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COMMUNICATION

[BEDT-TTF][Fe(C_2O_4)Cl_2]: An Organic-Inorganic Hybrid Semiconductive Antiferromagnet

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Cation radical salt composed of organic donor BEDT-TTF$^{1.0+}$ and one-dimensional inorganic anion [Fe(C_2O_4)Cl_2^-]$_n$ was obtained by electrocrystallization. It is semiconductor with σ_{300K} = 3.0 × 10^{-5} S/cm. A long-range magnetic ordering as canting antiferromagnet was observed at 5.5 K from ZFCM/FCM/RM measurement and confirmed by the *ac* measurement.

Dual-functional molecular crystal with magnetism such as antiferromagnetic, ferromagnetic to long-range ordering and conductivity from semiconductor, metal to superconductor is one of hot topic in material science for its potential usage for molecular spintronics.[1] Organic-inorganic hybrid is one of powerful method to design new dual-functional molecular crystal with magnetism and conductivity, and it is playing an important role on understanding the interplay between spin and electron. Organic unit with π-electrons provide rich organic conductor and superconductor when charge-transfer happened between organic unit and inorganic counterions.[2] Coordination ion from transition metal is a good candidate for magnetic unit. The interplay between donor and anion was discovered in charge-transfer salts of BEDT-TTF and $CuCl_4^{2-}$ anions through S¨Cl contacts, charge-transfer salts of BETS, EDO-TTF and $FeCl_4^-$/$FeBr_4^-$ through S/Se¨Cl/Br contacts.[3] The magnetic field induced molecular superconductor was discovered in λ-BETS$_2$FeCl$_4$ when artificial magnetic-field is high enough to overcome the inner field from π-d interaction inside crystal.[4] Hence, switching the electronic states by tuning the magnetic field become true in λ-BETS$_2$Fe$_{0.40}$Ga$_{0.60}$Cl$_4$.[5]This reveals its future application on molecular electronic and spintronics. Oxalato is one of popular magnetic ligands for construction not only one-dimension, two-dimension and three-dimension compounds with the long range magnetic ordering, but also two-dimension candidate quantum spin liquid through *d-d* superexchange.[6] The first molecular inorganic-organic metallic ferromagnet was founded in charge-transfer salt of two-dimensional [CrMn(C_2O_4)$_3^-$]$_n$ anion.[7] The one-dimensional coordination anion [Fe(C_2O_4)Cl_2^-]$_n$ as a combination of isolated MCl_4 anion and two-dimensional honeycomb oxalate anion successes in producing dual-functional molecular crystals. The insulator, semiconductor, conductor were obtained in charge-transfer salts of TTF derivatives, they show weak-ferromagnetism from π-d interaction between donor and anion.[8] A new radical cation salt of BEDT-TTF and [Fe(C_2O_4)Cl_2^-]$_n$ was presented here.

30 mg (Me_4N)Fe(C_2O_4)Cl_2 was dissolved in a mixture of 25 ml distilled C_6H_5Cl and 5 ml CH_3OH in an electrocrystallization cell. A total of 10 mg BEDT-TTF was place in the catholic compartment. The solution was subjected a constant current of 0.5 μA at room-temperature. Shiny tiny needle crystals were obtained on cathode after two weeks. The elemental analysis performed by EDS gave a composition with ratio S:Fe:O:Cl = 8:1:4:2, it means the ratio of donor and anion as 1:1.

A single crystal (0.18×0.06×0.02mm) was selected for the X-ray diffraction experiment. The data at 170 K was collected at Rigaku MM007HF diffractometer with Saturn 724+CCD detector and confused Mo Kα radiation. The data were corrected for Lorentz and polarization and finally for absorption using an empirical method.[9] Crystal structure was solved by direct methods and all of the non-hydrogen atoms were refined anisotropically by the full-matrix method.[10] The data was deposited in the Cambridge Crystallographic Data Centre (CCDC972917).

