to those found here in the common range, 700° and below. The shape of the liquidus curve in the present system suggests a more nearly ideal mixing than was seen with Na_3Bi.

The occurrence of two additional thermal arrests at 942 ± 1 and 731 ± 3° was unexpected, and these appeared more unusual when no X-ray evidence whatsoever could be found for any new phase. Powder patterns which were indistinguishable from the appropriate mixture of the NaI and Na_3Sb components were also obtained from a 90% composition equilibrated at either 1050 or 920° for 12 hr or a 80% composition held at 700° for 12 hr, each of these then being quenched by dropping the container into room-temperature silicone oil within the vacuum system. Similarly, equilibration of a 70% mixture 12 hr just above or below 731° made no difference in the relative magnitude of the eutectic arrest on subsequent cooling, contrary to expectation and experience when the cooling halt in question arises from the peritectic formation of an intermediate phase. The only explanation apparently left is that *the lower (731°) transition on cooling must result from the inverse peritectic decomposition of an intermediate phase formed at 942° back into the original components NaI and Na_3Sb.* The trends in the data obtained for the presumed decomposition (Figure 2) suggest that the presence of Na_3Sb(s) prevents supercooling or, more likely, that the intermediate phase exhibits some variable composition.

Problems of reactivity and containment have discouraged the verification of the existence of the new phase at temperature with X-rays. However, the flow properties of the system near the middle of the apparent 731–942° range of existence substantiate the presence of an all-solid system from Na_3Sb down to about the composition $NaI \cdot 5Na_3Sb$ (83.3 mol % Na_3Sb). For this examination containers were constructed of 3-in. lengths of 0.25-in. diameter tantalum tubing welded to the center of the bottom of a 6-in. length of a 0.5-in. diameter tube. The inner tube was filled with a mixture of the desired composition and the top of the outer was capped and welded. The components were then fused at 1010° for 1 hr, rapidly quenched upright in silicone oil, and then inserted into a preheated furnace and held at 820–840° for 3 hr. (This procedure was designed to give a uniform, intimate mixture which would readily reach equilibrium at temperature.) The crucible within the containing furnace was then tipped past the horizontal position for 3–5 hr, after which it was cooled in an upright position and opened in the drybox to look for evidence of flow. As denoted on Figure 2 by a cross no flow was evident for compositions containing 95, 93, 90, 88, 87, 86, and 85 mol % Na_3Sb. Flow was slight and questionable at 84% with two samples which had already received repetitive additions of NaI; however cumulative compositional errors or a slight oxidation had probably occurred during the run as another sample made up directly to 84 mol % did not flow but did so readily when the composition was reduced to 83 mol %. A control showed a partially liquid system was present at 680° with an 86 mol % Na_3Sb composition, consistent with the diagram shown.

The results for these two systems obviously raise questions concerning the nature of these solutions, particularly as to whether they may be considered akin to those (1) of the heavy alkali *metals* and their halides[6,7] or (2) of two *salts* of rather different melting points and properties. Present evidence suggests the latter may be somewhat more appropriate although the classification is by no means completely satisfactory.

The intermetallic phases used both have the Na_3As structure, which is the antitype of the tysonite structure common with the rare earth metal and actinide trifluorides. Neither phase exhibits any transition between room temperature and the ranges studied. The Na_3Sb is a semiconductor with a gap of *ca.* 1.1 eV,[12] while solid Na_3Bi is evidently metallic. Cryoscopic data for these compounds in dilute solution in sodium halides were earlier shown to be consistent with the formation of Sb^{3-} or Bi^{3-} anions therein.[3] A similar consideration of the solution of salt in metal is limited by the fact that an enthalpy of fusion is available only for Na_3Bi.[13] The lower dashed curve shown in Figure 1 is the depression therewith calculated for an ideal solution of a one-particle depressant (*i.e.*, I^- in Bi^{3-} or a molecular mixture). (The upper interrupted curve in this figure illustrates the relative effect of sodium metal.[10]) Only a limiting description seems at all feasible for the saltlike model, although the very applicability of this consideration may be questionable. On the other hand, use of the same entropy of fusion for Na_3Sb (6.32 eu) gives an *excellent* description of the observed liquidus curve in terms of an ideal solution up to about 12 mol % NaI.

The Na_3Sb and Na_3Bi phases themselves have large cohesive energies. This property is in considerable contrast with the low values considered important in the solution of the heavier alkali metals in their halides.[7] Although partial ionization of Y^{3-} to electrons and polymeric anions of the heavy metal cannot be eliminated in the more concentrated solutions of Na_3Y, the stability of the phases and the negligible tendency of the solutions to lose sodium make this seem unreasonable. Accordingly we are somewhat more inclined to view the liquid systems as a somewhat novel mixture of two saltlike materials, or at least phases which are potentially saltlike on dilution. This does not preclude some appreciable electronic conduction which seems particularly probable in the concentrated solutions of Na_3Bi. Some similarity to the conceptual problems of the solution of LaI_3 in the metallic $La^{3+}(I^-)_2e^-$, and *vice versa*,[14] is apparent.

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[12] W. E. Spicer, *Phys. Rev.*, **112**, 114 (1958).

[13] D. R. Frederickson, M. G. Chassonov, R. D. Barnes, and S. A. Johnson, *High Temp. Sci.*, **2**, 259 (1970).

[14] A. S. Dworkin, R. A. Sallach, H. R. Bronstein, M. A. Bredig, and J. D. Corbett, *J. Phys. Chem.*, **67**, 1145 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Synthesis of a Two-Metal Macrocyclic System

BY WILLIAM ROSEN[1]

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The preparation and investigation of macrocyclic metal complexes has been an area of intense study in

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recent years.[2] To date there is only one "example of a macrocyclic ligand which is able to circumscribe completely two metal ions."[3] We wish to report a second example in which two nickel atoms are encompassed by a single macrocycle, formed by a metal template promoted reaction of acetone with 1,4-dihydrazinophthalazine.

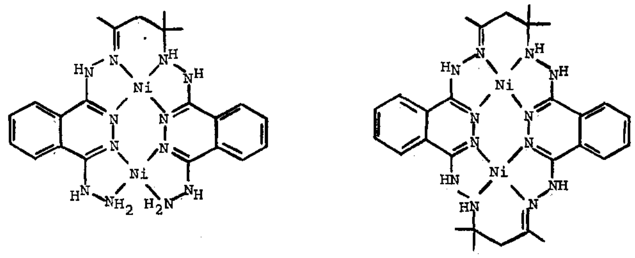
Experimental Section

The 1,4-dihydrazinophthalazine (dhph) used in the preparations was purchased from the Aldrich Chemical Co. as the hydrosulfate salt and freed by neutralization with aqueous KOH. Subsequent recrystallization from water gave yellow needles of dhph, mp 180° dec. A sample of $Ni_2(dhph)_2Cl_4 \cdot 6H_2O$ was prepared by the procedure of Ball and Blake.[4] Methanol was dried over Mg metal and distilled before use. The 2,2-dimethoxypropane used was freshly distilled. All infrared spectra were recorded on a Beckman IR-12 while visible–near-infrared spectra were obtained on a Cary 14 recording spectrophotometer. Magnetic susceptibility measurements were made by the Faraday method at room temperature (24.5°) and conductances were determined on 10^{-3} *M* aqueous solutions unless otherwise noted. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The ligands prepared are abbreviated taph and daph (taph = 6,7,8,9,12,19,20,21,22,25-decahydro-8,8,10,21,21,23-hexamethyl-5,26:13,18-bis(azo)dibenz[*i,t*][1,2,6,7,12,13,17,18]octaazacyclodocosine; daph = 4-[2-(4-hydrazino-1-phthalazinyl)hydrazino]-4-methyl-2-pentanone (4-hydrazino-1-phthalazinyl)hydrazone) and their structures are shown in Figure 1. Pertinent physical data are presented at the end of a preparation or in Table I.

