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Topological Features of both Electron Density and Electrostatic Potential in Bis(tiosemicarbazide)zinc(II) dinitrate Complex

Sladjana B. Novaković, Goran A. Bogdanović, Bernard Fraisse, Nour Eddine Ghermani, Nouzha Bouhmaida, Anne Spasojevic - de Biré

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Figure S5. Static deformation density maps of hydrogen bonds: in the N-H...O plane; orthogonal to N-H...O plane.

The results of the additional strategy which includes the refinement of the multipole parameters for Zn atom

Table S1. Crystallographic, data collection and reduction details.

Diffractometer		SMART CCD 1K				
Sample condition, temperature		N ₂ stream, 100 K				
Chemical formula		C ₂ H ₁₀ N ₂ S ₂ O ₆ Zn				
Molecular weight		371.7				
F ₀₀₀		752				
Density		2.15				
Crystal system		Monoclinic				
Space group		C 1 2/c 1				
Z		4				
Unit cell dimensions :	a (Å)	10.9541(3)				
	b (Å)	7.5673(2)				
	c (Å)	14.1753(3)				
	α (°)	90.000(2)				
	β (°)	101.630(2)				
	γ (°)	90.003(2)				
Volume (Å ³)		1150.90(6)				
Absorption coefficient μ (mm ⁻¹)		2.540				
Crystal dimensions: (mm) x (mm) x (mm)		0.47 x 0.43 x 0.30				
Colour		White translucent				
Wavelength (Å)		0.71073				
Detector-sample distance (cm)		4.082				
2θ-detector position (°)		0	28	-45	60	-75
Scan mode		ω				
Scan width (°)		-0.15				
Time per frame (s)		2	5	10	20	30
Number of measured frames		24000				
(sin θ/λ) _{max} (Å ⁻¹)		1.10				
h _{min} ; k _{min} ; l _{min}		-25 ; -17 ; -33				
h _{max} ; k _{max} ; l _{max}		24 ; 17 ; 33				
Integration box size X (°) x Y (°) x Z (°)		2.80 x 2.80 x 1.80			2.60 x 2.60 x 2.30	
I/σ threshold for the profile integration		10				
SADABS	Number of measured reflections	55584				
	R _{int} before SADABS	0.0623				
	R _{int} after SADABS	0.0195				
SORTAV	R ₁	0.0167				
	All data	53409				
	<N>, redundancy	7.4				
	Number of unique reflections	7616				
SHELXL	Number of measured reflections F ₀ > 4σ(F ₀)	7140				
	R ₁ (F ₀ > 4σ(F ₀))	0.0174				
	R ₁ (all)	0.0188				
	wR ₂	0.0444				
	goof	0.98				
	Number of refined parameters	108				

Table S2. Summary of the least-squares refinements.

	Spherical atom model	High Order	Pval-κ model	Multipolar model (strategy I)	Multipolar model (strategy II)
sinθ/λ range	0.05-1.10	0.80-1.11	0.05-1.10	0.05-1.10	0.05-1.10
Nobs (I>3σ _I)	5904	2517	5904	5904	5904
Npar	108	124	32	258	258
R[F]	1.66%	1.55%	1.63%	1.15%	1.15%
R _w [F]	2.00%	1.52%	1.97%	1.33%	1.33%
GoF	1.25	0.86	1.28	0.88	0.88

Table S3. Bond distances and angles.
(strategy I)

Bond	(Å)	Angle	(°)
Zn1-N1	2.0918(2)	N1-Zn1-S1	88.47(1)
Zn1-S1	2.2667(2)	N1-Zn1-S1_2	113.62(2)
N1-N2	1.4114(2)	N1-Zn1-N1_2	122.06(1)
C1-N2	1.3419(3)	S1-Zn-S1_2	134.59(1)
C1-N3	1.3274(3)	Zn1-N1-N2	110.68(1)
C1-S1	1.7194(2)	Zn1-S1-C1	95.37(1)
O1-N4	1.2561(2)	N1-N2-C1	121.64(2)
O2-N4	1.2568(3)	N2-C1-S1	123.61(2)
O3-N4	1.2418(3)	N2-C1-N3	117.45(2)
N1-H1a	0.997(10)	S1-C1-N3	118.94(2)
N1-H1b	1.030(9)	H1a-N1-H1b	107.97(2)
N2-H2	0.991(10)	N2-N1-H1a	109.92(2)
N3-H3a	1.006(10)	N2-N1-H1b	107.13(2)
N3-H3b	0.984(10)	Zn1-N1-H1a	114.34(2)
		Zn1-N1-H1b	106.47(2)
		N1-N2-H2	116.41(2)
		C1-N2-H2	121.67(2)
		H3a-N3-H3a	121.27(2)
		C1-N3-H3a	120.03(2)
		C1-N3-H3b	118.62(2)
		O1-N4-O2	120.20(2)
		O1-N4-O3	119.41(3)
		O2-N4-O3	120.38(3)

(strategy II)

Bond	(Å)	Angle	(°)
Zn1-N1	2.0918(2)	N1-Zn1-S1	88.47(1)
Zn1-S1	2.2667(2)	N1-Zn1-S1_2	113.62(2)
N1-N2	1.4114(2)	N1-Zn1-N1_2	122.06(1)
C1-N2	1.3419(3)	S1-Zn-S1_2	134.59(1)
C1-N3	1.3274(3)	Zn1-N1-N2	110.68(1)
C1-S1	1.7194(2)	Zn1-S1-C1	95.37(1)
O1-N4	1.2567(2)	N1-N2-C1	121.64(2)
O2-N4	1.2560(3)	N2-C1-S1	123.61(2)
O3-N4	1.2418(3)	N2-C1-N3	117.45(2)
N1-H1a	0.981(10)	S1-C1-N3	118.94(2)
N1-H1b	1.026(9)	H1a-N1-H1b	108.00(2)
N2-H2	0.976(10)	N2-N1-H1a	114.33(2)
N3-H3a	1.000(10)	N2-N1-H1b	107.14(2)
N3-H3b	0.974(10)	Zn1-N1-H1a	114.34(2)
		Zn1-N1-H1b	106.40(2)
		N1-N2-H2	116.50(2)
		C1-N2-H2	121.57(2)
		H3a-N3-H3a	121.38(2)
		C1-N3-H3a	120.00(2)
		C1-N3-H3b	118.55(2)
		O1-N4-O2	120.20(2)
		O1-N4-O3	119.41(3)
		O2-N4-O3	120.38(3)

Table S4. Topological proprieties of covalent bonds (strategy II).

