Two-dimensional metal–organic frameworks (MOFs) constructed from heterotrinuclear coordination units and 4,4′-biphenyldicarboxylate ligands†‡

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Three novel metal–organic frameworks (MOFs) formulated as $[Zn_2M(BPDC)_3(DMF)_2]\cdot 4DMF$ (M = Co^{II} **1**, Ni^{II} **2** or Cd^{II} **3**; BPDC = 4,4′-biphenyldicarboxylate; DMF = *N*,*N*′-dimethylformamide) have been prepared *via* solvothermal synthesis from mixtures of the corresponding transition metal salts and 4,4′-biphenyldicarboxylic acid (H_2BPDC). The framework structures are characterized by single-crystal X-ray diffraction analysis, IR and UV-vis diffuse reflectance spectroscopy, thermogravimetric analysis (TGA), and X-ray powder diffraction (XRPD). All three compounds possess essentially the same 2-D layered coordination framework consisting of linear heterotrinuclear secondary building units (SBUs) connected by rigid bridging BPDC ligands. Crystal data: for **1** ($C_{60}H_{66}CoN_6O_{18}Zn_2$): monoclinic, space group $P2_1/n$, $M = 1348.86$, $a = 20.463(4)$, $b = 14.819(3)$, $c = 23.023(5)$ Å, $\beta = 111.75(3)°$, $V = 6484(2)$ Å^3, $Z = 4$, $D_c = 1.382$ Mg m^{-3}. For **2** ($C_{60}H_{66}N_6NiO_{18}Zn_2$): monoclinic, space group $P2_1/n$, $M = 1348.64$, $a = 11.670(2)$, $b = 14.742(3)$, $c = 19.391(4)$ Å, $\beta = 102.29(3)°$, $V = 3259.5(11)$ Å^3, $Z = 2$, $D_c = 1.374$ Mg m^{-3}. For **3** ($C_{60}H_{66}CdN_6O_{18}Zn_2$): monoclinic, space group $P2_1/n$, $M = 1402.33$, $a = 11.491(2)$, $b = 14.837(3)$, $c = 19.386(4)$ Å, $\beta = 101.53(3)°$, $V = 3238.3(11)$ Å^3, $Z = 2$, $D_c = 1.438$ Mg m^{-3}.

Introduction

In recent years, metal–organic frameworks (MOFs) consisting of transition metal ions and organic ligands have attracted great interest due to their intriguing structural topologies[1] and potential applications in the areas of catalysis and materials science such as gas and liquid adsorption, nonlinear optics, magnetism, and molecular recognition.[2] Polycarboxylates have often been used as mono-, bi- or multi-dentate ligands to bind transition metal centers, leading to the formation of moderately robust metal–organic coordination frameworks.[3] Among these multi-carboxylate ligands, 1,4-benzenedicarboxylate (BDC) and 4,4′-biphenyldicarboxylate (BPDC) possess diverse bridging capabilities and have been employed as organic linkers to construct mono-, di- or poly-nuclear transition metal–organic polymeric structures with different dimensionalities[4] and to yield even some porous coordination frameworks[5] such as the well known MOF-5 $[Zn_4O(BDC)_3]$[5a] and IRMOF-9 $[Zn_4O(BPDC)_3]$[5b] reported by Yaghi and co-workers. Usually, the transition-metal carboxylate entities with simple geometry act as secondary building units (SBUs) which are further connected by the organic carboxylate linkers into MOF structures.[4c] However, the homopolynuclear MOFs thus built up contain only one kind of transition metal ion. To the best of our knowledge, there has been as yet no report on MOF-5 type or similar frameworks containing mixed transition metals although there are some simple discrete complexes comprised of mixed metals and monocarboxylates.[6]

In order to produce isorectangular frameworks with enhanced catalytic functions we were originally attempting to replace a single Zn ion within the $\{Zn_4O\}^{6+}$ coordination unit of IRMOF-9 by a redox-active transition metal ion such as Ni^{II}, Co^{II} or Cu^{II} (see Scheme 1). However, all our attempts to create heterotetranuclear frameworks which are isostructural with MOF-5 or IRMOF-9 have failed so far, presumably due to the preferential formation of structurally more stable heterotrinuclear frameworks, the crystal structures of which are described in this manuscript.

We report here three novel two-dimensional (2-D) layered metal–organic frameworks $[Zn_2M(BPDC)_3(DMF)_2]\cdot 4DMF$ (M = Co^{II} (**1**), Ni^{II} (**2**) or Cd^{II} (**3**), DMF = *N*,*N*′-dimethylformamide) generated from mixtures of transition metal ions and 4,4′-biphenyldicarboxylic acid (H_2BPDC) in solvothermal syntheses. To the best of our knowledge, these compounds are the first examples in which linear heterotrinuclear coordination units are connected by organic multicarboxylate linkers into metal–organic coordination frameworks (MOFs).

Experimental

General remarks

All starting materials were of reagent grade and used as received from the commercial supplier. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker IFS FT-IR spectrometer. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br). UV-vis diffuse reflectance spectra (DRS) were recorded on

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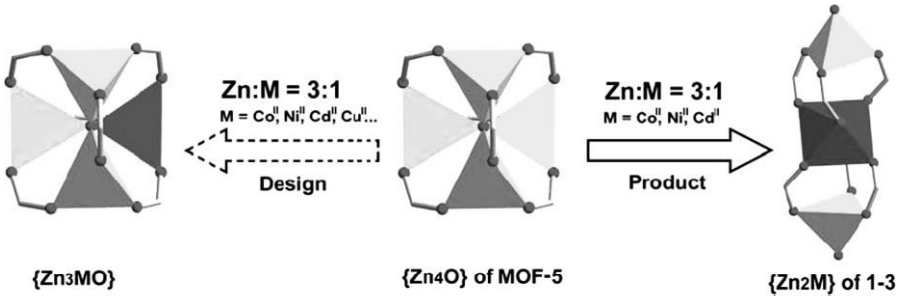
† The HTML version of this article has been enhanced with additional colour images.

