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Kakva je priroda vezivanja BF_4^-, NO_3^- i ClO_4^- za komplekse Cu(II) sa Žirarovim T hidrazidom? Kada mogu nastati binuklearni kompleksi?

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Četiri kompleksa, [Cu**L**Cl]BF_4, [Cu**L**Cl]NO_3, $[Cu_2$**L**$_2Cl_2](BF_4)_2$ i [Cu**L**Cl]ClO_4, sa istim $[Cu$**L**$Cl]^+$ fragmentom (**L**=(*E*)-*N*,*N*,*N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene) hydrazinyl)ethan-1-amin) su okarakterisani metodom difrakcije X-zraka. Na osnovu dužina veza, formule kompleksa su napisane tako da je $[Cu$**L**$Cl]^+$ unutrašnja sfera kompleksa, a $BF4^-$, $NO3^-$ i $ClO4^-$ pripadaju spoljašnjoj sferi. Proračuni zasnovani na Teoriji funkcionala gustine, u kojoj je disperzija korigovana na ne-lokalan način, na strukturama dobijenim difrakcijom X-zraka, su izvedeni u cilju razjašnjavanja prirode interakcija anjona sa Cu(II) jonom. Rezultati različitih analiza, kao što su dekompozicija interakcione energije, indeks nekovalentnih interakcija, model nezavisnog gradijenta i kvantna teorija atoma u molekulima, pokazuju da su anjoni u mononuklearnim kompleksima slabo koordinovani, dok je $BF4^-$ u binuklearnom kompleksu kontra jon, elektrostatički vezan za unutrašnju sferu. Takođe, proračuni objašnjavaju činjenicu da je samo kompleks $[Cu_2$**L**$_2Cl_2](BF_4)_2$ binuklearni sa mostnim Cl^- jonima. Ova studija pokazuje da se nedoumice oko koordinacionog broja u realnim kristalnim strukturama kompleksa mogu otkloniti detaljnom analizom elektronske gustine.

What is the nature of binding of BF_4^-, NO_3^- and ClO_4^- to Cu(II) complexes with Girard's T hydrazine? When can binuclear complexes be formed?

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Four complexes, [Cu**L**Cl]BF_4, [Cu**L**Cl]NO_3, $[Cu_2$**L**$_2Cl_2](BF_4)_2$ and [Cu**L**Cl]ClO_4 having the same $[Cu$**L**$Cl]^+$ moiety, (**L**=(*E*)-*N*,*N*,*N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene) hydrazinyl)ethan-1-amin), were characterized by single crystal X-ray diffraction methods. According to the bond distances, the formulas have been written such that $[Cu$**L**$Cl]^+$ is the inner sphere, while $BF4^-$, $NO3^-$ and $ClO4^-$ belong to the outer sphere. Non-local density-dependent dispersion corrected Density functional theory (DFT) calculations on the X-ray structures have been performed to rationalize interactions of anions to the Cu(II) ion. Results of analysis based on energy decomposition, Non-Covalent Interactions Index, Independent Gradient Model analysis, and Quantum Theory of Atoms in Molecules revealed that in mononuclear complexes, anions are weakly coordinated, while in binuclear complex, $BF4^-$ is counter-anion, electrostatically bonded to the inner sphere. Furthermore, DFT calculations rationalized the fact that only complex $[Cu_2$**L**$_2Cl_2](BF_4)_2$ is binuclear with bridging Cl^- ions. The present study shows that ambiguity about actual coordination number in the real crystal structures of coordination compounds can be solved with thorough analysis of the electron density.