Bond	length (Å)	d ₁	d ₂	ρ	∇ ² ρ	λ ₁	λ ₂	λ ₃	ε	G	V	H
Zn1-N1	2.0918(2)	0.999	1.093	0.52	7.18	-2.86	-2.67	12.72	0.07	234.17	-237.11	-38.94
Zn1-S1	2.2667(2)	1.050	1.217	0.40	5.06	-1.81	-1.68	8.56	0.07	158.97	-180.37	-21.40
N1-N2	1.4114(2)	0.695	0.716	2.06	-3.64	-16.17	-15.09	27.62	0.07	975.53	-2050.04	-1074.51
C1-N2	1.3419(3)	0.555	0.787	2.35	-22.32	-19.30	-16.71	13.69	0.15	892.59	-2395.55	-1500.03
C1-N3	1.3274(3)	0.552	0.775	2.43	-23.27	-20.63	-16.59	13.95	0.24	949.80	-2532.35	-1582.55
C1-S1	1.7194(2)	0.886	0.834	1.30	-2.60	-6.98	-5.64	10.02	0.23	436.44	-934.58	-507.14
O1-N4	1.2567(2)	0.624	0.632	3.06	-6.19	-26.33	-23.38	43.53	0.13	1904.85	-3905.11	-2000.26
O2-N4	1.2560(3)	0.622	0.635	3.06	-6.30	-26.49	-23.50	43.69	0.13	1901.96	-3972.22	-2070.26
O3-N4	1.2418(3)	0.622	0.620	3.19	-11.05	-28.22	-24.00	41.17	0.18	1958.49	-4217.44	-2258.95
N1-H1a	0.981(10)	0.726	0.268	2.15	-18.86	-28.77	-26.49	36.40	0.09	776.57	-2055.98	-1289.41
N1-H1b	1.026(9)	0.735	0.295	2.06	-16.69	-25.06	-23.17	31.73	0.08	738.97	-1931.76	-1192.79
N2-H2	0.976(10)	0.740	0.248	2.13	-21.27	-29.18	-26.72	33.85	0.09	715.60	-2009.57	-1293.97
N3-H3a	1.000(10)	0.726	0.240	2.12	-28.85	-29.30	-27.53	27.98	0.06	569.60	-1923.68	-1354.08
N3-H3b	0.974(10)	0.722	0.262	2.27	-24.96	-31.41	-29.18	34.94	0.08	771.98	-2222.65	-1450.67

d₁, d₂ are the distances from the critical point to atoms 1 and 2 in (Å); ρ is the electron density in (e.Å⁻³); ∇²ρ is the Laplacian in (e.Å⁻⁵), λ₁, λ₂, λ₃ are the principle curvatures in (e.Å⁻⁵), G, V, H are kinetic energy density, potential energy density and total energy density, respectively in (KJ.mol.borh⁻¹).

Table S5. Topological proprieties of hydrogen bonds (strategy II).

Bond	H...O (Å)	N-H...O (°)	d1	d2	ρ	∇ ² ρ	λ ₁	λ ₂	λ ₃	ε	G	V	H
N3-H3a...O2 ⁱ	1.8503(2)	175.58(1)	0.632	1.222	0.12	3.81	-0.62	-0.58	5.00	0.06	78.19	-53.04	25.15
N2-H2...O1 ⁱ	1.9382(3)	178.72(2)	0.703	1.225	0.14	2.90	-0.71	-0.69	4.30	0.03	64.25	-49.77	14.48
N1-H1a...O3 ⁱⁱ	2.0061(2)	158.97(2)	0.726	1.284	0.09	2.57	-0.47	-0.41	3.44	0.17	52.21	-34.57	17.64
N3-H3b...O1 ⁱⁱⁱ	2.0901(2)	156.42(2)	0.801	1.373	0.05	1.91	-0.27	-0.23	2.42	0.24	36.73	-20.71	15.20
N1-H1b...O3 ^{iv}	2.2981(2)	158.38(2)	0.905	1.478	0.03	1.12	-0.14	-0.05	1.31	0.67	21.21	-11.97	9.24
N1-H1b...O2 ^{iv}	2.4650(3)	108.32(2)	1.067	1.439	0.05	0.98	-0.24	-0.14	1.37	0.65	19.87	-13.10	6.77
N1-H1a...O1 ⁱⁱ	2.4710(3)	148.67(1)	1.031	1.612	0.02	0.57	-0.05	-0.04	0.68	0.57	10.79	-6.09	4.70
N3-H3a...O3 ^v	2.5737(3)	107.46(2)1	1.159	1.467	0.04	0.82	-0.14	-0.12	1.08	0.14	16.33	-10.37	5.96
N1-H1b...O2 ^{vi}	2.6111(3)	08.32(1)	1.211	1.501	0.04	0.71	-0.13	0.10	0.94	0.77	14.34	-9.38	4.96

(i) x,y,z; (ii) -x+0.5,-y+0.5,-z+1; (iii) x+0.5,y+0.5,z; (iv) x,y,z+0.5; (v) -x+0.5,y+0.5,-z+0.5; (vi) -x+0.5,y+0.5,-z+1.

Table S6. Net atomic charges.

ATOM	Strategy I		Strategy II	
	Kappa	AIM	Kappa	AIM
Zn1	1.45(4)	0.61	1.41(3)	0.63
S1	0.01(5)	0.12	0.03(4)	0.15
N1	-0.70(8)	-0.73	-0.69(2)	-0.72
N2	-0.24(7)	-0.83	-0.23(5)	-0.85
N3	-0.99(9)	-1.22	-0.99(7)	-1.29
N4	0.62(5)	0.65	0.58(7)	0.67
C1	0.15(8)	0.73	0.15(6)	0.67
O1	-0.59(4)	-0.54	-0.59(5)	-0.55
O2	-0.45(4)	-0.56	-0.45(4)	-0.56
O3	-0.53(4)	-0.57	-0.54(3)	-0.56
H1a	0.38(5)	0.53	0.39(5)	0.52
H1b	0.37(5)	0.45	0.36(5)	0.44
H2	0.28(5)	0.50	0.28(5)	0.523
H3a	0.45(6)	0.59	0.46(5)	0.65
H3b	0.53(5)	0.58	0.54(5)	0.61

Table S7a. Atomic coordinates, anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms after the multipolar refinement (strategy I).

	x	y	z	U(1.1)	U(2.2)	U(3.3)	U(1.2)	U(1.3)	U(2.3)
Zn1	0.50000	0.16713(1)	0.75000	0.00218(1)	0.00371(1)	0.00061(1)	0.00000	0.00027(1)	0.00000
N1	0.35667(2)	0.03320(3)	0.65767(1)	0.00219(1)	0.00365(2)	0.00091(1)	-0.00113(2)	0.00062(1)	0.00032(2)
N2	0.35293(2)	0.08165(3)	0.56097(2)	0.00181(1)	0.00404(2)	0.00078(1)	-0.00151(2)	0.00032(1)	-0.00010(2)
N3	0.42828(2)	0.22683(3)	0.44366(2)	0.00220(1)	0.00545(3)	0.00073(1)	-0.00135(3)	0.00033(1)	0.00031(2)
C1	0.43834(2)	0.19023(3)	0.53650(2)	0.00147(1)	0.00324(2)	0.00072(2)	-0.00016(2)	0.00033(1)	-0.00001(2)
S1	0.55857(1)	0.28277(1)	0.61841(1)	0.00146(1)	0.00401(1)	0.00080(1)	-0.00098(1)	0.00020(1)	0.00001(1)
N4	0.32555(2)	0.56438(3)	0.66716(1)	0.00155(1)	0.00300(2)	0.00087(1)	-0.00004(2)	0.00046(1)	-0.00001(2)
O1	0.33332(3)	0.60002(4)	0.58202(1)	0.00228(1)	0.00588(3)	0.00099(1)	-0.00108(3)	0.00086(1)	0.00066(2)
O2	0.27966(3)	0.41977(4)	0.68642(2)	0.00243(1)	0.00387(2)	0.00125(1)	-0.00158(3)	0.00031(1)	0.00060(2)
O3	0.36185(4)	0.67230(5)	0.73284(2)	0.00355(2)	0.00385(3)	0.00128(1)	-0.00065(4)	0.00023(2)	-0.00108(2)
H1a	0.3605(9)	-0.0981(13)	0.6641(7)	0.025(1)					
H1b	0.2744(9)	0.0753(12)	0.6749(7)	0.027(2)					
H2	0.2893(9)	0.0218(14)	0.5117(7)	0.024(2)					
H3a	0.3566(10)	0.1778(13)	0.3950(8)	0.022(2)					
H3b	0.4896(9)	0.3071(14)	0.4244(8)	0.025(2)					

