

$\text{Pd}_2\text{Cl}_4(\text{Ncy})_2$, 53111-33-4; $\text{PdCl}_2(\text{PPh}_3)(\text{Ncy})$, 53111-34-5; $\text{PdCl}_2(\text{PPh}_2\text{Me})(\text{Ncy})$, 53111-35-6; $\text{PdCl}_2(\text{PPhMe}_2)(\text{Ncy})$, 53111-36-7; Scy, 5362-78-7; Ncy, 3189-56-8; bis(dimethylphenylphosphine)dichloro- μ, μ' -dichloropalladium(II), 15699-80-6; bis(triphenylphosphine)dichloro- μ, μ' -dichloropalladium(II), 15134-30-2; bis(methyldiphenylphosphine)dichloro- μ, μ' -dichloropalladium(II), 29887-90-9; bis(benzonitrile)dichloropalladium(II), 14220-64-5.

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Investigation of the Second Coordination Sphere in Inorganic Complexes by Dynamic Nuclear Polarization (Dnp). Complexes with Electron Spin Residing on the Metal Atom¹

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The solvation of inert, low-spin Cr(I) complexes by nmr-active species in the second coordination sphere has been investigated by dynamic nuclear polarization (dnp), an nmr-esr double-resonance technique. At 75-G magnetic field, dipolar (through-space) and scalar (Fermi-contact) interaction between a nuclear spin and an electron spin on different molecules can be distinguished. Only dipolar coupling was observed for $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ and the nuclear test probes octafluoronaphthalene (OFN), trimethyl phosphite, Li^+ , and BF_4^- . There is little unpaired spin density at the periphery of the nitrosyl complex. The order of observed solvation interaction is $\text{BF}_4^- < \text{H}_2\text{O} < \text{Li}^+$, demonstrating electrostatic effects. With $\text{Cr}(\text{bipy})_3^+$, moderate scalar coupling is observed for OFN and the phosphite, indicating the presence of unpaired spin density in the plane of the bipyridyl ring, at the rim of the complex. With $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ serving as radical probe, strong scalar coupling by transient bonding interaction is observed for trimethyl phosphite and for BF_4^- . The absence of scalar coupling with OFN suggests a lack of unpaired spin density above the planes of the π -benzene rings. The data are consistent with penetration of small ligands into the space between the benzene rings and transient bond formation directly with the metal. The general applicability of dnp to the study of second coordination sphere molecular interactions having correlation times shorter than 10^{-8} sec is discussed.

Introduction

A metal complex in solution interacts with surrounding solvent molecules, counterions, or other dissolved species. The importance of this second coordination sphere (SCS) in ligand-exchange reactions, and to catalysis in general, is beginning to be realized.² Nmr is one of the few techniques that can yield information at the molecular level about interactions occurring at the outer fringes of a complex.^{2,3} Dipolar broadening of nmr lines sometimes allows the detection of preferential orientation of molecules near the surface of a paramagnetic complex.^{4,5} Distances of closest approach and solvation geometries can sometimes be deduced from dipolar

(pseudocontact) chemical shifts of solvent molecules positioned in the SCS of transition metal complexes exhibiting strong g -tensor anisotropy.^{2,6}

The present work examines the applicability of dynamic nuclear polarization (dnp), a double-resonance nmr-esr technique, as a tool for studying SCS interactions of paramagnetic ions in solution. Dnp measures the weak coupling between nuclear spins on one molecule and an electron spin on another molecule during encounters of the two species in solution. As the technique is only responsive to fast molecular interactions (correlation times shorter than 10^{-8} sec), it is especially suited for investigations of diffusion-controlled

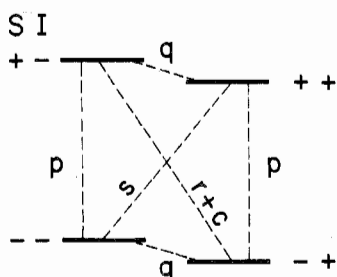


Figure 1. Combined energy states and relaxation probabilities for a system of unpaired electrons coupled weakly to spin $I = 1/2$ nuclei.

processes in the SCS. It is an ancillary benefit of low-field dnp that dipolar and scalar contributions to the intermolecular spin-spin coupling can be separated in a clear and unambiguous fashion for all nuclei studied so far.⁷⁻¹³

We wish to report dnp results at 75-G magnetic field for a series of low-spin Cr(I) complexes of differing geometries and with differing degrees of electron spin delocalization from the metal into the ligand framework. These properties were found to be important parameters for previous studies of fast molecular collision processes in solutions of organic free radicals.^{7a}

Theory

Dnp is a double-resonance technique that measures the weak coupling of a receptor nuclear spin on one molecule with an unpaired electron spin on another molecule during encounters of the two species in solution.¹⁴ Because of diffusion and tumbling of the two molecules, the nucleus and electron are in motion with respect to each other. This motion, essentially random in nature, modulates the electromagnetic coupling between the electron and the nucleus. Resultant modulation will, in fluids, usually contain frequency components which match the energy differences between levels of the coupled spin system (Figure 1) and thereby will allow transitions to be induced between the four levels of the coupled system. By saturation of the purely electronic transitions *p* (esr transitions) by means of radiofrequency power, the nuclear spin population distribution across the purely nuclear spin relaxation pathway *q* (nmr transitions) will be altered, and the intensity of the observed nmr signal will change accordingly.

