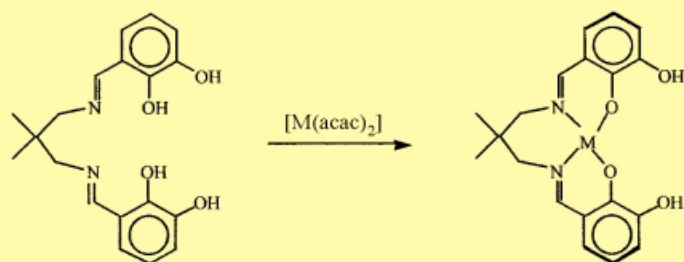
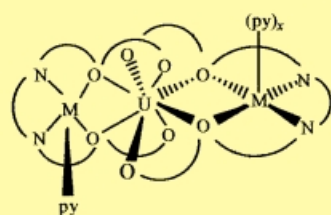


Heterobimetallic Compounds with Interesting Magnetic Properties

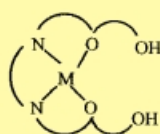


$[U(\text{acac})_4]$

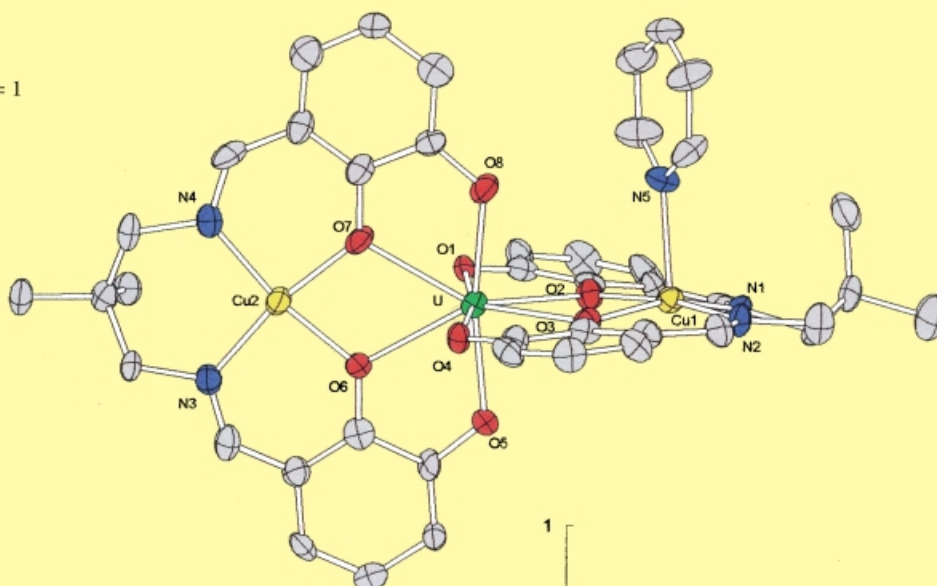


M = Co, Ni, Zn and $x = 1$

M = Cu and $x = 0$

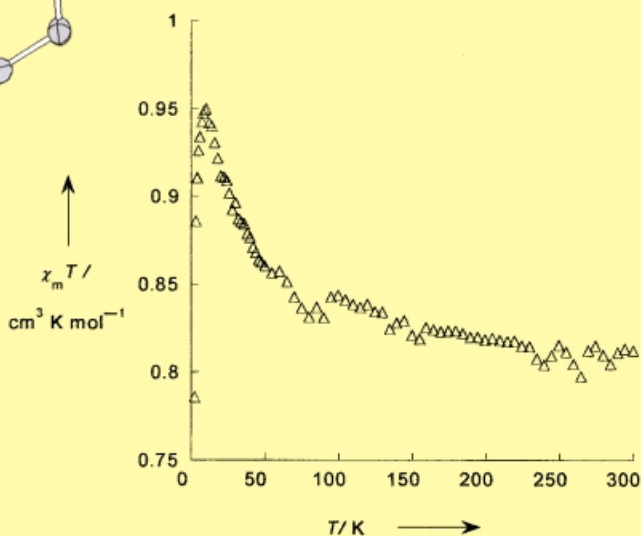


The hexadentate Schiff base ligand was used to synthesize a novel class of linear M_2U compounds



For more details see the following pages.

Comparison of the magnetic behavior the Cu_2U and Zn_2U compounds revealed the ferromagnetic U-Cu interaction



Syntheses, X-Ray Crystal Structures, and Magnetic Properties of Novel Linear $M_2^{II}U^{IV}$ Complexes ($M = Co, Ni, Cu, Zn$)

Thierry Le Borgne,^[a] Eric Rivière,^[b] Jérôme Marrot,^[c] Pierre Thuéry,^[a] Jean-Jacques Girerd,^{*[b]} and Michel Ephritikhine^{*[a]}

Abstract: Attempts to prepare heterobimetallic complexes in which 3d and uranium magnetic ions are associated by means of the Schiff bases H_2L^i derived from 2-hydroxybenzaldehyde or 2-hydroxy-3-methoxybenzaldehyde were unsuccessful because of ligand transfer reactions between $[ML^i]$ ($M = Co, Ni, Cu$) and UCl_4 that led to the mononuclear Schiff base complexes of uranium $[UL^iCl_2]$. The crystal structure of $[UL^3Cl_2(py)_2]$ [$L^3 = N,N'$ -bis(3-methoxysalicylidene)-ethylenediamine; $py =$ pyridine] was determined. The hexadentate Schiff base ligand N,N' -bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-pro-

panediamine (L) was useful for the synthesis of novel trinuclear complexes of the general formula $[[ML(py)]_2U]$ ($M = Co, Ni, Zn$) or $[[CuL(py)]M'\{CuL\}]$ ($M' = U, Th, Zr$) by reaction of $[M(H_2L)]$ with $[M'(acac)_4]$ ($acac = MeCOCHCOMe$). The crystal structures of the $Co_2U, Ni_2U, Zn_2U, Cu_2U,$ and Cu_2Th complexes show that the two ML fragments are orthogonal, being linked to the central actinide ion by the two pairs

of oxygen atoms of the Schiff base ligand. In each compound, the UO_8 core exhibits the same dodecahedral geometry, and the three metals are linear. The magnetic study indicated that the two Cu^{2+} ions are not coupled in the Cu_2Zr and Cu_2Th compounds. The magnetic behavior of the $Co_2U, Ni_2U,$ and Cu_2U complexes was compared with that of the Zn_2U derivative, in which the paramagnetic 3d ion was replaced with the diamagnetic Zn^{2+} ion. A weak antiferromagnetic coupling was observed between the Ni^{2+} and the U^{4+} ions, while a ferromagnetic interaction was revealed between the Cu^{2+} and U^{4+} ions.

Keywords: actinides · heteropolynuclear complexes · ions · magnetic properties · N,O ligands

Introduction

The objective of this work was to design and synthesize novel heterobimetallic compounds, in which 3d and uranium magnetic ions are in close proximity, and to determine the nature, antiferro- or ferromagnetic, of the exchange interaction between these ions.

Since the discovery, in 1985, of ferromagnetic coupling in Cu_2Gd complexes,^[1] many studies have been devoted to such compounds of the lanthanides (Ln) in order to understand the basics of the interaction of the 3d and 4f ions and to develop the molecular approach to magnetic materials with controlled and tunable properties.^[2] In contrast, virtually nothing is known about the magnetic behavior of molecular compounds containing simultaneously 3d and 5f ions, even though interesting magnetic properties should be anticipated, since the f electrons for the actinide ions are less shielded than they are for the lanthanide ions. This situation can be explained by two facts.

Magnetic properties of the most accessible uranium(IV) complexes (Th^{4+} is diamagnetic) are difficult to analyze because this $5f^2$ ion possesses a first-order orbital momentum, which prevents the use of a spin-only Hamiltonian for the description of the spectrum of the low-lying states;^[3] the temperature dependence of $\chi_M T$ (χ_M being the molar magnetic susceptibility and T the temperature) is due to both the thermal population of the excited states and the exchange interaction. It is for the same reason, that is, the lack of a general theoretical model to describe the magnetic susceptibility χ_M of a Ln^{3+} ion in its ligand field, that the magnetic

