



Article

Synthesis of New Derivatives of BEDT-TTF: Installation of Alkyl, Ethynyl, and Metal-Binding Side Chains and Formation of *Tris*(BEDT-TTF) Systems [†]

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[†] This paper is dedicated to the memory of Professor Peter Day FRS, who greatly encouraged and inspired our work in this area.



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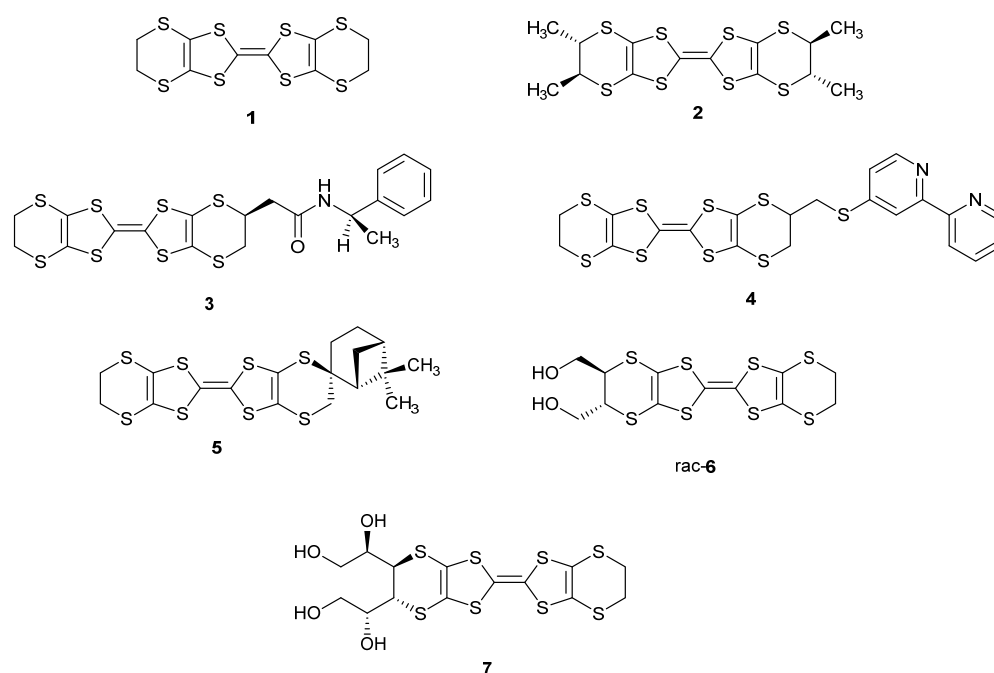
Abstract: The syntheses of new BEDT-TTF derivatives are described. These comprise BEDT-TTF with one ethynyl group (HC≡C-), with two (*n*-heptyl) or four (*n*-butyl) alkyl side chains, with two *trans* acetal (-CH(OMe)₂) groups, with two *trans* aminomethyl (-CH₂NH₂) groups, and with an iminodiacetate (-CH₂N(CH₂CO₂⁻)₂) side chain. Three transition metal salts have been prepared from the latter donor, and their magnetic properties are reported. Three *tris*-donor systems are reported bearing three BEDT-TTF derivatives with ester links to a core derived from benzene-1,3,5-tricarboxylic acid. The stereochemistry and molecular structure of the donors are discussed. X-ray crystal structures of two BEDT-TTF donors are reported: one with two CH(OMe)₂ groups and with one a -CH₂N(CH₂CO₂Me)₂ side chain.

Keywords: organic conductors; BEDT-TTF; synthesis; magnetism; crystal structures

1. Introduction

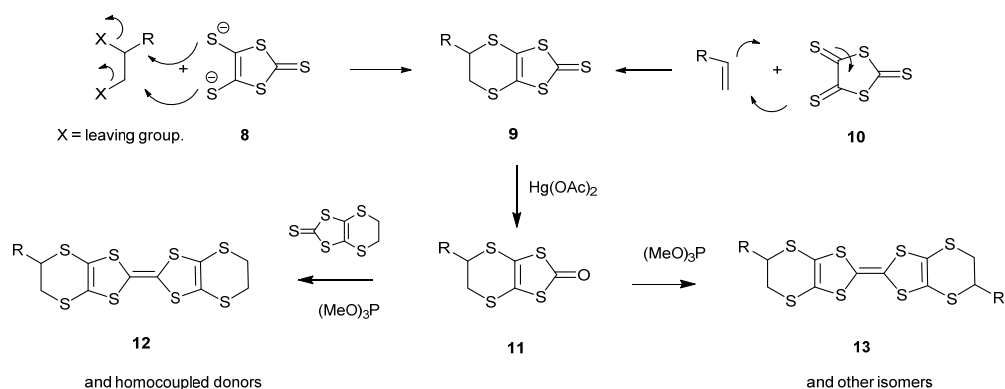
BEDT-TTF **1** has played a significant role in the development of electroactive organic materials. A very wide range of crystalline radical cation salts, with different stoichiometries, have been prepared, some of which are semi-conductors, conductors, or low temperature superconductors [1–4]. A range of different packing modes for the donors in these salts have been identified [5–7], which includes a κ -phase in the superconducting salts, such as (BEDT-TTF)₂Cu(NCS)₂, where the donors pack in face-to-face pairs but lie roughly perpendicular to their neighbouring pairs [8–10]. BEDT-TTF has been used to prepare hybrid materials with conducting and magnetic properties [11–14], as pioneered initially by Day et al. who prepared salts with iron *tris*(oxalate) salts which also showed low temperature superconductivity [11,12].

Following these studies on BEDT-TTF, a range of substituted BEDT-TTF derivatives that include compounds **2–5** have been reported (Scheme 1) [15]. Particularly notable examples are the enantiopure tetramethyl derivative **2** which forms a range of radical cation salts [16–19], the enantiopure amide **3** which forms a 4:1 TCNQ complex which changes from an insulator to an organic metal at 283 K and stays metallic down to ca. 4 K [20], the racemic bipyridylthiomethyl derivative **4** which forms capsular structures with metal ions [21], and the *spiro* chiral derivative **5** [22]. BEDT-TTF donors with one amino-methyl or -ethyl side chain [23], one hydroxy-methyl or -ethyl side chain [24,25], or with multiple hydroxymethyl or 1,2-dihydroxyethyl chains such as **6** and **7** have also been reported [26–28], as well as systems where the BEDT-TTF unit is fused to a thiophene or furan ring [29].



Scheme 1. Structures of donors 1–7.