TABLE I
PHYSICAL DATA ON NEW COMPLEXES

Compound	μ_{eff},[a] BM	Λ_M,[g] ohm^{-1}	ν_{max}, cm^{-1} Solid[c]	ν_{max}, cm^{-1} H_2O[d]
$Ni_2taph(BF_4)_4$	2.69	595	10,100 sh	10,200 (28) ν'_1
			13,300 ν_1	12,900 (14) ν'_2
			19,100 ν_2	17,900 (30) ν'_4
				30,300 (2600)
$Ni_2taph(NCS)_4$	2.77	8.0[b]	9,800 sh	9,900 (22)[e]
			12,900 ν_1	13,000 (28)
			19,100 ν_2	19,000 (31)
$Ni_2daph(ClO_4)_4$	2.76	620	10,000 sh	10,300 (10) ν'_1
			13,300 ν_1	12,900 (28) ν'_2
				13,700 (30) ν'_3
			19,100 ν_2	18,800 (19) ν'_4
$Ni_2daph(ClO_4)_4 \cdot 4H_2O$	2.73	635	10,300 ν'_1	10,200 (12) ν'_1
			12,900 ν'_2	12,900 (30) ν'_2
			13,700 ν'_3	13,800 (33) ν'_3
			18,900 ν'_4	18,900 (20) ν'_4
				31,300 (3400)
$Ni_2daph(NCS)_4$	2.81	*f*	10,000 sh	
			12,600 ν_1	*f*
			18,700 ν_2	

[a] A solid-state measurement made by the Faraday method (±0.02 BM). [b] A 10^{-3} *M* solution in methanol. [c] Diffuse transmittance of Nujol mulls. [d] Molar extinction coefficient in parentheses. [e] Methanol is the solvent. [f] Not soluble. [g] A 10^{-3} *M* aqueous $K_4Fe(CN)_6 \cdot 3H_2O$ solution has a Λ_M of 610 ohm^{-1}.



Ni_2daph^{+4} Ni_2taph^{+4}

Figure 1.—Proposed structures for the nickel(II) complexes of taph and daph.

Preparation of $Ni_2taph(BF_4)_4$.—To 9.5 g (0.05 mol) of dhph in 200 ml of dry methanol containing 15 ml of 2,2-dimethoxypropane was added 17.05 g (0.05 mol) of $Ni(BF_4)_2 \cdot 6H_2O$ in 300 ml of dry methanol containing a few drops of 48% HBF_4. This mixture was refluxed for 1 hr, filtered, and allowed to stand in a stoppered flask for 1 week. After 2 days crystals began to form on the walls of the flask and crystallization was complete at the end of the week whereupon the green crystals were removed by filtration, washed with dry methanol and anhydrous ether, and dried *in vacuo*. *Anal.* Calcd for $C_{28}H_{38}N_{12}Ni_2B_4F_{16}$: C, 33.45; H, 3.61; N, 16.72; Ni, 11.68; B, 4.30. Found: C, 34.09; H, 3.95; N, 16.87; Ni, 11.61; B, 4.06.

Preparation of $Ni_2daph(ClO_4)_4 \cdot 4H_2O$.—To 18.3 g (0.05 mol) of $Ni(ClO_4)_2 \cdot 6H_2O$ and 70 ml of 2,2-dimethoxypropane in 250 ml of absolute methanol was added 9.5 g (0.05 mol) of dhph and 15 ml of 2,2-dimethoxypropane in 200 ml of dry, boiling methanol. This mixture was cooled and then stirred at room temperature for 2 hr, and the green powder was removed by filtration, washed with dry methanol and anhydrous ether, and dried *in vacuo*. An analysis could not be performed because of the explosive nature of this compound at elevated temperatures. The compound is stable at room temperature but *caution should be exercised at all times*. Recrystallization of the green powder from aqueous methanol produced a blue, crystalline solid which was filtered, washed with dry methanol and anhydrous ether, and dried *in vacuo*. *Anal.* Calcd for $C_{22}H_{36}N_{12}Cl_4O_{20}$: C, 25.22; H, 3.56; N, 16.04; Ni, 11.21; Cl, 13.53. Found: C, 25.02; H, 3.29; N, 16.36; Ni, 11.42; Cl, 13.60. *Caution* must also be exercised with this blue compound as some small explosions were encountered when the temperature was raised rapidly but these were never as destructive as with its green precursor.

Preparation of $Ni_2taph(NCS)_4$ and $Ni_2(daph)(NCS)_4$.—These materials were prepared by the metathesis of aqueous solutions of $Ni_2taph(BF_4)_4$ and $Ni_2daph(ClO_4)_4$ with an aqueous KSCN solution. The light purple compounds, which are insoluble in water, were removed by filtration, washed with dry acetone, and dried *in vacuo*. *Anal.* Calcd for $C_{26}H_{28}N_{16}Ni_2S_4$: C, 38.55; H, 3.49; N, 27.72. Found: C, 38.04; H, 3.19; N, 27.50. Calcd for $C_{32}H_{36}N_{16}Ni_2S_4$: C, 43.16; H, 4.08; N, 25.17. Found: C, 42.92; H, 4.25; N, 25.25.

