Supporting information for

Description of the Ground State Wave Function of Ni Dithiolenes using Sulfur K-edge X-ray Absorption Spectroscopy

Robert K. Szilagyi, Booyong S. Lim, Thorsten Glaser, Richard H. Holm, Britt Hedman, Keith O. Hodgson, Edward I. Solomon

Table S1

Calculated S atomic charges (q, electron) by means of Mulliken (M), Hirshfeld (H) and Voronoi (V) population analyses, S 1s orbital energies (E(1s), eV) and estimated S 1s → 4p excitation energies (ΔE = E(4p) - E(1s), eV) for sulfide, thiolate and enedithiolate anions and Na salts (structures optimized at B88P86/BSIV level of theory, selected distances are given in Å unit)

anions		q^M	q^H	q^V	E(1s)	E(4p)	ΔE	S-C	C-C	Na...S
$[S]^{2-}$		-2.00	-2.00	-2.00	-2382.26	14.59	2396.85	-	-	-
	Δ	+1.22	+1.33	+1.29	-6.95		-1.7			
$[SC_2H_5]^-$		-0.78	-0.67	-0.71	-2389.21	5.94	2395.15	1.840	1.534	-
	Δ	+0.00	+0.01	+0.03	+3.04		-0.07			
$[S_2C_2Me_2]^{2-}$		-0.78	-0.66	-0.68	-2386.17	8.90	2395.08	1.786	1.386	-
Na salts		q^M	q^H	q^V	E(1s)	E(4p)	ΔE	S-C	C-C	Na...S
Na_2S		-0.75	-0.74	-0.76	-2393.35	4.59	2397.94	-	-	2.462
	Δ	+0.38	+0.27	+0.19	-0.82		+0.55			
$NaSC_2H_5$		-0.37	-0.47	-0.57	-2394.17	4.31	2398.49	1.844	1.527	2.396
	Δ	-0.06	+0.13	+0.20	-0.84		+0.66			
$Na_2S_2C_2Me_2$		-0.43	-0.34	-0.37	-2395.01	4.14	2399.15	1.810	1.378	2.623

Table S2

Basis set and population analysis calibration using the LUMO ($13b_{1g}$) of the $[Ni(S_2C_2Me_2)_2]^{2-}$ complex calculated at B88P86 level of theory by means of Mulliken (MPA), Weinhold's Natural (NPA) and Bader's Atoms-in-Molecule (AIM) methods

Slater-type all electron basis sets

	BSII	BSIII	BSIV	BSV
	MPA	MPA	MPA	MPA
Ni 3d, %	44	39	37	37
S 3p, %	49	51	52	52

Gaussian-type all electron basis sets

	BS2			BS5			BS6		
	MPA	NPA	AIM	MPA	NPA	AIM	MPA	NPA	AIM
Ni 3d, %	49	49	49	34	35	[a]	41	37	[a]
S 3p, %	41	42	45[b]	60	53	[a]	49	52	[a]

Effective core potentials with Gaussian-type valence electron basis sets

	ECP2			ECP5		
	MPA	NPA	AIM	MPA	NPA	AIM
Ni 3d, %	41	38	45	44	42	[a]
S 3p, %	49	53	48[b]	46	48	[a]

[a] not available due to convergence problems in AIM calculations
[b] contributions from other orbitals(mainly S 3s) are included

Table S3

Effect of various exchange and correlation density functionals on the LUMO ($13b_{1g}$) S 3p character (α^2, %) of $[Ni(S_2C_2Me_2)_2]^{2-}$ determined by means of Mulliken Population Analysis using BSIV

	α^2
VWN - B88 - P86 (reference)	52
variation of local functional	
Xα w/scaling of 0.7 - B88 - P86	49
VWN+Stoll correction - B88 - P86	50
variation of correlation functional	
VWN - B88 - LYP	53
VWN - B88 - PBE[a]	52
VWN - B88 - PW91	52
variation of exchange functional	
VWN - PW86 - P86	50
VWN - PW91 - P86	50
VWN - PBE - P86	50
VWN - PBE98- P86	48
VWN - PBE99- P86	49
VWN - LB94[b]- P86	63
VWN - SAOP[c] - P86	56