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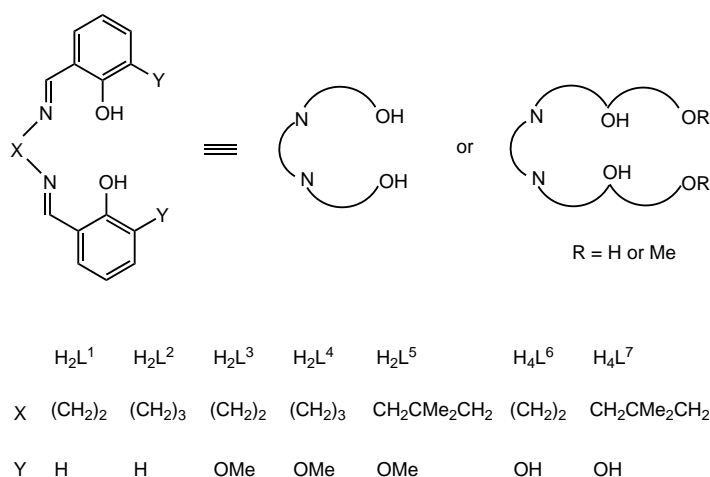
studies on 3d–4f complexes were at first essentially limited to the case in which the lanthanide(III) ion is the isotropic gadolinium(III), which has an $^8S_{7/2}$ single-ion ground state without first-order orbital momentum; in these complexes, the 3d ion is usually Cu^{2+} ,^[1, 4–6] but it can also be Co^{2+} , Ni^{2+} , Fe^{3+} , and the vanadyl ion VO^{3+} .^[7] Magnetic studies on $CuLn$ complexes other than those of Gd have been rather scarce.^[8] However, the problem of the spin-orbit coupling of the 4f ions was overcome by the empirical approach, proposed in 1998, in which one compares the magnetic properties of a 3d–4f complex with those of an isostructural derivative in which the paramagnetic ion, that is, Cu^{2+} , has been replaced with a diamagnetic ion, that is, low-spin Ni^{2+} or Zn^{2+} .^[9, 10] For this latter compound, that is, the $ZnLn$ compound, the deviation of χ_M with respect to the Curie law reflects the sole thermal population of the f ion Stark levels, and by transferring this information to the magnetic properties of the former 3d–4f complex, that is, the $CuLn$ complex, it is possible to determine the nature of the exchange interaction. This method, which was applied to two series of $CuLn$ ^[10] and Cu_3Ln_2 ^[9] compounds, is clearly transposable to uranium complexes, as demonstrated in this paper.

The other reason for the lack of magnetic studies on molecular 3d–5f complexes that is obviously related to the first one, is the scarcity of such compounds, which are interesting from a magnetic point of view; most of these complexes are organometallics with the 3d ion diamagnetic.^[11] Very recently, the MnU compound $[K_2Mn(C_2O_4)_4U] \cdot 9H_2O$ was synthesized, but no magnetic coupling was detected in this three-dimensional network of paramagnetic units.^[12] A large number of 3d–4f compounds have been synthesized with the aid of Schiff bases as dinucleating ligands, and we have considered this approach for the preparation of heteropolymetallic complexes containing both 3d and uranium ions, although U^{3+} and U^{4+} complexes with Schiff base ligands were quite uncommon.^[13–15]

Here we report the synthesis, crystal structures, and magnetic behavior of trinuclear complexes of the general formula $[(ML(py))_2U]$ ($M = Co, Ni, Zn$; $py = pyridine$) or $[(CuL(py))M'(CuL)]$ ($M' = U, Th, Zr$), in which the three metals are held together in a linear fashion by the hexadentate Schiff base ligand N,N' -bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine (L).^[16]

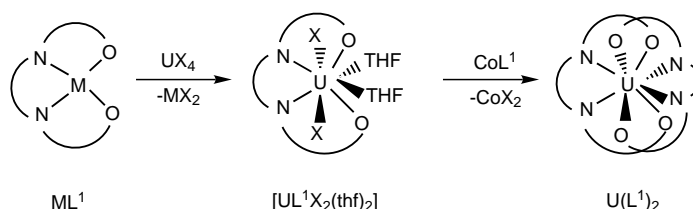
Results and Discussion

Synthesis and characterization of the complexes: Difficulties were encountered in the choice of the Schiff base ligand for the association of the 3d transition metal and uranium ions. Our first synthetic approaches relied on the stepwise complexation of Schiff base ligands derived from 2-hydroxybenzaldehyde (H_2L^i in Scheme 1, with $i = 1, 2$), which have been largely used as associating ligands for the synthesis of molecular 3d–4f compounds. In particular, L^1 (commonly called salen) is found in the trinuclear complex $[(CuL^1)_2Gd(H_2O)_3]^{3+}$ which was prepared by reaction of $[CuL^1]$ with $Gd(ClO_4)_3$; it is this complex, which permitted the discovery of the ferromagnetic interaction between the Cu^{2+}



Scheme 1. The Schiff bases H_2L^i ($i = 1–5$) and H_4L^i ($i = 6, 7$).

and Gd^{3+} ions.^[1] Replacement of $Gd(ClO_4)_3$ with GdX_3 ($X = NO_3, CF_3COCHCOCF_3$) in the above reaction led to the formation of the binuclear compounds $[(CuL^1)GdX_3]$, which also exhibit a ferromagnetic coupling.^[5] Moreover, treatment of $[NiL^1]$ with UCl_4 in dichloromethane was reported to give an insoluble orange precipitate, the elemental analyses of which are in agreement with the formula $[(NiL^1)UCl_4]$.^[14] In contrast to these results, we found that reactions of $[ML^1]$ ($M = Co, Ni, Cu$) with UX_4 ($X = Cl, OSO_2CF_3$) in THF did not afford the complexes $[(ML^1)UX_4]$, by addition through the oxygen atoms of the salicylidene groups, but gave invariably the uranium compound $[UL^1X_2(thf)_2]$ ^[14] with elimination of MX_2 (Scheme 2). Further reaction of $[UL^1Cl_2(thf)_2]$ with $[CoL^1]$ did not give the adduct $[(CoL^1)UL^1Cl_2]$ either, but led to the formation of $[U(L^1)_2]$.^[14] The same observations were made when L^1 was replaced with the homologue L^2 .

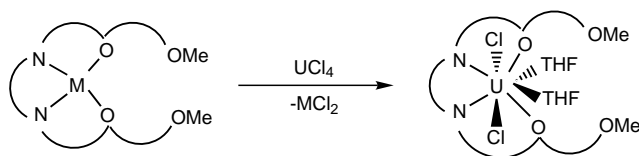


$M = Co, Ni, Cu$; $X = Cl, OSO_2CF_3$

Scheme 2. Ligand transfer reactions between $[ML^i]$ and UX_4 or $[UL^iX_2(thf)_2]$.

The hexadentate Schiff bases H_2L^i ($i = 3–5$, Scheme 1) were then considered for the synthesis of the binuclear complexes $[(ML^i)UCl_4]$ with the idea that the uranium ion would be stabilized by the two chelating methoxy groups at the 3-position of the salicylidene fragments. These Schiff bases possess two distinct cavities, the internal N_2O_2 cavity, which is adequate for the complexation of the 3d ion, and the external O_4 cavity, which is well suited for the f ion. Thus, the ligand L^5 was used in the preparation of the $CuGd$ complex, $[(CuL^5Cl_2)Gd(H_2O)_4]^+$, by reaction of $[CuL^5]$ with $GdCl_3$; in that case, migration of chloride ligands from Gd to Cu was

found to occur.^[6] However, reactions of $[ML^i]$ ($i=3-5$) with UCl_4 in THF afforded, here again, the mononuclear compounds $[UL^iCl_2(thf)_2]$ resulting from the displacement of the 3d ion out of the N_2O_2 cavity of the L^i ligand (Scheme 3).

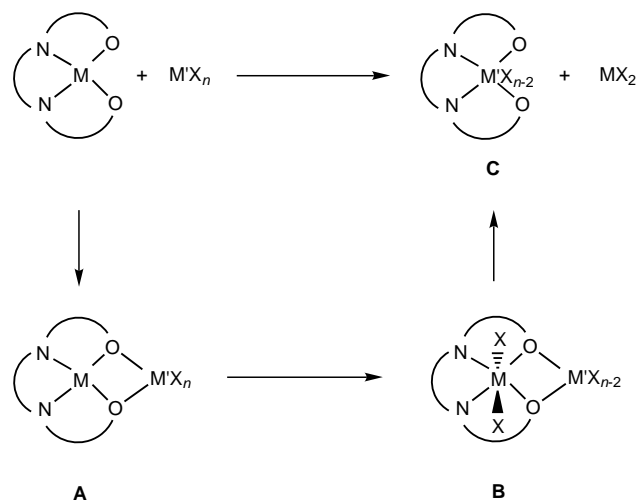


M = Co, Ni, Cu

Scheme 3. Ligand transfer reactions between $[ML^i]$ ($i=3-5$) and UCl_4 .

Such ligand transfer reactions between Schiff base complexes of main group or transition metals and metal halides have already been encountered. For example, treatment of $[Co(acen)]$ (acen = N,N' -ethylenebis(acetylacetonimine)) or $[ML^i]$ ($M = Sn, Ge$) with $TiCl_4$ gave $[Ti(acen)Cl_2]$ and $[TiL^iCl]^+$, respectively.^[17, 18] These exchange reactions of Schiff base complexes $[ML^i]$ with $M'X_n$ species very probably proceed by the initial formation of the adduct $[(ML^i)M'X_n]$ (**A** in Scheme 4), followed by migration of X from M' to M to give the intermediate (**B**), which is itself transformed into $[(ML^i)X_{n-2}]$ (**C**) with elimination of MX_2 .^[18] Compound **B** would be isolated in certain cases, as illustrated by the aforementioned complex $[(CuL^5Cl_2)Gd(H_2O)_4]^+$.^[6] The outcome of the reaction of $[ML^i]$ with $M'X_n$ and the relative stability of compounds **A**, **B**, and **C** are not always easily predictable as they are determined by a variety of factors: the nature and oxidation state of the metals, the coordinating ability of X and its affinity for M or M' , the polarity, and coordinating properties of the solvent, and the structure of the Schiff base, in particular the size of the heteroatom cavities.

