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Crystal structure of hetero(bi- and tetra-)metallic complexes of compartmental Schiff bases uniting uranyl and transition metal (Ni^{2+}, Cu^{2+}) ions

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Abstract

The first crystal structures of hetero(bi- and tetra-)metallic uranyl/3d metal ion complexes with hexadentate Schiff bases are reported. The two Schiff bases *N*,*N*′-bis(3-hydroxysalicylidene)-1,3-propanediamine (H_4L^1) and *N*,*N*′-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine (H_4L^2) have been used. Both ligands complex the 3d metal ion (Ni^{2+} or Cu^{2+}) in the inner N_2O_2 coordination site, with n additional axial pyridine ligands ($0 \leq n \leq 2$) and the uranyl ion in the outer O_4 cavity. In order to match the usual pentagonal bipyramidal geometry, the coordination sphere of the uranyl ion is completed by either a chlorine atom, giving the binuclear complex $[Ni(py)_2(L^1)UO_2Cl][Hpy]$, or by a water molecule, resulting in the hydrogen bonded binuclear dimer $[Ni(L^2)UO_2(H_2O)]_2$ or by a phenoxide oxygen atom of a second Schiff base in the tetranuclear $[Cu(py)(L^1)UO_2]_2$ species.

Keywords: Schiff bases; Heteropolymetallic complexes; Uranyl ions; Crystal structures

1. Introduction

The well-known requirement of the linear uranyl ion for pentagonal or hexagonal pseudo-planar equatorial environments makes this ion a well-suited target for complexation by Schiff bases. Mononuclear uranyl complexes with *N*,*N*′-bis(salicylidene)-1,2-ethylenediamine and *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine Schiff bases were synthesized and structurally characterized early [1,2]. In these compounds, the cation is bound in the N_2O_2 coordination site and completes its coordination sphere with a donor atom from a solvent molecule. In other complexes, the coordinating solvent is replaced by a donor atom included in the bridge linking the two imine nitrogen atoms, which ensures also a pentagonal environment [3–5]. Interest in these systems was renewed when it was demonstrated that, due to the cation Lewis acidic nature, several systems including uranyl-complexed functionalized Schiff bases could act as selective receptors for neutral molecules [6] or anions [7]. Heterobimetallic complexes uniting uranyl and 3d transition metal ions with compartmental Schiff bases have been synthesized [8] but, to the best of our knowledge, their crystal structure has never been determined. The only bimetallic species to date is a homobinuclear uranyl complex with a ligand which possesses an internal N_3O_2 site and an external O_4 one, the uranyl in the latter being further bound to a solvent molecule [3]. However, the present work proceeds from a different background. We recently used dinucleating hexadentate Schiff bases in order to synthesize heterobi- and heterotri-metallic complexes containing paramagnetic 5f (U^{IV}) and 3d metal ions, in order to investigate their magnetic behaviour [9]. In the course of this study, two heterobinuclear and one heterotetranuclear uranyl/3d metal ions complexes were obtained and their crystal structures are described herein. Two Schiff base ligands have been used: *N*,*N*′-bis(3-hydroxysalicylidene)-1,3-propanediamine and *N*,*N*′-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine, denoted H_4L^1 and H_4L^2, respectively (Scheme 1).

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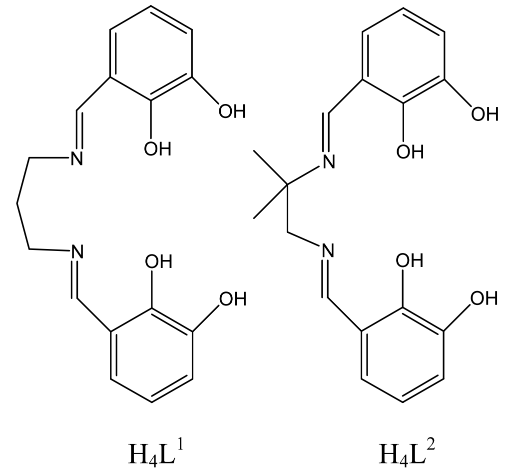

Scheme 1. The Schiff bases H_4L^1 and H_4L^2.

