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Nuclear Magnetic Resonance Contact Shifts of Nickel(II) Complexes of 4-Nitropyridine 1-Oxide and Benzonitrile

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Received July 23, 1965

Spin delocalization in a paramagnetic substance can be studied by e.p.r. if the electronic relaxation time is long or by n.m.r. if the effective electronic relaxation time is short.[1] The recent e.p.r. studies of the radical anions formed from 4-nitropyridine 1-oxide[2] and benzonitrile[3] prompt the present note on the n.m.r. spectra of octahedral nickel complexes containing these same ligands. Octahedrally coordinated nickel(II) is magnetically isotropic and for such complexes the observed isotropic n.m.r. shifts ($\Delta\nu_i = \nu_{\text{observed}} - \nu_{\text{diamagnetic}}$) are due only to the Fermi contact interaction. These contact shifts, like the e.p.r. hyperfine coupling constants, can be correlated with the electronic spin density at a given nucleus.

Experimental Results

A red solution of a complex of 4-nitropyridine 1-oxide with nickel acetylacetonate [$Ni(AA)_2$] was prepared by the addition of small amounts of $Ni(AA)_2$ to a deuteriochloroform solution saturated with 4-nitropyridine 1-oxide. The near-infrared and visible spectrum showed an absorption at 8760 cm.$^{-1}$. A second d–d transition normally found at 15,500 cm.$^{-1}$ was obscured by the beginning of a very strong absorption. Earlier work indicates such solutions involve mixtures of 2:1 and 1:1 ligand:$Ni(AA)_2$ complexes.[4] N.m.r. studies on the uncoordinated ligand show that its proton resonances form an A_2B_2 system which, when analyzed, yields chemical shifts of -8.13 and -8.27 p.p.m. All shifts were recorded using a Varian A-60 spectrometer and tetramethylsilane as an internal standard. The -8.13 p.p.m. shift was assigned to the 3 proton and the -8.27 p.p.m. shift to the 2 proton. Upon incremental addition of $Ni(AA)_2$ the peaks first coalesced and then moved away from each other. The peak shifted upfield was broadened more than the peak shifted downfield and was assigned to the 2 proton, which due to its proximity to the metal atom has a significantly shorter nuclear relaxation time. Although the absolute position of the peaks is dependent on the metal concentration, the ratio of the isotropic shifts is independent of concentration. A typical set of isotropic shifts ($\Delta\nu_i$) is given in Table I.

TABLE I
SPIN DENSITIES AND MAGNETIC RESONANCE DATA

Ligand	Position^{a}	A_i^{b}	$\Delta\nu_i$^{c}	$\rho\pi^*$^{d}	$\rho\pi$^{e}
4-$NO_2C_5H_4NO$	2	1.28^{f}	+0.95	0.010^{g}	0.087
4-$NO_2C_5H_4NO$	3	3.38^{f}	−0.68	0.098	0.008^{g}
C_6H_5CN	2	3.63	−5.63^{h}	0.107	0.094
C_6H_5CN	3	0.30	+0.83^{h}	0.045^{g}	0.057^{g}
C_6H_5CN	4	8.42	−3.75^{h}	0.243	0.267

[a] See structures I and II for numbering. [b] E.p.r. hyperfine coupling constant for radical anion, in gauss. [c] N.m.r. isotropic shifts, in p.p.m., for Ni(II) complexes. [d] M.O. spin density for lowest antibonding orbital. [e] M.O. spin density for highest bonding orbital. [f] Values of 3.58 and 1.58 gauss have been assigned to the 2 and 3 protons by comparison with M.O. calculations for 4-nitropyridine: M. Ito, T. Okamoto, and S. Nagakura, *Bull. Chem. Soc. Japan*, **36**, 1665 (1963). [g] These values may become negative by spin correlation. [h] Data obtained at −40°.

Benzonitrile does not coordinate strongly with $Ni(AA)_2$ and isotropic shifts, if present, are too small to be measured satisfactorily in this system. However, using the method by which Wickenden and Krause[5] prepared hexakis(acetonitrile)nickel(II) perchlorate (nitrile + $Ni(ClO_4)_2 \cdot 6H_2O$ dehydrated with P_2O_5) a blue or blue-green solution of what is presumed to be hexakis(benzonitrile)nickel(II) perchlorate in deuteriochloroform containing excess benzonitrile was obtained. This has near-infrared and visible absorption peaks at 10,200 and 17,500 cm.$^{-1}$ and a shoulder at 13,900 cm.$^{-1}$ in agreement with an octahedral structure.[5] The n.m.r. spectrum of the uncoordinated ligand in deuteriochloroform forms an AB_2C_2 system. Based on literature data as well as the present experiments the 2, 3, and 4 (*ortho*, *meta*, and *para*) proton chemical shifts were assigned as -7.58, -7.42, and -7.58 p.p.m. The complex with excess benzonitrile showed three n.m.r. absorptions at room temperature. The broad peak farthest downfield was assigned to the *ortho* proton, a second peak, half as intense and less broad, upfield from the first was assigned to the *para* proton, and the peak upfield from the diamagnetic position, of intensity comparable to the first peak but again not as broad, was assigned to the *meta* proton. At low temperature (−40°) the solution turns violet and four peaks are observed. The fourth resonance is a somewhat broadened peak at the diamagnetic position indicating that exchange between the coordinated and uncoordinated ligands is slow at this temperature. At 0° a broad intermediate spectrum is obtained. The ratios of the shifts are independent of concentration and are reproducible. As an excess of benzonitrile is added at ambient temperatures, the peaks coalesce to a single resonance at -7.60 p.p.m. at high benzonitrile to nickel(II) ratios.

Discussion

In a metal complex electron spin density can be transferred from the metal to the ligand either through π or σ orbitals. The nature of the isotopic shifts observed in the present work is in qualitative agreement with a π delocalization mechanism for both

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(1) Recent articles which contain more detailed discussion and leading references on this subject are (a) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); (b) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

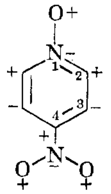
(2) J. M. Fritsch, T. P. Layloff, and R. N. Adams, *ibid.*, **87**, 1724 (1965).

(3) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

(4) R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

(5) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

ligands.[6] The expected shifts can be pictorialized using structures I and II for π delocation.[7] Here the α spin (α or $+$ spin signifies an electron spin vector parallel to that of the unpaired electrons on the metal atom) which is introduced onto the atom bonded to the metal distributes itself throughout the ligand in an alternating pattern due to electron correlation which puts β spin on the alternate atoms. This qualitative picture is in agreement with the observed signs of the n.m.r. contact shifts.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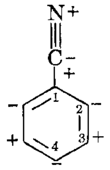
II

A more quantitative approach has been used with some success in the study of radical anions. In these systems the odd electron is assumed to be in a π antibonding molecular orbital. Spin density distributions can be estimated for such orbitals using any of several semi-empirical calculations and some electron correlation can also be introduced.[8] E.p.r. hyperfine coupling constants including those for nitrogen atoms have been correlated with these calculations. E.p.r. data, however, give only the magnitude of the coupling constant and do not indicate its sign. Thus n.m.r. data provide valuable additional information and moderate success has been reported in the correlation of both the sign and magnitude of isotropic shifts with spin densities calculated by the valence bond or molecular orbital methods.[9]

Table I includes, in addition to the reported e.p.r. hyperfine coupling constants and the presently observed n.m.r. contact shifts, calculated spin densities for the highest filled π bonding and lowest vacant π antibonding orbitals. The spin density data for 4-nitropyridine 1-oxide are Hückel calculations of Fritsch, Layloff, and Adams,[10] and those for benzonitrile are the squares of the atomic orbital coefficients reported for the S.C.F. orbitals of the neutral species by Peacock and Wilkinson.[11] Corrections for spin correlation are not included in these tabulated values but presumably the smallest values could become negative when spin correlation is introduced. Moderate agreement of the e.p.r. data with the calculated spin densities was reported for the lowest antibonding orbital corrected for spin correlation.[2,3]

It has been stated that in compounds such as octahedral nickel complexes, delocalization of spin into either a ligand π bonding or π antibonding orbital introduces excess α spin onto the ligand.[9c] Based on this premise, the n.m.r. data indicate that spin delocalization in 4-nitropyridine 1-oxide occurs by donation of a β spin electron from the ligand to the metal. Depending on the amount of spin correlation[12] introduced into the Hückel spin densities moderately good agreement of observed n.m.r. contact shift ratios to calculated spin density ratios can be obtained.

