out, and fresh sulfur dioxide was added. The above procedure was repeated five times, and the equilibrium pressure decreased each time until a value of 366 mm was duplicated in the two final additions. The solid complex (2.29 g) was removed from the flask. The product gave an acidic reaction in water and slowly lost sulfur dioxide on standing in air.

In a similar way, sulfur dioxide was absorbed by lithium, potassium, rubidium, and cesium azide.

Dibenzyldimethylammonium Azide–Sulfur Dioxide Complex. By the above procedure 3.0 g (11.2 mmoles) of anhydrous dibenzyldimethylammonium azide[6] was contacted with 4.2 g (66 mmoles) of sulfur dioxide to form a yellow solution. The vapor pressure at 25° in a 982–998-cc volume was noted as measured amounts of sulfur dioxide were removed from the system. The data are shown in Table II. When the mole ratio of sulfur dioxide to azide was decreased to 1, the mixture became solid. When the mole ratio was decreased to 0.7, the vapor pressure was 4 mm. The 3.5 g of solid (mp 75–80°) was removed from the flask. A comparison of the infrared spectrum of the product with that of the corresponding quaternary ammonium chloride and azide indicated the presence of bands due to the complex at 2010–2050 (doublet), 1190, 1110, and 985 cm^{-1}.

TABLE II

VAPOR PRESSURE OF THE SYSTEM $(C_6H_5CH_2)_2N^+(CH_3)_2N_3^- + SO_2$[a]

Total mmoles of SO_2	Vapor pressure, mm
7.84	4
8.33	10
9.82	30
17.6	156
37.3	394
47.0	456
51.8	526
59.1	624
66.4	710

[a] 25°, 982–998-cc volume, 11.2 mmoles of azide.

Dibenzyldimethylammonium chloride did not absorb sulfur dioxide, while ammonium azide and tetramethylammonium azide did.

Reaction of Sodium Azide and Triphenylphosphine in Liquid Sulfur Dioxide.—A mixture of 1.3 g (20 mmoles) of sodium azide, 5.24 g (20 mmoles) of triphenylphosphine, and 29 g of sulfur dioxide was stirred 7 days at 25° in a glass pressure flask. Periodically, the flask was cooled in liquid nitrogen, and the nitrogen generated in the reaction was pumped out. At the end of the reaction period, about 20 mmoles of nitrogen had formed. The sulfur dioxide was then distilled from the purple reaction mixture. The remaining solid was extracted with chloroform to leave a residue which was extracted into water and filtered. The water extract was evaporated to leave 0.7 g of a white solid which was shown to be sodium bisulfite by X-ray analysis. The chloroform extract was evaporated, and the solid was purified by fractional crystallization from methanol to yield 3.2 g of triphenylphosphine oxide and 1.5 g of triphenylphosphine sulfide which were identified by their melting points and infrared spectra.

Reaction of Sodium Azide and Phosgene in Liquid Sulfur Dioxide.—A mixture of 0.5 g (7.7 mmoles) of sodium azide, 2.1 g (21 mmoles) of phosgene, and 12.2 g of sulfur dioxide was stirred 21 hr at 25° in a glass pressure flask. The volatile portion of the mixture was distilled through a Dry Ice cooled trap on a high-vacuum line to collect 0.18 ml of a colorless liquid in the trap. Infrared analysis indicated that the product consisted of nearly equal amounts of carbonyl azide[8] and sulfuryl azide chloride.[6]

ω-Hydroperfluorononanoyl Azide.—ω-Hydroperfluorononanoyl chloride, prepared by the procedure of Carnahan and Sampson,[9] was isolated as a colorless liquid; bp 28° (0.5 mm); infrared peak at 1805 cm^{-1}. A mixture of 2.3 g (5.2 mmoles) of the acyl chloride, 0.4 g (6.1 mmoles) of sodium azide, and 20.5 g of sulfur dioxide was stirred overnight at room temperature. The sulfur dioxide was removed under vacuum and the residue was mixed with methylene chloride to extract the product. Distillation afforded 1.95 g (80%) of ω-hydroperfluorononanoyl azide; bp ~25° (0.06 mm). The product displayed infrared absorption at 2160–2190 (doublet), 1740–1749 (doublet), and 1110–1310 cm^{-1}.

