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Structure and magnetism of the first strictly dinuclear compound containing paramagnetic 3d and 5f metal ions. Major influence of the Cu^{II} ion coordination on the exchange Cu^{II}–U^{IV} interaction

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The dinuclear compound [$CuL^2(py)U(acac)_2$] has been synthesized by treating [$Cu(H_2L^2)$] with $U(acac)_4$ (L^2 = *N*,*N′*-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine) and shows the antiferromagnetic Cu–U interaction; the distinct magnetic behaviour of the trinuclear complexes [$(CuL^2)_2U$] (antiferromagnetic) and [$\{CuL^1(py)\}U\{CuL^1\}$] (ferromagnetic) revealed the major influence of the Cu^{II} ion coordination on the exchange interaction (L^1 = *N*,*N′*-bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine).

A great variety of heteropolymetallic compounds containing both 3d and 4f ions have been synthesized in order to develop the molecular approach to magnetic materials and to understand the mechanism of the exchange interaction.[1] Because the f electrons are less shielded in the actinide than in the lanthanide ions, it can be expected that complexes in which a paramagnetic 5f ion is interacting with another spin carrier would exhibit interesting magnetic properties. Such complexes are very rare: Sutter *et al.* prepared the three-dimensional network of [$K_2Mn(C_2O_4)_4U$]·$7H_2O$,[2] for which no magnetic coupling was observed, and we synthesized the trinuclear complexes [$\{ML^1(py)_x\}_2U$],[3] which revealed the antiferromagnetic Ni–U and ferromagnetic Cu–U interactions (L^1 = *N*,*N′*-bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine).

These intriguing results led us to prepare a discrete bimetallic Cu–U compound which would provide a more simple model for the study of the exchange interaction. This was possible by changing the diimino chain of the Schiff base ligand and here we present the synthesis, crystal structure and magnetic behaviour of [$CuL^2(py)U(acac)_2$] (**1**), the first strictly dinuclear compound of paramagnetic 3d and 5f ions (L^2 = *N*,*N′*-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine); we also compare the structures and magnetic properties of the Cu_2U complexes with the L^1 and L^2 ligands, revealing the major influence of the Cu^{II} coordination on the exchange interaction.

The synthesis of **1** could be achieved by using the hexadentate compartmental Schiff base H_4L^2 as the dinucleating ligand. A solution of [$Cu(H_2L^2)$] (150 mg) and $U(acac)_4$ (244 mg) in pyridine (20 mL) was heated at 60 °C for 12 h and after addition of pentane (20 mL), the brown powder of **1** was filtered off, washed with pyridine and dried under vacuum (55% yield); dark brown crystals were isolated after crystallization from pyridine. For the purpose of the magnetic studies (*vide infra*), the analogous yellow compound [$ZnL^2(py)U(acac)_2$] (**2**) was also prepared. These reactions are in striking contrast with those of [$M(H_2L^1)$] (M = Ni, Cu, Zn) and $M'(acac)_4$ (M′ = Zr, Th, U) which afforded directly the trinuclear compounds [$\{ML^1(py)_x\}_2M'$], without it being possible to observe the dinuclear intermediates.[3] The new compounds were characterized by their elemental analyses, ^1H NMR spectra,† and X-ray crystal structure.‡

The crystal structure of a pyridine solvate of **1** is represented in Fig. 1 together with selected data. The Cu^{II} and U^{IV} ions occupy respectively the N_2O_2 and O_4 cavities of the Schiff base ligand and are bridged by the two oxygen atoms O2 and O3 of the salicylidene fragments. The Cu^{II} ion adopts a square pyramidal coordination mode, being displaced from the N_2O_2 base by 0.266(3) Å towards the pyridine ligand. The eight oxygen atoms of the L^2 and acac ligands form a dodecahedron around the U^{IV} ion, the two trapezia O1–O2–O3–O4 and O5–O6–O7–O8 intersecting at an angle of 88.9(1)°. The structure of the zinc analogue **2** is very similar to that of **1**; in particular, the corresponding U–O bond lengths and O–U–O angles in the two complexes vary at the most by a value of 0.06 Å and 6°, respectively.

The nature of the exchange interaction between the U^{IV} and Cu^{II} ions in **1** was determined by the empirical method which was previously employed in the study of Cu_3Ln_2,[4] CuLn,[5] and M_2U compounds[3] (Ln = 4f ion, M = Ni, Cu). The magnetic behaviour of **1** and **2** is shown in Fig. 2 in the form of $\chi_M T$ versus T; the $\chi_M T$ values for **2**, $(\chi_M T)$(ZnU), only consist of the contribution of the U^{IV} ion. The difference $\Delta = (\chi_M T)(CuU) - (\chi_M T)(ZnU)$ is approximately constant from 300 to 100 K and equal to $0.40 \pm 0.05\ cm^3\ mol^{-1}\ K$, a value which corresponds to an isolated Cu^{II} ion. Below 100 K, Δ decreases to reach a minimum at 40 K and then increases to $0.40\ cm^3\ mol^{-1}$ K at 2 K. This profile of the Δ *vs.* T curve indicates that the U^{IV}–Cu^{II} interaction in **1** is antiferromagnetic.

