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A Radical-Radical and Metal–Metal Coupling Tetrathiafulvalene Derivative in which Organic Radicals Directly Coordinate to Cu^{II} Ions

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A new dinuclear metal complex including tetrathiafulvalene (TTF) radicals as ligands has been prepared and characterized, [{DMT-TTF(CONH$_2$)$_2$}$_2$Cu$_2$Cl$_6$] (**1**), DMT-TTF(CONH$_2$)$_2$ = *o*-bis(amido)-appended dimethylthio-tetrathiafulvalene. The compound is an uncommon example in which TTF radicals directly coordinate to the copper(II) halide by the amido group. Crystal structure analysis shows that it is a unique coordination bond/H-bond/S···S stacking cooperative system with two radicals and two paramagnetic transition metal ions, $TTF^{+\cdot}$–Cu^{II}–Cu^{II}–$TTF^{+\cdot}$. In the structure of **1**, the DMT-TTF units form dimers with very strong S···S interactions. The Cu^{II}–O(amide) distance of the coordination bond is 2.271(2) Å and the S···S stacking distances between the radicals are in the range 3.345–3.489 Å. The metal–metal ions are mildly antiferromagnetically coupled ($2J_1$ = –58.4 cm^{-1}), while the radical pairs are strongly antiferromagnetically coupled ($2J_2 > -1000$ cm^{-1}).

Introduction

Until the end of the twentieth century, the work on tetrathiafulvalene (TTF) chemistry was mostly concerned with the radical salts of magnetic molecular conductors.[1–5] In the crystals of these salts, the organic radicals and paramagnetic inorganic counterions are discretely arranged. Therefore, the interaction between them could only occur through space by weak intermolecular interactions, such as hydrogen bonding and stacking of atoms. With increasing light being shed on the interactions of TTFs with transition metals, recent interests of inorganic chemists are devoted to organic–inorganic hybrid TTF materials in which the synergy between organic and inorganic parts are through stronger covalent or coordination bonds. The incorporation of TTF units into dithiolate ligands ($TTFS_4^{4-}$ and $TTFS_2^{2-}$) is one of the successful strategies, and systems of single molecular complexes with d–π interactions have been reported.[6–10] Another strategy that has been popular is the design and synthesis of TTF derivatives that are substituted with heteroatom-based groups capable of coordinating to a metallic center, such as thioethers,[11–14] phosphanes,[15–18] pyridines,[19–24] alkylsilyls,[25] and stibines.[26] The corresponding coordination compounds have also been reported. The metal coordination of complexes with the TTF ligand offers a novel perspective on the modulation of the architecture and collective properties of molecular solids. However, to the best of our knowledge, the TTF moieties in most of the reported complexes are in the neutral state. Therefore, their direct applications as electronic or magnetic materials are limited. Very recently, an important step was reached by the synthesis and characterization of a radical electron/d electron directly cooperative complex, [Cu^{II}(hfac)$_2$(TTF-py)$_2$][PF$_6$]·2CH$_2$Cl$_2$, which has metal–radical and radical-radical couplings.[22] Besides the metal coordination, hydrogen bonds are also one of the successful strategies used to promote the properties of molecular solids. Some amide-functionalized TTFs have been prepared and their radical salts involving N–H···Cl/O hydrogen bonds were studied.[27–31]

What follows is a report on the preparation, crystal structure, and magnetic properties of a new TTF-amide derivative with two radicals and two paramagnetic transition metal ions, [{DMT-TTF(CONH$_2$)$_2$}$_2$Cu$_2$Cl$_6$] (**1**), DMT-TTF(CONH$_2$)$_2$ = *o*-bis(amide)-appended dimethylthio-tetrathiafulvalene. Complex **1** is a new dinuclear $TTF^{+\cdot}$–Cu^{II}–Cu^{II}–$TTF^{+\cdot}$ system with coordination bonds, H-bonds and S···S stacking, which is different from [Cu^{II}(hfac)$_2$-(TTF-py)$_2$][PF$_6$]·$_2$CH$_2$Cl$_2$, which has a mono-nuclear TTF–Cu^{II}–$TTF^{+\cdot}$ coordination system. The radical-radical and metal–metal magnetic couplings are also discussed.

