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Two-step construction of molecular and polymeric mixed-metal Cu(Co)/Be complexes employing functionality of a pyridyl substituted acetylacetonate†

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Received 2nd January 2003, Accepted 6th March 2003
First published as an Advance Article on the web 18th March 2003

The bifunctional exodentate ligand 3-(4-pyridyl)-2,4-pentanedione was exploited for the synthesis of mixed-metal (Co/Be and Cu/Be) and mixed-metal mixed-valence (Cu^ICu^{II}/Be) coordination compounds. The ligand was immobilized on a tetrahedral Be^{2+} matrix employing the β-diketonate function and the resulting complex BeL_2 was used as an extended connector for generation of Co(Cu)/Be alternating superstructures utilizing the pyridyl donor sites. Coordination compounds adopt either molecular ($Co\{BeL_2\}_2Cl_2$), and one- ($Cu_2X_3\{BeL_2\}_2$; X = Cl, Br) or two-dimensional ($Co\{BeL_2\}(CH_3OH)_2SO_4$, $Cu_2Br_2\{BeL_2\}_2$) polymeric patterns.

Introduction

In recent years many types of coordination polymers have been engineered under a strategy of supramolecular synthesis using a number of bi- and poly-dentate bridging ligands ("spacers") and different metal ions Co(II), Ni(II), Cu(I,II), lanthanides, *etc.*[1] In this case coordination driven polymerization leads to formation of many network solids with highly ordered structure by very simple self-assembly reactions between the components. The resulting metal–organic polymers display a variety of framework architectures,[1,2] some of which have an evident practical impact considering their inherent properties, *e.g.* chirality[3] and porosity.[4]

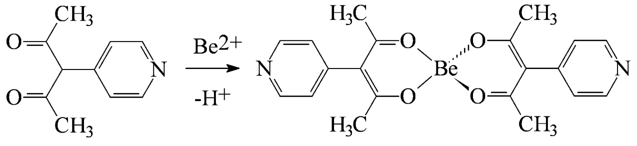
A novel synthetic scenario for generation of network solids with pre-programmed structure, extends this self-assembly methodology to step-by-step utilization of the ligand functionality ("metal complexes as ligands") and offers new significant potential for design of coordination compounds:[5]

$$L \xrightarrow{M^1} L{-}M^1{-}L \xrightarrow{M^2} \left(L{-}M^1{-}L{-}M^2\right)_n$$

Here is an evident possibility for construction of mixed-metal coordination polymers and multi-step complexation with different metal ions which could provide a high level of control over mutual disposition of coordination centres in space including designing of desired alternation of dia/paramagnetic centres. Control over the co-existence and distribution of different coordination geometries in the lattice is also important as a wide range of new network topologies may be anticipated for combination of net points of different connectivity under formation of mixed-metal polymers.[2,6] The multi-step approach presents a cost-effective alternative to the organic synthesis of desired molecular building blocks for modular construction of network polymers. It also offers an easy chemical access to families of molecular connectors of different geometry and functionality. An exceptional chemical paradigm for implementation of the multi-step strategy is a family of molecular complexones combining two of the most characteristic and typical ligand functions: the azine nitrogen atom and the β-diketonate group. Herein we report the 'engineering' of mixed-metal coordination polymers based upon 3-(4-pyridyl)-substituted acetylacetonate, that itself has a relatively unknown coordination chemistry.[7]

Results and discussion

The ligand was immobilized on a tetrahedral Be^{2+} matrix employing its β-diketonate function[8] and the resulting metallomolecule was used as an extended connector for generation of Co(Cu)/Be alternating superstructures by exploitation of the pyridyl donor sites.