[a] Perdew-Bruke-Ernzerhof;
[b] van Leeuwen - Baerends;
[c] Statistical Average of Orbital Potentials

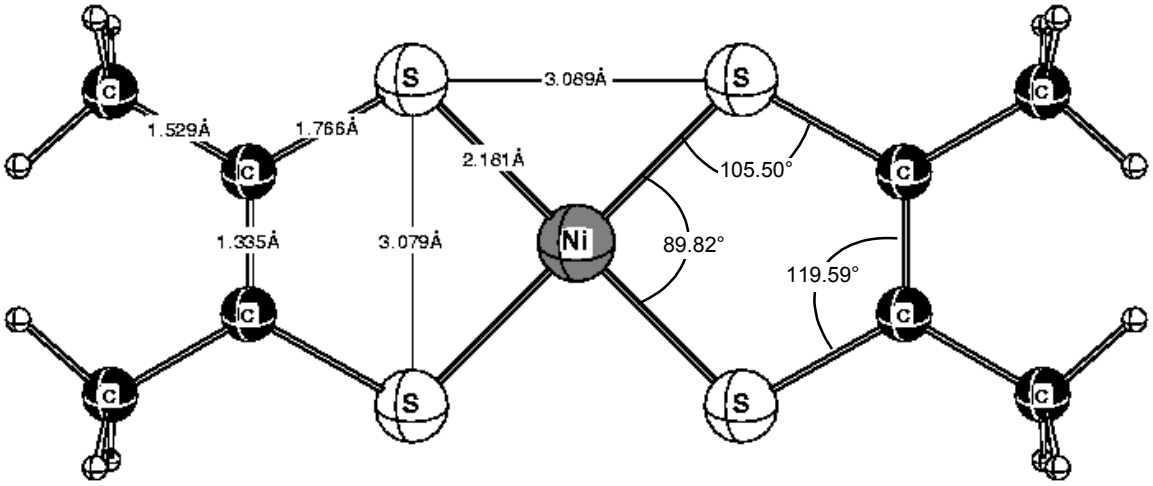
Table S4

Ground-state S 3p covalencies(α^2, %) by means of Mulliken Population Analysis calculated at LB94/BSIV level of theory

		α^2
Z = 2-	$13b_{1g}$	63
Z = 1-	$5b_{2g}$	66
	$13b_{1g}$	67
Z = 0	$5b_{2g}$	65
	$13b_{1g}$	67

Figure S1

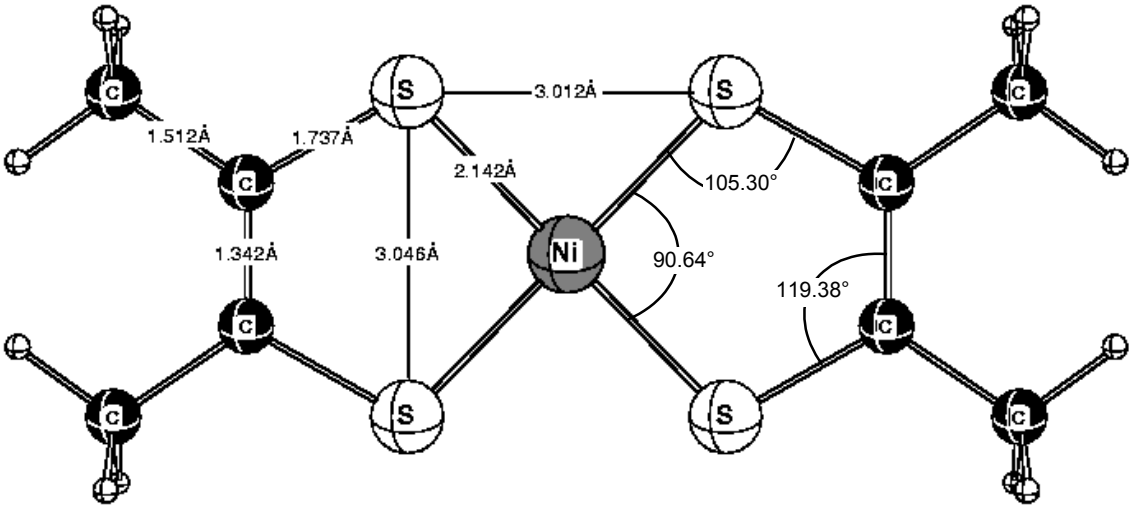
Symmetrized D_{2h} structure of $[Ni(S_2C_2Me_2]^{2-}$ with selected bond lengths (Å), bond angles (deg.) and Cartesian coordinates (Å)