Total signal enhancement of nucleus I at a given radiofrequency saturation power *P* is given by

$$G_I(P) = [A(P) - A(0)]/A(0) = U_\infty f S_e(P) \quad (1)$$

where *A*(*P*) and *A*(0) are the observed nmr signal intensities with and without saturating the esr lines, respectively. *S_e*(*P*) is the saturation function for the esr line, *f* is the spin "leakage" factor, and *U_∞* is the ultimate enhancement. The last is the nmr signal enhancement which would be attained at complete esr saturation, *S_e*(*P*) = 1, and complete domination of nuclear spin relaxation by its interaction with the electron, *f* = 1. These terms are further defined in eq 2-5; a more complete discussion

$$f = 1 - (T_1/T_{1b}) \quad (2)$$

$$S_e(P) = S/(S + 1) \quad (3)$$

$$S = \gamma_e^2 T_{1e} T_{2e} H_{1e}^2 \quad (4)$$

$$U_\infty = (\gamma_e/\gamma_I)(r - s + c)(2q + r + s + c)^{-1} \quad (5)$$

can be found elsewhere.⁷ *T₁* and *T_{1b}* are the nuclear relaxation times in the presence and in the absence of a radical species, respectively. It should be noted that high "leakage" factors for a nucleus I indicate strong interaction with and nuclear spin relaxation dominated by the radical species. The spin relaxation rates in (5) are depicted in Figure 1, with (*r* - *s*) being the net dipolar and *c* the scalar components of the total coupling. All other terms have their usual meanings.

At a magnetic field of 75 G, all relaxation pathways in Figure 1 are fully driven by diffusion-controlled molecular motions in the solution, with *2q*:*r*:*s* still very close to the zero field limit of 6:2:12. For pure dipolar coupling (*c* = 0), eq 5 requires negative signal enhancement with $U_\infty = -1/2(\gamma_e/\gamma_I)$, while for the scalar limit (*c* >> *r*, *s*) enhancements are positive, with $U_\infty = +(\gamma_e/\gamma_I)$. The difference in sign for the scalar and dipolar coupling components and the knowledge of their limiting values allow a clear separation of the two effects. The experimentally obtained dnp effect is proportional to the difference between the dipolar and scalar relaxation components. For a scalar component smaller than the dipolar term, negative enhancement of the nmr line is observed, while a larger scalar component gives rise to net positive enhancement. When scalar and dipolar terms are of approximately equal magnitude, the obtained *U_∞* values for a series of closely related solutions may be either small and positive or small and negative, with no intrinsic significance being attached to the sign of the enhancement itself. For protons in solutions of organic free radicals, *U_{∞H}* is very close to -330, the dipolar limit;⁷ for ⁷Li, on the other hand (for which the exact formulation of *U_∞* is similar to the *I* = 1/2 case), almost the total range in *U_{∞Li}* from the dipolar limit of -846.7 to the scalar limit of +1693.4 is known.^{11,15}

The respective dynamic strengths of dipolar and scalar components depend on their static energies and on interaction or correlation times. The dipolar term is almost always a simple function of molecular collision radii and diffusion times and varies in a relatively simple fashion. It depends merely on through-space spin-spin interaction with a *d*⁻⁶ distance dependence. The furthest distance at which radical-nuclear spin relaxation can compete with nuclear spin-nuclear spin relaxation lies near 10-12 Å or at the inner limit of the third coordination sphere. Dipolar dnp enhancements fall off with increasing fields as well-defined functions of the dipolar correlation time, which can then be deduced.^{7,16}

The scalar component, however, is transmitted by electron orbital interactions whose strength depends very much on the specific atomic species involved in the collision, unlike the dipolar case which is purely a function of the center-to-center distance between the electron and the nucleus.¹⁷ Scalar coupling may occur either by exchange polarization or by direct spin delocalization and orbital overlap during the formation of a transient bond between the radical and receptor molecules.

Any exact formulation for the scalar term *c* depends on the choice of model for the interaction,¹⁸ but for all models at low magnetic fields, *c* is proportional to *A_{iso}*²*τ_s*, where *A_{iso}* = $(8\pi/3)g_I\beta_I g_e\beta_e |\Psi(0)|^2$, with *A_{iso}* being the isotropic hyperfine coupling constant, *τ_s* the scalar correlation time, and $|\Psi(0)|^2$ the induced unpaired electron density at nucleus I.

Calculation of the peak scalar coupling energy during molecular collisions is complicated and at best semiquantitative. As an example of calculated values, the induced electron density of aromatic fluorines in σ collisions with *p*-benzosemiquinone at 2.5-Å separation is 0.001 electron; for π collision at 2.5 Å, 0.0001 electron.^{19a} These spin densities on the fluorocarbon would yield scalar hyperfine energies of about 50 and 5 MHz, respectively. The observed average value for hexafluorobenzene and chlorinated semiquinone is about 5 MHz for the scalar component and about 1.5 MHz for the dipolar hyperfine energy.^{18b} It is thus seen that even a very small induced spin density can rival or overwhelm the dipolar relaxation mechanism, depending on comparative correlation times.

