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

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Figure S4. Experimental density maps ($F_{\text{obs}} - F_{\text{calc}}$) for $[\text{Zn}(\text{TSC})_2](\text{NO}_3)_2$ (contours $0.1 \text{ e} \cdot \text{\AA}^{-3}$).

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) |

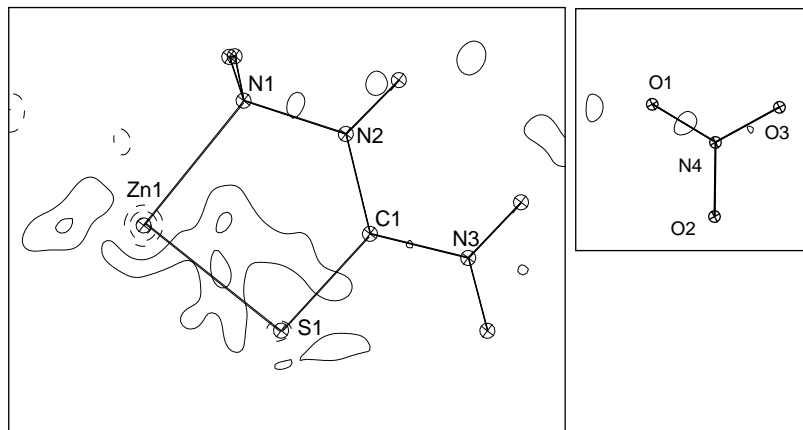
Table S10b. Multipolar refinement parameters for non-H atoms in $[\text{Zn}(\text{TSC})_2](\text{NO}_3)_3$ (Strategy II).

| | 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

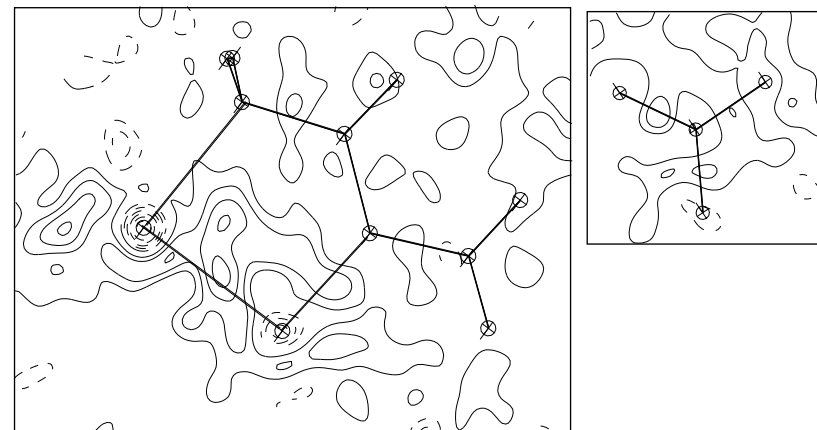
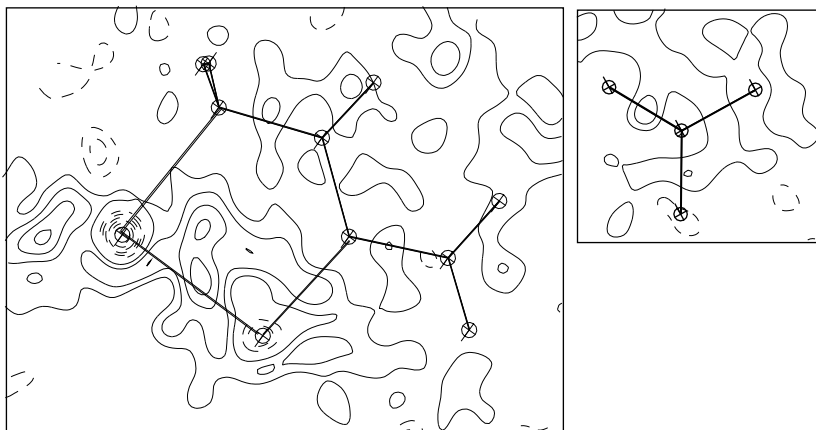
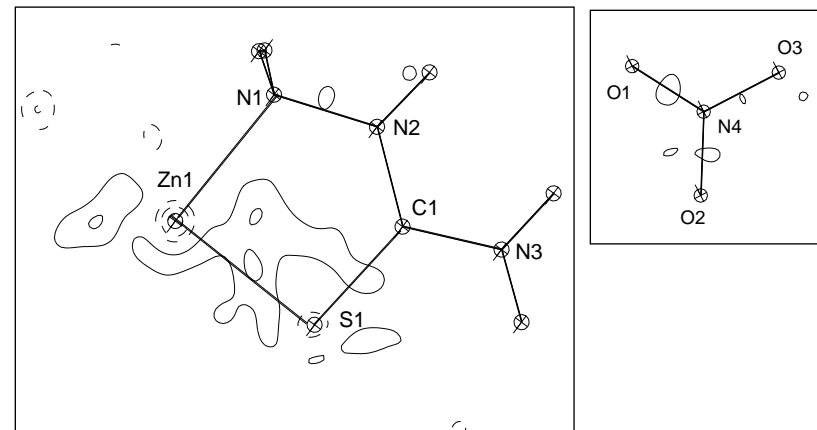