The compounds $[UL^iCl_2(thf)_2]$ ($i=1-4$) were found to be identical to those obtained directly by treatment of UCl_4 with H_2L^i and were characterized by their 1H NMR spectra; the signals corresponding to the $N(CH_2)_xN$ fragment ($x=2$ or 3)



Scheme 4. Plausible mechanism for the ligand transfer reactions.

are visible in the low-field region ($-70 < \delta < -60$), while the resonances of the aromatic and imino protons appear in the high-field region ($20 < \delta < 80$). The green product resulting from the reaction of UCl_4 with either H_2L^5 or $[ML^5]$ is insoluble in common organic solvents and was not further characterized. The pyridine adduct $[UL^3Cl_2(py)_2]$ was obtained by substitution of the THF ligands of $[UL^3Cl_2(thf)_2]$, and green crystals were suitable for X-ray diffraction analysis. The crystal structure, shown in Figure 1 together with selected

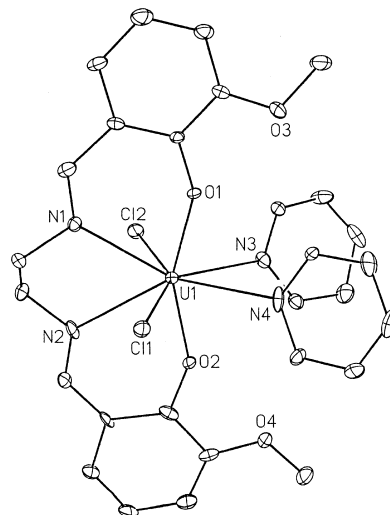


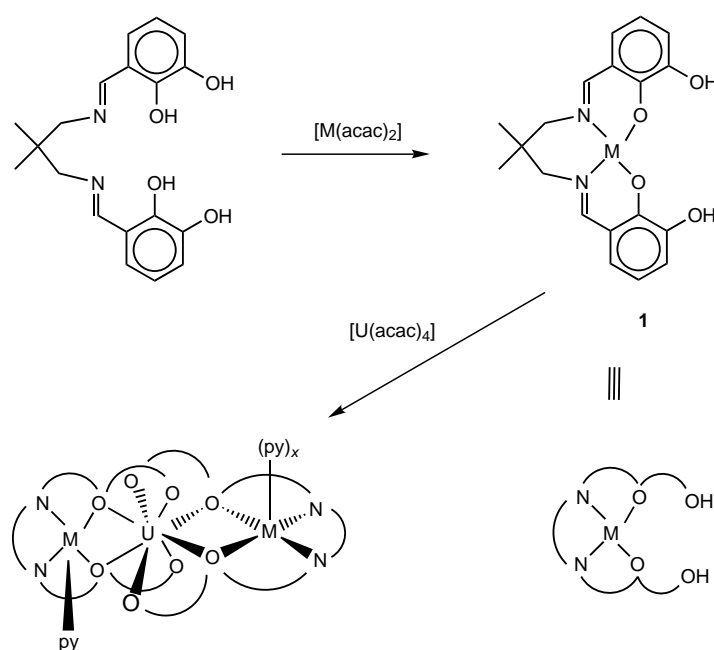
Figure 1. X-ray crystal structure of $[UL^3Cl_2(py)_2]$ (ellipsoids drawn at the 10% probability level). Selected bond lengths (Å) and angles ($^\circ$): U1–O1 2.152(10), U1–O2 2.197(11), U1–N1 2.598(13), U1–N2 2.647(12), U1–N3 2.661(11), U1–N4 2.708(11), U1–Cl1 2.755(3), U1–Cl2 2.707(4); O1–U1–O2 155.6(3), O1–U1–N1 69.8(4), O2–U1–N2 70.1(4), N1–U1–N2 65.2(5), N3–U1–N4 65.5(4), Cl1–U1–Cl2 147.95(12).

bond lengths and angles, resembles that of $[UL^1Cl_2(thf)_2]$,^[15] the only other Schiff base complex of uranium(IV) to have been crystallographically characterized. The uranium atom is in a dodecahedral environment defined by the two orthogonal trapezia O1O2N1N2 and Cl1Cl2N3N4. The U–O and U–N bond lengths in the L^3 ligand average 2.17(2) and 2.62(3) Å, respectively, and compare well with the corresponding values of 2.15(4) and 2.62(4) in $[UL^1Cl_2(thf)_2]$; the O–U–O, N–U–N, and O–U–N angles are also quite similar in both complexes, with mean values of 155.6(3), 65.2(5), and 69.95(10) $^\circ$ (L^3), and 154.8(8), 62.4(15), and 71.8(14) $^\circ$ (L^1). As noted in $[UL^1Cl_2(thf)_2]$, the U–Cl bond lengths of 2.707(4) and 2.755(3) Å are significantly longer, by 0.15 Å, than those usually found in uranium(IV) chloride complexes, and the Cl1–U–Cl2 angle of 147.95(12) $^\circ$ is close to the value of 155.6(3) $^\circ$ for the O1–U–O2 angle. The U–N(py) bond lengths are unexceptional, and the N3–U–N4 angle of 65.5(4) $^\circ$ is identical to the N1–U–N2 angle.

Since addition of the complexes $[ML^i]$ ($i=1-5$) to UX_4 did not afford the expected compounds $[(ML^i)UX_4]$ but gave the mononuclear species $[UL^iX_2]$ resulting from substitution of M for U, we pursued our studies by considering the Schiff bases H_4L^i ($i=6,7$) with the hope that the complexes $[(ML^i)UX_2]$, which could be synthesized by reacting $[M(H_2L^i)]$ with UX_4 , would be stable enough towards ligand transfer reactions; in

this case, the uranium atom is fixed inside the external O_4 cavity by two σ bonds with the phenoxide oxygen atoms at the 3-position of the salicylidene fragments. The Schiff base H_4L^6 was used to prepare a series of $CuGd$ complexes of the general formula $[CuX_3(H_2L^6)Gd] \cdot 2H_2O$ ($X = Cl, NO_3, ClO_4, CH_3CO_2$)^[19] and the CuY compound $[(CuL^6)Y(NO_3)(Me_2SO)_2]$,^[20] only this latter compound has been crystallographically characterized. Synthesis of $CuLn$ and $NiLn$ complexes with the hexadentate Schiff base H_4L^7 was reported without experimental details.^[21] Preliminary NMR experiments were carried out with the cobalt derivatives $[Co(H_2L^6)]$ and $[Co(H_2L^7)]$. Reaction of $[Co(H_2L^6)]$ with UCl_4 in THF led, here again, to the displacement of the cobalt ion and formation of the uranium complex $[U(H_2L^6)Cl_2]$, the 1H NMR spectrum of which is similar to that of the $[UL^6Cl_2]$ compounds. Treatment of $[Co(H_2L^6)]$ with $[U(acac)_4]$ in THF gave a precipitate, which was not identified. Reaction of $[Co(H_2L^7)]$ with UCl_4 in pyridine afforded a brown powder, the elemental analyses of which are in agreement with the formula $[(CoL^7)UCl_2(py)_2]$; however, the product could not be further characterized because of its insolubility in organic solvents. It is possible that this complex possesses a higher nuclearity due to di- or oligomerization of the initially formed dinuclear compound. Such dimerization of similar heterodinuclear compounds has already been observed, for example with the aforementioned CuY complex, $[(CuL^6)Y(NO_3)(Me_2SO)_2]$, obtained by treating $[Cu(H_2L^6)]$ with $Y(NO_3)_3$.^[20] The distinct reactions of UCl_4 with $[Co(H_2L^6)]$ and $[Co(H_2L^7)]$ clearly revealed that the length of the bridging chain between the nitrogen atoms of the Schiff base has a great influence on the nature of the products.

Eventually, reaction of $[Co(H_2L^7)]$ with $[U(acac)_4]$ in THF afforded a red precipitate, which could be dissolved in pyridine, and red microcrystals were deposited when the solution was heated under reflux. Only 0.5 equivalents of $[U(acac)_4]$ were necessary for the total conversion of $[Co(H_2L^7)]$, and this indicated that a trinuclear complex would be formed by chelation of a central uranium atom with two metalloligands $[Co(H_2L^7)]$ (Scheme 5). Green ($M = Ni, Cu$) or orange ($M = Zn$) compounds were obtained in the same way when $[Co(H_2L^7)]$ was replaced with the nickel, the copper, and also the diamagnetic zinc analogue. Their elemental analyses correspond to the formula $[(ML^7)_2U] \cdot 2py$ ($M = Co, Cu, Zn$) or $[(ML^7)_2U] \cdot 3py$ ($M = Ni$). All the complexes have been characterized by their 1H NMR spectra, which are similar and exhibit six resonances in a 3:2:1:1:1:1 intensity ratio, corresponding to equivalent L^7 ligands; the most shifted signal at approximately $\delta = 100$ and 400 are attributed to the methylene and imino protons of the $CH_2N=CH$ fragment, which are the closest to the paramagnetic $3d$ ion. The paramagnetic U^{4+} ion in these complexes could be changed for the diamagnetic Zr^{4+} or Th^{4+} ion. Thus, treatment of $[Cu(H_2L^7)]$ with $[Th(acac)_4]$ gave green crystals of $[(CuL^7)_2Th] \cdot 2py$, whereas a red ($M = Co$) or green ($M = Cu$) microcrystalline powder of $[(ML^7)_2Zr]$ was obtained by reaction of $[M(H_2L^7)]$ with $[Zr(acac)_4]$. These compounds were characterized by their elemental analyses; the 1H NMR spectra could be observed only for the Co_2Zr compound.



