

A chiral C_3 -symmetric hexanuclear triangular-prismatic copper(II) cluster derived from a highly modular dipeptidic N,N' -terephthaloyl-bis(S -aminocarboxylato) ligand^{†‡}

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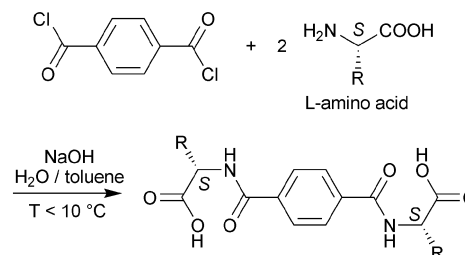
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The enantiomeric dipeptidic ligand N,N' -terephthaloyl-bis(L -phenylalaninato) (TBPh²⁻) reacts with copper(II) acetate in ethanol under the formation of the hexanuclear double-layered triangular-prismatic cluster $[Cu_2(\mu_4-TBPh-\kappa O : \kappa O' : \kappa O'' : \kappa O''')_2(EtOH)(H_2O)]_3 \cdot \sim 28(H_2O/0.33EtOH)$ with C_3 -symmetry, homochiral conformer assembly in the crystal and strong antiferromagnetic coupling within the $Cu_2(O_2CR)_4$ paddle-wheel unit ($J = -214$ K).

The construction of solvent-filled and potentially porous metal-organic frameworks,¹ or metallasupramolecular architectures,² such as molecular closed polyhedral coordination cages³ molecular open coordination polygons,⁴ and boxes⁵ is of contemporary interest for a variety of applications. The induction of chirality in any of the above compound classes is of added interest, *e.g.* for enantiomer recognition.^{6,7} Chiral microporous materials could be used in enantiomer separation or chiral synthesis.⁸ Furthermore, oligonuclear complexes feature prominently in crystal engineering⁹ and the well-known $Cu_2(O_2CR)_4$ paddle-wheel unit has recently been utilized successfully for the design of MOFs with large pores,^{1,10} porous polyhedra¹¹ and coordination polygons.¹²

Ongoing work on extended and molecular chiral metal complexes using easily accessible enantiopure aminocarboxylate ligands¹³ prompted us to utilize amino acids for the modification of terephthalate as a prototypical bridging ligand¹⁴ through amide formation.^{15,16} Such a terephthalate modification with proteinogenic α - and other amino acids leads to a large variety of highly modular C_2 -symmetric bridging ligands (Scheme 1).

Green crystals of $[Cu_2(\mu_4-TBPh-\kappa O : \kappa O' : \kappa O'' : \kappa O''')_2(EtOH)(H_2O)]_3 \cdot \sim 28(H_2O/0.33EtOH)$, **1** can be grown from an equimolar ratio of copper(II) acetate and TBPh₂ in ethanol.[‡] The crystal size depends on the water amount of the ethanol. Ethanol with 0.033% H₂O yielded fine needles while ethanol with 0.083% H₂O (determined by Karl-Fischer titration) gave larger needles suitable for single-



R = CH₃: N,N' -Terephthaloyl-bis(L -alanine), TBAAlaH₂
 R = CH(CH₃)₂: N,N' -Terephthaloyl-bis(L -valine), TBValH₂
 R = CH₂CH(CH₃)₂: N,N' -Terephthaloyl-bis(L -leucine), TBLeuH₂
 R = CH(CH₃)CH₂CH₃: N,N' -Terephthaloyl-bis(L -isoleucine), TB IleH₂
 R = CH₂Ph: N,N' -Terephthaloyl-bis(L -phenylalanine), TBPhH₂
 R = CH₂(C₈H₆N): N,N' -Terephthaloyl-bis(L -tryptophan), TBTrpH₂
 R = CH₂COOH: N,N' -Terephthaloyl-bis(L -aspartic acid), TBAspH₂
 R = CH₂C(O)NH₂: N,N' -Terephthaloyl-bis(L -asparagine), TBAsnH₂
 R = CH₂CH₂SCH₃: N,N' -Terephthaloyl-bis(L -methionine), TBMethH₂