Results and Discussion

Synthesis and General Discussion

The TTF derivative DMT-TTF(CONH$_2$)$_2$ was synthesized by a similar procedure described in the literature.[27]

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Compound **1** was prepared by the reaction of the TTF precursor with excess $CuCl_2$ using a diffusing method in ambient conditions (Scheme 1). The details are given in the experimental section. During the reaction the ligands are oxidized by Cu^{II} ions forming the radical cations and, hence, the charge distribution of **1** might be deduced as $[\{\text{DMT-TTF(CONH}_2)_2{}^{+\bullet}\}_2(\text{Cu}_2\text{Cl}_6)^{2-}]$.

$$\text{DMT-TTF(CONH}_2)_2 + \text{CuCl}_2 \longrightarrow [\text{DMT-TTF(CONH}_2)_2]^+ + [\text{CuCl}_2]^-$$

$$2\,[\text{DMT-TTF(CONH}_2)_2]^+ + [\text{Cu}_2\text{Cl}_6]^{2-} \longrightarrow (\text{DMT-TTF(CONH}_2)_2)_2\text{Cu}_2\text{Cl}_6$$

Scheme 1.

Copper(II) halides readily oxidize the TTF derivatives, providing a variety of charge-transfer (CT) salts that have conductive or semiconductive properties. Although a number of TTF CT compounds with copper(II) halides have been prepared, no cation-anion coordinated model has been found.[32–37] Due to the weak coordination of the TTF radicals with the Cu^{II} center (by the thioether or alkylthio group), the paramagnetic copper(II) halides, such as the familiar $Cu_2Cl_6{}^{2-}$ anion, are arranged discretely as counterions. However, anions of copper(I) halides, which can be formed from the reduction of Cu^{II} halides, are easily coordinated by the alkylthio group of the TTFs or its radicals. Some copper(I) halide-TTF complexes[11–14] or CT compounds[38–40] having S–Cu^I coordination bonds have been obtained. Compound **1** is an uncommon example where direct coordination of the copper(II) halide with the TTF radical occurs. In the case of **1** the TTF moieties are appended by two amido groups, which enable the Cu^{II} center to be bonded by the oxygen atom of the amide group.

Description of the Structures

The single crystal structure of **1** was solved by direct methods. A summary of the experimental details and crystal data for compound **1** is given in Table 1. Selected bond lengths, contact distances, bond angles, and torsion angles are listed in Table 2. The ligand, $\text{DMT-TTF(CONH}_2)_2$, in **1** adopts a conformation with an intramolecular hydrogen bond [N(1)–H···O(2), Figure 1], which has been observed for several TTF amides and their radical salts.[27–31] As a consequence of the intramolecular hydrogen bond, the two *ortho*-amido groups are fixed and form a seven-membered ring fused with the TTF moiety, which enables the conjugated π system to extend to the oxygen atoms of the amide groups.

Table 1. Crystallographic data for compound **1**.

Compound	**1**
Empirical formula	$C_{20}H_{20}Cl_6Cu_2N_4O_4S_{12}$
Formula mass	1104.90
Color, Habit	black, platelet
Crystal system	triclinic
Crystal size [mm]	0.3 × 0.2 × 0.02
Space group	$P\bar{1}$ (No. 2)
a [Å]	8.4564(12)
b [Å]	10.8253(19)
c [Å]	10.8817(18)
α [°]	111.302(4)
β [°]	90.645(4)
γ [°]	91.970(3)
Z	1
T [K]	193(2)
V [Å^3]	927.2(3)
$D_{\text{calcd.}}$ [g·cm^{-3}]	1.979
μ [mm^{-1}]	4.090
F(000)	552
Reflections collected	9242
Unique reflections	3371
Observations [$I > 2\sigma(I)$]	2996
Variables	220
$R1$ [$I > 2\sigma(I)$]	0.0308
wR_2	0.0754
Goodness of fit indicator	1.040

$R_1 = \Sigma\lVert F_o\rvert - \lvert F_c\rVert / \Sigma\lvert F_o\rvert$ and $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / \Sigma[w(F_o{}^2)^2]\}^{1/2}$

Table 2. Selected bond lengths, angles, torsion angles, contact distances, and hydrogen bonds.