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Electronic Supplementary Information (ESI) available: [IR spectrum on single crystal, and Table S1]. See DOI: 10.1039/x0xx00000x

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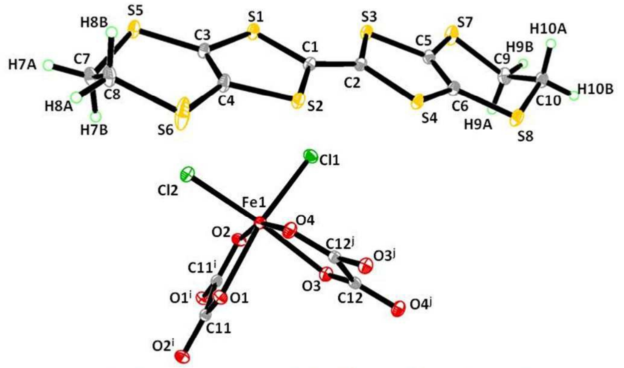
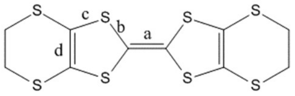


Figure 1. ORTEP drawing of compound **1** with 30% ellipsoid at 170K. Symmetry code for non-hydrogen atoms: i: 1-x, 1-y, 1-z; j: 2-x, 1-y, 1-z.

There is one BEDT-TTF and one $Fe(C_2O_4)Cl_2^-$ unit in an independent unit (Figure 1) as [BEDT-TTF][$Fe(C_2O_4)Cl_2$] (**1**). Except two ethylene groups, all of atoms on one of BEDT-TTF molecule are coplanar with a maximum deviation of 0.115 Å. The formal-charge of donor molecule is assigned to 1.0+ from bond length of TTF core as shown in Table 1.[11] In **1**, the mean planes of donors are parallel to the ($10\bar{1}$) plane. The structure consists of columns of donor cations, BEDT-TTF$^{1.0+}$, and anion chains $[Fe(C_2O_4)Cl_2^-]_n$, packed along the *a* axis. These organic and inorganic moieties arrange alternately along both the *a*- and *c*- axis. Within the donor column, donors are arranged in pairs where the two BEDT-TTF units are ring-over-bond mode with S···S contacts: S2···S3 3.594(1) Å and C–H···S contact C10–H10A···S5 2.91 Å /138.4°. The donor dimers arrange in a side-by-side mode with short contacts as: S3···S5 3.532(1) Å, and C7–H7A···S7 3.03 Å /109.4° along the *a* axis. There are short contacts between donor columns along the *c* axis: S2···S6 3.383(1) Å, S5···S8 3.422(1) Å, S6···S6 3.236(2) Å.

Table 1 Bond length of TTF core in **1**



δ = (b +c)- (a + d)
Q = 6.347 -7.463 δ

a	b	c	d	δ	Q
1.390	1.718 1.715 1.720 1.724	1.740 1.739 1.739 1.749	1.362 1.352	0.714	1.018 ~ 1.0 +

The inorganic anion is a one-dimensional zigzag chain consisting of Fe^{3+} bridged by oxalate dianions in *cis*-position and two terminal Cl atoms per Fe. Each iron atoms is in a distorted octahedral environment, being bonded to four oxygen atoms of two *cis*-oxalate and two Cl atoms as observed in ammonium salts and charge-transfer salts. The Fe–O bond lengths (2.041(2)~2.148(2) Å) and Fe–Cl bond lengths (2.256(1)~2.261(1) Å) are similar to those reported in the literature(Table S1).[8,12]

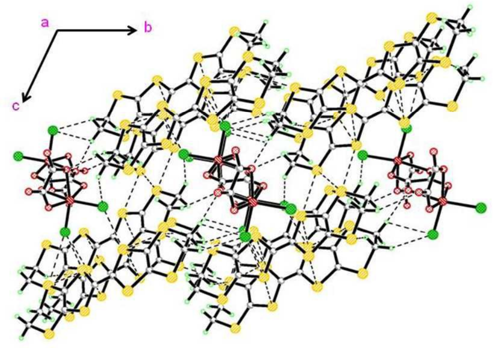


Figure 2. Crystal structure viewed along the *a* axis.

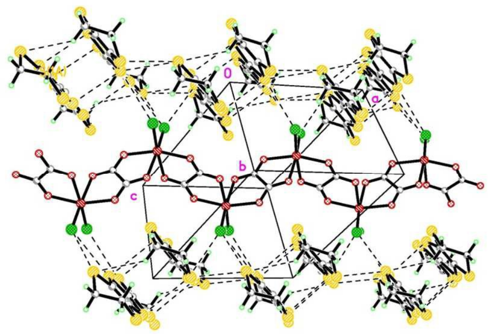


Figure 3. Crystal structure of **1** viewed along [$\bar{1}1\bar{1}$] direction.

