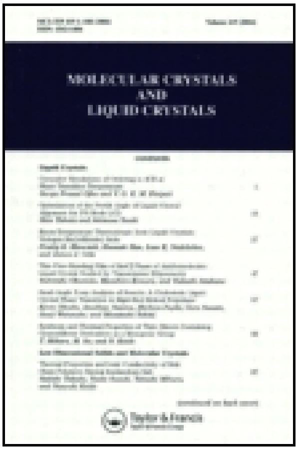


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Molecular Magnets Based on Organic Complexes

Akira Miyazaki [a], Takashi Umeyama [a], Toshiaki Enoki [a], Eiji Ogura [b], Yoshiyuki Kuwatani [b], Masahiko Iyoda [b], Hiroyuki Nishikawa [b], Isao Ikemoto [b] & Koichi Kikuchi [b]

[a] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152-8551, Japan

[b] Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan

Version of record first published: 24 Sep 2006

To cite this article: Akira Miyazaki, Takashi Umeyama, Toshiaki Enoki, Eiji Ogura, Yoshiyuki Kuwatani, Masahiko Iyoda, Hiroyuki Nishikawa, Isao Ikemoto & Koichi Kikuchi (1999): Novel Molecular Magnets Based on Organic Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 379-388

To link to this article: http://dx.doi.org/10.1080/10587259908023335

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 379-388
Reprints available directly from the publisher
Photocopying permitted by license only

Novel Molecular Magnets Based on Organic Complexes

AKIRA MIYAZAKI[a], TAKASHI UMEYAMA[a], TOSHIAKI ENOKI[a],
EIJI OGURA[b], YOSHIYUKI KUWATANI[b], MASAHIKO IYODA[b],
HIROYUKI NISHIKAWA[b], ISAO IKEMOTO[b] and KOICHI KIKUCHI[b]

[a]*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152–8551 Japan and* [b]*Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 192–0397 Japan*

The crystal structure and the physical properties of the radical ion salts BMT-TTFI_2•FeX_4 (X = Br, Cl) and $(DMET)_2FeBr_4$ are investigated. The structures of BMT-TTFI_2•FeX_4 are characterized as the sheets made of dimerized donor molecules and one-dimensional anion chains. These salts show three-dimensional Curie-Weiss behavior accompanied with antiferromagnetic transitions, with the highest Néel temperature (T_N= 15 K) among the π-*d* interaction based magnets for the $FeBr_4$ salt. Within a crystal of $(DMET)_2FeBr_4$, the donor molecules form one-dimensional columns, between which magnetic anion sheets are inserted. This salt is metallic down to T_{MI} = 200 K, above which the Curie-Weiss type magnetism is described in terms of donor and anion spins, in spite of the metallic conduction of the salt. Below T_{MI} the magnetism is governed by anion spins, and an antiferromagnetic phase transition takes place at T_N= 3.5 K.

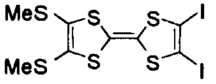
Keywords: molecular conductor; molecular antiferromagnet; π-*d* interaction

INTRODUCTION

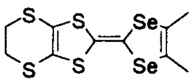
Organic radical ion salts have a large variety of low-dimensional electronic structures ranging from metals to insulators, whose electronic nature is easily controlled by changing external physical parameters, or chemical modification of the constituents. If the magnetic ions such as transition metal halides are introduced into molecular conductors having such a variety of electronic structures, the localized moments of *d*-electrons can interact with the aid of π-electrons in various ways. Molecular magnets based on organic complexes therefore have a possibility of realizing novel magnetic systems.

Focusing on this viewpoint, we have been searching the π-*d* interaction based molecular magnets using radical ion salts having magnetic anions[1,2], where a tetrahedral $FeBr_4^-$ anion is proved to be a good component for constructing molecular magnetic system. For example, a $FeBr_4$ salt of C_1TET-TTF (= bis(methylthio)ethylenedithiotetrathiafulvalene) has a weak ferromagnetic phase, whose origin is characterized as a Dzyaloshinsky-Moriya interaction between the localized moments on the anions[3]. $[M(dddt)_2]_2FeBr_4$ (M = Pt, Au; H_2dddt = dimercaptodihydrodithiin) also have an antiferromagnetic phase, where the exchange interaction between the magnetic $FeBr_4^-$ anions is mediated by the π-electrons on the donor layers.