Scalar coupling arising from formation of a transient chemical bond requires distances of closest approach between the radical source and the receptor nucleus or receptor molecule within the respective van der Waals radii, 2-4 Å. Chemical

bond formation can have two effects: overlap of orbitals will transmit a stronger scalar coupling pulse than is the case in simple nonbonding collisions (increase in A_{iso}^2), or a longer-lived attachment will occur which enables the scalar coupling term to be more effective through its augmented interaction time (increase in τ_s). In practice, the stronger electronic interactions which reflect bonding tendencies normally produce a longer-lived collision, so that dynamic scalar coupling is doubly augmented. This dual effect also reduces the need for multifield dnp studies in many situations of high chemical interest.¹⁹

Scalar coupling by exchange polarization occurs through slight unpairing of electrons around the nmr-active nucleus by the unpaired electron on the radical during an intermolecular collision or encounter. While the exact range over which intermolecular exchange coupling is felt has not been conclusively established, results from studies with trivalent phosphorus in solutions of TTBP (*vide infra*) suggest a limit somewhat above 7 Å.²⁰ It seems highly unlikely that exchange polarization between a radical and a nuclear probe should be mediated through an intervening molecule, so that this relaxation process should also require smaller collision radii and be restricted to SCS interactions.^{7a}

Scalar coupling is thus very sensitive to many aspects of chemical bonding. For interactions of a given nuclear test probe, an increase in A_{iso} upon change of radical would indicate greater unpaired electron density induced by the second radical at the I nucleus, while an increase in τ_s would indicate a tendency for the two species to stick together more tightly. Conversely, a decrease in A_{iso} or τ_s , as evidenced by diminution of scalar coupling compared to a suitable model radical, indicates either diminution of intermolecular interaction, unavailability of unpaired electron spin at the periphery of the radical, or both.

Dnp effectively monitors fast, transient bonding between a radical and other molecular species in the solution, a process which is not easily detected by other techniques. In order to observe any dnp effect in solution, correlation times for nuclear spin-electron spin interactions must be faster than 10^{-8} sec, while line broadening of esr spectra by the nuclear spin requires correlation times slower than about 10^{-8} sec. Dnp studies on paramagnetic complexes are limited to the compounds whose esr line can be at least partially saturated with feasible radiofrequency power levels ($T_{1e}T_{2e}$ above 10^{-15} sec²). As an additional limitation, chemical shifts at 75 G are small, so that only one unresolved nmr line is obtained for each nuclear species. Likewise, scalar shifts of the ¹⁹F nmr line for radical concentrations of 0.01 M would be about 0.1 ppm and thus unobservable;^{19b} a shift of 100 ppm is the minimum detectable at 75 G. However, the sensitivity of low-field dnp to scalar couplings which elude detection by nmr shift is magnified by the much more favorable dependence on correlation or sticking time, which amplifies the scalar component c of the nuclear relaxation. In contrast, the variation in collision time which greatly modifies the dnp signal affects scalar shifts hardly at all. The scalar shift is governed by the overall numerical partitioning between bound and free molecules, and the exact duration of the collision or complexation has only a very small effect in the rapid-mixing regime.

It should be noted that the dnp enhancement process occurs for a given molecule only while it is in the immediate proximity of the radical; but the polarized molecule retains its polarization for a substantial time after leaving the radical, because of relatively ineffective relaxation processes in the bulk liquid. The observed signal is therefore originating overwhelmingly from molecules in the bulk phase. This memory of collision effects gives dnp an unusual advantage by permitting a *post facto* study of molecular interactions. The remainder of the

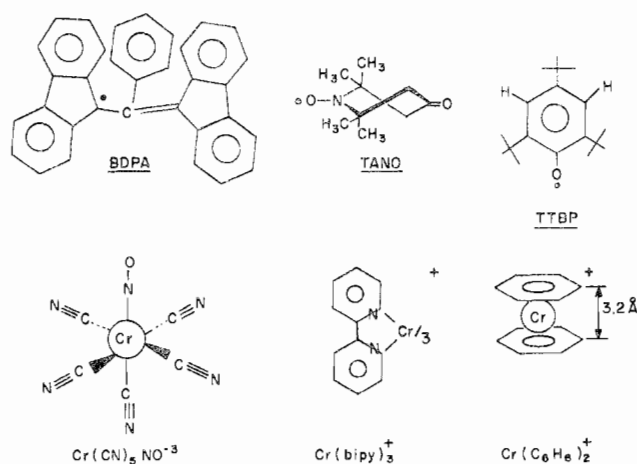


Figure 2. Investigated radicals and paramagnetic complexes.

species in the bulk of the solution cannot interfere in the detection of the interacting species, in contrast to other resonance techniques. Dnp thus provides valuable information on fast intermolecular collisions and interaction processes in solution which are not amenable to study by other resonance techniques.

Experimental Section

The basic apparatus for low-field dnp experiments has been described previously.⁷ All studies were performed at a magnetic field strength of 75 G, for which magnetic resonance frequencies in kHz are $\nu^1H = 319.7$, $\nu^{19}F = 300.8$, $\nu^{31}P = 129.41$, and $\nu^7Li = 124.01$. At this low magnetic field, chemical shifts are too small to be detected, so that only one unresolved nmr line is observed for each nucleus. To achieve a S/N (signal to noise ratio) of 8, unpumped ³¹P and ⁷Li signals (1 M solutions) typically required signal averaging over 3000–6000 traces with a computer of averaged transients (CAT) following lock-in detection of the signal. Only 16 and 64 traces respectively were required to achieve comparable S/N for ¹H (20–50 M) and for ¹⁹F (4–6 M). Signals with radiofrequency power applied were sufficiently resolved to be usable after four to eight sweeps.

