Formation of Coinage-Metal?Fullerene Adducts. Evaluation of the Interaction Nature between Triangular Coinage Metal Complexes (M3 = Cu, Ag, and Au) and C60 through Relativistic Density Functional Theory Calculations

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The recent formation of [M3(3,5-(CF3)2Pz)3]-C60 cocrystals in a 4:1 ratio have shown the coinage metal complex's ability to bind fullerene, acting as buckycatchers. Here, we clarify the nature of such interaction accounting for the stabilization of the whole assembly via two models of different 4:1 and 1:1 ratios, within the framework of relativistic dispersion-corrected density functional theory. Our results exhibit a strong van der Waals character in the interaction, supported by the electrostatic character of the acidic-M3 ring provided by coinage metals. This feature held constant throughout the coinage metal group, providing further guidance for explorative synthesis efforts seeking to increase the strength and versatility of the binding capabilities of coinage metal complexes, which is useful for predicting the rise of noncovalent interactions toward less symmetric fullerenes and endohedral metallofullerenes. In addition, the observed van der Waals character is retained in the hypothetical systems involving representative fullerene fragments, based on corannulene (C20H10) and sumanene (C21H12). These results highlight the versatility of trinuclear complexes which can adopt a convex distortion highly suitable for interacting with curved ?-surfaces. Moreover, the nature and strength of the interaction do not significantly vary with the number of [M3] complexes in the C60 fullerene case, suggesting that the number of coinage-metal units involved in the adduct formation is related to the ?-surface area available in the fullerene structure and the stoichiometry employed in the co-crystallization. Hence, we envisage the exploration of novel supramolecular arrays for the formation of structures featuring preorganized domains involving fullerenes and other appealing ?-systems.