ordering of the ferromagnetic planes *ab* would be due to the anisotropic component of the exchange.[30,31] It is likely relevant to recall here that two-dimensional ferromagnetism has been observed in A_2CrCl_4 compounds where A^+ is a bulky alkylammonium cation isolating magnetically the ferromagnetic $CrCl_4^{2-}$ layers,[32,34] as well as in similar tetrachlorocuprate compounds.[34,35]

One of the aspects of the discussion above deserves some additional comment, namely the ferromagnetism versus ferrimagnetism problem. Two nonequivalent spin sublattices NS_A and NS_B, with $S_A \neq S_B$, may interact to give either a ferromagnetic structure $N(S_A + S_B)$ or a ferrimagnetic structure $N(|S_A - S_B|)$. Thus, the only alternative to the ferrimagnetism is the ferromagnetism and not the antiferromagnetism. Consequently, it is quite appropriate to define the ground state of the $\mathrm{Mn^{II}Cu^{II}}$ ordered chains as one-dimensional ferrimagnetism. If the $\mathrm{Mn^{II}}$–$\mathrm{Cu^{II}}$ intrachain interaction was ferromagnetic instead of antiferromagnetic, we would speak of one-dimensional ferromagnetism. Let us consider now the interactions between the chains within the *ab* plane. We have seen that these interactions can lead either to the situation encountered in **1** with a cancellation of the spins or to that encountered in **2** with a parallel alignment of the $S_{Mn} = {}^5/_2$ spins. Since the former alternative clearly corresponds to antiferromagnetism, the latter one must be defined as ferromagnetism and it is correct to say that in **2** the ferrimagnetic chains couple ferromagnetically within the *ab* plane. Of course, if the interchain interactions in the *ab* plane became of the same order of magnitude as the intrachain interaction, the one-dimensional character of the system would vanish. In that case, it would be more appropriate to describe the situation in terms of ferrimagnetic *ab* planes.

Conclusion

In this paper, we have described an original strategy to design molecular-based systems ordering ferromagnetically. The basis idea is to assemble ferrimagnetic chains within the crystal lattice in a ferromagnetic fashion. Our approach has been the following: (i) The interaction within the chains should be as large as possible and the local spins of the adjacent ions as different as possible; these conditions led us to the choice of the systems $\mathrm{Mn^{II}Cu^{II}}$ with oxamato-type bridges. (ii) The shortest interchain metal–metal separations should be of the type Mn⋯Cu rather than Mn⋯Mn and Cu⋯Cu. By making some subtle chemical modifications, we have succeeded in synthesizing compound **2** with such relative positions of the chains along one of the directions of the lattice. This compound has actually been found to order ferromagnetically at $T_c = 4.6$ K. Below T_c, it exhibits a hysteresis loop rather typical of a soft magnet. The easy magnetization axis has been determined; it is the *c* axis. Unfortunately, due to the small size of the single crystals, we have not been able to plot the magnetization versus field curve along this axis. We have only investigated the magnetization of a polycrystalline sample. The magnetization is then restrained by the anisotropy field.

The area of the molecular ferromagnets is in its infancy. Several groups over the world work along this perspective by using various strategies. This emulation should favor a fast development. The main goals are first to shift T_c toward higher temperatures but also to design stable systems, given a well-defined hysteresis loop with large remnant magnetization and coercive field. We think that our approach utilizing both the efficiency of the organic based ligands to transmit the electronic effects on long distances and the specific ability of the d-metal orbitals to provide high magnetic moments will allow us to report on novel systems of this kind in the near future.

Acknowledgment. We thank Professor L. J. de Jongh for very stimulating discussions.

Registry No. **1**, 101935-07-3; **2**, 105121-18-4; **3**, 99387-35-6; **4**, 105139-32-0; 2-hydroxy-1,3-propylenediamine, 616-29-5; ethyl oxamate, 617-36-7.

Supplementary Material Available: Tables VI and VII giving anisotropic thermal parameters for Mn and Cu atoms and positional parameters for hydrogen atoms (2 pages). Ordering information is given on any current masthead page.

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The Generation, Microwave Spectrum, and Structure of Propadienethione, $H_2C{=}C{=}C{=}S$

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Abstract: The third member of the cumulene-thione series H_2C_nS, propadienethione, has been produced by pyrolysis of cyclopenteno-1,2,3-thiadiazole and detected by microwave spectroscopy. The rotational constants from a number of isotopomers have been used to derive a molecular geometry, which shows that propadienethione is a planar molecule of C_{2v} symmetry, unlike propadienone which is kinked. A fully optimized geometry from a set of ab initio calculations done at the MP3/6-31G** level is in agreement with the experimental results. The dipole moment has been calculated from the Stark effect to be 2.064 Debye.