Figure S1. Residual density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$, contours at $0.1 \text{ e.}\text{\AA}^{-3}$ (above) and $0.05 \text{ e.}\text{\AA}^{-3}$ (below).

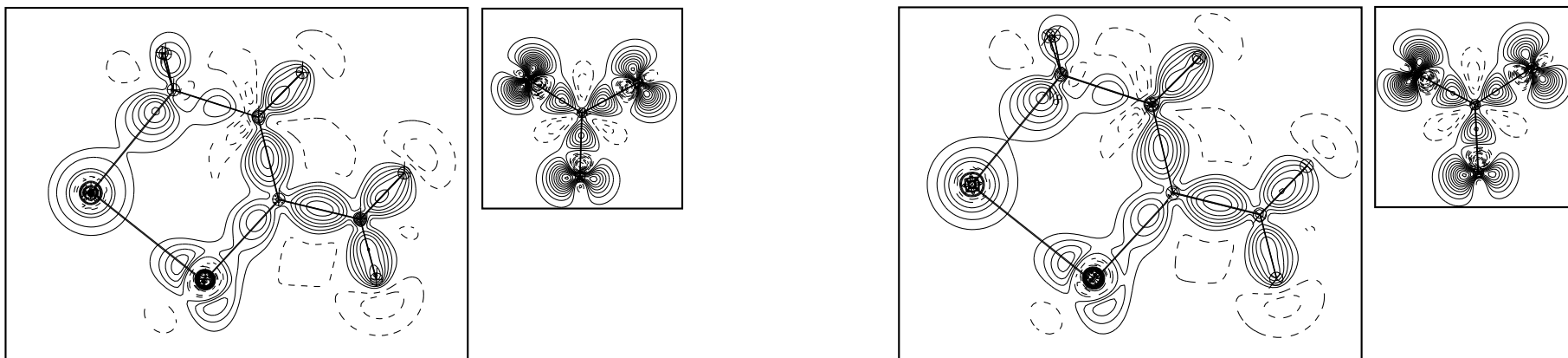


Figure S2. Static density maps for [Zn(TSc)₂](NO₃)₂ (contours 0.1e.Å⁻³).