Bond lengths [Å]			
Cu(1)–Cl(1)	2.3042(8)	Cu(1)–Cl(2)	2.2845(8)
Cu(1)–Cl(3)	2.2540(8)	Cu(1)–Cl(1^i)	2.3346(9)
Cu(1)–O(1)	2.271(2)	C(5)–C(6)	1.379(4)
Bond angles [°]			
Cu(1)–Cl(1)–Cu(1^i)	97.12(3)	O(1)–Cu(1)–Cl(1)	92.97(6)
O(1)–Cu(1)–Cl(1^i)	90.83(6)	O(1)–Cu(1)–Cl(2)	92.50(6)
O(1)–Cu(1)–Cl(3)	98.56(6)		
Torsion angles [°]			
N(1)–C(1)–C(3)–C(4)	22.8(5)	N(2)–C(2)–C(4)–C(3)	157.9(3)
Contact distances [Å]			
Cu(1)–Cu(1^i)	3.478	O(2)–S(6^{ii})	3.317
S(1)–S(6^{iii})	3.345	S(2)–S(5^{iii})	3.489
S(3)–S(4^{iii})	3.409		
Hydrogen bonds [Å, °]			
D–H···A	distance H···A	distance D···A	angle D–H···A
N(1)–H···O(2)	1.92	2.709(3)	148.7
N(1)–H···S(5^{ii})	2.92	3.524(2)	127.1
N(2)–H···Cl(2^v)	2.63	3.443(3)	154.6
N(2)–H···Cl(2^{iv})	2.42	3.288(2)	171.1

i: $-x + 1, -y, -z + 1$; ii: $x - 1, y - 1, z$; iii: $-x + 1, -y, -z$; iv: $-x + 1, -y - 1, -z$; v: $x, y, z - 1$

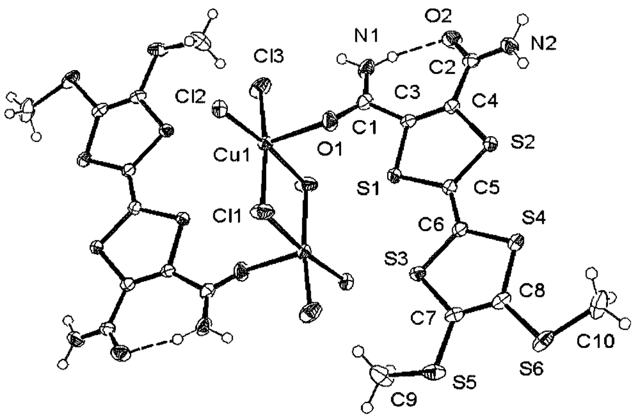

Figure 1. ORTEP view of **1**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The center of **1** is a dinuclear moiety of $Cu_2Cl_6^{2-}$, in which the Cu^{II} ions take on a quasi-square coordination and the two squares share a common edge of Cl(1)–Cl(1^i). The Cu–Cl distances are in the range 2.254–2.335 Å, and are comparable to those reported for the $Cu_2Cl_6^{2-}$ ion. However, the Cu(1)–Cl(1)–Cu(1^i) angle of 97.12(3)° is located at the top of the angle range compared with those of the corresponding compounds.[36,41,42] In addition to the coordination of chloride ions, the DMT-TTF$(CONH_2)_2$ coordinates to the Cu^{II} ions by the amide oxygen atom O(1), perpendicular to the square planes of the $CuCl_4$ moieties (see Figure 1). The 2.271(2) Å distance of Cu(1)–O(1) undoubtedly shows the formation of a strong coordination bond, which forces the $Cu_2Cl_6^{2-}$ ion to take on a quasi-planar geometry [atom Cl(3) is somewhat out of the square plane]. In contrast, the discrete $Cu_2Cl_6^{2-}$ ion adopts a structure with two distorted tetrahedra sharing a common edge.[36,43,44] The central C=C distance of the TTF moiety [C(5)–C(6), 1.379(4) Å], however, is longer than that found in the neutral TTF compounds (1.331 Å) but in accordance with that of the $TTF^{+\cdot}$ radicals (1.373–1.383 Å).[27]

All of the TTF units form dimers in the crystal structure **1** with very strong S···S stacking [Figure 2 (a)]. There are six S···S interactions between the TTF units of the dimer, in which the shortest one is 3.345 Å and the longest is 3.489 Å (average 3.414 Å, Table 2). The S···S interactions are considerably shorter than the sum of the van der Waals radii (3.60–3.70 Å), and they are related to the strong antiferromagnetic coupling of the organic radical dimer (vide infra).

