metric backbone conformation[12] for *cyclo*(Gly-Pro-Gly)$_2$ in DMSO-d_6 solution

	Gly$_1$	Pro	Gly$_2$
ϕ	$\sim$0°	120°	270°
ψ	$\sim$0°	300°	180°

Nmr spectra in aqueous solution suggest that the same skeletal conformation exists in this solvent.

The ^{13}C spectra of the enriched sample (Figure 2) permitted assignment of the highest field carbonyl resonance to the Gly$_1$ carbonyl carbon—the one involved in H bonding. This result is somewhat surprising, since shifts to lower field of 5–10 ppm have been reported for intermolecularly H-bonded carbonyl carbons,[13] although shielding due to magnetic anisotropy of the end peptide group of the β turn provides a possible explanation in this case.[14] Further, in spectra of the deuterated sample, both in DMSO-d_6 and in D$_2$O, it was noted that the central carbonyl resonance had markedly reduced intensity relative to the other carbonyls, while in the enriched sample (undeuterated) this was not the case.[15] Since the dominant ^{13}C spin-lattice relaxation mechanism is through neighboring protons, deuteration of the C$_\alpha$ of Gly$_2$ should lead to a less efficient relaxation (longer T_1) and, hence, to the observed reduced peak size. Thus, the Gly$_2$ C=O may be assigned to the central resonance, and the Pro C=O to the remaining downfield peak (Figure 2a and b).

Although the observed coupling constants are interpreted in terms of a single conformation for *cyclo*(Gly-Pro-Gly)$_2$, described by the ϕ,ψ angles indicated, the $J_{N\alpha}$ values are equally consistent with a weighted average of similar conformational states related by rotations (of perhaps ±30°) around the C$_\alpha$ bonds of the four glycyl residues. In contradistinction to the serine-containing cyclic hexapeptides,[3,4] *cyclo*(Gly-Pro-Gly)$_2$ showed no asymmetric conformations or structures containing *cis*-X-Pro peptide bonds in the solvents examined. The results with *cyclo*(Gly-Pro-Gly)$_2$[16] establish a general conformational preference for this class of proline-containing cyclic hexapeptides, which favors a trans′ orientation of the proline residue, and intramolecular H bonding of the residue *preceding* the proline.

Acknowledgments. We thank Dr. Eric T. Fossel for the ^{13}C nmr spectra. We also thank Dr. Aksel Bothner-by and Dr. Joseph Dadok of the Carnegie-Mellon University for making their 250-MHz nmr facility available to us. We acknowledge with thanks the use of the Varian XL-100-15 nmr instrument (provided by the National Science Foundation) at the Department of Chemistry. This work has been supported, in part, by U. S. Public Health Service Grants AM-07300 and AM-10794. One of us (L. G. P.) holds a National Science Foundation Predoctoral Fellowship.

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(12) The estimated uncertainty in all (ϕ,ψ) angles obtained from $J_{N\alpha}$ data is ±10°.

(13) F. A. Bovey in "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 233, and references therein.

(14) D. W. Urry and M. Ohnishi in "Approaches to Biomolecular Conformation," D. W. Urry, Ed., American Medical Association, Chicago, Ill., 1970, pp 263–299, and references therein.

(15) ^{13}C spectra of the deuterated sample taken with a longer pulse interval (acquisition time plus pulse delay = 8.5 sec) show recovery of the amplitude of the central resonance relative to the other carbonyl resonances. This result confirms that the observed effects are due to a change in T_1.

(16) Note Added in Proof. Professor Robert Schwyzer of the Eidg. Technische Hochschule, Zürich-Hönggerberg, has informed us that related investigations on this compound have recently been carried out in his laboratory (*Helv. Chim. Acta*, in press).

