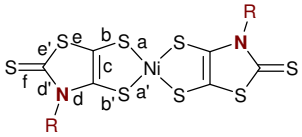
Electronic Supplementary Material (ESI) for Dalton Transactions.

Neutral, closed-shell nickel bis(2-alkylthio-thiazole-4,5-dithiolate) complexes as single component molecular conductors

Hadi Hachem, Zijun Xu, Nathalie Bellec, Olivier Jeannin, Pascale Auban-Senzier, Marc Fourmigué* and Dominique Lorcy*

SUPPLEMENTARY INFORMATION

Table S1 Bond distances within complexes $[C^+][Ni(R\text{-thiazdt})_2]^{2-,1-,0}$.



Complex	Ni–S (a,a')	S–C (b,b')	C=C (c)	C–N (d,d')	C–S (e,e')	C=S (f)	Ref
Neutral complex:							
R: Et	2.158(3)	1.686(3)	1.388(3)	1.378(3)	1.733(3)	1.640(2)	3
	2.158(1)	1.700(3)		1.372(3)	1.755(3)		
Monoanions:							
R: tBu	2.149(1)	1.717(6)	1.362(7)	1.440(8)	1.735(4)	(a)	this work
C^+: PPh_4^+	2.172(3)	1.733(5)		1.398(8)	1.731(14)		
R: tBu [(b)]	2.153(1)	1.715(4)	1.357(5)	1.422(4)	1.725(4)	1.671(4)	this work
C^+: PPh_4^+	2.162(1)	1.732(4)		1.367(5)	1.732(4)		
R: CH(Me)Ph	2.161(2)	1.708(6)	1.357(9)	1.399(8)	1.747(7)	1.645(7)	1
C^+: Et_4N^+	2.155(2)	1.709(7)		1.368(11)	1.746(7)		
R: Me	2.217(5)	1.713(6)	1.355(6)	1.395(5)	1.749(5)	1.658(3)	2
C^+: PPh_4^+	2.150(3)	1.719(6)		1.298(4)	1.779(3)		
R: Et [(c)]	2.156(1)	1.712(3)	1.356(3)	1.398(3)	1.739(2)	1.664(3)	3
C^+: PPh_4^+	2.178(2)	1.722(2)		1.362(4)	1.735(3)		
Dianions:							
R: Me	2.199(10)	1.735(10)	1.345(5)	1.405(9)	1.75(1)	1.678(10)	2
C^+: PPh_4^+	2.195(10)	1.732(9)		1.341(7)	1.751(6)		
R: Et	2.206(13)	1.735(11)	1.338(14)	1.409(12)	1.751(16)	1.692(15)	3
C^+: PPh_4^+	2.198(17)	1.741(12)		1.353(8)	1.732(18)		

[(a)] The C=S group is disordered. [(b)] Toluene solvate. (c) Acetonitrile solvate

References

[1] Y. Le Gal, A. Vacher, V. Dorcet, M. Fourmigué, J. Crassous and D. Lorcy, *New J. Chem.*, 2015, **39**, 122–129.

[2] S. Eid, M. Fourmigué, T. Roisnel and D. Lorcy, *Inorg. Chem.*, 2007, **46**, 10647–10654.

[3] A. Filatre-Furcate, N. Bellec, O. Jeannin, P. Auban-Senzier, M. Fourmigué, A. Vacher and D. Lorcy, *Inorg. Chem.*, 2014, *53*, 8681–8690.

Table S2 Calculated β interaction energies between frontier orbitals within nearest neighbors in crystalline [Ni(RS-tzdt)$_2$] (R = Me, Et) complexes. See Figure

	$\beta_{HOMO-HOMO}$	$\beta_{HOMO-LUMO}$	$\beta_{LUMO-HOMO}$	$\beta_{LUMO-LUMO}$
[Ni(MeS-tzdt)$_2$]				
Interaction I	–0.1709	–0.1131	+0.1131	+0.0345
Interaction II	–0.0397	–0.0343	+0.0343	+0.0268
Interaction III	–0.1293	–0.0050	–0.0050	+0.0235
[Ni(EtS-tzdt)$_2$]				
Interaction I	–0.1110	+0.3583	–0.3583	+0.2214
Interaction II	–0.0846	+0.0378	+0.0378	–0.0265
Interaction III	–0.1369	–0.0140	+0.0140	+0.0168

