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Ground electronic state description of thiourea coordination in homoleptic Zn²⁺, Ni²⁺ and Co²⁺ complexes using sulfur *K*-edge X-ray absorption spectroscopy

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SUPPORTING INFORMATION

Ground Electronic State Description of Thiourea Coordination in Homoleptic Zn(II), Ni(II), and Co(II) Complexes using Sulfur K-Edge X-Ray Absorption Spectroscopy

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Additional supporting information, such as normalized, and fitted S K-edge XANES spectra, XYZ coordinates of optimized molecular structures, formatted checkpoint files can be accessed at ZENODO, DOI: 10.5281/zenodo.4770724 or zenodo.org/record/4770724.

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Table S1. Peak heights (A), energy positions (E_0), line-widths (lw), Gaussian/Lorentzian ratios (G:L), and integrated peak intensity (D_0) for normalized spectra from Figures 5-10 (UDF stands for user-defined analytical fits of reference spectra). Averaged normalized pre-edge intensities were used to determine the experimental S 3p character in Co-S π/σ^* and Ni-S σ^* bonds.

		A , -	E_0 , eV	lw , eV	(G:L)	D_0 , -
free TU	C-S π^*	1.0	2472.1	1.0	0.5	1.33
ligand	C-S σ^*	2.1	2473.3	1.2	0.7	2.92
Fig.5	S 4p	1.2	2474.6	1.5	1.0	1.83
	edge position	1.0	2475.1	0.3		
[Zn(TU) ₄] ²⁺	TU UDF	1.8	2473.8			
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.4	2471.4	1.0	1.0	0.54
Fig.6B	TU UDF	1.0	2472.6			
[Ni(TU) ₆] ²⁺	Ni-S σ^*	0.4	2471.3	1.1	0.5	0.59
Fig.6C	TU UDF	1.1	2472.4			
[Zn(TU) ₄] ²⁺	C-S π^*	0.8	2472.7	1.1	0.5	1.44
Fig.7A	TU UDF	1.9	2473.5			
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.5	2471.4	1.0	0.5	0.61
Fig.7B	C-S π^*	0.8	2472.6	1.0	0.5	1.02
	TU UDF	1.9	2473.5			
[Ni(TU) ₆] ²⁺	Ni-S σ^*	0.4	2471.3	1.2	0.5	0.57
Fig.7C	C-S π^*	1.2	2472.5	1.2	0.5	1.82
	TU UDF	0.6	2472.3			
[Ni(TU) ₆] ²⁺	Ni-S σ^*	0.4	2471.3	1.1	0.5	0.51
C-S π^*/σ^*	C-S π^*	0.6	2472.3	1.0	0.5	0.71
ratio of 0.2	C-S σ^*	1.7	2473.4	1.8	0.5	3.79
Fig.8A	S 4p	0.7	2474.8	1.3	1.0	1.00
	edge position	1.0	2475.1	0.2		
[Ni(TU) ₆] ²⁺	Ni-S σ^*	0.4	2471.3	1.1	0.5	0.50
C-S π^*/σ^*	C-S π^*	0.7	2472.4	1.1	0.5	0.95
ratio of 0.3	C-S σ^*	1.6	2473.3	1.6	0.4	3.17
Fig.8B	S 4p	0.8	2474.7	1.6	1.0	1.33
	edge position	1.0	2475.1	0.2		
[Ni(TU) ₆] ²⁺	Ni-S σ^*	0.4	2471.3	1.2	0.5	0.53
C-S π^*/σ^*	C-S π^*	0.8	2472.4	1.2	0.5	1.12
ratio of 0.4	C-S σ^*	1.5	2473.4	1.5	0.5	2.90
Fig.8C	S 4p	0.8	2474.7	1.5	1.0	1.32
	edge position	1.0	2475.1	0.2		
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.4	2471.4	0.9	0.5	0.54
C-S π^*/σ^*	C-S π^*	0.8	2472.8	1.1	0.5	1.14
ratio of 0.2	C-S σ^*	1.5	2473.6	1.4	0.5	2.73
Fig.9A	S 4p	0.9	2474.9	1.4	0.5	1.58
	edge position	1.0	2475.2	0.2		
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.4	2471.4	1.0	0.5	0.54
C-S π^*/σ^*	C-S π^*	0.7	2472.8	1.0	0.5	0.97
ratio of 0.3	C-S σ^*	1.5	2473.5	1.5	0.4	2.97
Fig.9B	S 4p	0.9	2474.9	1.5	0.4	1.67
	edge position	1.0	2475.0	0.2		
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.4	2471.4	1.0	0.5	0.52
C-S π^*/σ^*	C-S π^*	0.7	2472.7	0.9	0.5	0.54
ratio of 0.4	C-S σ^*	1.7	2473.4	1.6	0.4	3.53
Fig.9C	S 4p	0.9	2475.0	1.6	0.4	
	edge position	1.0	2475.2	0.1		
[Co(TU) ₄] ²⁺	Co-S π/σ^*	0.4	2471.4	1.0	1.0	0.53
Fig.10B	[Zn(TU) ₄] ²⁺ UDF	0.9	2472.8			

