# Synthesis, Crystal Structure, and Magnetic Behavior of Linear $M^{II}_2U^{IV}$ Complexes ($M = Co, Ni, Cu, Zn$)

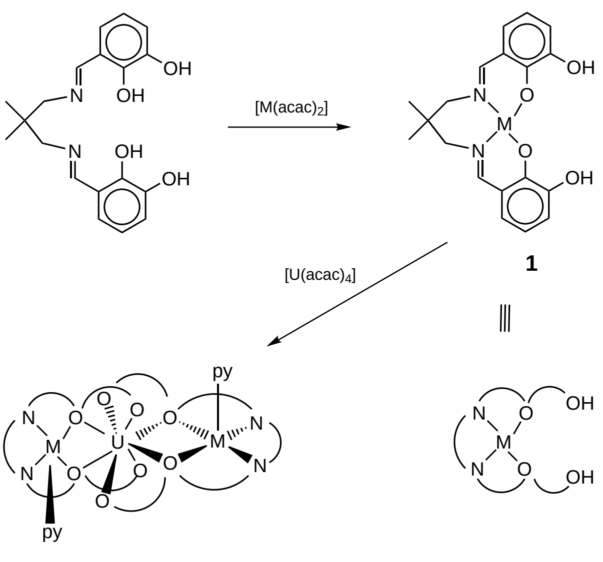
Thierry Le Borgne, Eric Rivière, Jérôme Marrot, Jean-Jacques Girerd,* and Michel Ephritikhine*

*In memory of Olivier Kahn*

Much attention has been paid to the design of novel molecular compounds containing both $3d^n$ transition metal and $4f^n$ lanthanide(III) ions in order to discover and/or understand rather unexpected magnetic and optical properties.[1] Most of the studies have been focused on the ferromagnetic M–Gd$^{III}$ pairs, M being usually Cu$^{II}$,[2] but also Co$^{II}$, Ni$^{II}$, Fe$^{III}$, and V$^{IV}$.[3] Very recent work has been devoted to the interaction between Cu$^{II}$ and lanthanide(III) ions other than Gd$^{III}$, which, because of the orbital contribution, is much more difficult to analyze and is subject to debate.[4, 5] In contrast, molecular compounds containing simultaneously paramagnetic $3d^n$ transition metal and $5f^n$ actinide ions are very rare,[6] and nothing is known about their magnetic behavior. In this context, we planned to prepare a series of new heteropolymetallic compounds in which the transition metal is in close proximity to uranium.

One of the methods for the synthesis of polymetallic compounds consists in utilizing compartmental ligands derived from Schiff base condensation.[7] By adopting this strategy, we succeeded in preparing unique examples of trimetallic complexes of general formula $[\{LM^{II}(py)\}_2U^{IV}]$ (M = Co, Ni, Cu; py = pyridine) in which the three metals are held together by the hexadentate compartmental ligand *N,N'*-bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine[8] (L) in a linear fashion. Our attempts to prepare U$^{III}$ complexes which would be the analogues of known M$^{II}$Ln$^{III}$ species have so far been unsuccessful.

The synthesis of the U$^{IV}$ compounds is represented in Scheme 1. The first step—the formation of complexes **1** by coordination of the transition metal into the inner $N_2O_2$ chamber of the hexadentate compartmental Schiff base—is similar to that used in the synthesis of the M$^{II}$Ln$^{III}$ compounds. Treatment of **1** with [U(acac)$_4$] (acac = acetylacetonate) afforded complexes **2**, which were isolated as red (M = Co) or green microcrystals (M = Ni, Cu). In fact, only 0.5 equiv of [U(acac)$_4$] was necessary for the total conversion of **1** into **2**, indicating that trinuclear complexes would be formed by chelation of a central uranium atom with two metalloligands **1**. Complexes **2** were characterized by elemental analysis (C, H, N) and $^1$H NMR spectroscopy; the spectra exhibited six resonances in a 3:2:1:1:1:1 intensity ratio, corresponding to equivalent L ligands.[9]



**1**

**2**

Scheme 1. Synthesis of the U$^{IV}$ complexes. M = Co, Ni, Cu, Zn.