Table S7b. Atomic coordinates with anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms after the multipolar refinement (strategy II).

	x	y	z	U(1.1)	U(2.2)	U(3.3)	U(1.2)	U(1.3)	U(2.3)
Zn1	0.50000	0.16711(1)	0.75000	0.00217(2)	0.00370(1)	0.00061(1)	0.00000	0.00026(1)	0.00000
N1	0.35667(2)	0.03320(3)	0.65767(1)	0.00219(1)	0.00365(2)	0.00091(1)	-0.00113(2)	0.00062(1)	0.00032(2)
N2	0.35293(2)	0.08165(3)	0.56097(2)	0.00181(1)	0.00404(2)	0.00078(1)	-0.00151(2)	0.00032(1)	-0.00010(2)
N3	0.42828(2)	0.22683(3)	0.44366(2)	0.00220(1)	0.00545(3)	0.00073(1)	-0.00135(3)	0.00033(1)	0.00031(2)
C1	0.43834(2)	0.19023(3)	0.53650(2)	0.00147(1)	0.00324(2)	0.00072(2)	-0.00016(2)	0.00033(1)	-0.00001(2)
S1	0.55857(1)	0.28277(1)	0.61841(1)	0.00146(1)	0.00402(1)	0.00080(1)	-0.00098(1)	0.00020(1)	0.00001(1)
N4	0.32555(2)	0.56438(3)	0.66716(1)	0.00155(1)	0.00300(2)	0.00087(1)	-0.00004(2)	0.00046(1)	-0.00001(2)
O1	0.33332(3)	0.60002(4)	0.58202(1)	0.00228(1)	0.00588(3)	0.00099(1)	-0.00108(3)	0.00086(1)	0.00066(2)
O2	0.27965(3)	0.41977(4)	0.68642(2)	0.00243(1)	0.00387(2)	0.00125(1)	-0.00158(3)	0.00031(1)	0.00060(2)
O3	0.36185(4)	0.67230(5)	0.73284(2)	0.00355(2)	0.00385(3)	0.00128(1)	-0.00065(4)	0.00023(2)	-0.00108(2)
H1a	0.3604(9)	-0.0976(13)	0.6641(7)	0.025(1)					
H1b	0.2747(9)	0.0753(12)	0.6749(7)	0.026(2)					
H2	0.2896(9)	0.0221(14)	0.5118(7)	0.025(2)					
H3a	0.3566(10)	0.1778(13)	0.3950(8)	0.020(2)					
H3b	0.4896(9)	0.3068(14)	0.4245(8)	0.024(2)					

Table S8 Gram-Charlier coefficients and their estimated standard deviations for anharmonic thermal vibration of Zn atom.

C ₂₂₂	.0050(6)
C ₁₁₂	-.004(1)
C ₂₃₃	.003(1)
C ₁₂₃	-.006(2)
C ₁₁₁₁	.0040(5)
C ₂₂₂₂	-.0017(5)
C ₃₃₃₃	.0013(4)
C ₁₁₁₃	.003(1)
C ₁₁₂₂	-.008(2)
C ₁₁₃₃	-.007(2)
C ₁₂₂₃	-.001(1)
C ₁₃₃₃	.001(1)
C ₂₂₃₃	-.005(2)
C ₂₂₂₂₂	-.0008(1)
C ₁₁₁₁₂	.0004(4)
C ₁₁₁₂₃	.0017(8)
C ₁₁₂₂₂	-.0017(5)
C ₁₁₂₃₃	-.0005(8)
C ₁₂₂₂₃	.00161(8)
C ₁₂₃₃₃	.0005(7)
C ₂₂₂₃₃	-.0007(4)
C ₂₃₃₃₃	-.0005(4)
C ₁₁₁₁₁₁	-.0007(2)
C ₂₂₂₂₂₂	.0006(1)
C ₃₃₃₃₃₃	-.0002(1)
C ₁₁₁₁₁₃	-.0012(4)
C ₁₁₁₁₂₂	.00016(6)
C ₁₁₁₁₃₃	.0004(6)
C ₁₁₁₂₂₃	.002(1)
C ₁₁₁₃₃₃	-.0009(6)
C ₁₁₂₂₂₂	.0020(5)
C ₁₁₂₂₃₃	.006(1)
C ₁₁₃₃₃₃	-.0003(5)
C ₁₂₂₂₂₃	-.0009(8)
C ₁₂₂₃₃₃	.0003(9)
C ₁₃₃₃₃₃	-.0002(3)
C ₂₂₂₂₃₃	.0020(5)
C ₂₂₃₃₃₃	.0011(5)

Table S9a. Multipolar refinement parameters for non-H atoms (Strategy I).

	Zn1	N1	N2	N3	C1	S1	N4	O1	O2	O3
κ	1.95(4)	0.974(4)	0.978(5)	0.982(5)	0.986(7)	1.056(4)	0.983(4)	0.985(2)	0.982(3)	0.985(3)
κ^2	1.00	0.76(1)	0.88(2)	0.82(2)	0.91(1)	0.82(2)	0.83(1)	1.03(2)	1.00(2)	1.21(2)
P_{val}	1.12(3)	5.59(8)	5.29(7)	5.43(9)	4.17(8)	5.96(5)	5.10(5)	6.35(4)	6.35(4)	6.37(4)
P_{00}	10.00									
P_{11}		-0.20(2)	0.00(16)	-0.05(2)	0.07(2)	-0.07(2)	0.01(1)	-0.11(1)	-0.09(1)	-0.09(1)
P_{1-1}		0.06(2)	0.13(16)	0.01(2)	-0.01(2)	0.03(2)	-0.02(1)	-0.03(1)	-0.01(1)	0.02(1)
P_{10}		0.03(3)	0.02(13)	0.03(1)	0.04(2)	-0.02(2)	-0.01(1)	-0.01(1)	-0.00(1)	0.05(1)
P_{20}		0.02(2)	0.03(14)	-0.05(2)	-0.31(2)	0.08(1)	-0.26(1)	-0.01(1)	-0.01(1)	-0.03(1)
P_{21}		-0.03(2)	0.01(12)	0.03(1)	0.01(2)	0.01(1)	-0.01(1)	-0.01(1)	-0.00(1)	0.00(1)
P_{2-1}		-0.02(2)	0.01(12)	0.02(1)	0.02(2)	-0.04(1)	-0.01(1)	-0.01(1)	0.00(1)	0.01(1)
P_{22}		-0.17(1)	0.01(12)	-0.04(2)	-0.01(2)	-0.14(1)	0.01(1)	-0.14(1)	-0.16(1)	-0.13(1)
P_{2-2}		-0.02(1)	0.04(13)	0.01(2)	-0.04(2)	0.01(1)	-0.01(1)	0.01(1)	0.01(1)	-0.01(1)
P_{30}		0.06(2)	0.02(14)	-0.01(2)	-0.01(2)	-0.05(2)	-0.01(1)	-0.01(1)	-0.02(1)	0.01(1)
P_{31}		-0.23(2)	0.03(14)	0.03(2)	0.01(2)	-0.01(1)	-0.03(1)	0.01(1)	0.01(1)	0.02(1)
P_{3-1}		-0.16(2)	0.01(14)	-0.01(2)	0.04(2)	-0.03(1)	0.01(1)	0.03(1)	-0.01(1)	0.04(1)
P_{32}		0.00(2)	0.01(14)	0.01(2)	0.02(2)	-0.04(1)	-0.01(1)	-0.02(1)	-0.02(1)	-0.03(1)
P_{3-2}		-0.03(2)	0.00(14)	-0.00(2)	-0.01(2)	-0.04(1)	-0.01(1)	-0.01(1)	-0.03(1)	0.01(1)
P_{33}		0.22(2)	0.25(14)	0.29(2)	0.38(2)	0.12(2)	0.45(1)	-0.01(1)	0.01(1)	0.01(1)
P_{3-3}		-0.02(2)	0.01(14)	-0.01(2)	0.02(2)	0.08(1)	0.01(1)	-0.01(1)	-0.02(1)	-0.00(1)