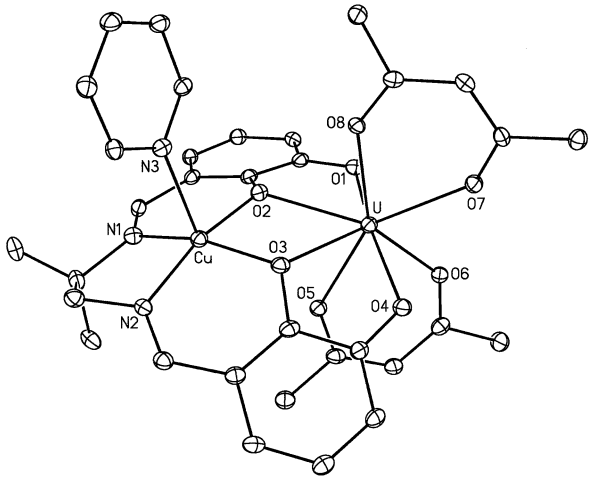

Fig. 1 View of the complex molecule in **1**·1.5py. Displacement ellipsoids are drawn at the 10% probability level. Selected distances (Å) and angles (°) in **1** and **2** (the latter in brackets): U–O1 2.282(5) [2.305(7)], U–O2 2.452(5) [2.428(8)], U–O3 2.497(5) [2.442(7)], U–O4 2.264(5) [2.280(7)], U–O5 2.345(5) [2.404(8)], U–O6 2.359(5) [2.364(7)], U–O7 2.367(5) [2.361(7)], U–O8 2.359(5) [2.398(7)], M–O2 1.912(5) [1.983(8)], M–O3 1.944(5) [1.971(7)], M–N1 1.941(7) [2.094(11)], M–N2 1.940(6) [2.063(11)], M–N3 2.320(6) [2.057(10)], U···M 3.574(1) [3.665(1)]; O1–U–O4 163.3(2) [169.4(3)], O2–U–O3 61.2(2) [60.0(3)], O5–U–O8 146.0(2) [148.3(3)], O6–U–O7 74.2(2) [71.4(2)], N1–M–N2 84.6(3) [85.0(3)], O2–M–O3 81.6(2) [76.1(3)].

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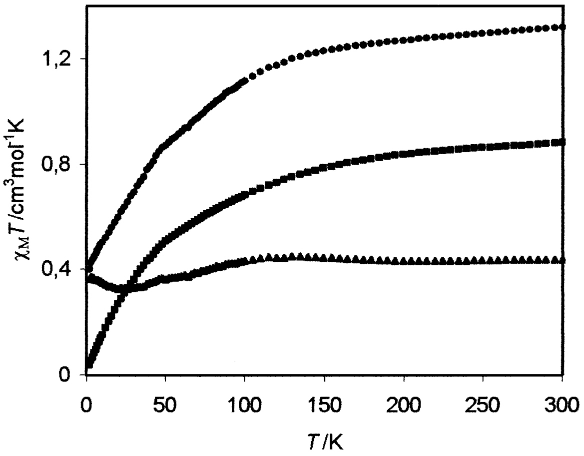

Fig. 2 Thermal dependence of $\chi_M T$ for the CuU and ZnU compounds **1** (●) and **2** (■) and the difference $\Delta = (\chi_M T)(\text{CuU}) - (\chi_M T)(\text{ZnU})$ (▲)