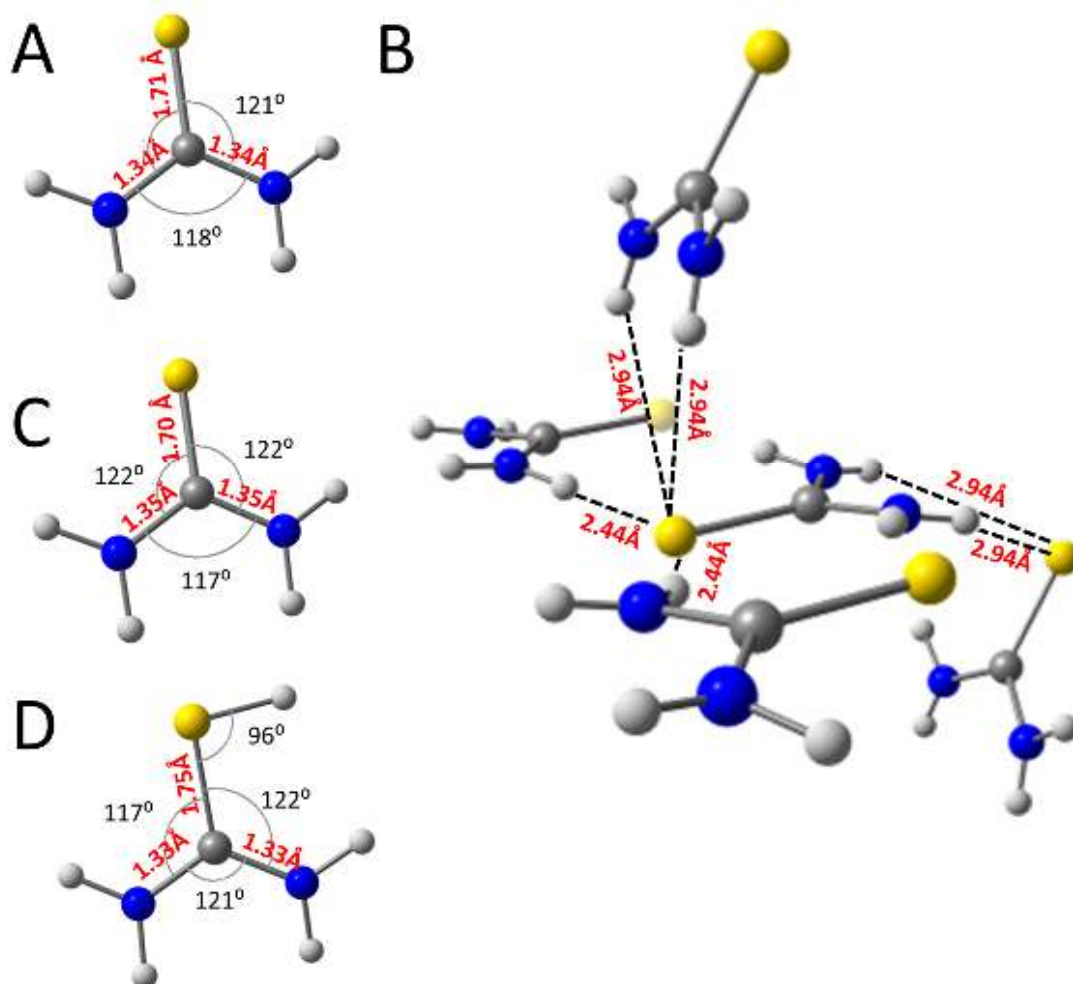


Figure S1. Thiourea geometry from the crystal structure (A),(Kumler & Fohlen, 1942) intermolecular H-bonding interactions in the TU crystal (B), optimized structure at BP86/def2-TZVP/PCM(CH₃CN) level without the presence of the crystal packing effects (C) and its S-protonated derivative (D) with representative bond lengths and angles.