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The beryllium based tecton exists as a neutral complex with the expected tetrahedral coordination[6b] around the metal atom and with non-coplanar orientation of two pyridyl groups (Fig. 1). In combination with transition metal ions the pyridyl moiety could serve as a monodentate or exo-bidentate ligand bridging a pair of metal atoms at a distance of *ca.* 18 Å. The two aromatic parts of the molecule are separated by a bulk beryllium diketonate "spacer", that precludes any close parallel alignment of the modules due to π-stacking interactions. This situation is typical of large polycyclic linkers bridging metal atoms and leads to a type of close packing in the crystal, rather than a generation of very open structures.[9] However, the packing patterns of BeL_2 based systems are also dominated by close parallel alignment. This is supported by a shape complementarity of the extended BeL_2 modules and a weak hydrogen bonding [CH ··· O] between the oxygen atom and the methyl hydrogen atoms of the beryllium diketonate fragment (for **1** CH ··· O 2.46 Å, C–H ··· O 169°, Fig. 1).[10] In all present systems Co(Cu) metal centres coordinate to only two pyridine

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† Electronic supplementary information (ESI) available: synthesis and crystallography. See http://www.rsc.org/suppdata/dt/b2/b212733d/

DOI: 10.1039/b212733d

Table 1 Selected bond distances (Å) and angles (°) for complexes **2**–**6**

Co{BeL$_2$}$_2$Cl$_2$·H$_2$O **2** (a: 1 − x, y, −0.5 − z)					
Co(1)–N(1)	2.037(2) (×2)	Be(1)–O	1.605(4)–1.621(4)	N(1)–Co(1)–N(1a)	110.81(12)
Co(1)–Cl(1)	2.2363(7) (×2)	O–Be(1)–O	106.1(2)–112.3(2)	Cl(1)–Co(1)–Cl(1a)	121.02(5)
Co{BeL$_2$}(CH$_3$OH)$_2$SO$_4$·H$_2$O·CH$_3$OH **3** (a: 1 + x, −1 + y, −1 + z)					
Co(1)–O(5)	2.070(3) (×2)	Co(1)–N(1)	2.198(3) (×2)	O(5)–Co(1)–N(1)	90.0(1)
Co(1)–O(9)	2.096(3) (×2)	Be(1)–O	1.598(8)–1.621(7)	O(5)–Co(1)–O(9)	88.4(1)
Cu$_2$Cl$_3${BeL$_2$}$_2$ **4** (a: 1 − x, y, 0.5 − z; b: 1.5 − x, 1.5 − y, −z; c: −0.5 + x, 1.5 − y, 0.5 + z)					
Cu(1)–N(1)	1.988(2) (×2)	Cu(2)–Cl(2)	2.2789(8)	N(1)–Cu(1)–Cl(1)	105.40(5)
Cu(1)–Cl(1)	2.4372(5) (×2)	Be(1)–O	1.603(3)–1.623(3)	Cl(1)–Cu(1)–Cl(1a)	95.33(2)
Cu(2)–N(2)	2.027(2) (×2)	O–Be(1)–O	105.5(2)–114.1(2)	N(2b)–Cu(2)–N(2c)	178.7(1)
Cu(2)–Cl(1)	2.4977(5) (×2)	N(1)–Cu(1)–N(1a)	120.1(1)	Cl(2)–Cu(2)–Cl(1)	133.84(1)
Cu$_2$Br$_3${BeL$_2$}$_2$ **5** (a: 2 − x, y, 1.5 − z; b: −0.5 + x, −0.5 − y, 0.5 + z; c: 2.5 − x, −0.5 − y, 1 − z)					
Cu(1)–N(1)	1.987(3) (×2)	Cu(2)–Br(2)	2.4249(8)	N(1)–Cu(1)–Br(1)	104.87(8)
Cu(1)–Br(1)	2.5598(5) (×2)	Be(1)–O	1.582(5)–1.631(5)	Br(1a)–Cu(1)–Br(1)	98.57(3)
Cu(2)–N(2)	2.034(3) (×2)	O–Be(1)–O	105.1(2)–115.0(3)	N(2b)–Cu(2)–N(2c)	178.0(2)
Cu(2)–Br(1)	2.6660(5) (×2)	N(1)–Cu(1)–N(1a)	121.4(2)	Br(2)–Cu(2)–Br(1)	133.30(1)
Cu$_2$Br$_2${BeL$_2$}$_2$·5.33CHCl$_3$ **6** (a: −x, 1 − y, 2 − z; b: 1 − x, −0.5 + y, 0.5 − z; c: −x, −y, 2 − z)					
Cu(1)–N	2.018(4), 2.042(4)	Cu(3)–Br	2.5195(8), 2.5393(8)	N(6b)–Cu(3)–N(2c)	120.7(2)
Cu(1)–Br	2.4413(8), 2.5312(8)	Be–O	1.598(9)–1.619(9)	Br(1)–Cu(1)–Br(1a)	111.14(3)
Cu(2)–N	2.009(4), 2.010(4)	O–Be–O	105.9(4)–114.1(5)	Br(2)–Cu(2)–Br(3)	114.73(3)
Cu(2)–Br	2.5093(8), 2.5293(8)	N(1)–Cu(1)–N(3)	111.7(2)	Br(3)–Cu(3)–Br(2)	114.02(3)
Cu(3)–N	2.017(4), 2.019(4)	N(4)–Cu(2)–N(5)	127.3(2)		

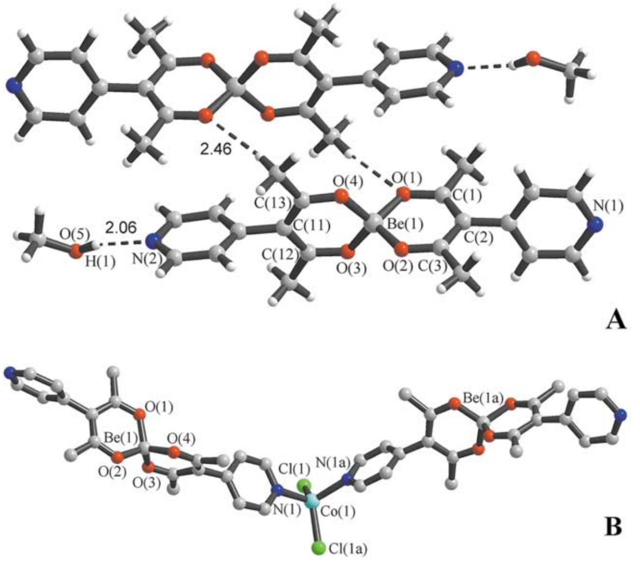

Fig. 1 Molecular structure of the [BeL$_2$·CH$_3$OH] complex (A) showing characteristic parallel alignment of the shape complementary molecules with weak hydrogen bonding C–H ··· O and the [Co{BeL$_2$}$_2$Cl$_2$·H$_2$O] complex (B) (hydrogen atoms are omitted for clarity).

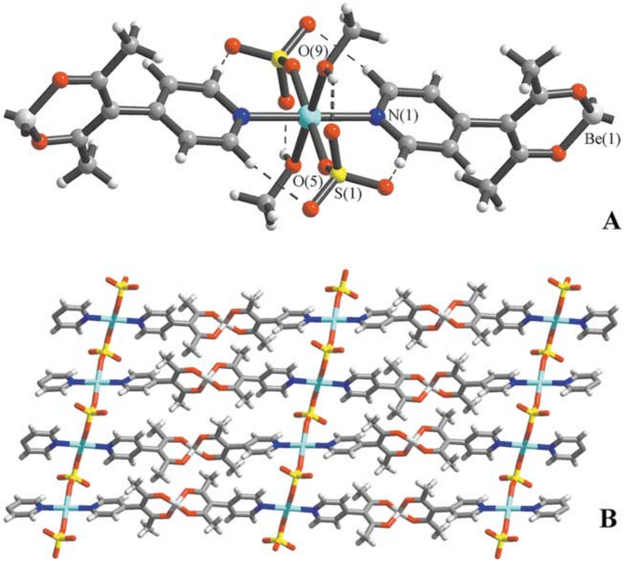

Fig. 2 (A) Octahedral coordination environment of cobalt in the structure of [Co{BeL$_2$}(CH$_3$OH)$_2$SO$_4$]·H$_2$O·CH$_3$OH **3** showing intramolecular hydrogen bonding. (B) Fragment of the 2D polymeric structure of the complex with bridging BeL$_2$ and sulfate groups.

groups and this may reflect the tendency to form coordination arrays of lower dimensionality and to prevent the formation of very open structures, that might have been anticipated in case of three- or four-fold connectivities.

Selected bond distances (Å) and angles (°) for complexes **2**–**6** are provided in Table 1.

Co{BeL$_2$}$_2$Cl$_2$·H$_2$O **2** illustrates monodentate coordination of the metalloligand and it exists as a molecular complex. Characteristic tetrahedral four-coordination around the cobalt atom comprises two nitrogen atoms provided by the metalloligands and uses only half of their functionality (Fig. 1(B)). The two-dimensional (2D) structure of the Co/Be coordination polymer was generated using a combination of bridging functions of the inorganic anion and the beryllium metalloligand. In the cobalt sulfate complex [Co{BeL$_2$}(CH$_3$OH)$_2$SO$_4$·H$_2$O·CH$_3$OH] **3**, the latter acts as a connector between two cobalt atoms separated by 18.41 Å with the generation of a mixed-metal metal–organic chain (Fig. 2). The coordination environment of the cobalt atom is completed with two *trans*-situated oxygen atoms of the bridging sulfate anions (Co ··· Co 5.39 Å) and two molecules of methanol. The relatively small size of the sulfate connector effects the dense packing of the [Co{BeL$_2$}]$_n$ chains with a parallel alignment of the BeL$_2$ ligands, that are shape complementary and interact through a set of weak hydrogen bonds between carbonyl oxygen and methyl hydrogen atoms of adjacent BeL$_2$ species: [CH ··· O 2.26 Å, C–H ··· O 162°].

An open 2D architecture may be expected for even a 1 : 1 metal–ligand ratio under "augmentation"[2] of the inorganic coordination centre. Attractive and realistic species in this context are copper(I) halogenides, the structural chemistry of which towards nitrogen donor ligands is essentially dominated by formation of molecular 'squares' of (Cu$_2$X$_2$) units[11] that are capable of coordinating four additional ligands. We have isolated both the copper(I) and mixed-valence copper(I,II) coordination polymers. Isomorphous complexes $Cu_2X_3(BeL_2)_2$ (X = Cl **4**, Br **5**) are the mixed-valence species with copper–halogenide linkages closely related to molecular 'diamonds'. The metal–halogen quadrangle involves both Cu(I) and Cu(II) atoms, the latter coordinating an additional halogen atom and thus the valence state of the two copper centres is easily distinguishable (Fig. 3(B)). This pattern is extremely rare and has only one structural precedent, $[Cu_2Cl_3(thiazole)_4]$.[12] The angles between vectors of the four Cu–N bonds correspond to "K-shape block" and at first glance they do not allow undesired parallel alignment of BeL_2 modules in the crystal. However, the compounds also adopt one-dimensional structures and exist as a double chain (Fig. 4) with the same set of H-bonding between neighbouring BeL_2 molecules as for the complex **3**: CH ··· O 2.57 Å, C–H ··· O 157°. Such an interlinking mode is feasible due to some conformational flexibility of the beryllium metalloligands themselves, which in the present case act as slightly angular connectors, with angles Cu(I)–Be–Cu(II) along the double chain at 153.7°.