The cumulenone series of molecules is of special interest, because in contradiction to the previously accepted theory of cumulated double bonds, the third member of the series, propadienone, has been shown to be kinked at the central carbon.[1-3] An analysis of the vibrational satellite spectra of H_2 and D_2 butatrienone, the fourth member of the series, has recently shown that the molecule is not kinked in its equilibrium configuration.[4]

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Table I. Rotational Transition Frequencies and $\nu_{obsd} - \nu_{calcd}$ of the Isotopomers of Propadienethione (MHz)

	$H_2C_3{}^{32}S$		$H_2C_3{}^{34}S$		$H_2{}^{13}CC_2S$		$H_2C^{13}CCS$		DHC_3S		D_2C_3S	
$5_{15}-4_{14}$	25215.039	-0.001	24600.051	0.034								
$5_{05}-4_{05}$	25274.703	0.025	24712.332	-0.039								
$5_{14}-4_{13}$			24656.818	0.001								
$6_{16}-5_{15}$	30257.997	-0.006					30030.771	-0.007				
$6_{34}-5_{33}$	30321.029	0.004					30092.781	-0.008				
$6_{33}-5_{32}$	30321.029	0.004					30092.781	-0.008				
$6_{25}-5_{24}$	30326.157	-0.005					30097.962	0.004				
$6_{24}-5_{23}$	30326.210	0.007					30097.962	0.004				
$6_{06}-5_{05}$	30329.564	0.005					30101.289	0.019				
$6_{15}-5_{14}$	30399.577	0.002					30170.275	-0.012				
$7_{17}-6_{16}$	35300.934	-0.008			34197.806	-0.006	35035.836	-0.004			32045.231	0.021
$7_{35}-6_{34}$	35374.469	-0.005			34266.887	0.011	35108.194	0.000	33672.344	-0.001	32171.472	0.005
$7_{34}-6_{33}$	35374.469	-0.005			34266.887	0.011	35108.194	0.000	33672.344	-0.001	32171.472	0.005
$7_{26}-6_{25}$	35380.460	0.007			34272.471	0.025	35114.232	0.014			32175.978	0.012
$7_{25}-6_{24}$	35380.534	0.006			34272.471	0.025	35114.232	0.014			32176.360	-0.018
$7_{07}-6_{06}$	35384.406	-0.004			34276.095	-0.005	35118.080	0.013	33678.047	-0.008		
$7_{16}-6_{15}$	35466.094	-0.015	34597.312	0.098	34352.736	-0.022	35198.576	-0.025	33785.710	0.005		
$8_{18}-7_{17}$			39359.835	0.003	39083.107	-0.012			38365.048	0.001	36623.014	0.009
$8_{36}-7_{35}$			39439.789	0.003	39162.017	-0.041			38482.604	0.002	36767.357	0.004
$8_{35}-7_{34}$			39439.789	0.003	39162.017	-0.041			38482.604	0.002	36767.357	0.004
$8_{27}-7_{26}$			39446.326	0.030	39168.441	0.023			38486.465	-0.005	36772.444	-0.008
$8_{26}-7_{25}$			39446.398	-0.048	39168.441	0.023			38486.745	-0.008	36773.063	-0.008
$8_{08}-7_{07}$			39450.596	-0.075	39172.617	0.042			38489.061	0.010	36775.873	-0.005
$8_{17}-7_{16}$			39539.642	0.043	39260.203	0.002			38612.130	-0.001	36927.769	0.007
$10_{29}-9_{28}$	50543.200	0.020										
$10_{28}-9_{27}$	50543.380	0.006										

Ab initio molecular orbital calculations taken to the Hartree–Fock level with substantial basis sets (6-31G**) failed to predict the bent structure of propadienone,[5] and it was only when electron correlation was included that the kinked geometry of propadienone was correctly predicted.[6,7] Initial ab initio calculations on butatrienone,[8] showing it to be strongly kinked have been shown to be unreliable,[4] a demonstration of the care that is necessary in carrying out and interpreting molecular orbital calculations on this type of molecule. It is clearly of interest to ascertain whether such structural peculiarities occur in related series, such as the cumulenethiones, a series in which only the first two members have hitherto been fully characterized. We report here the characterization of the third member of this series, propadienethione, by microwave spectroscopy. Preliminary results from the spectra of the major isotopic species and the ^{34}S substituted species have been presented elsewhere.[9]

Experimental Section

Materials. Cyclopenteno-1,2,3-thiadiozole was prepared from cyclopentanotosylhydrazone and freshly distilled thionyl chloride.[10,11] MS, m/z 126 (M^+, 9), 98 (7), 97 (8), 70 (H_2C_3S, 100).