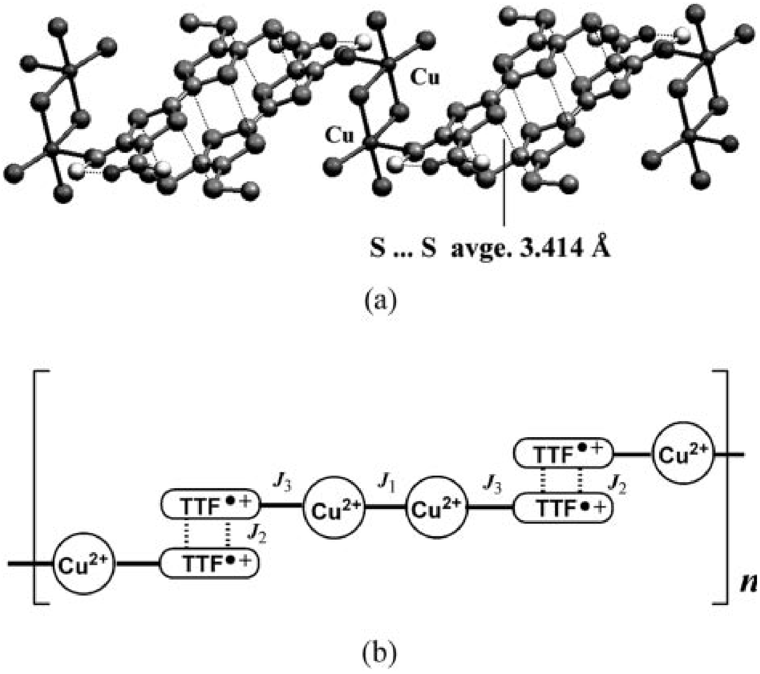

Figure 2. (a) One-dimensional structure of the molecules assembled by S···S stacking and metal coordination. (b) Schematic diagram of the two TTF radicals with the Cu^{II} system and the magnetic coupling constants.

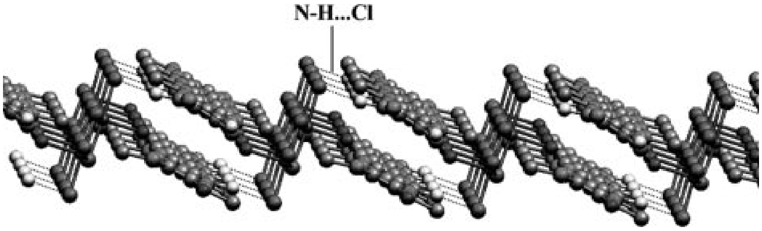

Figure 3. The inter-chain N(2)–H···Cl(2) (3.288 Å) hydrogen bonds of the assembled two-dimensional structure of the title compound.

Assembled by S···S stacking and Cu–O metal coordination, compound **1** forms an infinite chain propagating in the [101] direction. The crystal structure of **1** is further stabilized by inter-chain N(2)–H···Cl(2) hydrogen bonds (3.288 Å) and S(6)···O(2) contacts (3.317 Å), which assemble the molecules into two-dimensional slabs parallel to the plane (1–11) (Figure 3). It has been shown that the hydrogen-bond network is correlated with the density of states at the Fermi level and the spin susceptibility behavior.[31]