For benzonitrile the n.m.r. isotropic shifts are not in agreement with the calculated spin densities for either the π bonding or antibonding orbitals. Furthermore, it is not possible to bring the absolute magnitudes of isotropic shifts into good agreement with the calculated spin densities by any simple procedure such as including some σ spin delocalization using the spin density ratios found for σ spin delocalization in pyridine,[13] although the experimentally observed magnitudes $2 > 4 > 3$ can be corrected to the calculated order $4 > 2 > 3$ by this process. If the calculated spin densities are at least qualitatively correct for the metal complex the signs of the isotropic shifts are in agreement with the calculated data only if an excess of β spin is present on the ligand. This would indicate the transfer of β spin from the metal to the ligand π antibonding orbital as the alternate donation of α spin from the ligand to vacant metal orbitals is energetically unfavorable. Unfortunately, the experimental spin densities at the 1 position and on the cyano group necessary for confirming this hypothesis are not known.

Exact agreement between the reported e.p.r. hyperfine coupling constants or the observed n.m.r. contact shifts and the calculated M.O. spin densities cannot be expected. Perturbations due to the coordinated metal atom, differences in solvents, and errors inherent in the e.p.r. and n.m.r. measurements (for the n.m.r. measurements: uncertainty in the diamagnetic positions and centers of gravity of broad peaks, etc.) all contribute to the discrepancies. Of greater importance are the approximate nature of the semi-empirical calculations and the uncertainties in the spin delocalization mechanism. Thus although for radical anions spin density is apparently distributed in the lowest antibonding orbital, in metal complexes spin density can be distributed using σ, π, or π^* orbitals or some combination of these. For 4-nitropyridine 1-oxide the results appear to be in semiquantitative agreement with delocalization of spin in the highest filled bonding ligand π orbital. However, the presence of only 2 protons certainly does not provide a stringent test of the calculations. For benzonitrile the relative magnitudes for the n.m.r. shifts $2 > 4 > 3$ are similar to those observed for the isomeric phenylisocyanide[7] and in qualitative agreement with a valence bond calculation for the radical anion[14] but not in agreement with the reported e.p.r. or

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(6) See also footnote 23 in ref. 1b.

(7) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

(8) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(9) (a) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964); (c) D. R. Eaton, *ibid.*, **87**, 3097 (1965).

(10) These data are found in the supplement to ref. 2. The cation radical data were appended by Dr. Fritsch.

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

(14) J. C. Schug, T. H. Brown, and M. Karplus, *ibid.*, **37**, 330 (1962).

M.O. data spin density magnitudes which decrease in the order 4 > 2 > 3.

Acknowledgments.—Support of this research by the National Science Foundation through Grant No. NSF GP3397 is gratefully acknowledged. A preprint of ref. 9c was kindly supplied by Dr. Eaton.

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Donor Properties of Methyl Thiocyanate and Methyl Isothiocyanate

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Received August 2, 1965

The recent interest in the donor properties of the sulfur and nitrogen ends of the thiocyanate ion[1-4] toward metal ions prompts us to report the thermodynamics of 1:1 adduct formation of CH_3NCS and CH_3SCN with the acids iodine and phenol. This investigation was undertaken to determine the inherent donor properties of the sulfur and nitrogen ends of the thiocyanate group in a neutral environment. The neutral bases methyl thiocyanate and methyl isothiocyanate were studied, for they, respectively, have only the nitrogen or sulfur end of thiocyanate available for complex formation.

The thermodynamic properties of 1:1 adduct formation of these bases with I_2 have been determined by a spectrophotometric method. The shift in the phenol O–H stretching frequency upon complex formation has been used as a measure of the donor properties toward the hydrogen-bonding acid phenol.