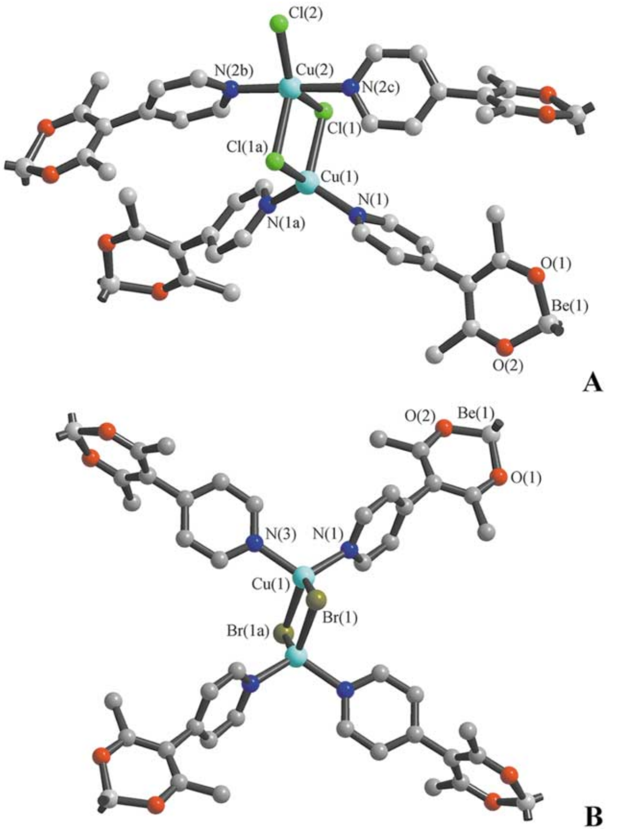

Fig. 3 View of Cu_2Cl_3 (A) and Cu_2Br_2 (B) molecular 'squares' coordinating four beryllium metalloligands BeL_2 in structures **4** and **6**.

Nevertheless, an open 2D structure was observed for the copper(I) compound involving the "square-like" (Cu_2Br_2) pattern. Within the coordination environment of the two copper(I) atoms can be seen two tetrahedra sharing the Br–Br edge and four additional Cu–N bonds aligned almost orthogonally. Thus in $[Cu_2Br_2\{BeL_2\}_2\cdot 5.33CHCl_3]$ **6**, the Cu_2Br_2 unit serves as a four-connected point for the 2D regular square-grid network in which beryllium metalloligands bridge pairs of copper atoms at distances of 18.1–18.5 Å, and the successive layers are separated by only 4.1 Å. The structure is very open, as each mesh of the network possesses inner cavities of *ca.* 12 × 12 Å size (the network solely occupies only 5468 Å^3 per unit cell or 54.1% of the crystal volume)[13] and enclathrates a set of guest molecules (Fig. 4). Unfortunately, removal of the accumulated chloroform molecules leads to disintegration of the network and a loss of crystallinity.