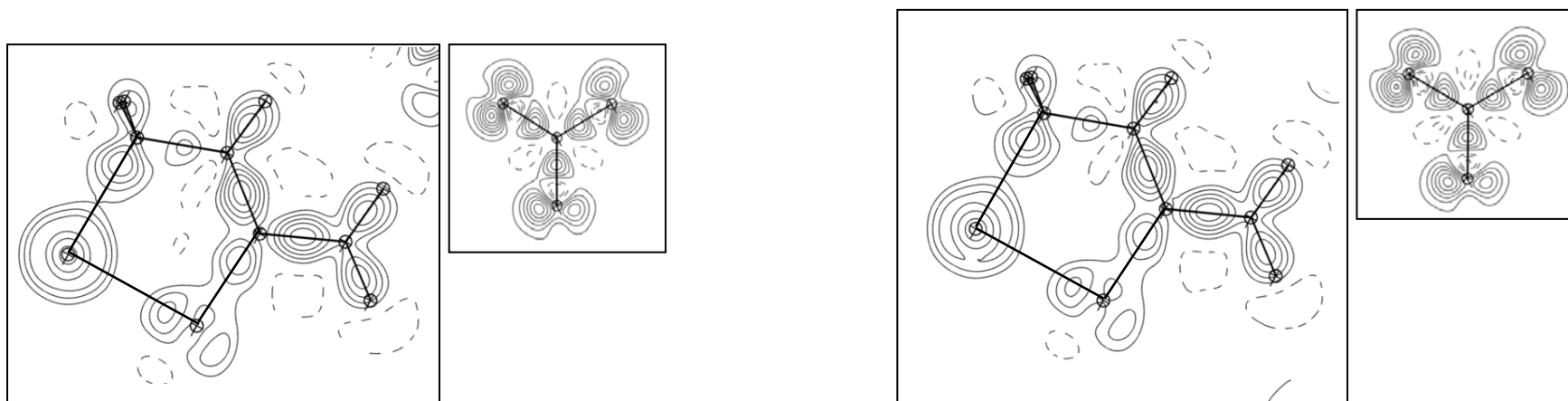


Figure S3. Dynamic density maps for [Zn(TSc)₂](NO₃)₂ (contours as above).