Two general synthetic routes have been used to prepare the aforementioned BEDT-TTF derivatives (Scheme 2) [15]. The first is via the dithiolate **8**, available from carbon disulphide and sodium, by double substitutions with dihalides or cyclic sulphate esters to give the bicyclic thione **9** [16,24]. The second is via the trithione **10**, which reacts with alkenes in a 4 + 2 electrocyclic reaction to also give the bicyclic thione **9** [22–28,30–34]. In both cases, the synthesis is completed by conversion of the thione to the oxo compound **11** by treatment with mercuric acetate, and then reaction with triethyl or trimethyl phosphite to form the homo-coupled BEDT-TTF system **13**. Cross-coupling of an oxo compound with a different thione is used to prepare an unsymmetrical derivative BEDT-TTF **12**.



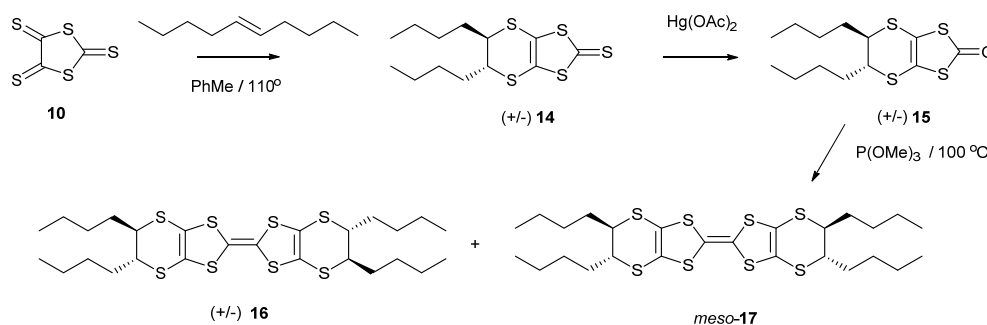
Scheme 2. Two general synthetic routes to BEDT-TTF derivatives.

In recent work, we have expanded our library of BEDT-TTF donors and now report the syntheses of a range of new racemic BEDT-TTF derivatives, prepared by the second synthetic strategy using the trithione intermediate **10**. This includes BEDT-TTFs substituted with an ethynyl side chain, **38**, or with metal binding groups, **48** and **53**, in addition to molecules bearing three BEDT-TTF units around a benzene ring core, **26–28**. Preliminary magnetic results for complexes of donor **53** with 3D transition metals are presented. Stereochemical aspects of substituted donors are also discussed. Full synthetic details are provided in Section 4 and in the Supplementary Information.

2. Results and Discussion

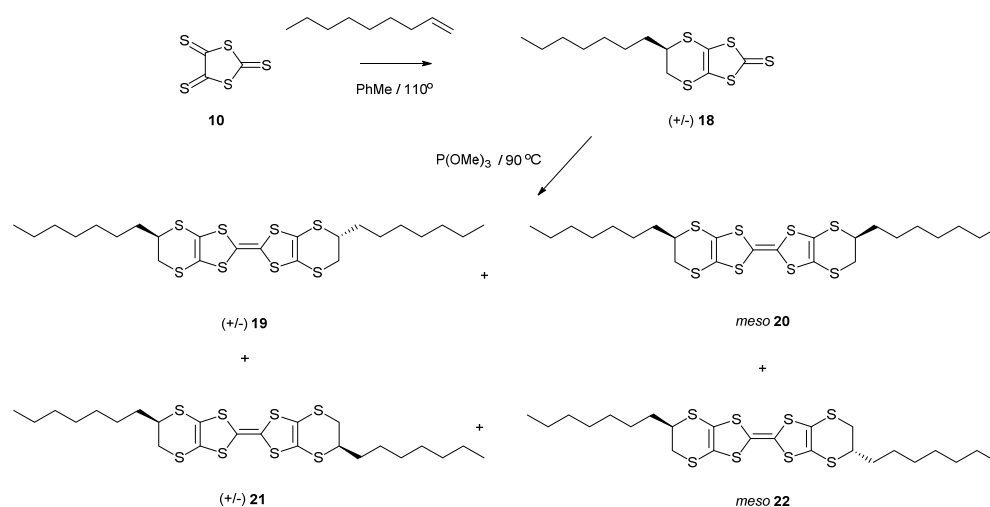
2.1. BEDT-TTF with Alkyl Chains

The installation of alkyl chains on a BEDT-TTF molecule should increase the solubility, which is very low for BEDT-TTF itself. Thus, the reaction of trithione **10** with *trans*-dec-5-ene gave the racemic thione **14** in 95% yield (Scheme 3). The treatment of this thione with mercuric acetate afforded the oxo compound **15** in an almost quantitative yield, which was homo-coupled using trimethyl phosphite to give the substituted BEDT-TTF in 57% yield as a mixture of stereoisomers. The configurations of the two stereogenic centres at one end of the molecule are the same but can be opposite to, or the same as, those at the other end. Thus, there are three stereoisomers: racemic (*R,R,R,R*)- and (*S,S,S,S*)-**16** and the *meso* compound (*R,R,S,S*)-**17**. Unfortunately, these are not separable by chromatography, but the structures are expected to have very similar shapes. In this respect, the conformation of the dithiin ring is typically an envelope or a half chair. Thus, the *R,R* and *S,S* configurations can position their side chains in similar pseudo-equatorial positions by adopting opposite conformations of their dithiin rings.



Scheme 3. Synthetic route to tetra-*n*-butyl-BEDT-TTF derivatives **16** and **17**.

Following the same synthetic strategy, the trithione **10** was reacted with non-1-ene to provide the bicyclic thione **18** with one heptyl side chain in 57% yield (Scheme 4). The thione was directly homo-coupled using trimethyl phosphite to give a mixture of two disubstituted BEDT-TTF donors (51%), each one having two diastereomers. The locations of the side chains could be at the top edge of the molecule, or one can be at the bottom edge, leading to the two differently substituted donors, each one of which has a racemic pair and a *meso* stereoisomer, **19–22**. Again, these were found to be inseparable. Both the **16–17** and **19–22** mixtures showed the expected two reversible oxidation peaks in their cyclic voltammograms (Table 1) at 0.47 and 0.89 V for **16–17** and 0.49 and 0.89 V for **19–22** (relative to Ag/AgCl).



Scheme 4. Synthetic routes to di-n-heptyl-BEDT-TTF derivatives **19–22**.

Table 1. Cyclic voltammetry data for selected BEDT-TTF derivatives ^a.

