e.g. in microelectronic devices, in chemical industry, aerospace technology and medicine. He also gave an impression of the many criteria that have to be optimized in industrial high-tech product development.

The framework of lectures complemented well the short contributions and poster presentations. A best-poster award was presented to *G. Hertel, H. Hoffmann* and *J. Kalus* (Univ. Bayreuth, FRG) for their neutron small-angle scattering study on the magnetic field alignment of the nematic phases of surfactants.

On the whole, the attempt to combine biological and technological aspects of liquid crystal research in one conference was well received and stimulated much discussion.

A book of abstracts is available from the author of this report.

Ferromagnetic and High Spin Molecular Based Materials in Dallas

By Joel S. Miller* and Dennis A. Dougherty*

The first symposium focusing on several aspects directly related to high spin and molecular/polymeric ferromagnets convened April 9–12, 1989 as part of the 197th National American Chemical Society meeting in Dallas, Texas, USA. This multidisciplinary meeting brought together inorganic, organic, organometallic, polymer, and physical chemists as well as theoretical and experimental condensed matter physicists from Japan, the USSR, the UK, France, Germany, Italy, Spain, Bulgaria, and the USA. The symposium was comprised of a tutorial and sessions devoted to the preparation and characterization of a 'designer magnet' from organic, organometallic, inorganic, and polymeric materials. This broad interdisciplinary symposium was unusual as it was co-sponsored by the Divisions of Inorganic, Organic, Polymer, and Physical Chemistry of the ACS and additionally supported by the Petroleum Research Fund and Gordon & Breach (Science Publisher). A total of 39 verbal and 25 poster papers were presented and the proceedings will be published as a forthcoming volume of *Molecular Crystals, Liquid Crystals.*

The tutorial session enabled attendees to appreciate the conceptual framework on which the current understanding of cooperative magnetic phenomena in molecular/organic/polymeric systems is based. *D. A. Dougherty* (Caltech) concisely reviewed the key criteria for stabilizing a triplet ground state, the building block of a high spin molecule or polymer. *J. S. Miller* (Du Pont) described the existing paradigms, while the fundamental physics of magnetism were reviewed by *A. J. Epstein* (Ohio State). Models for magnetic order and neutron diffraction aspects were presented by *P. Day* (Institut Laue-Langevin) and insight into the realities of opportunities for molecular based magnets was provided by *R. M. White* (Control Data Corp.). Due to their low density, high molecular weight, and low spin-orbit coupling, competition with existing magnets seems unlikely; however, opportunities might exist in fine particle and magnetooptic recording.

The strategies for designing molecular/polymeric materials with ferromagnetic coupling include: a) unpaired electrons in orthogonal orbitals sharing the same spatial region, b) Heitler-London spin exchange, c) antiferromagnetic coupling of sites with differing *S* values (ferrimagnet), d) conjugated odd-alternate hydrocarbons, e) polaronic, conjugated block copolymers, and f) configurational admixture of triplet charge transfer excited states. High spin systems demonstrating the feasibility of several of the strategies were discussed and a few high moment materials were described. It was emphasized universally that the rational design of solid state structures remains an art that limits our ability to prepare the secondary and tertiary structures needed to test many concepts in solid state science. Frequently, complex, solvated compositions with undesired or new structure types form instead of the desired phase. Additionally, several polymorphs may form in lieu of the desired structure type. This is particularly crucial for the formation of a bulk ferromagnet as ferromagnetism is a 3-D (bulk) not a 1-D property.

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The challenge of rationally controlled spin preferences of small organic molecules was addressed by *J. A. Berson* (Yale), *W. T. Borden* (Univ. Washington), *P. Dowd* (Pittsburgh) and *D. J. Klein* (Univ. Texas at Galveston). While there have been considerable successes, it is clear that for finely balanced systems, present computational methods cannot yet predict the singlet-triplet energy gap to better than a few kcal/mol for modest-sized molecules. A means to experimentally determine the singlet/triplet gap particularly for ground state triplet substances is unavailable, but would be of great value. *H. Iwamura* (Univ. Tokyo) and *K. Itoh* (Osaka City University) have prepared variously substituted extended carbene systems, reaching spin states as high as $S = 5$ in a pentacarbene. The spin coupling capacities of various π topologies were discussed, and the first ferrimagnetically coupled organic molecule was reported by *Itoh*. *Dougherty* described a high spin state ($S = 2$) in a partially localized system, involving ferromagnetic coupling through a cyclobutane ring.