Ferromagnetic Behavior of Phenanthrolineiron(II) Dichloride and Related Compounds

Sir:

Examples of inorganic ferromagnetic order among transition metal organometallic compounds are rare. The only such compound known to us is the five coordinate, spin $^3/_2$ bis(diethyl dithiocarbamato)iron(III) chloride studied by Wickman[1] and coworkers. This complex is not polymeric and thus the magnetic exchange is probably due to a weak (T_c = 2.5 K) interaction[2] between discrete molecules. In this communication we present Mössbauer and magnetic data for Fe(phen)Cl$_2$, in which a cooperative ferromagnetic behavior is observed, and for some similar systems.

Powder susceptibility measurements for analytically pure[3] samples of Fe(phen)Cl$_2$ over the temperature range 4.2–300 K and at various fields (Figure 1) have been made. Fits with a Curie–Weiss law yield a paramagnetic Curie temperature $\theta = +12 \pm 4$ K. The Curie–Weiss constant $C = 1.24 \times 10^{-2}$ emu/g determined at high temperatures ($T > 10\theta$) corresponds to an effective magnetic moment of 5.4 μB, consistent with quintet iron(II). This is also suggested by the iron-57 Mössbauer isomer shift [δ(300 K) = +1.04 mm/sec, ΔE = +1.45 mm/sec] relative to iron metal. The temperature dependence of dc magnetization at low fields (Figure 2) and ac susceptibility indicates a Curie temperature, $T_c = 8 \pm 2$ K. In addition, the field dependence of magnetization for high fields and $T <$ 4.2 K clearly shows that Fe(phen)Cl$_2$ is not completely saturated for fields up to 50 kG (Figure 3), and hysteresis is detected at low fields as expected for a ferromagnetic material. The low-field data in Figure 3 show a rapid rise of magnetic moment, σ, *vs.* applied field largely reflecting the demagnetizing field of the particular sample shape. The dashed initial portion indicates the region where hysteresis is observed and the region above $\sim$10 kG shows a gradual almost linear increase of σ *vs.* field. The moment σ = 55.6 emu/g at 48 kG corresponds to 3.07 μB/Fe atom in Fe(phen)Cl$_2$ and magnetic saturation is clearly not achieved. Similar data down to 1.4 K show the same general features with slightly (<5%) higher values of σ at high field. In order to saturate the Fe moment, these preliminary experiments must be extended to much higher applied fields. We also have made similar magnetic measurements for the complexes Fe(2,2′-bipy)Cl$_2$ and Fe(5,5′-diMe-2,2′-bipy)Cl$_2$.

Mössbauer spectroscopy confirms that Fe(phen)Cl$_2$ is ordered at 4.2 K. The well-resolved Zeeman spec-

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(1) H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, *Phys. Rev.*, **155**, 563 (1967).

(2) H. H. Wickman, *J. Chem. Phys.*, **56**, 976 (1972).

(3) Calculated % C = 46.95, H = 2.63, N = 9.12, Fe = 18.60; measured % C = 46.77, H = 2.66, N = 9.34, Fe = 18.20.

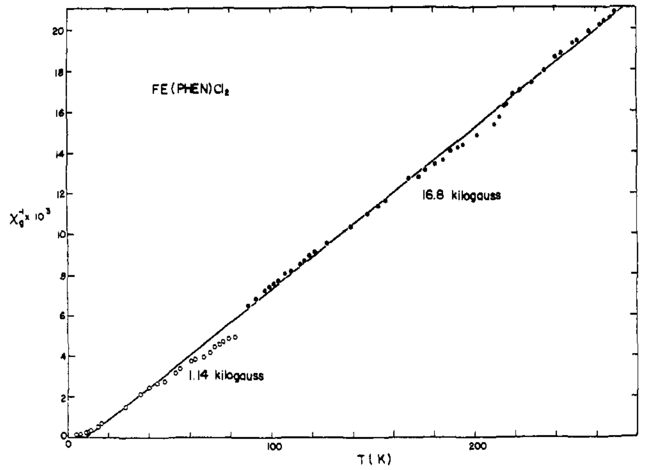

Figure 1. Inverse susceptibility per gram, χ_g^{-1}, *vs.* temperature, *T*, for Fe(phen)Cl_2 powder. Open circles are for applied fields of 1.14 kG.