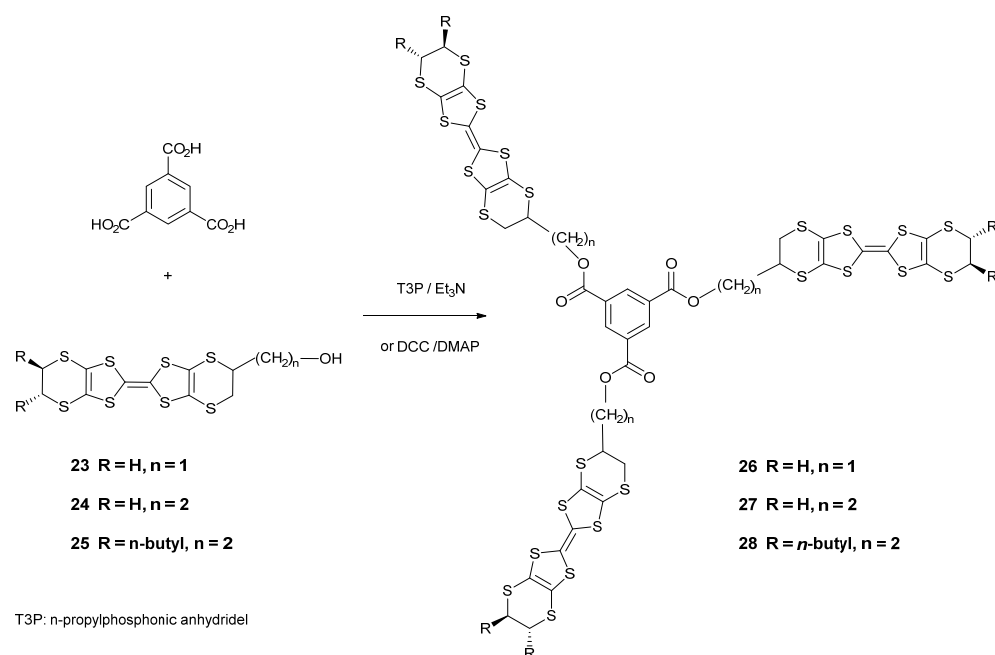
Donor	E ₁ (V)	E ₂ (V)
16–17	0.47	0.89
19–22	0.49	0.89
26	0.48, 0.55 ^b	0.88 ^b
27	0.44, 0.56 ^b	0.86 ^b
28	0.50	0.88
38	0.52	0.92
42	0.50	0.93
48	0.72 ^{b,c}	0.89 ^{b,c}
52	0.53	0.94

^a Measured in 0.1 M tetrabutylammonium hexafluorophosphate in DCM at 20 °C, substrate concentrations 0.01 mM, and scan rate of 0.1 V s^{−1}, unless otherwise stated; ^b irreversible; ^c in THF.

2.2. Tris-(BEDT-TTF) Donors

To provide systems which will show different packing arrangements versus the classical BEDT-TTF systems and which could also act as supramolecular synthons, e.g., for forming charge transfer complexes with fullerenes, three *tris*-donor systems **26–28** were prepared containing three donors appended to a benzene core. The synthetic route to these compounds involved the coupling of benzene-1,3,5-tricarboxylic acid with three equivalents of a BEDT-TTF donor bearing a hydroxyalkyl side chain using *n*-propyl phosphonic anhydride (“T3P”) or DCC (Scheme 5). Thus, donors **23** and **24** with a hydroxy-methyl or hydroxyethyl side chain afforded the *tris*-donors **26** and **27** in 22 and 33% yields, respectively. Interestingly, there are two racemic diastereomers for these two donors, one with the same configuration at all three stereogenic centres (*R,R,R*) and one with the same configuration at just two centres (*R,R,S*). However, the products proved to have low solubilities in common organic solvents, so the hydroxyethyl-BEDT-TTF donor **25**, functionalised with two *trans* oriented *n*-butyl side chains on the other ethylene bridge, was prepared and was coupled with the triacid to give the more soluble *tris*-donor **28** in 45% yield. The number of stereoisomers is increased over **26–27** because the three sets of butyl groups can have all six or just four configurations be the same. However, these stereochemical issues are unlikely to have a profound influence on the behaviour of the donor, due to the flexibilities of the dithiin rings, as discussed earlier. The structures were supported by their chemical analyses and spectral data, e.g., **26** showed a molecular ion in the mass spectrum, and **27–28** showed the three aromatic H atoms at ca. 8.8 ppm. The more soluble *tris* derivative **28** showed a reversible cyclic voltammogram with peaks at 0.50 and 0.88 V as expected of a BEDT-TTF derivative, but *tris* donors **26** and **27** showed irreversible volt-ammograms probably due

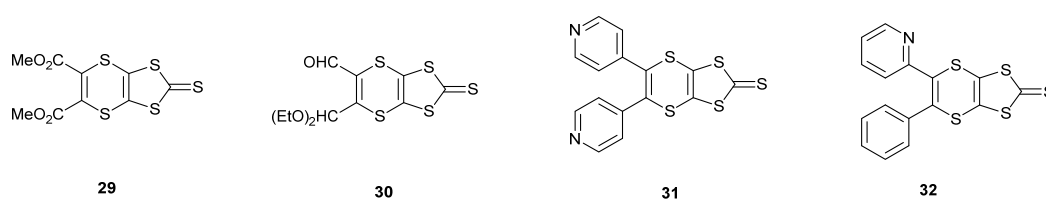
to the binding of the donor to the electrode, with two oxidation peaks between 0.44 and 0.56 V and another in the range 0.86–0.88 V on the outward scan.



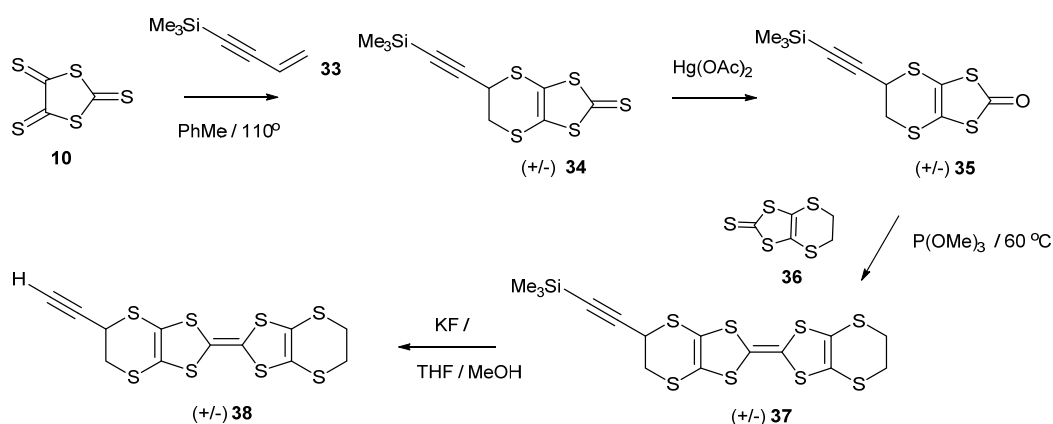
Scheme 5. Synthetic route to *tris*-BEDT-TTF derivatives **26–28**.