Samples of 6-ml total volume were prepared by dissolving the desired weight of radical or inorganic complex under an inert atmosphere. For air-stable radicals samples could also be deoxygenated by several freeze-pump-thaw cycles. Wherever possible, radical concentrations of 0.02 M were used to avoid spin leakage problems.¹³ To facilitate detection, the nuclear test probe concentration in the solvent was at least 1 M. The bulk solvent for $K_3Cr(CN)_5NO$ was a 1:1 water-acetone mixture to allow dissolution of the organic cosolvents; for all other radicals and complexes, CH_3CN was used to eliminate variations in solvent effects on dnp enhancements. Deuterated solvents or reagents were used to allow the detection of chemically different protons in the same solution. The complexes $K_3Cr(CN)_5NO$,²¹ $Cr(bipy)_3ClO_4$,²² and $Cr(C_6H_6)_2I^{23}$ were prepared by literature methods. ESR spectra were taken on a Varian V-4502 X-band spectrometer with dual sample cavity.

Evaluation of Dnp Data

Both magnitude and sign of the observed dnp effect depend on the nature of the radical, on the nature of the nmr-active nucleus, and on the specific interaction between the two species during intermolecular collisions or encounters. Nmr-active nuclei whose dnp enhancements are quite sensitive to the nature of the radical species are used as test probes, and the enhancements obtained with a given radical are compared to results with "model" radicals, whose dnp behavior is characteristic for a given type of interaction and whose behavior is already well understood. In this way, the interaction characteristics of the unknown radical can be defined.

Observed enhancements for selected nuclear test probes in solutions of the model radicals BDPA, TTBP, and TANO are shown in Table I, along with corresponding results for the inorganic complexes. The radicals and complexes studied are depicted in Figure 2.

Table I. 30-W Enhancements and Extrapolated U_{∞} Values for Systems Investigated

Radical	Receptor molecule								
	Solvent ^a G(30) ¹ H	OFN		P(OCH ₃) ₃		LiClO ₄		LiBF ₄	
		G(30) ¹⁹ F	U_{∞} ¹⁹ F	G(30) ³¹ P	U_{∞} ³¹ P	G(30) ⁷ Li	U_{∞} ⁷ Li	G(30) ¹⁹ F	U_{∞} ¹⁹ F
BDPA	-246	+219	+270	+745	+1000	-155	-230	-111	-175
TTBP	-240	-123	-180 ^d		+550 ^e	-305 ^e	-670 ^e	-130	-267
TANO	-20	-32.5	-75		+100 ^f	+60 ^e	+525 ^e	-20	-265
K ₃ Cr(CN) ₅ NO	-65	-55	-275	<i>b</i>	<i>b</i>	-88	-700	-34	-260
Cr(bipy) ₃ ClO ₄	-39	+2.3	+4.3	-10.6	-78	-18	-290	<i>b</i>	<i>b</i>
Cr(C ₆ H ₆) ₂ I	-10.3	-8.3	-280	+29	+900	-11.2	-450	+1.65	+65

^a For 0.02 M radical concentration. ^b Strongly dipolar. ^c Reference 11. ^d Reference 17. ^e Reference 10. ^f Reference 28b.

Nuclear Test Probes. For trivalent ³¹P such as in trimethyl phosphite, scalar coupling occurs predominantly *via* the lone pair, either in direct transient bonding¹⁰ or through exchange polarization.²⁰ Dnp with phosphine nuclear probes gauges the extent of lone-pair interaction with a radical or paramagnetic complex.²⁴ For F¹⁹ in the planar octafluoronaphthalene (OFN), strong scalar coupling is correlated with transient bonding interaction in strong plane-plane collisions with suitable radicals.²⁵ Results with OFN thus measure interaction with aromatic π orbitals. For ⁷Li in the solvated ion, scalar coupling may arise either through exchange polarization or through chemical bonding but fully manifests itself only when translational diffusion of the ion is not impeded.^{11,15} Dnp with ⁷Li measures, among other effects, interaction of radicals with positively charged species. For ¹⁹F in BF₄⁻, scalar coupling does not arise to any appreciable extent from exchange polarization, as attested by the low scalar component for interaction with TTBP, the model radical for exchange polarization. By comparison of dnp enhancements of Li⁺ and BF₄⁻ in solutions of charged radicals or paramagnetic complexes, ion pairing and other electrostatic effects can be detected. In almost all cases studied so far, intermolecular spin relaxation for ¹H occurs exclusively by the dipolar mechanism; scalar coupling contributions have only been observed in systems with strong hydrogen bonding, where the proton is polarized by spin transmission during molecular association with subsequent diffusion of the polarized species into the bulk of the solution.^{7,26}

Model Radicals. The efficiency with which a radical may induce scalar coupling depends on steric and electronic factors. The availability of unpaired electron density at the periphery of the radical, the ease with which the radical can be approached, and the distance of closest approach are principal parameters.²⁰ The model radicals below span a wide range of electronic spin delocalization and steric accessibility.