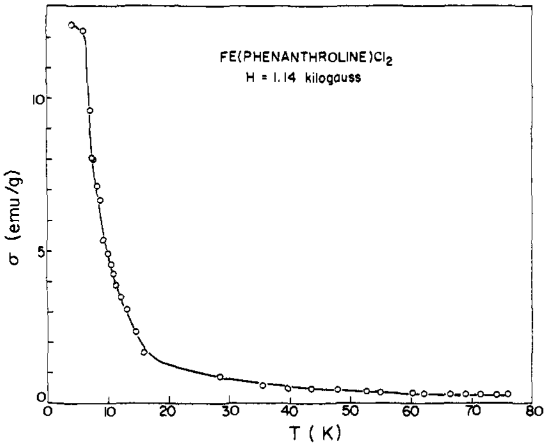

Figure 2. Magnetic moment per gram, σ, *vs.* *T* for Fe(phen)Cl_2 powder.

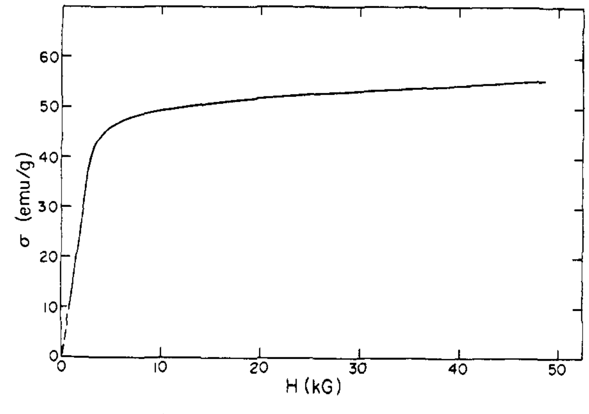

Figure 3. Magnetic moment *vs.* applied field at T = 3.0 K for Fe(phen)Cl_2 powder. Note that complete saturation of the Fe moment is not achieved at 48 kG.

trum (Figure 4) corresponds to an effective internal field of 116 kG at 4.2 K. An additional weak transition is observed at *ca.* 2.25 mm/sec, suggesting a nonzero asymmetry parameter (η) and absence of axial symmetry. However, the magnetically perturbed Mössbauer spectrum of Fe(phen)Cl_2 as well as Fe(2,2'-bipy)Cl_2 at 300 K (Figure 5) shows that V_{zz} is *positive* and $\eta \sim 0$. It might be argued that the Zeeman

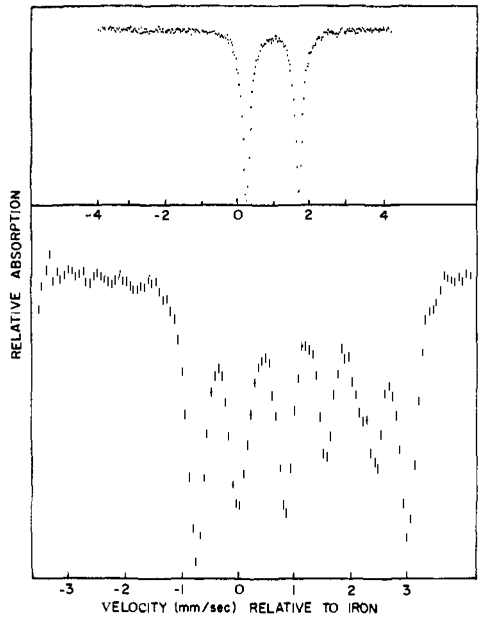

Figure 4. Mössbauer effect in Fe(phen)Cl_2. The upper spectrum shows the room temperature data and the lower data, taken at 4.2 K, show the well-resolved Zeeman spectrum of the ordered material.