Scheme 1 Synthesis of N,N' -terephthaloyl-bis(L -amino acids)[†]

crystal X-ray diffraction.[§] Increasing the percentage of water in ethanol led only to the precipitation of **1** as a powder. In pure water the ligand is not soluble. Hydrothermal techniques gave undefined reaction products. Removal of the crystals from the mother liquor leads to a largely amorphous material as shown by X-ray powder diffractometry.[‡]

The dinuclear paddle-wheel unit of copper acetate, $[Cu_2(OAc)_4]$ is preserved in the solid-state structure of **1** (Fig. 1). Pairs of copper(II) atoms are bridged by four carboxylate groups from four different TBPh²⁻ ligands. A terminal ethanol or aqua ligand completes the five-fold Cu coordination to a square pyramid. The Cu...Cu distance of 2.6309(2) Å is very similar to the distance in copper(II) acetate^{17,18} and related Cu carboxylates.^{10,11,12,19}

Three such Cu_2 units with six terephthaloyl-bis(L -phenylalaninato) ligands form a hexanuclear double-layer, triangular-prismatic cluster (Fig. 2a). The cluster exhibits three-fold rotational symmetry with a C_3 -axis of the space group $R3$ running through the center of the cluster.

A terminal aqua ligand of the Cu_2 units is oriented into the internal cavity of the cluster. An ethanol ligand is bound to the outside of the Cu_2 pair. These ethanol molecules are surrounded by three benzyl groups from the four coordinating TBPh ligands (Fig. 2a). The fourth benzyl group (C30-C35) is tangentially oriented away from the triangle.

There is a preferential canting of the six terephthaloyl aryl groups, such that they form a cone. The trigonal, non-centrosymmetric crystal symmetry requires all tangential benzyl groups and terephthaloyl aryl groups to be oriented in the same direction. The tangential

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[‡] Electronic supplementary information (ESI) available: Synthesis and analysis, structure determination and refinement, X-ray powder diffractogram, thermogravimetric analysis, table of hydrogen bonding interactions. See DOI: 10.1039/b717207a

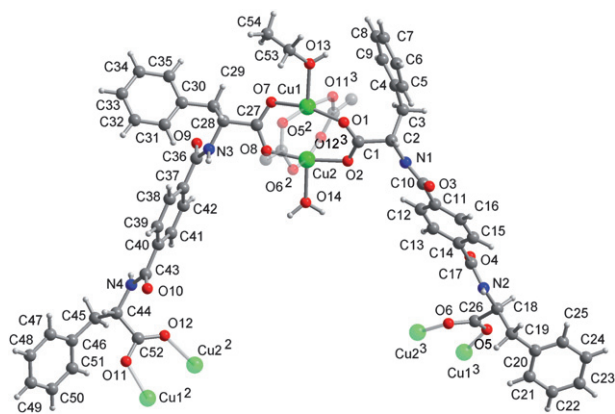


Fig. 1 Asymmetric unit and coordination environment for a copper paddle-wheel unit in **1**. Parts not belonging to the asymmetric unit are depicted as semi-transparent. Selected distances (Å) and angles (°): Cu1...Cu2 2.6309(2), Cu1–O1 1.9997(10), Cu1–O5² 1.9440(10), Cu1–O7 1.9916(11), Cu1–O11³ 1.9453(8), Cu1–O13 2.1366(10), Cu2–O2 1.9357(11), Cu2–O6² 2.0320(11), Cu2–O8 1.9344(10), Cu2–O12³ 2.0351(9), Cu2–O14 2.1172(10), O1–Cu1–O13 96.60(4), O5²–Cu1–O1 91.91(4), O5²–Cu1–O7 87.62(4), O5²–Cu1–O11³ 170.96(4), O5²–Cu1–O13 94.95(4), O7–Cu1–O1 163.67(3), O7–Cu1–O13 99.71(4), O11³–Cu1–O1 86.03(4), O11³–Cu1–O7 91.88(4), O11³–Cu1–O13 94.03(5), O5²–Cu1–Cu2 86.08(3), O11³–Cu1–Cu2 84.91(3), O7–Cu1–Cu2 82.27(2), O1–Cu1–Cu2 81.41(3), O13–Cu1–Cu2 177.80(4), O2–Cu2–O6² 92.02(4), O2–Cu2–O12³ 86.78(4), O2–Cu2–O14 96.04(5), O6²–Cu2–O12³ 162.68(4), O6²–Cu2–O14 98.20(5), O8–Cu2–O2 169.41(4), O8–Cu2–O6² 87.48(4), O8–Cu2–O12³ 90.55(4), O8–Cu2–O14 94.50(5), O12³–Cu2–O14 99.10(5), O8–Cu2–Cu1 84.60(3), O2–Cu2–Cu1 84.87(3), O6²–Cu2–Cu1 80.88(2), O12³–Cu2–Cu1 81.80(3), O14–Cu2–Cu1 178.74(4). Symmetry code: 2 = –y, 1 + x – y, z; 3 = –1 – x + y, –x, z.