Ni	0.00000	0.00000	0.00000
S	1.54430	1.53950	0.00000
S	1.54430	-1.53950	0.00000
C	3.07960	0.66770	0.00000
C	3.07960	-0.66770	0.00000
C	4.40070	1.43670	0.00000
C	4.40070	-1.43670	0.00000
H	4.45730	2.07680	0.90870
H	4.45730	2.07680	-0.90870
H	4.45730	-2.07680	0.90870
H	4.45730	-2.07680	-0.90870
H	5.24920	0.71650	0.00000
H	5.24920	-0.71650	0.00000
S	-1.54430	1.53950	0.00000
S	-1.54430	-1.53950	0.00000
C	-3.07960	0.66770	0.00000
C	-3.07960	-0.66770	0.00000
C	-4.40070	1.43670	0.00000
C	-4.40070	-1.43670	0.00000
H	-4.45730	2.07680	0.90870
H	-4.45730	2.07680	-0.90870
H	-4.45730	-2.07680	0.90870
H	-4.45730	-2.07680	-0.90870
H	-5.24920	0.71650	0.00000
H	-5.24920	-0.71650	0.00000

Figure S2

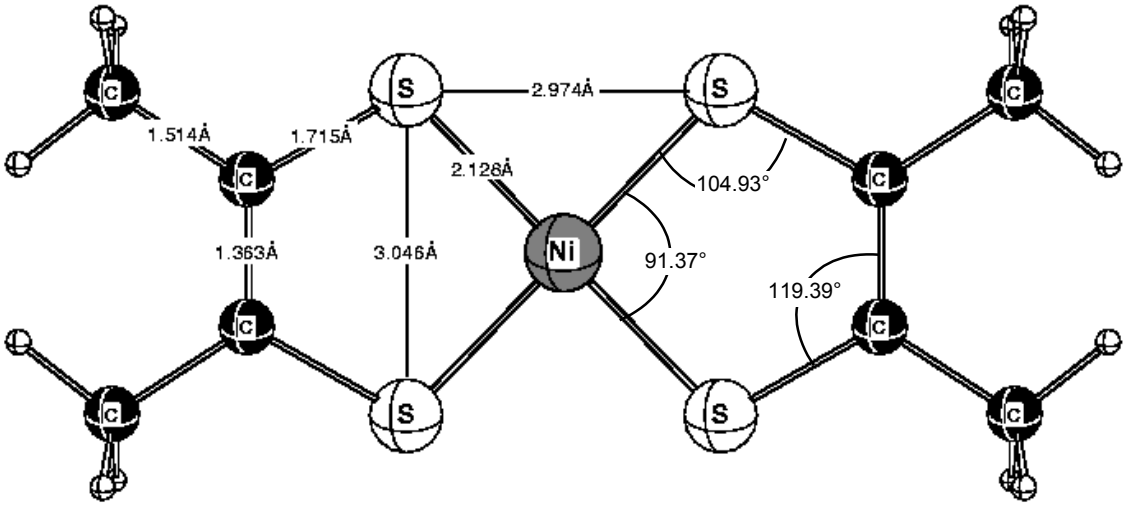
Symmetrized D_{2h} structure of $[Ni(S_2C_2Me_2]^{1-}$ with selected bond lengths (Å), bond angles (deg.) and Cartesian coordinates (Å)



