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## Synthesis, Structure, and Magnetism of Polynuclear Chelates. Bis(1,3,5-triketonato)dinickel(II) Chelates

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A new series of binuclear Ni(II) complexes has been prepared from substituted 1,3,5-triketone ligands, with the generalized formula  $Ni_2(1,3,5\text{-triketonato})_2B_4$ , where  $B = H_2O$  or  $py$ . The magnetic susceptibilities of all compounds were measured as a function of field strength and temperature from 77 to 420°K. For bis(1,5-diphenyl-1,3,5-pentanetrionato)tetraaquadinickel(II),  $Ni_2(DBA)_2(H_2O)_4$ , the susceptibilities were measured from 1.6 to 420°K. In the temperature region 300–420°K the Curie constant for  $Ni_2(DBA)_2(H_2O)_4$  is 1.50 corresponding to  $g = 2.46$  and a paramagnetic Weiss constant,  $\Theta_p$ , of –30°K. The  $\chi'_m$  in this temperature region can be calculated assuming  $d^8\text{--}d^8$  exchange with  $J = -15^\circ$  and  $N\alpha = 250 \times 10^{-6}$ . Below 150°K the slope of the  $\chi'_m^{-1}$  vs.  $T$  plot for  $Ni_2(DBA)_2(H_2O)_4$  is considerably different than in the high-temperature region, indicating a temperature-dependent  $J$  and/or  $g$ . The geometry of a representative member of this series,  $Ni_2(DBA)_2(py)_4 \cdot 4py$ , has been determined by single-crystal X-ray diffraction. The crystals are monoclinic,  $P2_1/n$ , with lattice constants  $a = 12.761$  (5),  $b = 17.903$  (7),  $c = 14.350$  (11) Å, and  $\beta = 102.32$  (6)°. The structure was refined by least-squares analysis to a discrepancy factor of 0.075 for 2567 independent diffractometric data. The molecular complex, possessing crystallographic site symmetry  $C_i-1$ , consists of two nickels coordinated to two 1,5-diphenyl-1,3,5-pentanetrionato ligands and to four pyridine ligands such that each Ni(II) has an octahedral environment of four coplanar oxygens and two pyridine nitrogens located above and below the metal–oxygen plane. The central oxygen donor in each 1,5-diphenyl-1,3,5-pentanetrionato ligand is bonded to both nickels thereby forming a four-membered ring containing two oxygens and two nickels. The Ni–Ni distance is 3.166 (3) Å and the intra-ring bond angles are O–Ni–O = 78.48 (24)° and Ni–O–Ni = 101.51 (24)°.

### Introduction

Kramers<sup>1</sup> first discussed magnetic exchange phenomena through bridging diamagnetic atoms in 1934. Sometime later Anderson<sup>2</sup> formalized a model for exchanging systems based largely on considerations of symmetry and orbital overlap between the metal ions and the bridging atoms. Although transition metal chemists have been interested in magnetic exchange through bridging atoms for some time, it is only recently that serious attempts have been made to apply Anderson's model to molecules in which the structural parameters are known.<sup>3–8</sup> However, it is presently not possible to state with certainty the effect of the metal–bridging atom(s)–metal bond angle or the effect of the spatial arrangement of the exchanging electrons on the magnetic exchange mechanisms.

Questions concerning the validity of Anderson's orbital model can only be resolved after much additional data are collected. An interesting system to study as a means of testing Anderson's model would be a series of binuclear complexes in which the microsymmetry of the exchanging metals is simple. In addition, if the ligands can be coordinated to several different metal ions, a series could be synthesized in which the complexes have similar stereochemistries but different numbers of d electrons available for exchange. The magnetic and structural properties of such a series could be used to assess critically the dependence of the magnetic exchange mechanism on the bridging bond angles, the number of unpaired d electrons, and the symmetry of the d electrons. A class of ligands based on 1,3,5-triketones satisfies many of

the prerequisites necessary to design a series of this type. The triketones in their dianionic form coordinate to two metal ions such that the central oxygen is bonded to both metals (Figure 1). The well-developed  $\pi$ -electron system in the coordinated ligand imparts a quite rigid planarity to the complex which makes the molecular symmetry relatively simple. Like the parent 1,3-diketones, the triketones can be expected to bond to a large number of different metal ions. To date, however, only a few reports of chelates of this potentially useful class of ligands have appeared in the literature.<sup>9–13</sup>

Although a great many magnetic exchange studies in dimeric Cu(II) systems have been carried out, very little is known about the magnetic properties of binuclear Ni(II) molecules. Several binuclear Ni(II) complexes have been reported;<sup>7,14–23</sup> however, only a small number have been thoroughly characterized magnetically.

The work reported herein represents an extension of 1,3,5-triketonato chemistry to the Ni(II) chelates and includes a thorough magnetic and structural investigation. To our

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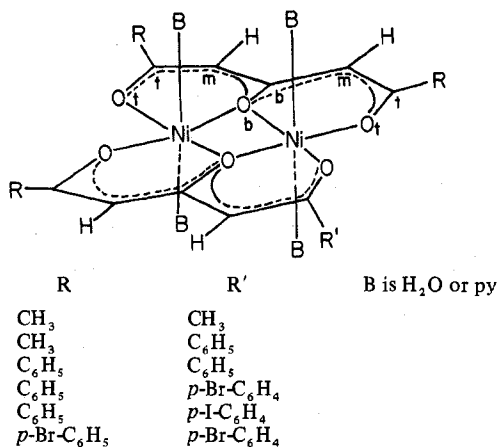


Figure 1. The generalized formula for the bis(1,3,5-triketonato)nickel(II) chelates. The conventions of terminal (t), bridging (b), and methine (m) atoms follow those in ref 12.

knowledge, no similar binuclear Ni(II) chelates have been reported.

### Experimental Section

**Ligands.** The ligand 1,5-diphenyl-1,3,5-pentanetrione was purchased from Eastman Organic Chemicals. The preparation of 2,4,6-heptanetrione from 2,6-dimethyl- $\gamma$ -pyrone (K and K Laboratories Inc.) is described in the literature.<sup>24</sup> All other triketones were prepared by the condensation of either 1-benzoylacetone (Aldrich Chemical Co.) or reagent grade acetone with the appropriate methyl ester using NaH as the condensing agent in refluxing monoglyme. This procedure has been described by Miles, Harris, and Hauser.<sup>25</sup> The purity of the ligands was established by elemental analysis.

**Binuclear Nickel(II) Chelates.** In general, the chelates were prepared by mixing a 1:1 molar ratio of ligand to metal in an alcohol-water or acetone-water system followed by addition of base. The chelates isolated have the general formula  $[\text{Ni}_2(1,3,5\text{-triketonato})_2(\text{H}_2\text{O})_4]$ . The waters are easily replaced by pyridines when the chelates are dissolved in pyridine. Isolation by concentrating the pyridine yields the pyridine adducts.

The preferred base in these preparations is NaOH. Syntheses using  $\text{NH}_4\text{OH}$  as the base result in products containing nitrogen. Ammonia can be detected over these compounds upon heating, indicating that the nitrogen is probably present as coordinated  $\text{NH}_3$  which has replaced a water molecule. The number of  $\text{NH}_3$  groups associated with the product is difficult to control under these conditions. Therefore, reproducibility using  $\text{NH}_4\text{OH}$  is not good.

In the following, the systematic nomenclature is given as well as abbreviated formulas which are based on trivial names for the triketones.<sup>26</sup>

**Bis(1,5-diphenyl-1,3,5-pentanetrionato)tetraaquodnickel(II),  $\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$ .** A solution of 1.8 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 ml of hot  $\text{CH}_3\text{OH}$  was added to 2.0 g of triketone in 250 ml of hot  $\text{CH}_3\text{OH}$ . When 0.65 g of NaOH in 10 ml of distilled  $\text{H}_2\text{O}$  was added, precipitation occurred immediately. The product was collected, dried, washed well with  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ , and dried *in vacuo*. The product changed from yellow to light brown between 100 and 150°. At about 290° a slight lightening of the brown color was observed, but no further change occurred up to 325°. *Anal.* Calcd: C, 56.87; H, 4.49; Ni, 16.43. Found: C, 57.08; H, 4.60; Ni, 16.40.

**Bis(1,5-diphenyl-1,3,5-pentanetrionato)tetrapyridinedinickel(II)-Tetrapyridine,  $\text{Ni}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$ .** One gram of  $\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$  was dissolved in 100 ml of pyridine. After concentration to 25 ml, an initial product was collected by filtration. A few crystals of the initial product were saved to seed another solution prepared in the same manner. The greenish yellow product of the second crystallization was filtered, air-dried, and stored in a well-stoppered bottle. *In vacuo* the crystals crumbled due to loss of the solvate molecules, and

(24) J. R. Bethell and P. Maitland, *J. Chem. Soc.*, 3755 (1962).

(25) M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, 30, 1007 (1965).