The structure of complexes **2** was confirmed by the X-ray crystallographic study of the cobalt derivative $[\{LCo(py)\}_2U]$ (Figure 1).[10] Each LCo unit is linked to the central uranium atom through two Co-O-U bridges, which are ensured by the oxygen atoms of the salicylidene fragments (O2,O3 and O6,O7), and also by two bonds between the uranium and the phenolate oxygen atoms at the 3-position of the L ligand (O1,O4 and O5,O8). The uranium atom is therefore surrounded by eight oxygen atoms in a dodecahedral arrangement defined by the two trapezia O1-O2-O3-O4 and O5-O6-O7-O8 intersecting at an angle of 88.2(3)°. The equivalent sites A and B of the dodecahedron are occcupied by the bridging and terminal oxygen atoms at an average distance from uranium of 2.45(1) and 2.31(3) Å, respectively. The pseudo $D_{2d}$ symmetry of the complex is broken by the presence of a single pyridine molecule attached to each cobalt atom. The cobalt ion thus adopts a square-pyramidal coordination mode, being displaced from the $N_2O_2$ base by 0.38(2) Å towards the axial pyridine ligand. The three metal centers are almost linear (Co1-U-Co2 171.84(2)°), with intramolecular U–Co separations of 3.68(2) Å. To our knowledge, species **2** represent unique examples of trinuclear complexes with a hexadentate Schiff base ligand; more generally, these are the only molecular compounds in which an f element is associated with two d transition metals in a linear arrangement.

For the purpose of magnetic studies, it was of interest to have at our disposal complexes **2** in which the paramagnetic centers have been replaced with diamagnetic ions. The orange $[\{LZn(py)\}_2U]$ and dark red $[\{LCu(py)\}_2Zr]$ compounds were prepared by the same synthetic route shown in Scheme 1. The Zn$_2$U complex is isostructural with $[\{LCo(py)\}_2U]$.

---

[*] Dr. M. Ephritikhine, T. Le Borgne
Service de Chimie Moléculaire
Bat. 125, DSM, DRECAM, CNRS URA 331, CEA Saclay
91191 Gif sur Yvette (France)
Fax: (+33) 1-69-08-66-40
E-mail: ephri@nanga.saclay.cea.fr

Prof. J.-J. Girerd, Dr. E. Rivière
Laboratoire de Chimie Inorganique
Institut de Chimie Moléculaire
CNRS UMR 8613, Université Paris-Sud
91405 Orsay Cedex (France)
Fax: (33) 01-69-85-55-36
E-mail: jjgirerd@icmo.u-psud.fr

Dr. J. Marrot
Institut Lavoisier, CNRS UMR C8637
Université de Versailles - Saint Quentin en Yvelines
45 avenue des Etats Unis, 78035 Versailles Cedex (France)