Ni	0.00000	0.00000	0.00000
S	1.50615	1.52309	0.00000
S	1.50615	-1.52309	0.00000
C	3.01982	0.67085	0.00000
C	3.01982	-0.67085	0.00000
C	4.26640	1.52565	0.00000
C	4.26640	-1.52565	0.00000
H	4.27566	2.16816	0.90874
H	4.27566	2.16816	-0.90874
H	4.27566	-2.16816	0.90874
H	4.27566	-2.16816	-0.90874
H	5.16579	0.87004	0.00000
H	5.16579	-0.87004	0.00000
S	-1.50615	1.52309	0.00000
S	-1.50615	-1.52309	0.00000
C	-3.01982	0.67085	0.00000
C	-3.01982	-0.67085	0.00000
C	-4.26640	1.52565	0.00000
C	-4.26640	-1.52565	0.00000
H	-4.27566	2.16816	0.90874
H	-4.27566	2.16816	-0.90874
H	-4.27566	-2.16816	0.90874
H	-4.27566	-2.16816	-0.90874
H	-5.16579	0.87004	0.00000
H	-5.16579	-0.87004	0.00000

Figure S3

Symmetrized D_{2h} structure of [Ni($S_2C_2Me_2$] with selected bond lengths (Å), bond angles (deg.) and Cartesian coordinates (Å)



Ni	0.00000	0.00000	0.00000
S	1.48676	1.52282	0.00000
S	1.48676	-1.52282	0.00000
C	2.98099	0.68130	0.00000
C	2.98099	-0.68130	0.00000
C	4.25030	1.50673	0.00000
C	4.25030	-1.50673	0.00000
H	4.27528	2.14882	0.90874
H	4.27528	2.14882	-0.90874
H	4.27528	-2.14882	0.90874
H	4.27528	-2.14882	-0.90874
H	5.13336	0.82929	0.00000
H	5.13336	-0.82929	0.00000
S	-1.48676	1.52282	0.00000
S	-1.48676	-1.52282	0.00000
C	-2.98099	0.68130	0.00000
C	-2.98099	-0.68130	0.00000
C	-4.25030	1.50673	0.00000
C	-4.25030	-1.50673	0.00000
H	-4.27528	2.14882	0.90874
H	-4.27528	2.14882	-0.90874
H	-4.27528	-2.14882	0.90874
H	-4.27528	-2.14882	-0.90874
H	-5.13336	0.82929	0.00000
H	-5.13336	-0.82929	0.00000

Figure S4

Representative fit for paramagnetic contamination corrected S K-edge pre-edge feature and second derivative of the $(Et_4N)_2[Ni(S_2C_2Me_2]$ compound