Here we have adopted following two approaches, in order to obtain π-d interaction-based systems with larger exchange interaction. The first is an introduction of iodine substituents to the TTF skeleton. The crystal structures of salts of iodine-substituted donors with anions are characterized as the presence of intermolecular –I···X– (X = CN, halogen) contacts[4]. Since these strong intermolecular contacts are also expected to be useful for making intermolecular exchange paths, we used BMT-$TTFI_2$ (= diiodo-bis(methylthio)tetrathiafulvalene) to make a radical ion salt. The second approach is the use of donor suitable for obtaining metallic salts. DMET (= dimethylethylenedithiodiselenadithiafulvalene) is known to give a number of metallic and superconducting salts[5], hence it can be a good building block for obtaining "molecular magnetic metal". In this paper, the crystal structure, transport and magnetic properties of FeX_4^- (X = Br, Cl) salts of these two donor molecules are described.



BMT-$TTFI_2$



DMET

EXPERIMENTAL

BMT-$TTFI_2$[6] and DMET[7] were prepared according to the literatures. Samples were grown with anodic oxidation of the donors, using n-$Bu_4N \cdot FeX_4$ (X = Cl, Br) as supporting electrolytes, chlorobenzene as a solvent.

The crystal structures are determined by single crystal X-ray diffraction method using *Rigaku* AFC-7 four-circle diffractometer. The structures were solved with direct methods (*SHELXS*-86), then refined with full-matrix least-squares method (*SHELXL*-93). DC electrical conductivity was measured using four-probe technique. Static magnetic susceptibilities were measured for single-crystalline oriented samples using Quantum-Design MPMS-5 SQUID magnetometer. The energy band structures of the salts were calculated based on the extended Hückel tight-binding approximation.[8] Coefficients for the Slater atomic orbitals were taken from Ref. [9].

RESULTS AND DISCUSSION

BMT-TTFI$_2$·FeX$_4$ (X = Br, Cl)

The salts have 1:1 stoichiometry and isomorphous, regardless of the counter anion. Figure 1 shows the crystal structure of BMT-TTFI$_2$·FeCl$_4$ viewed perpendicular to the molecular plane of the donor. The donor molecules are stacked along the *c*-direction forming head-to-tail dimers. The transfer integral between dimers (0.016 eV) is one tenth of that within the dimer (0.14 eV), showing the strong dimerization of the donors. The counter anions form zigzag chains extended along the $a + c$ direction by means of close halogen ··· halogen contacts, whose distances are 3.926(3) and 3.85(2) Å for the FeCl$_4$ and FeBr$_4$ salt, respectively. These chains are bridged by the

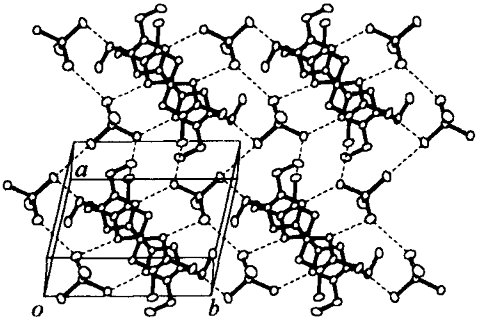


FIGURE 1 Crystal structure of BMT-TTFI$_2$·FeCl$_4$ projected perpendicular to the molecular plane of the donor. Dashed lines indicate close intermolecular contacts.

dimerized donors using a number of S ··· X and I ··· X contacts between the donors and anions. It is noteworthy that the distances for the I ··· X contacts ($\mathrm{FeCl_4}$: 3.251(1), $\mathrm{FeBr_4}$: 3.30(1) Å) are 0.5 Å shorter than van der Waals distances (I ··· Cl: 3.73, I ··· Br: 3.83 Å).[10] The anion chains and the donor dimers thus form sheets parallel to the (10$\bar{1}$) planes, between which the other weak halogen ··· halogen contacts exist ($\mathrm{FeCl_4}$: 4.312(3), $\mathrm{FeBr_4}$: 4.00(2) Å).

