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Extended coordination frameworks incorporating heterobimetallic squares†

Volodimir D. Vreshch,[a] Andrey B. Lysenko,[a] Alexander N. Chernega,[b] Judith A. K. Howard,[c] Harald Krautscheid,[d] Joachim Sieler[d] and Konstantin V. Domasevitch*[a]

[a] *Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev 01033, Ukraine. E-mail: dk@anorgchemie.univ.kiev.ua*
[b] *Institute of Organic Chemistry, Murmanskaya Str.4, Kiev 253660, Ukraine*
[c] *Dept. of Chemistry, University of Durham, Durham, UK DH1 3LE*
[d] *Institut für Anorganische Chemie, Universität Leipzig, Linnéstraße 3, D-04103 Leipzig, Deutschland*

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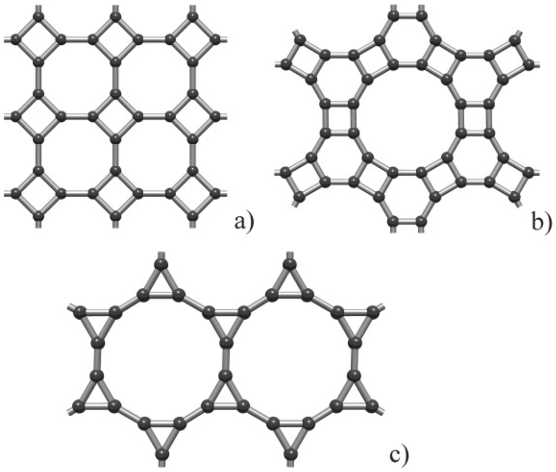
The molecular structure of aluminium and iron(III) complexes with 3-phenyl and 3-(4-pyridyl) (HL) substituted acetylacetonate ligands is appreciably distorted. For AlL_3 and FeL_3 this shows that the orientation of the side pyridyl-N donor atoms lone pairs is about 90 and 135° which favours the assembly of heterobimetallic square patterns in $Al(Fe)L_3$ complexes with metal ions. This was employed for the modular construction of semi-regular heterobimetallic networks, in which the pyridyldiketonate ligands bridge pairs of Fe(Al)/Cd(Co) metal ions and support the structure of 1D and 2D coordination polymers. The unprecedented 2D structure of $[Cd\{AlL_3\}(CH_3OH)\{NO_3\}_2]\cdot 2CHCl_3$ and $Cd\{AlL_3\}(CH_3OH)Br_2]\cdot 2CHCl_3\cdot 2CH_3OH$ is based upon plane tiling by a set of heterobimetallic squares and octagons, while $[Cd\{FeL_3\}_2(NO_3)_2]\cdot 2H_2O$ and $[Co\{AlL_3\}_2Cl_2]\cdot 4CHCl_3\cdot 2CH_3OH$ are 1D polymers and exist as chains of heterobimetallic squares sharing opposite vertices.

Introduction

Properties of network solids[1] originate in their structure and thus they can be designed in a rational manner using a crystal engineering approach.[1,2] Many important and attractive synthetic targets for the coordination frameworks are illustrated by 2D semi-regular topologies that are sustained with sets of closely packed (molecular triangles, squares) and very open (*cf.* molecular hexagons, octagons) regions within the network.[3] This feature could be especially suited for the construction of zeolite-like structures[4,5] that possess relatively low overall porosity while maintaining the large cages for guest molecules.[6] However, these clear prototypes still remain unexplored in the chemistry of coordination polymers[7] and it is difficult to anticipate such connectivity in metal–organic systems. For example, each of the semi-regular three-connected nets (Scheme 1) has angles at the net vertices that cannot be sustained with a typical coordination around metal ions.

A promising tool for tuning the coordination architecture may be found by incorporating into the network more than a single type of coordination geometry, if one can achieve a highly controllable assembly of heterometallic polymers with the desired distribution of different metal centers in the lattice and particularly employing secondary building blocks ('metal complexes as secondary ligands')[8] whose conformation inherently matches the metrics of the semi-regular nets. Thus, tridentate ligands supporting very uncommon binding directions, $\varphi = 90°$ and $2 \times 135°$, could favor the assembly of the square/octagonal net (Scheme 1(a)). We report an approach for modular engineering of such unprecedented semi-regular nets incorporating mixed-metal square motifs. This was feasible with two-step utilization of the ligand functionality and pre-construction of a suitable building block as an initial step.[9]



Scheme 1 Three-connected semi-regular nets. Angles at the net vertices are uncommon for coordination polymers: 90 and 2 × 135° (a); 90, 120 and 150° (b); 60 and 2 × 150° (c).