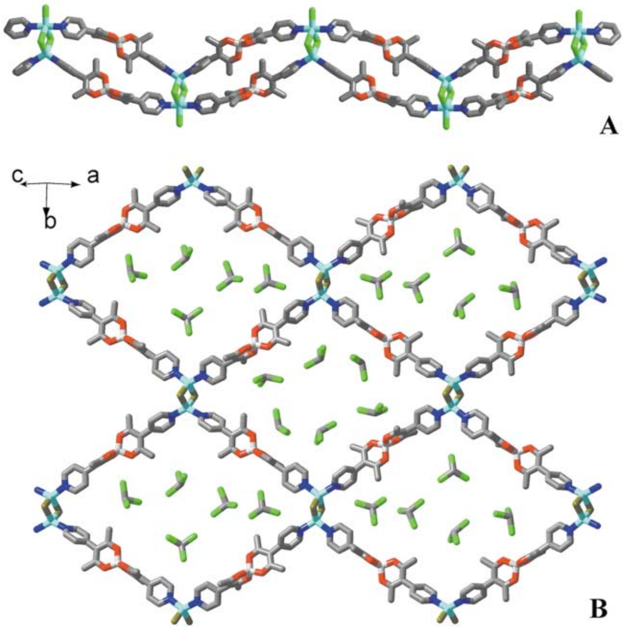

Fig. 4 View of the 1D double chain structure of the mixed-metal mixed-valence complex $[Cu_2Cl_3\{BeL_2\}_2]$ **4** (A) and the 2D square grid network in the complex $[Cu_2Br_2\{BeL_2\}_2\cdot 5.33CHCl_3]$ **6** (B). Note that the network is composed of two types of meshes, centrosymmetric (shown in the centre) and acentric, which incorporate different numbers of guest molecules.

Conclusion

Our results demonstrate a versatile and flexible approach for construction of mixed-metal complexes employing β-diketonate/pyridyl donor molecules. It can be also extended to other types of heteroaryl functionalized β-diketonates, many of which are readily available.[8] These species could provide an easy one-stage access to families of polypyridyl donor connectors that can be anticipated for the β-diketonate/pyridyl ligands complexed with tetra-, hexa- and octa-coordinate metal centres (*e.g.* Be^{2+}, Ga^{3+}, Fe^{3+}, Zr^{4+}, lanthanides). We are currently studying the utility of the approach for the rational design of mixed-metal coordination polymers involving d-, p- and f-block metal ions.

The reported system is important also concerning renewing interest[14] in the relatively poorly investigated chemistry of the extremely toxic beryllium, particularly in combination with 3d-block metal ions that can occur in many light-weight metal alloys widely used in industries.[15]

Experimental

The beryllium complex was prepared reacting 3-(4-pyridyl)-2,4-pentanedione (pyridylacetylacetone),[16] beryllium sulfate and pyridine in aqueous solution. To a well-stirred slurry of 6.72 g (37.9 mmol) of pyridylacetylacetone in 20 ml water and 8.0 ml pyridine 3.03 g (17.1 mmol) $BeSO_4\cdot 4H_2O$ in 15 ml water was added dropwise. The mixture was stirred for 30 min after which colorless deposit of the complex was filtered. Recrystallization from aqueous methanol afforded 2.5 g of pure BeL_2 **1** (40%) as thin lamellar platelets: $C_{20}H_{20}BeN_2O_4$, monoclinic, *C*2/*c*, $a = 18.597(4)$, $b = 11.487(2)$, $c = 20.168(4)$ Å, $\beta = 98.09(3)°$; crystal structure refinement gave relatively poor convergence ($R1 = 0.107$) and thus the structure of the non-coordinated metalloligand was redetermined using the methanol solvate $BeL_2\cdot CH_3OH$ obtained from dry methanol.

Cobalt complexes were synthesized reacting components in methanolic solution: $Co\{BeL_2\}_2Cl_2\cdot H_2O$ **2**, dark-blue; $Co\{BeL_2\}(CH_3OH)_2SO_4\cdot H_2O\cdot CH_3OH$ **3**, pink. Reactions of **1** with $CuCl_2$ and $CuBr_2$ using a layering technique gave Cu(I) or mixed-valence Cu(I)/Cu(II) species. In a typical synthesis, a