At this stage, it is not possible to determine whether the distinct magnetic properties of **1** (antiferromagnetic) and $[\{\text{CuL}^1(\text{py})\}\text{U}\{\text{CuL}^1\}]$ (ferromagnetic) could be related to the structural variations around the Cu^{II} or U^{IV} ion, or both. That the Cu^{II} environment has a major influence on the exchange interaction was revealed by the study of the trinuclear compound $[(\text{CuL}^2)_2\text{U}]$ (**3**). This Cu_2U complex was synthesized in 90% yield by using the same procedure as for **1**, from $[\text{Cu}(\text{H}_2\text{L}^2)]$ and U(acac)_4 in the molar ratio of 2 : 1 and by performing the reaction at 110 °C. In the crystal structure of **3** (Fig. 3), the dodecahedral configuration of the U^{IV} ion is identical to that found in $[\{\text{CuL}^1(\text{py})\}\text{U}\{\text{CuL}^1\}]$;[3] in particular, the O1–U–O4 or O5–U–O8 and O2–U–O3 or O6–U–O7 angles have mean values of 170(2) and 58.8(7)° respectively, while they are equal to 146.0(2) and 74.2(2)° in **1**. However, the Cu–U interaction in **3** is antiferromagnetic, as shown here again by the comparison of its magnetic behaviour with that of the zinc analogue $[\{\text{ZnL}^2(\text{py})\}_2\text{U}]$ (**4**); the plot of $\Delta' = (\chi_M T)(\text{Cu}_2\text{U}) - (\chi_M T)(\text{Zn}_2\text{U})$ *vs.* T has the same profile as that of Δ, with limit values of 0.8 cm^3 mol^{-1} K corresponding to two isolated Cu^{II} ions. It is noteworthy that, in contrast to what was observed in a series of CuGd complexes,[6] these differences do not seem to be connected with the dihedral angles between the two halves of the bridging CuO_2U core, which are very similar in both compounds (1.7(3) and 8.5(2)° in $[\{\text{CuL}^1(\text{py})\}\text{U}\{\text{CuL}^1\}]$ and 0.6(6) and 9.2(5)° in **3**). The most pertinent differences in the structures of the Cu_2U complexes with the L^1 and L^2 ligands concern the square planar coordination of the Cu^{II} ion, in particular the Cu–N distances and N–Cu–N angles which vary by *ca.* 0.06 Å and 10°, respectively. These variations, which are caused by the distinct structure of the diimino chain of the Schiff base ligand, should have a strong influence on the magnetic properties of the complexes. These results are in line with recent experimental and theoretical investigations on organic radical-Gd^{III} and Cu^{II}–Ln^{III} coordination complexes which indicate that slight modification of the ligands can lead to a drastic change in the sign and magnitude of the exchange interaction.[7,8]

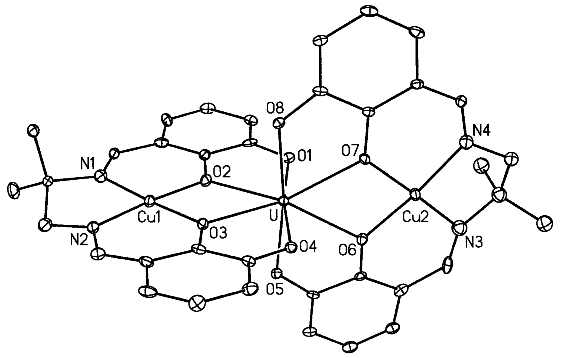

Fig. 3 View of the complex molecule in **3**·3py. Displacement ellipsoids are drawn at the 10% probability level. Selected distances (Å) and angles (°) in **3** and **4** (the latter in brackets): U–O1 2.320(10) [2.372(13)], U–O2 2.395(10) [2.400(12)], U–O3 2.417(10) [2.404(15)], U–O4 2.360(10) [2.392(13)], U–O5 2.325(9) [2.324(13)], U–O6 2.448(10) [2.402(13)], U–O7 2.417(9) [2.425(14)], U–O8 2.311(9) [2.332(13)], M1–O2 1.862(11) [1.985(17)], M1–O3 1.867(12) [2.032(14)], M1–N1 1.897(14) [2.03(2)], M1–N2 1.930(15) [2.12(2)], U···M1 3.536(2) [3.606(3)], M2–O6 1.858(10) [1.970(12)], M2–O7 1.870(10) [2.021(13)], M2–N3 1.933(7) [2.044(17)], M2–N4 1.942(8) [1.994(16)], U···M2 3.539(2) [3.661(2)]; O1–U–O4 171.8(4) [170.8(5)], O2–U–O3 58.9(4) [61.6(6)], O5–U–O8 172.1(3) [168.7(5)], O6–U–O7 58.8(3) [60.6(4)], N1–M1–N2 87.8(6) [82.2(10)], O2–M1–O3 78.7(5) [75.5(6)], N3–M2–N4 88.6(4) [82.2(7)] , O6–M2–O7 79.7(4) [75.2(5)].