Results and discussion

The desired irregular configuration of the tecton binding sites was readily accessible for functionally substituted metal tris-diketonates and considering metal 3-phenylpentane-2,4-dionates $Al(PhAcac)_3\cdot 2PhH$ **1** and $Fe(PhAcac)_3$ **2** as a suitable molecular model. Though the compounds exist as neutral complexes with expected octahedral six-fold coordination of the metal ion, the molecular structure at first glance is unusual. Two of three chelate metallocycles are non-planar, with an appreciable bend along the O···O line, and this facilitates the closer disposition of two coordinated ligands (Scheme 2, Fig. 1). Such a tight packing of two ligands within the coordination sphere allows the molecule to adopt a more compact configuration and it minimizes the moiety volume, *i.e.* leads to a "collapse" of the molecular structure. This was observed also for molecular metal complexes with a 3-(4-pyridyl) substituted acetylacetonate ligand that possesses a very similar shape and steric volume, $AlL_3\cdot 3H_2O$ **3** and FeL_3 **4**. The maximal deviation of the metal ion from the mean plane of the chelate fragment, 0.81 Å, was observed for **4**. The "collapsed structure" may be regarded as an inherent feature of metal tris-diketonates bearing large aromatic substituents in 3-position of the ligand and it is unlikely to be predetermined purely by packing effects since

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† Electronic supplementary information (ESI) available: Details for preparations, crystal structure determination and refinement. See http://www.rsc.org/suppdata/

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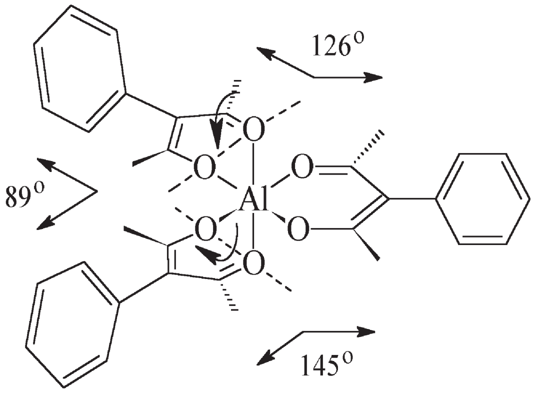


Scheme 2 Distortion of the molecular tris-diketonate structure.

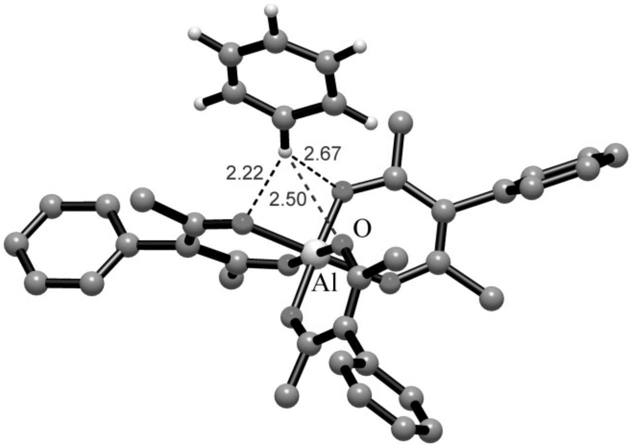


Fig. 1 The distorted structure of the aluminium complex **1** showing immobilization of the guest benzene molecule by trifurcated CH···O hydrogen bonding.[10] Bond lengths Al–O are in the range 1.858–1.882(2) Å.

either unsolvated complexes **2**, **4** or water and benzene solvates **3**, **1** manifest an equally appreciable distortion of the molecules.