Behavior of the Complexes.—Aqueous solutions of $Ni_2taph(BF_4)_4$ and $Ni_2daph(ClO_4)_4$ deposited an unidentified black solid when allowed to stand for a few days. In addition the former solid complex turned black on standing in moist air for a period of time: the chemical analysis and infrared spectral data indicated that water had been absorbed but to what extent was not known as it was a slow process. On the other hand, the thiocyanate complexes were insoluble in water and thus stable in the solid state. All of the complexes were very slightly soluble in methanol (stable if moisture is excluded) and insoluble in all other organic solvents with the exception of $Ni_2taph(NCS)_4$ which was soluble in methanol and like polar organic solvents.

Discussion

Stereochemistry about the Nickel Atoms.—All pertinent physical information is gathered in Table I and indicates that the nickel(II) ions are in a six-coordinate environment.[5] The visible–near-infrared spectra are typical of tetragonally or octahedrally substituted nickel(II) where the bands can be assigned as follows: for an NiN_6 octahedral field: ν_1, $^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; for an NiN_4O_2 tetragonal field: ν_1', $^3B_{1g} \rightarrow {}^3E_g$; ν_2', $^3B_{1g} \rightarrow {}^3B_{2g}$; ν_3', $^3B_{1g} \rightarrow {}^3A_{2g}$; ν_4', $^3B_{1g} \rightarrow {}^3E_g$. From the spectra and their assignments a value of 1310 cm^{-1} can be calculated for the Dq_{xy} of the macrocycle, which is consistent with values exhibited by other nitrogen donor macrocyclic ligands.[2] In

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(2) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967).

(3) K. Travis and D. H. Busch, *Chem. Commun.*, 1041 (1970).

(4) P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1415 (1969).

(5) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **2**, 134 (1959).

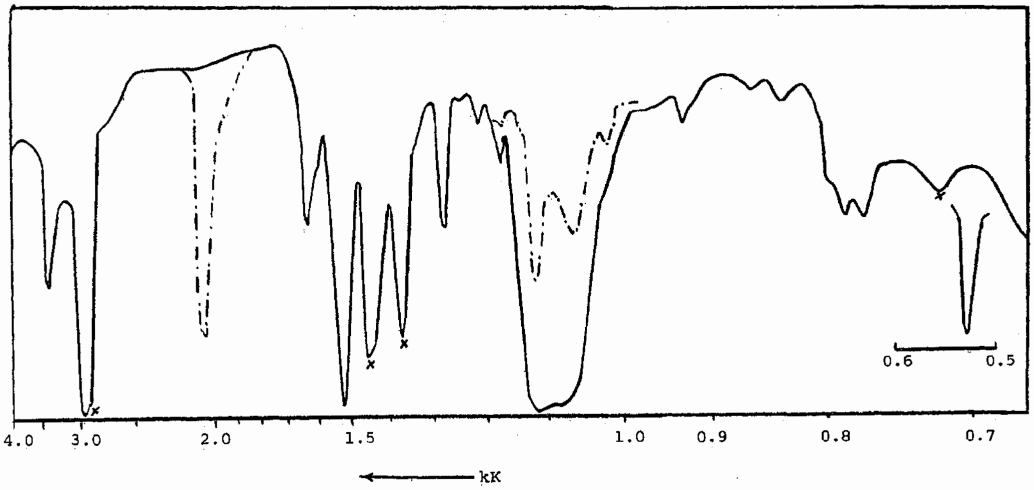

Figure 2.—Infrared spectra of Ni_2taphY_4 complexes: Y = NCS^-, —·—·—; Y = BF_4^-, ——. Nujol bands marked with ×. 1 kK = 1000 cm^{-1}.