In another experiment, the crude product from 0.8 g of sodium azide and 4.6 g of acyl chloride was extracted with toluene and heated until the solvent slowly refluxed. During 2-hr time, 225 cc (92%) of gas was evolved. The resulting solution of ω-hydroperfluorooctyl isocyanate was stirred 1 hr with 7 ml of anhydrous ethanol to form ethyl-ω-hydroperfluorooctyl carbamate. The carbamate was purified by distillation to yield 3.5 g (66%) of a solid, bp ~40° (0.005 mm), mp 43–45°. The product showed infrared absorption at 3360 and 1540 (NH), 1740 (C=O), and 1060–1350 cm^{-1}.

Anal. Calcd for $C_{11}H_7F_{16}NO_2$: C, 27.00; H, 1.45; F, 62.2; N, 2.90. Found: C, 27.00; H, 1.65; F, 60.5; N, 2.86.

In a like manner, benzyl azide, methanesulfonyl azide, and *p*-toluenesulfonyl azide were obtained in high yields.

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Proton Magnetic Resonance Shifts and Spin Delocalization in Nickel(II) Complexes with Macrocyclic Schiff Base Ligands

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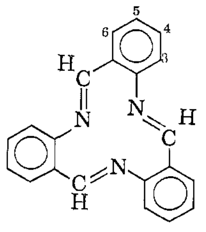
It has recently been shown that in the course of investigating the metal template effect on certain chemical reactions,[1,2] one of the products resulting from the self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) is a complex containing the macrocyclic ligand tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine, abbreviated TRI, with structure **1**.[3]



1

Several complexes containing this ligand have been prepared containing either one or two TRI molecules,[2–4] though the 5-Cl-substituted ligand, 5-Cl-TRI, has been prepared only with one TRI.[4] Both the magnetic and spectral data for $Ni[TRI]_2(NO_3)_2 \cdot H_2O$ are consistent with a pseudo-octahedral configuration about the

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[1] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

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[3] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

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metal.[2] As the infrared spectrum clearly indicated that the nitate was not coordinated, a sandwich structure was formulated for this chelate, while for the complexes with one TRI, the remaining three coordinating positions are occupied by nitrate and water in the crystal.[3]

Recent proton magnetic resonance studies on related nickel Schiff base complexes and others have revealed that the mechanism of spin transfer onto the ligand is a sensitive function of ligand type and coordination number.[5-9] In order to assess the importance of π bonding in this novel ligand, a pmr investigation was initiated for these paramagnetic[2,4] complexes. As illustrated previously, delocalization of the unpaired metal spins onto the ligand results in contact shifts[5-10] for the protons from the shifts observed in the diamagnetic ligand. From the signs and pattern of contact shifts, the spin-containing ligand orbital can be determined. For the case of π delocalization, the shifts are related to the spin densities, ρ, on the aromatic carbons by the equations[10,11]

$$\left(\frac{\Delta H}{H}\right)_i = -\frac{A_i \gamma_e g \beta S(S+1)}{\gamma_H 3kT} \qquad (1)$$

$$\rho_i = 2SA_i/Q \qquad (2)$$

where all symbols have their conventional meaning.[10,11] Effects from the dipolar interaction[10] can be neglected, since the g value of 2.08 obtained from the magnetic moments[2] is inconsistent with significant anisotropy.[12]

Experimental Section

The pmr spectra of the hexadeuteriodimethyl sulfoxide [Puriss, Fluka AG] solutions of $Ni[TRI][NO_3]_2[H_2O]_2$, $Ni[5\text{-}Cl\text{-}TRI][NO_3]_2 \cdot H_2O$, $Ni[TRI]_2[NO_3]_2 \cdot H_2O$, and $Ni[TRI]_2I_2 \cdot H_2O$, hereafter also called I, II, III, and IV, respectively, were recorded on a Varian DP-60 spectrometer, operating at 29°, and using TMS as the internal calibrant. Saturated solutions were necessary owing to very broad lines. The complexes are those reported elsewhere.[2,4]

Results

The pmr contact shifts for each of the complexes I, II, and III are given in Table I, as are the observed line widths and the relative line widths, with 4-H normalized to unity. III and IV, the two sandwich complexes, gave identical shifts for all peaks observed, such that only the shifts for III are listed. The lesser solubility of IV prevented the resolution of more than four of the peaks.