(Cyclopenteno-*4,4-d*$_2$)-1,2,3-thiadiazole. Cyclopentanone (10 g, 120 mmol) was stirred with D_2SO_4 (10 mL 99% + 90 mL of D_2O 99.9%) in a sealed flask. After 3 h the mixture was extracted with anhydrous ether (3×), the combined extracts were dried ($MgSO_4$), and the ether was removed by rotary evaporation. Mass spectrometric analysis indicated a product distribution of cyclopentanone-*2,2,4,4,-d*$_4$ (26%), cyclopentanone-*2,2,4,-d*$_3$ (40%), cyclopentanone-*2,4,-* and *-2,2-d*$_2$ (25%), and cyclopentanone-*2-d* (8%). A second exchange with a fresh sample of D_2SO_4/D_2O increased the proportion of cyclopentanone-d_4 to 70%. Reaction of cyclopentanone-d_4 with *p*-toluenesulfonylhydrazide in absolute ethanol (OD, 99%) gave (cyclopentanone-*2,2,4,4-d*$_4$)tosylhydrazone, which was treated with thionyl chloride as previously described[11] to give (cyclopenteno-*4,4-d*$_2$)-1,2,3-thiadiazole. MS, m/z 128 (M^+, 13), 127 (4), 100 (8), 99 (7), 72 (D_2C_3S, 68), 71 (HDC_3S,26), 70 (H_2C_3S,100).

(Cyclopenteno-*4-d*$_1$)-1,2,3-thiadiazole was prepared in a similar manner by using cyclopentanone after the first exchange reaction with D_2SO_4/D_2O.

Propadienethione was generated by pyrolysis of cyclopenteno-1,2,3-thiadiazole, which was expected to fragment as shown in Scheme I.

The microwave spectrometer was a standard Stark modulated instrument having a 1-m long G-band waveguide (47.55 × 22.15 mm) cell, and modulated at either 33 or 80 kHz. The microwave source was a phase-locked OKI klystron (47.5–52.5 GHz) or a microprocessor controlled synthesized source, designed and constructed at Monash University and utilizing a Y.I.G. oscillator (26.5–40.0 GHz). Frequencies were referenced to a laboratory standard which was periodically checked against the Australian frequency standard at C.S.I.R.O. Division of Applied Physics. The spectral data were collected and reduced on a VAX 11/750 computer system.

Because of the transient nature of propadienethione, the pyrolysate was continuously pumped through the cell whilst maintaining an inlet pressure of around 0.2 Pascal. The propadienethione was generated by pyrolysis of cyclopenteno-1,2,3-thiadiazole at 800 °C in a short quartz oven positioned at the inlet of the waveguide cell. Spectra of monodeuteriated and dideuteriated propadienethione were taken by using the isotopically substituted precursor samples, whilst the spectra of the ^{34}S and two ^{13}C species were measured in natural abundance by using computer averaging techniques. For Stark effect measurements the electric field calibration was based on measurements on OCS for which the electric dipole moment was taken to be 0.71521D.[12]

Ab Initio Molecular Orbital Calculations. Ab initio calculations were carried out by using the GAUSSIAN 82 suite of programs.[13] An initial optimization was done by using the double-ζ basis sets of Dunning[14] enhanced with one set of polarization functions (DZ + P) on a VAX 11/780 computer. The basis sets were contracted to 6s4p1d on sulfur, 4s,2p,1d on carbon, and 2s1p on hydrogen, and the geometry was restricted to be planar and of C_{2v} symmetry. The resultant structure was scaled and used to obtain an initial prediction of the rotational constants for the spectral search. More exhaustive optimizations requiring greater computing power than that available on a VAX 11/780 were carried out on an IBM 3090 system (These calculations were carried out under a joint research project with IBM Australia.) in order to determine whether propadienethione was predicted to have a kinked geometry. Three separate optimizations with a 6-31G** basis set, including valence correlations by Moller–Plesset perturbation theory[15] to third order (MP3) were