benzyl groups are always positioned to the left when looking inside the cone from its wide opening (Fig. 2b). This preferential orientation of the benzyl and aryl groups gives rise to a conformational chirality, with only one enantiomer allowed in the space group $R\bar{3}$. With the preset enantiomerically pure *S,S*-configuration of the amino carboxylate moieties, the triangular prisms with their two possible conformeric forms then represent diastereomers. For the structure elucidation of **1** three data sets were measured with three different crystals. All three data sets could be refined to the same conformeric form of the benzyl and aryl groups in the trigonal prism. Thus, the intermolecular forces appear strong enough to induce spontaneous resolution of one conformer within a single crystal and there may also be homochiral seeding.^{13c}

The hydrophilic part of the cluster is situated at the interior, whereas the exterior of the cluster is more hydrophobic (Fig. 2a,b). The remaining space inside the cluster is filled by highly disordered water or ethanol solvent of crystallization (Fig. 2c). The residual electron density within one cluster corresponds to about 28 oxygen atoms or the equivalent of C and O atoms of ethanol (at the most, about 9 EtOH molecules).[‡]

A thermogravimetric analysis of **1** (under nitrogen after a vacuum cycle) shows a weight loss up to 210 °C of 10.80%.[‡] This can be attributed to the loss of the terminal ligands of the {Cu₂(O₂CR)₄} paddle-wheel units (3 ethanol and 3 aqua ligands) together with about 10 remaining water molecules in the channel (calc. 10.63%). From 220 °C onwards the decomposition of the terephthaloyl-bis(*L*-phenylalaninato) ligand begins.

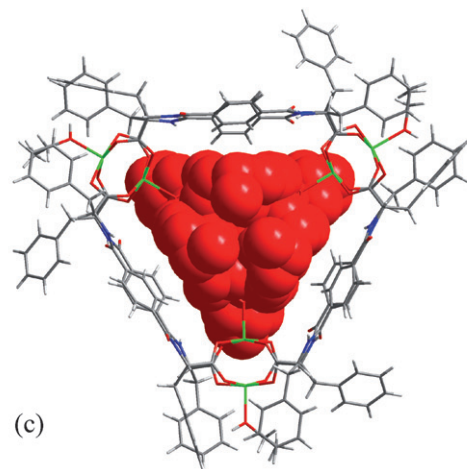
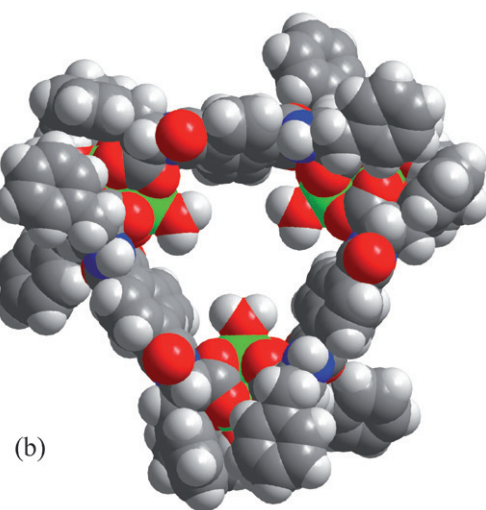
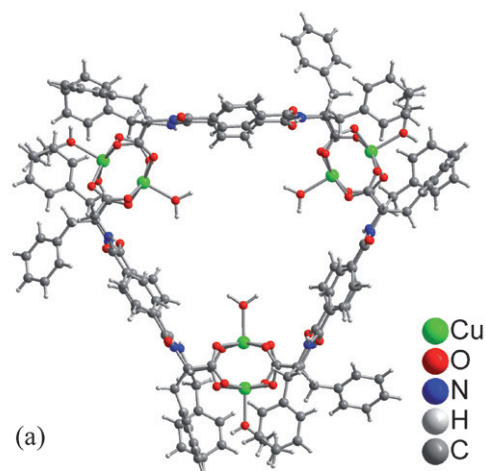


