

## **Observation of intramolecular vibrations cooperating with the magnetic phase transition in a nickel-bis-dithiolene compound**

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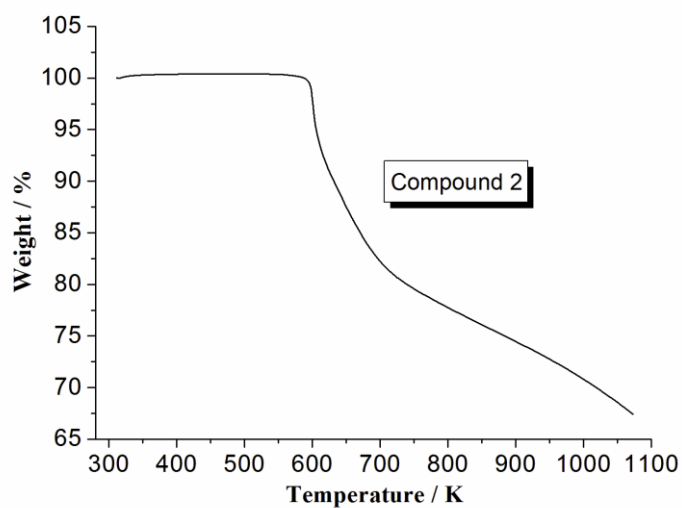
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**Table S1** Selected bond lengths [Å] and angles [°] for **2** at 296 K

Ni(1)-S(4)	2.1463(11)	Ni(1)-S(2)	2.1529(10)
Ni(1)-S(3)	2.1470(10)	Ni(1)-S(1)	2.1492(10)
S(1)-C(2)	1.725(4)	S(2)-C(3)	1.721(4)
S(3)-C(6)	1.714(4)	S(4)-C(7)	1.711(4)
N(1)-C(1)	1.142(5)	N(2)-C(4)	1.138(4)
N(3)-C(5)	1.136(4)	N(4)-C(8)	1.142(5)
N(5)-C(13)	1.305(4)	N(5)-C(16)	1.376(4)
N(5)-C(12)	1.472(4)	N(6)-C(13)	1.324(4)
N(6)-C(15)	1.344(4)	N(6)-C(14)	1.476(4)
C(1)-C(2)	1.428(5)	C(3)-C(2)	1.358(5)
C(3)-C(4)	1.432(5)	C(5)-C(6)	1.434(5)
C(6)-C(7)	1.358(4)	C(7)-C(8)	1.432(4)
C(9)-C(10)	1.511(4)	C(10)-C(11)	1.526(5)
S(4)-Ni(1)-S(3)	92.61(4)	S(4)-Ni(1)-S(1)	178.85(4)
S(3)-Ni(1)-S(1)	87.48(4)	S(4)-Ni(1)-S(2)	87.31(4)
S(1)-Ni(1)-S(2)	92.62(4)	S(3)-Ni(1)-S(2)	178.97(4)
C(2)-S(1)-Ni(1)	103.23(12)	C(3)-S(2)-Ni(1)	102.97(12)
C(6)-S(3)-Ni(1)	103.26(12)	C(7)-S(4)-Ni(1)	102.93(12)
C(13)-N(5)-C(16)	107.2(12)	C(13)-N(5)-C(12)	128.1(3)
C(16)-N(5)-C(12)	124.5(3)	C(13)-N(6)-C(15)	107.8(3)



**Figure S1** TGA curve for **2** in the temperature range of 311-1113 K

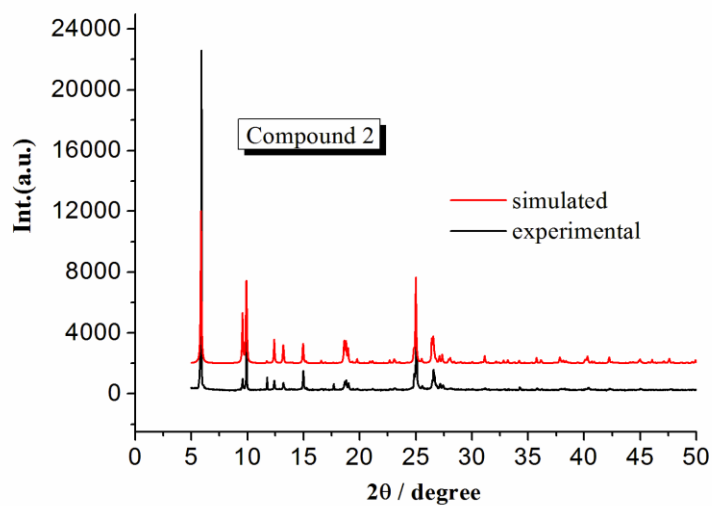


Figure S2 Powder X-ray diffraction profiles at 25 °C (experimental and simulated profiles) of **2**, indicating high phase purity of polycrystalline sample