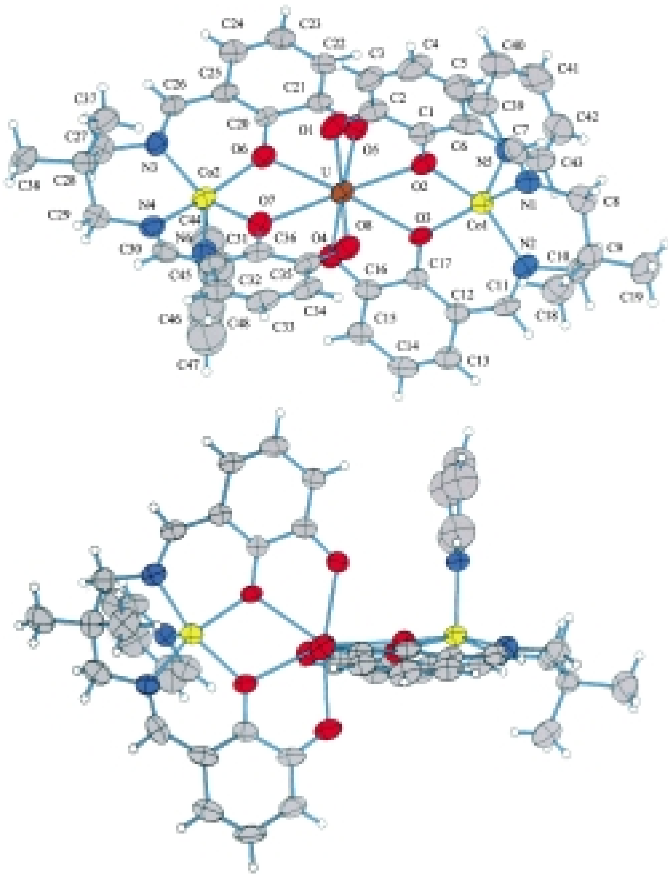


Figure 1. Structure of [{LCo(py)}$_2$U] in the crystal (ORTEP; thermal vibrational ellipsoids 30%). Selected bond lengths [Å] and angles [°]: U–O1 2.325(7), U–O2 2.450(8), U–O3 2.455(6), U–O4 2.286(7), U–O5 2.333(8), U–O6 2.457(7), U–O7 2.459(8), U–O8 2.316(7); O1-U-O4 167.5(3), O2-U-O3 60.4(2), O5-U-O8 165.3(3), O6-U-O7 60.4(2). The bottom view shows the orthogonality of the Schiff base ligands.