Fig. 2 Cluster structure of **1** formed from three Cu₂-units with six bridging ligands. (a) Ball-and-stick representation. (b) Space filling representation. (c) Stick representation of the cluster with the disordered solvent molecules (space filling representation) in the triangular-prismatic channel.

Without the disordered solvent molecules inside the trigonal prism there would be 23.4% potential solvent area volume as calculated by PLATON for Windows.²⁰ With the disordered solvent molecules this volume drops to 3.9% of the unit cell volume. An experimental nitrogen adsorption study on an evacuated sample (after 3 d at 30 °C) did not show any porosity. Hence, the solvent-depleted porous structure is not stable, as was also suggested from the loss of crystallinity seen by X-ray powder diffraction.‡

In space group *R*3 it is crystallographically required that neighboring cluster prisms are hexagonally packed in the *ab*-plane (Fig. 3) and are stacked on top of each other along *c* (Fig. 4). Neighboring clusters

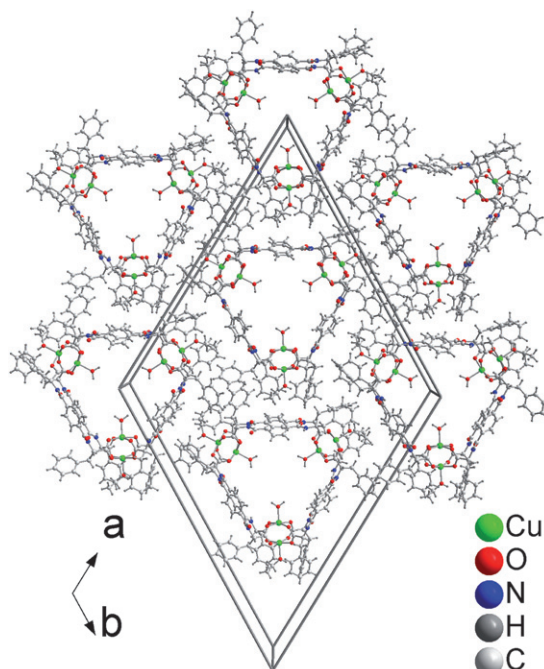


Fig. 3 Packing of the hexanuclear clusters in **1** in the *ab*-plane (disordered solvent omitted for clarity).

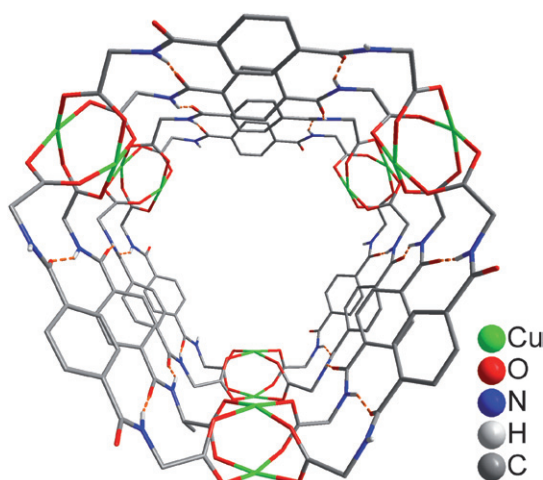


Fig. 4 Tube formation through hydrogen-bonding interactions (orange dashes) between the amine and carbonyl functions of TBPhe in **1**. For clarity the benzyl groups, aqua and ethanol ligands and aryl hydrogen atoms are not shown in the stick representation. Hydrogen bond distances and angles are given in ESI.‡