‡ Electronic supplementary information (ESI) available: TGA curves of compounds **1–3**, UV-vis DRS spectra of BPDC and compounds **1–3**, and XRPD patterns of compound **1** at elevated temperatures. See DOI: 10.1039/b609733b



Scheme 1

an Analytik Jena Specord 50 UV-vis spectrometer in the range of 190–1100 nm with $BaSO_4$-diluted samples ($BaSO_4$: sample = 1 : 1) and converted into normal absorption spectra with the Kubelka–Munk function.[7] The lamps change at 320 nm and the mirrors change at 370, 400, 700 and 900 nm. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed with a TGA/SDTA851 Mettler Toledo analyzer in a temperature range of 30–1100 °C in flowing nitrogen at a heating rate of 10 °C min^{-1}. X-Ray powder diffraction (XRPD) patterns were measured using a Panalytical X'Pert Pro powder diffractometer operated at 40 kV, 40 mA for Cu target (λ = 1.5406 Å) with a scan speed of 30 s $step^{-1}$ and a step size of 0.008°. The simulated powder patterns were calculated using single-crystal X-ray diffraction data and processed by the program PowderCell 2.3 ((c) by W. Kraus & G. Nolze (BAM Berlin)).

Syntheses

General comment. Initial experiments contained the compounds Zn/M (M = Co^{II}, Ni^{II}, Cu^{II} or Cd^{II})/H_2BPDC at a molar ratio of 3 : 1 : 3. However, the precipitated microcrystalline solids were mixtures consisting of compounds **1–3** as the main component and some unidentified by-products. In subsequent experiments the ratio of metal ions and organic linker was adjusted such as to optimise the yields of pure compounds **1–3**.

For the Cu containing precipitates we were not able to obtain single crystals suitable for X-ray structure analysis.

$[Zn_2Co(BPDC)_3(DMF)_2]\cdot 4DMF$ (1). A mixture of $Zn(NO_3)_2\cdot 4H_2O$ (0.0523 g, 0.2 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.0582 g, 0.2 mmol), and H_2BPDC (0.073 g, 0.3 mmol) was dissolved in 10 mL of *N*,*N*′-dimethylformamide (DMF) and the solution was placed in a pressure glass tube (30 mL). The tube was sealed and heated at a constant rate of 2 °C min^{-1} to 105 °C for 40 h, and then cooled to room temperature at a rate of 1 °C min^{-1}. The resulting dark purple block-like crystals were collected, washed quickly with DMF (3 × 2 mL), and dried in air for *ca.* 2–3 min (yield: 0.11 g, 81% based on Zn). The phase purity of the as-synthesized compound was confirmed by X-ray powder diffraction (XRPD) pattern, which is consistent with the simulated one from the single-crystal X-ray diffraction data (see Fig. 1). Since the fresh crystals lose solvent molecules to some extent upon drying in air, we were not able to obtain fully consistent data from elemental analysis. The same reason is also valid for compounds **2** and **3**.

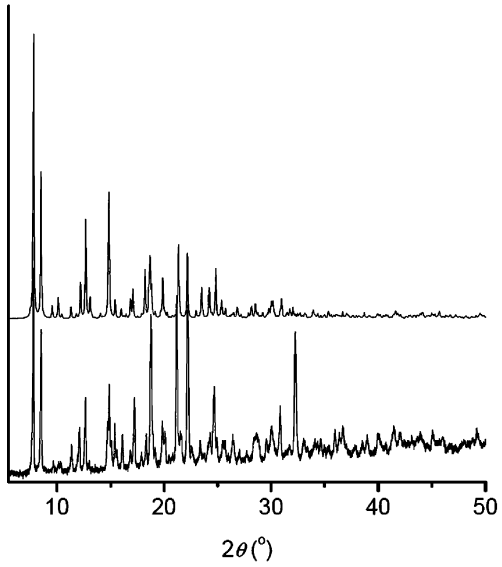


Fig. 1 Simulated (upper trace) and experimental (lower trace) X-ray powder diffraction patterns of compound **1**.

Calc. for $C_{60}H_{66}CoN_6O_{18}Zn_2$ (M = 1348.86): C, 53.43; H, 4.93; N, 6.23. Found: C, 52.91; H, 4.52; N, 5.58%. IR (KBr, cm^{-1}): 3424br, 3065w, 3001sh, 3065w, 2930w, 2856w, 1680s, 1606s, 1546m, 1498w, 1391vs, 1253w, 1177w, 1108w, 1088m, 1060w, 1021w, 1004w, 860m, 842m, 797w, 771s, 704w, 681m, 658w, 460m.

$[Zn_2Ni(BPDC)_3(DMF)_2]\cdot 4DMF$ (2). This compound was synthesized as light green block-like crystals by the procedure described for **1** except the addition of $Ni(NO_3)_2\cdot 6H_2O$ (0.0582 g, 0.2 mmol) instead of $Co(NO_3)_2\cdot 6H_2O$. Yield: 0.085 g, 63% based on Zn. Calc. for $C_{60}H_{66}N_6NiO_{18}Zn_2$ (M = 1348.64): C, 53.44; H, 4.93; N, 6.23. Found: C, 52.22; H, 4.64; N, 6.28%. IR (KBr, cm^{-1}): 3419br, 3062w, 2997w, 2929w, 2855w, 1677s, 1607s, 1546m, 1498w, 1393vs, 1253w, 1177w, 1111w, 1088m, 1060w, 1022w, 1005w, 861m, 842m, 771s, 703w, 682m, 658w, 459m.

