A Self-Assembled 2D Molecule-Based Magnet: The Honeycomb Layered Material $\{Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}$**

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Research in the area of molecule-based magnets is rapidly expanding, owing, in part, to numerous breakthroughs in the past decade.[1] The preparation of solid-state architectures of varying dimensionalities from specifically tailored paramagnetic building blocks has proven to be very successful, and also clearly multidisciplinary. Materials science and supramolecular chemistry efforts have joined forces with classical organic and inorganic chemistry in the design of solid-state materials whose magnetic properties rival, and sometimes even exceed, those of classic inorganic solids.[2] The molecule-based strategy allows for the preparation of unusual materials that cannot otherwise be obtained, for example, materials that combine two or more physical properties in the same compound[3] or molecules with magnetic bistability.[4] The solid-state structures of the majority of molecule-based magnetic materials consist of extended networks of paramagnetic metal ions held in close proximity by bridging ligands that allow for magnetic exchange. The dimensionality of the system dictates the overall magnetic properties and can be controlled by the use of capping ligands[5] or templating counterions.[6]

Unfortunately, few ligands are capable of mediating sufficiently strong magnetic interactions between metal ions such that bulk magnetic ordering can occur. Apart from monoatomic ligands (such as oxide or halide bridges), the most effective bridging groups with respect to magnetic exchange interactions are cyanide,[7] dicyanamide,[8] and oxalate.[9] Common features of these ligands are that they contain only a small number of atoms, and that they offer a π as well as a σ pathway for magnetic superexchange interactions. Organic radicals have also been successfully applied

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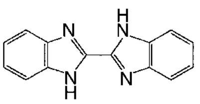
to the preparation of molecular magnets, with two of the best examples being families of metal–organic magnets based on TCNE and TCNQ.[10,11]

In our quest for new ligands to use as building blocks for new molecule-based magnets with new types of structural features, we discovered that 2,2′-bibenzimidazole (H_2bbiz, see structure) is capable of assembling homometallic structures that order ferromagnetically. This ligand and the related molecule 2,2′-biimidazole present multiple nitrogen-donor sites with the possibility of reversible protonation and deprotonation,[12] properties that have been capitalized upon in supramolecular chemistry for the preparation of multidimensional hydrogen-bonded networks.[13] The H_2bbiz molecule has also been used for the preparation of mononuclear,[14] dinuclear[15] and cyclic molecules[16] of second- and third-row metals with interesting photophysical properties, and in the preparation of models for bioinorganic systems.[17] Of more relevance to the present topic, we note that magnetic data for paramagnetic compounds of these ligands is limited to reports of a weakly antiferromagnetically coupled Ni dimer[18] and a poorly characterized magnet based on the bbiz ligand.[16a] Herein we present the synthesis, structural determination, and magnetic properties of a new molecule-based magnet based on Co^{II} ions and the $[Hbbiz]^-$ ligand.



The solvothermal reaction of $CoCl_2 \cdot x H_2O$ with H_2bbiz and KOH in a toluene/methanol mixture at 110 °C yields dark green single crystals of the title compound after several days. The structure of $\{Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2 \cdot 3\,C_7H_8 \cdot 9\,CH_3OH\}_\infty$, (**1**)[19] consists of neutral 2D layers (Figure 1) composed of octahedral units of $[Co^{II}(Hbbiz)_3]^-$ bridged by tetrahedral Co^{II} ions that are bound to the deprotonated N atoms of independent $Hbbiz^-$ ligands; Cl^- ions and water molecules complete the coordination sphere. The $[Co^{II}(Hbbiz)_3]^-$ moieties are in an octahedral environment with angles that deviate slightly from the ideal 90° (≈83° for the bite angle of the bibenzimidazole ligands) and regular Co–N bond lengths (1.92–1.95 Å). There are two crystallographically different tetrahedral sites, although the coordination environments for both sites are nearly identical, with two Cl^- ions and one water molecule being disordered over the three crystallographically unique positions. The tetrahedral sites clearly deviate from a regular tetrahedron as indicated by the different bond lengths observed for Co–N (2.01–2.03 Å) and the average Co–Cl/O separations (2.25–2.27 Å). The Cl^- ions and water molecules participate in hydrogen bonding to the remaining protons of the $Hbbiz^-$ molecules (Cl/O–N = 3.06 Å). The overall neutral framework consists of twelve-membered rings of alternating tetrahedral and octahedral Co^{II} ions, thereby creating an extended honeycomb hexagonal lattice. The three-atom bridge between metal centers leads to a short metal–metal separation of 5.79(2) Å.