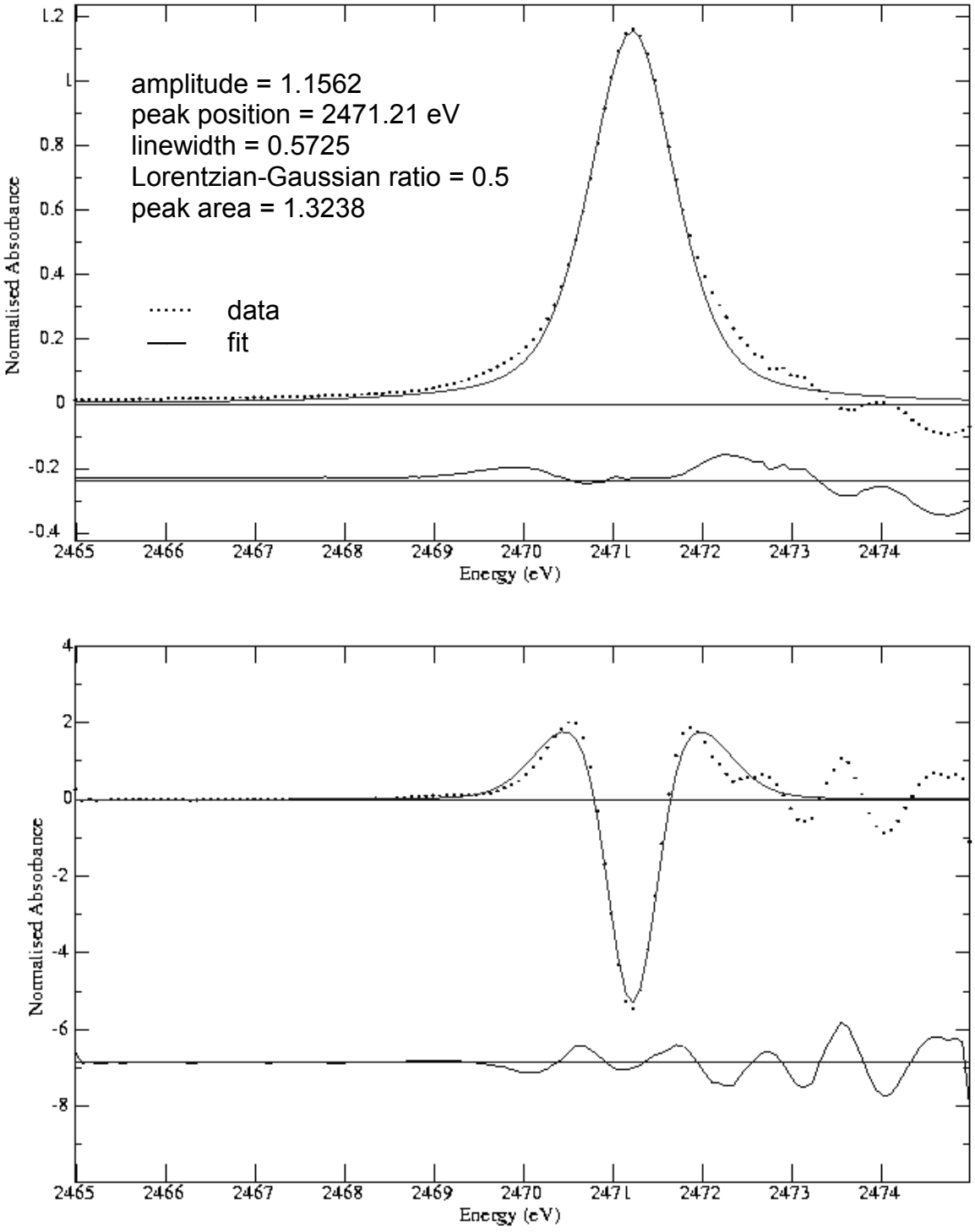


Figure S5

Representative fit for the S K-edge pre-edge features and second derivatives of the $(Et_4N)[Ni(S_2C_2Me_2]$ compound