There are several short donor-anion contacts: S1···Cl1 3.434(1) Å, S3···Cl1 3.483(1) Å, S3···Cl2 3.510(1) Å, S5···Cl1 3.543(1) Å, and C7–H7A···O1 2.55 Å /135.7°, C9–H9B···O2 2.52 Å /162.3°, C8-H8A···Cl2 2.69 Å /137.1°, C9–H9B···Cl2 2.90 Å /112.3°, C10–H10B···Cl1 2.77 Å /132.7°. One S atoms in a donor molecule could contact two anion chains along (011) direction, such as S3···Cl1, S3···Cl2, while S1 and S5 contact with one anion chain of S1···Cl1, S5···Cl1 on same side as S3···Cl2. The S···S, S···Cl short contacts and hydrogen bonds between donor and anion forms a three-dimensional network in crystal. These may induce the π-d interaction between donor and anion as observed in TTF[$Fe(C_2O_4)Cl_2$].[8]

The Raman spectra were measured on a Renishaw inVia Raman Microscope with λ = 514.5 nm at room temperature on the best developed surface of single crystal. In Raman spectrum, two bands were observed in 1419 and 1466 cm^{-1}, which is the same as that observed in charge-transfer salts of BEDT-TTF$^{1.0+}$ (Figure 4).[13] It is corresponded with the formal charge assigned from bond length of TTF core and confirmed the oxidation state of metal atoms is Fe^{3+}.

The measurement of the resistance was carried out on Keithley 4200 instrument by two-probe method with 15 μm Au wires attached by Au paste. The temperature was controlled by PPMS system. The room-temperature resistance of single crystal was about 3×10^{-5} S/cm. The resistance increased while temperature decreased with Eα = 0.35 eV (Figure 5, insert). It

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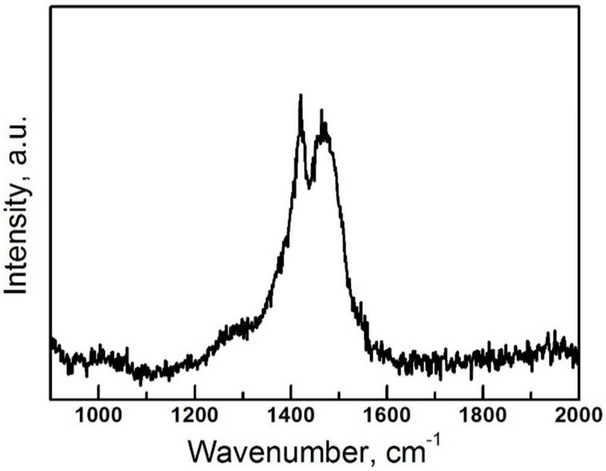

Figure 4. Raman spectra of **1** with λ = 514.5nm at room temperature.

is corresponded with oxidation state of donor as a wide band semiconductor.

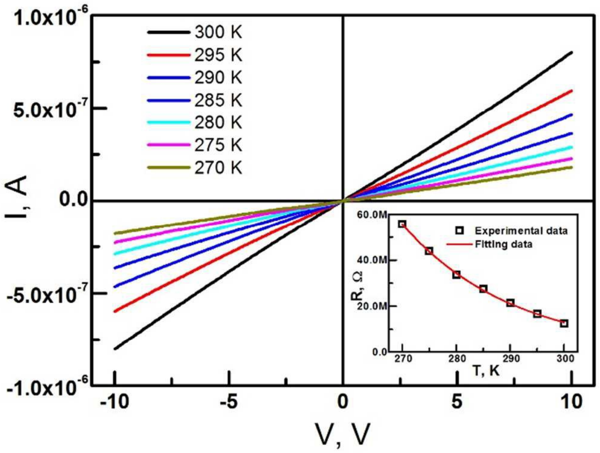

Figure 5. Temperature-depended I-V curves of **1**.

Magnetization measurements were performed on a MPMS SQUID system. The sample, consisting of 6.75 mg of tiny crystal was sealed by parafilm and placed inside a capsule. The as-measured data were finally corrected for the contributions of the signal of parafilm and capsule, and for the diamagnetism of the elements using Pascal's constants (–270.21 × 10^{-6} cm^3/mol).[14]