(26) The trivial nomenclature is as follows: 2,4,6-heptanetrione is diacetylacetone ( $\text{H}_2\text{DAA}$ ), 1-phenyl-1,3,5-hexanetrione is benzoyl-acetylacetone ( $\text{H}_2\text{BAA}$ ), 1,5-diphenyl-1,3,5-pentanetrione is dibenzoyl-acetone ( $\text{H}_2\text{DBA}$ ). The hydrogens represent the enolizable protons.

a powder which analyzed as  $\text{Ni}_2(\text{DBA})_2(\text{py})_4$  was formed. For long stability, the crystals should be stored in a pyridine atmosphere. *Anal.* Calcd for  $\text{Ni}_2(\text{C}_{17}\text{H}_{12}\text{O}_3)_2(\text{C}_5\text{H}_5\text{N})_4$ : C, 69.48; H, 5.01; N, 8.76; Ni, 8.95. Found: C, 69.11; H, 5.09; N, 8.53; Ni, 8.90.

**Bis(1-*p*-bromophenyl-5-phenyl-1,3,5-pentanetrionato)tetraaquodnickel(II),  $\text{Ni}_2(\text{p-Br(DBA)})_2(\text{H}_2\text{O})_4$ .** A solution of 1.1 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 10 ml of hot distilled  $\text{H}_2\text{O}$  was added to a solution containing 1.6 g of triketone in 100 ml of acetone and 0.37 g of NaOH in 5 ml of hot distilled  $\text{H}_2\text{O}$ . A yellow-green precipitate formed immediately. This was filtered, washed well with acetone and  $\text{H}_2\text{O}$ , and dried *in vacuo*. This chelate started decomposing at about 90°, and at 120° the color change from yellow to brown appeared complete. At about 300° the compound turned a lighter brown, but no further change was observed up to 335°. *Anal.* Calcd: C, 46.62; H, 3.45. Found: C, 46.21; H, 3.68.

**Bis(1-*p*-iodophenyl-5-phenyl-1,3,5-pentanetrionato)tetraaquodnickel(II),  $\text{Ni}_2(\text{p-I(DBA)})_2(\text{H}_2\text{O})_4$ .** To a solution of 1.5 g of triketone in 250 ml of hot acetone was added 0.3 g of NaOH and 10 ml of hot distilled water. A solution of 0.92 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 ml of hot absolute  $\text{CH}_3\text{OH}$  was then added and after about 5 min of stirring the yellow-green product precipitated. The precipitate was collected, washed well with acetone and  $\text{H}_2\text{O}$ , and dried *in vacuo*. *Anal.* Calcd: C, 42.11; H, 3.12. Found: C, 42.35; H, 3.16.

**Bis(1,5-di-*p*-bromophenyl-1,3,5-pentanetrionato)tetraaquodnickel(II),  $\text{Ni}_2(\text{di-p-Br(DBA)})_2(\text{H}_2\text{O})_4$ .** A solution of 0.27 g of NaOH in 5 ml of hot distilled water was added to 1.5 g of triketone in 275 ml of hot acetone. Then, a solution of 0.77 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 35 ml of hot  $\text{CH}_3\text{OH}$  was added. After about 30 sec of stirring a greenish yellow precipitate appeared and stirring was continued for a short period of time. The chelate was washed well with acetone and  $\text{H}_2\text{O}$  and dried *in vacuo*. *Anal.* Calcd: C, 39.51; H, 2.73. Found: C, 39.81; H, 3.03.

**Bis(1-phenyl-1,3,5-hexanetrionato)tetraaquodnickel(II) Hydrate,  $[\text{Ni}_2(\text{BAA})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ .** A solution of 2.4 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 ml of hot  $\text{CH}_3\text{OH}$  was added to 2.0 g of triketone in 250 ml of hot  $\text{CH}_3\text{OH}$ . To this solution 0.8 g of NaOH in 10 ml of distilled  $\text{H}_2\text{O}$  was added. Precipitation occurred immediately. The precipitate was washed well with benzene and  $\text{H}_2\text{O}$  and dried *in vacuo*. The greenish yellow product is relatively soluble in  $\text{CH}_3\text{OH}$ . It decomposes at about 90°. *Anal.* Calcd: C, 47.06; H, 4.90; Ni, 19.28. Found: C, 46.54; H, 4.86; Ni, 19.30.

**Bis(1,3,5-heptanetrionato)triquoamminednickel(II),  $\text{Ni}_2(\text{DAA})_2(\text{H}_2\text{O})_3(\text{NH}_3)_3$ .** Two grams of the triketone were dissolved in 250 ml of  $\text{CH}_3\text{OH}$ . To this solution 3.35 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 ml of  $\text{CH}_3\text{OH}$  was added. Upon addition of 1.1 g of NaOH in 10 ml of distilled  $\text{H}_2\text{O}$ , a fine green precipitate formed. The precipitate was filtered and washed well with an  $\text{NH}_4\text{OH}$  solution. It was necessary in this case to use the  $\text{NH}_4\text{OH}$  wash to eliminate  $\text{Ni}(\text{OH})_2$  from the precipitate. Preparation of this chelate is more difficult than the others reported herein. This may be due to the ease with which 2,4,6-heptanetrione cyclizes in basic solution. The yellow-brown product decomposes below 100°. *Anal.* Calcd: C, 35.82; H, 5.38; N, 3.00; Ni, 24.95. Found: C, 36.32; H, 5.69; N, 3.77; Ni, 24.18.

**Bis(1-*p*-iodophenyl-5-phenyl-1,3,5-pentanetrionato)tetrapyridinedinickel(II),  $\text{Ni}_2(\text{p-I(DBA)})_2(\text{py})_4$ .** One gram of  $\text{Ni}_2(\text{p-I(DBA)})_2(\text{H}_2\text{O})_4$  was dissolved in about 100 ml of pyridine. The solution was concentrated by boiling to about 25 ml. The remaining pyridine was evaporated at room temperature, and the product was air-dried. *Anal.* Calcd: C, 53.42; H, 3.49; N, 4.60. Found: C, 52.26; H, 3.49; N, 4.98.

**Bis(1,5-di-*p*-bromophenyl-1,3,5-pentanetrionato)tetrapyridinedinickel(II),  $\text{Ni}_2(\text{di-p-Br(DBA)})_2(\text{py})_4$ .** The same procedure used to prepare  $\text{Ni}_2(\text{p-I(DBA)})_2(\text{py})_4$  was used for this complex. *Anal.* Calcd: C, 50.75; H, 3.16; N, 4.38; Ni, 9.20. Found: C, 50.29; H, 3.47; N, 4.97; Ni, 9.36.

**Mononuclear Nickel(II) Chelates. Sodium Tris(2,4-pentanedionato)nickelate(II),  $\text{Na}[\text{Ni}(\text{acac})_3]$ .** The compound was prepared by modification of the synthesis of  $\text{Na}[\text{Co}(\text{acac})_3]$  reported by Ellern and Ragsdale.<sup>27</sup> A solution of 23.8 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 270 ml of  $\text{CH}_3\text{OH}$  was added dropwise over a 2-hr period with vigorous stirring to 24 g of NaOH and 60 g of 2,4-pentanedione in 400 ml of  $\text{CH}_3\text{OH}$ . The fine blue precipitate was washed with seven 100-ml portions of  $\text{CH}_3\text{OH}$  and four 50-ml portions of diethyl ether and then dried over sulfuric acid. The product yield was 97%. *Anal.* Calcd: C, 47.53; H, 5.60; Ni, 15.49. Found: C, 47.54; H, 5.88; Ni, 15.10.

**Bis(1,3-diphenyl-1,3-propanedionato)diaquonickel(II),  $\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$ .** Approximately equal volumes of two solutions, one containing 2.0 g of ligand and 0.5 g of KOH in  $\text{CH}_3\text{OH}$  and the other

(27) J. B. Ellern and R. O. Ragsdale, *Inorg. Syn.*, 11, 87 (1968).

containing 1.06 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , were mixed. A yellow-green compound precipitated immediately. This product was washed well with water and then with methanol and dried *in vacuo*. *Anal.* Calcd: C, 66.54; H, 4.81; Ni, 10.91. Found: C, 66.93; H, 5.30; Ni, 10.80.

**Magnetic Susceptibility Measurements.** Magnetic susceptibilities in the 77–421°K range were measured by both the Gouy and the Faraday methods using  $\text{Hg}[\text{Co}(\text{SCN})_6]$  as the calibrant.<sup>28</sup> The agreement between the two methods was within experimental error. The magnetic properties of each compound as a function of temperature were measured at least twice by each method. Temperature measurements were made with a copper-constantan thermocouple connected to a Leeds and Northrup temperature potentiometer, yielding an accuracy of  $\pm 0.5^\circ\text{K}$ . The measurements were taken with a Varian Associates Model V-4004 4-in. electromagnet set to a 2-in. pole gap. The resulting fields are about 8000 G.

Correction for diamagnetic effects were made using Pascal's constants. An experimental determination of the ligand diamagnetism for 1,5-diphenyl-1,3,5-pentanetrione yielded a result essentially identical with the value calculated from Pascal's constants,  $-137 \times 10^{-6}$  cgsu. The experimental value is  $-130 \times 10^{-6}$  cgsu.