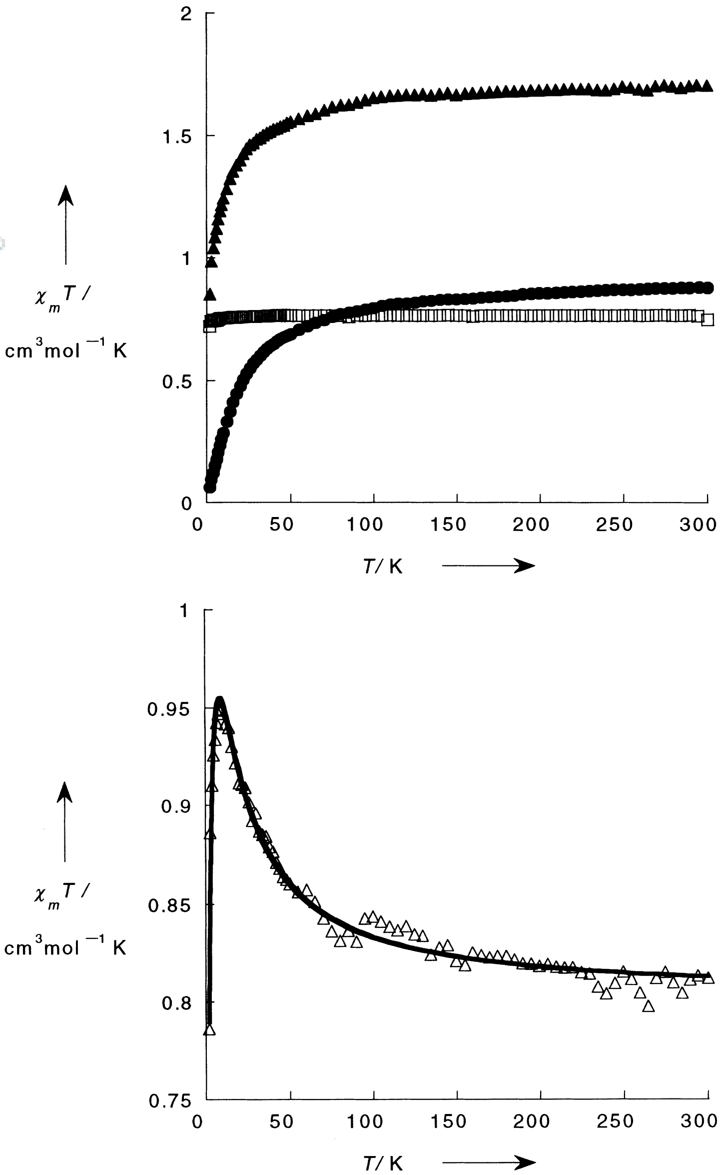


Figure 2. Thermal dependence of $\chi_M T$ for the Cu$_2$U (▲), Zn$_2$U (●), and Cu$_2$Zr (□) compounds (top) and the difference $\Delta = (\chi_M T)_{Cu_2U} - (\chi_M T)_{Zn_2U}$ (bottom). The solid curve was calculated as discussed in the text.

The magnetic behavior of the Cu$_2$U, Zn$_2$U, and Cu$_2$Zr complexes is shown in Figure 2 in the form of $\chi_M T$ versus $T$ ($\chi_M$ = molar magnetic susceptibility, $T$ = temperature). For the Cu$_2$Zr complex, $\chi_M T$ is essentially constant and equal to 0.77 cm$^3$ K mol$^{-1}$, a value which corresponds to that expected for two noninteracting Cu$^{II}$ ions; no ferromagnetic coupling is observed despite the orthogonality of the Cu$^{II}$ magnetic orbitals. The magnetic susceptibility of the Cu$_2$U and Zn$_2$U complexes decreases with the temperature, and in the latter compound this deviation from the Curie law results entirely from the crystal field effect of the U$^{IV}$ ion.

If it is assumed that the two Cu$^{II}$ ions are not coupled in the Cu$_2$U complex, as found in the Cu$_2$Zr analogue, the difference $\Delta = (\chi_M T)_{Cu_2U} - (\chi_M T)_{Zn_2U}$ should be due to the U–Cu interaction. At 300 K, the value of $\Delta$ corresponds to the contribution of two isolated Cu$^{II}$ ions, and this difference increases as $T$ is lowered to reach a maximum and then decreases at very low temperature. With this empirical approach, which has been designed recently for determining the nature of the Ln$^{III}$–Cu$^{II}$ interaction,[4, 5] the profile of the $\Delta$ versus $T$ curve might suggest that the U$^{IV}$–Cu$^{II}$ interaction in **2** is ferromagnetic. This amazing result, which cannot be explained with a simple theory, has to be confirmed, in particular by the study of discrete bimetallic U–Cu complexes. If it is now considered that the two copper(II) ions are coupled in **2**, it is most striking that the experimental $\Delta$ curve fits quite perfectly to the magnetic susceptibility equation valid for a Cu$^{II}$ dimer; the parameters corresponding to the best fit are $J_{CuCu} = 13.6$ cm$^{-1}$, $g = 2.07$, and $\theta = 0.7$ K with an agreement factor $R$ of $4.5 \times 10^{-5}$.

These data strongly suggest that the U$^{IV}$ center is able to mediate the ferromagnetic interaction between the two Cu$^{II}$ ions! This coupling exchange would involve the f orbitals of the U$^{IV}$ ion that have the appropriate energy and symmetry to overlap with the $d_{x^2-y^2}$ type magnetic orbitals centered on each Cu$^{II}$ ion; these are the $f_{x(y^2-z^2)}$ and $f_{y(x^2-z^2)}$ orbitals, which belong to the e irreducible representation in the symmetry group $D_{2d}$ (Figure 3). The ferromagnetism in **2** could then be explained either by a) the presence of two degenerate molecular orbitals of type e which would accomodate the two unpaired electrons