$[Zn_2Cd(BPDC)_3(DMF)_2]\cdot 4DMF$ (3). This compound was prepared as described for the previous compounds using a mixture of $Zn(NO_3)_2\cdot 4H_2O$ (0.0784 g, 0.3 mmol), $CdCl_2\cdot H_2O$ (0.02 g, 0.1 mmol), and H_2BPDC (0.073 g, 0.3 mmol). Colorless block-like crystals were obtained and collected in the same way as compound **1** (yield: 0.08 g, 81% based on Cd). Calc. for $C_{60}H_{66}CdN_6O_{18}Zn_2$ (M = 1402.33): C, 51.39; H, 4.74; N, 5.99. Found: C, 50.25; H, 4.65; N, 6.02%. IR (KBr, cm^{-1}): 3420br, 3064w, 2927w, 3001w, 2856w,

Table 1 Single-crystal data and refinement summary for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{60}H_{66}CoN_6O_{18}Zn_2$	$C_{60}H_{66}N_6NiO_{18}Zn_2$	$C_{60}H_{66}CdN_6O_{18}Zn_2$
M	1348.86	1348.64	1402.33
T/K	220(2)	193(2)	193(2)
λ/Å	0.71073	0.71073	0.71073
Crystal dimensions/mm	0.28 × 0.24 × 0.20	0.26 × 0.23 × 0.20	0.29 × 0.24 × 0.22
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	20.463(4)	11.670(2)	11.491(2)
b/Å	14.819(3)	14.742(3)	14.837(3)
c/Å	23.023(5)	19.391(4)	19.386(4)
β/°	111.75(3)	102.29(3)	101.53(3)
V/Å^3	6484(2)	3259.5(11)	3238.3(11)
Z	4	2	2
D_c/Mg m^{-3}	1.382	1.374	1.438
μ/mm^{-1}	1.059	1.088	1.132
F(000)	2796	1400	1440
θ Range/°	2.14–25.98	2.15–25.88	2.14–25.93
Measured reflections	50279	24998	25084
Independent reflections	12574	6008	6015
Data/restraints/parameters	12574/0/787	6008/33/394	6015/0/394
R_1 ($I > 2\sigma(I)$)[a]	0.0755	0.0838	0.0501
wR_2 (all data)[a]	0.2047	0.2515	0.1537
Goodness-of-fit on F^2	1.015	1.000	1.023
$\Delta\rho_{max,\,min}$/e Å^{-3}	1.098, −0.466	1.513, −0.973	1.151, −1.657

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

1665s, 1605s, 1542m, 1496w, 1388vs, 1251w, 1176w, 1090m, 1060w, 1024w, 1004w, 857w, 840w, 797w, 771m, 703w, 681m, 447m.

X-Ray crystallography

Single-crystal X-ray diffraction intensities were collected at 220 K on a STOE IPDS diffractometer employing monochromated Mo-Kα radiation (λ = 0.71073 Å). Initial structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using the SHELXL-97 program.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined using a riding model. Details of data collection and refinement of the compounds are summarized in Table 1. Selected bond distances and angles are given in Tables 2–4.

CCDC reference numbers 613447 (**1**), 613449 (**2**) and 613448 (**3**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609733b

Table 2 Selected bond lengths (Å) and angles (°) of compound **1**

Zn(1)–O(1)	1.919(5)	Co(1)–O(2)[b]	2.052(5)
Zn(1)–O(3)[a]	1.942(4)	Co(1)–O(4)[c]	2.066(5)
Zn(1)–O(5)	1.948(5)	Co(1)–O(4)[a]	2.066(5)
Zn(1)–O(7)	2.012(5)	Co(1)–O(6)[b]	2.094(5)
Co(1)–O(2)	2.052(5)	Co(1)–O(6)	2.094(5)
O(1)–Zn(1)–O(3)[a]	122.9(2)	O(2)–Co(1)–O(6)	93.8(2)
O(1)–Zn(1)–O(5)	112.8(2)	O(2)–Co(1)–O(2)[b]	180.0(1)
O(1)–Zn(1)–O(7)	94.4(2)	O(2)–Co(1)–O(4)[c]	88.3(2)
O(2)–Co(1)–O(4)[a]	91.7(2)	O(2)–Co(1)–O(6)[b]	86.2(2)

Symmetry transformations used to generate equivalent atoms: [a] $x + 1/2, -y + 3/2, z + 1/2$. [b] $-x + 1, -y + 2, -z + 1$. [c] $-x + 1/2, y + 1/2, -z + 1/2$.

Table 3 Selected bond lengths (Å) and angles (°) of compound **2**

Zn(1)–O(1)	1.934(5)	Ni(1)–O(2)[a]	2.004(6)
Zn(1)–O(3)[b]	1.942(5)	Ni(1)–O(4)[b]	2.022(8)
Zn(1)–O(5)	1.944(5)	Ni(1)–O(4)[c]	2.022(8)
Zn(1)–O(7)	2.012(6)	Ni(1)–O(6)	2.086(6)
Ni(1)–O(2)	2.004(6)	Ni(1)–O(6)[a]	2.086(6)
O(1)–Zn(1)–O(3)[b]	118.4(3)	O(2)–Ni(1)–O(6)	94.8(3)
O(1)–Zn(1)–O(5)	119.2(2)	O(2)–Ni(1)–O(2)[a]	180.0(4)
O(1)–Zn(1)–O(7)	95.9(2)	O(2)–Ni(1)–O(4)[c]	88.9(5)
O(2)–Ni(1)–O(4)[b]	91.1(5)	O(2)–Ni(1)–O(6)[a]	85.2(3)

Symmetry transformations used to generate equivalent atoms: [a] $-x, -y, -z$. [b] $x + 1/2, -y - 1/2, z - 1/2$. [c] $-x - 1/2, y + 1/2, -z + 1/2$.