The measurements recorded below 77°K were obtained using a zero-field induction bridge method and the same calibrant used in the Gouy and Faraday methods.

Values of the exchange integral,  $J$ , were calculated using the standard equation for two metal ions each with  $S = 1$ .<sup>7</sup>

**Spectra and Analysis.** Electronic absorption spectra were recorded for approximately  $1.0 \times 10^{-3} M$  pyridine solutions using a Cary 14 spectrophotometer. Mass spectra were recorded with an AEI MS 902 mass spectrometer. Infrared spectra were recorded on KBr pellets using a Perkin-Elmer Model 621 spectrophotometer.

All C, H, and N analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind. The metal analyses were by standard EDTA titration in our laboratory.

**X-Ray Study of  $\text{Ni}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$ . Single-Crystal Characterization and X-Ray Data Collection.** The procedures for isolation and mounting of single crystals in a pyridine atmosphere were similar to those described for  $\text{Co}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$ .<sup>12</sup> The crystal used for the X-ray study had dimensions of  $0.38 \times 0.27 \times 0.14$  mm. Their instability in the absence of pyridine precluded an experimental density determination.

Precession photographs taken with  $\text{Cu K}\alpha$  radiation showed approximate isomorphism of the  $\text{Co}(\text{II})$ <sup>12</sup> and  $\text{Ni}(\text{II})$  complexes. Both compounds crystallize in the monoclinic space group  $P2_1/n$  with systematic extinctions  $h + l = 2n + 1$  for  $\{h0l\}$  and  $k = 2n + 1$  for  $\{0k0\}$ . Accurate lattice constants were obtained from the least-squares refinement of 15 reflections centered with  $\text{Mo K}\alpha$  radiation ( $\lambda 0.71069 \text{ \AA}$ ) on a Syntex P2<sub>1</sub> computer-controlled diffractometer. The refined lattice constants are  $a = 12.761$  (5)  $\text{\AA}$ ,  $b = 17.903$  (7)  $\text{\AA}$ ,  $c = 14.350$  (11)  $\text{\AA}$ , and  $\beta = 102.32$  (6)°, with  $V = 3223.37 \text{ \AA}^3$ . The lattice constants of the cobalt analog are  $a = 12.778$  (7)  $\text{\AA}$ ,  $b = 17.919$  (10)  $\text{\AA}$ ,  $c = 14.373$  (7)  $\text{\AA}$ , and  $\beta = 120.54$  (6)°.

Intensity data were collected on the P2<sub>1</sub> diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation at a takeoff angle of 4°. A symmetric  $\theta$ - $2\theta$  scan of 2.0° (minimum) plus allowance for spectral dispersion was employed. The scan rate for each reflection was determined by counting for 2 sec at the peak maximum and using a slower scan rate for weaker data. A maximum scan rate of 3.99°/min was used for data with peak intensities greater than 750 Hz. For data with peak intensities less than 50 Hz, a minimum scan rate of 2.02°/min was used. Stationary backgrounds at each end of the scan were taken such that the ratio of total background counting time to scan time for each reflection was 0.4.

Independent data totaling 5262 reflections were collected in the quadrant ( $-h, -k, \pm l$ ) to a limiting  $2\theta$  of 50° ( $(\sin \theta)/\lambda < 0.596$ ). During the course of data collection, the intensities of five standard reflections were measured after every 100 reflections as a check on crystal and electronic stability. In the  $2\theta$  shell of data between 42 and 50°, the standards showed internally consistent decreased intensities to 88% of their initial intensities. The data in this region were scaled accordingly.

The intensity data were corrected<sup>29</sup> for background and Lorentz-polarization effects, and standard deviations of intensities were assigned as

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.05I)^2]^{1/2}$$

(28) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960.

where  $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$ ,  $I$  = net intensity,  $B$  = total background count, and  $K$  is the ratio of scan time to background counting time. The linear absorption coefficient for  $\text{Mo K}\alpha$  radiation is 6.5  $\text{cm}^{-1}$ . Since calculation showed the corrections for absorption were small, no corrections for absorption were deemed necessary.

Of the 5268 reflections examined, 2567 had  $I > 2.5\sigma(I)$  and were used for the solution and refinement of the structure.

**Structure Determination.** Although the structure was presumed to be isomorphous with the cobalt compound,<sup>12</sup> a systematic Patterson-Fourier solution was followed in order to avoid biasing the final results.

Three-dimensional Patterson techniques yielded the position of the independent nickel ion, which gave an unweighted discrepancy factor of 0.600 ( $R = \sum \|F_o| - |F_c| \| / \sum |F_o|$ ). Subsequent three-dimensional Fourier maps allowed positioning of the remaining atoms. Full-matrix isotropic least-squares refinement resulted in an  $R$  of 0.108 and a weighted discrepancy factor of  $R_w = 0.128$  ( $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ ). Unambiguous assignment of nitrogen positions in the free pyridine molecules was impossible. It is likely that each pyridine molecule is sixfold disordered.

A Fourier difference map revealed the positions of all hydrogen atoms except those on the solvent pyridine molecules. Two cycles of least-squares refinement, with anisotropic thermal parameters for the nickel atom and the atoms of the solvent pyridine rings, with anomalous scattering effects included for nickel, and with fixed contributions from the hydrogens, produced  $R^3 = 0.075$ ,  $R_w = 0.083$ , and an error of fit of 1.7884. The highest residual electron density from the final difference Fourier map was 0.48  $e/\text{\AA}^3$ .

An additional cycle of least-squares refinement varying anisotropic thermal parameters of the DBA ligands and coordinated pyridine groups, while holding all other parameters invariant, produced an  $R$  value of 0.065. In view of the data:parameter ratio, we report results from the penultimate cycle.

The discrepancy factors are analogous to those reported for the cobalt species<sup>12</sup> and may be attributed to the necessary pyridine atmosphere during data collection and to the possible disorder of the free pyridine molecules in the crystalline arrangement.

## Results

The generalized structural formulas of the nickel(II) triketonates studied are shown in Figure 1. Each nickel(II) ion is bonded to two terminal oxygen atoms and shares two bridging oxygen atoms with the other nickel(II) ion. Four molecules of water or pyridine presumably complete the coordination sphere about the metal ions, imparting an octahedral stereochemistry to each nickel(II) ion.

**Spectral Results.** The mass spectra of  $\text{Ni}_2(\text{DAA})_2(\text{H}_2\text{O})_3 \cdot (\text{NH}_3)$  and  $\text{Ni}_2(\text{BAA})_2(\text{H}_2\text{O})_4$  were recorded mainly to confirm the binuclear nature of this series of nickel chelates. Attempts to obtain the molecular ions from the mass spectra of the other compounds studied were unsuccessful. However, the dimeric nature of these nickel(II) triketonates is established by analogy to the compounds for which mass spectra could be obtained. At the high temperatures at which the spectra are run, the water molecules are lost and only molecular ions corresponding to the formula with two nickel ions and two triketonate ligands are observed.

A set of molecular ion peaks for  $\text{Ni}_2(\text{BAA})_2$  is observed at  $m/e$  520, 522, and 524. A similar set is observed for  $\text{Ni}_2(\text{DAA})_2$  at  $m/e$  396, 398, and 400. The ratio of intensities for these peaks is approximately 4:3:1 as expected for a species containing two nickel atoms whose major isotopes

(29) Local versions of the following programs were used in the solution and refinement of this structure: SYNCOR-W. Schomsee's program for the correction of diffractometer data and estimation of standard deviations; FORDAP-A. Zalkin's Fourier program; ORFLS and ORFFE-W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP-C. K. Johnson's program for drawing of crystal structures. Scattering factors (including anomalous dispersion for  $\text{Ni}^{2+}$ ) were taken from "The International Tables for X-Ray Crystallography," Vol. III, C. H. MacGillivray, G. D. Rieck, and K. Lonsdale, Ed., Kynoch Press, Birmingham, England, 1962, p 201.

(30) See paragraph at end of paper regarding supplementary material.

are  $^{58}\text{Ni}$  (68%) and  $^{60}\text{Ni}$  (26%). In addition, the spectra are rich in other high-mass species containing two nickel atoms and ligand fragments.

The electronic and infrared spectral data for these complexes were used mainly for identification purposes. No attempt has been made to analyze them in detail. The results are as expected for complexes of the type shown in Figure 1. The infrared spectra contain absorptions in the 1600–1400- $\text{cm}^{-1}$  region typical of coordinated carbonyl groups and ethylenic bonds. The presence of coordinated water is confirmed by a broad absorption ranging from 3700 to 2500  $\text{cm}^{-1}$ , typical of the O–H stretch in coordinated water.

The electronic spectra of the nickel(II) triketonates in pyridine (in the visible region) is as expected for nickel(II) in essentially  $D_{4h}$  symmetry. A very broad band ( $\epsilon_{\text{max}}$  12–15 per nickel ion) occurs in the 9800–9400- $\text{cm}^{-1}$  region. Another ligand field band of similar intensity occurs as a broad band or a well-defined shoulder in the 16,700–15,400- $\text{cm}^{-1}$  region. The positions and intensities of these bands are very similar to those found by Fackler<sup>31</sup> for the bis-pyridine adducts of some nickel(II) diketonato chelates. Very intense absorption begins at wavelengths lower than 500  $\mu\text{m}$ .