Experimental Section

Reagents and Solutions.—Reagent grade iodine was sublimed before use. Reagent grade phenol was distilled and sublimed once. The bases were obtained in reagent grade from Fisher. They were further purified by vacuum distillation. Fisher Spectroanalyzed carbon tetrachloride was used without further purification. All solutions were prepared and used within a 1-hr. period. No change in the electronic spectra of the solutions was observed over a 24-hr. period.

Apparatus.—Spectroscopic measurements were made with a Beckman DB spectrophotometer with a fluid-thermostated cell compartment. The temperature was measured by inserting a thermocouple directly into the cell. The temperature was maintained constant within ±0.1°. The solution concentrations were corrected for volume changes due to changing the temperature.

The phenol O–H frequency shifts were measured on a Perkin-Elmer 521 infrared spectrometer.

TABLE I

EQUILIBRIUM CONSTANTS FOR 1:1 ADDUCTS OF CH_3NCS AND CH_3SCN WITH IODINE (T = 25.0°, λ 450 mμ)

C_B, M	10^2C_A, M	$A - A^0$	$\epsilon_C - \epsilon_A$	K, M^{-1}
		$CH_3SCN–I_2$		
0.142	0.407	0.201		
0.177	0.407	0.250	1824	0.17 ± 0.02
0.710	0.407	0.920		
0.145	0.486	0.220		
0.181	0.486	0.270	1806	0.18 ± 0.02
0.361	0.486	0.526		
0.722	0.486	0.990		
		$CH_3NCS–I_2$		
0.074	0.314	0.166		
0.148	0.314	0.318		
0.185	0.314	0.387	1066	0.71 ± 0.01
0.371	0.314	0.690		
0.742	0.314	1.14		
0.075	0.354	0.185		
0.149	0.354	0.353		
0.186	0.354	0.430	1044	0.71 ± 0.01
0.373	0.354	0.770		
0.746	0.354	1.270		

TABLE II

EQUILIBRIUM CONSTANTS FOR 1:1 ADDUCTS OF CH_3NCS AND CH_3SCN WITH IODINE AT ELEVATED TEMPERATURE (λ 450 mμ)

C_B, M	10^2C_A, M	$A - A^0$	$\epsilon_C - \epsilon_A$	K, M^{-1}
		$CH_3SCN–I_2$ (T = 41.7°)		
0.144	0.486	0.176		
0.181	0.486	0.218	1820	0.14 ± 0.01
0.361	0.486	0.426		
0.722	0.486	0.810		
		$CH_3NCS–I_2$ (T = 39.5°)		
0.074	0.314	0.127	1050	0.54 ± 0.01
0.148	0.314	0.246		
0.185	0.314	0.304		
0.371	0.314	0.551		
0.742	0.314	0.952		

Procedure.—The equilibrium constants at 25.0° (Table I) were obtained by a least-squares fit of the absorbance data to a modified Ketelaar[5,6] equation

$$\frac{C_A}{A - A^0} = \frac{1}{K(\epsilon_C - \epsilon_A)}\frac{1}{C_B} + \frac{1}{\epsilon_C - \epsilon_A} \qquad (1)$$

where C_A is the initial acid concentration, C_B is the initial base concentration, $A - A^0$ is the difference in the absorbance of a solution of acid at concentration C_A and a solution of acid and base at concentrations C_A and C_B, and $\epsilon_C - \epsilon_A$ is the difference in molar absorptivity between the complex (C) and acid (A). The intercept and slope of the least-squares straight line were utilized, respectively, in the evaluation of $\epsilon_C - \epsilon_A$ and K. The error limits are reported at the 95% confidence level. The additional measurement of the equilibrium constants at an elevated temperature (Table II) was used to demonstrate that $\epsilon_C - \epsilon_A$ at 450 mμ was temperature independent over the range of temperatures studied.

The enthalpy measurements were made from the temperature dependence of the equilibrium constants. A single solution technique that utilizes the Rose–Drago equation was used in the enthalpy calculations.[6]

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