Magnetic Properties

Until now, work on TTF-containing π–d-type magnetic compounds has mostly been concerned with radical salts, except for the example reported recently by Ouahab et al., which has a mono-nuclear TTF–Cu^{II}–TTF$^{+\cdot}$ coordination system.[22] Compound **1**, reported here, has a new dinuclear TTF$^{+\cdot}$–Cu^{II}–Cu^{II}–TTF$^{+\cdot}$ coordination system [Figure 2 (b)]. The magnetic properties of **1** were measured with a SQUID magnetometer in the range 4–260 K (Figure 4). The magnetic moment (2.40 B. M. at room temperature) is considerably lower than the spin-only value, 6.92 B. M., for a noncoupling four-spin system (1.73 B. M. × 4), but the value of 2.40 B. M. corresponds to the value which is expected for a two-spin (S = 1/2) system with antiferromagnetic (AF) coupling (3.46 B. M. for a noncoupling two-spin system).

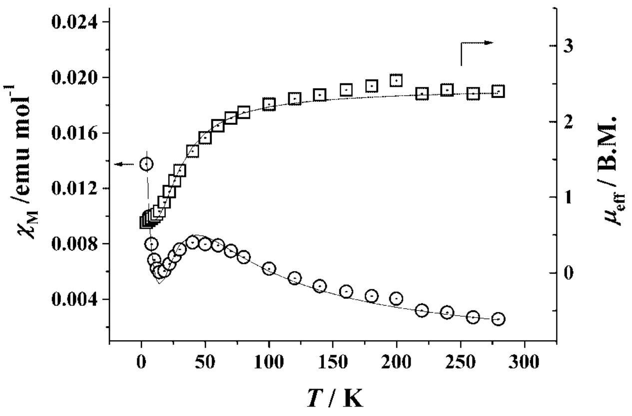

Figure 4. Variable-temperature magnetic susceptibility data and effective magnetic moments of **1** collected by a SQUID magnetometer in the range 4–260 K. The solid lines were calculated based on a singlet-triplet model.

A solid-state EPR spectrum (polycrystalline sample), which strongly supports the speculation, was measured at 110 K (Figure 5). Because the organic radicals are dimerized with very short S···S stacking and are strongly antiferromagnetically coupled no sharp radical signal is observed in the EPR spectrum. The spectrum only shows a parallel and perpendicular split of Cu^{II} character with g values of 2.045 and 2.246 for $g_{\parallel}$ and $g_{\perp}$, respectively. This result means that the two TTF radicals are AF coupled with $2J_2 > -1000\ \text{cm}^{-1}$. In addition, because the spin density of the radical is mainly located on the central TTF core and the amide oxygen atom of **1** coordinates to the Cu^{II} center of the Cu$_2$Cl$_6$ plane along the axial position, the interaction of the radicals with the metal ions should be very weak. Therefore, the J_3 coupling can be neglected in the fitting procedure. Consequently, this compound can be described as a system that has a strongly coupled TTF$^{+\cdot}$ (J_2) dimer and a mildly coupled Cu$_2$Cl$_6$ (J_1) dimer with very weak radical-metal interaction (J_3) [Figure 2 (b)]. From a simplified calculation, considering the antiferromagnetic coupling intensity, the magnetic susceptibility of compound **1** can be fitted by a Cu$_2$Cl$_6$ dimer model with spin-exchange Hamiltonian $\hat{H} = -2J_1\hat{S}_{Cu1}\hat{S}_{Cu2}$, where J_1 is the spin-exchange coupling constant between the two Cu^{II} ions (Figure 4). The susceptibility data were fitted using Equation (1) containing the paramagnetic impurity term ρ. The best least-squares fit gave $J_1 = -29.2\ \text{cm}^{-1}$, $g = 2.08$, $\rho = 0.08$ and the consistent factor $R = \Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}^2 = 3.85 \times 10^{-3}$. The structural-magnetic correlation for the Cu$_2$Cl$_6^{2-}$ ion has been intensively discussed elsewhere.[45,46] The present result of $2J_1 = -58.4\ \text{cm}^{-1}$ supports the structure in which the copper(II) center adopts a square-planar geometry.

$$\chi_M = \frac{2Ng^2\beta^2}{KT}\left[\frac{1}{3+\exp(-2J_1/KT)}\right](1-\rho) + \frac{Ng^2\beta^2}{2KT}\rho + N_\alpha \quad (1)$$