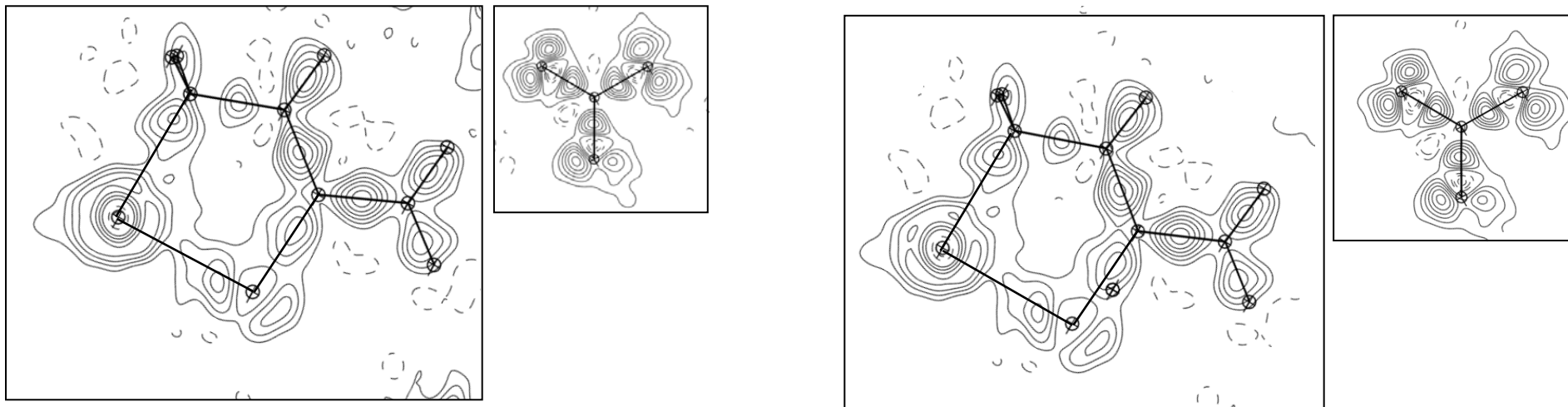
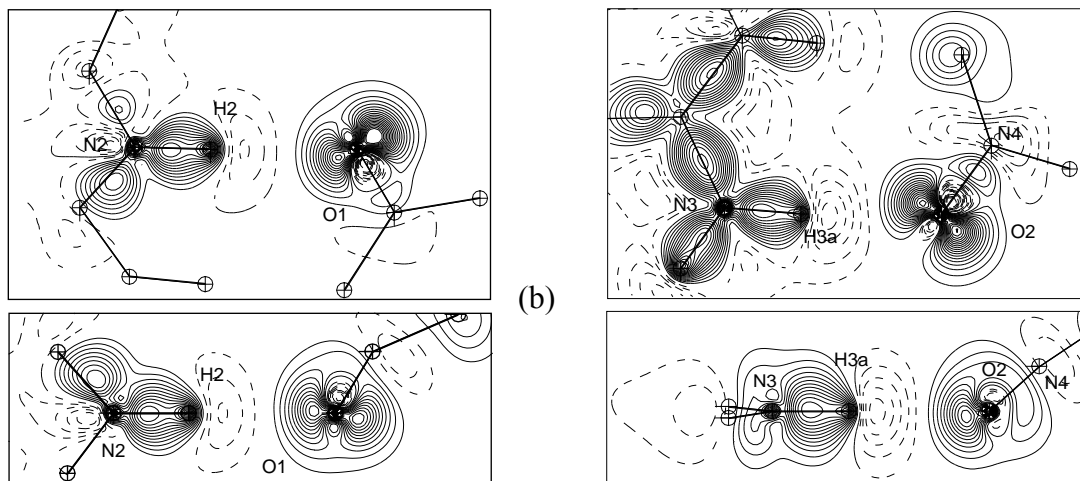
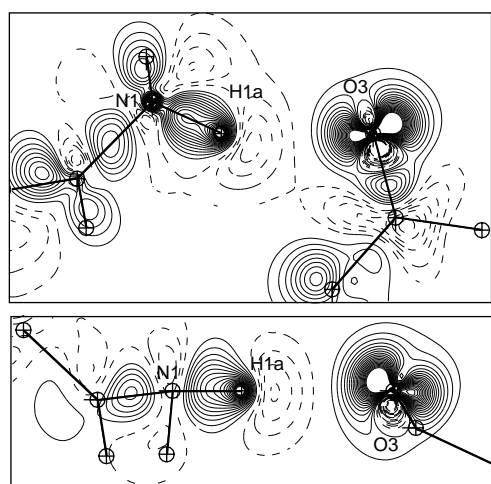


Figure S4. Experimental density maps ($F_{\text{obs}} - F_{\text{calc}}$) for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours as above).

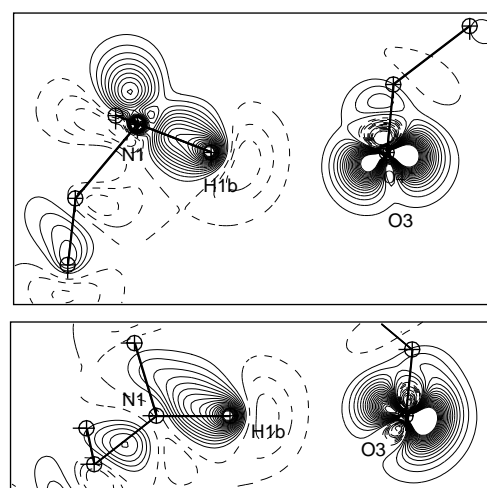


(a)

(b)



(c)



(d)