2.3. New Functionalised BEDT-TTFs: Ethynyl and Acetal Substituted Derivatives

There are several examples of the cyclisation of the trithione **10** with alkynes (Scheme 6), in particular with those where the triple bond bears two carbonyl or acetal functionalities, affording thiones such as **29** and **30** [35–37]. The electron deficient diarylethynes also react with the trithione **10**, giving access to thiones such as **31** and **32** [38,39]. An interesting case, therefore, would be the reaction with 4-trimethylsilyl-1-buten-3-yne **33**, which has both an alkene and an alkyne group, to determine which group preferentially reacts with the trithione **10** (Scheme 7). Refluxing the two materials together gave a 55% yield of the bicyclic trithione **34** in which the alkene, and not the alkyne, had reacted. The reaction of the trimethylsilylethynyl thione with mercuric acetate gave the oxo compound **35** in an almost quantitative yield, without affecting the triple bond, and this material was cross-coupled with the unsubstituted thione **36** to give the trimethylsilylethynyl substituted BEDT-TTF donor **37** in 45% yield. Treatment with potassium fluoride in THF/methanol gave the deprotected ethynyl-BEDT-TTF donor **38** in 88% yield. This shows the greater reactivity of the alkene over the alkyne with the trithione. This has provided an interesting donor which has the potential for connecting to larger molecular systems, either preserving the triple bond by substitution of the ethynyl H atom, e.g., by a Sonogashira reaction, or using the triple bond as a substrate for click chemistry with azide-functionalised materials.



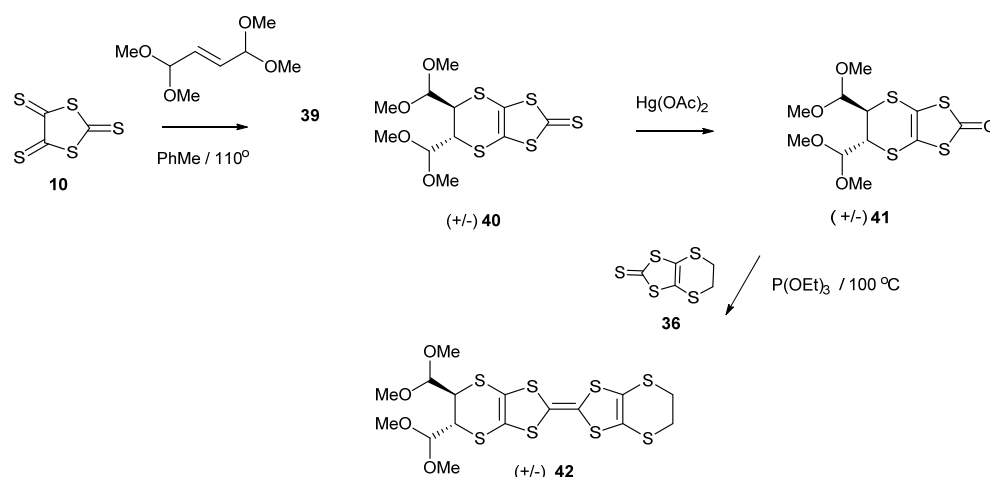
Scheme 6. Structures of thiones prepared from trithione **10** and various disubstituted alkynes.



Scheme 7. Synthetic route to ethynyl-BEDT-TTF **38**.

We were interested in making BEDT-TTF with two aldehyde groups attached, which could facilitate further ring constructions or the attachment of side chains. Thus, we targeted the corresponding *bis*(dimethylacetal) containing donor **42**. The reaction of the corresponding alkene, the *bis*-dimethylacetal of fumaraldehyde **39**, with trithione **10** gave the disubstituted thione **40** in a low yield of 17%, which was converted to the oxo compound **41** in almost quantitative yield (Scheme 8). The donor **42** was obtained by the cross-coupling of oxo compound **41** with the unsubstituted thione **36** in 49% yield. However, all attempts to hydrolyse the acetal groups with HCl or tosic acid in a range of concentrations failed to give the corresponding dialdehyde. Similar experiences have been reported on organosulphur donors containing acetal or ketal functionality [24,40]. It may be that these donor molecules stack together in clumps and isolate themselves from the acidic environment. Nevertheless, it is quite remarkable that these groups are resistant to hydrolysis, when dilute acid is usually quite sufficient. The cyclic voltammograms of BEDT-TTF derivatives **38** and **42** showed the expected two reversible oxidation peaks (Table 1).

Single crystals suitable for X-ray diffraction of **42** were grown from CH₃CN, and the molecular structure of the donor was determined (Figure 1). The substituted dithiin ring adopts a half-chair conformation and directs the acetal groups into pseudo-axial positions. The organosulphur moiety adopts a bowed shape with inflexions about the S...S vectors across the two dithiole rings of 19.6 and 17.2°. In the crystal structure, the donors pack in centrosymmetric slipped pairs to accommodate the side chains, with the shortest C...C contact of 3.546 Å between the TTF cores.



Scheme 8. Synthetic route to the BEDT-TTF derivative functionalised with two *trans*-oriented, dimethylacetal groups **42**.

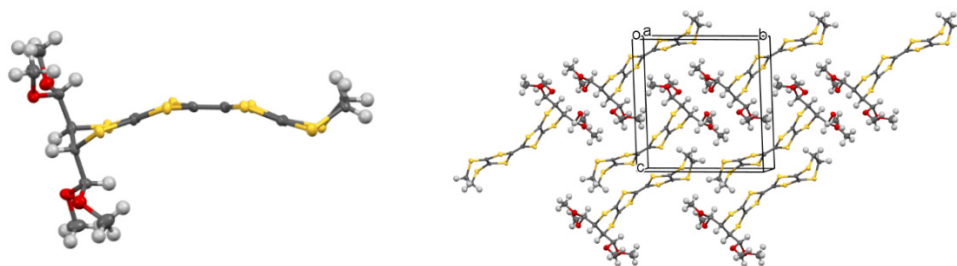
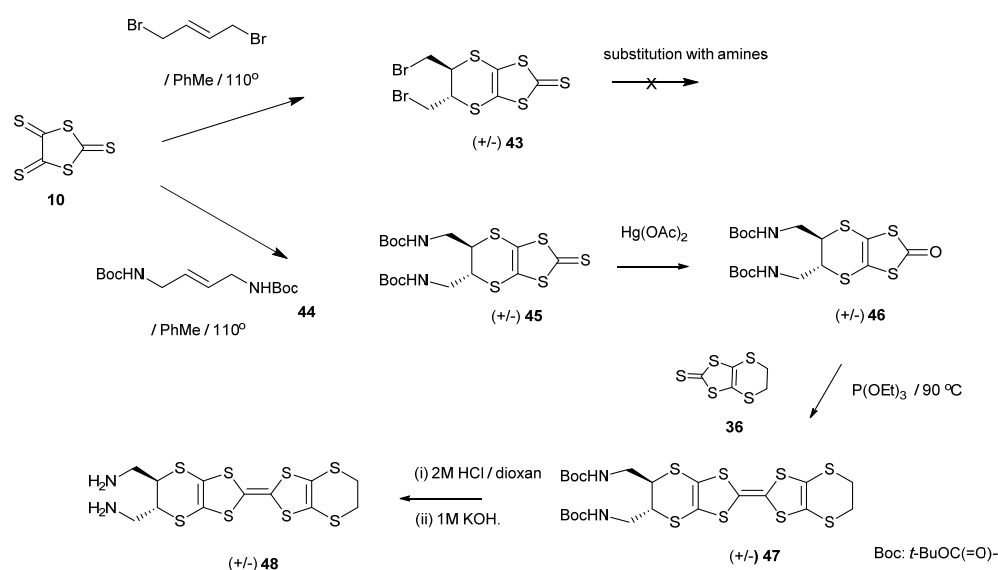


Figure 1. Molecular structure of donor **42** (left) and its crystal packing arrangement (right).

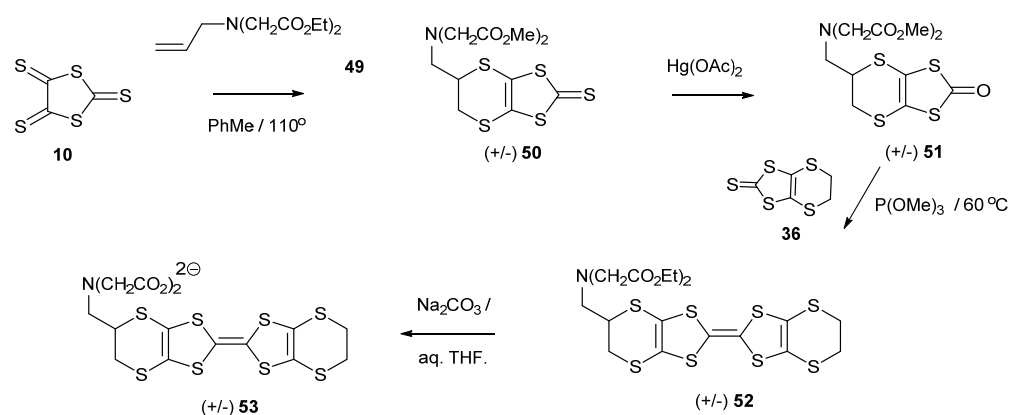
2.4. Donors with Metal Ion Binding Potential and the First Salts and Their Magnetic Properties

The BEDT-TTF donor **48** with *trans* aminomethyl groups was an interesting target, both for further synthetic elaborations and for the binding of metal ions. In a first approach, which we hoped would have a wide scope, thione **10** was reacted successfully with *trans*-1,4-dibromobut-2-ene to give the *trans* bis(bromomethyl)thione **43**. However, attempts to substitute the bromide groups of this material with amines were unsuccessful, with the amine probably causing the elimination of HBr. Therefore, to synthesize the donor with two aminomethyl groups **48**, the trithione **10** was reacted with the *bis*-N-boc derivative of *trans*-but-2-en-1,4-diamine **44** to give the thione **45** in 53% yield (Scheme 9). The corresponding reaction of the trithione with the readily obtained *bis*-phthalimido derivative of *trans*-but-2-en-1,4-diamine was unsuccessful. Following the established procedure, the thione **45** was converted to the oxo compound **46** which was cross-coupled with the unsubstituted thione **36** to give the *bis*-N-Boc donor **47** in 63% yield. Deprotection of this donor with HCl in dioxane followed by basification gave the *bis*(aminomethyl)BEDT-TTF **48** in 78% yield. The cyclic voltammogram of **48** in THF showed broad irreversible peaks, probably due to the donor binding to the electrode.



Scheme 9. Synthetic route to *trans*-bis-(aminomethyl)-BEDT-TTF **48**.

Installing an iminodicarboxylate dianion group on the side chain of BEDT-TTF could provide another BEDT-TTF donor with potential metal binding properties, so donor **53** with just a methylene between the donor and the metal binding group was prepared. This was synthesized following the synthetic strategy outlined in Scheme 10. The attachment of an allyl group to diethyl iminodiacetate gave alkene **49** which reacted with trithione **10** to give the substituted thione **50** in high yield. Conversion to the corresponding oxo compound **51** and subsequent cross-coupling with the unsubstituted thione **36** afforded the BEDT-TTF donor **52** with an imino diethyl ester group in the side chain in 34% yield.



Scheme 10. Synthetic route to the disodium salt of BEDT-TTF-methylamino-*N,N*-dicarboxylate **53**.

Single crystals of **52** were grown from DCM, and the crystal structure was determined by single crystal X-ray diffraction (Figure 2). The BEDT-TTF moiety adopts a bowed structure, with inflexions about the two S...S vectors in the dithiole rings of 14.6 and 23.3°. The unsubstituted ethylene bridge is disordered between two half-chair conformations (62:38). On the other bridge the carbon bearing the side chain and its attached hydrogen atom are disordered between two positions (82:18) which correspond to the structures of opposite enantiomers of the donor. This illustrates how the bridge can flex to accommodate both enantiomers without affecting the positions of either the main parts of the organosulphur system or the side chain. The donors are packed in centrosymmetric pairs with the shortest C...C distance between the TTF cores of 3.42 Å.

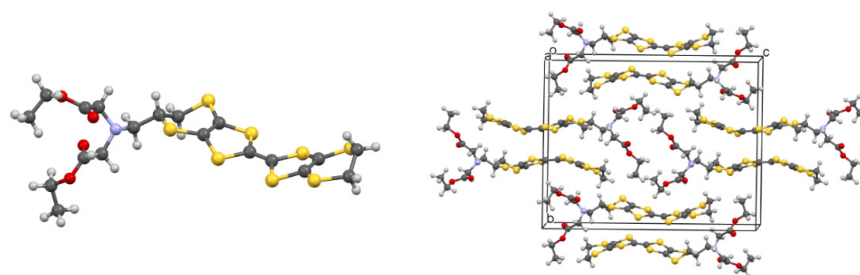


Figure 2. Crystal structure of donor **52**, showing the main molecular conformation (**left**) and the crystal packing arrangement (**right**).