As a result of the "molecular collapse", the angles between the vectors of nitrogen atoms lone pairs for 4-pyridyl functionalized species **3** (φ = 88.6, 134.5, 136.9°) and **4** (φ = 71.7, 135.3, 152.9°) are far from evident values of 3 × 120° (Fig. 2). There are no suitable structural prototypes for direct comparison, while 64 of 67 neutral metal tris-diketonate moieties observed as yet in crystal structures[11] had a simple regular geometry (120 ± 10°). The only exceptions are somewhat more distorted iron(III) and manganese(III) dipivaloylmethanides[12] and a bismuth(III) compound, in which a lone pair of the metal ion is stereoactive.[13]

Mixed-metal coordination frameworks

The above features of the molecular structure are a key pre-requisite for the rational application of the 'triangular' building blocks ML_3, for the design of semi-regular coordination polymers, using coordination of the side pyridyl-N donors to additional octahedral metal ions. Supramolecular structures of the resulting heterobimetallic compounds thus could be pre-programmed at the molecular level since facile orthogonal orientation (φ = 90°) of the peripheral pyridyl groups within the ML_3 tecton frame predetermines the formation of the densest mixed-metal squares, instead of regular open hexagons, with φ = 120° (Fig. 2). A target 2D semi-regular topology originates in combination of the 'collapsed triangles' ML_3 with T-shape $[M'N_3]$ metal ion coordination, while square planar $[M'N_4]$ centres can not afford a 2D net and a simpler 1D chain may by anticipated as a structure motif (Scheme 3). We therefore explored the binding of ML_3 to octahedral metal ions, which typically adopt either T-shape $[M'N_3]$ or planar $[M'N_4]$ coordination geometries with the pyridyl N-donor ligands.[14,15] That the molecular metal complexes of this type retain donor properties of the pyridyl functions and can be exploited as efficient bridging metalloligands were proved by examination of the simpler ML_2 (M = Be, Cu) systems.[16]

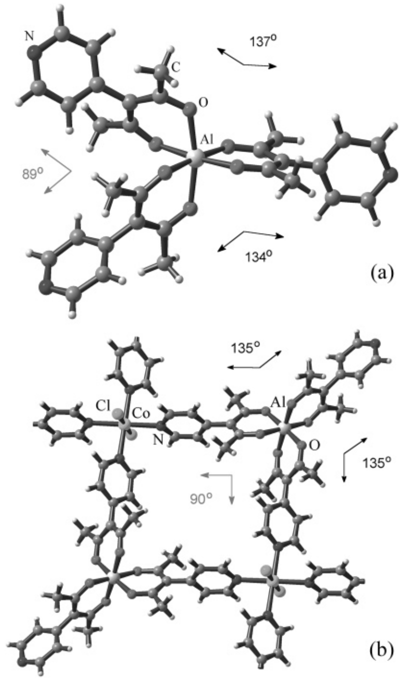
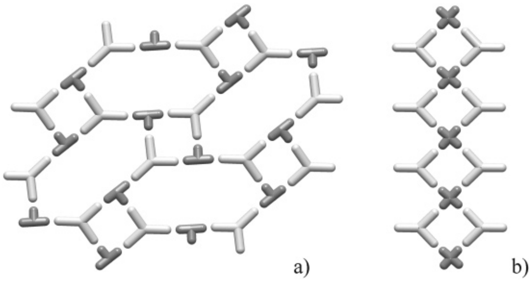


Fig. 2 Inherent conformation of the tris-complexes ML_3 (M = Al **2**) (a) facilitates assembly of heterobimetallic squares with d-metal ions coordinating side nitrogen atoms of the ML_3 tecton, for example the Co_2Al_2 square pattern seen in structure **6** (b).



Scheme 3 Network topologies originating in combination of the 'collapsed triangles' ML_3 and T-shape $[M'N_3]$ (a) and square $[M'N_4]$ (b) coordination of octahedral metal ions.

Heterobimetallic squares are a basic motif for the coordination networks based upon ML_3 building blocks. The structure of $[Cd\{FeL_3\}_2(NO_3)_2]\cdot 2H_2O$ **5** with alternating Cd and Fe centres exemplifies a 1D array of heterobimetallic squares sharing opposite vertices (Fig. 3). FeL_3 units serve as angular bidentate connectors (φ = 87.6°) and the organic ligands bridge pairs of Fe and Cd atoms at 10.0 Å. The typical six-fold coordination of the cadmium atoms includes pyridyl nitrogen atoms (Cd–N 2.33, 2.37 Å) of four FeL_3 molecules and two *trans*-situated nitrate groups (Table 1). The non-coordinated pyridine groups form hydrogen bonds with water of crystallization, that preclude interdigitation of the coordination bands $[Cd\{FeL_3\}_2(NO_3)_2]_n$ in a fashion found for the 1D 'railroad motifs' formed by 4,4′-bipyridine.[17] Actually the same structure was observed for Co/Al complex $[Co\{AlL_3\}_2Cl_2]\cdot 4CHCl_3\cdot 2CH_3OH$ **6**. Chloride ions, which are *trans*-coordinated to cobalt(II) centres (Co–Cl 2.44 Å, Fig. 2(b)), have a smaller size than the nitrate groups in **5**, and in the present case, the liberated crystal volume is occupied by guest chloroform molecules, four per cobalt atom.