Table 4 Selected bond lengths (Å) and angles (°) of compound **3**

Zn(1)–O(1)	1.935(3)	Cd(1)–O(2)[a]	2.171(3)
Zn(1)–O(3)[b]	1.952(3)	Cd(1)–O(4)[b]	2.177(4)
Zn(1)–O(5)	1.934(3)	Cd(1)–O(4)[c]	2.177(4)
Zn(1)–O(7)	2.007(3)	Cd(1)–O(6)	2.205(3)
Cd(1)–O(2)	2.171(3)	Cd(1)–O(6)[a]	2.205(3)
O(1)–Zn(1)–O(3)[b]	117.7(1)	O(2)–Cd(1)–O(6)	93.1(1)
O(1)–Zn(1)–O(5)	115.5(1)	O(2)–Cd(1)–O(2)[a]	180.0(2)
O(1)–Zn(1)–O(7)	94.6(1)	O(2)–Cd(1)–O(4)[c]	87.2(1)
O(2)–Cd(1)–O(4)[b]	92.8(1)	O(2)–Cd(1)–O(6)[a]	86.9(1)

Symmetry transformations used to generate equivalent atoms: [a] $-x, -y, -z$. [b] $x + 1/2, -y - 1/2, z - 1/2$. [c] $-x - 1/2, y + 1/2, -z + 1/2$.

Results and discussion

Synthesis and characterization

In recent years solvothermal synthesis has been applied quite successfully to prepare a host of structurally different

metal–organic coordination frameworks.[3c,4c,d,9c] It was found that many parameters such as reaction time, temperature, solvent, and molar ratio of reactants may have an effect on the final reaction product. In our approach towards the synthesis of heteronuclear MOFs, changing the molar ratio of the reactants (Zn^{II} : M^{II} : H_2BPDC = 2 : 1 : 3, 3 : 1 : 3 or 2 : 2 : 3) under solvothermal reaction conditions (reactions carried out in 10 mL of DMF under autogenic pressure at T = 105 °C for 40 h) did not significantly alter the formation of different products, but all lead to preferential formation of the structurally similar compounds **1–3**, with the general formula $[Zn_2M(BPDC)_3(DMF)_2]\cdot 4DMF$ (M = Co^{II} (**1**), Ni^{II} (**2**) or Cd^{II} (**3**)). This fact strongly indicates that the type of MOF structure we describe here is the thermodynamically most stable framework under these reaction conditions. In addition, one may notice that although the three compounds have analogous molecular formulae their crystal lattices are not all isostructural. The cell volume of **1**, for instance, is twice the volume of **2** and **3** (Table 1), and thus compound **1** represents a crystal polymorph of the lattice type found in the compounds **2** and **3**. Interestingly, it is possible to switch between these polymorphs by adjusting the ratio of Zn^{II} and M^{II} ions, since we have also been able to grow crystals of the Cd- or Ni-containing frameworks which are isostructural with compound **1** (*vide infra*). These facts indicate that the Zn^{II}–M^{II}–H_2BPDC reaction system in our case yields only one kind of MOF structure although the compounds might crystallize in different polymorphic crystal lattices depending on reactant ratios. Further, none of the compounds **1–3** is soluble in water or common organic solvents, which is normal for the products obtained from solvothermal reactions.

The IR spectrum of compound **1** shows characteristic strong bands of the carboxylate groups at 1606 and 1546 cm^{-1} as well as at 1391 cm^{-1} for the asymmetric and symmetric stretching vibrations, respectively.[9] Similar values are found for compound **2**: 1607, 1546, 1393 cm^{-1}, and for compound **3**, respectively: 1605, 1542, 1388 cm^{-1}. The separations (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ of the carboxylate groups for compounds **1–3** are 155, 153, and 154 cm^{-1}, all similar to that of an ionic carboxylate. The missing absorption band at a wavenumber around 1700 cm^{-1} (indicative of a carboxylic acid group) demonstrates that complete deprotonation of the BPDC ligands occurs upon reaction with the transition metal ions.

The UV-vis diffuse reflectance spectra (DRS) of the three compounds all display two similar absorption bands in the UV region at around 39 525 (253) and 28 248 (354 nm) cm^{-1}, which correspond to the intraligand n→π* and π→π* transitions, respectively.[10] In addition, compounds **1** and **2** also exhibit well-developed bands in the range of 9000–25 000 cm^{-1} owing to the d–d transitions of Co^{II} and Ni^{II} ions.[11] Compound **1**, which contains an octahedrally coordinated Co^{II} ion, shows one main absorption in the visible region (at 18 939 cm^{-1}, 528 nm) as well as one weak and broad absorption in the red end of the visible region (at 9225 cm^{-1}, 1084 nm), which can be attributed to the spin allowed transitions from $^4T_{1g}(F)$ to $^4T_{1g}(P)$ (ν_3) and to $^4T_{2g}(F)$ (ν_1), respectively. The values of Dq (1052 cm^{-1}) and B (723 cm^{-1}) which have been estimated from these transitions are typical for six-coordinate octahedral Co^{II} complexes.[11] Compound **2** shows two absorption bands at 12 674 (789 nm) and 23 529 cm^{-1} (425 nm) due to the spin allowed transitions from $^3A_{2g}$ to $^3T_{1g}(F)$ (ν_2) and $^3T_{1g}(P)$ (ν_3), respectively. The Dq value (763 cm^{-1}) calculated from these transitions is comparable to those of other six-coordinate octahedral Ni^{II} complexes.[11] All the spectral data mentioned above provide substantial evidence for the fact that the Co^{II} and Ni^{II} centers are octahedrally coordinated in the present MOF structures. Based on UV-vis spectroscopic data, even a partial replacement of the tetrahedrally coordinated Zn ion by Co or Ni ions in the heterotrinuclear units might be ruled out, since tetrahedrally coordinated Co^{II} and Ni^{II} centers would become immediately apparent in the UV-vis spectra, due to their much more intense ("Laporte allowed") absorption bands (typically by a factor between 10 and 50 for similar sets of ligands). Thus, in the X-ray structure analysis of compounds **1–3**, the tetrahedral coordination sites were exclusively occupied by zinc metal centers.