2. Experimental

2.1. Synthesis

UCl_4 [10], $U(acac)_4$ (acac = acetylacetonato) [11] and $U(OTf)_4$ ($OTf = CF_3SO_3$) [12] were synthesized as reported in the literature. The complexes $[MH_2L^i]$ (NiH_2L^1, NiH_2L^2 and CuH_2L^1) were synthesized by reaction of H_4L^i with 1 equiv. $M(acac)_2$ in THF. The mononuclear metal complexes were mixed in a 1:1 ratio with UX_4 in pyridine (X = Cl, acac or OTf). In all cases, adventitious traces of oxygen or water probably entered the reaction flask during prolonged heating at 80 °C, which resulted in U^{IV} oxidation to give U^{VI} in the form of uranyl ions. Dark orange single crystals of $[Ni(py)_2(L^1)UO_2Cl][Hpy]\cdot 2py$ (**1**) were obtained from NiH_2L^1 and UCl_4, dark brown single crystals of $[Ni(L^2)UO_2(H_2O)]\cdot 2py$ (**2**) from NiH_2L^2 and $U(acac)_4$ and dark red single crystals of $[Cu(py)(L^1)UO_2]_2\cdot 2py$ (**3**) from CuH_2L^1 and $U(OTf)_4$.

2.2. Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer [13] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were introduced in glass capillaries with a protecting ‘Paratone-N’ oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. A 180° φ-range was scanned with 2° steps during data collection, with a crystal-to-detector distance fixed to 28 mm. The data were processed with DENZO-SMN [14]. The structures were solved by direct methods with SHELXS-97 [15] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 [15]. Absorption effects were corrected empirically with the program DELABS from PLATON [16]. In compound **1**, the central carbon atom of the diimino chain is disordered over two positions which have been refined with occupancy factors constrained to sum to unity. In compound **2**, the distance between the two central atoms of the diimino chain is abnormally short (1.38 Å) and the highest residual electron density peaks are located near these atoms, which likely indicates the presence of unresolved disorder. All non-hydrogen atoms were refined with anisotropic displacement parameters, except the disordered ones when present. Some restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in the disordered parts. Hydrogen atoms bound to nitrogen and oxygen atoms were found on Fourier-difference maps and the other ones were introduced at calculated positions, except in the disordered parts when present. All protons were treated as riding atoms with a displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with SHELXTL [17]. All calculations were performed on a Silicon Graphics workstation.

3. Discussion

The binuclear complex $[Ni(py)_2(L^1)UO_2Cl][Hpy]\cdot 2py$ (**1**) is represented in Fig. 1. The $[Ni(py)_2(L^1)UO_2Cl]$ group is anionic and its charge is compensated by that of a pyridinium ion which is hydrogen bonded to a phenoxide oxygen atom [N5···O4 2.584(8), N5–H 0.98, H···O4 1.61 Å, N5–H···O4 172°]. The nickel atom occupies the inner N_2O_2 coordination site whereas the uranium atom lies in the outer O_4 one, as usual [9]. A chlorine atom completes the uranium coordination sphere, resulting in a pentagonal bipyramidal environment. The five donor atoms define a mean plane with a maximum deviation of 0.039(4) Å, the uranium atom being at 0.059(2) Å from this plane. The four U–O bond lengths have a mean value of 2.39(4) Å, with only U–O1 being slightly lower than the others (Table 2). This is at variance with the homobimetallic uranyl complexes previously described [3], in which the cation in the external site displays two long bond lengths with the internal oxygen atoms (2.52–2.54 Å) and two shorter ones with the external oxygens (2.25–2.27 Å), with however an identical overall mean value of 2.40(15) Å. However, it must be noted that the Schiff base geometries are somewhat different, the present one being hexadentate whereas that in the previous study is heptadentate, with a much longer bridge between the imine functions, which results in different sizes for the O_4 site. The O···O distances between adjacent oxygen atoms are O1···O2 2.559(8), O3···O4 2.589(7), O2···O3 2.508(7) and O1···O4 4.701(8) Å in **1**, the corresponding

