is in a $\sigma$ orbital, there are $\pi$ orbitals close to it in energy. The INDO calculations are in much better agreement with experiment than extended Hückel MO calculations. However, neither takes the metal orbitals into consideration. It is not particularly surprising that the contact shift data for the adducts of $Ni(i\text{-}C_3H_7dtp)_2$ do not differ remarkably from comparable data for bis(acetylacetonato)nickel(II) adducts with pyridine and picoline. Crystallographic work has shown[6,28] that the Ni–N distance in the bis-pyridine adducts of both $Ni(i\text{-}C_3H_7dtp)_2$ and $Ni(acac)_2$ is 2.11 Å.

**Thermogravimetric and Dsc Results.**—Thermal decomposition of dialkyldithiophosphate complexes is known to lead to the elimination of olefins.[9,29] In this report we were only interested in the decomposition of the complex with regard to the elimination of the adduct and not the decomposition of the bis complex. The decomposition reaction studied is

$$\underset{\text{green crystals}}{Ni(i\text{-}C_3H_7dtp)_2 \cdot 2L} \xrightarrow{\Delta} \underset{\text{purple solid}}{Ni(i\text{-}C_3H_7dtp)_2} + 2L(g)\uparrow \qquad (1)$$

The usefulness of differential scanning calorimetry (dsc) in measuring the energies associated with this type of thermal decomposition has been well established.[30] The adducts, pyridine, $\beta$-picoline, and $\gamma$-picoline, were investigated but the corresponding complex with $\alpha$-picoline could not be examined. The thermogravimetric curve for a typical adduct is shown in Figure 2 with the corresponding dsc and derivative thermogravimetric curve. Weight loss data indicate a stoichiometry of two nitrogen donor ligands per mole of $Ni(i\text{-}C_3H_7dtp)_2$ for each of the adducts studied.

The use of the derivative of the tg curve is well known as a technique to distinguish weight changes that follow each other closely in the heating curve. Referring to Figure 2 it is apparent from the dtg curve that no stepwise loss of adduct was observed in these decomposition reactions.

The energies, $\Delta H_R$ (kcal/mol), associated with reaction 1 are presented in Table III. Typical differential

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TABLE III

THERMAL DATA

| Ligand | $H_R$, kcal/mol | $H_A$, kcal/mol |
|---|---|---|
| Pyridine | 24.0 ± 0.7 | 25.9 ± 0.3 |
| β-Picoline | 25.3 ± 0.8 | 20.2 ± 0.4 |
| γ-Picoline | 15.4 ± 0.9 | 17.1 ± 0.5 |

scanning calorimetric curves for the loss of adduct ligands are shown in Figure 3 for each of the adducts studied.

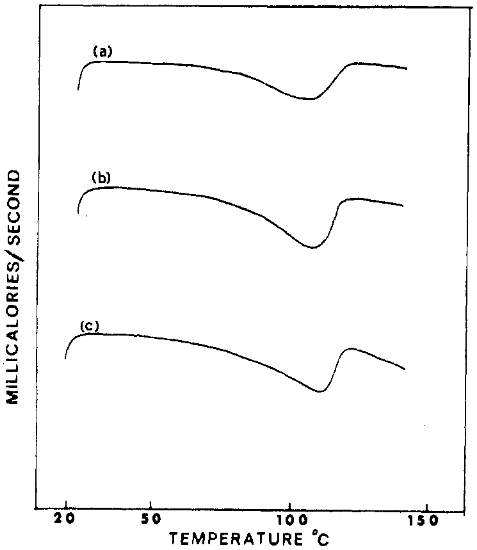

Figure 3.—Differential scanning calorimetry curves for vaporization of the amine in (a) $Ni(i\text{-}C_3H_7dtp)_2 \cdot 2py$, (b) $Ni(i\text{-}C_3H_2dtp)_2 \cdot 2\beta\text{-pic}$, and (c) $Ni(i\text{-}C_3H_7dtp)_2 \cdot 2\gamma\text{-pic}$.

The values for the pyridine and β-picoline adducts are comparable with values obtained by Beech and coworkers for the related $NiL_4Cl_2$ complexes. These workers found a value of 24.5 kcal/mol for the loss of two pyridine ligands and a value of 25.7 kcal/mol for the corresponding reaction with β-picoline.[31] The $\Delta H_R$ values are indicative of the expected trend in stability, that is, γ-picoline > β-picoline > pyridine, in agreement with the increased donor power of the nitrogen atom due to the substitution of the methyl group.