Coordination of the remaining third binding site of the ML_3 module could increase the dimensionality of the structure and allow the generation of extended arrays, while preserving the basic heterobimetallic squares, unlike those for simpler bifunctional self-assembly ligands.[18] The configuration of the binding sites that are situated at the angles 90° and 2 × 135°, is especially suitable for generation of semi-regular three-connected topologies supporting metal–organic squares and octagons (Scheme 3). This new possibility has been demonstrated by the 2D network formed in

Table 1 Selected bond distances (Å) and angles (°) for complexes **5–8**

$[Cd\{FeL_3\}_2(NO_3)_2]\cdot 2H_2O$ **5**			
Cd(1)–N(3)	2.333(3) × 2	Fe(1)–O	1.978(3)–2.019(3)
Cd(1)–N(1)	2.373(3) × 2	N(3)–Cd(1)–N(1)	93.20(13)
Cd(1)–O(7)	2.396(7) × 2	N(3)–Cd(1)–O(7)	89.40(19)
		N(1)–Cd(1)–O(7)	101.2(2)
$[Co\{AlL_3\}_2Cl_2]\cdot 4CHCl_3\cdot 2CH_3OH$ **6**			
Co(1)–N(1)	2.232(4) × 2	Al(1)–O	1.859(4)–1.896(5)
Co(1)–N(2)	2.203(7) × 2	N(2)–Co(1)–N(1)	86.4(2)
Co(1)–Cl(1)	2.445(1) × 2	N(1)–Co(1)–Cl(1)	91.1(1)
		N(2)–Co(1)–Cl(1)	90.0(1)
$[Cd\{AlL_3\}(CH_3OH)\{NO_3\}_2]\cdot 2CHCl_3$ **7**			
Cd(1)–N(1)	2.390(4)	Al(1)–O	1.861(3)–1.886(3)
Cd(1)–N(2)	2.361(4)		
Cd(1)–N(3)	2.374(4)	N(3)–Cd(1)–N(1)	88.5(1)
Cd(1)–O(8)	2.453(6)	N(2)–Cd(1)–N(3)	90.1(1)
Cd(1)–O(10)	2.415(8)	N(2)–Cd(1)–N(1)	164.3(1)
Cd(1)–O(13)	2.348(4)	N(3)–Cd(1)–O(8)	89.08(19)
$[Cd\{AlL_3\}(CH_3OH)Br_2]\cdot 2CHCl_3\cdot 2CH_3OH$ **8**			
Cd(1)–N(1)	2.386(7)	Al(1)–O	1.854(6)–1.883(6)
Cd(1)–N(2)	2.374(8)		
Cd(1)–N(3)	2.376(7)	N(2)–Cd(1)–N(3)	91.7(3)
Cd(1)–O(7)	2.389(7)	N(2)–Cd(1)–N(1)	87.7(2)
Cd(1)–Br(1)	2.706(1)	N(3)–Cd(1)–N(1)	174.2(3)
Cd(1)–Br(2)	2.689(1)	Br(2)–Cd(1)–Br(1)	172.09(4)

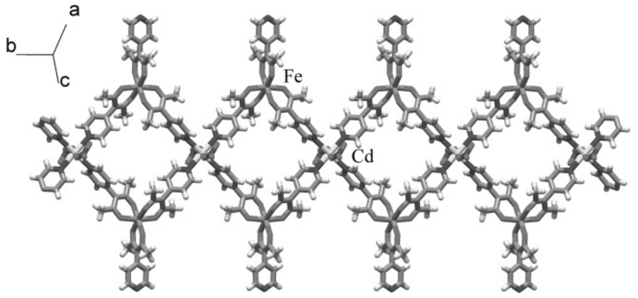


Fig. 3 One-dimensional motif incorporating Cd/Fe heterobimetallic squares in structure **5**.