Table 1
Crystal data and structure refinement details

	1	2	3
Chemical formula	$C_{42}H_{40}ClN_7NiO_6U$	$C_{28}H_{28}N_4NiO_7U$	$C_{54}H_{48}Cu_2N_8O_{12}U_2$
M (g mol^{-1})	1071.00	829.28	1604.14
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.0545(6)	11.4453(6)	10.754(2)
b (Å)	17.8471(13)	22.3006(13)	15.779(3)
c (Å)	22.7500(13)	12.0090(7)	16.111(3)
β (°)	100.049(4)	114.905(3)	107.61(2)
V (Å^3)	4019.7(4)	2780.1(3)	2605.8(9)
Z	4	4	2
D_{calc} (g cm^{-3})	1.770	1.981	2.045
μ (Mo Kα) (mm^{-1})	4.616	6.549	7.073
Crystal size (mm)	0.10 × 0.10 × 0.05	0.22 × 0.20 × 0.10	0.15 × 0.10 × 0.05
$F(0\,0\,0)$	2104	1600	1532
θ Range (°)	2.8–25.7	2.6–25.7	2.7–25.7
T (K)	100(2)	100(2)	100(2)
Number of data collected	27 517	18 927	16 547
Number of unique data	7499	5259	4799
Number of 'observed' data [$I > 2\sigma(I)$]	4851	3736	1984
R_{int}	0.135	0.089	0.114
Number of parameters	524	372	352
R_1 [a]	0.050	0.046	0.074
wR_2 [b]	0.088	0.096	0.111
S	1.011	1.019	0.959
$\Delta\rho_{min}$ (e Å^{-3})	−0.83	−1.68	−1.29
$\Delta\rho_{max}$ (e Å^{-3})	0.68	1.82	1.06

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

distances in the previous examples being O1···O2 (or O3···O4) 2.628–2.686, O2···O3 2.805–2.848 and O1···O4 4.415–4.447 Å, showing as expected a lessened difference between the O2···O3 and O1···O4 separations, which may account for a slightly different uranium location. A similar mean U–O bond length of 2.37(6) Å is found in the U^{IV} complexes of Schiff bases recently reported [9]. It has been noted, in the case of the mononuclear uranyl complex of *N*,*N′*-bis(salicylidene)-1,2-ethylenediamine, that involvement of a phenoxide donor in an intermolecular hydrogen bond results in a lengthening of the corresponding U–O bond (by about

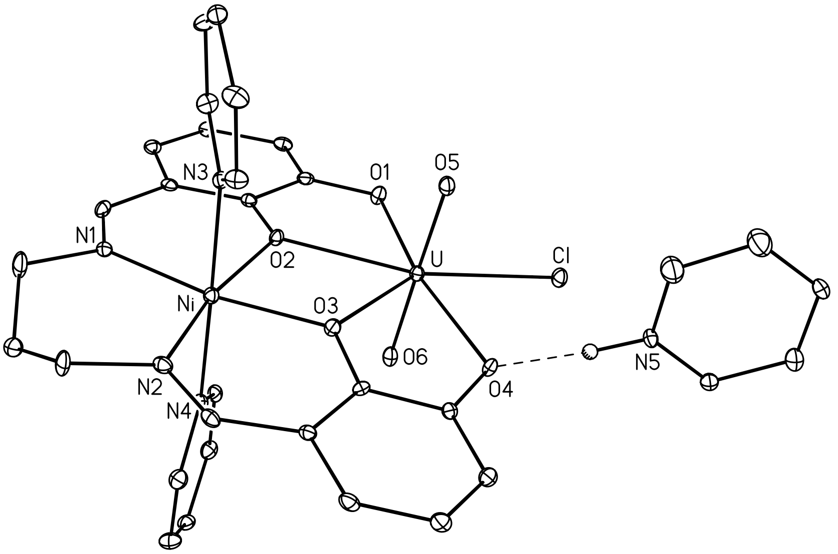

Fig. 1. View of the complex $[Ni(py)_2(L^1)UO_2Cl][Hpy]\cdot 2py$ (**1**). Hydrogen atoms (except the pyridinium one) and solvent molecules omitted for clarity. Hydrogen bond represented as a dashed line. Ellipsoids drawn at the 10% probability level.