Table S9a. Multipolar refinement parameters for H atoms (Strategy I).

	H1a	H1b	H2n	H3a	H3b
κ	1.49(8)	1.38(7)	1.30(6)	1.25(6)	1.42(8)
P_{val}	0.61(5)	0.49(5)	0.63(5)	0.61(6)	0.53(5)
P_{11}	0.15(3)	0.12(3)	0.09(2)	0.16(2)	0.16(2)

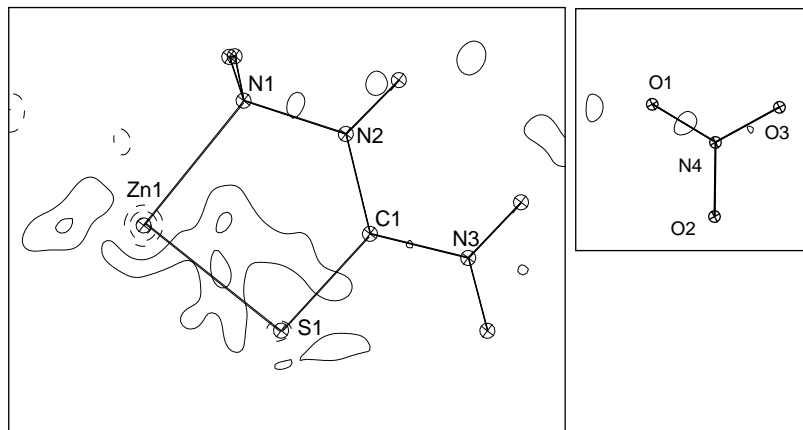
Table S10b. Multipolar refinement parameters for non-H atoms in $[\text{Zn}(\text{TSC})_2](\text{NO}_3)_3$ (Strategy II).

	Zn1	N1	N2	N3	C1	S1	N4	O1	O2	O3
κ	1.92(4)	0.974(4)	0.978(5)	0.982(5)	0.986(7)	1.056(4)	0.983(4)	0.983(3)	0.980(3)	0.981(3)
κ^2	1.00	0.77(1)	0.89(2)	0.83(2)	0.92(1)	0.81(2)	0.82(1)	1.04(2)	1.00(2)	1.21(2)
P_{val}	1.10(3)	5.59(8)	5.31(7)	5.46(9)	4.17(8)	6.00(5)	5.10(5)	6.30(4)	6.31(4)	6.30(4)
P_{00}	10.00									
P_{11}		-0.20(2)	0.01(2)	-0.04(2)	0.07(2)	-0.06(2)	0.01(1)	-0.11(1)	-0.09(1)	-0.09(1)
P_{1-1}		0.06(2)	-0.13(3)	0.01(2)	-0.01(2)	0.03(2)	-0.02(1)	-0.03(1)	-0.01(1)	0.02(1)
P_{10}		0.03(2)	0.02(1)	0.03(1)	0.04(2)	-0.02(2)	-0.01(1)	-0.01(1)	-0.00(1)	0.05(1)
P_{20}		0.02(2)	0.03(1)	-0.05(2)	-0.31(2)	0.09(1)	-0.26(1)	-0.01(1)	-0.01(1)	-0.03(1)
P_{21}		-0.03(2)	0.00(1)	0.03(1)	0.01(2)	0.01(1)	-0.01(1)	-0.01(1)	-0.00(1)	0.00(1)
P_{2-1}		-0.03(2)	0.01(1)	0.02(1)	0.02(2)	-0.03(1)	-0.01(1)	-0.01(1)	0.00(1)	0.01(1)
P_{22}		-0.17(1)	0.01(1)	-0.04(1)	-0.01(2)	-0.14(1)	0.01(1)	-0.14(1)	-0.16(1)	-0.13(1)
P_{2-2}		-0.02(1)	0.04(1)	0.01(1)	-0.04(2)	0.00(1)	-0.01(1)	0.01(1)	0.01(1)	-0.01(1)
P_{30}		0.06(2)	-0.02(1)	0.01(2)	-0.01(2)	-0.05(2)	-0.01(1)	-0.01(1)	-0.02(1)	0.01(1)
P_{31}		-0.23(2)	0.03(1)	0.03(2)	0.01(2)	-0.00(2)	-0.03(1)	0.01(1)	0.01(1)	0.02(1)
P_{3-1}		-0.16(2)	-0.01(1)	-0.01(1)	0.04(2)	-0.03(2)	0.01(1)	0.03(1)	-0.01(1)	0.04(1)
P_{32}		0.01(2)	-0.01(1)	0.01(2)	0.02(2)	-0.04(2)	-0.01(1)	-0.02(1)	-0.02(1)	-0.03(1)
P_{3-2}		-0.02(2)	-0.01(1)	-0.01(1)	-0.01(2)	-0.04(2)	-0.01(1)	-0.01(1)	-0.03(1)	0.01(1)
P_{33}		0.21(2)	0.24(1)	0.28(2)	0.38(2)	0.13(2)	0.45(1)	-0.01(1)	0.01(1)	0.01(1)
P_{3-3}		-0.02(2)	0.00(1)	-0.02(1)	0.02(2)	0.08(2)	0.01(1)	-0.01(1)	-0.02(1)	-0.00(1)

Table S10b. Multipolar refinement parameters for H atoms (Strategy II).