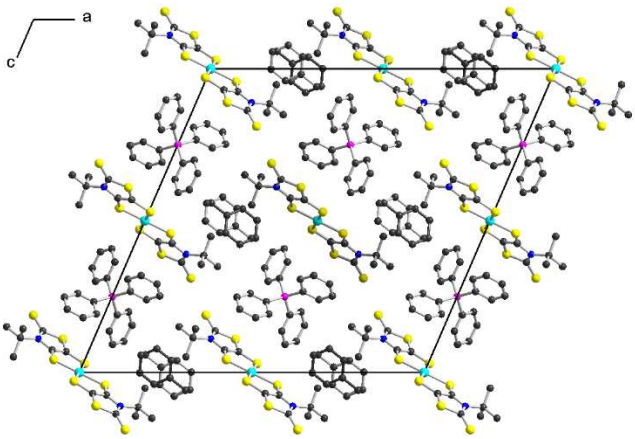


Fig. S1 Projection view along *b* of the unit cell of $[PPh_4][Ni(t\text{Bu-thiazdt})_2]$•toluene. Hydrogen atoms have been omitted for clarity. Bonds within the inversion centered disordered toluene molecules are highlighted in light and dark grey.

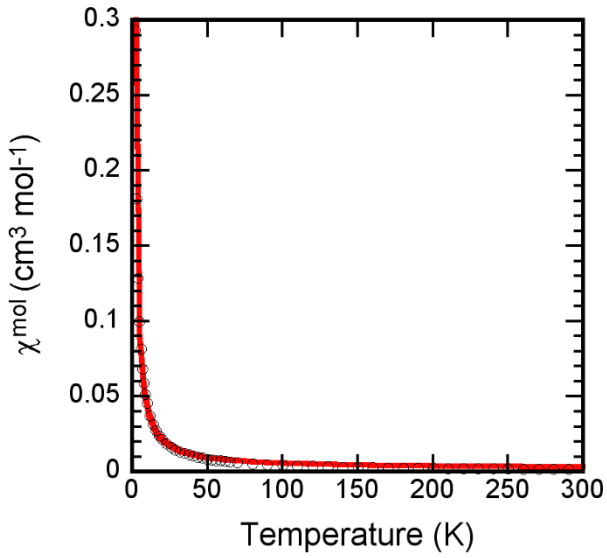


Fig. S2 Temperature dependence of the magnetic susceptibility of $[PPh_4][Ni(t\text{Bu-thiazdt})_2]$, with the Curie Weiss fit (see text).

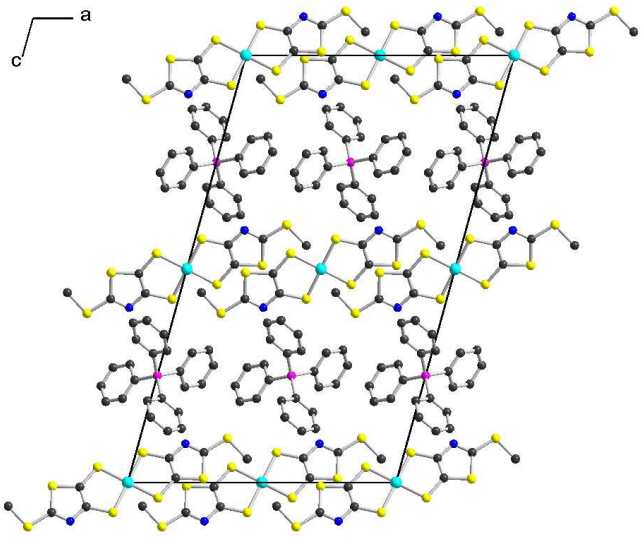


Fig. S3 Projection view along *b* of the unit cell of $[PPh_4][Ni(MeS\text{-}tzdt)_2]$. Hydrogen atoms have been omitted for clarity.