BDPA. The sterically exposed planar π -allyl radical bis(diphenylene)phenylallyl is capable of strong bonding interactions. The allyl carbons share 30–50% of the unpaired spin density, with the remainder being distributed throughout the benzene rings. Because of the wide exposure of electron density above and below the plane of the radical, nonstereospecific, random-bounce collisions should be effective in transmission of scalar coupling.²⁴ Especially high scalar coupling is obtained for interactions where randomly occurring plane-plane collisions provide good overlap between π orbitals of suitable energies on the colliding molecules.^{18,19}

TTBP. About 30% of unpaired spin density in the planar tri(*tert*-butyl)phenoxy radical is located on the oxygen atom, with the remainder distributed throughout the phenyl ring.^{7a} In contrast to BDPA, approach of other species to within bonding distance of the radical is either precluded or hindered by the shielding *tert*-butyl groups. Consequently, scalar contributions to total coupling are usually much smaller than with BDPA and arise mostly from exchange polarization. Stereospecific interactions, as exemplified by the interaction of the oxyl group with phosphines,²⁰ may raise the level of

Table II. Per Cent Contribution of Scalar Coupling to Total Coupling: $100c/(2q + r + s + c)$.

Radical	Receptor molecule			
	OFN	P(OCH ₃) ₃	LiClO ₄	LiBF ₄
	Nuclear probe			
	¹⁹ F	³¹ P	⁷ Li	¹⁹ F
BDPA	60	74	24	17
TTBP	16	56	7	8
TANO	26	37	65	8
K ₃ Cr(CN) ₅ NO	1	<5	6	8
Cr(bipy) ₃ ClO ₄	33	30	28	
Cr(C ₆ H ₆) ₂ I	7	70	16	40

observed scalar coupling. Hydrogen bonding has been demonstrated to occur with secondary phosphites, where the proton can overcome the steric shielding of TTBP, leading to polarization of the phosphorus atom by an intramolecular spin transmission pathway *via* the secondary H atom.^{10,24}

TANO. Unpaired spin density on 2,2,6,6-tetramethyl-4-piperidone-1-oxyl is localized on the polar nitroxide, which is only moderately shielded by the flanking methyl groups. As a consequence of the localized nature of the unpaired electron, scalar interactions with species such as OFN and phosphines are generally diminished compared to those with BDPA,²⁷ except where highly stereospecific point-to-point bonding²⁸ or electrostatic interactions¹¹ can occur.

Results

Table I gives the observed enhancements and extrapolated U_{∞} values for the systems investigated. The ratio method was used to obtain U_{∞} values for ³¹P and ¹⁹F, using the techniques previously described.¹³

Observed proton enhancements in solutions of paramagnetic complexes are generally smaller than in solutions of organic radicals. As seen from eq 1–5, enhancements obtained while saturating an esr line at a given power level are a function of the electronic $T_{1e}T_{2e}$ product, which is usually significantly shorter for paramagnetic metal complexes than for organic radicals.²⁹ Proton enhancements for 0.02 M solutions of Cr(bipy)₃³⁺ and Cr(C₆H₆)₂²⁺ indicate $T_{1e}T_{2e}$ values that respectively are 16% and 4% of the $T_{1e}T_{2e}$ product in 0.02 M BDPA solution. However, 0.02 M solutions of [Cr(CN)₅NO]³⁻ have an electronic $T_{1e}T_{2e}$ value of about twice that for BDPA, possibly because of the low degree of spin delocalization from the metal atom and minimal intermolecular spin-spin interaction in the chromium complex (*vide infra*).

Error analysis of the obtained data suggests that scalar coupling components calculated to be below 10% are of questionable significance, due to uncertainties in unpumped signal intensities $A(0)$ and slightly diminished leakage factors even at the high radical concentrations employed in the present work. As can be seen in Table II, scalar coupling components for inorganic complexes span about the same range as those for organic radicals, with only [Cr(CN)₅NO]³⁻ exhibiting almost exclusively dipolar coupling. Solvent proton enhancements in all systems are completely dipolar within experimental error, confirming that the observed polarization

is not due to penetration of the first coordination sphere and bonding to the metal. For protons in $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, positive enhancement due to intramolecular scalar coupling of the metal with the bound solvent had been observed.³⁰

Discussion

$[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$. Ultimate enhancements for all nuclear test probes lie near or approach the dipolar limit. This absence of a scalar component has no parallel among organic radicals. Steric factors cannot be held responsible, as the approach of other species both to the equatorial cyanide ligands and to the axial nitrosyl oxygen is completely unhindered. However, it is quite obvious that the nitroxide group in TANO is not a suitable analog for the nitrosyl group in the chromium complex. The results of Table II and experiments with other nuclear test probes indicate that the unpaired electron must be much better shielded than in TTBP or in TANO, or it cannot reach the periphery of the complex. The latter conclusion is substantiated by esr evidence.³¹ The unpaired electron is in an equatorial d_{xy} orbital; intramolecular exchange polarization is thought to be responsible for the small (-0.076) unpaired electronic spin in the axial nitrosyl nitrogen p orbitals. Esr hf ^{14}N ($I = 1$) splitting of 5.25 G is far below the 15.8 G observed for aliphatic nitroxides such as TANO. Lack of significant ^{14}N hf splitting for the cyanide ligands completes the evidence that the unpaired electron must be localized on the metal ion. Intermolecular electronic spin-spin interaction is small, as seen by the low degree of dipolar broadening. Nitrosyl ^{14}N hf components are still distinct in esr spectra of 0.02 M aqueous solutions, while hf components in TANO have broadened into a single peak at the same concentration.