	H1a	H1b	H2n	H3a	H3b
κ	1.47(9)	1.37(7)	1.31(6)	1.30(7)	1.46(8)
P_{val}	0.62(6)	0.49(5)	0.60(5)	0.57(6)	0.51(5)
P_{11}	0.15(3)	0.13(3)	0.09(2)	0.18(3)	0.17(3)

Strategy I



Strategy II

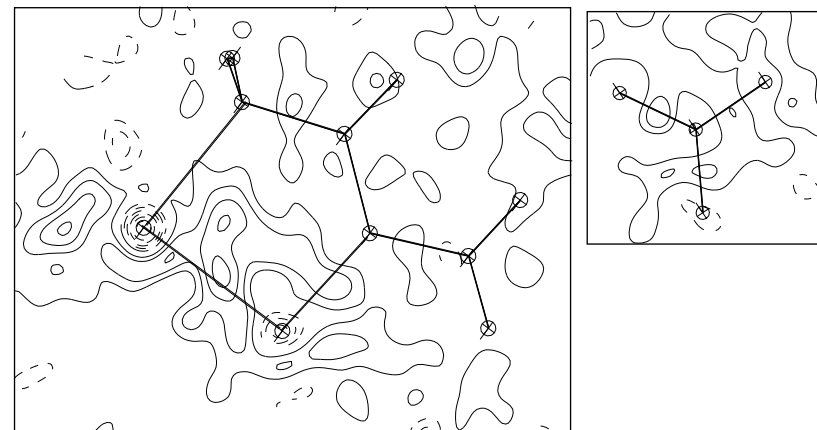
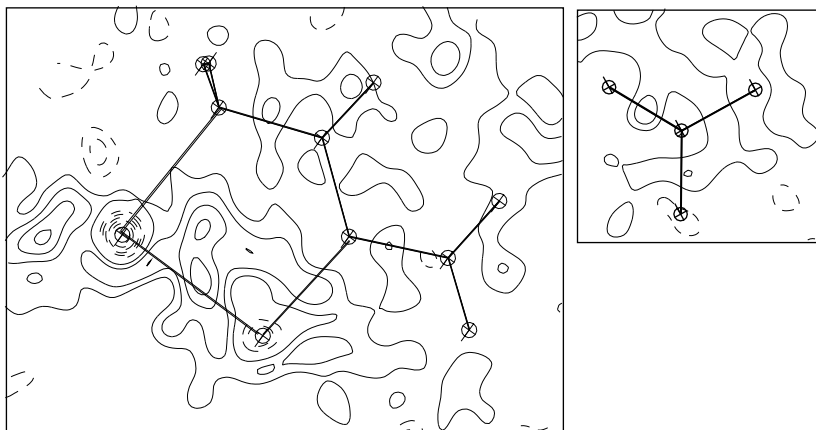
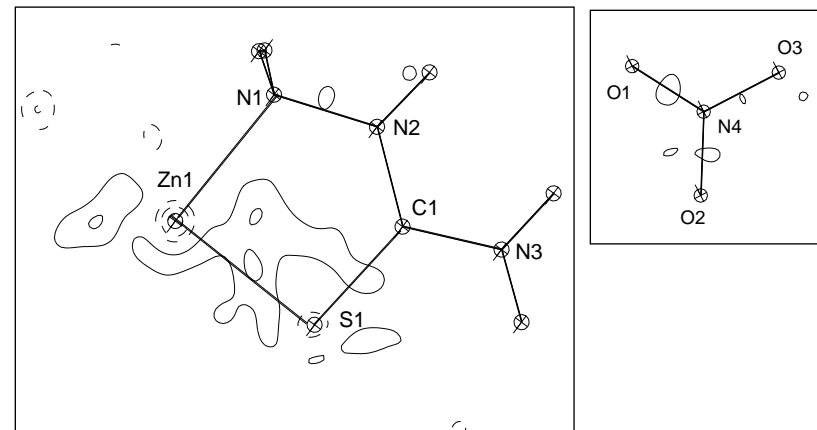


Figure S1. Residual density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$, contours at $0.1 \text{ e.}\text{\AA}^{-3}$ (above) and $0.05 \text{ e.}\text{\AA}^{-3}$ (below).

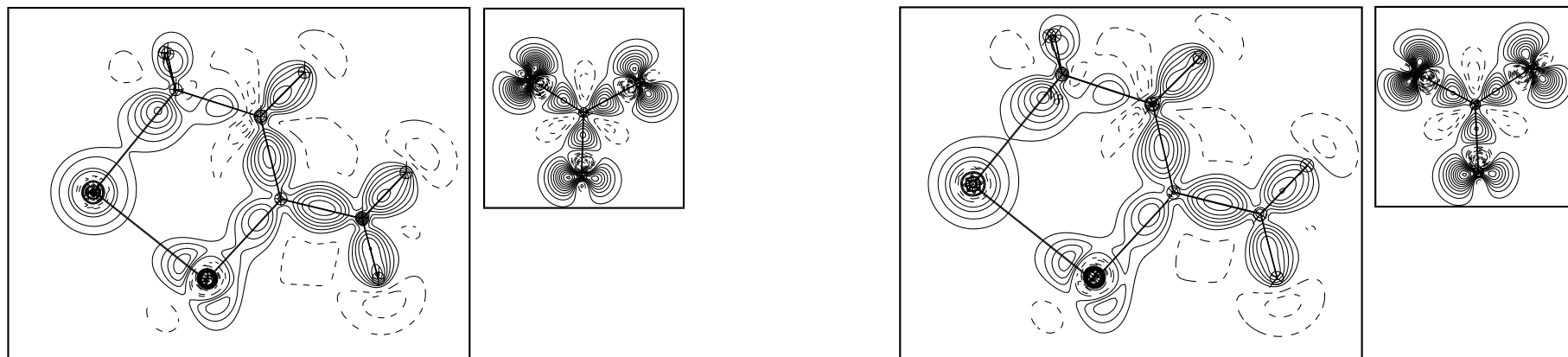


Figure S2. Static density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours $0.1\text{e}\cdot\text{\AA}^{-3}$).

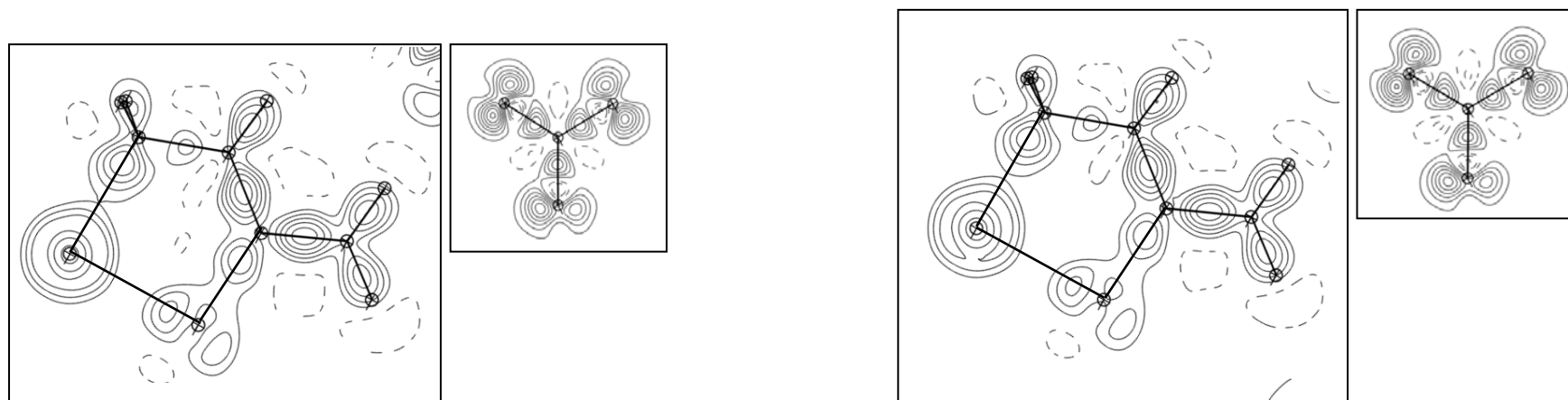


Figure S3. Dynamic density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours as above).