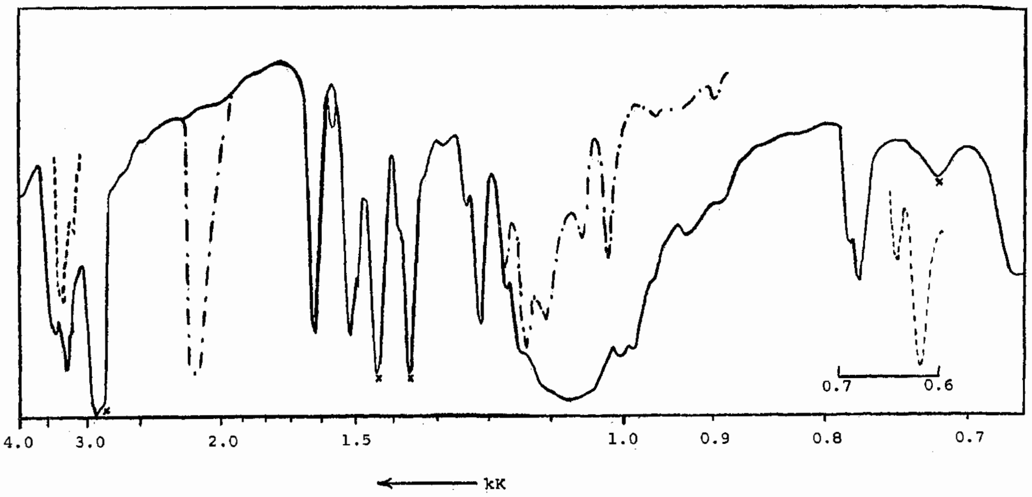

Figure 3.—Infrared spectra of Ni_2daph$Y_4 \cdot zH_2O$ complexes: Y = ClO_4^-, z = 0, - - - - - -; Y = ClO_4^-, z = 4, ——; Y = NCS^-, z = 0, —·—·—. Nujol bands marked with ×. 1 kK = 1000 cm^{-1}.

addition to the bands which have the above assignments there is a shoulder on the low-energy side of ν_1. Speculation has been offered as to the origin of this shoulder in other systems but to date no conclusive evidence has been presented.[5,6]

All of the complexes are paramagnetic and exhibit magnetic moments which are slightly below the accepted range for six-coordinate nickel(II).[7] Blake and coworkers[4,8] have explained this lowering as being due to an antiferromagnetic coupling of the metal atoms through the backbone of the ligand and our values are similar to theirs indicating that the same mechanism is operative. Indeed, the same basic ligand structure is involved in the backbone and one would therefore predict that the magnetic moment should be lowered by an amount similar in magnitude to that of $Ni_2(dhph)_2Cl_4 \cdot 6H_2O$.

The paramagnetism and six-coordinated spectral behavior of the anhydrous complexes $Ni_2taph(BF_4)_4$ and $Ni_2daph(ClO_4)_4$ in the solid state is surprising as one might expect these compounds to be square planar and diamagnetic. The infrared spectra of these complexes (see Figures 2 and 3) display bands typical of ionic BF_4^- and ClO_4^- which excludes the possibility of coordination by the anions.[9] A plausible explanation is that the uncoordinated hydrazine amine groups are bonded in the fifth- and sixth-coordination sites of the metals. This type of bonding produces a staggered, stacked arrangement of the macrocycles in a polymeric array and is compatible with the observation that dissolution in water shifts the visible spectral bands toward the spectrum displayed by the tetragonal tetraaquo species, a consequence of the destruction of the polymer in favor of the hydrated complex, $Ni_2daph(ClO_4)_4 \cdot 4H_2O$, being the isolated example.

The conductance data are also consistent with the formulated structures, shown in Figure 1, where Ni_2taph^{4+} and Ni_2daph^{4+} are completely hydrated and thus 4:1 electrolytes. The thiocyanate moieties remain coordinated in methanol resulting in tetragonal nonelectrolytes.

The Ligands.—The structures of the ligands, shown

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[6] W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970).

[7] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

[8] J. E. Andrew, P. W. Ball, and A. B. Blake, *Chem. Commun.*, 143 (1969).

[9] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965); **5**, 492 (1966).

in Figure 1, are based on the chemical analysis and infrared spectral information. These structures are reminiscent of the macrocycles made by Curtis and coworkers over the past 10 years[10] in which various diamines and carbonyl compounds are condensed about a metal template. In the present work 2,2-dimethoxypropane is used both as a dehydrating agent and as a source of acetone for the acid-catalyzed condensation with dhph. The fact that both taph and daph can be isolated from two different reactions is attributed to the solubility properties of the derived complexes in methanol.