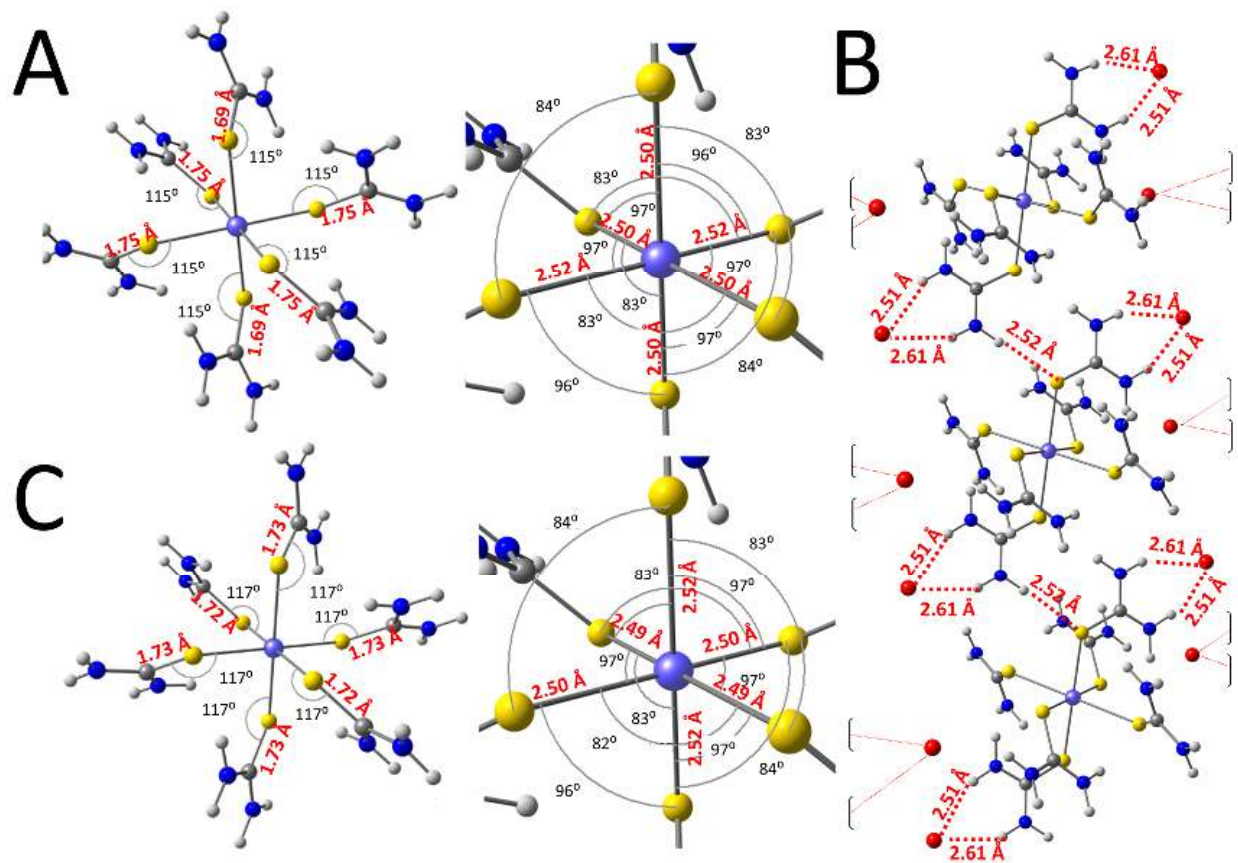


Figure S2. $[\text{Ni}(\text{TU})_6]^{2+}$ coordination geometry from the crystal structure (A), (Weininger *et al.*, 1969) crystal packing (B), and the BP86/def2-TZVP/PCM(CH_3CN) optimized structure (C) of with representative bond lengths and angles.

