

Dioxygen adducts of lacunar cobalt(II) cyclidene complexes.

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The factors controlling the reversible dioxygen binding in lacunar cobalt(II) cyclidene complexes (Figure1) have been examined. Extensive structural variation reveal that the dioxygen affinity can be controlled by both steric and electronic means. The dioxygen affinity decreases monotonically with the length of a polymethylene bridging group (R^* , Figure1) from octamethylene to tetramethylene; no binding occurs with the still shorter trimethylene bridge. From the analysis of a large array of experimental data, the effect of the R^2 and R^3 substituents on dioxygen affinity are found to be mainly electronic; for example, electron-withdrawing groups at the R^2 and R^3 positions decrease the affinity.

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