$M = Co, Ni, Zn$ and $x = 1$

$M = Cu$ and $x = 0$

Scheme 5. Synthesis of the M_2U complexes.

The Schiff base H_4L^7 was thus found to be appropriate for the synthesis of a series of trinuclear $M_2^IIM^{IV}$ complexes ($M = Co, Ni, Cu, Zn$ and $M' = U$; $M = Cu$ and $M' = Zr, Th$) by reaction of the metalloligand $[M(H_2L^7)]$ with $[M'(acac)_4]$. These are unique examples of trinuclear complexes with a hexadentate Schiff base ligand. It is likely that their formation proceeded via the binuclear intermediate $[(ML^7)M'(acac)_2]$, which rapidly reacted with a second molecule of the metalloligand to give the trinuclear product.

X-ray crystal structures of the M_2U ($M = Co, Ni, Cu, Zn$) and Cu_2Th complexes: The crystal structures of $[(ML(py))_2U]$ ($M = Co, Ni, Zn$), $[(NiL(py))_2U] \cdot py$, and $[(CuL(py))An\{CuL\}] \cdot 2py$ ($An = U, Th$) have been determined (hereafter, the ligand L^7 is called L). The Co_2U , Ni_2U , and Zn_2U compounds are isostructural, as well as the Cu_2U and Cu_2Th complexes. The crystal structures of $[(NiL(py))_2U]$ and $[(CuL(py))U\{CuL\}]$ are shown in Figure 2 and Figure 3, respectively; selected bond lengths and angles are listed in Table 1. All the complexes are built up by two LM units, which are linked to the central actinide ion by two pairs of oxygen atoms: the phenoxide oxygen atoms at the 3-position of the L ligand (O1, O4, and O5, O8) and the oxygen atoms of the salicylidene fragment (O2, O3 and O6, O7), which are in bridging positions between the $3d$ and An ions. The An atom is therefore found in a dodecahedral arrangement defined by the two orthogonal trapezia (O1O2O3O4 and O5O6O7O8). The equivalent sites A and B of the dodecahedron are occupied by the bridging and terminal oxygen atoms, respectively. The orthogonal arrangement of the two ML moieties

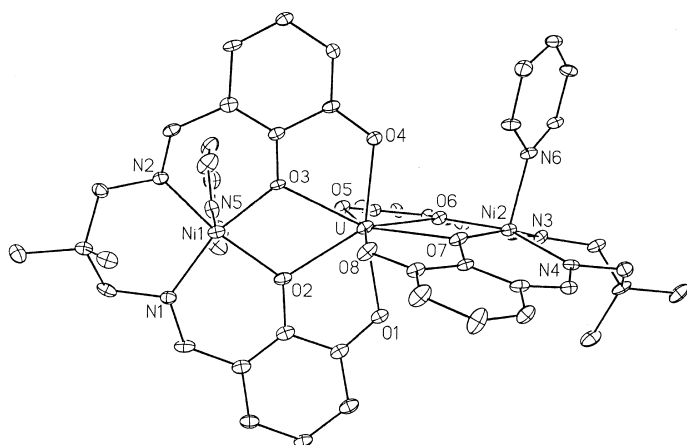


Figure 2. X-ray crystal structure of $[[\text{NiL}(\text{py})]_2\text{U}]$ (ellipsoids drawn at the 10% probability level).

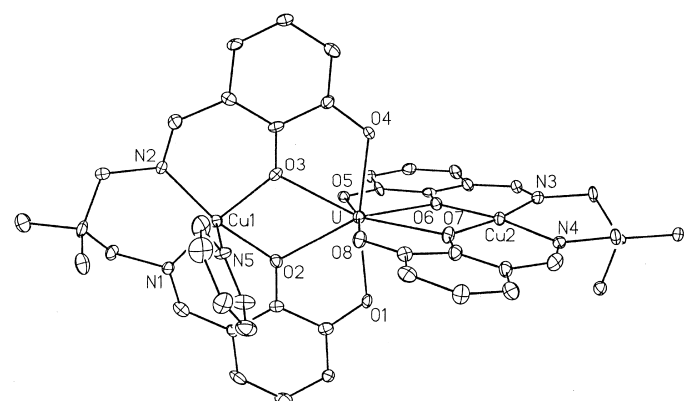


Figure 3. X-ray crystal structure of $[[\text{CuL}(\text{py})]\text{U}\{\text{CuL}\}]$ (ellipsoids drawn at the 20% probability level).

Table 1. Selected bond lengths [Å] and angles [°] in the trinuclear complexes.

	Co ₂ U	Ni ₂ U	Zn ₂ U	Cu ₂ U	Cu ₂ Th
An–O1	2.325(7)	2.324(8)	2.271(9)	2.319(6)	2.395(7)
An–O2	2.450(8)	2.413(11)	2.430(8)	2.434(6)	2.477(7)
An–O3	2.455(6)	2.429(8)	2.433(10)	2.433(6)	2.477(8)
An–O4	2.286(7)	2.316(8)	2.311(10)	2.310(6)	2.361(7)
An–O5	2.333(8)	2.321(8)	2.321(10)	2.312(6)	2.376(7)
An–O6	2.457(7)	2.434(8)	2.439(9)	2.465(6)	2.512(8)
An–O7	2.459(8)	2.432(10)	2.463(12)	2.453(6)	2.484(7)
An–O8	2.316(7)	2.312(7)	2.325(8)	2.274(6)	2.327(8)
M1–O2	2.013(8)	2.004(10)	2.033(9)	1.947(6)	1.951(8)
M1–O3	1.991(7)	1.971(8)	2.040(12)	1.952(6)	1.967(7)
M1–N1	2.050(9)	2.018(11)	2.085(12)	1.983(8)	1.966(9)
M1–N2	2.070(9)	2.002(10)	2.058(12)	1.992(7)	1.994(10)
M1–N5	2.143(9)	1.990(12)	2.114(13)	2.293(8)	2.311(9)
M2–O6	1.988(7)	1.966(9)	2.016(10)	1.925(6)	1.931(7)
M2–O7	1.997(7)	1.987(10)	2.027(11)	1.912(6)	1.929(8)
M2–N3	2.098(9)	2.038(10)	2.122(12)	1.976(7)	1.972(10)
M2–N4	2.036(10)	2.016(10)	2.061(12)	1.970(8)	1.979(9)
M2–N6	2.042(10)	2.032(11)	2.03(2)		
O1–An–O4	167.5(3)	164.1(4)	167.0(3)	168.4(2)	171.6(3)
O2–An–O3	60.4(2)	61.1(3)	60.6(3)	59.5(2)	59.0(2)
O5–An–O8	165.3(3)	166.4(3)	165.0(4)	170.2(2)	172.9(3)
O6–An–O7	60.4(2)	60.5(3)	60.8(3)	58.2(2)	57.7(2)
M1–O2–An	111.3(3)	110.4(4)	112.5(4)	111.6(3)	111.8(3)
M1–O3–An	111.9(3)	110.9(3)	112.1(5)	111.4(3)	111.3(3)
M2–O6–An	110.7(3)	111.8(3)	111.1(4)	111.8(3)	111.9(3)
M2–O7–An	110.2(3)	111.1(4)	109.8(5)	112.8(3)	113.1(3)
M1–An–M2	171.84(2)	172.28(3)	170.9(3)	177.27(3)	176.97(3)