**Magnetic Properties of the Bis(1,3,5-triketonato)dinickel(II) Chelates.** The magnetic susceptibilities and moments of some triketonatonickel(II) chelates are listed in Table I. The values reported at room temperature are the averages of determinations at six different field strengths ranging from about 3000 to 9000 G. None of the samples exhibited any appreciable field strength dependence in the range studied. The magnetic properties reported in Table I were calculated on a per Ni(II) basis as

$$\chi_g(\text{mol wt})/2 = \chi_m$$

$$\chi_m - \chi_d = \chi'_m$$

$$\chi'_m = C/(T - \Theta) + N\alpha$$

$$N\alpha \cong 250 \times 10^{-6} \text{ cgsu}$$

$$\mu_{\text{eff}} = 2.83[(\chi'_m - N\alpha)T]^{1/2}$$

where  $\chi_g$  is the gram-susceptibility,  $\chi_d$  is the diamagnetic contribution,  $N\alpha$  is the temperature independent paramagnetism, and  $\chi'_m$  is the corrected molar susceptibility.

In general, the high-temperature data given in Table I represent the maximum temperature that could be attained without decomposition. For example, it was possible to obtain reproducible results at 421°K for  $\text{Ni}(\text{DBA})_2(\text{H}_2\text{O})_4$ , but  $\text{Ni}(\text{DAA})_2(\text{H}_2\text{O})_3(\text{NH}_3)$  decomposed rapidly at 350°K. Decomposition was confirmed by observation on the heating stage of a melting point apparatus. The weights of the samples were checked after heating to ensure that no decomposition had taken place before the susceptibility was measured.

#### Magnetic Properties of Some Nickel(II) 1,3-Diketonates.

In order to understand the exchange phenomenon in the binuclear triketonates, the magnetic properties of some related mononuclear Ni(II) chelates were studied. Two 1,3-diketonates were examined:  $\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$  and  $\text{Na}[\text{Ni}(\text{acac})_3]$ . The first was selected since the Ni(II) environment is very similar to the Ni(II) environment in  $\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$ . The second was selected since reliable esr data are available. It is worth noting that even though the magnetic properties of mononuclear octahedrally coordinated Ni(II)

**Table I.** Magnetic Susceptibilities (cgsu) and Moments (BM) for Some Bis(1,3,5-triketonato)dinickel(II) Chelates

Compd	Temp, °K	$10^6 \chi'_m$	$\mu_{\text{eff}}$
$\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$	421	3,486	3.30
	393	3,709	3.30
	350	4,257	3.35
	333	4,474	3.36
	297	4,819	3.30
	276	4,904	3.21
	195	6,510	3.13
	77	9,934	2.44
	60	10,550	2.25
	50	11,000	2.10
	40	11,500	1.92
	30	12,800	1.43
10	13,600	1.04	
4.2	14,244	0.67	
$\text{Ni}_2(\text{BAA})_2(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$	393	3,555	3.23
	350	4,075	3.23
	333	4,305	3.29
	297	4,810	3.29
	276	4,885	3.20
	195	6,890	3.22
	77	13,140	2.82
$\text{Ni}_2(\text{DAA})_2(\text{H}_2\text{O})_3(\text{NH}_3)$	297	4,235	3.08
	195	5,185	2.78
	77	10,155	2.47
$\text{Ni}_2(\text{di-}p\text{-Br}(\text{DBA}))_2(\text{py})_4$	333	3,995	3.16
	297	4,545	3.20
	276	4,665	3.12
	195	6,480	3.12
	77	10,510	2.52
$\text{Ni}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$	298	3,163	2.75
	273	3,615	2.71
	195	4,435	2.63
	77	7,451	2.14

**Table II.** Magnetic Properties of  $\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$  and  $\text{Na}[\text{Ni}(\text{acac})_3]$

T, °K	$\chi'_m$ , cgsu	$\mu_{\text{eff}}^a$ , BM	$\mu'_{\text{eff}}^b$ , BM
$\text{Na}[\text{Ni}(\text{acac})_3]$			
421	2,962	3.04	3.07
393	3,127	3.02	3.06
350	3,421	2.99	3.04
333	3,669	3.04	3.08
297	4,079	3.04	3.08
273	4,320	2.99	3.05
195	5,690	2.92	3.01
77	14,577	2.98	3.21
50	19,920	2.81	3.08
$\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$			
350	3,738	3.13	
333	3,907	3.12	
297	4,383	3.14	
276	4,587	3.10	
195	6,587	3.15	
77	15,583	3.08	

<sup>a</sup> Calculated from  $\mu_{\text{eff}} = 2.83[(\chi'_m - N\alpha)T]^{1/2}$  where  $N\alpha = 225 \times 10^{-6}$  cgsu. <sup>b</sup> Calculated from  $\mu'_{\text{eff}} = 2.83[(\chi'_m - N\alpha)(T - \Theta)]^{1/2}$  where  $N\alpha = 225 \times 10^{-6}$  cgsu and  $\Theta = -10^\circ\text{K}$ .

are generally considered to be well understood, very few studies have been reported in which the temperature has been varied over a significant range. The magnetic susceptibilities and moments for  $\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$  and  $\text{Ni}[\text{Ni}(\text{acac})_3]$  are given in Table II.

The magnetic properties of  $\text{Ni}(\text{DBM})_2(\text{H}_2\text{O})_2$  are adequately described by the simple Curie relationship,  $\chi'_m = C/T + N\alpha$ , in the temperature range studied. The susceptibility of  $\text{Na}[\text{Ni}(\text{acac})_3]$  follows a Curie-Weiss relationship,  $\chi'_m = C/(T - \Theta) + N\alpha$ , between 50 and 420°K. The value of  $\Theta$  measured from the  $\chi^{-1}$  vs.  $T$  plot is  $-10^\circ\text{K}$ . In addition, the  $g$  factor

(31) J. T. Hashagen and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **87**, 2821 (1965).

**Table III.** Magnetic Properties of Some Mono- and Binuclear Ni(II) Complexes in the Paramagnetic Temperature Region

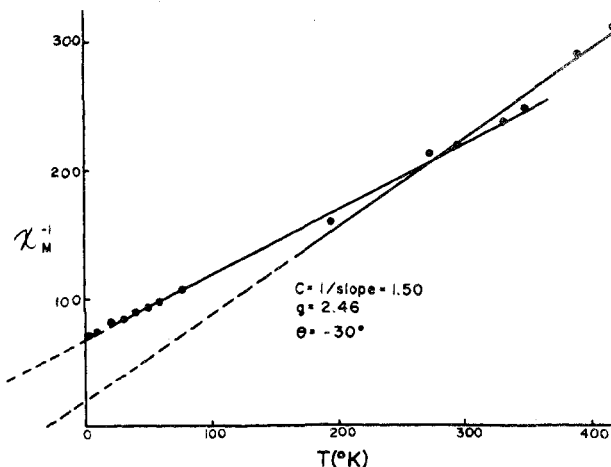
No.	Compd	Slope of $\chi^{-1}$ vs. $T^a$	Temp. range, $^{\circ}\text{K}^b$	$C^c$	$g_{av}^d$	$1 - 4\lambda/10Dq^e$	$10Dq^f$	$10^6 N\alpha^g$	$\mu_{eff}$ , BM	
									Calcd <sup>h</sup>	Exptl <sup>i</sup>
1	Na[Ni(acac) <sub>3</sub> ]	0.846	50–421	1.18	2.17	1.085	9300	225	3.07	3.06
2	Ni(DBM) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	0.825	77–350	1.21	2.20	1.10	9100	230	3.11	3.12
3	Ni <sub>2</sub> (DBA) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	0.667	297–421	1.50	2.46	1.23	>8000	261	3.48	3.46
4	Ni <sub>2</sub> (BAA) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ·H <sub>2</sub> O	0.681	77–400	1.47	2.42	1.21	>8000	261	3.42	3.44

<sup>a</sup> Before plotting  $\chi'_m$  was corrected for  $N\alpha$ . <sup>b</sup> The slope of  $\chi^{-1}$  vs.  $T$  was determined from data only within the temperature range shown. <sup>c</sup> The Curie constant,  $C$ , is equal to the reciprocal of the slope of the  $\chi^{-1}$  vs.  $T$  plot in the paramagnetic temperature region. <sup>d</sup> Calculated from  $C = N\beta^2 g^2 [S(S+1)]/3k$  where  $S = 1$ . <sup>e</sup> Calculated from  $g = 2.0(1 - 4\lambda/10Dq)$ . <sup>f</sup> Unpublished results from our laboratory. <sup>g</sup> Calculated from  $N\alpha = 8N\beta^2/10Dq$ . <sup>h</sup> Calculated from  $\mu_{eff} = (1 - 4\lambda/10Dq)[4S(S+1)]^{1/2}$ . <sup>i</sup> Average values calculated from experimental determinations of  $\chi'_m$ ,  $N\alpha$ , and  $\Theta_p$  according to the formula  $\mu_{eff} = 2.83[(\chi'_m - N\alpha)(T - \Theta_p)]^{1/2}$ ;  $\Theta_p$  values for compounds 1–4 are  $-10$ ,  $0$ ,  $-30$ , and  $-30^{\circ}\text{K}$ , respectively. These values were determined from data in the temperature range indicated.

has been accurately determined by esr at  $4^{\circ}\text{K}$  to be  $g_{\perp} \approx g_{\parallel} = 2.20$ .<sup>32</sup> Using this value together with the measured value of  $10Dq = 9300 \text{ cm}^{-1}$ <sup>33</sup> and the equation  $g = 2.00(1 - 4\lambda/10Dq)$ , the calculated value of  $\lambda$  is  $-233 \text{ cm}^{-1}$ . This represents a significant reduction in magnitude from the free ion value of  $-315 \text{ cm}^{-1}$ . These electron spin resonance and electronic absorption spectral results are in good agreement with the magnetic susceptibility results shown in Table III.