Each layer is chiral, with all octahedral sites maintaining the same chirality, namely Δ or Λ. The overall structure is achiral, however, with alternating layers being of opposite chirality. The layers are offset from one other (Figure 2) in such a way that the phenyl rings point to the interstices of the cavities created by the interlocked rings in adjacent layers (≈18 Å diameter).

Magnetic susceptibility measurements carried out on 5 mg of crushed single crystals of $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2 \cdot 3\,C_7H_8 \cdot 9\,CH_3OH\}_\infty$ with an applied field of 1000 G revealed a room temperature $\chi_m T$ value of 14.2 emu K mol^{-1} (see Supporting Information). This value is higher than the

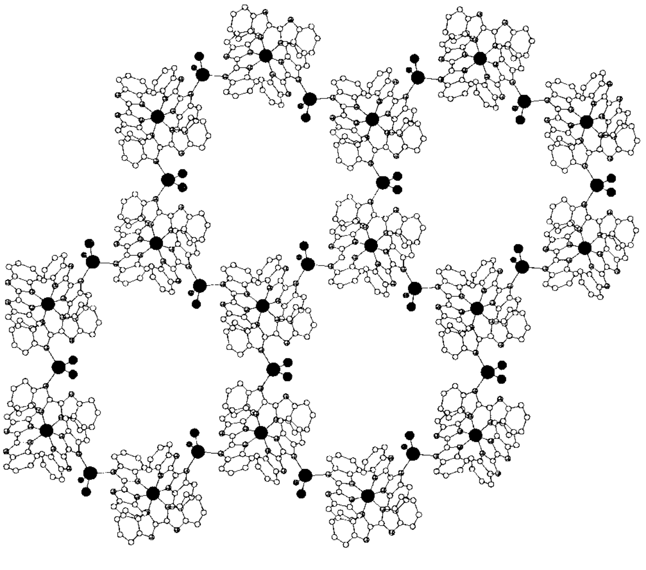


Figure 1. Top view of the 2D structure of the title compound $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}_\infty$.

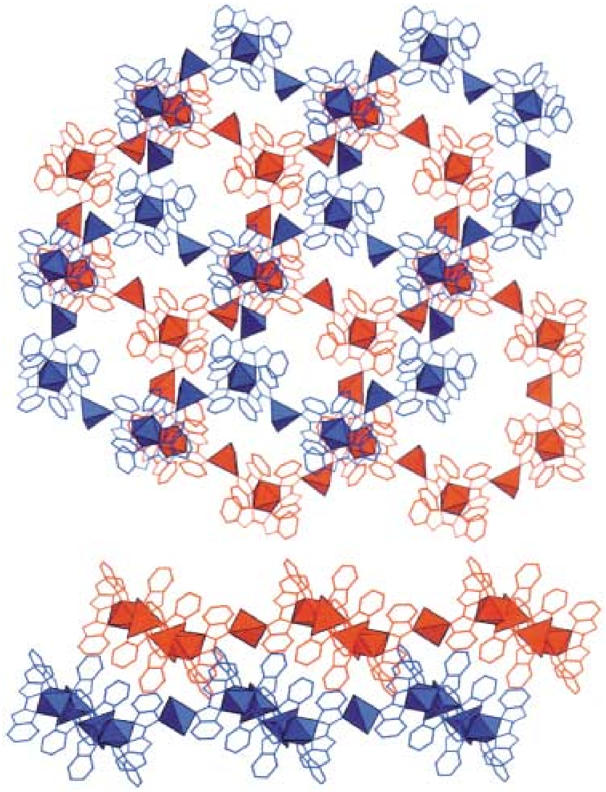


Figure 2. Top and side views of alternating layers in the title compound $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}_\infty$ showing the registry between layers.