Thermogravimetric analysis (TGA) was performed on polycrystalline samples of compounds **1–3** in a nitrogen atmosphere and the TGA curves are displayed in the ESI.† Four weight loss steps can be observed in the TGA curve of **1**. The first two steps in the temperature ranges of 70–225 and 226–400 °C are due to the loss of approximately four isolated and two coordinated DMF molecules, respectively. Concomitant with the second weight loss step, compound **1** began to lose its crystallinity and thus its structural integrity, as revealed by XRPD patterns measured at elevated temperatures (>200 °C, ESI,‡ Fig. S10). The final two weight losses in the ranges 401–580 and 580–920 °C are ascribed to the decomposition of BPDC units and the polymeric coordination framework. The TGA curve of **2** also shows a continuous four-step weight loss process as follows. Step 1 in the range 37–238 °C and step 2 from 239 to 389 °C correspond to the loss of approximately four isolated and two coordinated DMF molecules, respectively, while the separate steps 3 and 4 in the ranges of 390–580 and 581–890 °C are attributed to decomposition of the BPDC ligands and thus the MOF framework. As for the TGA curve of **3**, it indicates three weight loss steps. The first step occurred over the temperature range 35–380 °C owing to the continuous removal of about four isolated and two coordinated DMF molecules. The final two steps took place in the ranges 381–579 and 579–1045 °C due to the decomposition of the BPDC groups and thus the MOF framework.

Crystal structures

Since single-crystal X-ray diffraction analysis reveals that compounds **1–3** possess essentially the same 2-D metal–organic coordination frameworks, herein we limit the description of crystal structures to that of compound **1**, which contains the building unit shown in Fig. 2. This coordination unit consists of a heterotrinuclear cluster which comprises a centrosymmetric linear array of two Zn centers and one Co^{II} center which are bridged by BPDC ligands through carboxylate oxygen atoms. In the crystal structure the Co^{II} ion occupies a crystallographic center of inversion and adopts a slightly distorted octahedral coordination geometry, being coordinated by six carboxylate oxygen atoms from six different BPDC ligands. The Co–O bond lengths are in the range of 2.052(5)–2.094(5) Å and the O–Co–O bond angles range from 86.2(2) to 180.0(1)°. The two symmetry-related Zn^{II} centers reside in an appreciably distorted tetrahedral coordination environment. Each Zn center is bound to three carboxylate oxygen atoms from three distinct BPDC groups and one oxygen stemming from a monodentately coordinated DMF molecule. The

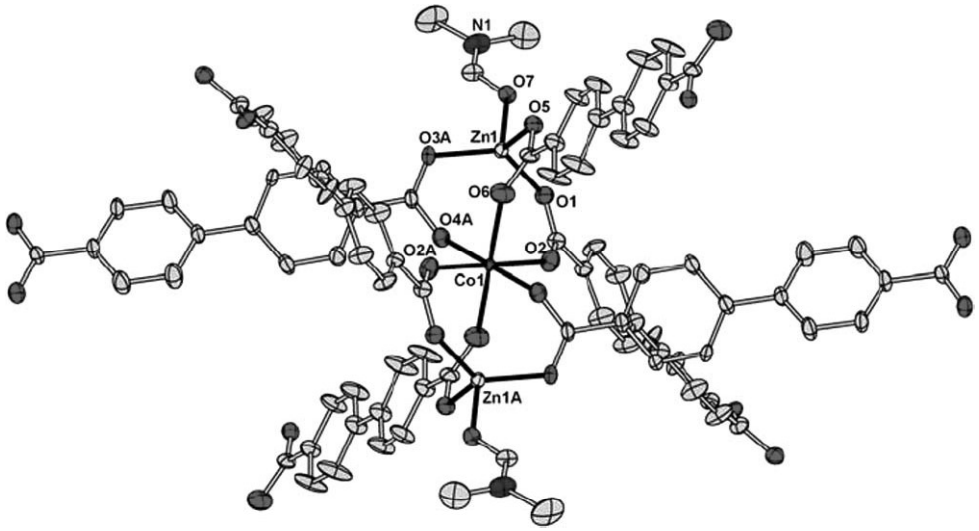


Fig. 2 ORTEP representation of compound **1** showing the local coordination environments of the metal centers with thermal ellipsoids at 30% probability. H atoms are omitted for clarity.