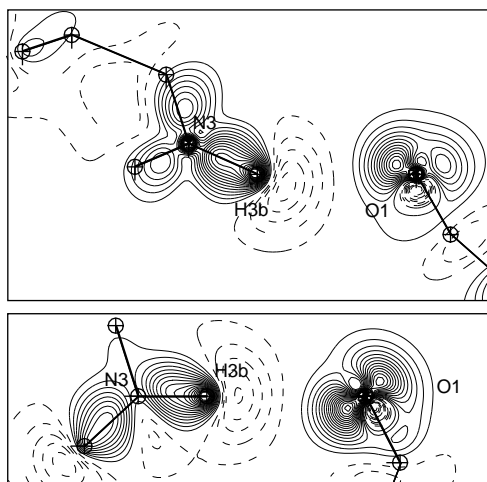


Figure S5. Static deformation density maps of hydrogen bonds: in the N-H...O plane; orthogonal to N-H...O plane (below). (contours $0.05e.\text{\AA}^{-3}$).

(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) |

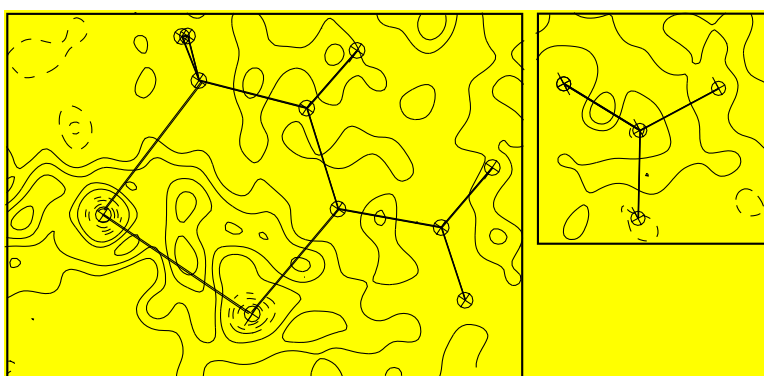
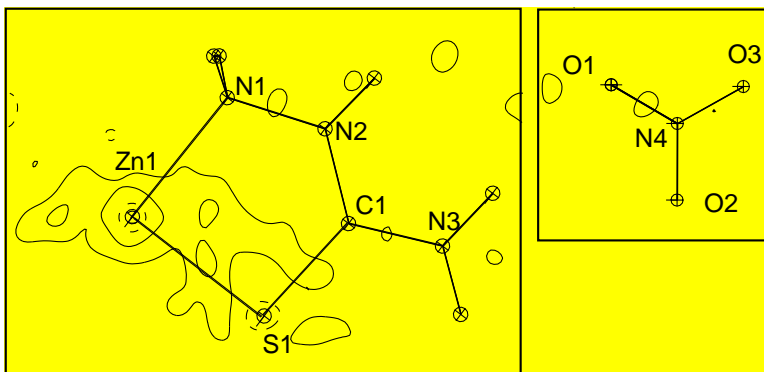


Figure S6. Residual density maps for [Zn(TSc)₂](NO₃)₂, contours at 0.1 e.Å⁻³ (above) and 0.05 e.Å⁻³ (below)

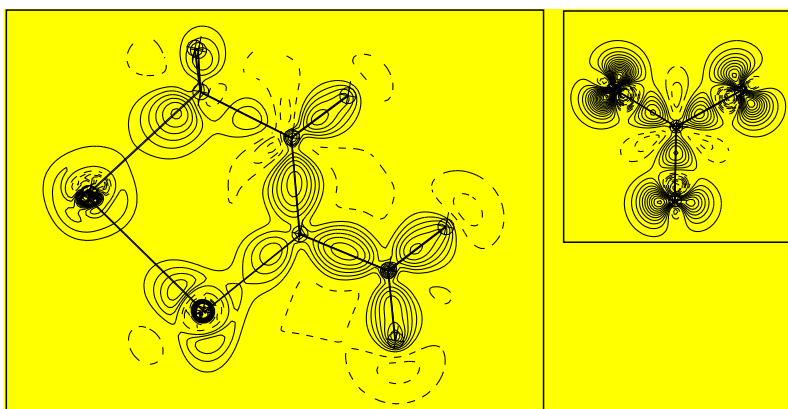


Figure S7. Static density maps for [Zn(TSc)₂](NO₃)₂ (contours 0.1 e.Å⁻³)