Dnp enhancements at 10-W esr saturation power over the range of 65–85 G trace out the three hf components of the esr absorption. Ultimate enhancements for protons at the center of the hf components extrapolate to -100 , -120 , and -95 , respectively, indicating the expected³² one-third saturation for each component of a triplet in which the tails of the lines overlap only slightly. Aliphatic nitroxides, in contrast, extrapolate to higher U_∞ values for each hyperfine component of the esr spectrum.³³

The strength of dipolar coupling interactions between the complex and molecules in the SCS is a straightforward function of distance of closest approach and of correlation or interaction times. The absence of a scalar component makes this chromium(I) nitrosyl complex highly attractive for studies of solvation, molecular-caging, and ion-pairing effects in the SCS. As previously concluded from esr evidence in solvated crystals, $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ does not form strong H bonds.^{31b} Electron spin induced nuclear relaxation for protons in H_2O -acetone- d_6 mixture is not significantly more effective than for protons in D_2O -acetone solution of the nitrosyl complex. In contrast to these observations, solutions of aliphatic nitroxide radicals give rise to greater relaxation for H-bonding solvent protons,^{33,34} and water is known to be a much better ligand than acetone for inner-sphere solvation.^{3b} Radical-induced nuclear relaxation times for ^7Li and ^{19}F in 1 M solutions of LiBF_4 in dilute $\text{K}_3\text{Cr}(\text{CN})_5\text{NO}$ aqueous solution (0.003 M) are much faster for the cation than the anion, giving spin leakage values of 0.4 for the anion, 0.6 for the solvent protons, and 0.9 for the cation. For radical concentrations at which nuclear spin-nuclear spin intermolecular relaxation has become the dominant mechanism for the anion, 90% of the nuclear spin relaxation for the cation is still occurring by interaction with the electron spin on the chromium complex. Dnp is thus quite sensitive to electrostatic and ion-pairing effects.

$\text{Cr}(\text{bipy})_3^+$. The planar radical bipyridyl anion by itself is capable of strong plane-plane collisions with OFN and in general exhibits dnp enhancements similar to the values observed with BDPA.³⁵ In distinction, the chromium(I)

bipyridyl complex exhibits only moderate scalar coupling with the test probes in Tables I and II. The bound rings in $\text{Cr}(\text{bipy})_3^+$ face the SCS edgewise, with the aromatic π orbitals unavailable for bonding interactions. The most favorable scalar coupling mechanism, spin transfer in plane-plane bonding interactions, seemingly can no longer take place. Recent nmr results indicate that only very small solvent molecules may penetrate into the crevices between the ligand paddle wheels,³⁶ so that penetration of the test probes into the regions of higher unpaired spin density should be precluded. Interaction between unpaired electrons in the $\text{Cr}(\text{bipy})_3^{2+}$ species with molecules in the SCS occurs *via* the para position of the pyridine ring,³⁶ and not by direct interaction with the metal. Most likely, scalar coupling with the $\text{Cr}(\text{bipy})_3^+$ complex also proceeds by electron spin-nuclear spin coupling at the rim of the bipyridyl rings. The unpaired electron is in an a_1 orbital of the D_3 molecule.^{37,38} Electronic spectra,³⁷ esr,³⁸ and infrared data³⁹ suggest that considerable electron delocalization into the rings occurs both in the electronic ground state and in excited states of the complex. Esr data indicate a 1.1% admixture of metal 4s character for the unpaired electron and strong bonding between the metal 4s orbitals and ligand MO states of like symmetry.³⁷ There is also ample evidence for σ delocalization of unpaired spin density in metal complexes with pyridine-type ligands.⁴⁰ As intermolecular transfer or induction of only 0.001 unpaired spin density onto the nucleus is required to give some observable scalar coupling, the edges of the bipyridyl rings should indeed be able to induce a moderate scalar coupling pulse.

As a consequence of the described steric and electronic factors, the scalar coupling component is smaller than in BDPA but is by no means insignificant. The observed positive enhancements with OFN make scalar coupling by exchange polarization an unlikely mechanism, although the average degree of scalar coupling with the receptor test probes in Table II resembles the values obtained with TTBP, the model radical for exchange polarization. Requirements for scalar coupling by exchange polarization are a delocalized electron spin, the existence of low-lying excited states, and steric hindrance that prevents close approach and bonding interaction between radical and nuclear spin species.²⁰ OFN exhibits a larger scalar coupling component with $\text{Cr}(\text{bipy})_3^+$ than with TTBP, which is sterically shielded, or with TANO, where the unpaired spin is sterically available but quite localized. The amount and distribution of unpaired spin density at the rim of the spherical $\text{Cr}(\text{bipy})_3^+$ is obviously sufficient to induce electron spin transfer in collisions with the OFN planes. Dnp results confirm the presence of unpaired spin density at the periphery and in the plane of the bound bipyridyl ligand and indicate substantial interaction between the complex and species in the SCS.