the Cd/Al complexes $[Cd\{AlL_3\}(CH_3OH)\{NO_3\}_2]\cdot 2CHCl_3$ **7** and $[Cd\{AlL_3\}(CH_3OH)Br_2]\cdot 2CHCl_3\cdot 2CH_3OH$ **8** (Fig. 4), where all available side functionality of the metalloligand is employed for binding with cadmium atoms and results in the generation of the polymer (**7**: $\varphi = 95.2, 126.1, 138.6°$). In **7** the cadmium atoms adopt a distorted hepta coordination including three pyridyl nitrogen atoms ("T-shape") and oxygen atoms of monodentate and asymmetric-bidentate nitrate groups and a methanol molecule, while for **8** the six-fold coordination of the cadmium atoms is retained with two *trans*-situated bromine atoms and also with three equatorial pyridyl N-donors and a methanol molecule (Fig. 4(a)). Thus both the aluminium and cadmium atoms provide three-connected vertices for the polymeric structure.[19]

The resulting coordination network is very open and for **7** it occupies 3117.9 Å^3 per unit cell or only 59.8% of the crystal volume (62.0% for network in **8**).[20] It is even more interesting that, unlike the more usual three-connected 4,4′-bipyridine polymers,[1,7,15] the network consists of two kinds of regions in equal proportions—dense molecular squares and very open octagons, and only the octagons provide large enough voids, *ca.* 21 × 7 Å, for hosting the guest molecules (Fig. 4(b)). This topology is unprecedented for metal–organic polymers and it may be related to the tellurium sublattice in the Cs_3Te_{22} structure.[21]

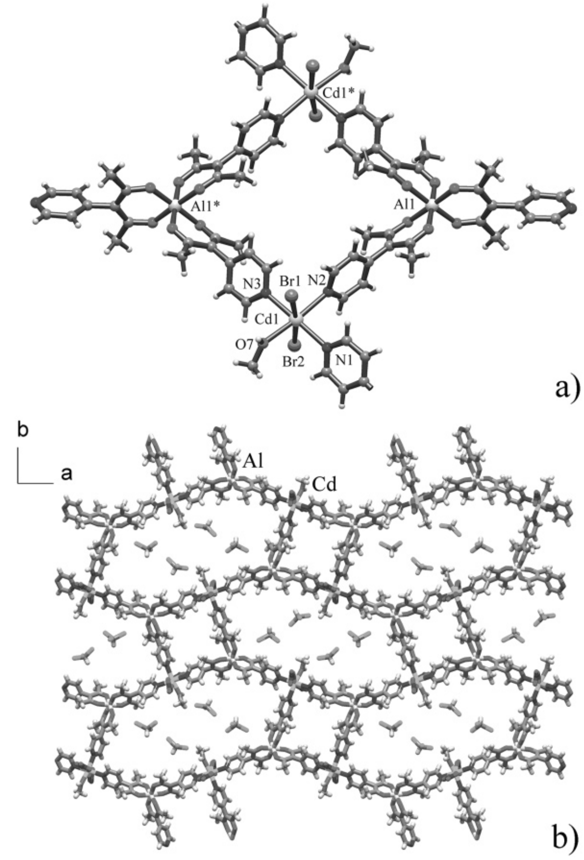


Fig. 4 Cd/Al heterobimetallic squares sustained with T-shape $[CdN_3]$ coordination of cadmium atoms in structure **8** (a) and resulting 2D coordination pattern in the form of a semi-regular net (b). Each large octagonal Cd_4Al_4 void is populated with four chloroform molecules.

Conclusion

Our study suggests wider possibilities for the construction of a number of semi-regular networks incorporating dense molecular squares and larger polygons that were categorized by Wells,[3] but currently are relatively unknown. Either 1D or 2D networks designed using 'triangular building blocks' ML_3 have an imprint of the inherent symmetry and the configuration of the ML_3 molecules and these topologies are clearly predictable on the basis of molecular structure. The results demonstrate a potential of the multi-step approach towards heterometallic coordination polymers that could be anticipated for ambifunctional ligands bridging pairs of suitable tetra-, hexa- and octa-coordinate p-and d-metal ions (*cf.* Al^{3+}, Ga^{3+}, Fe^{3+}, Zr^{4+}, lanthanides). Pre-assembly of the secondary tectons using coordination interactions illustrates also cost- and time-effective alternatives to common organic preparations of desired tectons and will simplify many other tasks of supramolecular synthesis.