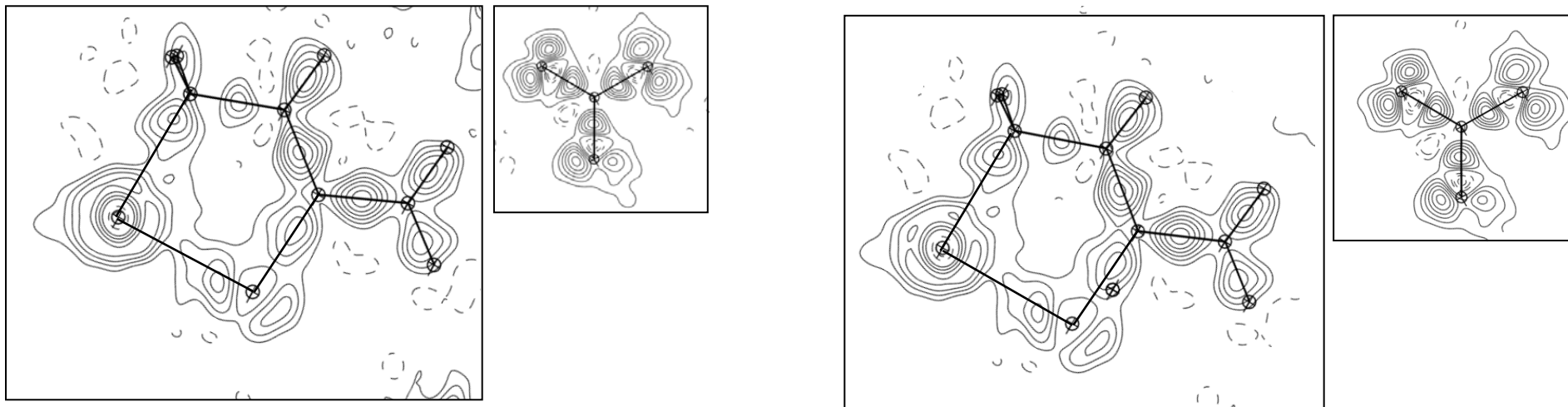
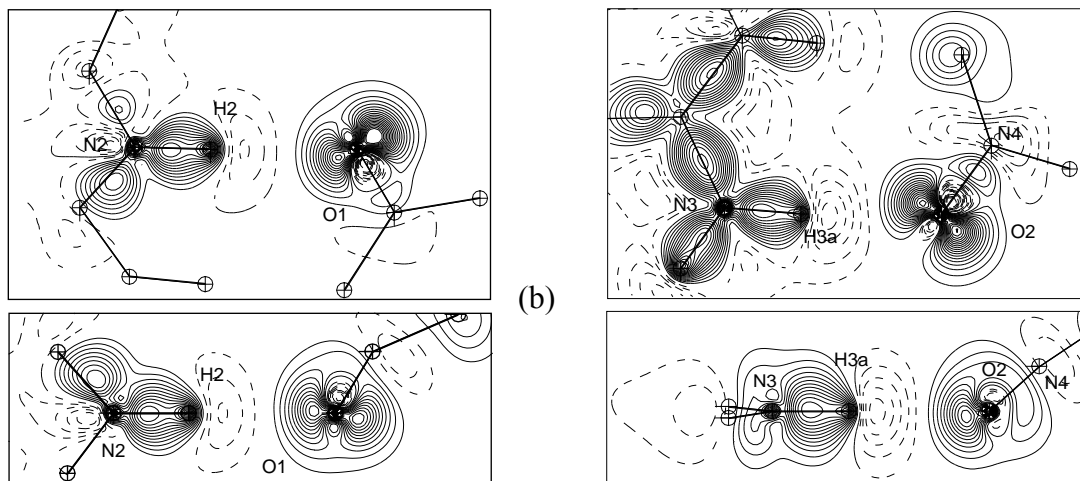
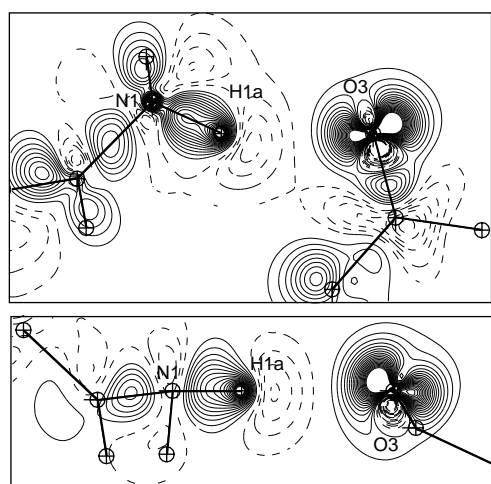


Figure S4. Experimental density maps ($F_{\text{obs}} - F_{\text{calc}}$) for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours as above).

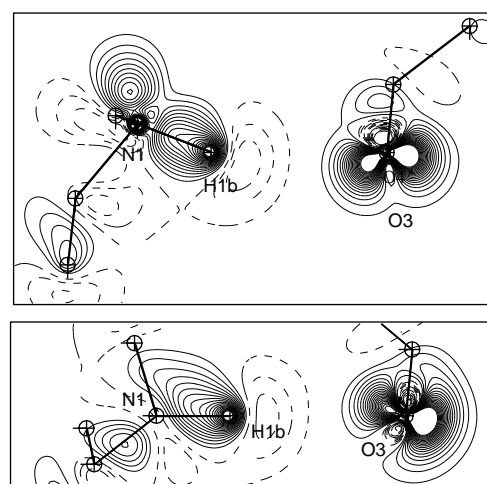


(a)

(b)



(c)



(d)

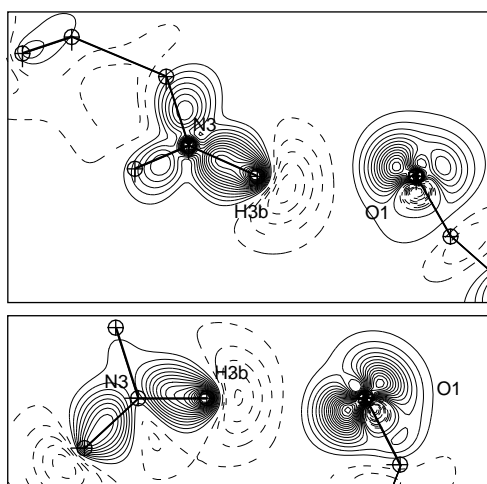


Figure S5. Static deformation density maps of hydrogen bonds: in the N-H...O plane; orthogonal to N-H...O plane (below). (contours $0.05e.\text{\AA}^{-3}$).

(f)

The results of the additional strategy which includes the refinement of the multipole parameters for Zn atom

Table S11. Bond distances and angles.