Sealed sample pans provided a means of obtaining latent heats of fusion of the $Ni(i\text{-}C_3H_7dtp)_2$ complexes, $\Delta H_A$. These values are listed in Table III. The magnitude of the energy required to melt the crystals can be related to the compactness of the crystals. The ordering of the $\Delta H_A$ fusion energies, with a considerably larger value for the pyridine adduct, is in accordance with the less bulky character of pyridine as compared with the picolines.

Enthalpy values were also obtained for the purple $Ni(i\text{-}C_3H_7dtp)_2$ complex, $\Delta H = 10.1 \pm 0.5$ kcal/mol. This is in close agreement with the energy required to melt the residue from reaction 1 ($\Delta H = 10.5$ kcal/mol). We conclude from these values that the residue product was the starting complex $Ni(i\text{-}C_3H_7dtp)_2$.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
BROOKHAVEN NATIONAL LABORATORY,
UPTON, NEW YORK 11973

# Induction of the Thallium(I)–Thallium(III) Exchange by Iron(II)[1]

BY BJÖRN WARNQVIST AND R. W. DODSON*[2]

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The oxidation of iron(II) by thallium(III) is believed to proceed *via* thallium(II) as an intermediate.[3] The thallium(I)–thallium(III) electron exchange is accelerated by irradiation with X-rays[4] and with ultraviolet light.[5] This effect has been ascribed to the formation of thallium(II) and rapid exchange reactions between this species and the 1+ and 3+ oxidation states. It is therefore to be expected that iron(II) will accelerate the thallium(I)–thallium(III) exchange. The present work was undertaken to investigate this possibility.

## Experimental Section

**Materials.**—Baker Analyzed perchloric acid was used. Sodium perchlorate solutions were prepared from reagent grade sodium carbonate and perchloric acid. Thallous perchlorate was precipitated with perchloric acid from a solution of thallous nitrate and was recrystallized three times. A thallic perchlorate stock solution was prepared by anodic oxidation of thallous perchlorate. Iron(II) and iron(III) perchlorates were recrystallized from perchloric acid solution. The $^{204}Tl$ tracer, obtained in nitrate solution from Oak Ridge, was converted to thallous perchlorate with perchloric acid. Methyl isobutyl ketone (Eastman White Label) was passed through neutral alumina under argon immediately before use. Tributyl phosphate (Fisher Purified) and benzene (B & A reagent) were used without purification.

**Procedure.**—All runs were made in dark vessels, under argon, at 25°. Tracer was added in the form of a thallium(I)-204 perchlorate solution. In some runs the exchange was followed for about 1 hr before the addition of iron(II). Then iron(II) was added, and measurements were continued for several hours. In other runs, iron(II) was added 2 min before the tracer. The sequence of addition of iron(II) and tracer had no discernible effect on the results. Aliquots of the reaction mixture were removed at suitable time intervals and mixed with dilute hydrochloric acid. Thallium(III) was extracted, either with methyl isobutyl ketone or with a 20 vol % tributyl phosphate–benzene mixture. Liquid samples were counted in well-type sodium iodide scintillators, with circuitry adjusted for the Hg X-rays emitted in the decay of $^{204}Tl$. In most runs both phases were counted. With the ketone extractant the organic-phase count was corrected for the slight extraction of thallium(I). With the tributyl phosphate–benzene mixture the thallium(I) was removed by backwashing with dilute hydrochloric acid before counting. An aliquot of the reaction mixture was counted without chemical separation. The counting rate per unit volume was multiplied by $[Tl(III)]/([Tl(III)] + [Tl(I)])$ to calculate $x_\infty$, the "infinite time" counting rate of the thallium(III) fraction. Because $[Fe^{II}]$ was always much less than $[Tl^{III}]$, the variation of $x_\infty$ during a run was small enough to be neglected. The exchange fraction $F$ was taken as $x/x_\infty$, where $x$ is the counting rate of the thallium(III) fraction at time $t$.

## Results and Discussion

The addition of iron(II) caused a marked increase in the rate of conversion of thallium(I) to thallium(III).

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(2) Author to whom correspondence should be addressed.

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