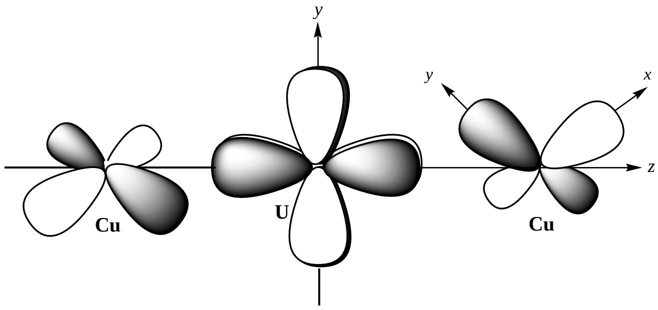


Figure 3. Role of the $f_{x(y^2-z^2)}$ $U^{IV}$ orbital in coupling the two $d_{x^2-y^2}$ orbitals containing the two $Cu^{II}$ unpaired electrons. The planes of the Cu orbitals are 45° above and below the horizontal plane.

from the $Cu^{II}$ ions, leading to a triplet state,[11] or b) within a more localized picture and in line with the proposed mechanism of the $Ln^{III}-Cu^{II}$ interaction,[12] the transfer of the unpaired electron of $Cu^{II}$ towards an empty 5f orbital of $U^{IV}$. This process would force the d and f electrons to align parallel and, in the case of a Cu-U-Cu triad, would lead to the parallel alignment of the $Cu^{II}$ electrons.

In conclusion, the use of a hexadentate compartmental Schiff base ligand permitted the synthesis of the first complexes in which an uranium(IV) ion is located between two paramagnetic divalent metallic ions—these are unique molecular compounds exhibiting a linear arrangement of an f element and two d transition metals. The comparative magnetic study of the $Cu_2U$, $Zn_2U$, and $Cu_2Zr$ compounds revealed that the f orbitals of the $U^{IV}$ center would mediate ferromagnetic interaction within the Cu-U-Cu triad.

## *Experimental Section*

All experiments were carried out under argon (< 5 ppm oxygen and water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use.

$[\{LCo(py)\}_2U]$: A mixture of $LH_4$ (306 mg, 0.89 mmol) and $[Co(acac)_2]$ (230 mg, 0.89 mmol) in THF (50 mL) was stirred for 1 h at 20 °C. The red solution was evaporated to dryness, leaving **1** (M = Co), which was then treated with $[U(acac)_4]$ (283 mg, 0.44 mmol) in THF (50 mL). After 2 h at 20 °C, the red powder of $[\{LCo(THF)\}_2U]$ was filtered off, washed with THF, and dried under vacuum. This powder was dissolved in pyridine (5 mL), and the red microcrystals of **2** (M = Co) that deposited after 12 h at 110 °C were filtered off and dried under vacuum (441 mg, 83 %).

The $Ni_2U$, $Cu_2U$, $Zn_2U$, and $Cu_2Zr$ analogues were synthesized by the same procedure.

Received: December 6, 1999 [Z 14357]

---

[1] R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, *27*, 447.

[2] a) A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* **1985**, *107*, 8128; b) M. Sakamoto, Y. Kitakami, H. Sakiyama, Y. Nishida, Y. Fukuda, M. Sakai, Y. Sadaoka, A. Matsumoto, H. Okawa, *Polyhedron* **1997**, *16*, 3345; c) I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930; d) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 3429.

[3] a) J.-P. Costes, A. Dupuis, J.-P. Laurent, *Eur. J. Inorg. Chem.* **1998**, 1543; b) J.-P. Costes, A. Dupuis, J.-P. Laurent, *J. Chem. Soc. Dalton Trans.* **1998**, 735; c) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, C. R. Seances, *Acad. Sci*. Ser *IIc* **1998**, 417; d) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 4284.

[4] M. L. Kahn, C. Mathonière, O. Kahn, *Inorg. Chem.* **1999**, *38*, 3692.