Up to now it has not been possible to measure directly the effect of collision attitude upon dnp enhancements for a planar radical such as BDPA. Collision of a molecule with the plane of the radical, the sterically preferred mechanism, leads to strong scalar coupling by transient bonding interactions.²⁵ From the results with $\text{Cr}(\text{bipy})_3^+$, it may be concluded that collisions with the edge of a planar radical lead only to moderate scalar coupling. As previously assumed, the experimentally obtained strong scalar coupling of planar radicals with OFN must therefore be due to interactions with the spin-rich planes of the radical.⁷

$\text{Cr}(\text{C}_6\text{H}_6)_2^+$. The complex exhibits strong scalar coupling with the phosphite and fluoroborate nuclear test probes and almost pure dipolar coupling with OFN. The bis(π -benzene) complex is sterically accessible from all sides; the inter-ring distance of about 3.2 Å even exposes the chromium ion to attack by solvent molecules.⁴¹ In contrast to $\text{Cr}(\text{bipy})_3^+$, the stacked benzene rings provide ample opportunity for plane-plane collisions with species such as OFN. The neutral

bis(benzene) complex is known to form charge-transfer complexes with nitrobenzenes and tetracyanoethylene to give the chromium complex cation and planar anions.⁴² The absence of scalar coupling with OFN must be a consequence of electronic factors, as the geometry of the complex is well suited for the type of plane-plane collision which gives rise to the strong scalar coupling of OFN with BDPA. The observed dipolar coupling with OFN indicates the absence of unpaired electron density in the plane of the benzene rings and above these planes. According to esr evidence, the unpaired electron is in an a_{1g} ($3d_{z^2}$) orbital of the Cr atom, with about 2.2% metal 4s admixture.⁴³ In agreement with our dnp results, the esr studies indicate that there is little charge on the rings and little delocalization of unpaired electron density into the rings.

The extremely high degree of scalar coupling with the phosphine and with BF_4^- must be accounted for by a different interaction mechanism. *A priori*, both exchange polarization and chemical bonding interactions may be expected to contribute to scalar coupling in the case of ^{31}P and ^7Li . However, BF_4^- does not show significant scalar coupling with TTBP, with which any propensity for exchange polarization should be fully realized. The high scalar component in the ^{19}F coupling with the $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ complex must be attributed to bonding interactions. In order for scalar coupling by bonding interaction to be observable, distances of closest approach must be about 2–3 Å, and correlation or sticking times for the interaction must exceed 10^{-10} sec.^{7,15} The most obvious mode of interaction by which OFN alone among the nuclear test probes cannot be polarized efficiently is direct intrusion of a molecular species into the space between the benzene rings and direct bonding with the metal located in the xy plane of the complex, the region of high unpaired spin density. A similar bonding interaction with the metal has been postulated for the ligand-exchange reactions of $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$.⁴⁴ Bonding with the BF_4^- anion is most likely due to electrostatic attraction to the chromium cation. The slight scalar component for ^7Li in turn may be due to ion pairing with the fluoroborate anion, attracting Li^+ to an area of high unpaired spin density. Scalar coupling of the phosphine ^{31}P is most likely a result of bonding interaction of the exposed chromium atom with the phosphine lone pair.

Molecular interaction between $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ and SCS species is thus characterized by weak solvation of the benzene rings and by strong transient bonding of the sandwiched chromium atom with negatively charged groups or atoms and with lone pairs of suitable ligands.

Conclusions

Intermolecular encounter or collision between an inorganic or organometallic paramagnetic complex and other species in solution may give rise to both dipolar and scalar coupling of electron and nuclear spin. The relative contribution of either component can be measured by low-field dnp. Protons generally exhibit only dipolar coupling in intermolecular interactions, while ^7Li , ^{19}F , and ^{31}P may exhibit moderate to strong scalar coupling. The extent of the latter relaxation process depends on the availability of unpaired electron density at the periphery of the complex, the possibility of close approach to within the effective limits for scalar coupling, and the presence of chemical or physical forces encouraging close and protracted approach.

The presence of scalar coupling either from exchange polarization effects or from the presence of bonding interactions between the paramagnetic complex and molecules in the SCS allows a qualitative description of these molecular interactions. Nuclear test probes can trace out the availability of unpaired electron density at the surface of a paramagnetic complex in which the unpaired electron resides primarily on the metal.

Results from dnp experiments are in agreement with conclusions reached from esr evidence.

Although dnp is not sensitive to angular variations in intermolecular encounters in the same way as pseudocontact chemical shift techniques,^{2a} stereospecific intermolecular bonding effects can frequently be identified. Ion-pairing and ion-repulsion effects are graphically demonstrated in the intermolecular encounters between electrically charged radicals or paramagnetic complexes and ionic nuclear test probes. Detailed information on fast molecular interactions between radical inorganic complexes and molecular species in the solvation shell can be obtained as in previous studies on organic radicals.^{7a}

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Registry No. BDPA, 2152-02-5; TTBP, 2525-39-5; TANO, 2896-70-0; $\text{K}_3\text{Cr}(\text{CN})_5\text{NO}$, 14100-08-4; $\text{Cr}(\text{bipy})_3\text{ClO}_4$, 14524-27-7; $\text{Cr}(\text{C}_6\text{H}_6)_2\text{I}$, 12089-29-1; OFN, 7789-25-5; $\text{P}(\text{OCH}_3)_3$, 121-45-9; LiClO_4 , 7791-03-9; LiBF_4 , 14283-07-9; ^{31}P , 7723-14-0; ^7Li , 13982-05-3.