in the *ab*-plane are packed through C–H··· π interactions.‡,²¹ There is no π ··· π -stacking.²² A triangular tube is established along *c* through intra- and intercluster hydrogen-bonding interactions between the carbonyl and amine functions (Fig. 4).‡

Magnetic interactions in binuclear copper(II) carboxylate complexes with the $\text{Cu}_2(\text{O}_2\text{CR})_4$ paddle-wheel unit have been intensely studied.^{18,23} The magnetic properties of a dried sample of **1** with the approximate composition $[\text{Cu}_2(\text{TBPhe})_2(\text{EtOH})(\text{H}_2\text{O})]_3 \cdot 10 \text{H}_2\text{O}$ (from TGA and elemental analysis) were investigated in the solid state.† In the following we will scale all magnetic properties to asymmetric units of dried samples of **1** consisting of one third of the given formula and displaying dimeric copper pairs as outlined above. The measured susceptibility data were corrected for the constant diamagnetic contribution (–0.480 memu per asym. unit) applying the rough estimate $\chi_{\text{dia}} = -0.79Z_i \times 10^{-6} (r/la_0)^2$ emu per asym. unit, where Z_i is the sum of all electrons per asymmetric unit and $(r/la_0)^2 = 1$ where a_0 is the Bohr radius. Upon lowering the temperature, the magnetic susceptibility χ first increases very smoothly and then decreases rapidly with a broad maximum around 260 K (Fig. 5). This behavior characterizes strong antiferromagnetic correlations within the Cu_2 pairs. An intramolecular coupling between copper(II) atoms through the TBPhe bridging ligand can be excluded because of the long distance (>10.8 Å). At temperatures below 60 K, χ increases again (Fig. 5). This residual paramagnetic tail can be attributed to small amounts of paramagnetic impurities ($S = 1/2$) (see, for example, ref. 24).

The fit was carried out with the Bleaney-Bowers formula for Cu_2 dimers in which both copper atoms possess a spin of $S = 1/2$.²⁵ The fit parameters give a measure of the gyromagnetic constant $g = 2.29$, a paramagnetic impurity $\rho = 4\%$ and a TIP (temperature independent paramagnetism) of 0.23 memu per asym. unit. The negative coupling constant $J = -214 \text{ K}$ ($= -149 \text{ cm}^{-1}$) is indicative of the antiferromagnetic interaction as expected from the curve progression. The typical value in copper(II) acetate complexes is $-2J = 300 - 320 \text{ cm}^{-1}$.^{18,23} The temperature dependence of χT reflects the antiferromagnetic coupling within the Cu_2 dimers as well (Fig. 6). The χT value at room temperature of 0.61 emu K per asym. unit is much lower than the expected value for two non-interacting isolated copper(II) atoms of 0.90 emu K/2Cu,²⁶ which corroborates antiferromagnetic correlations even at 300 K. With decreasing temperature χT decreases. This is a clear evidence for enhanced coupling within the dimers at lower temperatures.

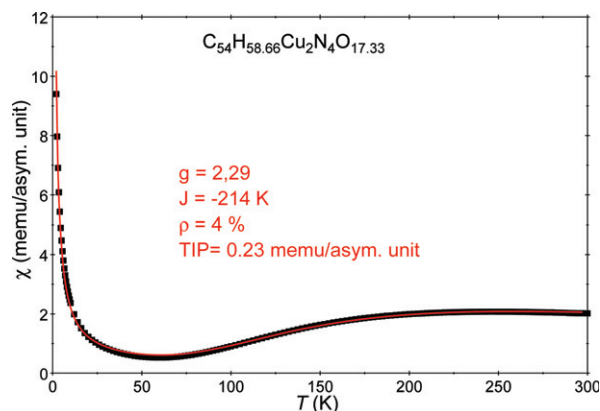


Fig. 5 Temperature-variable magnetic susceptibility of a dried sample of **1**. The red line is the best fit to the Bleaney-Bowers formula.

