

Synthesis and characterization of the cobalt complexes of new BF_2^+ bridged, anthracene substituted bis(α -dioxime) macrocycles.

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Streszczenie

The synthesis, characterization and structure are described for new cobalt complexes, with a BF_2^+ bridged, bis(α -dioxime) ligand, based upon a sterically demanding framework derived from an anthracene Diels-Alder adduct. The ligand provides a deep cleft within which axial ligands and/or O_2 can bind. The crystal structures of the bis- and mono(BF_2^+) bridged complexes have space groups $P2_1/c$ and $P1$, respectively, with unit cell dimensions $a = 12.662(2) \text{ \AA}$, $b = 16.430(3) \text{ \AA}$, $c = 10.438(3) \text{ \AA}$, $\beta = 103.51(2)^\circ$, $a = 12.046(1) \text{ \AA}$, $b = 17.596(3) \text{ \AA}$, $c = 9.939(1) \text{ \AA}$, $\alpha = 105.15(1)^\circ$, $\beta = 102.87(1)^\circ$, and $\gamma = 78.13(1)^\circ$, respectively. For both complexes $Z = 2$ and the residuals R and R_w were 0.070, 0.104, and 0.059, 0.075, respectively. ESR studies show that the cobalt(II) complexes have a strong tendency to bind two axial nitrogen bases, adopting a coordination number of six. The dioxygen affinity of the new cobalt(II) dioxygen carrier is limited by the competition between axial base binding and O_2 binding. This extends the understanding of correlations between electrode potentials and O_2 affinities and possible sources of apparent contradictions.

Słowa kluczowe

Cobalt complex, macrocycle, dioxygen binding, ESR study, X-ray crystal structure

Adres publiczny

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