expected spin-only value, in accordance with the well-documented orbital contribution of octahedral Co^{II} ions. Upon lowering the temperature, $\chi_m T$ decreases, a feature that can be attributed to the spin–orbit coupling of the octahedral Co^{II} sites. The $\chi_m T$ value reaches a minimum at 42 K (11.8 emu K mol^{-1}) and then rapidly increases to a maximum of 19.2 emu K mol^{-1} at 7.5 K. These features correspond to an abrupt increase in χ_m around 15 K, which is an indication of the onset of magnetic ordering. Indeed, the AC magnetic susceptibility data (Figure 3) confirm the presence of net magnetization, as the data show a peak in both the χ_m' (in-phase) and χ_m'' (out-of-phase) signals below a $T_c = 9.0$ K (T_c = Curie temperature). The position of the maxima shows negligible frequency dependence over the range 1–1000 Hz. At very low temperatures χ_m' undergoes a slight increase which could be because of the presence of a paramagnetic contribution arising from defects in the crystal structure.

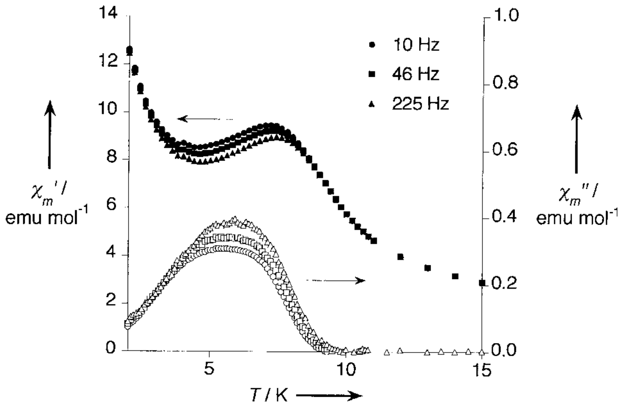


Figure 3. AC magnetic susceptibility (χ_m'; χ_m'' = out-of-phase) measurements for the title compound $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}_\infty$. T = temperature.

The magnetization of the sample at 2 K increases rapidly at low fields, with no saturation observed up to 5 T. The maximum value observed of 11.3 μ_B is lower that the expected value for a ferromagnetic ground state (~15 μ_B). The compound exhibits a hysteresis loop at 2 K (Figure 4) with a small coercive field of 155 G. These data do not allow for a precise understanding of the nature of the magnetic ordering. Based on the occupancy of the magnetic orbitals, it is reasonable to expect ferromagnetic superexchange to occur. The tetrahedral Co^{II} cations contain three unpaired electrons in the t_2 levels whereas the octahedral Co^{II} cations have one unpaired electron in a t_{2g} orbital set and two unpaired electrons in the e_g symmetry orbitals. The orthogonality of the t_2 and e_g orbitals is expected to favor ferromagnetic interactions, and, indeed, this pathway was found to dominate in compounds containing tetrahedral and octahedral Co^{II} ions,[20] although this factor depends on the relative orientation of the magnetic orbitals. If the ordering is ferromagnetic as proposed, the low saturation value for the magnetization is expected to be a consequence of the magnetic anisotropy of the octahedral Co^{II} ions in conjunction with strong spin canting within the layers which are noncentrosymetric. The structure of the magnet is quite complex, a fact that leads to questions about the exact dimensionality of the magnetic interactions in this system. Without pathways for magnetic exchange between the layers, the magnetic ordering could be quasi-2D.