These salts are semiconductive, whose conductivity (1×10^{-6} Scm^{-1} at room temperature) and activation energy (4.6×10^{3} K) are independent of the counter anion. Their low electrical conductivies and high activation energies are consistent with the 1:1 stoichiometry and the strong dimerization of the donor units. Namely, the electronic state of the π-system for these salts is regarded as closed-shell singlet state with relatively high excitation energy, which leads to the absence of the conduction electron.

Figure 2 shows the static magnetic susceptibilities of single crystalline samples for the $\mathrm{FeX_4}$ salts, after the subtraction of the Pascal's core diamagnetic contribution. In the high temperature region ($T > 50$ K) the susceptibility of both salts obeys the Curie-Weiss law. Their Curie constants (4.3 emu K mol^{-1}) indicate that the magnetic moments originate from the high-spin ($S = 5/2$) $\mathrm{FeX_4^-}$ anion, which are consistent with the singlet nature of the π-electron system. For the $\mathrm{FeCl_4}$ salt, a broad hump of the susceptibility originating from short-range order is observed around 3 K, and an antiferromagnetic transition takes place at 2.5 K. For the $\mathrm{FeBr_4}$ salt, an

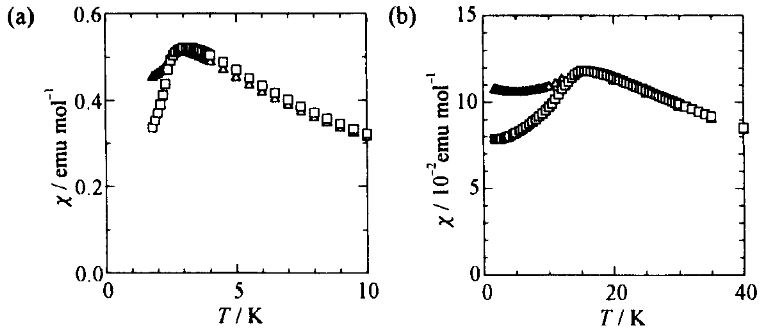


FIGURE 2 Magnetic susceptibility of (a) BMT-$\mathrm{TTFI_2 \cdot FeCl_4}$ and (b) BMT-$\mathrm{TTFI_2 \cdot FeBr_4}$ in a field of H = 1 T (△: $H \parallel b$, □: $H \parallel c$).

antiferromagnetic transition occurs at 15 K showing only a symptomatic short-range order. In the magnetization curve at 2 K (not shown in the figures), spin-flop transitions are observed at H_{SF} = 1.8 T for the $FeCl_4$ salt, whereas no spin flop transition is observed up to 5 T for the $FeBr_4$ salt.

Despite the one-dimensional alignment of the magnetic anions, the susceptibility shows three-dimensional Curie-Weiss behavior, and their Néel temperatures ($FeCl_4$ salt: 2.5 K, $FeBr_4$ salt: 15 K) are suppressed from the Weiss temperatures ($FeCl_4$: –4.6 K, $FeBr_4$: –23.8 K). Both of these are well explained by considering the presence of the Fe–X ··· $(donor)_2$ ··· X–Fe superexchange paths. The paths between anion chains raise dimensionality of the magnetic system, which prevents the emergence of the short-range order on the susceptibility. Moreover, superexchange paths connecting second-nearest neighbor sites within an anion chain frustrates Fe^{3+} spins to diminish the Néel temperature.

The large difference in the Néel temperatures between the $FeCl_4$ and $FeBr_4$ salts can be understood by comparing their crystal structures. The distance of the halogen ··· halogen contacts for the $FeBr_4$ salt between the anion chains (3.85(2) Å) is shorter than the corresponding value for the $FeCl_4$ salt (3.926(3) Å). Since the intermolecular I ··· X contacts between the donor and anion molecules strongly bind neighboring FeX_4^- anions to one donor molecule, the distance between the neighboring anions is nearly the same for the both salts. Taking the Fe–X bond length into consideration, the $FeBr_4$ salt has shorter halogen ··· halogen intermolecular distance, which leads to the large exchange interaction between the localized spins. The relative magnitude of the exchange interaction can be obtained from the magnetic anisotropy in their antiferromagnetic phases. From the dipole-sum calculation, the anisotropy field H_A is estimated at 0.27T for these salts. Using the spin flop field H_{SF} ($FeCl_4$: 1.8 T, $FeBr_4$: > 5T), their exchange field H_E is estimated at 6 T for the $FeCl_4$ salt and > 45 T for the $FeBr_4$ salt. The exchange interaction between $FeBr_4^-$ anions is therefore four times larger than $FeCl_4^-$ anions, which qualitatively corresponds to the tendencies of the Weiss and Néel temperatures.

Finally, we comment on the role of the iodine substituents to the magnetic properties of these salts. The extended Hückel molecular orbital calculation reveals that the $5p_z$ orbitals of iodine atoms little contribute to the HOMO of the donor (atomic orbital coefficient = 0.064). Consequently, the exchange interactions through I ··· X (X = Cl, Br) paths between a donor and an anion are regarded as weak ones. On the other side, the remarkably short I ··· X contacts makes the distance between FeX_4^- anions considerably reduced and, as a consequence, the large exchange interaction between the localized moments on the counter anion is achieved. This "chemical pressure effect" gives the highest Néel temperature of BMT-TTFI$_2$·FeBr$_4$ among the *π-d* interaction-based molecular antiferromagnets within the authors' knowledge.

$(DMET)_2FeBr_4$

Figure 3 shows the crystal structure of $(DMET)_2FeBr_4$ projected along the *b*-axis[11]. The donors are stacked to form uniform one-dimensional columns without any dimerization. The column located at $z \sim 0$ and $z \sim 1/2$ are extended along the $a + b$ and $a - b$ directions, respectively. These columns then interact through close Se···S intermolecular contacts (distance: 3.72(1)Å) to form a sheet structure. The extended Hückel MO calculation shows the presence of strong (~0.6eV) intra-chain transfer integrals for the face-to-face intermolecular contacts, and the strengths of the inter-chain interactions (0.06 to 0.1eV) are 10 – 20% of the intra-chain ones. The calculated band structure of this salt suggests a 3/4-filled one-dimensional semimetallic state. The tetrahedral $FeBr_4^-$ anions form a distorted square lattice formed by Br ··· Br contacts (distance: 3.882(7)Å). The donor sheets interact with the anion sheets

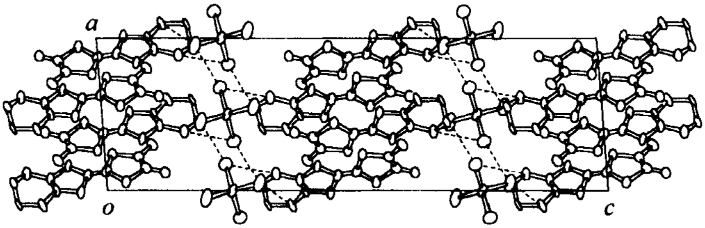


FIGURE 3 Crystal structure of $DMET_2FeBr_4$ viewed along the *b*-axis. Dashed lines indicate close intermolecular contacts.

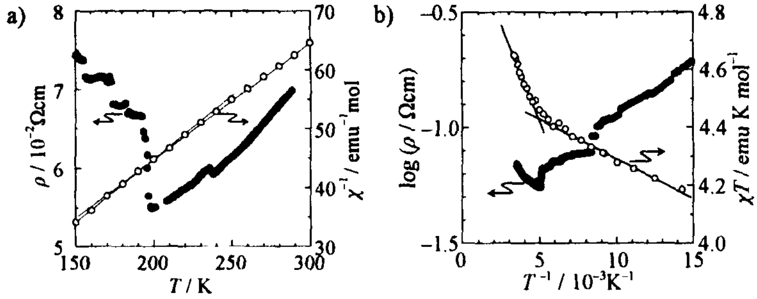


FIGURE 4 (a) The temperature dependence of the resistivity (●) and the reciprocal magnetic susceptibility (○). (b) log ρ (●) and χT (○) plotted against T^{-1}. The solid lines are Curie-Weiss fittings above and below 200 K.

are interacted through Br ··· S contacts, whose distance (3.76(1)Å) is comparable to the corresponding van der Waals distance (3.65Å)[10].