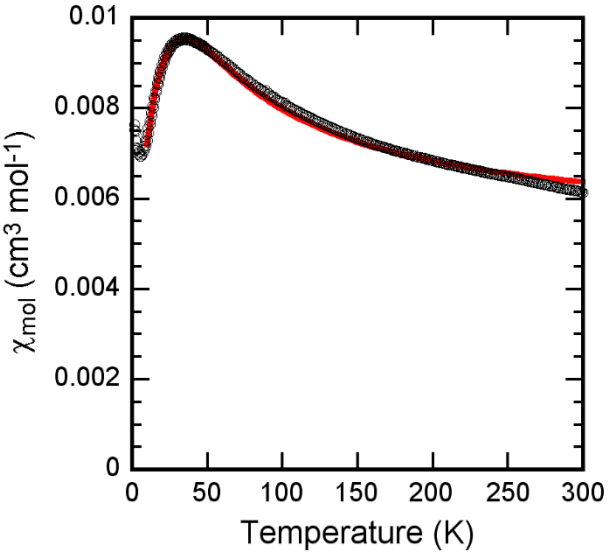


Fig S4 Temperature dependence of the magnetic susceptibility of $[PPh_4][Ni(MeS\text{-}tzdt)_2]$, with the Bonner-Fisher fit (red curve) for a uniform $S = ½$ spin chain. Note a large temperature independent paramagnetism (TIP) $\chi_0 = 5.3\times10^{-3}$ cm^3 mol^{-1} (see text).

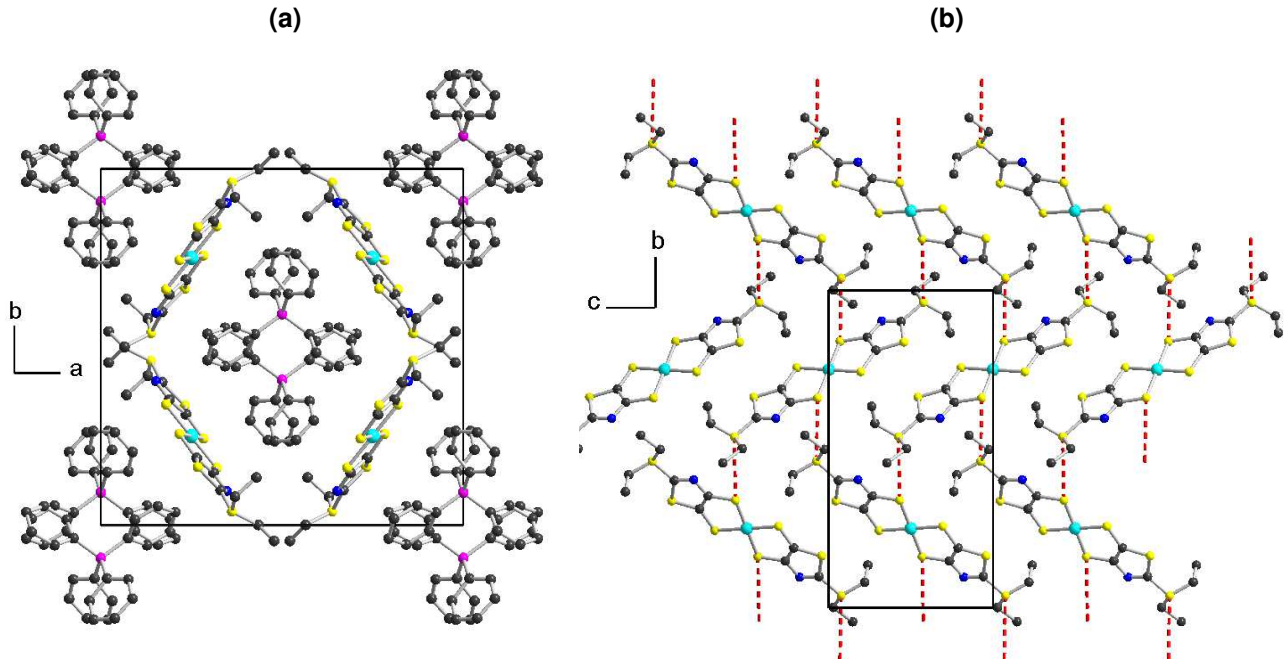


Fig. S5 (a) Projection view along *c* of the unit cell of $[PPh_4][Ni(EtS\text{-}tzdt)_2]$. Only one position of the disordered PPh_4^+ cation is shown. (b) Detail of the solid state organization of the radical anions within (bc) planes. The red dotted lines are associated with a short S•••S intermolecular contact at 3.823 Å. Hydrogen atoms have been omitted for clarity.