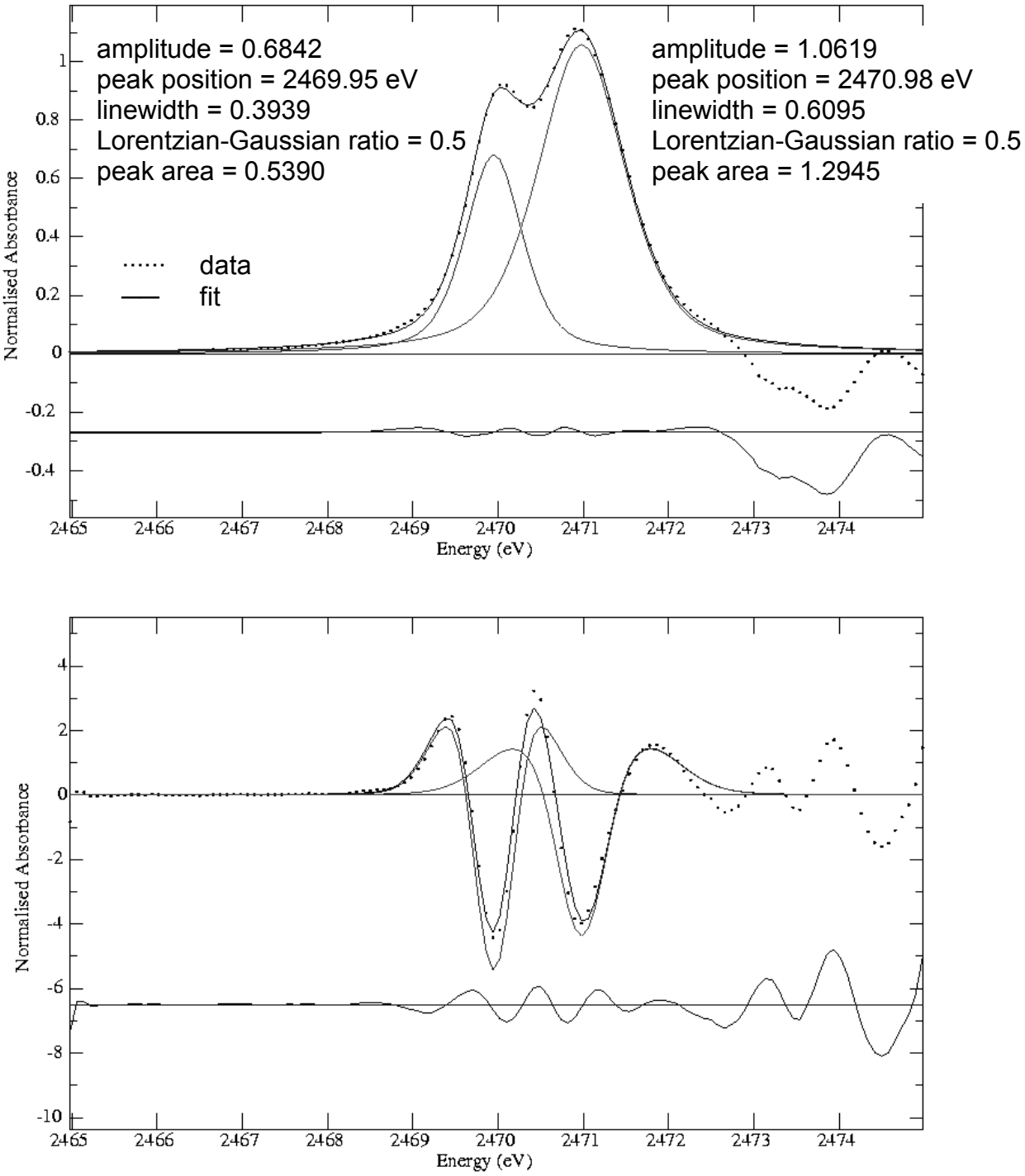


Figure S6

Representative fit for the S K-edge pre-edge features and second derivatives of the [Ni($S_2C_2Me_2$] compound