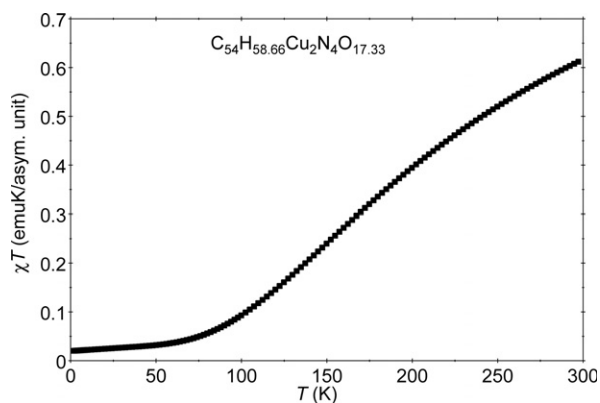


Fig. 6 Temperature variation of χT of a dried sample of 1.

Acknowledgements

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Notes and references

§ X-Ray data for 1: $C_{163}H_{156}Cu_6N_{12}O_{70}$, 3784.24 g mol⁻¹, trigonal, R_3 , $a = b = 39.7978(3)$, $c = 10.1735(2)$ Å, $Z = 3$, $V = 13954.7(3)$ Å³, $R_1/wR_2 [I > 2\sigma(I)] = 0.0579/0.0952$, Flack parameter 0.012(12). CCDC reference number 666735.

- Xiang Lin, Jinhua Jia, P. Hubberstey, M. Schröder and N. R. Champness, *CrystEngComm*, 2007, **9**, 438; Chaoying Gao, Shuxia Liu, Linhua Xie, Yuanhang Ren, Jianfang Cao and Chunyan Sun, *CrystEngComm*, 2007, **9**, 545.
- C. H. M. Amijs, G. P. M. van Klink and G. van Koten, *Dalton Trans.*, 2006, 308.
- N. P. Power, S. J. Dalgarno and J. L. Atwood, *New J. Chem.*, 2007, **31**, 17; T. K. Ronson, H. Adams and M. D. Ward, *CrystEngComm*, 2006, **8**, 497; I. M. Müller and D. Möller, *Angew. Chem., Int. Ed.*, 2005, **44**, 2969; I. M. Müller, S. Spillmann, H. Franck and R. Pietschnig, *Chem.–Eur. J.*, 2004, **10**, 2207; D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185.
- R.-D. Schnebeck, L. Randaccio, E. Zangrando and B. Lippert, *Angew. Chem., Int. Ed.*, 1998, **37**, 119; J. R. Hall, S. J. Loeb, G. K. H. Shimizu and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 1998, **37**, 121; M. A. Ali, P. V. Bernhardt, C. L. Kiem and A. H. Mirza, *Aust. J. Chem.*, 2004, **57**, 409.
- Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 2001, **123**, 980; M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 371.
- Chiral MOFs: P. Thuéry, *CrystEngComm*, 2007, **9**, 460; Zhen-Feng Chen, Shu-Feng Zhang, Hai-Sheng Luo, B. F. Abrahams and Hong Liang, *CrystEngComm*, 2007, **9**, 27.
- Chiral polygon: O. Mamula and A. von Zelewsky, *Coord. Chem. Rev.*, 2003, **242**, 87; E. Barea, J. A. R. Navarro, J. M. Salas,

