Answer on Question#41646-Chemistry-Inorganic Chemistry

Question

Thiocyanate (SCN-) has the potential to coordinate metals either via N-atom or S-atom linkage. Predict the coordination linkage (N-atom or S-atom) and geometry for Zn (II) and Cu (I).

Answer

The general rule based on the experimental evidence states that class A metals (forming hard acids) tend to form N-bonded thiocyanate complexes, whereas class B metals (forming soft acids) tend to form S-bonded thiocyanate complexes.

This classification is based on the HSAB (hard and soft (Lewis) acids and bases) concept, which is also known as the Pearson acid base concept. According to it:

Type of Acid	CHARACTERISTICS	EXAMPLES
Hard acids	* Atomic centres of small ionic radii (<90 pm). * High positive charge. * Empty orbitals in their valence shells. * Low electronegativity (0.7-1.6) and low electron affinity. * Likely to be strongly solvated. * High energy LUMO.	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+} Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Ir^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO^{2+}, UO_2^{2+} $BeMe_2$, BF_3, BCl_3, $B(OR)_3$, $AlMe_3$
Soft acids	* Large radii (>90 pm). * Low or partial positive charge. * Completely filled orbitals in their valence shells. * Intermediate electronegativities (1.9-2.5) * Low energy LUMO's with large magnitude of LUMO coefficients.	**Cu^+**, Ag^+, Au^+, Hg^+, Cs^+, Tl^+, Hg^{2+}, Pd^{2+}, Cd^{2+}, Pt^{2+} Metal atoms in zero oxidation states
Borderline acids		Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, **Zn^{2+}**, Pb^{2+}, $B(CH_3)_3$, SO_2, NO^+

Since Cu^+ is a class B metal (forming soft acid), it forms S-bonded thiocyanate: Cu–S–C≡N

Zn^{2+} is a borderline acid, so it forms both S-bonded and N-bonded thiocyanates:

N≡C–S–Zn–S–C≡N

S=C=N–Zn–N=C=S

S=C=N–Zn–S–C≡N

Geometry of thiocyanate ion, whatever resonance structure ($N{\equiv}C{-}S^-$ or $S{=}C{=}N^-$), is linear, and geometry around the atom bonded to the metal is bent due to the lone pair of electrons on N and two lone pairs on S: