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$[W(bipy)(CN)_6]^-$: A Suitable Metalloligand in the Design of Heterotrimetallic Complexes. The First $Cu^{II}Ln^{III}W^{V}$ Trinuclear Complexes

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Supporting Information

ABSTRACT: The first 3d−4f−5d heterotrimetallic complexes using $[W^{V}(bipy)(CN)_6]^-$ as a metalloligand were synthesized (bipy = 2,2′-bipyridine). The structural and magnetic properties of three $[Cu^{II}Ln^{III}W^{V}]$ complexes (Ln = Gd, Ho, Tb) are discussed.

Polynuclear complexes containing two different paramagnetic metal ions have played a crucial role in the development of molecular magnetism.[1] The most attractive combinations consist of metal ions with orthogonal magnetic orbitals (ferromagnetic coupling) or with a big and a small spin size, respectively (antiferromagnetic coupling). An important condition to be fulfilled by a synthetic strategy is to avoid the scrambling of the metal ions that leads to the formation of mixtures of homo- and heterometallic complexes. It is obvious that the rational synthesis of heterotrimetallic species is even more complicated. The increasing difficulties encountered when three different spin carriers have to be confined within the same molecular entity represent the main reason for the limited number of heterotrimetallic complexes reported to date.[2] Very efficient synthetic routes toward heterotrimetallics consist of self-assembly processes involving preformed heterobimetallic species and a metalloligand carrying the third metal ion.[2a−l] We have illustrated this strategy with several 3d−3d′−3d″, 3d−3d′−4f, and 3d−4f−4d complexes.[2d−i] The use of cyanido complexes as metalloligands is very appealing because of the well-known ability of the cyanide group to mediate exchange interactions between the paramagnetic centers. A plethora of heterometallic complexes with exciting magnetic properties have been obtained using stable homoleptic anions as tectons ($[M(CN)_6]^{3-}$, M^{III} = Fe, Cr; $[M(CN)_8]^{3-}$, M^{V} = Mo, W).[3] Heteroleptic cyanido complexes are also employed as metalloligands.[4] The presence of coligands within the coordination sphere of the cyanido building block decreases the dimensionality of the coordination polymers when fully solvated metal ions are used in the assembly process. The formation of low-nuclearity species is favored if both the metalloligand and the assembling cationic complex contain blocking ligands. To the best of our knowledge, there is only one example of a heterotrimetallic complex that has been obtained using a 3d heteroleptic cyanido metalloligand[2l] and none with 4d or 5d heteroleptic species. Cyanido complexes of 4d and 5d metal ions are very attractive for the building of heterometallic systems because of the expected stronger exchange interactions with respect to the 3d counterparts.[3c] However, the 4d and 5d heteroleptic metalloligands have rarely been used as tectons in the design of heterometallic complexes, as illustrated by the paucity of reports on 5d−3d bimetallic polynuclear complexes with $[W(bipy)(CN)_6]^-$.[5]

Herein we report the first complexes containing three different paramagnetic metal ions (3d−4f−5d), which have been synthesized using $[W(bipy)(CN)_6)]^-$ as a metalloligand: $[(CN)_5(bipy)W(CN)Cu(3\text{-}MeOsalpn)Ln(O_2NO)_2(H_2O)]\cdot 3MeCN$ [Ln = Gd (**1**), Tb (**2**), and Ho (**3**); $3\text{-}MeOsalpn^{2-}$ = *N*,*N*′-propylenebis(3-methoxysalicylideneiminate)]. The compounds have been obtained by reacting the binuclear 3d−4f complex $[Cu(3\text{-}MeOsalpn)Ln(O_2NO)_3]$, formed in situ from $[Cu(3\text{-}MeOsalpn)]$ and lanthanide nitrate, with $(AsPh_4)[W(bipy)(CN)_6]$. IR spectra show the characteristic bands of the bridging and terminal cyanido groups (see the Supporting Information, SI).

Compounds **1**−**3** are isostructural and crystallize in the triclinic system, space group $P\bar{1}$, with cell parameters and other pertinent crystallographic data given in Table S1 (SI). Their structure consists of neutral $[Cu^{II}Ln^{III}W^{V}]$ heterotrimetallic units (Figure 1) and three acetonitrile molecules. The $[W(bipy)(CN)_6]^-$ metalloligand is coordinated through one cyanido group to the apical position of the Cu^{II} ion. Because compounds **1**−**3** are isostructural, only the structure of the

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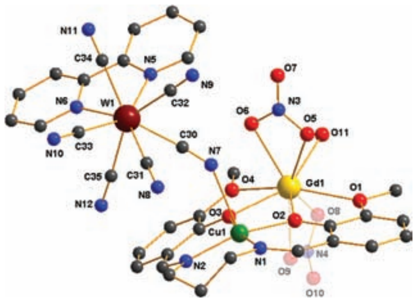

Figure 1. Perspective view of **1** along with the atom numbering scheme. The solvent molecules and H atoms are omitted for clarity.

gadolinium derivative **1** will be discussed. The $\{W(CN)_6(bipy)\}$ moiety adopts a distorted square-antiprism coordination geometry (normalized bite $b = 1.19$).[6] The Cu^{II} ion, which is located in the inner compartment of the Schiff base ligand, has a square-pyramidal environment with two N and two O atoms from the Schiff base in the basal plane and the bridging cyanido group occupying the apical position [$Cu1-N7_{ax} = 2.536(7)$ Å]. The value of the $Cu1-N7_{ax}-C30$ angle is 145.9°, and the intramolecular distance between Cu^{II} and W^{V} across the cyanido bridge is 5.586(1) Å.

The Gd^{III} ion is surrounded by nine O atoms arising from the large compartment of the ligand, a aqua ligand, and two bidentate nitrato groups. The distance of Cu1···Gd1 within the trinuclear unit is 3.4656(10) Å. Selected bond distances are gathered in Table S2 (SI).

Analysis of the crystal packing reveals the formation of supramolecular double chains, running along the crystallographic *a* axis, which are assembled from neutral heterotrimetallic entities connected through hydrogen bonds and $\pi-\pi$ stacking interactions (Figures S1 and S2 in the SI).

In addition to studying the magnetic properties of **1**–**3**, which are detailed herein, and looking for a better understanding of them, we have also investigated the magnetic and electron paramagnetic resonance (EPR) properties of the mononuclear W^{V} metalloligand.

The $\chi_M T$ versus T plot of the W^{V} precursor (χ_M is the molar magnetic susceptibility) is shown in Figure S4 (SI). Analysis of the magnetic data of this mononuclear complex through a Curie law for a spin doublet leads to the following best-fit parameters: $g = 1.96(1)$, $\theta = -0.65(1)$ K, and TIP $= 137 \times 10^{-6}$ $cm^3\ mol^{-1}$. θ is the Weiss parameter, which takes into account the intermolecular magnetic interactions. The X-band EPR spectrum of a polycrystalline sample at 5.0 K (Figure S3 in the SI) exhibits a rhombic pattern with the following set of components of the **g** tensor and hyperfine constants [$I(^{183}W) = {}^{1}/_{2}$]: $g_1 = 1.956$, $g_2 = 1.953$, $g_3 = 1.946$, $A_1 = 17$ G, $A_2 = 85$ G, and $A_3 = 82$ G. These values are comparable to those reported for the parent $[W(CN)_8]^{3-}$ species.[7]

We started the investigation of the magnetic properties of the series of $[Cu^{II}Ln^{III}W^{V}]$ trinuclear complexes with the gadolinium derivative: the lack of orbital momentum for Gd^{III} allows treatment of the magnetic data using the Heisenberg–Dirac–Van Vleck Hamiltonian. The temperature dependence of the $\chi_M T$ product per trinuclear unit of **1** is depicted in Figure 2. $\chi_M T$ at room temperature is 8.65 $cm^3\ mol^{-1}$ K, as is expected for a set of two spin doublets ($S_{Cu} = {}^{1}/_{2}$ and $S_W = {}^{1}/_{2}$) and a spin octet ($S_{Gd} = {}^{7}/_{2}$) all magnetically noninteracting. Upon cooling, $\chi_M T$ continuously increases to reach a maximum value of 9.95 $cm^3\ mol^{-1}\ K^{-1}$ at 14.0 K and finally decreases to 6.76 $cm^3\ mol^{-1}$ K at 1.9 K. This plot is indicative of a dominant ferromagnetic interaction, with the decrease of $\chi_M T$ in the low-temperatures domain being due to weak antiferromagnetic interactions and/or zero-field-splitting (ZFS) effects. The magnetization (M) versus H plot for **1** at 2.0 K (see the inset of Figure 2) tends to a saturation value close to $S = 9$ μ_B. The fact that such a plot is slightly below the curve for a magnetically noninteracting set of two spin doublets ($S_{Cu} = S_W = {}^{1}/_{2}$) and one octet ($S_{Gd} = {}^{7}/_{2}$) and also far from the plot for $S = {}^{9}/_{2}$ is indicative of very weak intramolecular ferromagnetic coupling together with intermolecular antiferromagnetic interactions (or ZFS effects) in **1**. The magnetic coupling between the Cu^{II} and Gd^{III} pair in **1** is expected to be ferromagnetic, as is illustrated by a large number of magnetostructural reports with similar systems.[2f] As far as the magnetic coupling between Cu^{II} and W^{V} through the single cyanido bridge is concerned, its nature and strength are dependent on several structural features: first, the two metal ions interact through a cyanide bridge pointing to the apical position of Cu^{II}, and this interaction is expected to be small; second, recent magnetostructural correlations on $Cu^{II}-\mu\text{-}NC-W^{V}$ (with an axial $Cu-N_{cyano}$ bond) complexes have shown that the value of the Cu–N–C angle is crucial, with smaller bending angles at the Cu^{II} side causing a nonzero orbital overlap, which favors antiferromagnetic interaction.[8] In the case of complex **1**, the bending of the Cu–N–C angle (ca. 145.9°), together with the apical coordination to Cu^{II} of the cyanido group and the quite long $Cu^{II}-N7$ distance, account for the weak antiferromagnetic coupling between the two spin doublets.

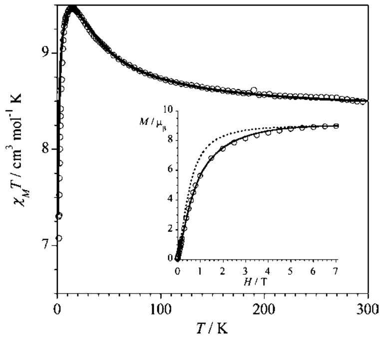

Figure 2. $\chi_M T$ versus T plot for **1**: (circles) experimental data; (solid line) best-fit curve. Inset: M versus H plot at 2.0 K: (circles) experimental data; (dashed line) Brillouin function for a spin $S = {}^{9}/_{2}$ with $g = 2.0$; (solid line) Brillouin function for a magnetically isolated three-spin set of $S_{Cu} = {}^{1}/_{2}$, $S_W = {}^{1}/_{2}$, and $S_{Gd} = {}^{7}/_{2}$.

The magnetic data for **1** were analyzed through the isotropic spin Hamiltonian shown in eq 1.

$$\mathbf{H} = -J\mathbf{S}_{Cu}\cdot\mathbf{S}_{Gd} - j'\mathbf{S}_{Cu}\cdot\mathbf{S}_{W} + \beta H(g_{Gd}\mathbf{S}_{Gd} + g_{Cu}\mathbf{S}_{Cu} + g_{W}\mathbf{S}_{W}] \quad (1)$$

The magnetic data have been simulated through numerical matrix diagonalization techniques using the Fortran program *VMPAG*.[9] Two sets of best-fit parameters with similar quality fits were obtained: $g_{Cu} = 2.14$, $g_{Gd} = 2.00$, and $g_W = 1.95$ (values common for both fits) with $J = +8.67$ cm^{-1}, $j = -1.52$ cm^{-1}, and $\theta = -0.45$ K (in one case) or $J = +8.90$ cm^{-1}, $j = -0.83$ cm^{-1}, and $D = 1.85$ cm^{-1}. θ is the Curie–Weiss term accounting for intermolecular interactions, and D is the ZFS parameter. It is clear that the value of the J parameter is in line with Costes' magnetostructural correlations for $Cu^{II}Gd^{III}$

complexes with similar ligands.[2i] Such a parameter follows the variation of the dihedral angle formed by the halves (O−Cu−O) and (O−Gd−O) of the bridging network: lowering the bending of the CuO_2Gd core causes ferromagnetic interaction to increase. In our case, the dihedral angle is 12.8°, and the value of J is close to those observed for complexes with similar bridging geometries (the highest J value, +10.1 cm^{-1}, was observed for a dihedral angle of 1.7°).[10] As far as the j parameter is concerned, we are faced with a very weak antiferromagnetic coupling, and its value is not as reliable as that of J. However, it agrees with the considerations formulated above for an axial-exchange pathway.

The temperature dependences of the $\chi_M T$ product for **2** and **3**, together with their M versus H plots at 2.0 K, are shown in Figure S5 (SI). At room temperature, $\chi_M T$ is equal to 13.40 (**2**) and 15.10 cm^3 mol^{-1} K (**3**). These values are as expected for a Tb^{III} (**2**) or Ho^{III} (**3**) and one Cu^{II} and a W^{V} magnetically isolated centers [$\chi_M T$ = 12.56 (**2**) and 14.80 cm^3 mol^{-1} K (**3**) for the corresponding ground states $^7F_6$ ($g_6 = {}^3/_2$) and $^5I_8$ ($g_8 = {}^5/_4$), respectively, assuming a contribution of the Cu^{II}−W^{V} pair of ca. 0.75 cm^3 mol^{-1} K ($S_{Cu} = S_W = {}^1/_2$)]. Upon cooling, $\chi_M T$ remains constant for **2** until 20 K, and it further decreases to 8.80 cm^3 mol^{-1} K at 1.9 K. In the case of **3**, $\chi_M T$ continuously decreases to reach a minimum value of 10.0 cm^3 mol^{-1} K at 1.9 K.

The presence of crystal-field effects and very large orbital moments for Tb^{III} and Ho^{III} in contrast to Gd^{III} masks the visualization of the possible magnetic interactions in **2** and **3** and also precludes the analysis of their magnetic data because of the large number of variable parameters whose weights are certainly greater than those of the magnetic couplings to be computed. However, in the case of **3**, the Curie law behavior observed in the high-temperature domain points toward the occurrence of an intramolecular ferromagnetic coupling, with the expected increase of $\chi_M T$ being compensated for by the decrease caused by the ligand field. The greater orbital contribution in the case of Ho^{III} with respect to Tb^{III} would account for the continuous decrease of $\chi_M T$ for **3** from room temperature. Compounds **2** and **3** do not show out-of-phase alternating-current signals, and therefore no single-molecule magnet (SMM) behavior.

In conclusion, we have illustrated for the first time the ability of $[W^V(bipy)(CN)_6]^-$ to generate heterotrimetallic complexes. The resulting 3d−4f−5d compounds are different from those obtained using the same 3d−4f precursor and $[M(CN)_8]^{3-}$ metalloligands (M = Mo, W).[2e] Other heterobinuclear, 3d−3d′, precursors can be employed as well. Further work on such heterotrimetallic complexes with interesting magnetic properties, especially SMM or single-chain magnetic behavior, is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Kahn, O. *Adv. Inorg. Chem.* **1995**, *43*, 179. (c) Beltran, L. M. C.; Long, J. R. *Acc. Chem. Res.* **2005**, *38*, 325. (d) Wang, X.-Y.; Avedaño, C.; Dunbar, K. R. *Chem. Soc. Rev.* **2011**, *40*, 3213.

(2) (a) Verani, C. N.; Rentschler, E.; Weyhermüller, T.; Bill, E.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **2000**, 4263. (b) Kou, H.-Z.; Zhou, B. C.; Gao, S.; Wang, R.-J. *Angew. Chem., Int. Ed.* **2003**, 3288. (c) Shiga, T.; Ohkawa, H.; Kitagawa, S.; Ohba, M. *J. Am. Chem. Soc.* **2006**, *128*, 16426. (d) Andruh, M. *Chem. Commun.* **2007**, 2565. (e) Visinescu, D.; Madalan, A. M.; Andruh, M.; Duhayon, C.; Sutter, J.-P.; Ungur, L.; Van den Heuvel, W.; Chibotaru, L. F. *Chem.—Eur. J.* **2009**, *15*, 11808. (f) Andruh, M.; Costes, J.-P.; Díaz, C.; Gao, S. *Inorg. Chem.* **2009**, *48*, 3342. (g) Andruh, M.; Branzea, D. G.; Gheorghe, R.; Madalan, A. M. *CrystEngComm* **2009**, 2571. (h) Gheorghe, R.; Madalan, A. M.; Costes, J.-P.; Wernsdorfer, W.; Andruh, M. *Dalton Trans.* **2010**, *39*, 4734. (i) Andruh, M. *Chem. Commun.* **2011**, *47*, 3025. (j) Sutter, J.-P.; Dhers, S.; Rajamani, R.; Ramasesha, S.; Costes, J.-P.; Duhayon, C.; Vendier, L. *Inorg. Chem.* **2009**, *48*, 5820. (k) Gao, T.; Yan, P.-F.; Li, G.-M.; Zhang, J.-W.; Sun, W.-B.; Suda, M.; Einaga, Y. *Solid State Sci.* **2010**, *12*, 597. (l) Wang, H.; Zhang, L.-F.; Ni, Z.-H.; Zhong, W.-F.; Tian, L.-J.; Jiang, J. *Cryst. Growth Des.* **2010**, *10*, 4231. (m) Nesterov, D. S.; Graiff, C.; Tiripicchio, A.; Pombeiro, A. J. L. *CrystEngComm* **2011**, *13*, 5348. (n) Long, J.; Chamoreau, L.-M.; Mathonière, C.; Marvaud, V. *Inorg. Chem.* **2009**, *48*, 22.

(3) (a) Shatruk, M.; Avendano, C.; Dunbar, K. R. *Prog. Inorg. Chem.* **2009**, *56*, 155. (b) Visinescu, D.; Desplanches, C.; Imaz, I.; Bahers, V.; Pradhan, R.; Villamena, F. A.; Guionneau, P.; Sutter, J.-P. *J. Am. Chem. Soc.* **2006**, *128*, 10202. (c) Sieklucka, S.; Podgajny, R.; Korzeniak, T.; Nowicka, B.; Pinkowicz, D.; Kozieł, M. *Eur. J. Inorg. Chem.* **2011**, 305.

(4) (a) Lescouëzec, R.; Toma, L. M.; Vaissermann, J.; Verdaguer, M.; Delgado, F. S.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2005**, *249*, 2691. (b) Toma, L. M.; Toma, L. D.; Delgado, F. S.; Ruiz-Pérez, C.; Sletten, J.; Cano, J.; Clemente-Juan, J. M.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2006**, *250*, 2176. (c) Wang, S.; Ding, X.-H.; Zuo, J.-L.; You, X.-Z.; Huang, W. *Coord. Chem. Rev.* **2011**, *255*, 171.

(5) (a) Yoon, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2005**, *44*, 7714. (b) Yoon, J. H.; Lim, J. H.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2006**, *45*, 9613. (c) Yoon, J. H.; Lim, J. H.; Choi, S. W.; Kim, H. C.; Hong, C. S. *Inorg. Chem.* **2007**, *46*, 1529. (d) Kim, J. I.; Yoon, J. H.; Kwak, H. Y.; Koh, E. K.; Hong, C. S. *Eur. J. Inorg. Chem.* **2008**, 2756. (e) Choi, S. W.; Kwak, H. Y.; Yoon, J. H.; Kim, H. C.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2008**, *47*, 10214. (f) Choi, S. W.; Ryu, D. W.; Lee, J. W.; Yoon, J. H.; Kim, H. C.; Lee, H.; Cho, B. K.; Hong, C. S. *Inorg. Chem.* **2009**, *48*, 9066.

(6) Ribas Gispert, J. *Coordination Chemistry*; Wiley-VCH: Weinheim, Germany, 2008; p 33.

(7) McGarvey, B. R. *Inorg. Chem.* **1966**, *5*, 476.

(8) Korzeniak, T.; Desplanches, C.; Podgajny, R.; Giménez-Saiz, C.; Stadnicka, K.; Rams, M.; Sieklucka, B. *Inorg. Chem.* **2009**, *48*, 2865.

(9) Cano, J. *VMPAG package*; University of Valencia: Valencia, Spain, 2003.

(10) Costes, J.-P.; Dahan, F.; Dupuis, A. *Inorg. Chem.* **2000**, *39*, 165.