**Treatment of Data in the High-Temperature, Paramagnetic Region.** The magnetic properties of antiferromagnets at temperatures well above the Neel point,  $T_N$ , may be treated as simple paramagnets. The treatment outlined below makes use of this fact and is consistent with basic effective molecular field theory. For the simple, mononuclear nickel(II) 1,3-diketones the results of a treatment may be checked with the results of spectral studies. The magnetic moments indicate that Ni(DBM)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is a simple paramagnet while Na[Ni(acac)<sub>3</sub>] may be a weak antiferromagnetic. These conclusions are supported by the  $\chi'_m$  vs.  $T$  plots, whose  $T$  intercept is equal to the paramagnetic Weiss constant,  $\Theta_p$ , and whose reciprocal slope is  $C$ , the Curie constant. For Ni(DBM)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, the  $\chi'_m$  vs.  $T$  plot yields  $\Theta_p = 0^{\circ}$  and  $C = 1.21$ , values which are theoretically consistent with a simple paramagnet with  $g = 2.20$ . For Na[Ni(acac)<sub>3</sub>], the plot of  $\chi'_m$  vs.  $T$  yields  $\Theta_p = -10^{\circ}$  and  $C = 1.18$ . The value of  $-10^{\circ}$  for  $\Theta_p$  indicates some antiferromagnetism as does the magnetic moment at low temperatures. From  $C = 1.18$ , the value of  $g$  is calculated to be 2.17 in good agreement with the value of 2.20 measured by esr at  $4.2^{\circ}\text{K}$ .<sup>32</sup> Plotting the same data as  $\chi$  vs.  $T^{-1}$  and extrapolating to  $T^{-1} = 0$  results in a straight line which intersects the  $\chi'_m$  ordinate at a positive value of  $\chi'_m$ . The value of  $\chi'_m$  at  $T^{-1} = 0$  is the susceptibility at infinitely high temperature, i.e., the temperature-independent paramagnetism or  $N\alpha$ . A totally independent value of  $N\alpha$  can be calculated provided  $10Dq$  is known using the relationship  $N\alpha = 8N\beta^2/10Dq$ . The experimental determination of  $N\alpha$  from  $\chi$  vs.  $T^{-1}$  plots is in good agreement with the calculated values although this method involves a long extrapolation if the maximum temperature is only  $420^{\circ}\text{K}$ . As a result, the accuracy of the determination from  $\chi$  vs.  $T^{-1}$  plots is not considered to be high. With these experimental data two independent values of  $\mu_{eff}$  can be calculated. The excellent agreement between these two values for Na[Ni(acac)<sub>3</sub>] and Ni(DBM)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is shown in Table III.

The results for the mononuclear Ni(II) complexes are compared to those from a similar treatment for two binuclear nickel(II) triketonates in Table III. The plot of  $\chi'_m$  vs.  $T$  for Ni<sub>2</sub>(DBM)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> is shown in Figure 2. It should be emphasized that the results in Table III are for the high-



**Figure 2.** Plot of  $\chi'_m$  vs.  $T$  for Ni<sub>2</sub>(DBA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> from 4.2 to  $421^{\circ}\text{K}$ .

temperature, paramagnetic region only. At lower temperatures this treatment would, of course, not be valid. Inspection of the data in Table III shows that the unusually high moments for the triketonates at high temperatures are the result of a relatively low  $10Dq$  and high  $\lambda$ , i.e., a large  $g$  factor. Electron spin resonance verification of the high values of  $g$  in Table III has not been possible since no spectra are observed in frozen solutions down to  $4^{\circ}\text{K}$ . The paramagnetic Weiss constants determined in the high-temperature region for both binuclear Ni(II) complexes are  $-30^{\circ}\text{K}$ . The magnetic moments reported in Table III are calculated by alternative methods to the common  $\mu_{eff} = 2.83[(\chi'_m - N\alpha)T]^{1/2}$  relationship in order to show the close agreement between moments calculated from measured  $g$  factors, i.e.,  $\mu_{eff} = (1 - 4\lambda/10Dq)[4S(S+1)]^{1/2}$ , and experimental  $\chi'_m$  and  $\Theta_p$  values, i.e.,  $\mu_{eff} = 2.83[(\chi'_m - N\alpha)(T - \Theta_p)]^{1/2}$ . Both expressions are equivalent to stating that in this paramagnetic region  $\mu_{eff} = (8C)^{1/2}$ .

**Treatment of the Data for Ni<sub>2</sub>(DBA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> in the Low-Temperature Region.** The variation of  $\chi'_m$  with temperature for Ni<sub>2</sub>(DBA)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> has been measured by the induction bridge method from 77 to  $1.6^{\circ}\text{K}$ . Nowhere in that region was a susceptibility maximum observed. This is a perplexing result considering the obvious decrease in the moments of all the triketonates at temperatures below  $200^{\circ}\text{K}$ . The absence of a susceptibility maximum may be due to a slight impurity of paramagnetic Ni(II). A maximum can be predicted by correcting the experimental results for a few per cent paramagnetic impurity. Corrections for 3% paramagnetic Ni(II) have been made in Table IV using the relationship

$$0.97\chi'_{(AF)} + 0.03\chi'_{(para)} = \chi'_{(obsd)}$$

(32) M. Peter, *Phys. Rev.*, **116**, 1432 (1959).

(33) J. R. Kline and R. L. Lintvedt, unpublished results.

**Table IV.** Low-Temperature Susceptibility ( $\times 10^6$ ) of  $\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$  Corrected for the Presence of 3% Paramagnetic Ni(II) Impurity

$T, ^\circ\text{K}$	cgsu		
	$\chi'_m(\text{para})^a$	$\chi'_m(\text{obsd})$	$\chi'_m(\text{AF})$
195	6,455	6,510	6,511
77	15,064	9,934	9,811
60	20,417	10,550	10,349
50	24,445	11,000	10,726
40	30,500	11,500	11,112
30	40,583	12,100	11,518
20	60,750	12,800	11,821
10	121,250	13,600	11,403
4.2	288,345	14,244	8,650

<sup>a</sup> Calculated from  $\chi'_m(\text{para}) = C/T + N\alpha$  where  $C = 1.210$  and  $N\alpha = 250 \times 10^{-6}$  cgsu.

The corrected susceptibility is  $\chi'_m(\text{AF})$ .

The plot of  $\chi^{-1}$  vs.  $T$  for the observed susceptibility,  $\chi'_m(\text{obsd})$ , between 4.2 and 330°K yields a straight line with a slope of 0.528 (Figure 2). Extrapolation of this line results in  $\Theta = -124^\circ\text{K}$  and  $\chi^{-1}$  at  $T = 0^\circ\text{K}$  of 65 cgsu<sup>-1</sup>.

**The Exchange Constant,  $J$ .** The values of  $\mu_{\text{eff}}$  in Table I indicate an antiparallel spin arrangement at low temperatures. The high-temperature values of most compounds, however, seem more typical of paramagnetic Ni(II). In order to investigate this temperature dependence further, the exchange constant,  $J$ , was calculated for the most thoroughly studied complex,  $\text{Ni}_2(\text{DBA})_2(\text{H}_2\text{O})_4$ . This was done using the standard susceptibility equation for a Ni(II) dimer. All symbols

$$\chi'_m/\text{Ni} = \frac{3K}{T - \Theta_1} \left[ \frac{1 + 5e^{4J/kT}}{3 + 5e^{4J/kT} + e^{-2J/kT}} \right] + N\alpha$$

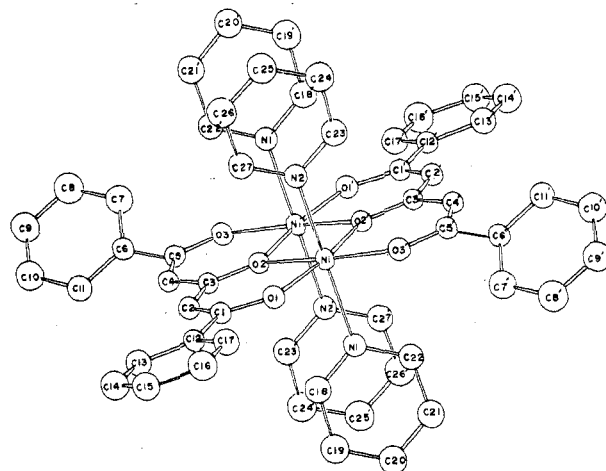
have their usual significance. The temperature-independent susceptibility,  $N\alpha$ , is taken to be  $250 \times 10^{-6}$  cm<sup>3</sup> g-atom<sup>-1</sup> and  $K = g^2 N\beta^2 / 3k$ . The Weiss constant,  $\Theta_1$ , is an indication of intermolecular exchange and is assumed to be 0. This Weiss constant should not be confused with the  $\Theta_p$  derived from  $1/\chi$  vs.  $T$  plots which is a function of exchange between the Ni(II) ions within one molecule.