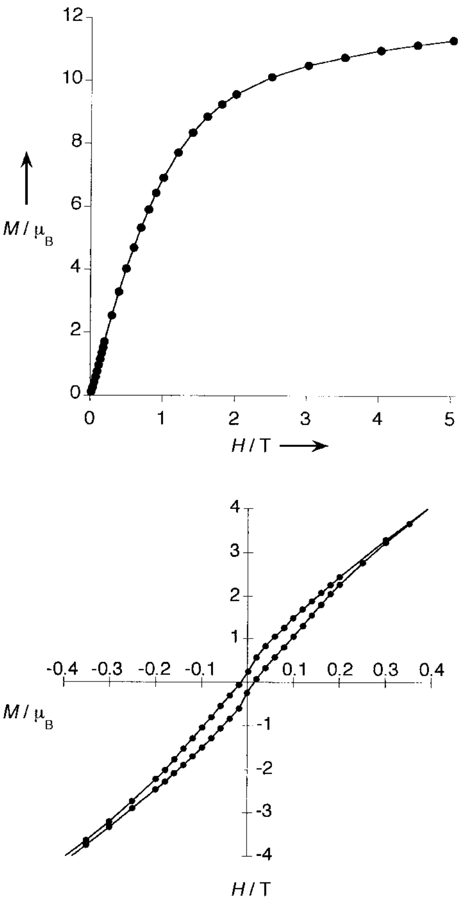


Figure 4. Field dependence of the magnetization (M; top) and hysteresis loop (bottom) at 2 K for the title compound $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}_\infty$. H = magnetic field strength.

The possibility of antiferromagnetic exchange, and ferrimagnetic ordering, seems less plausible than ferromagnetic interactions. In these cases, the three tetrahedral Co^{II} ions would align in an antiparallel fashion with the two octahedral Co^{II} cations. This situation would lead to very low magnetization values (~3 μ_B per one net Co^{II} atom which is far from the 11.3 μ_B observed at 5 T), and the slope would also be less steep owing to the field working against the antiferromagnetic interactions in the solid. In any case, to determine the sign of the magnetic exchange, either a model dimer compound or neutron diffraction studies will be needed.

In conclusion, $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2\}_\infty$ is the first molecule-based magnet of the 2,2′-bibenzimidazole ligand. The fact that the compound contains only one type of metal ion is important, as it represents a new strategy for preparing a family of magnetic materials with different paramagnetic transition metals. Preliminary data indicate that other homometallic compounds exhibit magnetic ordering as well, with critical temperatures as high as 40 K for the Mn^{II} derivative. The possibility of fully deprotonating the ligand is being contemplated as a means to produce additional novel architectures. Finally, it is noted that bimetallic networks should also be possible to prepare with this ligand, and these may prove to have even more interesting magnetic properties such as higher ordering temperatures, higher remnant magnetization and larger coercivities.

Experimental Section

The ligand 1,10-bibenzimidazole (H_2bbiz) was prepared according to a literature procedure.[21] $CoCl_2 \cdot 6\,H_2O$ (1 g, 4.2 mmol), H_2bbiz (0.09 g, 0.4 mmol) and KOH (0.2 g, 3.5 mmol) were suspended in a mixture of methanol (30 mL) and toluene (50 mL), and placed in a sealed teflon vessel. The suspension was heated to 110 °C under autogeneous pressure. After seven days, chunky prismatic dark green crystals of $\{[Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2 \cdot 3\,C_7H_8 \cdot 9\,CH_3OH\}_\infty$ (**1**), were removed by filtration, washed with methanol and water, and dried in air. Elemental analysis for $C_{114}H_{118}Cl_4Co_5N_{24}O_{11}$: calcd: C 56.19, H 4.88, N 13.80; found: C 56.12, H 4.88, N 13.83.

CCDC-191616 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[1] "Magnetism: A Supramolecular Function": *NATO ASI Ser. C* **1996**, *484*.

[2] *MRS Bull.* **2000**, 21–71 special issue Eds.: J. S. Miller, A. J. Epstein).

[3] a) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García,, V. Laukhin, *Nature* **2000**, *408*, 447–449; b) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704–705; c) K. Awaga, E. Coronado, M. Drillon, *MRS Bull.* **2000**, 52–57.

[4] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141–143;b) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301–317.

