Communication

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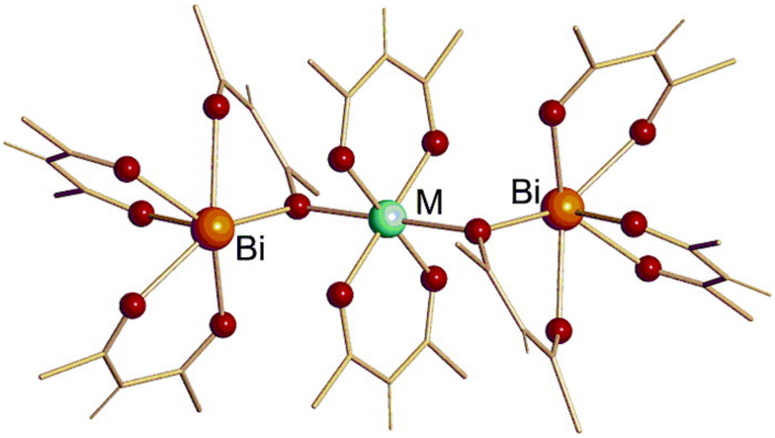

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Heterometallic Bismuth-Transition Metal Homoleptic β-Diketonates

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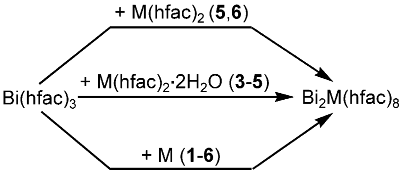
Metal β-diketonates have received much attention because of their use as MOCVD precursors for oxide materials.[1] Due to their chelating character, β-diketones are not generally considered as proper ligands for the formation of heterometallic species. Thus, only a few examples of heterometallic β-diketonate complexes have been reported to date. The first group of bimetallic diketonates described in the 1960s includes Cs[M(hfac)$_4$] (M = Y, Eu, Am; hfac = hexafluoroacetylacetonate)[2] compounds that can be formulated as built of Cs^+ cations and $[M(hfac)_4]^-$ anions, with Cs···F and Cs···O distances being in the range of 3.10−3.50 Å. Recently, a similar complex, K[Mn(hfac)$_3$], having a polymeric structure and stronger K···O contacts (2.75−2.82 Å) has been reported.[3] Another example found in earlier literature is the Co(acac)$_3$Eu(fod)$_3$ complex[4] in which Co and Eu units are connected through Eu···O_{acac} interactions of 2.59 Å. At the same time, a number of homometallic β-diketonates are known to maintain polynuclear structures in the absence of solvent donor molecules through strong Lewis acid−base interactions[5] or through the formation of oxo-(hydroxo) bridges[6] that strengthen the connections between metal atoms.

We were particularly interested in targeting bimetallic bismuth-transition metal complexes[7] as potential single-source precursors for crystalline oxide phases. A number of bismuth-transition metal oxide materials are known[8] to exhibit desirable properties, including oxide-ion conductivity, catalysis, ferroelectrics, high T_c superconductivity, and nonlinear optics. Several heterobimetallic bismuth compounds have been reported as precursors for bismuth oxide materials,[9] none of which are homoleptic diketonates. In this communication, we report a general synthetic approach and characterization of the first family of heterobimetallic homoleptic diketonates, Bi$_2$M(hfac)$_8$, that contain bismuth(III) and the first row divalent transition metals, M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Cu (**5**), and Zn (**6**).

Three major synthetic routes (Scheme 1), all using Bi^{III} hexafluoroacetylacetonate[10] as starting material, were employed for the synthesis of the target Bi$_2$M(hfac)$_8$ complexes. The most efficient method (ca. 90% yield) was a direct reaction between Bi(hfac)$_3$ and anhydrous M(hfac)$_2$ (M = Cu and Zn)[11] performed in a sealed ampule at 60 °C. We also found in the case of **5** that this reaction can be readily carried out at room temperature in noncoordinating solvents. Taking into account the limited availability of metal diketonates without exogenous ligands, we have developed yet another approach for **3**−**5** using the corresponding aqua bis-adducts, M(hfac)$_2$·2H$_2$O.[11a,12] In the latter reaction, which proceeds in an evacuated ampule at ca. 85 °C, Bi(hfac)$_3$ effectively substitutes the coordinated water molecules, giving yields of about 50%. Finally, in the most general synthetic method, Bi(hfac)$_3$ reacts in the solid state with pure finely divided metals at 70−90 °C to produce the title compounds Bi$_2$M(hfac)$_8$ (**1**−**6**) in 50−80% yield. In all of the above solid-state reactions, the heterobimetallic diketonates are deposited in the cold end (ca. 5 °C lower) of the ampule in the form of large prismatic crystals.

Scheme 1



All of the heterobimetallic diketonates **1**−**6** are volatile and can be further purified by an additional sublimation if needed. The compounds are relatively stable and can be handled quickly in dry air. They are readily soluble in coordinating solvents, such as acetone and THF. The solubility in noncoordinating solvents, such as dichloromethane and chloroform, is limited; nevertheless, we have shown that the heterometallic complexes can be recrystallized from the latter. According to TGA/DTA data, the thermal decomposition of compounds **1**−**6** on heating in nitrogen proceeds in three or four steps beginning at 80−90 °C and completing at 300−350 °C and shows no apparent loss of β-diketonates to sublimation.

Single-crystal X-ray analysis of compounds **1**−**6** revealed that the solid-state structure of all complexes is represented by trinuclear molecules in which a planar M(hfac)$_2$ unit is sandwiched between two Bi(hfac)$_3$ groups (Figure 1a,b shows representative structures). The heterometallic molecule is held together by two M−O contacts between the central transition-metal atom and one of the oxygens on a bismuth-chelating diketonate ligand. The coordination of the M^{II} atom is thus octahedral, while the bismuth atom maintains a distorted pentagonal pyramidal coordination with two β-diketonate ligands approximately located in the basal plane and the third ligand being in a vertical mirror plane.

Heterobimetallic complexes **1**−**6** crystallize in the triclinic space group $P\bar{1}$ with one trinuclear molecule per unit cell. The M^{II} atom resides on an inversion center, and the two Bi(hfac)$_3$ units are symmetry-related. Compounds **1**−**4** and **6** are isostructural, while the copper structure **5** is unique. In the former cases, the bridging oxygen atom belongs to one of the basal plane ligands (Figure 1b), but in the latter it comes from the vertical mirror plane ligand (Figure 1a). The molecules of **1**−**4** and **6** all have bismuth-bound nonbridging diketonate groups disordered over two rotational orientations indicating the statistical distribution of enantiomeric forms of the coordinated Bi(hfac)$_3$ unit in the crystal structure.

When comparing structures of heterobimetallic compounds **1**−**6** with the homometallic parent diketonates, we found that the geometry of Bi(hfac)$_3$ (Figure 1c) is only slightly affected. The changes correspond to elongation of both Bi−O distances for the bridging ligand. At the same time, the geometry of the M(hfac)$_2$ unit may experience substantial changes. While coordination of the Cu atom in pure Cu(hfac)$_2$ is square planar[11a] as in **5**, coordination of zinc in Zn(hfac)$_2$,[11b] without additionally bound donor molecules, is tetrahedral (Figure 1d), which is typical for the d^{10} configuration.