Figure 4(a) presents the temperature dependence of the electrical resistivity and the reciprocal magnetic susceptibility. The resistivity at room temperature is $7\times10^{-2}\Omega$cm, which is comparable to the other metallic DMET salts[5], and shows metallic behavior above $T_{\mathrm{MI}} = 200$ K. Below T_{MI}, the sample shows semiconductive behavior with the activation energy $E_{\mathrm{A}} \approx 130$ K. The magnetic susceptibility obeys the Curie–Weiss low with an anomaly at the metal–insulator transition point, which is more clearly seen in the χT vs. T^{-1} plot in Fig. 4(b). The Curie constant above 200 K is estimated at 4.7 emu K mol^{-1}, which is in good agreement with the calculated value with the coexistence of donor ($S = 1/2$) and anion ($S = 5/2$) contributions. It is noteworthy that the localized magnetic moments exist on the donor layer even in the metallic phase. In the semiconductive phase, the Curie constant is 4.4 emu K mol^{-1}, which corresponds to value only with the anion spins.

Now we discuss the origin of the metal–insulator transition of this salt. Peierls-type instability caused by a lattice distortion is ruled out because of the semimetallic electronic structure. Although the resistivity data shows a leap at T_{MI} which is characteristic of a first-order transition, the metal–insulator transition cannot be explained solely from the structural aspect. An isomorphous radical ion salt $(DMET)_2GaBr_4$ has nearly the same lattice constant as the $FeBr_4$ salt, whereas it shows a metal–insulator transition at 100 K[12]. If the metal–insulator transition of the $FeBr_4$ salt were caused by a structural change of the donor columns, this large difference in T_{MI} for these two isomorphous salts could not be explained. Therefore, the magnetic moments localized on the counter anion should play a role in the phase transition mechanism of the $FeBr_4$ salt. This situation is similar to the case of λ-$(BETS)_2FeCl_4$ [9], whose metallic state is destroyed at a temperature at which localized moments on the counter anions order antiferromagnetically. Namely, the conduction π-electrons are perturbed by the exchange field of the localized spins, which is caused by the presence of short chalcogen ··· halogen intermolecular contacts between donors and anions. Since λ-$(BETS)_2FeCl_4$ has a stable two-dimensional electronic structure in the metallic phase[9], the ordering of the localized moments on the counter anion is necessary for destroying its metallic state. On the other hand, $(DMET)_2FeBr_4$ has quasi one-dimensional semimetallic electronic structure which is relatively unstable, hence even a small exchange field caused by the magnetic anions can influence severely the electronic structure of the π-electron system.

The presence of localized magnetic moments on the donor layer in the metallic phase can be explained in terms of the Coulomb interaction between the π–electrons. For one-dimensional quarter-filled systems, the on-site (U) and the inter-site (V) Coulomb interactions, are essential parameters for describing their electronic structure. In such cases, the ground state is achieved by allocating a hole to every two donors[13], which corresponds a Wigner lattice state where a localized spin feature appears. The sliding motion of the Wigner lattice contributes to electron transport, giving a metallic feature above T_{MI}.