In the high-temperature, paramagnetic region from 297 to 421°K the observed susceptibilities can be calculated to within  $\pm 100 \times 10^{-6}$  cgsu when  $g = 2.46$ ,  $J = -15^\circ$ ,  $\Theta_1 = 0$ , and  $N\alpha = 250 \times 10^{-6}$  cgsu using the susceptibility equation given above. The value of  $g$  agrees well with the experimental value of  $2.46 \pm 0.02$  determined from the  $\chi'_m$  vs.  $T$  plot between 297 and 421°K (Table III). Thus, both  $g$  and  $N\alpha$  can be considered to be experimentally determined. At lower temperatures, however, calculation of the observed susceptibilities requires different values of  $g$  and/or  $J$ .

A similar treatment of the 77–393°K data for  $\text{Ni}_2(\text{BAA})_2 \cdot (\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$  gives a good fit of the experimental data when  $g = 2.40$ ,  $J = -11.3^\circ$ ,  $\Theta_1 = 0$ , and  $N\alpha = 250 \times 10^{-6}$  cgsu. The value of  $g$  is supported by the experimental value of 2.42 calculated from the  $\chi'_m$  vs.  $T$  plot (Table III).

Interesting differences are observed between the complexes with all oxygen donors and  $\text{Ni}_2(\text{DBA})_2(\text{py})_4$  which contains both oxygen and nitrogen donor atoms. The magnetic data for  $\text{Ni}_2(\text{DBA})_2(\text{py})_4$  are reproduced when  $g = 2.0$ ,  $J = -18^\circ$ ,  $\Theta_1 = 0$ , and  $N\alpha = 250 \times 10^{-6}$  cgsu. The value of  $J$  is not unlike that found in the previously discussed compounds, but the value of  $g$  is very different.

**Description of the Structure of  $\text{Ni}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$ .** The structure of  $\text{Ni}_2(\text{DBA})_2(\text{py})_4 \cdot 4\text{py}$  is similar to that determined previously for the corresponding cobalt(II) complex.<sup>12</sup> The molecular configuration of bis(1,5-diphenyl-1,3,5-

**Figure 3.** Molecular structure and atomic identification scheme for  $\text{Ni}_2(\text{DBA})_2(\text{py})_4$ .

pentanetrionato)tetrapyridinedinickel(II) is shown in Figure 3. Parameters are listed in Table V and important bond distances and angles are presented in Tables VI and VII.

The molecular complex, possessing crystallographic site symmetry  $C_2$ -T, consists of two nickels coordinated to two 1,5-diphenyl-1,3,5-pentanetrionate ligands and to four pyridine nitrogens located above and below the metal-oxygen plane. In light of the previous discussion,<sup>12</sup> we shall concentrate on a comparison of critical features with those of the cobalt(II) complex.

The Ni-N distances (2.155 (8) Å (average)) and the Ni-O<sub>b</sub> distances (2.044 (6) Å (average)) are approximately 0.05 Å shorter than the corresponding distances in the Co(II) complex.<sup>12</sup> This has resulted in a Ni-Ni distance of 3.166 (3) Å which is 0.106 Å shorter than the Co-Co distance. However, the metal-O<sub>t</sub> distances are virtually the same in the two compounds (2.014 (6) Å (average)). The varying sensitivity of these differing types of metal-ligand distances to the nature of the metal ion is not readily explained by us in terms of either bonding or magnetic interactions.

The other dissimilarity between the two compounds is the O<sub>t</sub>-M-O<sub>t</sub> angle which is 102.30 (23)° in the Ni compound and 106.60 (30)° in the Co compound.<sup>12</sup> This contraction is accomplished at no cost in planarity about the metal ion and is absorbed in the other angles about the metal. The smaller angle in the Ni compound is reflected in a 0.09 Å smaller interligand O<sub>t</sub> ··· O<sub>t</sub> distance, bringing it closer to the "bite" of a diketone group.

The parameters which characterize the ligands show no significant differences between the nickel and cobalt compounds. The bond lengths and angles in the 1,3,5-pentanetrionato fragments are virtually invariant in the two compounds and are consistent with a delocalized  $\pi$ -electron system, as is the essential planarity ( $\pm 0.006$ ) of the metals and the triketonate chelate rings.

## Discussion

In many respects, binuclear complexes of pseudo-octahedral Ni(II) represent the simplest case of magnetic exchange after binuclear Cu(II) complexes. For molecular symmetry such as is present in the bis(1,3,5-triketonato)dinickel(II) chelates, one unpaired electron from each Ni(II) ion is directed at the bridging ketonic oxygens and is in the plane of the metal ions and the organic ligands. The other unpaired electron is directed at the axial ligands and is therefore out of the plane of the bridging system. The in-plane electrons (one from

Table V. Positional<sup>a</sup> and Thermal Parameters<sup>b,c</sup> with the Estimated Standard Deviations of the Last Digit in Parentheses

	x	y	z	B, Å <sup>2</sup>		x	y	z
Ni	0.1240 (1)	0.0083 (1)	0.0450 (1)		H(1)	0.0900	0.1100	0.2170
O(1)	0.2431 (5)	0.0392 (3)	-0.0190 (4)	3.36 (13)	H(2)	0.0680	0.2320	0.2570
O(2)	0.0167 (4)	0.0213 (3)	-0.0817 (4)	3.04 (12)	H(3)	0.1200	0.3330	0.1570
O(3)	-0.2025 (4)	0.0080 (3)	-0.1807 (4)	3.36 (12)	H(4)	0.1650	0.2960	0.0
C(1)	0.2331 (7)	0.0573 (5)	-0.1076 (6)	2.90 (19)	H(5)	0.1620	0.1600	-0.0470
C(2)	0.1380 (7)	0.0602 (5)	-0.1767 (6)	2.96 (30)	H(6)	0.1420	-0.1420	0.1410
C(3)	0.0338 (7)	0.0424 (5)	-0.1642 (6)	2.92 (18)	H(7)	0.1700	-0.2690	0.1380
C(4)	-0.0530 (7)	0.0460 (5)	-0.2442 (6)	3.15 (19)	H(8)	0.1850	-0.3200	-0.0500
C(5)	-0.1594 (7)	0.0268 (5)	-0.2508 (6)	3.15 (19)	H(9)	0.1580	-0.3010	-0.1380
N(1)	0.1082 (6)	0.1243 (4)	0.0820 (5)	3.49 (17)	H(10)	0.1780	-0.0820	-0.1220
N(2)	0.1557 (6)	-0.1057 (4)	0.0135 (6)	3.64 (17)	H(11)	-0.1630	0.1080	-0.4050
C(6)	-0.2309 (7)	0.0224 (5)	-0.3477 (6)	3.42 (20)	H(12)	-0.2410	0.0940	-0.5600
C(7)	-0.3098 (9)	-0.0329 (6)	-0.3624 (8)	5.07 (26)	H(13)	-0.4200	-0.0050	-0.6080
C(8)	-0.3736 (11)	-0.0435 (7)	-0.4578 (9)	6.60 (28)	H(14)	-0.4140	-0.0410	-0.4370
C(9)	-0.3567 (9)	0.0033 (7)	-0.5289 (8)	5.99 (26)	H(15)	-0.3220	-0.0720	-0.2120
C(10)	-0.2827 (9)	0.0572 (6)	-0.5142 (8)	5.40 (28)	H(16)	0.4100	0.0700	0.0
C(11)	-0.2170 (8)	0.0684 (5)	-0.4231 (7)	4.33 (23)	H(17)	0.5920	0.1100	-0.0200
C(12)	0.3377 (7)	0.0784 (5)	-0.1350 (6)	3.19 (19)	H(18)	0.6400	0.1200	-0.1890
C(13)	0.3429 (9)	0.1012 (6)	-0.2264 (7)	4.52 (24)	H(19)	0.4580	0.1530	-0.3190
C(14)	0.4427 (10)	0.1156 (6)	-0.2488 (8)	5.42 (28)	H(20)	0.2550	0.1200	-0.2820
C(15)	0.5367 (9)	0.1084 (6)	-0.1795 (8)	4.97 (27)	H(21)	0.1420	0.0810	-0.2610
C(16)	0.5329 (9)	0.0857 (6)	-0.0882 (8)	5.57 (29)	H(22)	-0.0230	0.0600	-0.3050
C(17)	0.4312 (9)	0.0715 (6)	-0.0664 (7)	4.51 (24)				
C(18)	0.1234 (9)	0.1782 (6)	0.0209 (7)	4.71 (25)				
C(19)	0.1307 (9)	0.2537 (6)	0.0435 (8)	5.39 (26)				
C(20)	0.1206 (9)	0.2747 (6)	0.1331 (8)	5.40 (26)				
C(21)	0.1061 (9)	0.2215 (6)	0.1975 (8)	5.25 (25)				
C(22)	0.0992 (8)	0.1461 (6)	0.1685 (7)	4.25 (23)				
C(23)	0.1553 (8)	-0.1600 (6)	0.0780 (8)	4.76 (25)				
C(24)	0.1781 (9)	-0.2350 (6)	0.0629 (8)	5.53 (28)				
C(25)	0.1981 (9)	-0.2528 (6)	-0.0239 (9)	5.81 (28)				
C(26)	0.1977 (10)	-0.1994 (7)	-0.0938 (8)	5.96 (29)				
C(27)	0.1752 (8)	-0.1259 (6)	-0.0704 (7)	4.39 (23)				
C(28)	0.0170 (36)	0.2093 (21)	0.5207 (27)					
C(29)	-0.0596 (32)	0.2188 (14)	0.4441 (40)					
C(30)	-0.0876 (28)	0.1592 (36)	0.3773 (22)					
C(31)	-0.0235 (46)	0.0966 (22)	0.4039 (35)					
C(32)	0.0523 (27)	0.0978 (20)	0.4806 (45)					
C(33)	0.0744 (21)	0.1490 (27)	0.5402 (19)					
C(34)	0.6252 (18)	0.1548 (27)	0.2561 (18)					
C(35)	0.5971 (31)	0.2168 (21)	0.2735 (13)					
C(36)	0.4974 (41)	0.2404 (11)	0.2574 (23)					
C(37)	0.4172 (17)	0.1962 (30)	0.2114 (17)					
C(38)	0.4463 (35)	0.1242 (23)	0.1908 (14)					
C(39)	0.5512 (44)	0.1065 (13)	0.2141 (23)					