Discussion

All complexes display both upfield and downfield shifts, indicating that π delocalization predominates.[5-9] The delocalization mechanism also appears to be insensitive to the number of TRI ligands, though the shifts for I and II are some 10% greater than for the sandwich complexes. Only for I was it possible to resolve all six expected peaks, as either the sparing solubility or the great line widths failed to resolve the —N=CH peak in the remaining complexes. The shifts for the 5-Cl-TRI complex, II, clearly identify the 5-H resonance, and the water resonance is located by area comparison and by addition of a minute excess of water, but neither multiplet structure nor other substituents are available to allow conventional assignment for the remaining protons. Simple McLachlan-type Hückel theory[9,13] predicts upfield shifts for 3-H and 5-H and downfield shifts for 4-H and 6-H for the highest bonding orbital, HBO, with essentially shifts of opposite signs for the lowest antibonding orbital, LAO. The observed upfield 5-H shift indicates the spin to reside in the HBO. A convincing assignment for all protons can be effected on the basis of line widths.

For a paramagnetic complex, the excess line widths are determined[14] by either the contact or the dipolar interaction. The former mechanism predicts line widths proportional to contact shifts, while the latter produces a line-width dependence on R_i^{-6}, where R_i is the proton–metal distance.[14] Inspection of Table I shows that the dipolar term is dominant. Thus the observed line widths should correspond to the relative values for R_i^{-6} for the various protons. The metal–proton distances were estimated using published data.[3] The calculated relative line widths, as reflected by R_i^{-6}, are also included in Table I. The order of increasing relative widths was found to be insensitive to parameters, except for 4-H and 5-H, which were always nearly equal. Upon comparing the observed and calculated line widths, assignments for the remaining protons are easily made. The ambiguity for the 4-H and 5-H peaks is removed by the 5-Cl-TRI complex. This analysis also indicates why the N=CH peak was not observed in the sandwich complexes, as its width is predicted to be some 1500–2000 cps.

The large difference in line width between the complexes with one and two TRI ligands does not seem to reflect differences in the R_i^{-6} term, since their contact shifts are nearly identical. Rather, it appears probable that the characteristic correlation times for the electron relaxation, τ_c, are different.[14] For a zero-field splitting relaxation mechanism,[15] the larger $Ni[TRI]_2^{2+}$ ion would have a longer tumbling time and hence a longer electron relaxation time and broader pmr line.

The observed shifts are therefore consistent only with spin in the ligand HBO in all complexes. This was also the case in the related tetrahedral salicylaldimine compounds,[5] though spin also appears to be in the LAO for the octahedral analogs.[5,7,8] σ delocalization in the six-membered rings is negligible but apparently domi-

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TABLE I

PMR CONTACT SHIFTS AND LINE WIDTHS FOR Ni–TRI COMPLEXES

Complex		3-H	4-H	5-H	6-H	N=CH	H_2O
I	ΔH^a	+938	−1166	+522	−518	3700	0 ± 3[e]
	ρ^b	+6.78	−8.43	+3.77	−3.74	. . .	. . .
	δ^c	185 ± 15	48 ± 5	51 ± 5	125 ± 10	220 ± 25	15 ± 3
	Rel δ^d	3.85	1.0	1.03	2.6	4.5	. . .
II	ΔH	+955	−1114	. . .	−554	. . .	0 ± 3
	ρ	+6.91	−8.05	. . .	−4.00	. . .	. . .
	δ	165 ± 15	40 ± 5	. . .	105 ± 10	. . .	15 ± 3
	Rel δ	4.1	1.0	. . .	2.6	. . .	. . .
III	ΔH	+860	−1089	+448	−458	. . .	0 ± 3
	ρ	+6.22	−7.87	+3.24	−3.31	. . .	. . .
	δ	1000 ± 200	170 ± 15	170 ± 15	460 ± 50	. . .	45 ± 5
	Rel δ	6.1	1.0	1.0	2.7	. . .	. . .
Estd R_i		4.7	6.5	6.6	5.2	4.1	. . .
Calcd rel R_i^{-6}		7.0	1.0	0.9	3.8	16.0	. . .

