Five-coordinate complexes of 21-thiaporphyrin : preparations, spectra, and structures of iron(II), nickel(II), and copper(II) complexes.

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Streszczenie

Insertion of Fe(II), Ni(II), and Cu(II) as their chloride salts into tetraphenyl-21 -thiaporphyrin, STPPH, yields Feu(STPP)Cl (S = 2, Meff = 5.2 mb), Nin(STPP)Cl (S =1, Meff = 3.3 mb)> and Cun(STPP)Cl (5 = '/2). Electronic spectra of these complexes show porphyrin-like behavior with a strong Soret peak at 400 nm. The Móssbauer spectrum for Fen(STPP)Cl (QS = 3.93 mm/s, IS = 0.88 mm/s at 295 K) is characterized by a large quadrupolar splitting found for related high-spin iron(II) complexes. The structures of these three isomorphous compounds (triclinic, /) have been determined by X-ray diffraction: Fen(STPP)Cl(CH3CN), a = 10.059 A, b = 13.661 (4) A, c = 15.033 (5) A, a = 102.53 (2)°, ß = 104.16 (2)°, y = 106.37 (2)°, Z = 2 at 130 K, least-squares refinement of 240 parameters using 3034 reflections, R = 0.077; Nin(STPP)Cl, a = 10.154 (3) A, b = 13.687 (4) A, c = 15.064 (4) A, a = 101.97 (2)°, ß = 103.62 (2)°, = 105.90 (2)°, Z = 2 at 293 K, least-squares refinement of 489 parameters with 4860 reflections, R = 0.053; Cun(STPP)Cl(CH3CN), a = 10.061 (6) A, b = 13.646 (7) A, c = 14.930 (8) A, a = 102.12 (4)°, ß = 104.02 (4)°, y = 108.20 (4)°, Z = 2 at 130 K, least-squares refinement of 228 parameters with 3951 reflections, R = 0.084. The complexes share a basic five-coordinate structure with approximately square-pyramidal geometry and an apical chloride. The thiophene ring is bent from the plane of the remainder of the STPP" ligand core and is rj'-bound to the metal through a pyramidal sulfur.