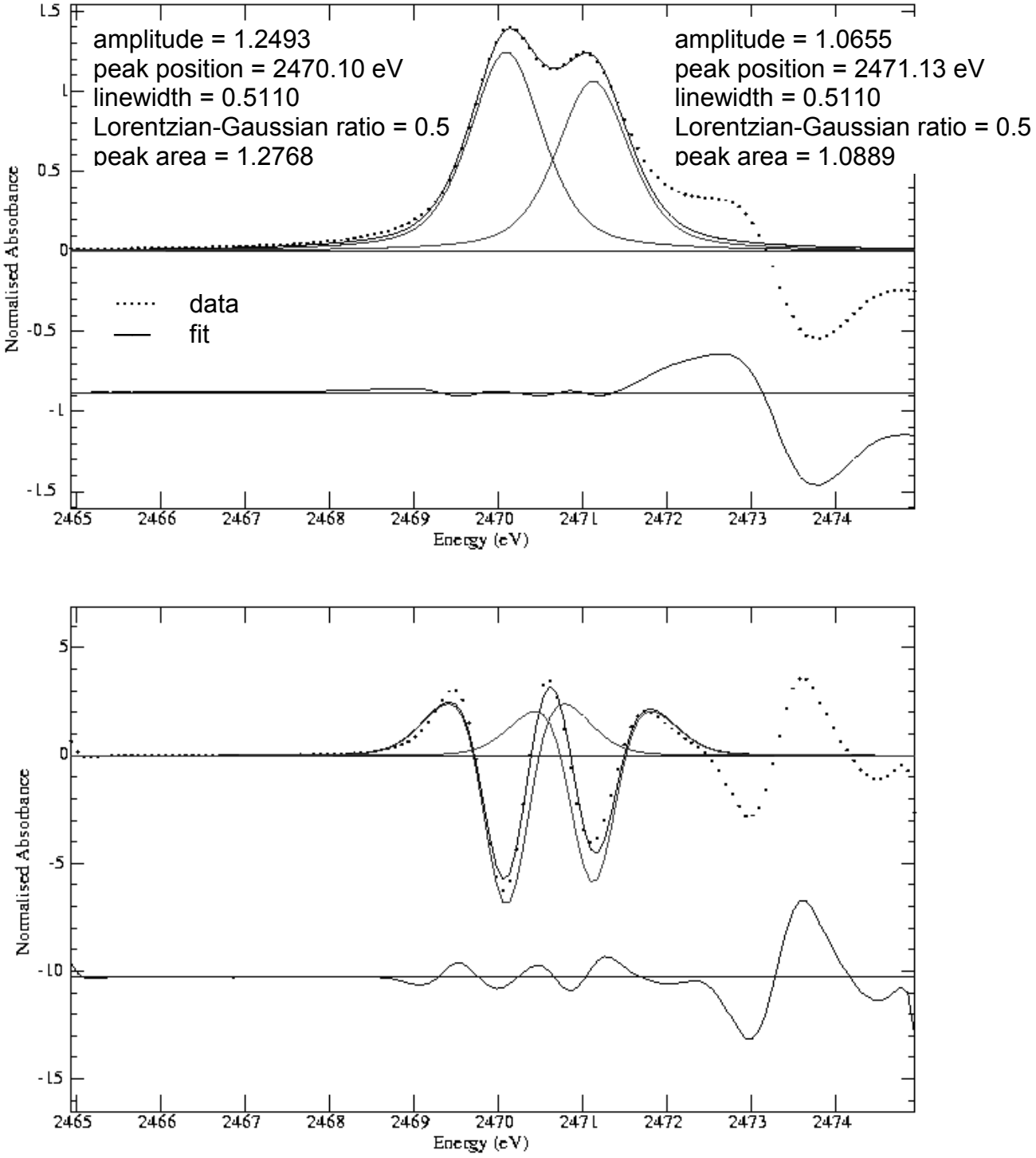


Figure S7

Nickel K-edge spectra of $(Et_4N)_2[Ni(S\text{-}2Ph\text{-}C_6H_4)_4]$ (solid line), $(Et_4N)_2[Ni(S_2C_2Me_2)_2]$ (dashed line), $(Et_4N)[Ni(S_2C_2Me_2)_2]$ (dotted line), and $[Ni(S_2C_2Me_2)_2]$ (dashed-dotted line) compounds with Ni 1s → $4p_z$ transitions indicated for the dithiolene complexes