Hydrolysis of the imino diethyl ester substituted donor **52** with sodium hydroxide gave the dianion **53** as a disodium salt in high yield. The reaction of this donor with a range of transition metal salts afforded precipitates which were all insoluble in a wide range of solvents, and from which single crystals could not be obtained. Thus, assignments of compositions are tentative, based only on chemical analysis, magnetic measurements, and infrared spectra, and we acknowledge that the structural topologies may be more complex. Ligand **53** can show a number of coordination modes (Figure 3). It can act as tridentate dianion (L^{2-}) binding by two oxygens and nitrogen; be protonated once (HL^-), on nitrogen or oxygen, and act as a bidentate or tridentate monoanion, respectively; or be protonated twice and coordinate as a neutral ligand (H_2L). Such behaviours are seen with simpler N-alkylated iminodiacetate ligands [41–43]. It can also act as just a bridging ligand [44]. Furthermore, binding to the outer set of the BEDT-TTF unit's sulphur atoms cannot be excluded, as has been observed with copper(I) and silver(I) [45–47]. Details of three of the coordination complexes obtained are provided in Table 2. With zinc triflate, the CHN data are consistent with the product **54** containing two equivalents of the HL^- monoanion coordinated to Zn(II). With $MnCl_2$, the product **55** contains two neutral H_2L ligands along with $MnCl_2$ and two waters. For the $MnCl_2$ complex, at room temperature, the value of the χT product ($4.4 \text{ cm}^3 \text{ K mol}^{-1}$) is in excellent agreement with the theoretical expected value for an isolated HS octahedral Mn(II) ion ($4.375 \text{ cm}^3 \text{ K mol}^{-1}$) with a g value of 2.00. Similarly, for the second Mn(II) complex **56** prepared from $Mn(hfac)_2$, the room temperature χT product of $4.5 \text{ cm}^3 \text{ K mol}^{-1}$ is again very reasonable for an isolated HS Mn(II) ion in octahedral geometry, where compared to complex **55**, the $hfac$ ions replace the chlorides, though with one less H_2L ligand and one less water molecule. For both Mn(II) complexes, dc magnetic studies reveal that the χT product is temperature independent down to ca. 50 K, after which time it rapidly decreases, which is consistent with the presence of antiferromagnetic interactions.

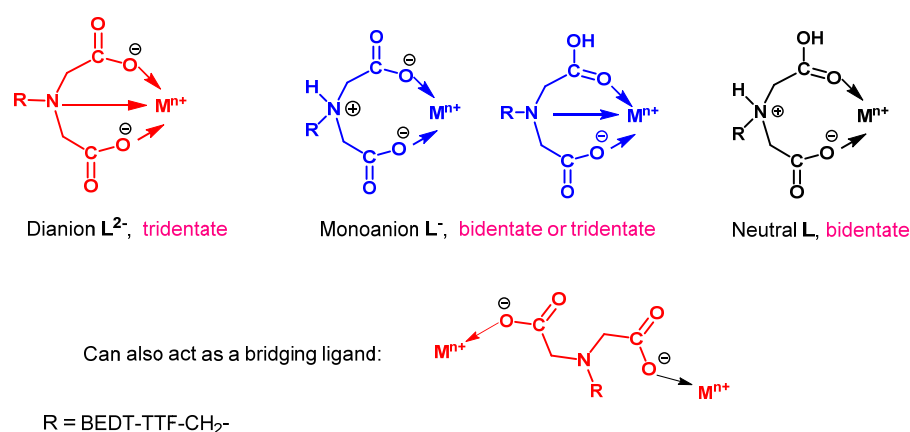


Figure 3. Possible binding modes of donor **53** to a metal ion, depending on its degree of protonation.

Table 2. Proposed compositions, magnetic data, and chemical analysis for the reaction of ligand **53** with Zn(II) and Mn(II) salts.

Metal salt, Colour.	Proposed Composition, Compound number, RMM.	Magnetic properties: ^a χT (cm ³ K mol ^{−1}); C (cm ³ K mol ^{−1}); θ (K).	Found CHN (%)	Calculated CHN (%)
Zn(II)triflate Red/pink.	Zn(HL) ₂		C: 31.95	C: 32.09
	54		H: 2.41	H: 2.51
	RMM 1121.4		N: 2.64	N: 2.49
MnCl ₂ Red.	Mn(H ₂ L) ₂ Cl ₂ ·2H ₂ O	χT : 4.4	C: 29.28	C: 29.50
	55	C: 4.47	H: 2.57	H: 2.81
	RMM 1220	θ : −6.07	N: 2.58	N: 2.29
Mn(hfac) ₂ Orange /brown.	Mn(H ₂ L)(hfac) ₂ ·H ₂ O	χT : 4.5	C: 29.58	C: 29.53
	56	C: 4.66	H: 1.88	H: 1.88
	RMM 1016.8	θ : −7.72	N: 1.48	N: 1.38

^a Plots of $1/\chi$ vs. T, and χT vs. T are provided in the ESI.

3. Conclusions

The synthesis of a range of new BEDT-TTF derivatives, which are substrates for the formation of charge transfer salts as well as for incorporation in more complex systems, has been described. The development of conducting and hybrid materials is highly dependent on the availability of new donor systems, and such syntheses are often not straightforward. For example, the trithione **10** does not react with all alkenes, and the presence of the BEDT-TTF unit can disrupt apparently standard synthetic manipulations to side chain functionalities. The possibility of forming hybrid materials between the donor bearing an iminodiacetate function **53** and metal ions has been demonstrated and will be extended in the future to the *bis*(diaminomethyl) donor **48**, though methods for forming crystalline products, e.g., by hydrothermal synthesis, need to be developed. Furthermore, to produce conducting materials, an oxidation step needs to be included. Of particular note is that the flexibility of the ethylene bridges of BEDT-TTF donors results in both enantiomers of the substituted BEDT-TTF being close to superimposable, as shown in the crystal structure of **52**. This indicates that to prepare systems with chiral packing arrangements, the stereogenic feature might be more effective in the side chain. However, we note that the first observation of magnetochiral anisotropy in organic conductors was in the perchlorate salts of enantiomers of dimethyl EDT-TTF, where the chirality was on the donor [48].

4. Materials and Methods

General. Solution NMR spectra were measured on either a Jeol ECLIPSE ECX or ECZ spectrometer operating at 400 MHz for ¹H and at 100.6 MHz for ¹³C, using CDCl₃ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in hertz. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using attenuated total reflection sampling on solids or oils and are reported in cm^{−1}. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea or on a Waters Xevo QTOF G2 XS using an ESI source with a Waters Acquity UPLC system at NTU. Chemical analysis data were obtained from London Metropolitan University and Nottingham University, UK. Flash chromatography was performed on 40–63 μ m silica gel obtained from Fluorochem Ltd. (Hadfield, Glossop, Derbyshire, UK).

Magnetic Measurements: Variable-temperature dc magnetic measurements were performed on a Quantum Design SQUID MPMS magnetometer in an applied field of 0.1 T, from 2 to 300 K. The experimental data were corrected for the diamagnetism and signal of the sample holder.

Full details of the synthetic procedures and further details of the magnetic data are provided in the ESI. The syntheses of **49–56** are given below to illustrate the general methods.