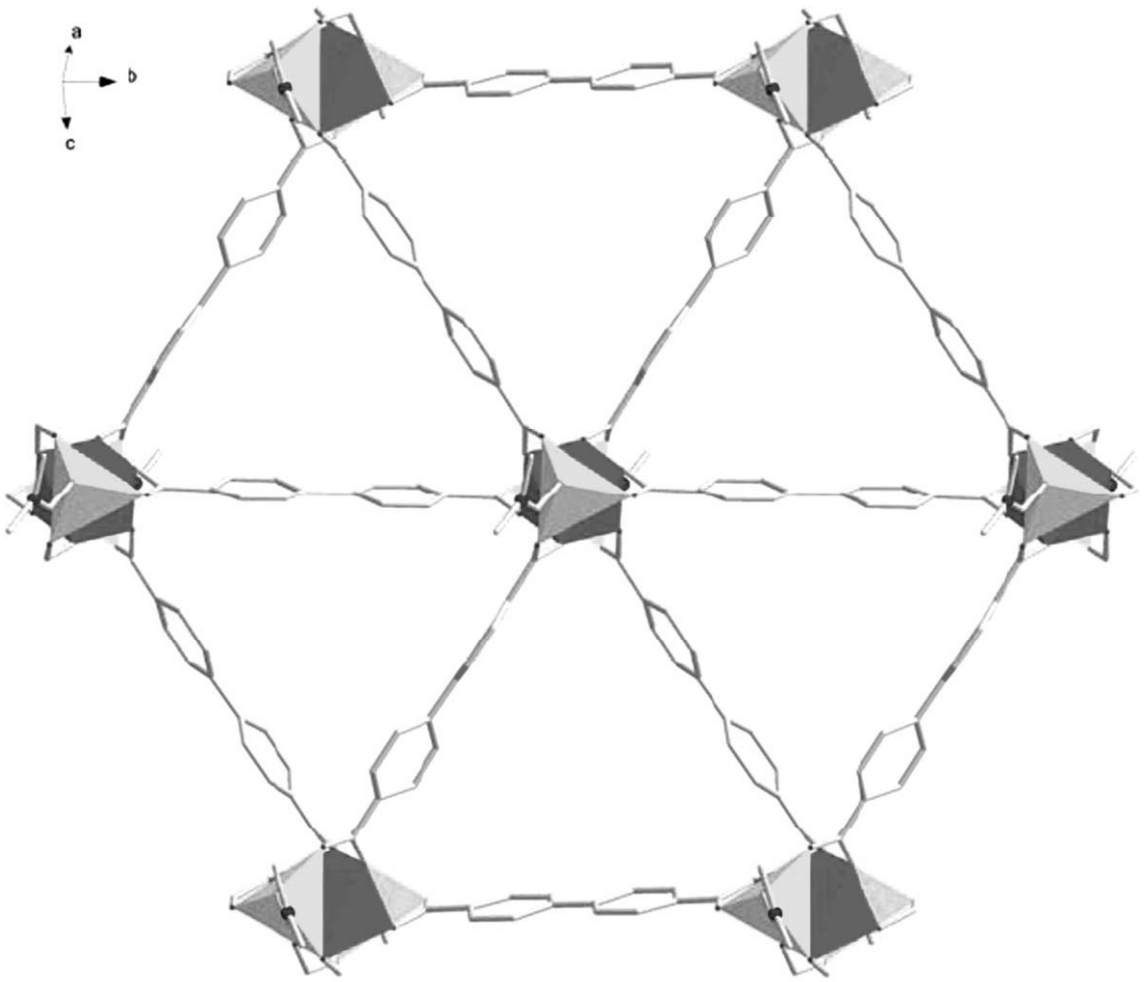


Fig. 3 Polyhedral representation of individual 2-D network of compound **1** with triangular grids. $\{ZnO_4\}$ and $\{CoO_6\}$ are depicted as light tetrahedra and dark octahedra, respectively.