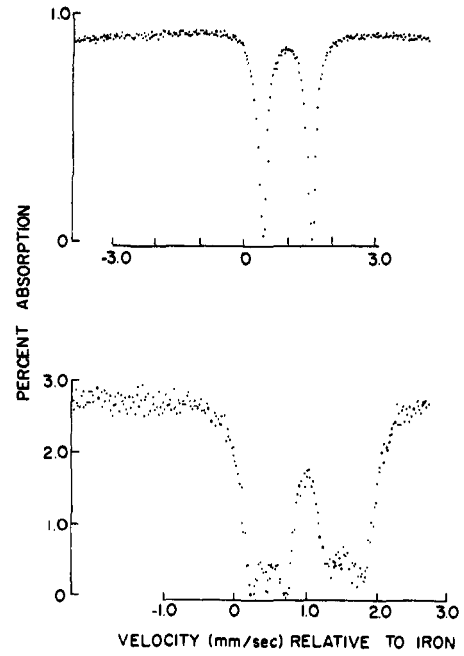

Figure 5. Mössbauer spectra of Fe(2,2'-bipy)Cl_2 at room temperature: top, $-H_{\text{applied}} = 0$; bottom, $-H_{\text{applied}} = \sim 18$ kG.

spectrum of Figure 4 is the result of a slowly relaxing paramagnet. However, the magnetically dilute, monomeric,[4] pseudotetrahedral paramagnet Fe(2,9-diMephen)Cl_2 shows[5] no such Zeeman splitting at 4.2 K. The complex Fe(2,2'-bipy)Cl_2 exhibits a Zeeman splitting at 4.2 K similar to that of the phenanthroline (effective field = 96 kG) and a longitudinally applied field of 35 kG has the effect expected for ferromagnetic behavior, *i.e.*, the observation of still *only six transitions*

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(4) H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. A*, 1956 (1969).

(5) W. M. Reiff, 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972, No. 160, Inorganic Division.

with 2 and 5 of reduced intensity. This observation of incomplete saturation at 35 kG is consistent with magnetic moment data which also shows incomplete magnetic saturation of the powder at this field and temperature. Fe(4,4′-diMe-2,2′-bipy)Cl_2 and the 5,5′-dimethyl analog, both of which show large quadrupole effects (3.5 mm/sec), also exhibit magnetic hyperfine splitting at 4.2 K.

In an effort to determine T_c more precisely for the preceding materials, the temperature dependence of the Mössbauer spectra over the range 2–10 K is presently under investigation. X-Ray, near-infrared, and other spectral data bearing on the structure of and nature of ferromagnetic interaction in the foregoing materials have been completed and will be published elsewhere. The X-ray data and near-infrared–visible spectral absorptions at ~6000 and 10,000 cm^{-1} confirm solid state association through bridging chlorines resulting in a polymer containing iron(II) having either five or six coordination. An extensive new series of mono-polyimine ferrous halides having a variety of electron-releasing and -withdrawing substituents and of structure similar to Fe(phen)Cl_2 has been prepared.[5] Investigation of the variation of T_c in this group should provide a novel method of studying substituent electronic and packing effects.

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Chemically Induced Polarization of Fluorine-19 Nuclei. Fluorine-Substituted Phenyl Radicals

Sir:

Chemically induced dynamic nuclear polarization (CIDNP)[1] is a sensitive indicator for radical-pair reactions. The theory underlying this effect has been developed to a stage where the experimentally observed signal directions and intensity patterns can be used to derive the initial spin multiplicity of the radical pair or the esr parameters of the individual radicals.[2] The application of CIDNP to the determination of the *signs* of hyperfine coupling constants (*a* values) can be of particular interest, since the magnitudes of these parameters are available directly from esr spectra, whereas their signs are less readily accessible and subject occasionally to controversy. Examples of the use of the CIDNP technique to establish or confirm the signs of electron–hydrogen hyperfine interactions include the hydroxybenzyl,[3a] phenoxyl,[3b] and cyclopropyl[3c] radicals.