around the central uranium ion is rather exceptional; it has been encountered very recently in the compound $[(\text{NiL}^4)_2\text{Na}]^+$, prepared by addition of NiL^4 to NaL .^[22] The dodecahedral geometry of the UO_8 core, although less common than the square antiprismatic arrangement of the tetrakis(β -diketonato) actinide complexes, is classical; it has been found, for example, in the tetrakis(salicylaldehydato) compounds of thorium and uranium.^[23] In the M_2U compounds, the U–O(bridging) bond lengths range from 2.413(11) to 2.455(6) Å with a mean value of 2.43(3) Å, whereas the U–O(terminal) bond lengths vary from 2.271(9) to 2.325(7) Å and average 2.30(3) Å. These distances are slightly longer in the thorium complex, 2.38(1) and 2.48(8) Å, and this reflects the difference in the ionic radii of Th^{4+} (1.05 Å) and U^{4+} (1.00 Å).^[24] The ratio of the mean U–O(bridging) and U–O(terminal) bond lengths is equal to 1.06, close to the value of 1.03 in the ideal dodecahedron. The O(bridging)–An–O(bridging) angles vary from 164.1(4) to 172.9(3)°, with a mean value of 167(6)°, and the O(terminal)–An–O(terminal) angles lie between 57.7(2) and 61.1(3)° and average 59(2)°; the corresponding values in the ideal dodecahedron are 147 and 70°. The 3d ion is found, in all complexes, inside the cavity formed by the two nitrogen and two bridging oxygen atoms of the Schiff base ligand. In the Co_2U , Ni_2U , and Zn_2U complexes, a pyridine molecule is attached to each 3d ion, which adopts a square pyramidal coordination mode, and the 3d ion is displaced from the N_2O_2 base towards the axial pyridine ligand by a distance of 0.38(2), 0.29(1), and 0.45(2) Å, respectively. Only one Cu^{2+} ion coordinates a pyridine molecule in the Cu_2An compounds; the other ion is in a square planar configuration. In all complexes, the three metal centers are almost linear with M–An–M angles lying between 170.9(3) and 177.27(3)°, and the M–An distances range from 3.640(7) to 3.70(2) Å. Such molecular compounds, in which an f element is associated with two d transition metals, are quite rare and, with the exception of the Cu_2U complex, $[(\text{PPh}_3)_3\text{Cu}(\text{SPh})_2\text{U}]$,^[11b] the three metal centers in these complexes are not linear. The compounds $[[\text{ML}(\text{py})_x]_2\text{U}]$ are the only trinuclear compounds which exhibit a linear arrangement of paramagnetic 3d and 5f ions. It is important for the magnetic studies that the uranium ion adopts, in all these M_2U complexes and in particular the Zn_2U derivative, the same dodecahedral configuration. The coordination mode of the 3d ion, square pyramidal or square planar depending on whether a pyridine molecule is attached to it or not, has little influence on the dodecahedral arrangement of the eight oxygen atoms around the central U^{4+} ion; the corresponding U–O bond lengths and O–U–O angles in the complexes $[[\text{CuL}(\text{py})]\text{U}\{\text{CuL}\}]$ and $[[\text{ZnL}(\text{py})]_2\text{U}]$ vary at the most by a value of 0.05 Å and 5°, respectively (Table 1). The intermetallic distances between two distinct molecules are larger than 6.5 Å, so that the trinuclear entities may be considered to be magnetically isolated.

Magnetic studies: The magnetic behavior of the Cu_2U , Cu_2Th , and Cu_2Zr complexes is shown in Figure 4 in the form of $\chi_M T$ versus T . For the Cu_2Th and Cu_2Zr compounds, $\chi_M T$ is essentially constant and equal to 0.77 $\text{cm}^3 \text{K mol}^{-1}$, a value

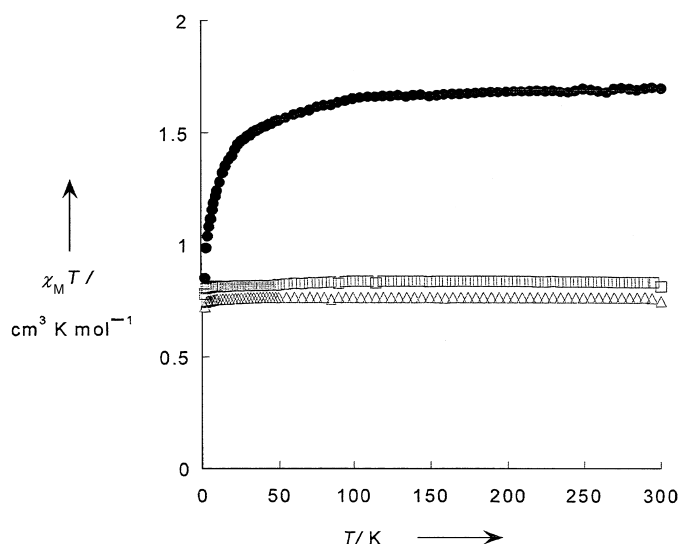


Figure 4. Thermal dependence of $\chi_M T$ for the Cu_2U (●), Cu_2Th (□), and Cu_2Zr (△) compounds.

close to that expected for two noninteracting Cu^{2+} ions. The $\chi_M T$ product for the Cu_2U complex is equal to $1.7 \text{ cm}^3 \text{ K mol}^{-1}$ between 300 and 100 K and then decreases with the temperature to reach the value of $0.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The curves of $\chi_M T$ versus T for the Zn_2U and Cu_2U complexes (Figure 5)

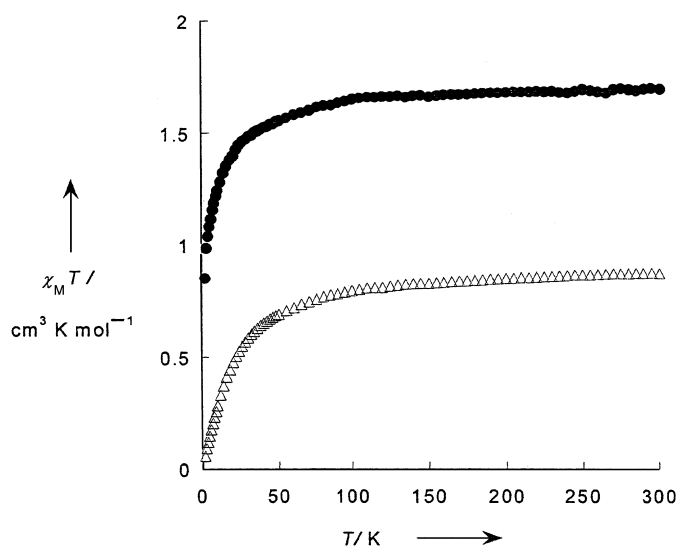


Figure 5. Thermal dependence of $\chi_M T$ for the Cu_2U (●) and Zn_2U (△) compounds.

are roughly parallel between 300 and 100 K, and the difference $\Delta(\chi_M T) = (\chi_M T)(\text{Cu}_2\text{U}) - (\chi_M T)(\text{Zn}_2\text{U})$ is equal to approximately $0.8 \text{ cm}^3 \text{ K mol}^{-1}$. Below 100 K, this difference, which is represented in Figure 6, increases as T is lowered to reach a maximum value of $0.95 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K, and then drops to $0.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. At this temperature, the field dependence of the difference $\Delta M = M(\text{Cu}_2\text{U}) - M(\text{Zn}_2\text{U})$, M being the magnetization, closely follows the Brillouin function for two noninteracting Cu^{2+} ions with $S = 1/2$ (Figure 7).

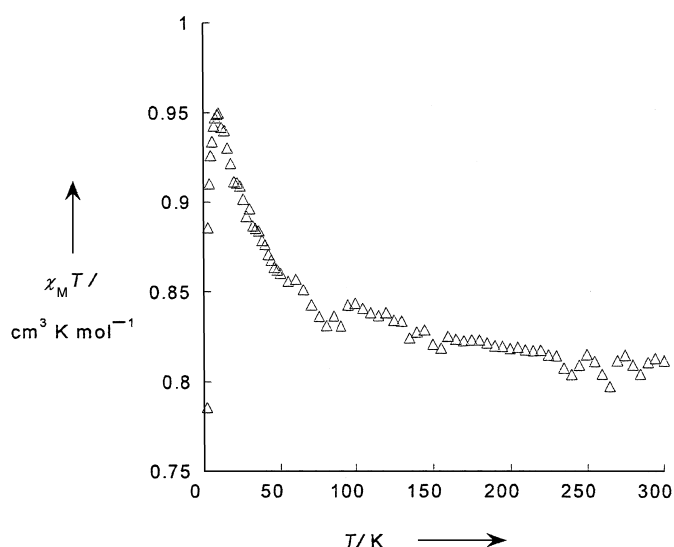


Figure 6. Thermal dependence of $\Delta(\chi_M T) = (\chi_M T)(\text{Cu}_2\text{U}) - (\chi_M T)(\text{Zn}_2\text{U})$.

Together these experiments indicate that:

- 1) no Cu–Cu interaction through Zr^{IV} or Th^{IV} is detected, from which it can be inferred that the same situation holds for U^{IV} .
- 2) the $^3\text{H}_4$ level of U^{IV} is split by crystal field effects in such a manner that no Curie law is observed for the Zn_2U compound.
- 3) the increase of the difference $\Delta(\chi_M T) = (\chi_M T)(\text{Cu}_2\text{U}) - (\chi_M T)(\text{Zn}_2\text{U})$ when T decreases proves that a ferromagnetic interaction exists between the Cu^{2+} and U^{4+} ions.