[a] Observed contact shifts in cps, referenced against diamagnetic positions taken as −430 cps from TMS for all ring protons. [b] Spin density × 10^3, calculated from eq 1 and 2 [c] Observed line width at peak half-height, in cps [d] Observed relative line widths, with 4-H normalized to unity. [e] Diamagnetic position of H_2O with respect to TMS in DMSO was taken as −200 cps and determined by adding minute amounts of water to DMSO solution with TMS.

nant for the azomethine proton, as observed in all related systems.[5,7,8] Simple MO calculations indicate that the spin distributions for salicylaldimine and *o*-aminobenzaldehyde do not differ appreciably within the Hückel framework.[9] The observed shift patterns for the TRI complexes and the tetrahedral salicylaldimine chelates[5] also do not differ much. Therefore it should be permissible to estimate the extent of spin delocalization by comparing the observed spin densities, given in Table I, with those of the valence bond calculation for salicylaldimine. This yields an estimate of approximately $^1/_{20}$ unpaired spin per ligand, such that there is appreciable covalency comparable to that for the tetrahedral chelates.[5] A direct covalency comparison with salicylaldimine complexes is not really warranted, as a comparison with the yet unprepared paramagnetic *o*-aminobenzaldehyde complexes would be more appropriate. It has been observed previously, however, that the contact shifts are usually greater in ligands bonded to the metal only through nitrogens[6,16,17] than for a combination of nitrogens and oxygens[5,7–9] which might be attributed to the greater tendency toward covalency on the part of nitrogen.

It is somewhat surprising that the H_2O molecules in the complexes with one TRI ligand display no contact shifts, since X-ray work[3] has shown the water to be coordinated in the crystal. Previous work with octahedral nickel complexes has indicated that coordinated water has a contact shift of some ∼−500 cps.[18] The absence of even a very small contact shift for water, plus the fact that its line width is considerably smaller than that of the relatively far removed ligand protons, strongly suggests that, in dimethyl sulfoxide solution, the three remaining coordination positions in the Ni[TRI]$^{2+}$ complexes are occupied only by nitrate ions, and the water is essentially free.[19]

A comment on the spin-transfer mechanism is appropriate. Octahedral nickel(II) has its unpaired spins in dσ orbitals, such that π delocalization is not expected. The symmetry for the Ni[TRI]$^{2+}$ complexes is so low that π overlap with the normally dσ orbitals is conceivable. However, since the Ni[TRI]$_2^{2+}$ and Ni[TRI]$^{2+}$ complexes show almost identical shifts, their delocalization mechanisms must also be very similar. For the sandwich complexes, first assuming a planar ligand, the *meso* form[2] has symmetry D_{3d}, for which the spin-containing metal orbitals have symmetry e_g,[20] though the ligand HBO and LAO are both a_{1g}, such that π delocalization of unpaired spin into the HBO is forbidden. As the sense of the net ligand spin density is positive, a σ–π polarization mechanism is unlikely.[9,21] The previously suggested mechanism for π-spin transferral in octahedral nickel complexes,[9] involving unpairing of the t_{2g} electrons *via* spin–orbit coupling,[22] also seems unable to account for so much spin delocalization. Since extensive π delocalization is observed, it appears that the propeller-like distortion[3] of the TRI ligand destroys the symmetry sufficiently to allow significant π overlap with the "e_g" orbitals. Thus the spin delocalization for the TRI ligand seems to be dependent only on the conformation of the ligand and not on the nature of the three remaining coordinated atoms or ligands.

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(19) It is possible that impurity water in the DMSO solvent could partially average out a contact shift through fast exchange with the coordinated water. However, for the concentration of complex I in DMSO used in this study, the maximum reported water content in the solvent (Fluka Puriss) could produce only about 2 equiv of excess water. This excess water could reduce the shift by a maximum of a factor of 3, such that the zero contact shift observed really should reflect the absence of bonding.

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