[5] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Chem. Eur. J.* **1998**, *4*, 1616.

[6] a) F. T. Edelmann in *Comprehensive Organometallic Chemistry, Vol. 4* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1995**, p. 11; b) M. Ephritikhine *New J. Chem.* **1992**, *16*, 451.

[7] a) D. E. Fenton, P. A. Vigato, *Chem. Soc. Rev.* **1988**, *17*, 69; b) U. Casellato, P. Guerriero, S. Tamburini, S. Sitran, P. A. Vigato, *J. Chem. Soc. Dalton Trans.* **1991**, 2145; c) U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, C. Benelli, *Inorg. Chim. Acta* **1993**, *207*, 39; d) F. Calderazzo, M. Pasquali, T. Salvatori, *J. Chem. Soc. Dalton Trans.* **1974**, 1102.

[8] A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, *Inorg. Chim. Acta* **1992**, *202*, 157.

[9] $^1H$ NMR data for complexes **2** (200 MHz, $[D_5]$pyridine, 30 °C, TMS): M = Co: $\delta = 402$ (4H, $W_{1/2} = 160$ Hz; N=CH), 133.0 (8H, $W_{1/2} = 200$ Hz; $CH_2$), 48.7, 9.6, and −2.4 (3 × 4H; aromatic CH), −11.8 (12H, $W_{1/2} = 95$ Hz; $CH_3$); M = Ni: $\delta = 409$ (4H, $W_{1/2} = 2500$ Hz; N=CH), 102 (8H, $W_{1/2} = 540$ Hz; $CH_2$), 46.5, 10.7, and 9.6 (3 × 4H, aromatic CH), −4.3 (12H, $W_{1/2} = 135$ Hz; $CH_3$); M = Cu: $\delta = 423$ (4H, $W_{1/2} = 3000$ Hz; N=CH), 96 (8H, $W_{1/2} = 325$ Hz; $CH_2$), 47.5, 16.0, and 4.38 (3 × 4H; aromatic CH), −7.0 (12H, $W_{1/2} = 50$ Hz; $CH_3$); M = Zn: $\delta =$ 24.0, 14.2, 5.1, and 0.3 (4 × 4H; CH), −7.4 (8H; $CH_2$), −7.9 (12H; $CH_3$). When not specified, $W_{1/2} = 5-40$ Hz.

[10] Crystal structure analysis of **2** (M = Co): Siemens diffractometer, $Mo_{K\alpha}$ radiation, measurement temperature 296(2) K, crystal dimensions 0.28 × 0.24 × 0.22 $mm^3$, orthorhombic, space group *Pna*2 (no. 1), $a = 27.4586(2)$, $b = 13.8515(2)$, $c = 13.9874(2)$ Å, $V = 5320.01(11)$ $Å^3$, $Z = 4$, $\rho = 1.487$ $g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.705$ $mm^{-1}$, $2.96 < 2\theta < 59.26°$; of 34624 measured reflections, 12594 were independent and 7380 with $I > 2\sigma(I)$; 566 parameters, multiscan absorption correction (R. H. Blessing, *Acta Cryst. Sect. A* **1995**, *51*, 33; $T_{max} = 0.453$, $T_{min} = 0.336$), $R1 = 0.0520$, $wR2 = 0.1324$, GOF = 0.986; max./min. residual electron density 1.179/−0.517 $e\,Å^{-3}$. The structure was solved with direct methods and refined against $F^2$ for all observed reflections. Hydrogen atoms were introduced at calculated positions and constrained to ride on their parent carbon atom. Software used: SHELXTL94, SHELXS86, SHELXL93 (G. M. Sheldrick, Universität Göttingen). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136721. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). .

[11] Two degenerate molecular orbitals could also be built up from the $d_{x^2-y^2}$ Cu orbitals and the filled $5d_{xz}$ and $5d_{yz}$ orbitals of uranium.

[12] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.*, **1993**, *115*, 1822.