The bridging M−O interactions are significantly different for the trinuclear molecules **1**−**6**. In the unique copper structure **5**, the Cu−O contacts are the longest (2.588(2) Å), while for the nickel

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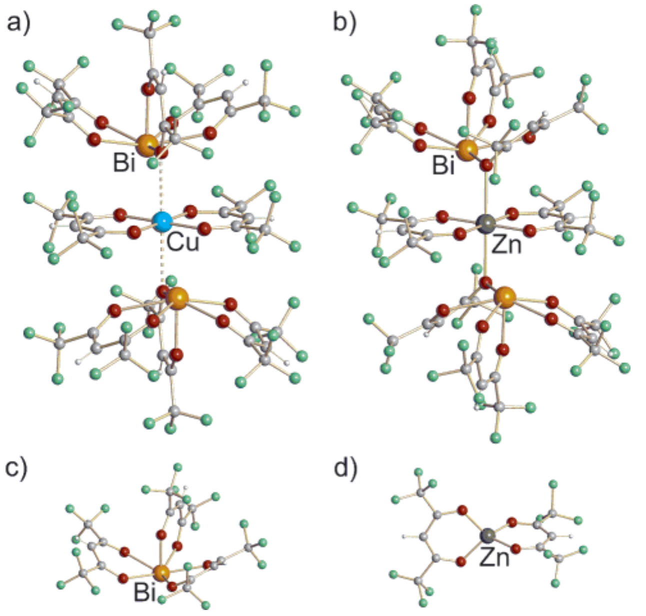

Figure 1. Trinuclear molecules of heterobimetallic homoleptic β-diketonates (a) $[Bi_2Cu(hfac)_8]$ (**5**) and (b) $[Bi_2Zn(hfac)_8]$ (**6**). Coordination of metal atoms in the structures of parent homometallic β-diketonates (c) $Bi(hfac)_3$ and (d) $Zn(hfac)_2$.

structure **4**, these distances are just 2.163(4) Å. The M−O interactions gradually lengthen from cobalt (**3**, 2.229(3) Å) through iron (**2**, 2.250(3) Å) to manganese (**1**, 2.307(3) Å). The Zn−O distances in **6** are also in that range, measured at 2.296(3) Å.

The retention of the trinuclear structure in noncoordinating solvents has been confirmed by the following observations. First, we demonstrated that heterobimetallic β-diketonates can be recrystallized from dichloromethane solution. Second, the IR data for the solid species appear to be identical to the solution spectra. Finally, the behavior of $Bi_2Zn(hfac)_8$ (**6**) in solution has been studied by proton NMR. The ^1H NMR spectrum of **6** in CD_2Cl_2 reveals the presence of two CH resonances at $\delta = 6.41$ and 6.32 ppm that correspond to a downfield shift versus free $Bi(hfac)_3$ ($\delta = 6.31$ ppm) and $Zn(hfac)_2$ ($\delta = 6.23$ ppm). On the contrary, in a coordinating solvent such as acetone, the two proton signals ($\delta = 6.14$ and 6.02 ppm) are consistent with the collapse of the trinuclear structure and the formation of acetone adducts of the homometallic diketonates.

The ^1H NMR spectra of **6** revealed only a single chemical environment for the Bi-bound hfac sites, characterized by a broad singlet, thus suggesting that the diketonate ligands, inequivalent in the solid-state structure, are fluxional in solution on the NMR time scale.

In summary, the Lewis acidity of the first row transition-metal(II) centers in their hexafluoroacetylacetonates allows for the facile formation of heterobimetallic coordination complexes with bismuth(III) β-diketonate. Stable Bi:M = 2:1 (M = Mn, Fe, Co, Ni, Cu, Zn) complexes that represent rare examples[9a] of heterometallic compounds that are compositionally rich in bismuth have been obtained in good yields under relatively mild conditions. The various synthetic techniques employed in this work appear to be general for the preparation of compounds incorporating a wide range of main group elements and transition metals. This simple approach opens broad opportunities for producing single-source precursors for multimetallic oxide and oxofluoride materials.

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Supporting Information Available: Preparative details, analytical and spectroscopic data, TGA traces of the thermal decomposition, and X-ray structural data for **1**-**6**, $Bi(hfac)_3$, and $Zn(hfac)_2$ (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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