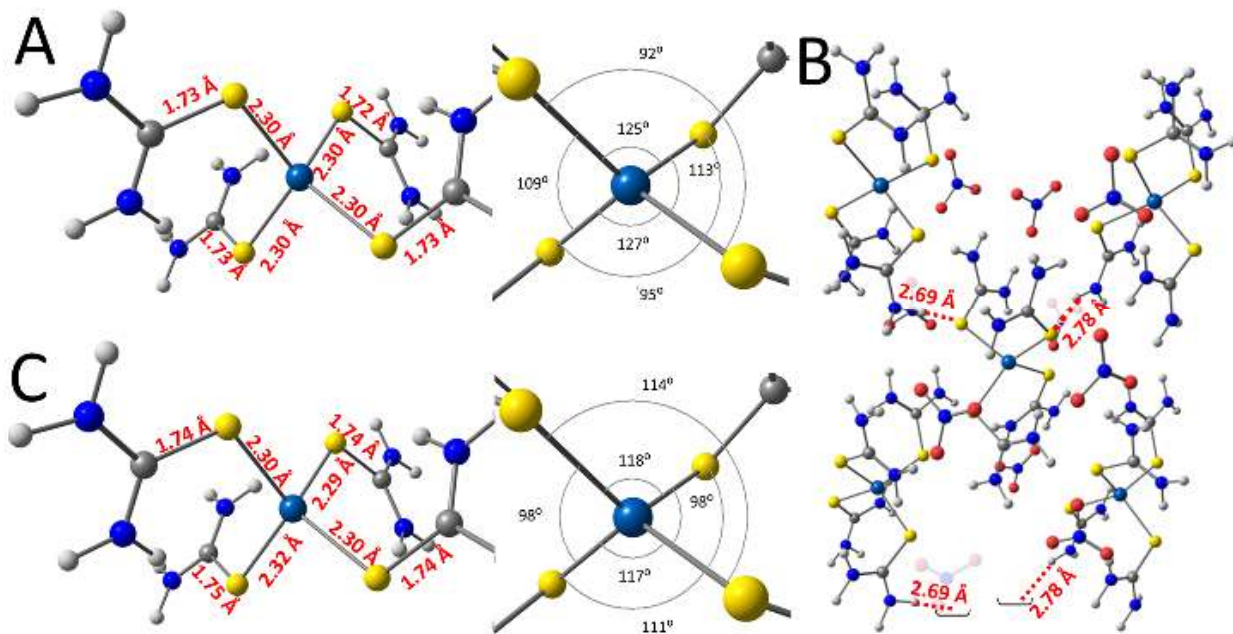


Figure S3. $[\text{Co}(\text{TU})_4]^{2+}$ coordination geometry from the crystal structure (A), (Cotton *et al.*, 1964) crystal packing (B), and the BP86/def2-TZVP/PCM(CH_3CN) optimized structure (C) with representative bond lengths and angles.

Calculated Molecular Geometries. In order to correlate bonding information from S K-XANES data with indirect structural information from IR vibrational spectroscopy (El-Bahy et al., 2003; Cotton et al., 1964), we carried out geometry optimizations and comparison of the calculated and experimental vibrational spectra (Table S2). Using the TU crystal structure (Kumler & Fohlen, 1942) as a starting point for geometry, calculations at the BP86/def2-TZVP/PCM(CH₃CN) level were used to obtain optimized TU structure (Figure S1). The BP86/def2-TZVP/PCM(CH₃CN) optimization reproduces the geometry of the TU crystal structure to within 0.01 Å and 1° for bond lengths and bond angles, respectively. This remarkable agreement suggests that the simulated acetonitrile dielectric environment in combination with the pure GGA functional and large basis set mimics well the structural effects of the S...H-N in-plane and out-of-plane H-bonding network in the TU crystal (Figure S1B). The S-protonated TU (Figure S1D) exaggerates the shift in the resonance structure (Scheme 1) toward the protonated or coordinated thiolate form. Upon protonation, the thione C=S bond is elongated by 0.05 Å (1.75 Å vs. 1.70 Å, Figure S1D vs. Figure S1A) and the N–C–N bond angle changes by 5° (117° versus 122°) relative to the optimized structure (Figure S1C). Parallel with IR data, (Yamaguchi *et al.*, 1958; Kumler & Fohlen, 1942; El-Bahy *et al.*, 2003) upon shifting from the thione to the thiolate form, the C–N bond order increases and bond length shortens by 0.02 Å.