Table 2 Crystal data for $Al(PhAcac)_3 \cdot 2PhH$ **1**, $Fe(PhAcac)_3$ **2**, $AlL_3 \cdot 3H_2O$ **3**, FeL_3 **4**, $[Cd\{FeL_3\}_2(NO_3)_2] \cdot 2H_2O$ **5**, $[Co\{AlL_3\}_2Cl_2] \cdot 4CHCl_3 \cdot 2MeOH$ **6**, $[Cd\{AlL_3\}(MeOH)\{NO_3\}_2] \cdot 2CHCl_3$ **7** and $[Cd\{AlL_3\}(MeOH)Br_2] \cdot 2CHCl_3 \cdot 2MeOH$ **8**

	1	2	3	4	5	6	7	8
Formula	$C_{45}H_{45}AlO_6$	$C_{33}H_{33}FeO_6$	$C_{30}H_{36}AlN_3O_9$	$C_{30}H_{30}FeN_3O_6$	$C_{60}H_{64}CdFe_2N_8O_{20}$	$C_{66}H_{72}Al_2Cl_{14}CoN_6O_{14}$	$C_{33}H_{36}AlCdCl_6N_5O_{13}$	$C_{35}H_{44}AlBr_2CdCl_6N_3O_9$
M	708.83	581.47	609.60	584.42	1441.29	1782.49	1062.75	1162.63
T/K	293	120	223	293	293	293	293	173
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group, Z	$P\bar{1}$, 2	$P2_1/c$, 4	$P\bar{1}$, 2	$P2_1/n$, 4	$P\bar{1}$, 1	$P\bar{1}$, 1	$P2_1/n$, 4	$P2_1/n$, 4
a/Å	12.150(2)	11.8040(5)	10.682(1)	11.2540(7)	12.479(1)	12.026(2)	11.8236(9)	11.7982(6)
b/Å	13.128(2)	21.333(1)	11.481(1)	20.724(1)	13.492(1)	13.712(2)	25.833(2)	25.504(1)
c/Å	14.446(2)	12.8103(6)	13.563(1)	12.8035(7)	14.086(1)	14.192(3)	17.228(2)	16.0778(9)
α/°	90.46(1)		76.403(2)		92.760(5)	96.589(8)		
β/°	104.85(1)	112.940(2)	84.815(2)	106.987(6)	107.627(5)	103.894(5)	97.84(1)	97.889(3)
γ/°	115.09(1)		81.933(2)		105.936(4)	108.249(5)		
U/Å^3	1999.1(6)	2970.7(2)	1597.9(2)	2855.9(3)	2150.9(4)	2111.3(6)	5212.8(8)	4792.0(4)
μ(Mo-Kα)/cm^{-1}	8.12[a]	5.50	1.19	5.75	6.37	7.26	7.98	25.26
D_c/g cm^{-3}	1.178	1.300	1.267	1.359	1.113	1.402	1.354	1.612
θ_{max}/°	57.23	28.82	29.17	26.73	25.51	26.03	25.68	25.68
Data/parameters	4003/469[b]	3035/361[b]	7660/397	5840/361	7314/439	7655/461	9211/509	8635/515
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.056, 0.063[b]	0.052, 0.053[b]	0.053, 0.139	0.033, 0.077	0.051, 0.115	0.076, 0.183	0.053, 0.112	0.080, 0.168
Max., min. peak/e Å^{-3}	0.30, −0.31	−0.59, 0.55	0.72, −0.23	0.26, −0.21	0.30, −0.23	0.45, −0.71	0.41, −0.40	1.59, −1.68

[a] Cu-Kα radiation. [b] R_w is based upon F for observed reflections with $I > 3\sigma(I)$.

Experimental

3-Phenylpentane-2,4-dione[22] and 3-(4-pyridyl)pentane-2,4-dione (HL)[23] were prepared according to the literature methods.