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Table II. Rotational and Centrifugal Distortion Constants of Propadienethione (MHz)[a]

	I	II	III	IV	V	VI
A	328500 (26700)	328500[b]	328500[b]	328500[b]	214806 (1400)	149963 (3155)
B	2539.276 (1)	2476.927 (5)	2459.383 (5)	2520.081 (3)	2421.049 (2)	2317.593 (2)
C	2515.681 (1)	2454.456 (5)	2437.248 (5)	2496.829 (3)	2390.164 (2)	2279.498 (2)
D_J	0.000162 (5)	0.000143 (14)	0.000198 (46)	0.000172 (31)	0.000180 (11)	0.000115 (18)
D_{JK}	0.0654 (4)	0.0627 (19)	0.0598 (12)	0.0624 (5)	0.0410 (7)	0.0599 (3)
H_{KJ}	−0.00157 (5)	−0.00152 (20)	−0.00155 (13)	−0.00184 (5)	−0.00058 (7)	−0.00046 (1)

[a] I, $H_2C{=}C{=}C{=}S$; II, $H_2C{=}C{=}C{=}{}^{34}S$; III, $H_2{}^{13}C{=}C{=}C{=}S$; VI, $H_2C{=}{}^{13}C{=}C{=}S$; V, $DHC{=}C{=}C{=}S$; VI, $D_2C{=}C{=}C{=}S$. [b] Held at value for main species.

Table III. Harmonic Frequencies from 6-31G** Calculation

assignment	frequency, cm^{-1}	vibrational mode	
ν_{12} (b_2)	208.2	C=C=C=S	cis bend out of plane
ν_{11} (b_2)	568.3	C=C=C=S	trans bend out of plane
ν_{10} (b_2)	1110.7	CH_2	wag
ν_9 (b_1)	209.0	C=C=C=S	cis bend in plane
ν_8 (b_1)	422.4	C=C=C=S	trans bend in plane
ν_7 (b_1)	1135.7	CH_2	rock
ν_6 (b_1)	3378.6	C–H	asymmetric stretch
ν_5 (a_1)	741.0	C=C=C=S	concerted stretch
ν_4 (a_1)	1463.4	C=C=C	stretch − scissor
ν_3 (a_1)	1666.9	C=C=C	stretch + scissor
ν_2 (a_1)	2280.3	C=C=C=S	out-of-phase stretch
ν_1 (a_1)	3293.4	C–H	symmetric stretch

Scheme I

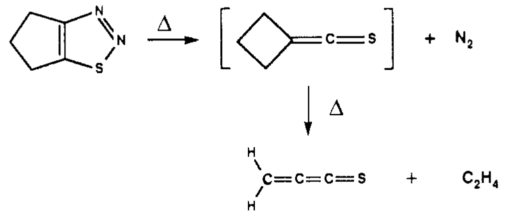

Table IV. Geometric Parameters of Propadienethione (pm)

	r_s[a]	r_0[a]	DZ + P	6-31G**	MP3/6-31G**
$r_{C{=}S}$	157.2	157.3	156.5	156.8	157.4
$r_{C{=}C({=}S)}$	127.4	127.1	127.2	126.1	127.6
$r_{C{=}C({=}C)}$	131.9	131.9	131.8	130.6	132.6
r_{C-H}	109.5	111.0	108.7	107.7	108.2
⟨HCH	117.9	119.0	117.2	117.2	116.8

[a] See text for a description of how these geometries were derived.

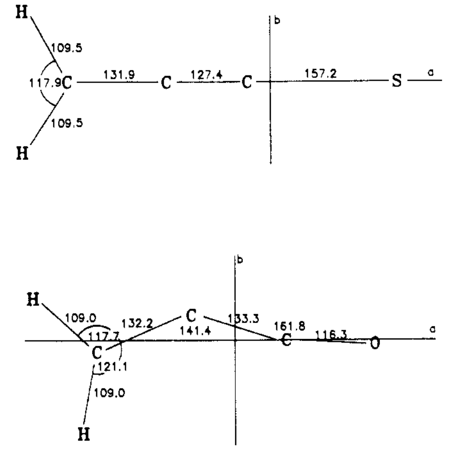

Figure 1. The r_s geometries of propadienone and propadienethione. Bond lengths are in pm; bond angles are in deg.

done: the first with C_{2v} symmetry, the second with C_s planar symmetry, and the third with C_s nonplanar symmetry. The geometries which were used to start the C_s optimizations had angles deviating from the C_{2v} angles by up to 10°. The results showed that the C_{2v} structure is a local minimum to an accuracy of better than 0.1 pm in the bond lengths, 0.1° in bond angles, and 1 μE_H in energy. An analytical frequency calculation was performed at a HF/6-31G** optimized geometry.