Table 2 Crystal data for $BeL_2 \cdot CH_3OH$ **1**, $Co\{BeL_2\}_2Cl_2 \cdot H_2O$ **2**, $Co\{BeL_2\}(CH_3OH)_2SO_4 \cdot H_2O \cdot CH_3OH$ **3**, $Cu_2Cl_3\{BeL_2\}_2$ **4**, $Cu_2Br_3\{BeL_2\}_2$ **5** and $Cu_2Br_2\{BeL_2\}_2 \cdot 5.33CHCl_3$ **6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{20}H_{20}BeN_2O_4 \cdot CH_4O$	$C_{40}H_{40}Be_2Cl_2CoN_4O_8 \cdot H_2O$	$C_{22}H_{28}BeCoN_2O_{10}S \cdot CH_4O \cdot H_2O$	$C_{40}H_{40}Be_2Cl_3Cu_2N_4O_8$	$C_{40}H_{40}Be_2Br_3Cu_2N_4O_8$	$C_{40}H_{40}Be_2Br_2Cu_2N_4O_8 \cdot 5.33CHCl_3$
M	393.43	870.63	630.52	956.21	1089.59	1646.31
T/K	153	200	223	153	223	153
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/c$
a/Å	9.6272(3)	27.473(2)	9.549(1)	26.9766(8)	27.199(3)	21.0193(9)
b/Å	10.6028(3)	11.2165(5)	10.780(1)	10.9883(3)	11.075(1)	25.180(1)
c/Å	11.3100(5)	13.786(1)	15.713(1)	14.3431(4)	14.516(2)	21.7707(9)
α/°	94.020(2)		82.427(4)			
β/°	114.827(1)	103.000(8)	86.698(5)	104.073(1)	102.649(2)	118.618(1)
γ/°	102.168(1)		71.158(5)			
U/Å^3	1007.73(6)	4139.3(4)	1517.2(3)	4124.1(2)	4266.7(8)	10114.7(7)
Z	2	4	2	4	4	6
μ(Mo-Kα)/cm^{-1}	0.92	6.02	6.93	12.83	38.62	24.98
$2\theta_{max}$/°	61.0	56.0	53.0	61.0	56.0	61.0
Meas./Unique reflns.	12286/6048	12187/4881	8474/5018	15058/6254	13615/5126	93413/30833
R_{int}	0.018	0.041	0.019	0.064	0.025	0.067
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.052, 0.153	0.046, 0.111	0.065, 0.145	0.042, 0.118	0.038, 0.091	0.076, 0.210

solution of 0.034 g (0.20 mmol) of $CuCl_2 \cdot 2H_2O$ in 5 ml methanol was layered over a solution of 0.080 g (0.22 mmol) of **1** in 5 ml methanol and 5 ml chloroform. Slow interdiffusion of the layers afforded crystallization of the yellow–brown mixed-valence complex $Cu_2Cl_3\{BeL_2\}_2$ **4** (yield: 0.038 g, 40%). Under the same conditions copper(II) bromide produces the univalent complex $Cu_2Br_2\{BeL_2\}_2 \cdot 5.33CHCl_3$ **6**, brown blocks (30%), in a mixture with non-crystalline unidentified products, while the reaction in ethanol–chloroform solution afforded the bromide analog of complex **4**, $Cu_2Br_3\{BeL_2\}_2$ **5**, as brown prisms.

Crystallographic measurements were made using a Siemens SMART CCD area-detector diffractometer (empirical absorption corrections using SADABS) and Stoe IPDS diffractometer for **2** (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-86 and SHELXL-93[17] (Table 2). All hydrogen atoms were placed in calculated positions with their isotropic U values set to be 1.2 times greater then U_{eq} of the corresponding carbon atom. In structure **6** part of the guest chloroform moieties are disordered. In the structure **3** the guest methanol molecule is disordered over three overlapping sites and the corresponding atoms were left isotropic; also one of the acetyl groups within the BeL_2 core is disordered over two closely situated positions and was refined with partial contributions at 0.5. Graphical visualisation of the structures was made using program Diamond.[18]

CCDC reference numbers 200510–200515.

See http://www.rsc.org/suppdata/dt/b2/b212733d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

The work was in part supported by grant from the Deutsche Forschungsgemeinschaft (J. S. and K. V. D.), Royal Society Fellowship (A. N. Ch.) and INTAS Fellowship grant (K. V. D.) YSF 2002–310. J. A. K. H. acknowledges the EPSRC for a Senior Research Fellowship.

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