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ni	0.0048 (1)	0.0026 (0)	0.0034 (1)	-0.0002 (1)	0.0011 (1)	0.0001 (1)
C(28)	0.0206 (40)	0.0082 (16)	0.0170 (33)	-0.0038 (17)	0.0070 (28)	-0.0020 (15)
C(29)	0.0170 (30)	0.0058 (11)	0.0246 (36)	-0.0009 (14)	0.0102 (26)	0.0053 (19)
C(30)	0.0216 (36)	0.0155 (22)	0.0124 (19)	-0.0101 (26)	0.0024 (20)	0.0038 (19)
C(31)	0.0311 (63)	0.0097 (17)	0.0209 (37)	-0.0049 (28)	0.0183 (38)	-0.0074 (23)
C(32)	0.0143 (28)	0.0069 (15)	0.0317 (52)	0.0000 (17)	0.0135 (30)	-0.0003 (23)
C(33)	0.0130 (22)	0.0084 (14)	0.0173 (23)	-0.0023 (16)	0.0038 (18)	0.0011 (17)
C(34)	0.0131 (21)	0.0113 (17)	0.0085 (17)	0.0048 (18)	0.0033 (14)	0.0051 (15)
C(35)	0.0181 (31)	0.0085 (13)	0.0078 (11)	-0.0048 (15)	0.0037 (17)	-0.0023 (11)
C(36)	0.0275 (37)	0.0056 (9)	0.0145 (24)	0.0037 (18)	0.0113 (29)	0.0005 (11)
C(37)	0.0096 (17)	0.0170 (22)	0.0083 (15)	0.0024 (17)	0.0029 (12)	0.0011 (15)
C(38)	0.0233 (33)	0.0111 (15)	0.0086 (13)	-0.0099 (18)	0.0084 (20)	-0.0048 (12)
C(39)	0.0328 (45)	0.0046 (9)	0.0138 (24)	0.0036 (17)	0.0142 (30)	0.0023 (11)

<sup>a</sup> All atoms are in the general positions  $\pm(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z)$ . <sup>b</sup> Anisotropic temperature factors of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  were used for the Ni(II) ion and the uncoordinated pyridine molecules; the resulting thermal coefficients, with standard deviations of the last significant figure given in parentheses, are given in this table. <sup>c</sup> The isotropic thermal parameters for the hydrogen atoms were set to 6.0 Å<sup>2</sup>.

each Ni) may be expected to engage in exchange which is governed by the  $\sigma$ -bonding system between the metal ions and the bridging oxygens. Mechanisms for exchange between the out-of-plane electrons (one from each Ni) would necessarily be quite different. The two unpaired electrons on any one Ni(II) are, of course, coupled to one another by Hund's rule considerations. The geometry of the bridging system is such that the M-O-M bond angle is 101.51 (24)<sup>o</sup> and the bridging O-M-bridging O angle is 78.48 (24)<sup>o</sup>. Thus,

there are important deviations from the simplest possible geometry in which the angles would all be 90<sup>o</sup>. Nonetheless, it is reasonable to treat each Ni(II) as having an <sup>3</sup>A<sub>2</sub> ground state in which case the magnetic moment would be temperature independent except for the effect of magnetic exchange. Although the structure of the H<sub>2</sub>O adducts is not known with certainty, it is reasonable to assume from the structure of Ni<sub>2</sub>(DBA)<sub>2</sub>(py)<sub>4</sub> that the waters are coordinated in the axial positions. This assumption results in treating

Table VI. Bond Distances (Å) and Angles (deg) within 1,5-Diphenyl-1,3,5-pentanetrionate

Part A. Bond Distances					
Bond classification	Results		Bond classification	Results	
C <sub>t</sub> -R	C(5)-C(6)	1.494 (12)	C <sub>m</sub> -C <sub>b</sub>	C(3)-C(4)	1.416 (12)
	C(1)-C(12)	1.518 (12)		C(2)-C(3)	1.416 (12)
	Av	1.506 (12)		Av	1.416 (12)
C <sub>t</sub> -C <sub>m</sub>	C(4)-C(5)	1.384 (12)	C <sub>t</sub> -O <sub>t</sub>	C(5)-O(3)	1.289 (9)
	C(1)-C(2)	1.394 (11)		C(1)-O(1)	1.291 (9)
	Av	1.389 (12)		Av	1.290 (9)
			C <sub>b</sub> -O <sub>b</sub>	C(3)-O(2)	1.304 (9)
Part B. Bond Angles					
Angle classification	Results		Angle classification	Results	
R-C <sub>t</sub> -O <sub>t</sub>	C(6)-C(5)-O(3)	115.8 (8)	C <sub>m</sub> -C <sub>b</sub> -O <sub>b</sub>	C(4)-C(3)-O(2)	119.8 (8)
	C(12)-C(1)-O(1)	114.2 (8)		C(2)-C(3)-O(2)	121.5 (8)
	Av	115.0 (8)		Av	120.6 (8)
O <sub>t</sub> -C <sub>t</sub> -C <sub>m</sub>	O(3)-C(5)-C(4)	126.0 (8)	C <sub>t</sub> -C <sub>m</sub> -C <sub>b</sub>	C(3)-C(4)-C(5)	129.0 (9)
	O(1)-C(1)-C(2)	126.7 (8)		C(1)-C(2)-C(3)	126.9 (8)
	Av	126.4 (8)		Av	128.0 (9)
Part C. Oxygen-Oxygen Distances <sup>a</sup>					
	O(1)-O(3')	3.129 (6)	O(1)-O(2)	2.836 (6)	
	O(2)-O(2')	2.589 (6)	O(2)-O(3)	2.867 (6)	
			Av	2.851 (6)	

<sup>a</sup> The primed atoms in this and other tables correspond to atoms related to the unprimed atoms by the center of inversion located at the origin.