In our previous communication we suggested that the two Cu^{2+} ions could be coupled ferromagnetically through the 5f orbitals. This possibility does not seem to us likely now since the Th^{IV} derivative, that we specially prepared to check this hypothesis, exhibits no coupling. We thus consider that the coupling we observed occurs between the 3d unpaired electron on Cu^{2+} and the U^{4+} 5f electrons. It is interesting to

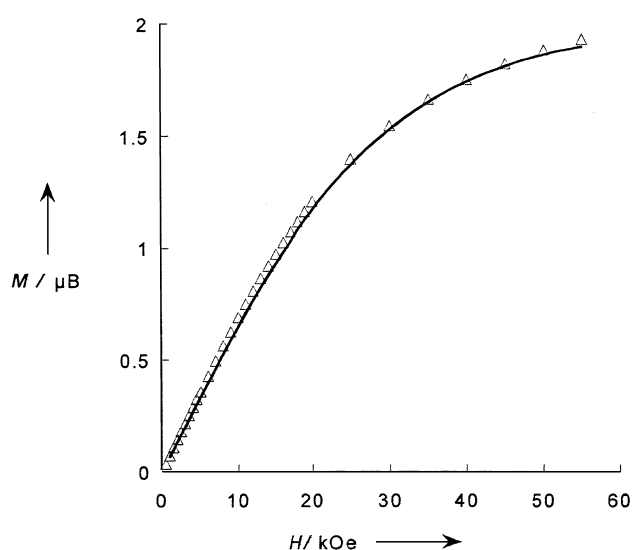


Figure 7. Field dependence of $\Delta M = M(\text{Cu}_2\text{U}) - M(\text{Zn}_2\text{U})$ at 2 K. The solid line corresponds to the Brillouin function for two noninteracting Cu^{2+} ions.

note that at low temperature, when U^{4+} becomes diamagnetic, the two Cu^{2+} ions are magnetically isolated, as now demonstrated by the magnetization curve of the Cu_2U compound at 2 K (Figure 7).

The dependence of $\chi_M T$ as a function of T for the Ni_2U and Co_2U complexes, with the variation of $\Delta(\chi_M T) = (\chi_M T)(M_2U) - (\chi_M T)(Zn_2U)$ ($M = Ni, Co$), is represented in Figure 8 and Figure 9, respectively. For $M = Ni$, $\chi_M T$ is equal

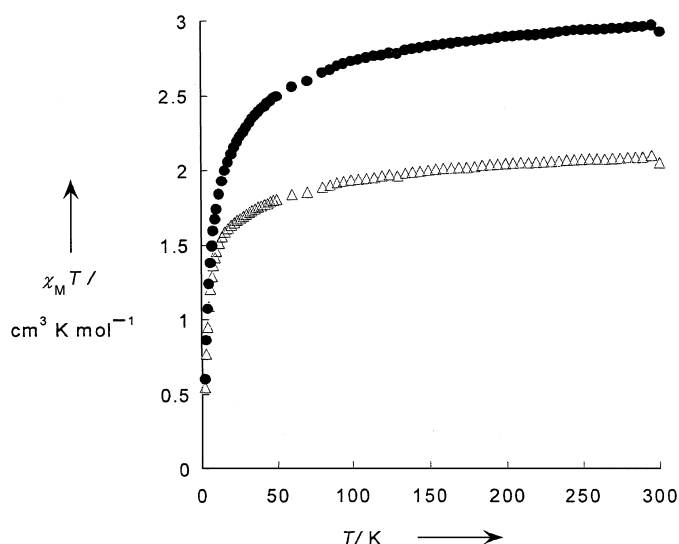


Figure 8. Thermal dependence of $\chi_M T$ for the Ni_2U complex (●) and the difference $\Delta(\chi_M T) = (\chi_M T)(Ni_2U) - (\chi_M T)(Zn_2U)$ (Δ).

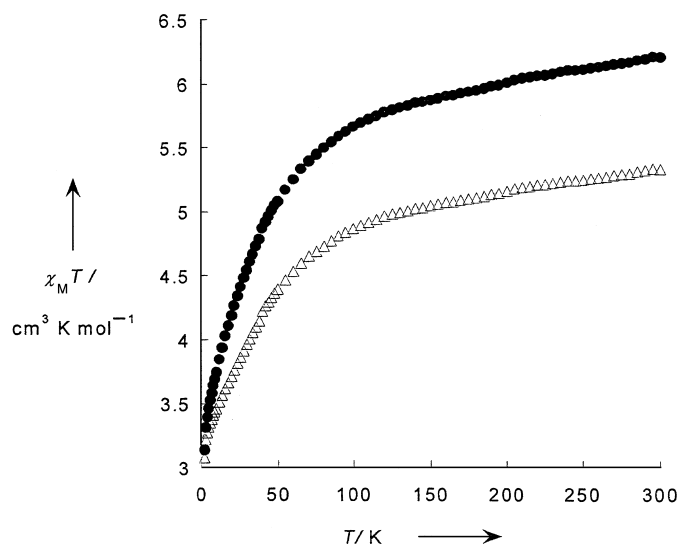


Figure 9. Thermal dependence of $\chi_M T$ for the Co_2U complex (●) and the difference $\Delta(\chi_M T) = (\chi_M T)(Co_2U) - (\chi_M T)(Zn_2U)$ (Δ).

to $2.9 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature and decreases continuously as T is lowered to reach $0.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The profile of the $\chi_M T$ versus T curve is similar for $M = Co$, with values of 6.3 and $3.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 and 2 K, respectively. The difference $\Delta(\chi_M T)$ decreases as T is lowered. For $M = Ni$, the value of $2 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K is close to that expected for two independent Ni^{2+} ions ($S = 1$). However, it was not possible to reproduce the decrease of $\Delta(\chi_M T)$ by a zero-field effect on Ni^{2+} ; in fact, the data start to decrease from room

temperature, and this is incompatible with a zero-field effect. This strongly suggests that an antiferromagnetic coupling exists between the Ni^{2+} and U^{4+} ions. For $M = Co$, the value of the difference $\Delta(\chi_M T)$ of $5.3 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is compatible with that for two isolated high-spin Co^{2+} ions ($S = 3/2$). High-spin Co^{2+} in an octahedral field has a degenerate ${}^4T_{1g}$ ground state for the orbitals, and the Curie law is then not obeyed.^[25] For a tetragonally distorted Co^{2+} ion as is the case here, $\chi_M T$ is approximately equal to $2.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K and goes to $1.7 \text{ cm}^3 \text{ K mol}^{-1}$ at low temperature, with the corresponding values of 5.0 and $3.4 \text{ cm}^3 \text{ K mol}^{-1}$ determined for two Co^{2+} ions. The low-temperature value of $\Delta(\chi_M T)$ is in agreement with that last value but it is very difficult to come to a conclusion about the absence or presence of coupling between the Co^{2+} and U^{4+} ions from this crude analysis.

It thus appears that the coupling in the $Ni-U$ pair is antiferromagnetic and ferromagnetic in the $Cu-U$ pair. It is too early to rationalize these differences. Other heterobimetallic compounds associating 3d and uranium magnetic ions, in particular strictly dinuclear complexes, have to be prepared and studied before reaching an understanding of the interaction between 3d and 5f electrons.

Conclusion

The use of an hexadentate bicompartamental 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 crystal structures of the homologous M_2U compounds ($M = Co, Ni, Cu, Zn$) showed that the uranium atom adopts the same dodecahedral configuration. Assuming that the crystal field effects on uranium are the same in the different complexes, we could apply the empirical approach recently designed for determining the nature of the magnetic interaction. Thus, comparison of the magnetic behavior of the Cu_2U , Cu_2Th , Cu_2Zr , and Cu_2Zn compounds revealed that the Cu^{2+} and U^{4+} ions are ferromagnetically coupled. On the other hand, the $Co-U$ pair was found to be weakly antiferromagnetically coupled. The amazing ferromagnetic coupling observed for the $Cu-U$ pair, which cannot be explained with a simple theory, has to be confirmed, in particular by the study of discrete bimetallic $Cu-U$ complexes.

Experimental Section

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

The 1H NMR spectra were recorded on a Bruker DPX200 instrument and referenced internally by using the residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$, $20^\circ C$). Magnetic susceptibility data were collected by using a powdered sample of the compound with a SQUID-based sample magnetometer Quantum design MPMS5. Elemental

analyses were performed by Analytische Laboratorien at Lindlar (Germany).

The Schiff bases H₂Lⁱ (*i* = 1, 2,^[25] 3,^[26] 4,^[27] and 5^[6]) and H₄Lⁱ (*i* = 6 and 7)^[27] were synthesized by published methods. The acac compounds [M(acac)₂] (M = Co, Ni, Cu, Zn) and [Zr(acac)₄]·H₂O (Aldrich) were used without purification. The complexes [MLⁱ] (*i* = 1–5) and [M(H₂Lⁱ)] (*i* = 6, 7) were synthesized by reaction of H₂Lⁱ or H₄Lⁱ with 1 equiv [M(acac)₂] in THF. UCl₄,^[28] [U(OSO₂CF₃)₄],^[29] [U(acac)₄],^[30] [Th(acac)₄],^[30] and [UL¹Cl₂(thf)₂] and [U(L¹)₂]^[14] were prepared as previously reported.