Table 2
Environment of the uranium and 3d transition metal atoms in compounds **1**–**3**: selected distances (Å) and angles (°)

1				
	U–O1	2.321(5)	Ni–O2	2.001(6)
	U–O2	2.406(5)	Ni–O3	2.021(5)
	U–O3	2.412(5)	Ni–N1	2.032(7)
	U–O4	2.412(5)	Ni–N2	2.013(7)
	U–O5	1.790(6)	Ni–N3	2.167(7)
	U–O6	1.759(6)	Ni–N4	2.218(7)
	U–Cl	2.707(2)		
	U···Ni	3.6232(11)		
	O1–U–O2	65.5(2)	O2–Ni–N1	90.7(2)
	O2–U–O3	62.8(2)	N1–Ni–N2	100.7(3)
	O3–U–O4	64.9(2)	N2–Ni–O3	91.4(3)
	O4–U–Cl	79.31(14)	O3–Ni–O2	77.2(2)
	Cl–U–O1	87.45(14)	N3–Ni–N4	178.1(3)
	O5–U–O6	178.4(3)		
2				
	U–O1	2.310(6)	Ni–O2	1.829(7)
	U–O2	2.424(6)	Ni–O3	1.831(6)
	U–O3	2.419(6)	Ni–N1	1.807(9)
	U–O4	2.396(6)	Ni–N2	1.861(10)
	U–O5	1.786(6)		
	U–O6	1.790(6)		
	U–O7	2.368(5)		
	U···Ni	3.5298(12)		
	O1–U–O2	65.1(2)	O2–Ni–N1	98.0(4)
	O2–U–O3	57.7(2)	N1–Ni–N2	87.5(5)
	O3–U–O4	64.5(2)	N2–Ni–O3	95.2(4)
	O4–U–O7	80.7(2)	O3–Ni–O2	79.3(3)
	O7–U–O1	92.5(2)		
	O5–U–O6	178.2(3)		
3				
	U–O1	2.271(13)	Cu–O2	1.952(14)
	U–O2	2.411(11)	Cu–O3	2.005(11)
	U–O3	2.412(12)	Cu–N1	1.993(16)
	U–O4	2.427(10)	Cu–N2	1.976(17)
	U–$O4^{a\prime}$	2.380(11)	Cu–N3	2.300(14)
	U–O5	1.735(11)		
	U–O6	1.763(11)		
	U···Cu	3.608(3)		
	U···$U^{a\prime}$	3.9336(15)		
	O1–U–O2	65.8(4)	O2–Cu–N1	92.2(7)
	O2–U–O3	62.0(4)	N1–Cu–N2	97.1(7)
	O3–U–O4	65.8(4)	N2–Cu–O3	90.2(5)
	O4–U–$O4^{a\prime}$	70.2(5)	O3–Cu–O2	77.7(5)
	$O4^{a\prime}$–U–O1	96.4(4)		
	O5–U–O6	178.7(6)		

Symmetry code: $a' = 2-x, -y, -z$.

0.09 Å) [1b]. A similar observation can be made in compound **1** since U–O4 is larger by 0.09 Å than U–O1. The O–U–O angles are in the 63–66° range, but the Cl–U–O1 and Cl–U–O4 angles differ by about 8° one from the other. The nickel atom is in a square bipyramidal environment with two axial pyridine ligands (mean equatorial and axial bond lengths 2.02(1) and 2.19(4) Å, respectively). As a result of this bipyramidal geometry, the metal atom is close to the mean N_2O_2 plane, with a separation of 0.024(3) Å only, whereas it amounts to 0.29(1) when only one axial pyridine is present [9a]. The two coordination planes N_2O_2 and O_4 in **1** define a dihedral angle of 7.5(2)°. The Schiff base is in the so-called *umbrella* conformation, with a dihedral angle of 13.3(3)° between the two aromatic rings.