Notes and references

† *Characterizing data*: ^{1}H NMR (200 MHz, 30 °C in [^{2}H$_5$]pyridine, except **2** at 10 °C): **1**, δ −16.5 (12 H, acac), −8.7 (2 H, acac), −7.71 (6 H, Me), 11.24, 23.9 and 66.0 (3 × 2 H, aromatic H), 81 (2 H, NCH$_2$) ; **2**, δ −23.5 (3 H, acac), −21.01 (6 H, acac), −14.5 (3 H, acac), −12.70 and −10.62 (2 × 1 H, acac), −10.20 (3 H, Me), −9.36 and −6.16 (2 × 1 H, NCH$_2$), −5.35 (3 H, Me), 4.15 and 4.58 (2 × 1 H, CH=N), 11.72, 12.12, 25.30, 25.66, 52.40 and 52.62 (6 × 1 H, aromatic H); **3**, δ −8.40 (12 H, Me), 4.85, 5.14, 15.93, 16.26, 45.54 and 46.14 (6 × 2 H, aromatic H), 66.9 (4 H, NCH$_2$); **4**, δ −8.57 (4 H, NCH$_2$), −7.45 (12 H, Me), 0.19 and 0.56 (2 × 2 H, CH = N), 5.16 and 13.97 (2 × 4 H, aromatic H), 23.38 and 23.58 (2 × 2 H, aromatic H). Elemental analyses (%) (calculated values in parentheses). **1**: C, 43.7 (43.9); H, 3.9 (3.9); N, 4.8 (4.65). **2**: C, 44.0 (43.8); H, 4.05 (3.9); N, 4.8 (4.6). **3**·py: C, 45.6 (45.05); H, 3.7 (3.4); N, 6.4 (6.4). **4**: C, 48.5 (47.0); H, 4.1 (3.6); N, 7.1 (7.15).

‡ *Crystal data*: for compound **1**·1.5py: $\text{C}_{40.5}\text{H}_{42.5}\text{CuN}_{4.5}\text{O}_8\text{U}$, M = 1021.86, triclinic, space group $P1$, a = 10.6528(5), b = 13.4546(7), c = 16.1262(9) Å, α = 102.667(3), β = 107.410(3), γ = 109.447(3)°, V = 1944.6(2) Å^3, Z = 2, D_c = 1.745 g cm^{-3}, μ = 4.764 mm^{-1}, $F(000)$ = 1004, $T_{\min}$ = 0.38, $T_{\max}$ = 0.68. R_1 = 0.047, wR_2 = 0.098, S = 0.993, $\Delta\rho_{\max}$ = 1.00 e Å^{-3} for 6798 independent reflections (R_{int} = 0.060) and 503 parameters.

For compound **2**: $\text{C}_{33}\text{H}_{35}\text{N}_3\text{O}_8\text{UZn}$, M = 905.04, orthorhombic, space group $Pbca$, a = 14.1052(7), b = 16.7914(5), c = 26.9961(13) Å, V = 6393.9(5) Å^3, Z = 8, D_c = 1.880 g cm^{-3}, μ = 5.866 mm^{-1}, $F(000)$ = 3520, $T_{\min}$ = 0.36, $T_{\max}$ = 0.63. R_1 = 0.063, wR_2 = 0.104, S = 1.088, $\Delta\rho_{\max}$ = 1.91 e Å^{-3} for 5870 independent reflections (R_{int} = 0.083) and 428 parameters.

For compound **3**·1.5py: $\text{C}_{43.5}\text{H}_{39.5}\text{Cu}_2\text{N}_{5.5}\text{O}_8\text{U}$, M = 1132.42, monoclinic, space group $P2_1/c$, a = 10.3373(5), b = 13.4223(11), c = 31.0552(14) Å, β = 90.315(5)°, V = 4308.9(5) Å^3, Z = 4, D_c = 1.746 g cm^{-3}, μ = 4.786 mm^{-1}, $F(000)$ = 2212, $T_{\min}$ = 0.51, $T_{\max}$ = 0.79. R_1 = 0.070, wR_2 = 0.150, S = 1.029, $\Delta\rho_{\max}$ = 1.63 e Å^{-3} for 7837 independent reflections (R_{int} = 0.099) and 548 parameters.

For compound **4**·3py: $\text{C}_{61}\text{H}_{57}\text{N}_9\text{O}_8\text{UZn}_2$, M = 1412.93, orthorhombic, space group $Pca2_1$, a = 20.150(2), b = 14.634(2), c = 19.291(1) Å, V = 5688.3(9) Å^3, Z = 4, D_c = 1.650 g cm^{-3}, μ = 3.741 mm^{-1}, $F(000)$ = 2808, $T_{\min}$ = 0.31, $T_{\max}$ = 0.96. R_1 = 0.074, wR_2 = 0.128, S = 0.956, $\Delta\rho_{\max}$ = 1.24 e Å^{-3} for 9915 independent reflections (R_{int} = 0.079) and 736 parameters.

Data for all compounds were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). Absorption effects were empirically corrected.

CCDC 200802–200805. See http://www.rsc.org/suppdata/cc/b2/b212635d/ for crystallographic data in .cif or other electronic format.

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