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Photochemistry of the Group VI Hexacarbonyls in Low-Temperature Matrices.

II. ¹ Infrared Spectra and Structures of ¹³CO-Enriched Hexacarbonyls and Pentacarbonyls of Chromium, Molybdenum, and Tungsten

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The infrared spectra of the ¹³CO-enriched metal hexacarbonyls and pentacarbonyls have been studied in Ar and CH₄ matrices at 20 K. The hexacarbonyl spectra can be fitted very accurately in frequency and intensity using a CO-factored force field. The spectra of the pentacarbonyls are inconsistent with a *D*_{3h} structure but can be fitted accurately using a *C*_{4v} structure. Using intensity data, axial-radial bond angles (*C*_{4v} structure) between 90 and 95° are calculated. The structure and force constants are almost independent of the matrix material.

Chromium, molybdenum and tungsten pentacarbonyls have been generated by *uv* photolysis of the hexacarbonyls in hydrocarbon glasses² at 77 K and in argon matrices¹ at 20 K. In the ir spectra three bands were observed in the C–O stretching region (e.g., Cr(CO)₅ in Ar: 2093 (v_w), 1965.6 (s), 1936.1 (m) cm⁻¹). The bands were assigned to the A₁, E, and A₁ bands, respectively, of a square-pyramidal (*C*_{4v}) molecule. The evidence for this structure as opposed to that for a *D*_{3h} structure was based on the presence of the very weak high-frequency band and on the intensity ratio of the low-frequency bands. During investigation of the *uv* spectra of the pentacarbonyls in different matrices,³ it became essential to have stronger evidence that the *D*_{3h} structure was incorrect and to estimate bond angles for a *C*_{4v} structure.

In the experiments described below, the ir spectra of ¹³CO-enriched metal pentacarbonyls were studied using the methods of analysis developed by Haas and Sheline,⁴ Bor,⁵ and Darling and Ogden.⁶ The results prove that the *C*_{4v} structure for photochemically generated M(CO)₅ is indeed correct.

Analysis of Spectra

When a metal carbonyl is enriched to approximately 50% ¹³CO, all possible isotopic molecules (M(¹²CO)_x(¹³CO)_{n-x}, *x* = 0, 1, ..., *n*) are present in a scrambled mixture whose composition is determined by the statistical weights of the different molecules. Since the vibrational symmetry is lowered by ¹³CO substitution, the ir spectrum in the C–O stretching region consists of the sum of the superimposed spectra of all the individual molecules, each of which has a different vibrational pattern.

Darling and Ogden⁶ have calculated the patterns of the isotopic spectra of metal carbonyls for those cases in which the parent molecule has no permanent dipole moment and all CO groups are equivalent (i.e., M(¹²CO)_x(¹³CO)_{n-x}; *n* = 2, *D*_{∞h} geometry; *n* = 3, *D*_{3h} geometry; *n* = 4, *T*_d or *D*_{4h}; *n* =

6, *O*_h). In such molecules there is only one C–O stretching force constant and not more than two CO–CO interaction constants. Such calculations have been used to assign the spectra of a number of metal carbonyls and dinitrogen species.⁷

M(CO)₅ presents a more complex case because it must have at least two different CO stretching force constants and three interaction constants whether the molecular symmetry is *D*_{3h} or *C*_{4v}. In intensity calculations for the *C*_{4v} geometry we must include bond angle and bond moment data.⁸ The distinction between *C*_{4v}, *D*_{3h}, or any geometry of lower symmetry rests on detailed comparison of experimental spectra and a range of possible theoretical spectra. We assume that the molecule has the simplest structure for which the experimental spectra can be matched (i.e., the structure with the minimum number of force constants).

Such an assignment depends on having an estimate of the errors expected in the prediction of the isotopic spectra. There have been a number of studies of isotopically enriched carbonyls in solution but most have involved only partial enrichment.⁹ Ni(CO)₄ and Co(CO)₃NO⁵ have been examined with more extensive enrichment but these compounds have relatively few bands; Noack and Ruch¹⁰ studied Fe(CO)₅ but did not optimize the force constants. Johnson, *et al.*,¹¹ have examined the spectrum of Mn(CO)₅Br in chloroform during C¹⁶O–C¹⁸O exchange and have refined the Cotton–Kraihanzel parameters and calculated intensity data; the spectra however were only of moderate resolution. Darling¹² has generated C¹⁸O-substituted Cr(CO)₆ in Kr matrices by cocondensation of Cr atoms and CO–Kr mixtures, but the spectra are not sharp enough to merit complete analysis. We therefore decided to analyze the M(CO)₆ species in low-temperature matrices as a check on our calculations and to obtain an estimate of the systematic errors in the method. (Details of the methods of calculation of frequency and intensity are given in Appendix 2.)

Low-temperature matrices have the advantage that the