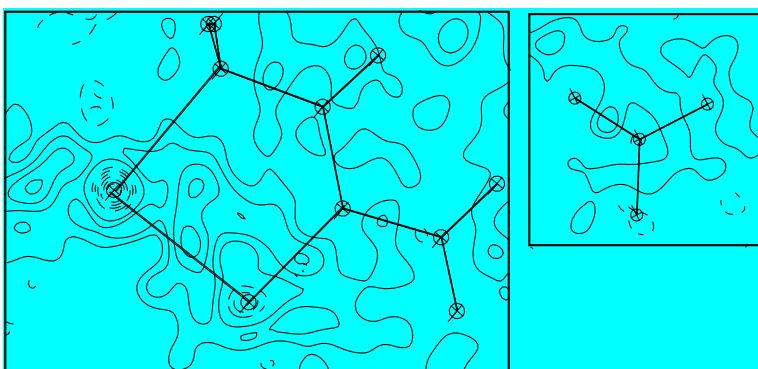
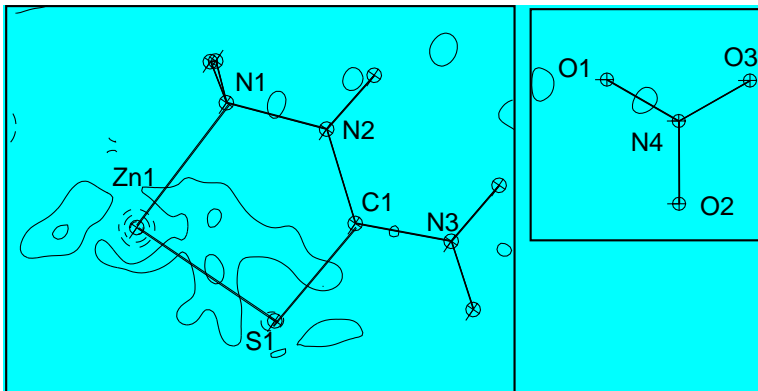


Figure S8. Residual density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$, contours at $0.1\text{e}\cdot\text{\AA}^{-3}$ (above) and $0.05\text{e}\cdot\text{\AA}^{-3}$ (below)

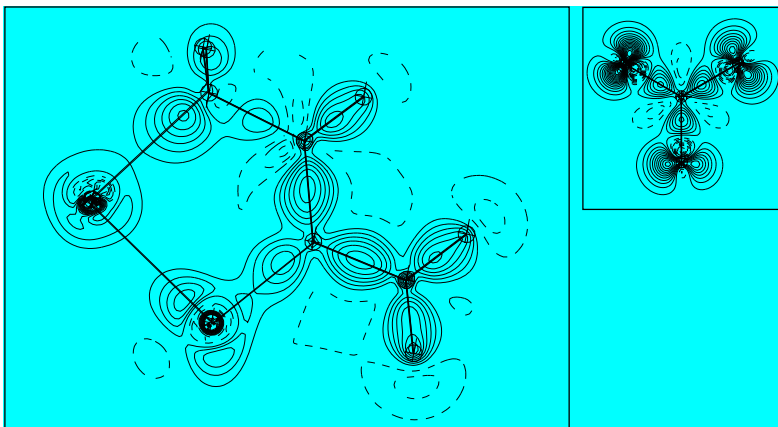


Figure S9. Static density maps for $[\text{Zn}(\text{TSc})_2](\text{NO}_3)_2$ (contours $0.1\text{e}\cdot\text{\AA}^{-3}$)

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 |