Diethyl allylamino-N,N-diacetate, 49: To a stirred solution of diethyl amino-N,N-diacetate (3.04 g, 16.1 mmol) in THF (50 mL), allyl bromide (2.20 mL, 25.3 mmol) was slowly added followed by addition of K_2CO_3 (3.42 g, 24.7 mmol), and the resulting suspension was warmed up to reflux and left to stir for 20 h. The reaction mixture was cooled to room temperature, and THF was evaporated under reduced pressure. DCM was added to the residue (100 mL) and the organic layer was washed with water (100 mL) and brine (100 mL) and dried over Na_2SO_4 . Evaporation of DCM afforded diethyl allyl-amino-N,N-diacetate **49** (3.16 g, 86%) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$): 5.88 (1H, m, $-CH=CH_2$), 5.22 (1H, dd, $J = 18.8, 1.7$ Hz, $-CH=CH_{trans}H$), 5.17 (1H, dd, $J = 10.1, 1.8$ Hz, $-CH=CH_{cis}H$), 4.17 (4H, q, $J = 7.2$ Hz, $-O-CH_2-CH_3$), 3.57 (4H, s, $2 \times -N(CH_2COOEt)_2$), 3.38 (2H, d, $J = 6.7$ Hz, $-CH_2-CH=$), 1.27 (6H, t, $J = 7.0$ Hz, $2 \times -CH_3$); δ_C : (100 MHz, $CDCl_3$): 170.6 ($2 \times -C=O$), 134.9 ($=CH$), 118.0 ($=CH_2$), 60.0 ($2 \times -O-CH_2-CH_3$), 57.0 ($=CH-CH_2-N-$), 53.8 ($2 \times -N-CH_2CO$), 13.8 ($2 \times -CH_3$); ν_{max} : 2981, 1737, 1674, 1399, 1333, 1190, 714; HRMS: (ASAP) found: 230.1383 (100%), $C_{11}H_{20}NO_4 + H$: requires: 230.1387; found C, 57.69; H, 8.36; N, 6.19%; $C_{11}H_{20}NO_4$ requires C, 57.64; H, 8.29; N, 6.11%.

Diethyl (+/-)-5,6-dihydro-2-thioxo-1,3-dithiol[4,5-b]1,4-dithiin-5-methylamine-N,N-diacetate, 50: Diethyl allyl-amino-N,N-diacetate **49** (1.17 g, 5.0 mmol) was added to a suspension of trithione **10** (3.25 g, 17.0 mmol) in toluene (100 mL), and the resulted suspension was warmed up to reflux and left to stir overnight under a nitrogen atmosphere. The solid formed during the reaction was filtered off and washed with $CHCl_3$ until washes ran clear. The combined filtrates were evaporated under reduced pressure to give the desired thione **50** as a dark red oil (2.09 g, 96%). δ_H (400 MHz, $CDCl_3$): 4.10 (4H, q, $J = 7.0$ Hz, $-O-CH_2-CH_3$), 3.72 (1H, m, 5-H), 3.51 (4H, s, $2 \times (-N-CH_2-C=O)$), 3.43 (1H, dd, $J = 13.4, 6.1$ Hz, 5-($CH_\alpha H$)-N), 3.29 (1H, dd, $J = 13.3, 2.8$ Hz, 5-($CH_\beta H$)-N), 3.13 (1H, dd, $J = 13.8, 8.7$ Hz, 6- H_α), 3.05 (1H, dd, $J = 13.8, 6.5$ Hz, 6- H_β), 1.20 (6H, t, $J = 7.2$ Hz, $2 \times -CH_3$); δ_C : (100 MHz, $CDCl_3$): 208.0 ($C=S$), 170.9 ($2 \times C=O$), 123.6, 122.2 (3a-, 7a-C), 60.8 ($2 \times -O-CH_2$), 58.7 (5- CH_2-N), 56.2 ($2 \times -N-CH_2-C=O$), 42.6 (5-C), 31.9 (6-C), 14.2 ($2 \times -CH_3$); ν_{max} : 2975, 1729, 1483, 1368, 1259, 1180, 1140, 1054, 883, 799, 512; HRMS: (ASAP) found: 425.9995 (100%), $C_{14}H_{19}NO_4S_5 + H$: requires: 425.9990; found C, 39.55; H, 4.51; N, 3.35%, $C_{14}H_{19}NO_4S_5$ requires C, 39.53; H, 4.47; N, 3.29%.

Diethyl (+/-)-5,6-dihydro-2-oxo-1,3-dithiol[4,5-b]1,4-dithiin-5-methylamine-N,N-diacetate, 51: To a solution of thione **50** (1.88 g, 4.40 mmol) in $CHCl_3$ (100 mL), mercury (II) acetate (3.54 g, 11.0 mmol) was added, and the suspension was left stirring for 3 h at room temperature under a nitrogen atmosphere. The solid formed during the reaction was filtered off and washed with $CHCl_3$ until washes ran clear. The combined filtrates were washed with saturated sodium hydrogen carbonate solution (5×50 mL). The organic layer was washed with water (50 mL) and brine (50 mL) and dried over $MgSO_4$. Evaporation of the chloroform yielded the desired oxo-compound **51** as a brown oil (1.71 g, 91%). δ_H (400 MHz, $CDCl_3$): 4.17 (4H, q, $J = 7.1$ Hz, $-O-CH_2-CH_3$), 3.82 (1H, m, 5-H), 3.59 (4H, s, $2 \times -N-CH_2-C=O$), 3.49 (1H, dd, $J = 13.3, 6.2$ Hz, 5-($CH_\alpha H$)-N), 3.39 (1H, dd, $J = 13.3, 3.1$ Hz, 5-($CH_\beta H$)-N), 3.23 (1H, dd, $J = 13.8, 8.7$ Hz, 6- H_α), 3.13 (1H, dd, $J = 13.8, 6.4$ Hz, 6- H_β), 1.28 (6H, t, $2 \times -CH_3$); δ_C (100 MHz, $CDCl_3$): 188.8 ($C=O$), 171.0 ($2 \times -C=O(OEt)$), 113.7, 111.8 (3a-, 7a-C), 60.8 ($2 \times -O-CH_2-CH_3$), 58.8 ($-CH_2-N-$), 56.2 ($2 \times -N-CH_2C=O$), 44.1 (5-C), 32.9 (6-C), 14.2 ($2 \times -CH_3$); ν_{max} : 2978, 1731, 1670, 1443, 1411, 1368, 1186, 1139, 1024, 762, 463; HRMS: (ASAP) found: 410.0208, $C_{14}H_{19}NO_5S_4 + H$: requires: 410.0219; found C, 40.94; H, 4.72; N, 3.50%, $C_{14}H_{19}NO_5S_4$ requires C, 41.07; H, 4.64; N, 3.42%.