The most extensively characterized organic, organometallic, and inorganic high spin compounds exhibiting magnetic or incipient magnetic order were galvinoxyl [*M. Kinoshita* (Univ. Tokyo)], decamethylferrocenium tetracyanoethenide [DMeFc][TCNE] (*Epstein* and *Miller*) and $Mn^{II}Cu^{II}$[oxamido-*N,N'*-bis(2-benzoato)] · H_2O, [*O. Kahn* (Univ. Paris, South)] and Mn(hexafluoroacetylacetonate)$_2$tetramethyl-*n*-propylnitronylnitroxide [*D. Gatteschi* (Florence)]. Galvinoxyl exhibits strong ferromagnetic coupling (Curie-Weiss $\theta = +19$ K), however, a still to be understood phase transition, which can be suppressed by doping with hydroxygalvinoxyl, occurs at ~85 K. The Mn^{II} containing coordination polymers exhibit spontaneous magnetization in accord with ferrimagnetic ordering at 14 and 8.6 K, respectively. The most extensively characterized molecular magnet, [DMeFc][TCNE] [i.e., $\theta = +30$ K, 1 kOe coercive field, $\alpha-\delta$ critical constants, and ferromagnetic ordering at 4.8 K confirmed by neutron diffraction], comprises isolated radical cations and radical anions without the benefit of an extended network solid state structure. Substitution of chemically important features of [DMeFc][TCNE] lead to the characterization of several ferromagnetically coupled systems. An additional bulk ferromagnet, however, remains elusive. The extended McConnell model of the configurational admixture of triplet charge transfer excited states appears at present to provide the best understanding of the mechanism of ferromagnetic coupling for this system and enables the prediction of magnetic coupling for related systems.

Based upon this McConnell model several groups have targeted the preparation of radicals to test the model and its special cases. Three-fold or higher symmetry donors containing nitrogen were discussed by *R. Breslow* (Columbia) and *D. A. Dixon* (Du Pont), whereas *L. Y. Chiang* (Exxon) reported on an oxygen containing donor and *F. Wudl* (UCSB), *J. Yamaguchi* (Kyoto), and *J. P. Morand* (Bordeaux) described their successes in preparing sulfur containing donors. *Wudl* also elaborated upon the preparation of 1,3,5,-tris(tricyanovinyl)benzene. In the best characterized system, the six-fold symmetric hexaazaoctadecahydrocoronene system, *Breslow* and *Dixon* noted that distortions to the diamagnetic dication readily occurred and conjectured that this distortion may be circumvented by going to a three-fold symmetric system. Ferromagnetically coupled systems, however, have yet to be prepared with such donors.

Two unusual ferromagnetically coupled high spin polynuclear clusters were reported. *D. C. Johnston* (Iowa) and *D. N. Hendrickson* (UCSD) reported $S = 6$ $[Cr_4^{III}S(O_2CMe)_8(H_2O)_4]^{2\oplus}$ and $S = 14$ $[Mn_8^{III}Mn_4^{IV}O_{12}(O_2CPh)_{16}(H_2O)_4]$, respectively. A microscopic understanding of the mechanism of spin exchange is unknown; however, the 'orbital ordering' mechanism described by *Day* in for example Rb_2CrCl_4 may be applicable. Additionally, a ferromagnetically coupled $S = 9/2$ $Cr^{III}Ni_3^{II}$ cluster was described by *Kahn* and a $S = 12$ $[Mn^{II}(\text{nitronylnitroxide})]_6$ ferrimagnetic ring was presented by *Gatteschi* and *Rey*. Novel liquid crystals (*W. Haase*, Darmstadt) exhibiting antiferromagnetic and ferromagnetic order and monomolecular films (*H. M. McConnell*, Stanford) exhibiting long range order captured the imagination of the audience.

The preparation of organic polymers exhibiting high spin if not ferromagnetic order is attracting significant attention. *Iwamura* described materials based on polyacetylenes with radical pendant groups. *A. L. Buchachenko* (Institute of Chemical Physics, USSR), *M. Ota* (Gumna U.), *A. A. Ovchinnikov* (Institute of Chemical Physics, USSR), and *J. B. Torrance* (IBM) described their respective approaches, i.e., silicone based polymers, photooxidation of triarylmethane based polymers, pyrolysis of polyacrylonitrile, polymerization of nitroxyl containing diacetylenes, and iodine oxidation of 1,3,5-triaminobenzene. A reproducibly prepared, well characterized system has been elusive. In post deadline poster contributions *D. W. Wiley* (Du Pont) and *C. J. O'Connor* (Univ. New Orleans) independently reported that prototype dinitroxyl diacetylenes monomers (each crystallizing into two polymorphs) to test the concept of preparing high spin polymer, could not be topochemically polymerized and did not exhibit high spin, ferromagnetically coupled behavior. Theoretical guidance for designing new polymers was additionally described by *N. N. Tyutyukov* (Bulgaria Academy of Science) and *T. Hughbanks* (Texas A & M at College Station).

Clearly the embryonic quest for molecular/polymer based magnetic materials is a thriving area of research. The synthetic challenges are formidable as ferromagnetism, being a bulk and not a molecular property, requires that materials with specific primary, secondary, and tertiary structures be made. The rational design of solids remains an art that limits our ability to prepare such structures.

Nonetheless, several examples of deliberately designed high moment, magnetically ordered materials have been prepared and we look toward a future where ferromagnetic phenomena can be added to the repertoire of physical properties enjoyed by molecular/polymeric materials.