Results

The spectra of the monodeuteriated and dideuteriated species were assigned by their Stark effects in the same manner as those of the main species.[9] For the ^{13}C species a search was carried out in the relevant spectral regions and the computer averaged spectra assigned by their Stark effects and intensities relative to the main species transitions. No conflicting lines of the correct intensity and Stark effect were found in these narrow regions. The rotational transition frequencies for all the isotopomers studied are presented in Table I, and the rotational and centrifugal distortion constants from a least-squares fit to Watson's S-reduced Hamiltonian are presented in Table II. The dipole moment, obtained by analysis of the Stark effect of the 5_{05}–4_{04} and 5_{15}–4_{14} transitions, is 2.064 Debye. The results of the ab initio frequency calculations are presented in Table III.

Discussion

The rotational constants have been used to derive the geometry of propadienethione in a number of different ways. A near r_s structure has been calculated by using Kraitchman's substitution equations for the substituted atoms and the first moment equation for the third carbon atom. (Kraitchman's equations are not applicable for atoms that are situated very close to the center of mass.) Due to the indeterminancy of the *A* rotational constant it is necessary to make an assumption in order to calculate the distance of the hydrogen atoms from the *a* inertial axis. In Table IV the r_s structure has been calculated by assuming that the inertial defects ($\Delta = I_c - I_a - I_b$) of the main species, monodeuteriated and dideuteriated species, are the same as the respective averages of the inertial defects of the related molecules ketene and thioketene. This method of calculating a value for I_a should give greater accuracy than simply assuming that the molecule is planar and assigning the value zero to the inertial defect. The r_0 structure has been calculated by fitting the geometric parameters to the experimental *B* and *C* rotational constants in a least-squares procedure. The equilibrium geometries of the ab initio calculations are in good agreement with the experimentally derived r_0 and r_s geometries.

The structure of propadienethione, unlike propadienone, which is kinked, as seen in Figure 1, has the heavy atoms in a linear chain and two equivalent hydrogen atoms. The equivalent hydrogens result in an alternation in the intensities of the microwave transitions due to nuclear spin statistics. This intensity alternation is evident in the experimental spectra. For H_2C_3S the lines of odd K_p and even K_p alternate in a 3:1 ratio, whilst for D_2C_3S the alternation is 1:2. Further evidence for the ground-state equilibrium geometry having C_{2v} symmetry comes from the vibrational satellite spectra. Although as yet unassigned, these strong satellite lines all appear at higher frequencies than the lines assigned to the ground state. For propadienone where the equilibrium geometry is kinked, the opposite is the case, and the major satellite

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Table V. Dipole Moments of the Two Cumulene-Based Series (Debye)

molecule	X = O	X = S
$H_2C{=}X$	2.332^{16}	1.647^{16}
$H_2C{=}C{=}X$	1.422^{16}	1.021^{17}
$H_2C{=}C{=}C{=}X$	$2.297^{a,2}$	2.064
$H_2C{=}C{=}C{=}C{=}X$	1.9767^{18}	

[a] $\mu_a = 2.156$; $\mu_b = 0.791$.

progressions occur at frequencies lower than those of the ground state. Relative intensity measurements on the most intense $K_p = 2$ propadienethione vibrational satellite lines gives a frequency of ~250 cm^{-1} for the lowest bending mode, which because of spin statistics arguments must be an out-of-plane motion. This frequency is close to that predicted by the ab initio calculations in Table III for both the in-plane and out-of-plane bends.

The dipole moment of 2.064 D for propadienethione is about the value expected when the trends in the dipole moments of the two cumulene series are examined as in Table V. The alternation in size of the dipole moment with odd and even numbers of carbon atoms is evident in both series.

Acknowledgment. Financial support by ARGS is acknowledged. We thank IBM Australia for access to their 3090 computer system under a joint research program.