Bond	(Å)	Angle	(°)
Zn1-N1	2.0918(2)	N1-Zn1-S1	88.47(1)
Zn1-S1	2.2667(1)	N1-Zn1-S1_2	113.62(2)
N1-N2	1.4114(2)	N1-Zn1-N1_2	122.06(1)
C1-N2	1.3419(3)	S1-Zn-S1_2	134.59(1)
C1-N3	1.3274(3)	Zn1-N1-N2	110.68(1)
C1-S1	1.7194(2)	Zn1-S1-C1	95.37(1)
O1-N4	1.2561(2)	N1-N2-C1	121.64(2)
O2-N4	1.2567(3)	N2-C1-S1	123.61(2)
O3-N4	1.2417(3)	N2-C1-N3	117.45(2)
N1-H1a	0.997(10)	S1-C1-N3	118.94(2)
N1-H1b	1.030(9)	H1a-N1-H1b	107.97(2)
N2-H2	0.991(10)	N2-N1-H1a	109.92(2)
N3-H3a	1.006(10)	N2-N1-H1b	107.13(2)
N3-H3b	0.984(10)	Zn1-N1-H1a	114.34(2)
		Zn1-N1-H1b	106.47(2)
		N1-N2-H2	116.41(2)
		C1-N2-H2	121.67(2)
		H3a-N3-H3a	121.27(2)
		C1-N3-H3a	120.03(2)
		C1-N3-H3b	118.62(2)
		O1-N4-O2	120.20(2)
		O1-N4-O3	119.41(3)
		O2-N4-O3	120.38(3)

Table S12. Net atomic charges.

ATOM	Kappa	AIM
Zn1	1.59(4)	0.61
S1	0.10(5)	0.12
N1	-0.71(8)	-0.71
N2	-0.24(7)	-0.83
N3	-0.94(9)	-1.20
N4	0.60(5)	0.66
C1	0.18(8)	0.73
O1	-0.55(4)	-0.54
O2	-0.57(4)	-0.56
O3	-0.57(4)	-0.57
H1a	0.35(5)	0.50
H1b	0.38(5)	0.45
H2	0.29(5)	0.49
H3a	0.41(6)	0.58
H3b	0.52(5)	0.55

Table S13. Topological proprieties of covalent bonds

Bond	length (Å)	d_1	d_1	ρ	$\nabla^2\rho$	λ_2	λ_2	λ_3	ε	G	V	H
Zn1-N1	2.0918(2)	0.977	1.115	0.47	7.90	-2.36	-2.67	12.94	0.13	231.93	-249.06	-17.12
Zn1-S1	2.2667(2)	1.038	1.230	0.37	5.12	-1.72	-1.62	8.46	0.07	152.36	-165.51	-13.14
N1-N2	1.4114(2)	0.695	0.716	2.05	-3.46	-16.13	-14.93	27.60	0.08	970.39	-2034.90	-1064.48
C1-N2	1.3419(3)	0.547	0.796	2.32	-22.99	-19.32	-16.69	13.02	0.16	852.96	-2331.05	-1478.09
C1-N3	1.3274(3)	0.548	0.779	2.41	-23.21	-20.63	-16.59	14.01	0.23	932.12	-2495.35	-1563.23
C1-S1	1.7194(2)	0.885	0.834	1.28	-2.64	-6.97	-5.55	9.88	0.25	423.38	-918.55	-495.16
O1-N4	1.2567(2)	0.625	0.631	3.06	-6.07	-26.33	-23.38	43.53	0.13	1904.13	-3973.31	-2069.18
O2-N4	1.2560(3)	0.622	0.634	3.07	-6.32	-26.48	-23.49	43.69	0.13	1910.58	-3993.00	-2082.42
O3-N4	1.2418(3)	0.622	0.620	3.19	-11.05	-28.22	-24.00	41.17	0.18	1958.49	-4217.44	-2258.95
N1-H1a	0.981(10)	0.726	0.268	2.16	-18.92	-28.81	-26.49	36.36	0.09	784.18	-2082.81	-1298.64
N1-H1b	1.026(9)	0.735	0.295	2.05	-16.69	-25.06	-23.17	31.73	0.08	730.57	-1914.95	-1184.39
N2-H2	0.976(10)	0.743	0.245	2.13	-21.19	-29.10	-26.71	33.85	0.09	717.06	-2010.99	-1293.24
N3-H3a	1.000(10)	0.755	0.246	2.13	-26.94	-29.08	-27.25	29.39	0.07	612.82	-1958.18	-1345.36
N3-H3b	0.974(10)	0.722	0.262	2.30	-25.52	-31.41	-29.18	35.07	0.08	788.90	-2271.73	-1482.83

Table S14. Atomic coordinates, anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms after the multipolar refinement.

	x	y	z	U(1.1)	U(2.2)	U(3.3)	U(1.2)	U(1.3)	U(2.3)
Zn1	0.50000	0.16713(1)	0.75000	0.00218(1)	0.00371(1)	0.00061(1)	0.00000	0.00027(1)	0.00000
N1	0.35667(2)	0.03320(3)	0.65767(1)	0.00220(1)	0.00367(2)	0.00091(1)	-0.00113(2)	0.00062(1)	0.00032(2)
N2	0.35293(2)	0.08165(3)	0.56097(2)	0.00182(1)	0.00404(2)	0.00079(1)	-0.00151(2)	0.00032(1)	-0.00010(2)
N3	0.42828(2)	0.22683(3)	0.44366(2)	0.00220(1)	0.00546(3)	0.00073(1)	-0.00135(3)	0.00033(1)	0.00031(2)
C1	0.43834(2)	0.19023(3)	0.53649(2)	0.00147(1)	0.00325(2)	0.00072(2)	-0.00016(2)	0.00033(1)	-0.00001(2)
S1	0.55857(1)	0.28277(1)	0.61841(1)	0.00146(1)	0.00403(1)	0.00080(1)	-0.00098(1)	0.00020(1)	0.00001(1)
N4	0.32555(2)	0.56438(3)	0.66716(1)	0.00155(1)	0.00301(2)	0.00088(1)	-0.00004(2)	0.00046(1)	-0.00001(2)
O1	0.33332(3)	0.60002(4)	0.58202(1)	0.00228(1)	0.00588(3)	0.00099(1)	-0.00108(3)	0.00086(1)	0.00066(2)
O2	0.27965(3)	0.41977(4)	0.68642(2)	0.00244(1)	0.00388(2)	0.00125(1)	-0.00158(3)	0.00032(1)	0.00060(2)
O3	0.36184(4)	0.67230(5)	0.73284(2)	0.00356(2)	0.00385(3)	0.00128(1)	-0.00066(4)	0.00023(2)	-0.00108(2)
H1a	0.3605(9)	-0.0981(13)	0.6641(7)	0.025(1)					
H1b	0.2744(9)	0.0753(12)	0.6749(7)	0.027(2)					
H2	0.2893(9)	0.0218(14)	0.5117(7)	0.024(2)					
H3a	0.3566(10)	0.1778(13)	0.3950(8)	0.022(2)					
H3b	0.4896(9)	0.3071(14)	0.4244(8)	0.025(2)					

Table S16. Multipolar refinement parameters for H atoms.