From the infrared spectra of the complexes, Figures 2 and 3, it is clear that the ligands taph and daph are closely related. The bands between 3200 and 3350 cm^{-1} are attributed to the N–H stretching frequencies. The ligand taph has only secondary amine groups and displays only one type of N–H stretch while daph has both primary and secondary amine groups and correspondingly shows two different bands. In the range 1630–1650 cm^{-1} is found the imine stretch which is the normal position for this moiety.[11] A strong band appears at 1510 cm^{-1} in all of the complexes and is associated with the phthalazine ring system since complexes of dhph show a similar band. This information when coupled with the chemical analyses and the methods of preparation places the proposed structures on firm ground.[12]

The availability of these ligands now makes it possible to study the effects that macrocyclic ligands have on two metal ions which are in close proximity to one another.

Acknowledgment.—We wish to thank Dr. Kurt L. Loening, Nomenclature Director, Chemical Abstracts Service, for help in naming the ligands.

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[10] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 33 (1968).

[11] The weak intensity of the imine frequency in taph is attributed to the polymeric nature of the complex.

[12] The disposition of the imine linkages with respect to one another is only speculative in taph.

Correspondence

Spin Delocalization in σ Systems

Sir:

Large isotropic nuclear resonance shifts[1] are often observed in paramagnetic systems owing to an electron–nuclear hyperfine contact interaction (dipolar shifts[2] which arise in magnetically anisotropic systems will be ignored for the present discussion). In transition metal complexes such shifts occur when unpaired electron spin density is transferred, by whatever mechanism, from the central metal to the ligand nucleus in question. It has been customary to describe electron spin delocalization according to the symmetry (σ or π) of the ligand orbitals involved in the process. The early work in this area was devoted almost entirely to proton resonance and the systems most extensively studied such as salicylaldimine and aminotropone imine complexes of nickel(II)[3] exhibit isotropic shift patterns which are generally attributed[4] to spin delocalization in ligand π orbitals. Several features lead to this conclusion: (i) the shifts alternate in sign between adjacent positions on an aromatic fragment, (ii) no particular attenuation in shift magnitude is observed as the protons become further removed from the metal, (iii) the shifts are interpretable in a semiquantitative manner by VB[5] and MO[6] calculations considering the π-electron system alone, and (iv) substitution of a methyl group for a proton results in a methyl proton resonance shift in the direction opposite to that of the replaced proton, as required by the hyperconjugative model for the interaction of a pπ electron with methyl protons.[7] The aforementioned features have generally been taken as diagnostic of π-spin delocalization.

On the other hand, the downfield shifts experienced by pyridine protons, which decrease in magnitude in the order $\alpha > \beta > \gamma$ when this ligand is coordinated to nickel(II) acetylacetonate, $\mathrm{Ni(acac)_2}$, were attributed in 1963 by Happe and Ward[8] to spin delocalization in the ligand σ system. This intuitively reasonable conclusion has been cited on numerous occasions as diagnostic of σ-spin delocalization. Furthermore it is usually, though not invariably,[9] observed for saturated aliphatic groups that proton resonance shifts are downfield and attenuate rapidly in magnitude as the number of bonds intervening between the metal and the proton increases. In an early attempt to interpret σ-spin delocalization *via* a theoretical model, Holm, Everett, and Horrocks carried out an extended Hückel (EHMO) calculation on pyridine.[10] This calculation predicted the magnitude of the downfield shifts in the order $\gamma > \alpha > \beta$ for direct spin delocalization in the highest filled σ MO, in poor agreement with experiment. It was noted however that the proton shifts paralleled quite closely the hyperfine interaction constants observed in an epr experiment[11] for the phenyl radical, a σ species.

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[1] For a review see D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance* **1**, 103 (1965).

[2] For a recent discussion see W. DeW. Horrocks, Jr., *Inorg. Chem.* **9**, 690 (1970).

[3] See R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969), for a discussion and leading references.

[4] See, however, D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 4484, 5255 (1970).

[5] (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); **39**, 3513 (1963); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964).

[6] G. N. La Mar, *Mol. Phys.*, **12**, 427 (1967).

[7] (a) A. D. McLachlan, *ibid.*, **1**, 233 (1958); (b) D. B. Chestnut, *J. ibid.*, **29**, 43 (1958).

[8] J. A. Happe and R. L. Ward, *ibid.*, **39**, 1211 (1963).

[9] (a) D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Amer. Chem. Soc.*, **89**, 4040 (1967); (b) T. Yonezawa, I. Morishima, and Y. Ohmori, *ibid.*, **92**, 1267 (1970).

[10] R. H. Holm, G. W. Everett, Jr., and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1071 (1966).

[11] (a) W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965); (b) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).