For preparation of the complex **1**, solid $NaHCO_3$ (0.56 g, 6.67 mmol) was added, in several portions during 20 min period, to a well-stirred solution of 1.2 g (6.77 mmol) 3-phenylpentane-2,4-dione in 15 ml MeOH and 5 ml H_2O. Then the mixture was combined with a solution of 0.68 g (1.8 mmol) $Al(NO_3)_3 \cdot 9H_2O$ in 6 ml H_2O and the colorless precipitate was recrystallized from benzene to give 0.82 g (64% yield) of pure $Al(PhAcac)_3 \cdot 2PhH$ **1**. The solvate loses the incorporated solvent in air within hours. The complex **3** was prepared similarly and was recrystallized from aqueous methanol to give $AlL_3 \cdot 3H_2O$ (60%). The iron(III) diketonates were synthesized in a similar fashion, reacting the components in a water–methanol mixture. Brown precipitates were dissolved in dry methanol and slowly evaporated to *ca.* 2 ml volume, yielding pure complexes **2** (88%) and **4** (39%). The compounds **1**–**4** are soluble in methanol and chloroform.

For preparation of $[Cd\{FeL_3\}_2(NO_3)_2] \cdot 2H_2O$ **5**, 10 mg (0.032 mmol) $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in 5 ml MeOH and mixed with a solution of 20 mg (0.035 mmol) FeL_3 in 4 ml MeOH. The resulting orange mixture was filtered and left overnight giving 15 mg of brown platelets **5** in a 60% yield. It was not possible to obtain the Al analog in the same fashion, using the AlL_3 tecton.

Crystals of the compounds **6**–**8** were obtained using a layering technique. In a typical synthesis, a solution of 40 mg (0.08 mmol) $CoCl_2 \cdot 6H_2O$ in 4 ml MeOH was layered over a solution of 70 mg (0.126 mmol) AlL_3 in 1 ml MeOH and 3 ml $CHCl_3$. Slow interdiffusion of the layers, in a 7–8 days period, led to crystallization of 45 mg (40% yield) of the light-blue prisms $[Co\{AlL_3\}_2Cl_2] \cdot 4CHCl_3 \cdot 2CH_3OH$ **6**. Compounds $[Cd\{AlL_3\}(CH_3OH)\{NO_3\}_2] \cdot 2CHCl_3$ **7** and $[Cd\{AlL_3\}(CH_3OH)Br_2] \cdot 2CHCl_3 \cdot 2CH_3OH$ **8** were synthesized in a similar way, in 40–45% yields.

Complexes **6**–**8** readily lose incorporated solvent molecules with disintegration of the structure. They are also unstable under the mother solution since the initially formed crystals lose crystallinity and dissolve in a period of 15–20 days. It was not possible to obtain any crystals by the layering method for any mixed-metal FeL_3 species and the only isolable materials were isomorphous products of the ion exchange: $M\{L\}_2(H_2O)_2 \cdot 3H_2O$, M = Cd and Co (trigonal, space group $R\bar{3}$, $a = 22.350(3)$, $c = 13.222(2)$ Å).

Crystallography

The data were collected using CAD-4 Enraf Nonius (**1**, Cu-Kα, $\lambda = 1.54178$ Å), Siemens SMART CCD (**2**–**3**, **5**–**7**) and Stoe IPDS (**4**, **8**) diffractometers (Mo-Kα, $\lambda = 0.71073$ Å) (Table 2). The structures were solved by direct methods and refined by least-squares techniques using SHELXS-86, SHELXL-97[24] and CRYSTALS (**1**, **2**).[25] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added as fixed contributions with invariant isotropic U values at 0.08 Å^2. The hydrogen atoms of solvate methanol and water molecules in **5**, **6** and **8** were not included. One of three solvate water molecules in **3** is disordered and corresponding hydrogen atoms were not included. In **5** the coordinated nitrate groups are disordered over two positions that were resolved with partial contributions of 0.75 and 0.25 and fixed standard geometry of NO_3^- ions. Thermal parameters for one of two coordinated nitrate groups in **7** also were suggestive of possible disorder, but we were not successful in resolving it. The geometry of the nitrate group was constrained, N–O 1.25(3), and this led to a stable model. Part of solvate chloroform molecules in structures **6**–**8** were refined with restrained geometry (C–Cl 1.74(1) Å) in order to improve the refinement stability.

CCDC reference numbers 224037–224041 and 238710–238712.

See http://www.rsc.org/suppdata/dt/b4/b407244h/ for crystallographic data in CIF or other electronic format.

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