Diethyl (+/-)-BEDT-TTF-methylamino-N,N-diacetate, 52: Oxo compound **51** (2.01 g, 5.0 mmol) and 5,6-dihydro-dithiol[4,5-b]dithiin-2-thione **36** (1.79 g, 8.0 mmol) were heated together in freshly distilled triethyl phosphite (50 mL) at 90 °C for 6.5 h under a nitrogen atmosphere. The solid formed was filtered and washed with $CHCl_3$, and the combined filtrates were concentrated under reduced pressure. The triethyl phosphite was distilled off using a Kugelrohr apparatus. The residue was purified by flash chromatography (6:1 = cyclohexane: ethyl acetate) to give the substituted BEDT-TTF **52** as an orange solid (0.99 g, 34%), m.p. 107–108 °C; δ_H (400 MHz, $CDCl_3$): 4.09 (4H, q, $J = 7.1$ Hz, $2 \times -O-$

CH₂-CH₃), 3.64 (1H, m, 5-H), 3.50 & 3.51 (2 × 2H, 2 × s, 2 × (-N-CH₂-C(O))), 3.33 (1H, dd, J = 13.0, 6.0 Hz, 5-(CH_αH)-N), 3.21 (4H, s, (5'-, 6'-CH₂)), 3.20 (1H, dd, J = 13.0, 3.1 Hz, 5-(CH_βH)-N), 3.03 (2H, m, 6-H₂), 1.20 (6H, t, J = 7.2 Hz, 2 × -CH₃); δ_C (100 MHz, CDCl₃): 171.0 (2 × C=O), 113.8, 113.7, 112.5, 111.5, 109.8 (2-, 2'-, 3a-, 7a-, 3'a-, 7'a-C), 60.6 (2 × O-CH₂-CH₃), 58.7 (5-CH₂-N-), 56.1 (2 × N-CH₂-C=O), 42.6 (5-C), 32.5 (6-C), 30.1 (5'-, 6'-C), 14.1 (2 × -CH₃); ν_{max}: 2921, 1733, 1449, 1412, 1372, 1190, 1022, 770; found C, 39.16; H, 4.00; N, 2.29%; C₁₉H₂₃NO₄S₈ requires C, 38.97; H, 3.93; N, 2.39%.

Disodium (+/−)-BEDT-TTF-methylamino-N,N-dicarboxylate 53 as a tetrahydrate, Na₂L·4H₂O: The di-ester donor **52** (0.37 g, 6.40 mmol) was dissolved in THF (10 mL), and an aqueous solution of NaOH (5 mL, 0.256 M, 12.8 mmol) was added. The suspension was warmed to 50 °C and left stirring overnight. The THF was evaporated, and the solid filtered and washed successively with DCM (3 × 5 mL), water (3 × 5 mL), and ether (3 × 10 mL). Filtration gave **53** (0.41 g, quantitative) as a highly insoluble red solid, m.p. 240 °C (dec). ν_{max}: 2917, 1582, 1400, 1326, 1122, 995, 904, 771, 669; found C, 28.16; H, 3.03; N, 2.38%, C₁₅H₁₃NO₄S₈Na₂·4H₂O required C, 27.90; H, 3.28; N, 2.17%.

Preparation of metal salts of 53: (a) with zinc(II) triflate to give 54: To a suspension of sodium salt **53** (77 mg, 0.12 mmol) in dry MeOH (8 mL) at room temperature under a nitrogen atmosphere, zinc triflate (25 mg, 0.069 mmol) was added, and immediately after the addition, a brown suspension was formed. The reaction mixture was left to stir for 1 h, and then the solid was filtered off, washed with diethyl ether, and left to dry in air to give Zn(HL)₂, **54**, (45 mg, 58%); m.p. 243–244 °C (dec.), ν_{max}: 2950, 2854, 1596 (C=O), 1422, 1398, 1342, 1143, 996, 893, 766, 748; found C, 31.94; H, 2.41; N, 2.64%; C₃₀H₂₈N₂O₈S₁₆Zn requires C, 32.09; H, 2.51; N, 2.49%.

(b) with manganese(II) chloride to give 55: To a suspension of sodium salt **53** (0.212 g, 0.33 mmol) in distilled water (5 mL) at room temperature, MnCl₂·4H₂O (0.035 g, 0.18 mmol) was added, and immediately after the addition, a red precipitate was formed. The obtained solid was filtered and washed with diethyl ether and left to dry in air to give Mn(H₂L)₂Cl₂·2H₂O, **55**, (147 mg, 68%), m.p. 206–207 °C (dec). ν_{max}: 3321, 2914, 1595 (C=O), 1399, 1364, 1194, 1143, 996, 892; found C, 29.28; H, 2.57; N, 2.58%; C₃₀H₃₀O₈S₁₆N₂Cl₂Mn·2H₂O required C, 29.50; H, 2.81; N, 2.29%.

(c) with manganese(II) (hfac)₂ to give 56: To a suspension of sodium salt **53** (26.0 mg, 0.052 mmol) in dry MeOH (6 mL) at room temperature under a nitrogen atmosphere, Mn(hfac)₂·3H₂O (24 mg, 0.046 mmol) was added. Immediately after the addition, a brown solid precipitated out from the mixture. The reaction was left to stir for 1 h, and then the solid was filtered. The brown precipitate was collected, washed with diethyl ether, and left to dry in air to give Mn(H₂L)(hfac)₂·H₂O, **56**, (22 mg, 48%), m.p. 137–140 °C; ν_{max}: 3296, 1601, 1401, 1319, 1054, 994, 902, 771; found C, 29.61; H, 1.76; N, 1.81%; C₂₅H₁₇NO₈F₁₂S₈Mn·H₂O requires C, 29.53; H, 1.88; N, 1.38%.

X-ray Crystallography. X-ray diffraction data (MoKα) were measured at low temperature for **42** (120 K) and **52** (150 K). Structures were solved and refined using the SHELXS and SHELXL suite of programs [49,50] using the XSEED interface [51]. Molecular illustrations and geometric analysis were made with Mercury [52]. Data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC 2083578–2083579.

Crystal data for **42**: C₁₆H₂₀O₄S₈, M_r = 532.80, triclinic, *a* = 6.3985(4), *b* = 12.6825(11), *c* = 13.4735(10) Å, α = 89.198(4), β = 81.424(5), γ = 87.025(5)°, *V* = 1079.66(14) Å³, *Z* = 2, *P*-1, *D*_c = 1.64 g cm^{−3}, μ = 0.849 mm^{−1}, *T* = 120(2) K, 4995 unique reflections (*R*_{int} = 0.078), 3422 with *F*² > 2σ, *R*(*F*, *F*² > 2σ) = 0.059, *R*_w (*F*², all data) = 0.13. Crystal from acetonitrile.

Crystal data for **52**: C₁₉H₂₃NO₄S₈, M_r = 585.8, monoclinic, *a* = 6.5481(4), *b* = 17.6090(16), *c* = 22.2441(14) Å, β = 97.298(5)°, *V* = 2544.1(3) Å³, *Z* = 4, *P*₂₁/*c*, *D*_c = 1.53 g cm^{−3}, μ = 0.729 mm^{−1}, *T* = 150(2) K, 5831 unique reflections (*R*_{int} = 0.090), 4196 with *F*² > 2σ, *R*(*F*, *F*² > 2σ) = 0.085, *R*_w (*F*², all data) = 0.23. Crystal from dichloromethane.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/magnechemistry7080110/s1>, S1: full experimental details for the syntheses not described in Section 4; S2: magnetic data for **55** and **56**; S3: references for S1–S2.

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Data Availability Statement: Crystallographic information files for **42** and **52** are available at The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, with numbers: CCDC 2083578-2083579.

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