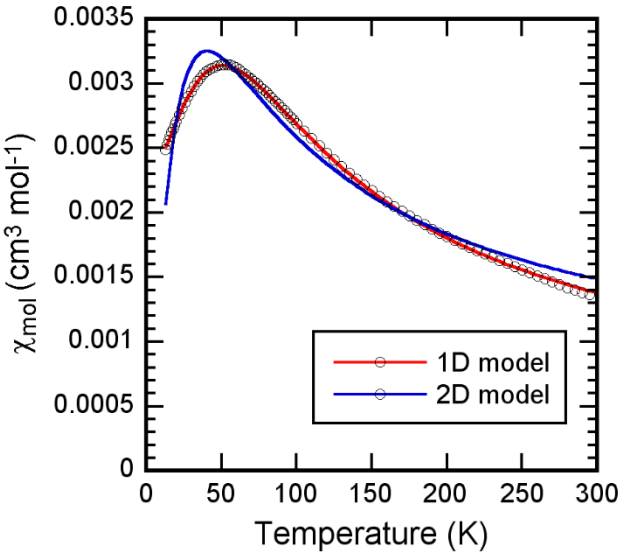


Fig S6 Temperature dependence of the magnetic susceptibility of $[PPh_4][Ni(EtS\text{-}tzdt)_2]$, with two different fits, the 1D Bonner-Fisher fit (red curve) for a uniform $S = ½$ spin chain, and the 2D $S = ½$ spin square lattice. The temperature independent paramagnetism (TIP) with the 1D model amounts to $\chi_0 = 3.1\times10^{-4}$ cm^3 mol^{-1} (see text).

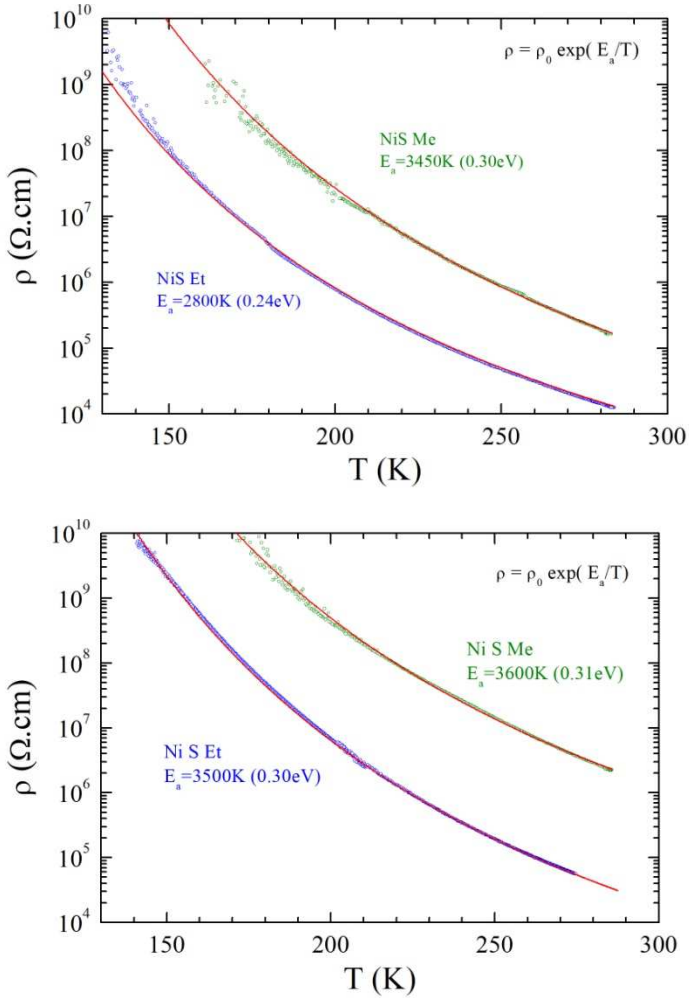


Fig S7 Temperature dependence of the resistivity of [Ni(EtS-tzdt)$_2$] and [Ni(MeS-tzdt)$_2$]. The red lines are the Arrhenius fits to the data giving the activation energies. Measurements performed without gold pads (top) and with gold pads (bottom).