We have observed ^{19}F polarization in coupling and radical-transfer products derived from pentafluorophenyl and monofluorophenyl radicals and, on the basis of the spectral patterns, have determined the signs of the hyperfine coupling constants for fluorine nuclei in the ortho, meta, and para positions of these radicals.

When a solution of di(pentafluorobenzoyl) peroxide (**1**) in tetrachloromethane was photolyzed in the probe of an nmr spectrometer,[4] seven enhanced multiplets were observed (Figure 1). Three multiplets represented the phenoxyl segment of pentafluorophenyl pentafluorobenzoate (**2**): the ortho and meta nuclei appeared in enhanced absorption (A), the *p*-fluorine in emission (E). A fourth, very weak multiplet (E) was assigned to the *o*-fluorines of the benzoyloxy fragment of **2**. The remaining three multiplets had the chemical shifts of the radical-transfer product, chloropentafluorobenzene (**3a**); their polarization was opposite to the corresponding nuclei of **2** (F_o, F_m, E; F_p, A). Decomposition of **1** in protio- or deuteriotrichloromethane produced similar spectra with **2** and **3b** or **3c** as spin-polarized products. All signals appear to show only net polarization (*e.g.*, Figure 2).

We explain the observed polarization as being induced in the radical pair, pentafluorobenzoyloxy–pentafluorophenyl[5] (Scheme I). Generated in the singlet state[5b,c] this pair can couple to yield **2**. Pentafluorophenyl radicals escaping from their partners can form the radical-transfer products, **3a–c**. The pentafluorobenzoyloxy radical should have a considerably larger *g* factor than the pentafluorophenyl radical. If these apparently reasonable assumptions are correct, the signal directions observed for coupling product **2** and radical-transfer product **3** indicate that the fluorine hyperfine coupling constants of the pentafluorophenyl radical are positive in the ortho and meta positions ($a_F{}^o$, $a_F{}^m > 0$), but negative for the para position ($a_F{}^p < 0$). From the intensity of the CIDNP spectra it appears that $a_F{}^o > a_F{}^m > |a_F{}^p|$. Because of possible relaxation effects we did not attempt to determine the exact ratios of these coupling constants.[6]

We also studied the photodecomposition of the symmetrical di(fluorobenzoyl) peroxides in tetrachloromethane. The polarized products observed in these reactions indicated that the fluorine hyperfine interactions of both *o*- and *p*-fluorophenyl radicals are

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(1) (a) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch., A*, **22**, 1551 (1967); (b) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(2) (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969); (c) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (d) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (e) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970).

(3) (a) G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7229 (1970); (b) M. L. Kaplan and H. D. Roth, *Chem. Commun.*, 970 (1972); (c) R. Kaptein, Ph.D. Thesis, Leiden, The Netherlands, 1971.

(4) The nmr spectra were recorded on a Jeolco C-60 HL spectrometer at 56 MHz. This instrument contained a quartz probe and was fitted with two mirrors to permit uv irradiation (200-W high-pressure mercury lamp) of the samples in the area of the receiver coil. All samples were deaerated with argon. Products 2 and 3 were identified by comparison of their chemical shifts with those of authentic materials.

(5) *Cf.* (a) E. Lippmaa, T. Pehk, A. L. Buchachenko, and S. V. Rykov, *Dokl. Akad. Nauk SSSR*, **195**, 632 (1970); *Chem. Phys. Lett.*, **5**, 521 (1970); (b) R. Kaptein, J. A. Den Hollander, D. Antheunis, and L. J. Oosterhoff, *Chem. Commun.*, 1687 (1970); (c) S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

(6) To our knowledge, no esr study of the pentafluorophenyl radical has as yet been published. Upon photolysis of 1 at −196° in a benzene matrix, an esr spectrum was observed with $g = 2.0015$ and an apparent 1:2:1 triplet splitting of ~20 G. We are indebted to Mr. J. H. Marshall for informing us of these results.