Registry No. $H_2C_3{}^{34}S$, 112196-93-7; $H_2{}^{13}CC_2S$, 112196-92-6; $H_2C^{13}CCS$, 112196-91-5; DHC_3S, 112196-90-4; D_2C_3S, 112196-89-1; H_2C_3S, 83797-23-3; cyclopenteno-1,2,3-thiadiazole, 56382-73-1; (cyclopenteno-*4,4-d*$_2$)-1,2,3-thiadiazole, 112196-87-9; (cyclopenteno-*4-d*$_1$)-1,2,3-thiadiazole, 112196-88-0.

Phase Transition in the Conductive Molecular Crystals Bis(tetramethyltetraselenafulvalene)[bis(trifluoromethyl)ethylene]diselenolatonickel and -platinum, $[TMTSF]_2[M(tds)_2]$, M = Ni, Pt. Relation to the Copper Analogue

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Abstract: A series of quasi-two-dimensional molecular conductors with formula $[TMTSF]_2[M(tds)_2]$ (TMTSF = tetramethyltetraselenafulvalene; tds = [bis(trifluoromethyl)ethylene]diselenolato; M = Ni, Pt, Cu) are described. All have $\sigma_{RT} = 20–100\ \Omega^{-1}\ cm^{-1}$ with metal-like character near room temperature. When M = Ni or Pt, there is a novel first-order structural transition (at $T_c = 275$ and 245 K, respectively) in which the low-temperature state exhibits enhanced conductivity; no corresponding transition occurs when M = Cu. At room temperature the three compounds are isostructural. The structure of M = Ni at 293 K consists of segregated stacks (along *c*) of TMTSF cations that are flanked by parallel chains of $M(tds)_2$ anions so as to form a two-dimensional anion–cation network parallel to the (010) plane. Crystal data: triclinic, space group C_i^1-$P\bar{1}$; $a = 11.503$ (18), $b = 12.465$ (20), $c = 7.885$ (13) Å; $\alpha = 96.39$ (4), $\beta = 109.57$ (4), $\gamma = 77.92$ (4)°; $V = 1040.7$ Å^3; $Z = 1$. ESR and magnetic susceptibility measurements are consistent with the formulation $[(TMTSF)^{0.5+}]_2[[M(tds)_2]^-]$, where the anions have an open-shell, paramagnetic ($S = {}^1/_2$) configuration when M = Ni or Pt but are closed-shell and diamagnetic when M = Cu. Thus, the existence of a transition correlates with the electronic structure of the anion. The conductivity arises from a three-fourths-filled band associated with the TMTSF stacks; for M = Ni or Pt, the carrier spins are exchange-coupled to the localized anion moments. Interestingly, the structure of the low-temperature phase of M = Ni, determined at 116 K, is disordered; it is derived from the room-temperature structure by uncorrelated translations of the individual stacks and chains by $\pm{}^1/_8c$ along *c*. Crystal data: triclinic, space group C_i^1-$P\bar{1}$; $a = 11.346$ (21), $b = 12.171$ (34), $c = 7.719$ (11) Å; $\alpha = 95.30$ (34), $\beta = 108.75$ (13), $\gamma = 79.90$ (25)°; $V = 993.0$ Å^3; $Z = 1$. The altered disposition of the stacks and chains in the disordered low-temperature structure enhances the intermolecular contacts within the two-dimensional anion–cation network.

In recent years, the field of molecular solid-state chemistry has experienced considerable growth fueled by the discovery of molecular crystals that exhibit metallic conductivity.[1,2] Of particular interest here are the organic superconductors,[3] which are salts of the heterofulvalene donor species tetramethyltetraselenafulvalene (TMTSF)[4] and bis(ethylenedithio)tetrathiafulvalene. The crystal structures of these compounds exhibit an enhanced multidimensional character, arising from intermolecular chalcogen–chalcogen interactions, that is believed to contribute substantially to the unusual physical properties.

The observation[5] that the nature of the anions plays an important role in modulating the dimensionality of such materials

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(4) Abbreviations used in text: TMTSF, tetramethyltetraselenafulvalene; TTF, tetrathiafulvalene; TMPD, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; TCNQ, tetracyanoquinodimethane; $(TCNQ)Br_2$, 2,5-dibromotetracyanoquinodimethane; DMTM, *N,N*-dimethylthiomorpholinium; dmit, isotrithionedithiolato; mnt, maleonitriledithiolato; bds, *o*-benzenedithiolato; tds, bis(trifluoromethyl)ethylenediselenolato.

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