Table VII. Description of Nickel Coordination Sphere

Part A. Bond Distances						
Bond classification	Results		Bond classification	Results		
Ni-O <sub>t</sub>	Ni-O(3')	2.013 (6)	Ni-Ni		3.166 (3)	
	Ni-O(1)	2.014 (6)		Ni-N	Ni-N(1)	2.163 (8)
	Av	2.014 (6)			Ni-N(2)	2.148 (7)
Ni-O <sub>b</sub>	Ni-O(2')	2.046 (6)	Av	2.155 (8)		
	Ni-O(2)	2.042 (6)				
	Av	2.044 (6)				
Part B. Bond Angles						
Angle classification	Results		Angle classification	Results		
O <sub>t</sub> -Ni-O <sub>b</sub>	O(1)-Ni-O(2)	89.46 (23)	O <sub>t</sub> -Ni-O <sub>t</sub>	O(1)-Ni-O(3')	102.30 (23)	
	O(3')-Ni-O(2')	89.76 (22)	O <sub>b</sub> -Ni-O <sub>b</sub>	O(2)-Ni-O(2')	78.48 (24)	
	Av	89.61 (22)	Ni-O <sub>b</sub> -Ni	Ni-O(2)-Ni'	101.51 (24)	

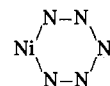
the Ni(II) as having a <sup>3</sup>A<sub>2</sub> ground state and makes intermolecular exchange relatively unimportant due to the large distance between Ni(II) ions in adjacent molecules.<sup>34</sup>

Despite the relative simplicity, magnetic exchange in d<sup>8</sup>-d<sup>8</sup> systems is not well characterized. The studies of binuclear nickel compounds carried out by Ginsberg, *et al.*,<sup>23</sup> are interpreted in terms of ferromagnetic *intracluster* interactions (positive exchange integral) and one or both of a much weaker antiferromagnetic *interdimer* interaction (negative Θ<sub>i</sub>) and zero-field splitting. The μ<sub>eff</sub> at room temperature for [Ni<sub>2</sub>(en)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub> is 3.12 BM and goes to a maximum of 3.57 BM at ~20°K. The room-temperature μ<sub>eff</sub> of [Ni<sub>2</sub>(en)<sub>4</sub>(SCN)<sub>2</sub>]I<sub>2</sub> is 3.06 BM and increases to 3.34 BM at ~7°K after which it falls off sharply. The increase in μ<sub>eff</sub> with decreasing temperature is a consequence of the increasing population of the S = 2 molecular ground state. The combined effect of zero-field splitting and lattice antiferromagnetism causes the rapid low-temperature decrease in μ<sub>eff</sub>. Parallel spin coupling takes place through the two essentially 90° monoatomic

(34) The possibility that the waters may be weakly bonded has been pointed out by A. P. Ginsberg in a private communication. A distortion of this type could perhaps account for the apparent temperature dependence of *g* and/or *J*. This model is under further consideration.

bridges of [Ni<sub>2</sub>(en)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub>. The other complex, [Ni<sub>2</sub>(en)<sub>4</sub>(SCN)<sub>2</sub>]I<sub>2</sub>, has a polynuclear bridge; however, the coupling can still be described as e<sub>g</sub> || p<sub>y</sub> || p<sub>z</sub> || e<sub>g</sub>'. This description of the exchange coupling leads to the conclusion that the essential requirement for ferromagnetic coupling between metal atoms in a cluster is the availability of connecting orbitals of proper symmetry.

Ball and Blake<sup>16</sup> have studied some binuclear nickel(II) complexes containing the bridging system



They found *J* values ranging from -8 to -34°. These were the first examples of antiferromagnetic coupling between Ni(II) ions within a molecular species except for the weak interaction of the terminal nickel of Ni<sub>2</sub>(acac)<sub>6</sub>.<sup>6</sup> Ball and Blake<sup>16</sup> have speculated that an important part of the superexchange mechanism in at least some of their complexes must involve excitation of an electron from the t<sub>2g</sub> into the e<sub>g</sub> orbital of Ni<sup>2+</sup>. The unpaired spins in the t<sub>2g</sub> orbitals then are believed to couple by virtue of their overlap with the π MO's of the bridging ligand. The p<sub>π</sub> orbital of the ligand is orthogonal



to the metal  $e_g$  orbitals but nonorthogonal to one member of each  $t_{2g}$  subset.

The magnetic results of  $Ni_3(acac)_6$  have been explained by a ferromagnetic interaction between neighboring nickel ions ( $+26 \text{ cm}^{-1}$ ) and antiferromagnetism between the terminal nickel ions ( $-7 \text{ cm}^{-1}$ ). The tetrameric nickel compound,  $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ ,<sup>35</sup> which has a "cubane" arrangement, is explained by intramolecular ferromagnetism. There is an additional, much weaker, lattice ferromagnetism which is detected at very low temperatures. In a very recent paper, Duggan, Barefield, and Hendrickson<sup>36</sup> reported oxalate- and squarate-bridged Ni(II) dimers which exhibit antiferromagnetic exchange. The observed susceptibilities in these complexes are quite well described by the model proposed by Ginsberg, *et al.*<sup>23</sup>

The magnetic moments of the binuclear nickel(II) triketonates reported in Table I indicate antiferromagnetic coupling between the Ni(II) ions. In order to investigate this coupling the exchange constant,  $J$ , was calculated. It is obvious that in such calculations it is desirable to have experimental values of  $g$ ,  $N\alpha$ , and  $\Theta_i$ . When these values, together with  $T$  and  $\chi'_m$ , are known,  $J$  may be calculated directly. Without experimental values one is faced with achieving "best fits" by varying as many as four parameters. In the present work  $g$  is obtained by determining the value of the Curie constant,  $C$ , from the reciprocal slope of  $\chi^{-1}$  vs.  $T$  plots in the high-temperature region where lattice and zero-field effects are negligible. The value of  $N\alpha$  is obtained from  $\chi$  vs.  $T^{-1}$  plots and the relationship  $N\alpha = 8N\beta^2/10Dq$ . The intermolecular exchange is accounted for by  $\Theta_i$  in the exchange equation. Since the intermolecular Ni-Ni distance is on the order of 8–10 Å the value of  $\Theta_i$  is assumed to be zero.

The calculation of  $J$  for  $Ni_2(DBA)_2(H_2O)_4$  presents some unusual difficulties since the  $\chi^{-1}$  vs.  $T$  plot is not a straight line throughout the high-temperature region. In fact, there appear to be two distinct straight-line regions, one from about 300 to 420°K and another from about 40 to about 300°K (Figure 2). These results have been duplicated several times with samples from different preparations. Since the (slope)<sup>-1</sup> is  $C$ , the most obvious explanation is that the effective  $g$  factor is different in the high-temperature region than in the low-temperature region. The high-temperature region is of interest since the compound behaves as a simple paramagnet with an average  $\mu_{\text{eff}}$  of 3.32 BM (Table I). In addition,  $g = 2.46$  and  $\Theta_p = -30^\circ\text{K}$  as determined graphically. The susceptibilities in this region are well reproduced by  $g = 2.46$ ,  $J = -15^\circ$ ,  $N\alpha = 250 \times 10^{-6}$  cgsu, and  $\Theta_p = 0^\circ$  (Table VIII). These values, however, in no way account for the suscep-

**Table VIII.** Comparison of Calculated and Observed Susceptibilities for  $Ni_2(DBA)_2(H_2O)_4$  with  $g = 2.46$ ,  $J = -15^\circ$ ,  $N\alpha = 250 \times 10^{-6}$  cgsu, and  $\Theta = 0^\circ$  from 421 to 297°K

$T, ^\circ\text{K}$	$10^6 \chi'_m, \text{cgsu}$		
	Calcd	Obsd	$\Delta$
421	3593	3486	107
393	3810	3709	101
350	4213	4257	-44
333	4395	4474	-79
297	4836	4819	17

tibilities at the lower temperatures. In order to achieve fits in the lower temperature region  $g$  and/or  $J$  must be temperature dependent.

The results between 1.6 and 77°K are unusual in that antiparallel spin alignment is obvious, but no maximum is observed in the  $\chi$  vs.  $T$  plot. A logical explanation for the absence of a susceptibility maximum is that the samples contain a few per cent of paramagnetic Ni(II). The impurity most likely to be responsible is the mononuclear triketonate  $Ni(HDBA)_2(H_2O)_2$ . The presence of 2–3% of the Ni(II) in this paramagnetic impurity could account for the absence of a maximum. After correcting the observed values, a susceptibility maximum appears at 24°K.

At present the authors know of no completely satisfactory model to explain the magnetic behavior of  $Ni_2(DBA)_2(H_2O)_4$  throughout the temperature range studied. Models such as proposed by Ginsberg, *et al.*,<sup>23</sup> have been applied without success particularly if the possibility of strong intermolecular exchange is discounted.

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**Registry No.**  $Ni_2(DBA)_2(H_2O)_4$ , 42087-54-7;  $Ni_2(DBA)_2(py)_4 \cdot 4py$ , 42087-55-8;  $Ni_2(p\text{-BrDBA})_2(H_2O)_4$ , 42087-56-9;  $Ni_2(p\text{-IDBA})_2(H_2O)_4$ , 42087-57-0;  $Ni_2(di\text{-}p\text{-BrDBA})_2(H_2O)_4$ , 42087-58-1;  $[Ni_2(BAA)_2(H_2O)_4] \cdot H_2O$ , 42151-53-1;  $Ni_2(DAA)_2(H_2O)_3(NH_3)$ , 42055-44-7;  $Ni_2(p\text{-IDBA})_2(py)_4$ , 42055-45-8;  $Ni_2(di\text{-}p\text{-BrDBA})_2(py)_4$ , 42055-46-9;  $Na[Ni(acac)_3]$ , 42230-53-5;  $Ni(DBM)_2(H_2O)_2$ , 42055-47-0.

**Supplementary Material Available.** A listing of structure factor amplitudes as well as bond distances and angles in phenyl and pyridine groups will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-18.

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