The optimized structure for the [Ni(TU)₆]²⁺ complex at the BP86/def2-TZVP/PCM(CH₃CN) level (Figure S2) shows only borderline acceptable agreement in bond lengths (0.04 Å), but acceptably small deviation for bond angles (2°) to the experimental structure. In addition to the limitations of DFT to capture fully the ground electronic state, crystal packing is also a source of error, as it involves axial hydrogen bonding interactions with the inner-sphere, coordinated sulfur ligands that leads to C=S bond elongation in going from the free TU (1.71 Å) to the coordinated (as long as 1.75 Å). This elongation in both optimized and crystal structures corresponds to shift in the preference of resonance structures from thione toward thiolate.

Figures S3A and S3C compares the experimental and BP86/def2-TZVP/PCM(CH₃CN) optimized structures of [Co(TU)₄]²⁺. The calculated bond lengths show good agreement with the crystal structure within 0.02 Å. However, the bond angles differ considerably by 15°. There is an axial compression in the calculated structures, since the S–Co–S bond angles change from 92° and 95° in the crystal structure to 111° and 114° at DFT/def2-TZVP/PCM(CH₃CN) level. This difference between the experimental and calculated structures can be correlated with the presence of H-bonding interactions in the crystal packing of the [Co(TU)₄]²⁺ crystal structure (Figure S3B). When compared to crystal structure of the free TU ligand, we observe an elongation of the C=S bond in the [Co(TU)₄]²⁺ complex (1.73 Å vs. 1.70 Å), which is along the distortion coordinate between the thione and the thiolate resonance forms of TU (Scheme 1 and Figures S1B and S1C).

Table S2. Calculated (BP86/def2-TZVP/PCM(CH₃CN)) and experimental (El-Bahy *et al.*, 2003; Cotton *et al.*, 1964) vibrational frequencies for the free TU ligand, [Ni(TU)₆]²⁺, and [Co(TU)₄]²⁺ complexes as independent experimental validation from the XAS results on the weakening of the C=S bond upon coordination to Ni²⁺ and Co²⁺ transition metal ions.

free TU, cm ⁻¹		[Ni(TU) ₆] ²⁺ , cm ⁻¹		[Co(TU) ₄] ²⁺ , cm ⁻¹		assignment
exp.	calc.	exp.	calc.	exp.	calc.	
3380	3474	3400	3488	-	3480	N-H stretching
1620	1600	1619	1586	-	3328	C-N-H bending
1477	1432	1483	147	-	1470	N-C stretching vibration (N-C-N symmetric)
1414	1431	1398	1347	1350	1351	NH ₂ rocking, C-S stretching N-C-N asymmetric stretching
1082	1044	1089	1046	1049	1072	NH ₂ rocking, C=S/C-N stretching
730	728	710	710	700	684	C=S stretching (C=S)

Vibrational Analysis. Frequency calculations were performed for the BP86/def2-TZVP/PCM(CH₃CN) optimized structures of the free TU ligand, [Ni(TU)₆]²⁺, and [Co(TU)₄]²⁺ complexes. The calculated IR frequencies and their assignments are summarized in Table S2 that were in qualitative agreement with the experimentally measured values; however, absolute errors up to 100 cm⁻¹ were also observed. Specifically, the calculated C=S stretching frequency in the [Co(TU)₄]²⁺, and [Ni(TU)₆]²⁺ complexes, 684 cm⁻¹, and 710 cm⁻¹, respectively, gave a notable agreement with the experimental values (700 cm⁻¹ and 710 cm⁻¹, respectively). These values corresponds to a red shift from their respective free ligand values by ~20-30 cm⁻¹, which indicates a weakening of the S=C bond upon coordination and parallels the elongation of C-S bond lengths relative to the free ligand both in the experimental structures and in calculations. The N-H stretching modes in [Ni(TU)₆]²⁺ were blue shifted both experimentally and computationally, which is an indication for the formation of the M-S(TU) bond along with opposite changes in the bond order of C-N versus C-S bonds (El-Bahy *et al.*, 2003). The qualitative agreement is meaningful between the free TU and its Ni²⁺/Co²⁺ complexes; however, the absolute agreement could not be achieved due to the limitations of DFT to describe the ground state electronic structures of these complexes with rather complex M-L interactions.

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