Ferro and Antiferromagnetic Couplings in Trinuclear M^{II}-U^{IV}-M^{II} Complexes.

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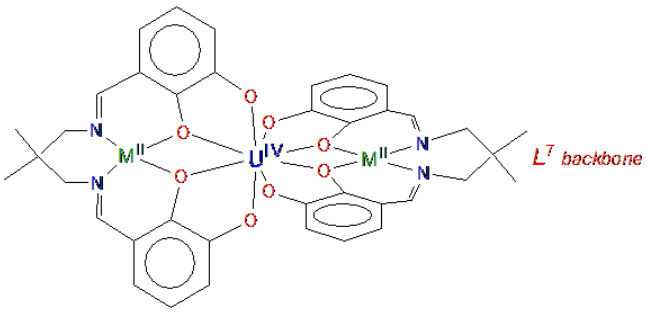
ABSTRACT

The magnetic properties of the trinuclear Schiff base complexes, M_2AnL^i (M^{II} = Zn,Cu; An^{IV} = Th, U; L^i = Schiff base; i = 1-4,6,7,9), and M_2UL^7 (M^{II} = Co, Ni, Cu; L^7 =*N,N'*-bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine), exhibiting the $[M(\mu\text{-}O)_2]_2U$ core structure (3d-5f-3d subsystem), have been investigated theoretically using scalar relativistic ZORA/DFT computations, combined with the Broken Symmetry approach. The calculated coupling constants J_{CuU} between the Cu and U atoms, agree with the observed shift from the antiferromagnetic (AF) character of the $L^{1,2,3,4}$ complexes to the ferromagnetic (Ferro) of the $L^{6,7,9}$ ones [1]. Moreover, the calculated coupling constants J_{MU} agree with the AF character of the Ni_2UL^7 one, consistent with the experimentally observed AF behaviour for Co_2UL^7.The natural populations, bond orders and the magnetic molecular orbital analyses, reveal the driving role, regarding the Ferro or AF character, of the U(5f) covalent contribution to the bonding within the M-O-U coordination. The analyses are supported by the study of the mixed $ZnMUL^7$ and M_2ThL^7 systems, where the Co^{II} ($3d^7$) and Ni^{II} ($3d^8$) paramagnetic ions are replaced by the diamagnetic Zn^{II}($3d^{10}$) one, whereas in the second complex, the U^{IV}($5f^2$) paramagnetic center is replaced by the diamagnetic Th^{IV}($5f^0$) one.



References

[1] Meskaldji, S.; Belkhiri, L.; Maurice R.; Costuas, K.; Le Guennic, B.; Boucekkine, A.; Ephritikhine, M. Electronic structure and magneto-structural correlations study of Cu_2UL trinuclear Schiff base complexes: a 3d-5f-3d case. *J. Phys. Chem.* A **2023**, 127, 1475–1490