The magnetic susceptibility data measured in an applied field of 1000 Oe from 2 to 300 K exhibit a broad peak centred around 50 K, as shown in Figure 6. At room temperature, the χT value is 4.15 cm^3 mol^{-1}, which is close to one S = 5/2 localized spin system with g = 2.00. It is lower than 4.83 cm^{3}mol^{-1} as was observed in charge-transfer salt TTF[Fe(C_2O_4)Cl_2] with contribution from donor of S = 1/2 and anion of S = 5/2 with g = 2. It is in the same range as observed in solvent included charge-transfer salt [BEDT-TTF][Fe(C_2O_4)Cl_2]·CH_2Cl_2 with 4.38 cm^{3}mol^{-1}. The broad peak around 50 K is similar with reported ammonium salts of [Fe(C_2O_4)Cl_2^{-}]$_n$ and charge-transfer salts of [Fe(C_2O_4)Cl_2^{-}]$_n$.[8,12] The data above 80 K were fitted with Curie-Weiss well and give C = 5.95(2) cm^3 ml^{-1}, θ = –126(1) K, and R = 4.26×10^{-5}. The negative θ value means the strong antiferromagnetic interaction in crystal, which should be contributed of two main contributions. The first is the interaction between metal atoms through oxalate anion along the zigzag chain. The second should be interaction between metal atoms through donor as Cl···S interaction, which is always called π-d interaction.

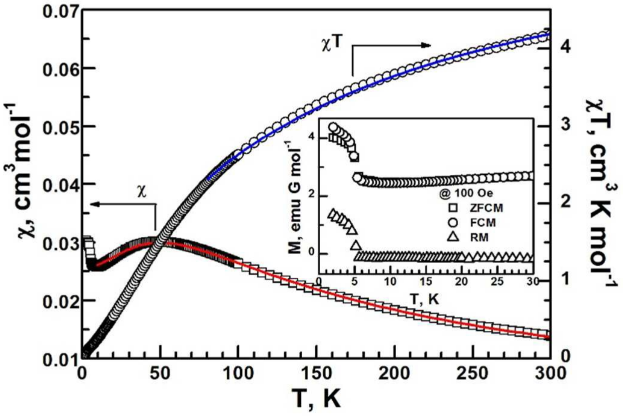

Figure 6. χ-vs-T (empty square) and χT-vs-T (empty circle) plot of **1**. Blue solid line: Curie-Weiss fitting. Red solid line: fitting with Heisenberg model. Insert: ZFCM/FCM/RM at low –temperature range.

In the χ vs. T plot, the data above 10 K fitted a one-dimensional isotropic S = 5/2 Heisenberg model with J = –4.150(9) cm^{-1}, g = 2.178(2) and R = 4.2×10^{-5}.[15] The J value is in the same range of –5.10(3) cm^{-1} found for TTF[Fe(C_2O_4)Cl_2], –12.5 cm^{-1} for BETS$_2$[Fe(C_2O_4)Cl_2], –3.89 cm^{-1} for (BEDT-TTF)[Fe(C_2O_4)Cl_2](CH_2Cl_2) and ammonium salts as reported by other groups.[8,12]

In order to check the existence of long-range ordering, the ZFCM/ZFCM/RM measurement was carried out under 100 Oe between 2 to 50 K. The bifurcation was observed at 5.5 K (Figure 6, insert). This means a spin-canted antiferromagnetic long range ordering (LRO) occurred in **1**.

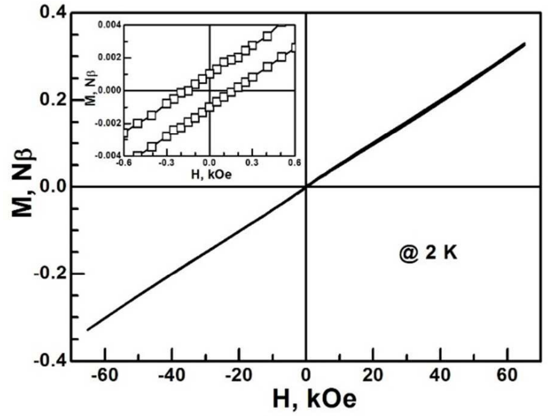

Figure 7. Isothermal magnetization at 2 K. Insert: low-field range.

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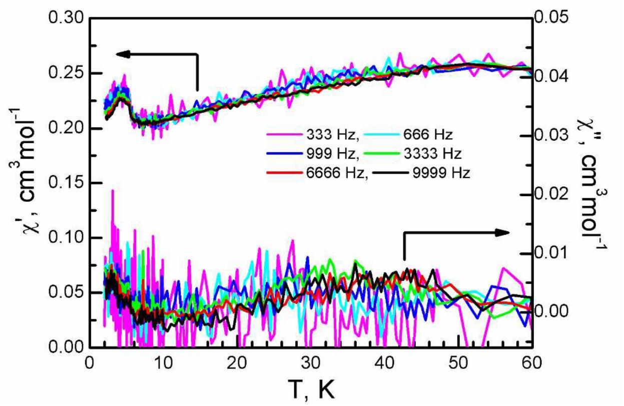

Figure 8. The *ac* susceptibility of **1** at 0 Oe.