	H1a	H1b	H2n	H3a	H3b
κ	1.48(8)	1.37(7)	1.32(6)	1.30(6)	1.48(8)
Pval	0.62(5)	0.50(5)	0.60(5)	0.58(6)	0.51(5)
P ₁₁	0.15(3)	0.11(3)	0.08(2)	0.16(2)	0.16(2)

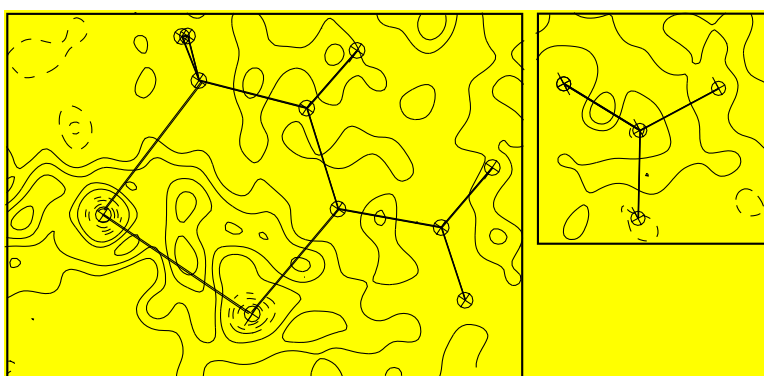
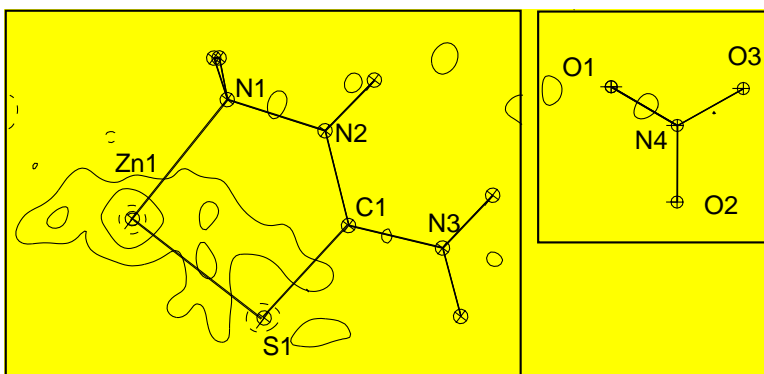


Figure S6. Residual density maps for [Zn(TSc)₂](NO₃)₂, contours at 0.1 e.Å⁻³ (above) and 0.05 e.Å⁻³ (below)

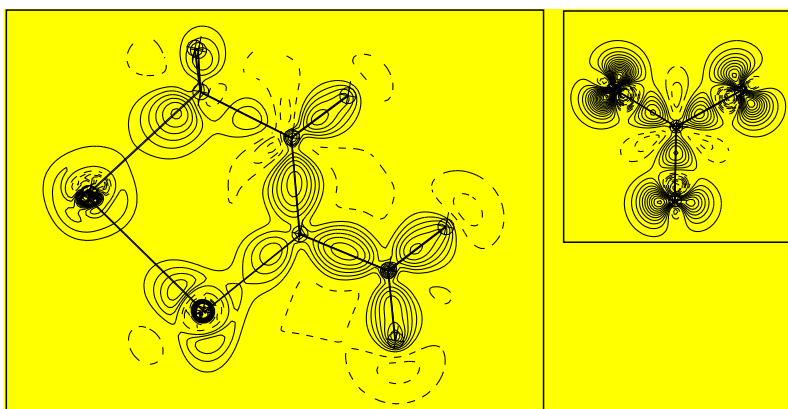


Figure S7. Static density maps for [Zn(TSc)₂](NO₃)₂ (contours 0.1 e.Å⁻³)

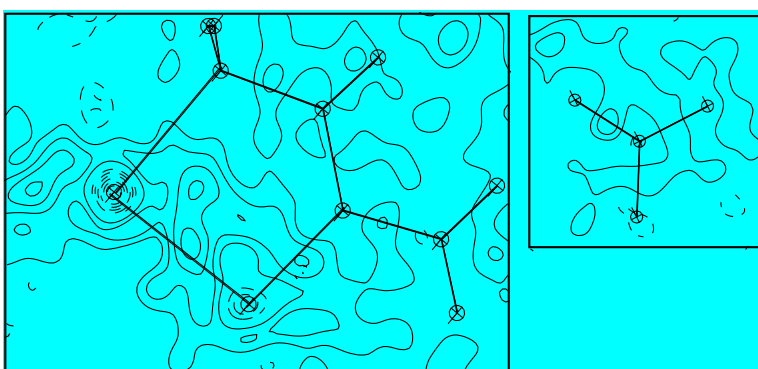
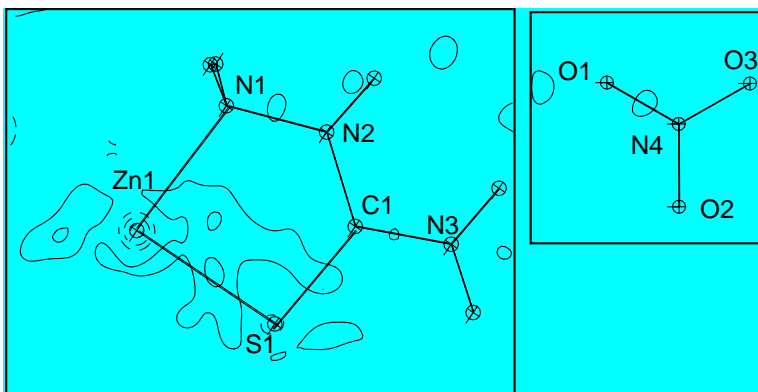


Figure S8. Residual density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$, contours at $0.1\text{e}\cdot\text{\AA}^{-3}$ (above) and $0.05\text{e}\cdot\text{\AA}^{-3}$ (below)

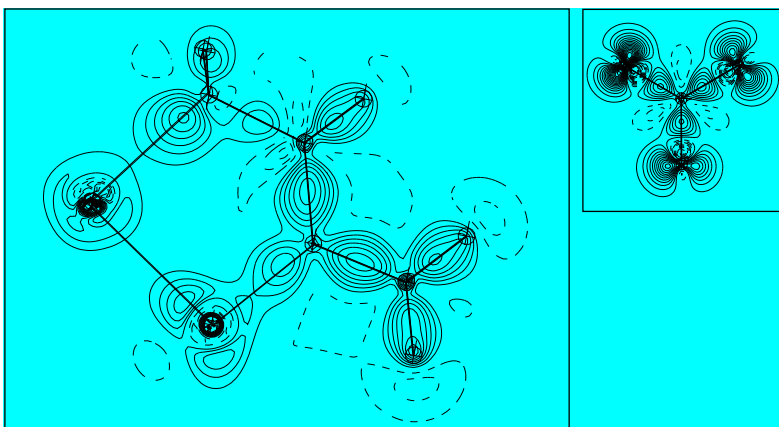


Figure S9. Static density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours $0.1\text{e}\cdot\text{\AA}^{-3}$)

Table S17. Topological proprieties of coordination bonds

Bond	length (Å)	d₁	d₁	ρ	∇²ρ	λ₂	λ₂	λ₃	ε	G	V	H
Zn1-N1	2.0918(2)	0.980	1.113	0.47	7.82	-2.36	-2.67	12.85	0.13	230.48	-248.33	-17.84
Zn1-S1	2.2667(2)	1.041	1.227	0.37	5.08	-1.73	-1.62	8.43	0.07	151.64	-165.15	-13.50