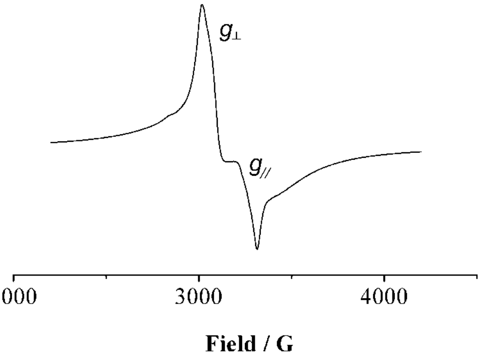

Figure 5. Solid-state EPR spectrum of the title compound measured at 110 K.

Conclusion

Prior to the report of Ouahab et al., where the TTF radicals directly coordinate to the paramagnetic ions,[22] the charge transfer TTF compounds containing paramagnetic inorganic ions were radical salts in which the cations and anions are discretely arranged. The compound **1** reported here is a new example in which the TTF radicals directly coordinate to the paramagnetic ions. Crystal structure analysis showed that it is a unique coordination bond/H-bond/S···S stacking cooperative system with two radicals and two paramagnetic transition metal ions, TTF$^{+\cdot}$–Cu^{II}–Cu^{II}–TTF$^{+\cdot}$. Although the direct coordination of the TTF(CONH$_2$)$_2^{+\cdot}$ radical to the paramagnetic transition metal anion, (Cu$_2$Cl$_6$)$^{2-}$, does not improve the interaction of the radical electrons and the d electrons in this case, because of the strong antiferromagnetic coupling within the radical pairs (TTF radical couples) the preparation of materials with direct coordination of TTF radicals to transition metal anions is still an attractive strategy for chemists in molecular design.

Experimental Section

General Remarks: All analytical grade chemicals were obtained commercially and used for synthesis directly without further purification. Elemental analyses of C, H, and N were performed using an MOD 1106 elemental analyzer. The IR spectra were recorded as KBr discs with a Nicolet Magma 550 FT-IR spectrometer. Solid-state EPR spectra were recorded with an EMX-10/12 spectrometer at 110 K and at a frequency of 9.4852 GHz. The magnetic properties were measured with a SQUID magnetometer (Quantum Desigen, MPMS-2) in the range 3.99–278 K, with an applied field of 10000 gauss.

Synthesis of Compounds

DMT-TTF(CONH$_2$)$_2$ (Ligand): The ligand was synthesized by a similar procedure described in the literature.[27] A purple powder was obtained (yield 79%). $C_{10}H_{10}N_2O_2S_6$ (382.56): calcd. C 31.24, H 2.64, N 7.33; found C 32.09, H 2.87, N 6.60. IR (KBr): $\tilde{\nu}$ = 3375–3189 (NH$_2$), 1675–1662 (C=O) cm^{-1}.

$(C_{10}H_{10}N_2O_2S_6)_2Cu_2Cl_6$ (1): Well-defined black platelet crystals of **1** were obtained by a diffusing method with an acetonitrile solution of CuCl$_2$ (4×10^{-2} M) and a THF solution of the ligand (5×10^{-3} M). $C_{20}H_{20}Cl_6Cu_2N_4O_4S_{12}$ (1104.93): calcd. C 21.83, H 1.83, N 5.09; found C 21.56, H 2.05, N 4.89. IR (KBr): $\tilde{\nu}$ = 3329–3149 (NH$_2$), 1671–1660 (C=O) cm^{-1}.

X-ray Crystallographic Study: All measurements were carried out with a Rigaku Mercury CCD diffractometer at 193 K with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. X-ray Crystallographic data of compounds **1** were collected and processed using CrystalClear (Rigaku).[47] The structures were solved by direct methods with SHELXS-97[48] and the refinements against all reflections of the compound were performed using SHELXL-97.[49] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the theoretical riding model. The final cycle of full-matrix least-squares refinement was done on the basis of 3371 independent reflections and 220 variable parameters. The weighted R factor (wR) and goodness of fit (S) were obtained on the basis of 2996 [$I > 2\sigma(I)$] reflections. The calculations were performed using the CrystalStructure software package.[50]

CCDC-268681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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