The complex unit in $[Ni(L^2)UO_2(H_2O)]\cdot 2py$ (**2**) is neutral, the chlorine atom of **1** being replaced by a water molecule (Fig. 2). The uranyl ion is in the usual pentagonal bipyramidal environment, with a mean U–O(phenoxide) bond length of 2.39(5) Å and with the uranium and water oxygen atoms displaced by 0.039(4) and 0.37(1) Å, respectively, from the O_4 plane (largest deviation 0.046(4) Å). The U–O4 bond length is larger by about 0.09 Å than U–O1, which is likely due to the involvement of O4 in a strong hydrogen bond with the water molecule of a neighbouring, centrosymmetrically-related, molecule (O7···$O4^{a\prime}$ 2.608(8), O7–H1 0.95, H1···$O4^{a\prime}$ 1.70 Å, O7–H1···$O4^{a\prime}$ 158°). The large displacement of the water oxygen atom out of the uranyl equatorial plane may be accounted for by its involvement in a second strong hydrogen bond with a pyridine molecule (O7···N3 2.750(10), O7–H2 0.95, H2···N3 1.81 Å, O7–H2···N3 173°). The nickel atom is in a square planar environment, with a mean Ni–(N,O) bond length of 1.83(2) Å and a displacement of 0.021(4) Å from the mean N_2O_2 plane. The Schiff base is close to planarity, with a dihedral angle of 6.7(7) Å between the two aromatic rings. The water–phenoxide hydrogen bonds result in the formation of centrosymmetrical dimers held by feeble interactions, with formation of a central eight-membered ring containing the two uranium atoms.

$[Cu(py)(L^1)UO_2]_2\cdot 2py$ (**3**) is a tetranuclear complex built from two centrosymmetrically related binuclear units (Fig. 3). Each uranium atom is bound to the four phenoxide oxygen atoms of one Schiff base molecule and to one ($O4^{a\prime}$) from the second, with a mean U–O bond length of 2.38(6) Å, the distances involving the bridging atom O4 being larger by about 0.13 Å than that with its non-bridging counterpart O1. The uranium atom is displaced by 0.025(4) Å from the mean equatorial O_5 plane (maximum deviation 0.075(8) Å). The O–U–O angles involving O1, O2, O3 and O4 in adjacent positions are in the range 62–66°, whereas the two angles involving $O4^{a\prime}$, and particularly O1–U–$O4^{a\prime}$, are larger. It may be noted that the U···Ni distance is larger by about 0.09 Å in compound **1** than in **2**. Such a difference, which results from the variation in the diimino chain length, has also been observed in Cu(II)–U(IV) complexes with the same Schiff bases [9c]. The central bimetallic U_2O_8 core in **3** is roughly planar. The copper atom is in a square pyramidal environment, with a mean Cu–(N,O) bond length in the basal plane of 1.98(2) Å and a displacement from the N_2O_2 plane of 0.217(7) Å towards the pyridine ligand. The Schiff base is in an *umbrella* conformation with a dihedral angle of 27.1(7)° between the two aromatic rings. The present