At 2 K, a hysteresis loop with coercive field of 150 Oe was observed at the lower field range (Figure 7, insert). The isothermal magnetization at 2 K reached 0.33 N_β at 65 kOe, which is about 6.6% of 5 N_β if the moments were all aligned parallel. These are characteristic of weak ferromagnetism. The canting angle was estimated as 0.01°.

The antiferromagnetic LRO was further confirmed by alternating-current (ac) susceptibility under zero field (Figure 8). The *ac* response was weak and the response increased below 5.5 K. There is a sharp peak observed around 4.3 K for χ' and 3.0 K for χ''. No frequency dependence of the temperature-dependent feature was observed among 333, 666, 999, 3333, 6666, 9999Hz.

The π-d interaction between donor and anion through S¨Cl and S¨O was calculated with the Hückel method and yield $J_{\pi d}$ = 6.55 K (4.55 cm^{-1}).[16] It is stronger than 0.075 K in (BEDT-TTF)[$Fe(C_2O_4)Cl_2$](CH_2Cl_2), in the same range of 7.77 K in TTF[$Fe(C_2O_4)Cl_2$], weaker than 16.72 K in λ-$BETS_2FeCl_4$ and 25.82 K in β”-(BEDT-TTF)$_3$($FeCl_4$)$_2$. This confirmed the antiferromagnetic behaviour of **1** is contributed from both intra-chain interactions through the oxalate-bridge and π-d interaction through donor and anion. It shows the possibility to control the conductivity states with magnetic field as in λ-$BETS_2Fe_{0.40}Ga_{0.60}Cl_4$ ($J_{\pi d}$ = 6.69 K). And information could be remained well in low field range, such as 100 Oe at 2 K. So it should be a good candidate for molecular spintronics.

Conclusions

The single crystal of [BEDT-TTF][$Fe(C_2O_4)Cl_2$] (**1**) was obtained by electrocrystallization method. It is composed of segregated columns of pairs of BEDT-$TTF^{1.0+}$ as donor and anion chain [$Fe(C_2O_4)Cl_2^-$]$_n$. It is a wide-band semiconductor. The interaction between donor and anion through S¨Cl as the π-d interaction produces the long range ordering as canted antiferromagnet at 5.5 K.

Acknowledgements

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Notes and references

§ Crystallographic data of **1**: $C_{12}H_8Cl_2FeO_4S_8$, F.W = 599.41, triclinic, *a* = 8.896(2) Å, *b* = 11.401(3) Å, *c* = 11.427(3) Å, α = 112.062(2)°, β = 103.775(2)°, γ = 100.328(4)°, *V* = 995.7(5) Å^3, 170 K, $P\bar{1}$, *Z* = 2, total 17763, 4554 unique, 4300 $I \geq 2\sigma(I_0)$, R_{int} = 0.0441, *R* = 0.0354 ($I \geq 2\sigma(I_0)$), *S* = 1.141, CCDC972917.