Reactions of [ML¹] (M = Co, Ni, Cu) with UCl₄: An NMR tube was charged with [CoL¹] (4.0 mg, 0.012 mmol) and UCl₄ (4.6 mg, 0.012 mmol) in [D₈]dichloromethane (0.3 mL). No reaction was observed after refluxing for 12 h. The solvent was evaporated off and replaced with [D₈]THF. The color of the solution turned immediately from orange to green, and the spectrum showed the quantitative formation of [UL¹Cl₂(thf)₂]; ¹H NMR ([D₈]THF): δ = −62.2 (s, 4H; CH₂N), 32.5, 45.4, 46.1, 51.5 and 77.7 (s, 5 × 2H; aromatic H and CH=N). Similar reactions of [NiL¹] (6.4 mg, 0.020 mmol) or [CuL¹] (6.6 mg, 0.020 mmol) with UCl₄ (7.6 mg, 0.020 mmol) in [D₈]THF (0.3 mL) also readily afforded [UL¹Cl₂(thf)₂] in quantitative yield.

Reaction of [NiL¹] with [U(OSO₂CF₃)₄]: An NMR tube was charged with [NiL¹] (3.3 mg, 0.010 mmol) and [U(OSO₂CF₃)₄] (8.3 mg, 0.010 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [UL¹(OSO₂CF₃)₂(thf)₂]; ¹H NMR ([D₈]THF): δ = −63.3 (s, 4H; CH₂N), 29.6, 46.2, 48.7, 54.5 and 72.3 (s, 5 × 2H; aromatic H and CH=N).

Reaction of [CoL¹] with [UL¹Cl₂(py)₂]: An NMR tube was charged with [CoL¹] (3.2 mg, 0.010 mmol) and [UL¹Cl₂(py)₂] (7.3 mg, 0.010 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [U(L¹)₂]; ¹H NMR ([D₅]pyridine): δ = −38.3 (s, 4H; CH₂N), 10.8, 11.5, 12.1, 14.5 and 15.7 (s, 5 × 2H; aromatic H and CH=N).

Reactions of [ML²] (M = Ni, Cu) with UCl₄: An NMR tube was charged with [NiL²] (7.5 mg, 0.022 mmol) or [CuL²] (7.6 mg, 0.022 mmol) and UCl₄ (8.6 mg, 0.022 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [UL²Cl₂(thf)₂]. This latter compound was also obtained from the reaction of H₂L² and UCl₄; ¹H NMR ([D₈]THF): δ = −67.6 (s, 4H; CH₂N), −43.2 (s, 2H; CH₂), 30.5, 43.2, 44.0, 52.5 and 72.5 (s, 5 × 2H; aromatic H and CH=N).

Reaction of [CuL³] with UCl₄: An NMR tube was charged with [CuL³] (7.4 mg, 0.020 mmol) and UCl₄ (7.6 mg, 0.020 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [UL³Cl₂(thf)₂]. This latter compound was also obtained from the reaction of H₂L³ and UCl₄; ¹H NMR ([D₈]THF): δ = −62.8 (s, 4H; CH₂N), 24.2 (s, 6H; Me), 32.9, 45.7, 48.4, 52.9 (s, 4 × 2H; aromatic H and CH=N).

Reactions of [ML⁴] (M = Co, Ni, Cu) with UCl₄: An NMR tube was charged with [ML⁴] (7.7 mg (Co), 7.7 mg (Ni), 7.8 mg (Cu), 0.020 mmol) and UCl₄ (7.6 mg, 0.020 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [UL⁴Cl₂(thf)₂]. This latter compound was also obtained from the reaction of H₂L⁴ and UCl₄; ¹H NMR ([D₈]THF): δ = −70.9 (s, 4H; CH₂N), −41.8 (s, 2H; CH₂), 21.5 (s, 6H; Me), 31.3, 43.5, 44.3 and 55.2 (s, 4 × 2H; aromatic H and CH=N).

Reaction of [Co(H₂L⁶)] with UCl₄: An NMR tube was charged with [Co(H₂L⁶)] (7.2 mg, 0.020 mmol) and UCl₄ (7.6 mg, 0.020 mmol) in [D₈]THF (0.3 mL). After 15 min at 20 °C, the spectrum of the green solution showed the quantitative formation of [U(H₂L⁶)Cl₂(thf)₂]; ¹H NMR ([D₈]THF): δ = −60.9 (s, 4H; CH₂N), 31.4, 43.4, 46.0 and 49.5 (s, 4 × 2H; aromatic H and CH=N).

Reaction of [Co(H₂L⁷)] with UCl₄: A flask was charged with H₄L⁷ (184.8 mg, 0.54 mmol) and [Co(acac)₂] (138.8 mg, 0.54 mmol), and THF (40 mL) was condensed in it. After 2 h at 20 °C, the solvent was evaporated off, and this left the red powder of [Co(H₂L⁷)]. UCl₄ (205 mg, 0.54 mmol) was introduced into the flask, and pyridine (40 mL) was condensed in it. The reaction mixture was stirred for 2 h at 20 °C; the brown precipitate was filtered off, washed with THF (20 mL), and dried under vacuum. The product was found to be insoluble in organic solvents. Its elemental analyses corresponded to the formula [(CoL⁷)UCl₂(py)₂]; elemental

analysis calcd (%) for C₂₉H₂₈CoCl₂N₄O₄U (864): C 40.30, H 3.20, N 6.48, Cl 8.20; found: C 40.68, H 3.27, N 6.12, Cl 8.13.

Synthesis of [(CoL⁷(py))₂U]: A flask was charged with H₄L⁷ (306 mg, 0.9 mmol) and [Co(acac)₂] (230 mg, 0.9 mmol), and THF (40 mL) was condensed in it. The reaction mixture was stirred for 1 h at 20 °C, and the red solution was evaporated to dryness, and this left the red powder of [Co(H₂L⁷)]. [U(acac)₄] (283 mg, 0.44 mmol) was introduced into the flask, and pyridine (40 mL) was condensed in it. The reaction mixture was stirred for 2 h at 20 °C; the red precipitate was filtered off, washed with THF (20 mL), and dried under vacuum. The precipitate was dissolved in the minimum quantity of pyridine (ca. 10 mL). Red crystals were deposited from the red solution upon heating for 12 h at 110 °C; these were filtered off and dried under vacuum (441 mg, 84%). The ¹H NMR spectrum was recorded with the powder before crystallization from pyridine; ¹H NMR ([D₅]pyridine): δ = −11.8 (s, w_{1/2} = 95 Hz, 12H; CH₃), −2.4, 9.6 and 48.7 (s, 3 × 4H; aromatic CH), 133 (s, w_{1/2} = 200 Hz, 8H; CH₂), 402 (s, w_{1/2} = 160 Hz, 4H; CH=N); elemental analysis calcd (%) for C₄₈H₄₆Co₂N₆O₈U (1191): C 48.30, H 3.81, N 7.05; found: C 45.10, H 3.53, N 7.52.

Synthesis of [(NiL¹(py))₂U]·py: The Ni₂U compound was synthesized by using the same procedure as for the Co₂U complex, starting from H₄L¹ (375.2 mg, 1.1 mmol), [Ni(acac)₂] (282 mg, 1.1 mmol), and [U(acac)₄] (347.8 mg, 0.55 mmol). Green crystals (475 mg, 68%) were obtained by crystallization from pyridine; ¹H NMR ([D₅]pyridine): δ = −4.6 (s, w_{1/2} = 135 Hz, 12H; CH₃), 9.6, 10.7 and 46.5 (s, 3 × 4H; aromatic CH), 102 (s, w_{1/2} = 540 Hz, 8H; CH₂), 409 (s, w_{1/2} = 2500 Hz, 4H; CH=N); elemental analysis calcd (%) for C₅₃H₅₁N₇Ni₂O₈U (1267): C 50.20, H 4.0, N 7.73; found: C 50.28, H 4.11, N 7.95.

Synthesis of [(CuL⁷(py))U(CuL⁷)]·py: The Cu₂U compound was synthesized by using the same procedure as for the Co₂U complex, starting from H₄L⁷ (200 mg, 0.58 mmol), [Cu(acac)₂] (152 mg, 0.58 mmol), and [U(acac)₄] (185 mg, 0.29 mmol). Green crystals of [(CuL⁷(py))U(CuL⁷)]·2py were obtained by crystallization from pyridine; these were transformed into the monosolvated Cu₂U complex upon drying under vacuum (251 mg, 72%); ¹H NMR ([D₅]pyridine): δ = −7.0 (s, w_{1/2} = 135 Hz, 12H; CH₃), 4.4, 16.0 and 47.5 (s, 3 × 4H; aromatic CH), 96 (s, w_{1/2} = 325 Hz, 8H; CH₂), 423 (s, w_{1/2} = 3000 Hz, 4H; CH=N); elemental analysis calcd (%) for C₄₈H₄₆Cu₂N₆O₈U (1199): C 48.0, H 3.83, N 7.0; found: C 47.76, H 3.79, N 6.85.