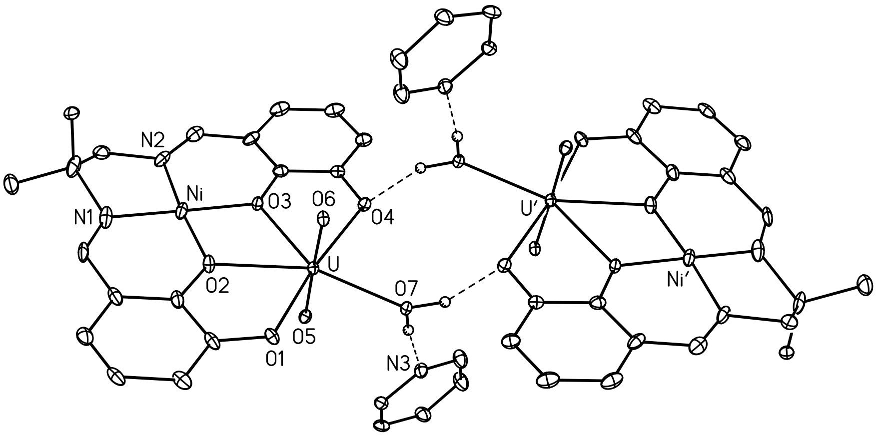

Fig. 2. View of the hydrogen bonded dimeric structure of the complex $[Ni(L^2)UO_2(H_2O)]\cdot 2py$ (**2**). Hydrogen atoms (except those of water) and non-hydrogen bonded pyridine molecules omitted for clarity. Hydrogen bonds represented as dashed lines. Ellipsoids drawn at the 10% probability level. Symmetry code: a′, 2−*x*, 1−*y*, 2−*z*.

tetranuclear arrangement with two central phenoxide bridges is analogous to that found in the roughly planar mixed copper/yttrium complex of *N*,*N*′-bis(3-hydroxysalicylidene)-ethanediamine [8] in which yttrium replaces uranium, with its coordination sphere completed by a nitrate ion and a dmso molecule. It is also reminiscent, albeit to a lesser degree, of the mixed cobalt/sodium complex of *N*,*N*′-bis(3-methoxysalicylidene)-ethanediamine [18], but in this case the complex is no more planar, the central Na_2O_2 square being much inclined with respect to the Schiff bases. No other example of a similar geometry is present in the Cambridge Structural Database (Version 5.24 [19]).

Apart from some differences in the nature of the 3d metal ion and in the Schiff base diimino chain, which appear of secondary importance since they have little or no effect on the uranyl ion environment, the three compounds reported herein display three architectures of progressive complexity, from the simple binuclear complex **1** to the loosely associated bis(binuclear) complex **2** and the genuine tetranuclear assembly **3**. The latter, with its bridging phenoxides, evidences the assembling ability of hexadentate Schiff bases, which has recently been demonstrated in the case of a cluster of eight Zn^{2+} ions and four Schiff bases [20].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 205724–205726 for compounds **1**–**3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

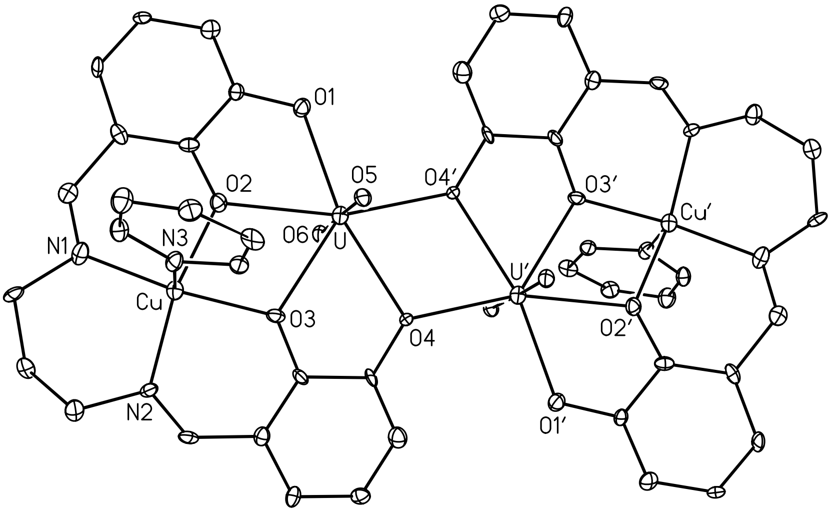

Fig. 3. View of the dimeric complex $[Cu(py)(L^1)UO_2]_2\cdot 2py$ (**3**). Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids drawn at the 10% probability level. Symmetry code: a′, 2−*x*, −*y*, −*z*.

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