- M. Quirós, M. Willermann and B. Lippert, *Chem.–Eur. J.*, 2003, **9**, 4414.
- C.-D. Wu and W. Lin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1075; B. Y. Lou, X. Huang and X. Lin, *Z. Anorg. Allg. Chem.*, 2007, **633**, 372; B. Y. Lou, R. H. Wang, D. Q. Yuan, B. L. Wu, F. L. Jiang and M. C. Hong, *Inorg. Chem. Commun.*, 2005, **8**, 971; J. Zhang, Y. Kang, R. B. Zhang, Z. J. Li, J. K. Cheng and Y. G. Yao, *CrystEngComm*, 2005, **7**, 177; V. Balamurugan and R. Mukherjee, *CrystEngComm*, 2005, **7**, 337; R. Peng, T. Wu and D. Li, *CrystEngComm*, 2005, **7**, 595; J. Weng, M. Hong, Q. Shi, R. Cao and A. S. C. Chan, *Eur. J. Inorg. Chem.*, 2002, 2553; C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431.
- M. Andruh, *Chem. Commun.*, 2007, 2565.
- A. Pichon, C. M. Fierro, M. Nieuwenhuyzen and S. L. James, *CrystEngComm*, 2007, **9**, 449.
- M. Eddaoudi, Jaheon Kim, J. B. Wachter, H. K. Chae, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 4368.
- K. Seok Jeong, S. Young Kim, Youjin Oh, D. Won Min, Jaheon Kim and N. Jeong, *CrystEngComm*, 2007, **9**, 273.
- (a) B. Wisser, Y. Lu and C. Janiak, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1189; (b) L. F. Ma, L. Y. Wang, J. G. Wang, Y. F. Wang and X. Feng, *Z. Anorg. Allg. Chem.*, 2006, **632**, 487; (c) M. Enamullah, A. Sharmin, M. Hasegawa, T. Hoshi, A.-C. Chamayou and C. Janiak, *Eur. J. Inorg. Chem.*, 2006, 2146; (d) G. Vujevic and C. Janiak, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2585.
- C. Janiak, *Dalton Trans.*, 2003, 2781.
- Terephthaloyl-bis(glycinato): G. E. Kostakis, L. Casella, N. Hadjiliadis, E. Monzani, N. Kourkoumelis and J. C. Plakatouras, *Chem. Commun.*, 2005, 3859; Hong-Tao Zhang and Xiao-Zeng You, *Acta Crystallogr., Sect. E*, 2005, **61**, m1163.
- C. S. Cleaver and B. C. Pratt, *J. Am. Chem. Soc.*, 1955, **117**, 1544.
- J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, 1953, **6**, 227.
- M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259.
- B. Kozlevčar, I. Leban, M. Petriček, O. Roubeau, J. Reedijk and P. Šegedin, *Inorg. Chim. Acta*, 2004, **357**, 4220; R. Cejudo, G. Alzuet, J. Borrás, M. Liu-González and F. Sanz-Ruiz, *Polyhedron*, 2002, **21**, 1057; V. Calvo-Pérez, A. Vega and E. Spodine, *Organometallics*, 2006, **25**, 1953; B. J. Hathaway, *Compr. Coord. Chem.*, 1996, **5**, 635.
- A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34; *PLATON Version 1.11, 31-05-07. Windows implementation*, L. J. Farrugia, University of Glasgow, Scotland, 2007.
- M. Nishio, *CrystEngComm*, 2004, **6**, 130; M. Nishio, M. Hirota and Y. Umezawa, *The CH/π Interaction*, Wiley-VCH, New York, 1998; C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann and O. M. Zippel, *Eur. J. Inorg. Chem.*, 2000, 1229.
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, 1972, 428; R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209; C. Oldham, *Compr. Coord. Chem.*, 1996, **2**, 440; J. Mroziński, *Coord. Chem. Rev.*, 2005, **249**, 2534; M. Gerloch and J. H. Harding, *Proc. R. Soc. London, Ser. A*, 1978, **A360**, 211.
- A. J. Blake, C. M. Grant, E. J. L. McInnes, F. E. Mabbs, P. E. Y. Milne, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1996, **21**, 4077.
- B. Bleaney and K. D. Bowers, *Proc. R. Soc. Lond.*, 1952, **A214**, 451.
- K. C. Dash and Ch. K. C Mohapatra, *Transition Met. Chem.*, 1977, **2**, 155.