1 F. Palacio, J. S. Miller, *Nature*, 2000, **408**, 421; T. Sugawara, H. Komatsu, K. Suzuki, *Chem. Soc. Rev*., 2011, **40**, 3105; H. Sandrine, *Nat. Mater*., 2015, **14**, 967.
2 T. Ishiguro, K. Yamaji, G. Saito, *Organic Superconductors*, Springer, 1998.
3 P. Day, M. Kurmoo, T. Mallah, I. R. Marsden, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseau, J. Gaultier, G. Bravic, L. Ducasse, *J. Am. Chem. Soc*., 1992, **114**, 10722; A. Kobayashi, T. Udagawa, H. Tomita, T. Naito, H. Kobayashi, *Chem. Lett*., 1993, 2179; T. Hayashi, X. Xiao, H. Fujiwara, T. Sugimoto, H. Nakazumi, S. Noguchi, T. Fujimoto, S. Yasuzuka, H. Yoshino, K. Murata, T. Mori, H. Aruga-Katori, *J. Am. Chem. Soc.*, 2006, **128**, 11746; G. Kawaguchi, M. Maesato, T. Komatsu, H. Kitagwa, T. Imakubo, A. Kiswandhi, D. Graf, J. S. Brookes, *Angew. Chem. Int. Ed.,* 2015, **54**, 10169.
4 S. Uji, H. Shinagawa, T. Herashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, H. Kobayashi, *Nature,* 2001, **410**, 908.
5 B. Zhang, H. Tanaka, H. Fujiwara, H. Kobayashi, E. Fujiwara, A. Kobayahsi, *J. Am. Chem. Soc*., 2002, **122**, 9982.
6 M. Clemente-Leon, E. Coronado, C. M. Gastdaldo, F. M. Romero, *Chem. Soc. Rev*., 2011, **40**, 473; E. Pardo, C. Train, K. Boubekeur, G. Gontard, J. Cano, F. lloret, K. Nantani, M. Verdaguer, *Inorg. Chem*., 2012, **51**, 11582; B. Zhang, Y. Zhang, Z. Wang, P. Baker, F. Pratt, D. Zhu, *Sci. Rep*., 2014, **4**: 6451.
7 H. Tamaki, Z. Zhang, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, H. Okawa, *J. Am. Chem. Soc*., 1992, **114**, 6974
8 B. Zhang, Z. Wang, H. Fujiwara, H. Kobayashi, K. Inoue, T. Mori, S. Gao, Y. Zhang, D. Zhu, *Adv. Mater.* 2005, **17**, 1988; B. Zhang, Z. Wang, Y. Zhang, K. Takahashi, Y. Okano, H. Cui, H. Kobayashi, K. Inoue, M. Kurmoo, F. L. Pratt, D. Zhu, *Inorg. Chem.* 2006, **45**, 3275; B. Zhang, Y. Zhang, Z. Gao, G. Chang, S. Cu, D. Wang, Y. Guo, D. Zhu, *Euro. J. Inorg. Chem*., 2014, 4028.
9 Rigaku Inc., *CrystalClear*, 2007, Version 1.4.0. Tokyo, Japan.
10 G. M. Sheldrick, *Shelx2014*.
11 P. Guinneau, C. J. Kepert, G. Bravic, D. Chasseau, M. R. Truter, M. Kurmoo, P. Day, *Synth. Met.* 1997, **86**, 1973.
12 H. Xu, T. Liu, Z. Wang, S. Gao, *Inorg. Chem.,* 2007, **46**, 3089; D. Armentano, T. F. Mastropietro, G. D. Munno, P. Rossi, F. Lloret, M. Julve, *Inorg. Chem*., 2008, **47**, 3772.
13 H. H. Wang, J. R. Ferraro, J. M. Williams, U. Geiser, J. A. Schlueter, *J. Chem. Soc., Chem. Commun.* 1994, 1893.
14 Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993, p.15
15 J. C. Bonner, M. E. Fisher, *Phys. Rev.* 1964, **135**, A640; O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993, p. 258.
16 T. Mori, M. Katsuhara, *J. Phys. Soc. Jpn.* 2002, **71**, 826.

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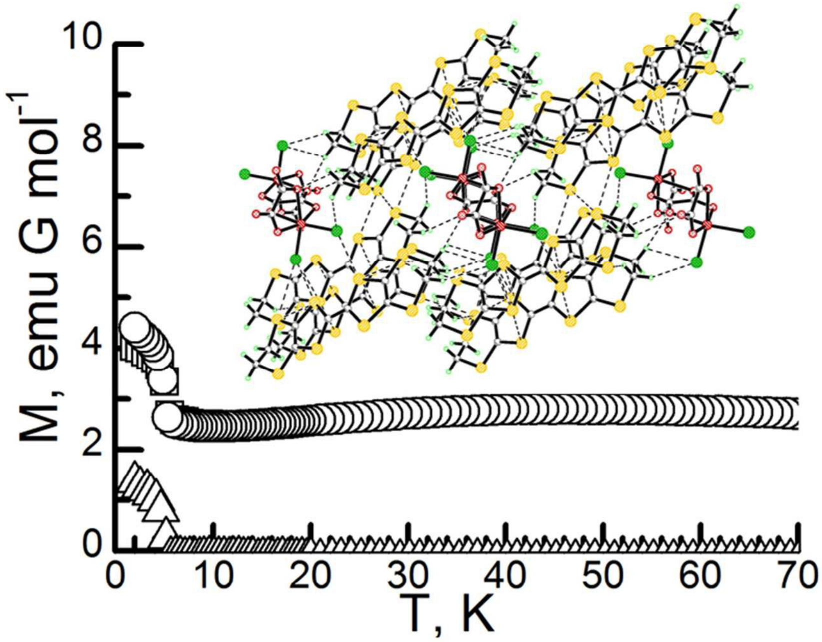

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