Synthesis of [(ZnL⁷(py))₂U]: The Zn₂U compound was synthesized by using the same procedure as for the Co₂U complex, starting from H₄L⁷ (245 mg, 0.71 mmol), [Zn(acac)₂] (187 mg, 0.71 mmol), and [U(acac)₄] (227 mg, 0.35 mmol). Orange crystals (228 mg, 54%) were obtained by crystallization from pyridine; ¹H NMR ([D₅]pyridine): δ = −7.9 (s, 12H; CH₃), −7.4 (s, 8H; CH₂), 0.3, 5.1, 14.2 and 24.0 (s, 4 × 4H; aromatic CH and CH=N); elemental analysis calcd (%) for C₄₈H₄₆N₆O₈UZn₂ (1199): C 47.9, H 3.8, N 6.98; found: C 48.11, H 3.64, N 7.23.

Synthesis of [(CuL⁷)₂Zr]: The Cu₂Zr compound was synthesized by using the same procedure as for the Co₂U complex, starting from H₄L⁷ (219 mg, 0.64 mmol), [Cu(acac)₂] (168.2 mg, 0.64 mmol), and [Zr(acac)₄]·H₂O (162 mg, 0.32 mmol). The green powder (240 mg, 84%) was not recrystallized. No signal was visible on the ¹H NMR spectrum; elemental analysis calcd (%) for C₃₈H₃₆Cu₂N₄O₈U (886): C 51.4, H 4.0, N 6.3; found: C 51.05, H 4.49, N 5.61.

Synthesis of [(CuL⁷(py))Th(CuL⁷)]·py: The Cu₂Th compound was synthesized by using the same procedure as for the Co₂U complex, starting from H₄L⁷ (180 mg, 0.52 mmol), [Cu(acac)₂] (138 mg, 0.52 mmol), and [Th(acac)₄] (167 mg, 0.26 mmol). Green crystals of [(CuL⁷(py))U(CuL⁷)]·2py were obtained by crystallization from pyridine; these were transformed into the monosolvated Cu₂Th complex upon drying under vacuum (156 mg, 50%). No signal was visible on the ¹H NMR spectrum; elemental analysis calcd (%) for C₄₈H₄₆Cu₂N₆O₈Th (1196): C 48.2, H 3.8, N 7.0; found: C 47.67, H 3.51, N 6.99.

Crystal structure determination for [UL³Cl₂(py)₂] and [(ZnL⁷(py))₂U]: The crystals were introduced in Lindemann glass capillaries with a protecting “Paratone” oil (Exxon Chemical Ltd.) coating. The data were recorded on a Siemens Smart area detector diffractometer by using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The unit cell parameters were determined from the reflections collected on 45 frames and were then refined on all data. The data were recorded in ω-scan mode (180° range, 0.3° steps, exposure time 10 s per frame) and processed with SHELXTL.^[26] The structures were solved by direct methods with SHELXS-97^[27] and

subsequent Fourier-difference synthesis and refined by the full-matrix least-squares method on F^2 with SHELXL-97.^[28] A semiempirical absorption correction based on symmetry equivalent reflections was applied by using the program SADABS.^[29] All non-hydrogen atoms were refined with anisotropic displacement parameters, except the carbon atoms of the pyridine molecules in the Zn_2U complex. All hydrogen atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom. The absolute structure of the Zn_2U complex was determined from the value of the Flack parameter,^[30] 0.009(9). The crystals of [UL³Cl₂(py)₂] were of a rather low quality, and the presence of a disordered solvent molecule, which cannot be properly resolved, was likely. The presence of a free pyridine molecule in the structure of the Zn_2U and Co_2U complexes, located as in the isomorphous Ni_2U complex (vide infra), but not resolved from data recorded at ambient temperature, was also possible. Crystal data and structure refinement details for the Zn_2U compound are given in Table 2. Crystal data for [UL³Cl₂(py)₂]: $C_{33}H_{38}Cl_2N_4O_4U$, $M = 863.60$, monoclinic, space group $P2_1/n$, $a = 10.0550(1)$ Å, $b = 12.3059(2)$ Å, $c = 30.0314(1)$ Å, $\beta = 94.641(1)^\circ$, $V = 3703.78(7)$ Å³, $Z = 4$, $F(000) = 1688$, $\rho_{\text{calcd}} = 1.549$ g cm⁻³, μ_{Mo} = 4.565 mm⁻¹, crystal size = 0.28 × 0.24 × 0.20 mm, $T_{\text{min}}/T_{\text{max}} = 0.361/0.462$, 2θ range = 3–59°, $T = 296(2)$ K, 23 867 reflections collected, 9375 independent reflections ($R_{\text{int}} = 0.243$), 2754 “observed” reflections [$I > 2\sigma(I)$], 388 parameters refined, $R_1 = 0.084$, $wR_2 = 0.179$, $S = 0.824$, $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} = 5.88/-4.01$ e Å⁻³ (highest residual density peaks located near the uranium atom).

Crystal structure determination for [(NiL⁷(py))₂U]·py and [(CuL⁷(py))₂U]·2py (An = U, Th): The crystals were introduced into Lindemann glass capillaries with a protecting “Paratone” oil (Exxon Chemical Ltd.) coating. The data were collected on a Nonius Kappa-CCD area detector diffractometer^[31] by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were determined from the reflections collected on ten frames and were then refined on all data. The data were recorded in ϕ -scan mode (180° range, 2° steps, exposure time 10 to 20 s per frame) and processed with DENZO-SMN.^[32] The structures were solved by direct methods with SHELXS-97^[27] and subsequent Fourier-difference synthesis and refined by the full-matrix least-squares method on F^2 with SHELXL-97.^[28] Absorption effects were corrected empirically with the program MULABS from PLATON.^[33] All non-

hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced at calculated positions as riding atoms with an isotropic displacement parameter equal to 1.2 (CH, CH₂) or 1.5 (CH₃) times that of the parent atom. The absolute structure of the Ni_2U complex was determined from the value of the Flack parameter,^[30] 0.003(10). The molecular plots were drawn with SHELXTL.^[26] Crystal data and structure refinement details for the trinuclear compounds are given in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169408 ([UL³Cl₂(py)₂]), 169409 (Ni_2U), 169410 (Zn_2U), 169411 (Cu_2U), and 169412 (Cu_2Th). 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).

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Table 2. Crystallographic data of the trinuclear complexes.

	[[CoL(py)) ₂ U]	[[NiL(py)) ₂ U]·py	[[ZnL(py)) ₂ U]	[[CuL(py))U{CuL}]·2py	[[CuL(py))Th{CuL}]·2py
chemical formula	C ₄₈ H ₄₆ Co ₂ N ₆ O ₈ U	C ₅₃ H ₅₁ N ₇ Ni ₂ O ₈ U	C ₄₈ H ₄₆ N ₆ O ₈ UZn ₂	C ₅₃ H ₅₁ Cu ₂ N ₇ O ₈ U	C ₅₃ H ₅₁ Cu ₂ N ₇ O ₈ Th
M [g mol ⁻¹]	1190.80	1269.46	1203.68	1279.12	1273.13
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$P2_1/n$	$P2_1/n$
a [Å]	27.4586(2)	27.156(2)	27.2759(9)	13.5992(9)	13.676(1)
b [Å]	13.8515(2)	13.6128(8)	13.8672(4)	13.1624(9)	13.1207(8)
c [Å]	13.9874(2)	13.717(1)	13.9425(4)	27.941(2)	27.999(3)
β [°]				103.490(3)	104.006(4)
V [Å ³]	5320.0(1)	5070.6(6)	5273.6(3)	4863.5(6)	4874.6(7)
Z	4	4	4	4	4
ρ_{calcd} [g cm ⁻³]	1.487	1.663	1.516	1.747	1.735
μ (Mo K_{α}) [mm ⁻¹]	3.705	3.982	4.018	4.252	3.971
crystal size [mm]	0.28 × 0.24 × 0.22	0.24 × 0.20 × 0.18	0.24 × 0.20 × 0.10	0.15 × 0.15 × 0.08	0.18 × 0.15 × 0.12
$T_{\text{min}}/T_{\text{max}}$	0.336/0.453	0.430/0.488	0.446/0.689	0.540/0.712	0.533/0.621
$F(000)$	2344	2520	2368	2528	2520
2θ range [°]	3–59	6–51	3–59	5–51	5–51
T [K]	296(2)	100(2)	296(2)	100(2)	100(2)
no. of data collected	34 624	31 712	35 272	32 329	29 827
no. of unique data	12 594	8927	13 194	9088	8887
observed data [$I > 2\sigma(I)$]	7380	6065	5927	5658	5561
R_{int}	0.047	0.097	0.092	0.088	0.086
no. of parameters	566	628	541	641	640
R_1 ^[a]	0.052	0.057	0.062	0.060	0.071
wR_2 ^[b]	0.132	0.119	0.142	0.117	0.143
S	0.986	1.002	0.942	0.982	1.006
$\Delta\rho_{\text{min}}$ [e Å ⁻³]	-0.52	-1.16	-0.56	-1.59	-1.68
$\Delta\rho_{\text{max}}$ [e Å ⁻³]	1.18	0.88	1.19	1.35	1.20

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (observed reflections). [b] $wR_2 = [\sum w |F_o|^2 - |F_c|^2 / \sum w |F_o|^2]^{1/2}$ (observed reflections).

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