Figure 5 shows the temperature dependence of the susceptibility below 10 K. When the field is applied parallel to the $a + b$ direction, the susceptibility shows a peak at 3.5 K and then it approaches zero as the temperature goes to 0 K. On the other side, the susceptibility becomes constant in a field parallel to the $a - b$ axis. The presence of this magnetic

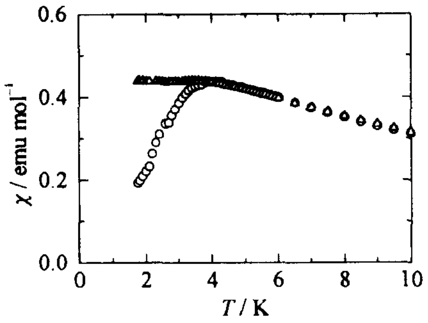


FIGURE 5 The temperature dependence of the magnetic susceptibility of $(DMET)_2FeBr_4$ in a field of $H = 1$ T (○: H // $a+b$, △: H // $a-b$).

anisotropy proves the antiferromagnetic ordering. Since the short range order hump is absent in the susceptibility, the magnetic system can be treated as a three-dimensional system, where donor π-electrons bridging anion quasi-square lattice work to give inter-layer superexchange paths. Based on the molecular field approximation, the Weiss ($\Theta = -5.7$ K) and the Néel temperature ($T_N = 3.5$ K) give the estimation of the exchange interaction J, $J' \sim 0.1$ K for intra- and inter-layer paths, respectively. This demonstrates the importance of the π-electrons on the donor molecules for achieve the three-dimensional exchange path network even in the insulator phase.

SUMMARY

We investigated the crystal structure and the transport and magnetic properties of the two groups of the radical ion salts: $BMT\text{-}TTFI_2{\cdot}FeX_4$ (X = Cl, Br) and $(DMET)_2FeBr_4$. Within the crystals of the former salts, the magnetic counter anions form one-dimensional chains by means of close X ··· X contacts, which are then bridged by the dimerized donor units to form sheet structure. Their magnetic susceptibilities have three-dimensional character, suggesting the coexistence of the Fe–X ··· X–Fe and Fe–X ··· $(Donor)_2$ ··· X–Fe exchange paths. These salts undergo antiferromagnetic transitions, with notably high Néel temperature for the $FeBr_4$ salt. This is explained as a result of a chemical pressure effect caused by the close intermolecular I ··· Br contacts. The crystal structure of $(DMET)_2FeBr_4$ consists of an alternating stack of donor sheets and magnetic anion sheets. A metal–insulator transition occurs at $T_{MI} = 200$ K, above which the magnetic susceptibility is described as a sum of the Curie–Weiss terms of donor and anion spins. The metallic state carrying localized moments of π-electrons can be explained by the sliding motion of the Wigner lattice state. In the insulator phase the donor π-electrons disappear, and the magnetic moments on the anions show antiferromagnetic order at $T_N = 3.5$ K.

Acknowledgement

The authors would like to express their sincere thank to Prof. H. Fukuyama and Mr. H. Seo for fruitful discussion. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

[1] A. Miyazaki, M. Enomoto, M. Enomoto, T. Enoki and G. Saito, *Mol. Cryst. Liq. Cryst.*, **305**, 425 (1997).
[2] T. Enoki, J.-I. Yamaura and A. Miyazaki, *Bull. Chem. Soc. Jpn.*, **70**,2005 (1997).
[3] M. Enomoto, A. Miyazaki and T. Enoki, in these proceedings.
[4] T. Imakubo, H. Sawa and R. Kato, *Synth. Metals*, **73**, 117 (1995).
[5] K. Kikuchi, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro and K. Kobayashi, *Synth. Metals*, **27**, B269 (1988), and references cited therein.
[6] U. Kux, H. Suzuki, S. Sasaki and M. Iyoda, *Chem. Lett.*, 183 (1995).
[7] K. Kikuchi, T. Namiki, I. Ikemoto and K. Kobayashi, *J. Chem. Soc. Chem. Commun.*, 1474 (1986).
[8] T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57**, 627 (1984).
[9] H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe and P. Cassoux, *J. Am. Chem. Soc.*, **118**, 368 (1996).
[10] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
[11] T. Enoki, T. Umeyama, A. Miyazaki, H. Nishikawa, I. Ikemoto and K. Kikuchi, *Phys. Rev. Lett.*, submitted.
[12] K. Enomoto, A. Miyazaki and T. Enoki, in preparation.
[13] H. Seo and H. Fukuyama, *J. Phys. Soc. Jpn.*, **66**, 3352 (1997).