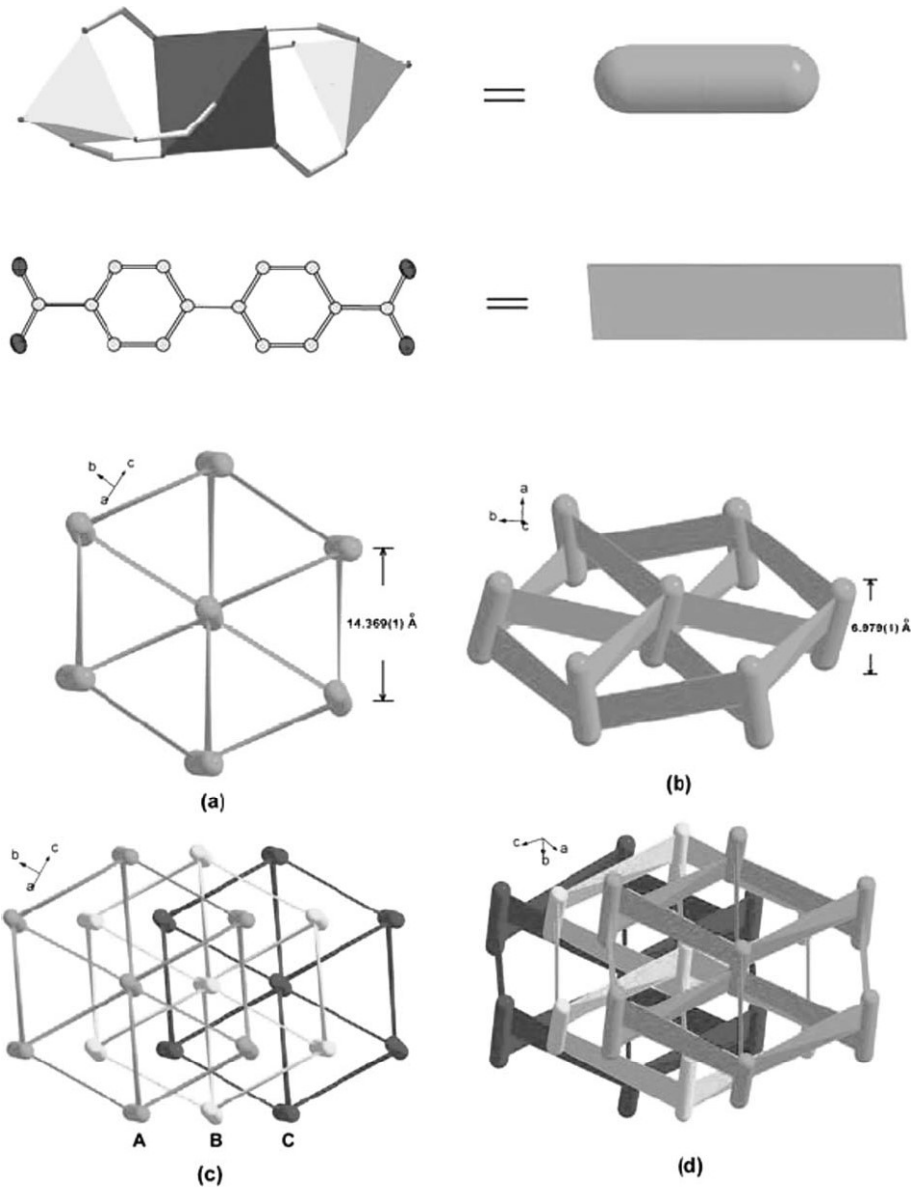


Fig. 4 The 2-D network and the packing arrangements of compound **1** with the secondary building unit (SBU) represented by solid rods and BPDC ligand displayed as flat ribbons.

Zn–O bond lengths are in the range of 1.919(5)–2.012(5) Å and the O–Zn–O bond angles range from 94.4(2) to 122.9(2)°. All BPDC ligands in compound **1** adopt only one coordination mode, namely the bridging bis-bidentate mode, for connecting two different transition metal centers. Analogous bis-bidentate coordination modes have been observed for the BDC ligand in some coordination polymers.[9a,c] The two DMF molecules in the building unit serve as terminal ligands to complete the tetrahedral coordination geometry of Zn centers. The linear heterotrinuclear coordination units connected by BPDC ligands can be regarded as secondary building units (SBUs) $Zn_2Co(\mu_2\text{-}O_2CR)_6$. These SBUs are connected by rigid organic linkers (BPDC) to yield a 2-D layered metal–organic coordination framework with triangular meshes, as shown in Fig. 3. With the SBU represented by solid rods and the BPDC ligand by flat ribbons, the 2-D layered structure with its triangular meshes is schematized in Fig. 4. The distance between two adjacent SBUs is 14.369(1) Å and the thickness of a single 2-D layer is about 6.979(1) Å. In the crystal, adjacent 2-D layers are stacked in an ABCABC$\cdots$ staggering mode, leading to a 3-D structure (see Fig. 4(c) and (d)). A closer examination of the 2-D layered structure as indicated in Fig. 5 reveals that solvent (DMF) molecules reside in the open cavities of the crystal lattice that occur between adjacent 2D layers. It is noteworthy that the coordinated DMF molecules protrude in an upward or a downward direction into the triangular cavities formed by the coordination framework. Based on C$\cdots$O distance calculations there are weak hydrogen bonding interactions between the occluded and the coordinated DMF molecules and also the BPDC groups, which might contribute to stabilization of the whole MOF structure (Table T1, ESI‡).

Although structurally similar *homo*trinuclear SBUs have been observed in a few MOF structures constructed from zinc centers

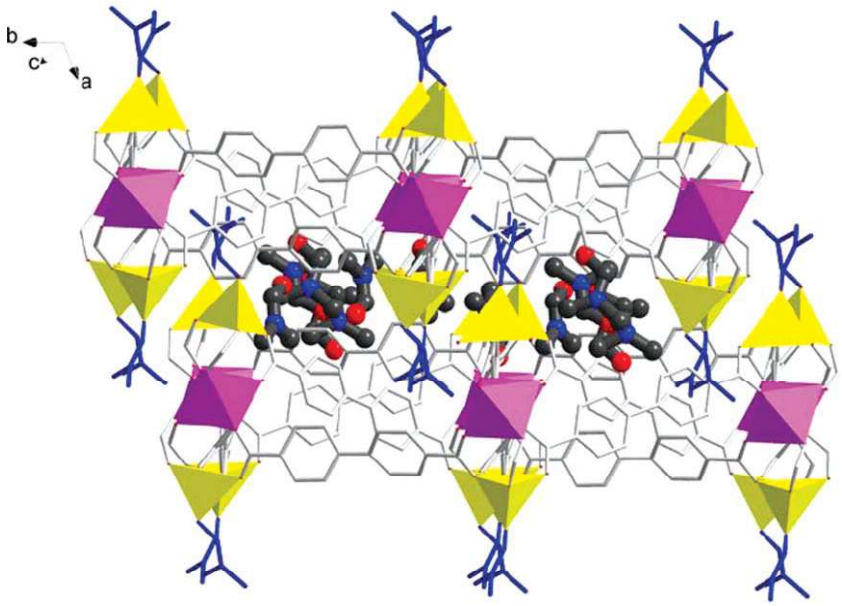


Fig. 5 The packing arrangement of compound **1** viewed along the *b* axis showing the positions of solvent DMF molecules. The coordinated DMF molecules are shown as blue capped sticks; the solvent DMF molecules are shown as ball and stick models.

and BDC ligands,[4d,e,5d] and discrete *hetero*trinuclear complexes of the general formula $Zn_2M(\mu\text{-}O_2CR)_6$ (M = Zn, Co, Ni, Cd, Mg, Ca or Sr) are known,[6] in which six monofunctional carboxylate groups bind to a trinuclear unit in a similar way, the heterotrinuclear $[Zn_2M(BPDC)_3(DMF)_2]\cdot 4DMF$ ($M = Co^{II}$ **1**, Ni^{II} **2** and Cd^{II} **3**) MOFs containing mixed transition metals connected by BPDC ligands and the 2-D layered MOF structures thus constructed are unprecedented in present MOF structural chemistry. The fact that MOFs can be constructed from SBUs containing different metal ions, which are placed in different coordination environments without scrambling of metal sites to occur is one of the most interesting feature of compounds **1–3**. This feature demonstrates that catalytically active MOFs comprising precisely defined bi- or polymetallic redox-active sites are a realistic task and might become reality in the near future.