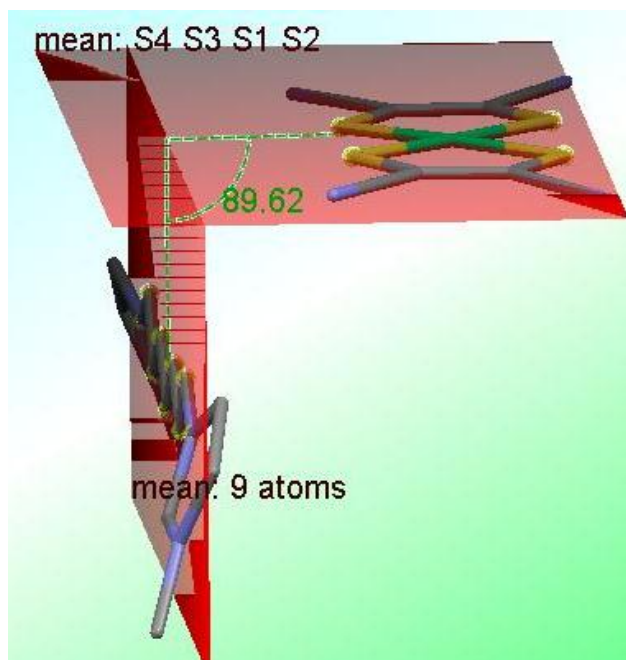


Figure S3 The plane consisted of the carbon atoms in hydrocarbon chain is approximately perpendicular to the anion plane in the crystal of **2** at room temperature

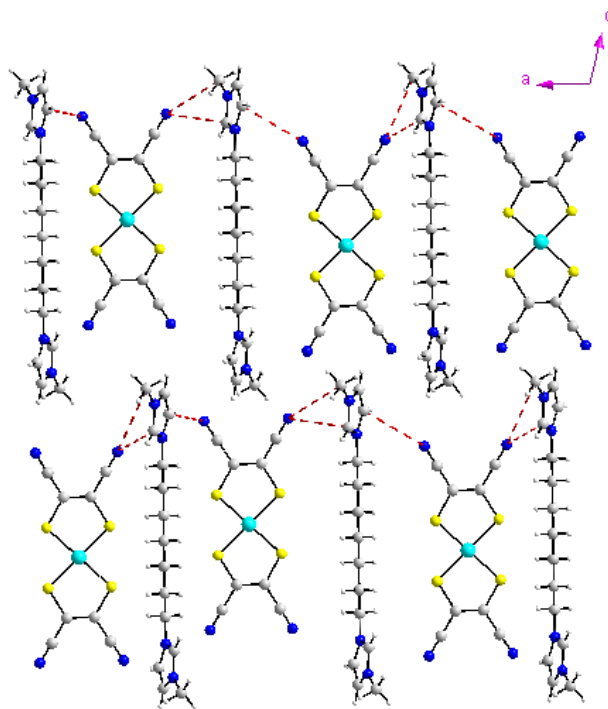
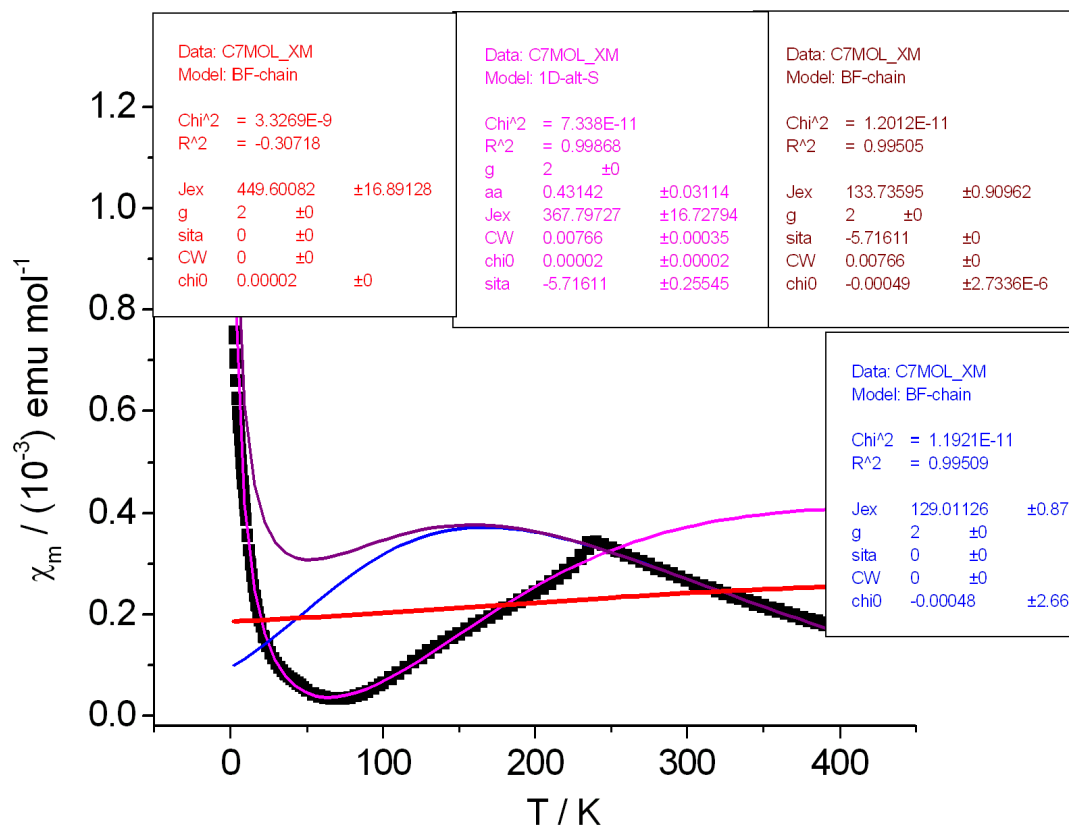


Figure S4 C-H...N interactions between the adjacent anionic and cationic stacks in **2**.



**Figure S5** Plot of  $\chi_m$  vs.  $T$  for **2** (the solid squares: experimental data over the temperature range 1.8-400 K; red, blue, wine and magenta lines: theoretically reproduced curves using the fitted parameters in the temperature range 245-400 K and 1.8-195 K, respectively; more details see the main text).