Conclusion

We have demonstrated the solvothermal synthesis and structural characterization of three novel metal–organic frameworks with the formula of $[Zn_2M(BPDC)_3(DMF)_2]\cdot 4DMF$ ($M = Co^{II}$, Ni^{II}, or Cd^{II}; BPDC = 4,4′-biphenyldicarboxylate; DMF = *N*,*N*′-dimethylformamide). All three compounds exhibit a two-dimensional layered coordination framework consisting of linear heterotrinuclear coordination units linked by bridging bis-bidentate BPDC ligands. The successful preparation of these three compounds containing mixed transition metals and dicarboxylate ligands may provide a new route for the design and synthesis of novel redox- and catalytically active metal–organic frameworks.

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References

1 Reviews: M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; M. J. Zaworotko, *Chem. Commun.*, 2001, 1; P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 283; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3.

2 O. M. Yaghi, in *Access in Nanoporous Materials*, ed. T. J. Pinnavaia and M. F. Thorpe, Plenum, New York, 1995, p. 111; M. Zaworotko and R. D. Rogers, in *Synthesis of New Materials by Coordination Chemistry Self-Assembly and Template Formation*, ACS Symposium, Anaheim, 1999; N. Guillou, S. Pastre, C. Livage and G. Férey, *Chem. Commun.*, 2002, 2358; B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; O. Kahn and C. Martinez, *Science*, 1998, **279**, 44; O. R. Evans, R. Xiong, Z. Wang, G. K. Wong and W. Lin, *Angew. Chem., Int. Ed.*, 1999, **38**, 536; W. Lin, O. R. Evans, R. Xiong and Z. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13272; K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem., Int. Ed.*, 2002, **41**, 281; B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angew. Chem.*, 2005, **117**, 4823, (*Angew. Chem., Int. Ed.*, 2005, **44**, 4745); J. L. C. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, *J. Am. Chem. Soc.*, 2004, **126**, 5666; N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127.

3 (*a*) O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096; (*b*) H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571; (*c*) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239; (*d*) D. T. Vodak, M. E. Braun, J. Kim, M. Eddaoudi and O. M. Yaghi, *Chem. Commun.*, 2001, 2534; (*e*) S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen and W.-T. Wong, *Inorg. Chem.*, 2004, **43**, 830; (*f*) X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem., Int. Ed.*, 2004, **43**, 5036; (*g*) X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li, Z.-M. Su, L. Xu and L. Carlucci, *Angew. Chem., Int. Ed.*, 2005, **44**, 5824.

4 (*a*) J. Chen, Z. Liu, T. Yu, Z. Chen, J. Sun, L. Weng, B. Tu and D. Zhao, *Chem. Lett.*, 2003, **32**, 474; (*b*) S. Y. Yang, L. S. Long, R. B. Huang

and L. S. Zheng, *Chem. Commun.*, 2002, 472; (*c*) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504; (*d*) A. D. Burrows, K. Cassar, R. M. W. Friend, M. F. Mahon, S. P. Rigby and J. E. Warren, *CrystEngComm*, 2005, **7**, 548; (*e*) M. Edgar, R. Mitchell, A. M. Z. Slawin, P. Lightfoot and P. A. Wright, *Chem.–Eur. J.*, 2001, **7**, 5168; (*f*) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Angew. Chem.*, 2002, **114**, 294, (*Angew. Chem., Int. Ed.*, 2002, **41**, 284); (*g*) R. H. Groeneman, L. R. MacGillivray and J. L. Atwood, *Inorg. Chem.*, 1999, **38**, 208; (*h*) G. Guilera and J. W. Steed, *Chem. Commun.*, 1999, 1563; (*i*) C. S. Hong and Y. Do, *Inorg. Chem.*, 1997, **36**, 5684; (*j*) L. Deakin, A. M. Arif and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 5072; (*k*) H. K. Fun, S. S. S. Raj, R. G. Xiong, J. L. Zuo, Z. Yu and X. Z. You, *J. Chem. Soc., Dalton Trans.*, 1999, 1915.

5 (*a*) H. L. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (*b*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*c*) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651; (*d*) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186.

6 W. Clegg, I. R. Little and B. P. Straughan, *Inorg. Chem.*, 1988, **27**, 1916; W. Clegg, I. R. Little and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1986, 1283; B. Singh, J. R. Long, F. F. de Biani, D. Gatteschi and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 7030.

7 W. W. Wendlandt and H. G. Hecht, in *Reflectance Spectroscopy*, Interscience Publishers/John Wiley & Sons, New York, 1966.

8 G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

9 (*a*) J. Tao, M.-L. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 3669; (*b*) X.-M. Zhang, M.-L. Tong, M.-L. Gong and X.-M. Chen, *Eur. J. Inorg. Chem.*, 2003, 138; (*c*) W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H.-M. Yuan, J.-S. Chen and S.-N. Wang, *Inorg. Chem.*, 2003, **42**, 944.

10 A. Gilbert and J. Baggott, in *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, FL, 1991, pp. 87–89.

11 (*a*) A. B. P. Lever, in *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company, Amsterdam, 1968, ch. 9, pp. 317–349; (*b*) The *Dq* and *B* values were estimated by using the transition energy ratio diagrams on pp. 393–400 of the same book as in ref. 11*a*.