[5] a) M. Ohba, H. Okawa, *Coord. Chem. Rev.* **2000**, *198*, 313–328; b) J. A. Smith, J. R. Galán-Mascarós, R. Clérac, K. R. Dunbar, *Chem. Commun.* **2000**, 1077–1078; c) H. Z. Kou, S. Gao, B. Q. Ma, D. Z. Liao, *Chem. Commun.* **2000**, 1309–1310; d) F. Bellouard, M. Clemente-León, E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, F. Romero, K. R. Dunbar, *Eur. J. Inorg. Chem.* **2002**, 1603–1606; e) E. Colacio, M. Ghazi, H. Stoeckli-Evans, F. Lloret, C. Perez, *Inorg. Chem.* **2001**, *40*, 4876–4883.

[6] a) M. Pilkington, M. Gross, P. Franz, M. Biner, S. Decurtins, H. Stockli-Evans, A. Neels, *J. Solid State Chem.* **2001**, *159*, 262–267; b) E. Coronado, M. Clemente-León, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, E. Martínes-Ferrero, *J. Chem. Soc. Dalton Trans.* **2000**, 3955–3961.

[7] a) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283–391; b) W. R. Entley, G. S. Girolami, *Inorg. Chem.* **1994**, *33*, 5156–5166; c) S. Ferlay, T. Mallah, R. Ouahés, P. Veillet, N. Verdaguer, *Nature* **1995**, *378*, 701–703.

[8] a) M. Kurmoo, C. J. Kepert, *New J. Chem.* **1998**, *22*, 1515–1524; b) J. L. Manson, C. R. Kmety, Q. Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein, J. S. Miller, *Chem. Mater.* **1998**, *10*, 2552–2560; c) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.* **1998**, 439–440.

[9] a) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, J. M. Martínez-Agudo, *Inorg. Chem.* **2001**, *40*, 113–120; b) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, J. Ensling, P. Gütlich, *Chem. Eur. J.* **2000**, *6*, 552–563; c) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwan, Y. Hashimoto, H. Okawa, *J. Am. Chem. Soc.* **1992**, *114*, 6974–6979.

[10] a) J. S. Miller, A. J. Epstein, *Angew. Chem.* **1994**, *106*, 399–432; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385–415; b) J. Zhang, J. Ensling, V. Ksenofontov, P. Gütlich, A. J. Epstein, J. S. Miller, *Angew. Chem.* **1998**, *110*, 676–679; *Angew. Chem. Int. Ed.* **1998**, *37*, 657–660; c) G. T. Yee, J. M. Manriquez, D. Dixon, R. S. McLean, D. M. Groski, R. B. Flippen, K. S. Narayan, A. J. Epstein, J. S. Miller, *Adv. Mater.* **1991**, *3*, 309–311.

[11] a) "Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets": K. R. Dunbar, J. Cowen, H. Zhao, R. A. Heintz, X. Ouyang, G. Grandinetti, *NATO ASI Ser. Ser. C* **1999**, *518*,353; b) J. Cowen, R. Clérac, R. A. Heintz, S. A. O'Kane, X. Ouyang, H. Zhao, K. R. Dunbar, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1999**, *334*, 825–844; c) S. A. O'Kane, R. Clérac, H. Zhao, X. Ouyang, J. R. Galán-Mascarós, R. Heintz, K. R. Dunbar, *J. Solid State Chem.* **2000**, *152*, 159–173.

[12] T. Akutagawa, G. Saito, M. Kusunoki, K. Sakaguchi, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2487–2511.

[13] a) M. Tadokoro, K. Nakasuji, *Coord. Chem. Rev.* **2000**, *198*, 205–218; b) M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro, K. Nakasuji, *Angew. Chem.* **1999**, *111*, 102–106; *Angew. Chem. Int. Ed.* **1999**, *38*, 95–98; c) M. Tadokoro, T. Shiomi, K. Isobe, K. Nakasuji, *Inorg. Chem.* **2001**, *40*, 5476–5478; d) C. A. Hester, R. G. Baughman, H. L. Collier, *Polyhedron* **1997**, *16*, 2893–2895.

[14] a) S. Rau, T. Büttner, C. Temme, M. Ruben, H. Görls, D. Walther, M. Duati, S. Fanni, J. G. Vos, *Inorg. Chem.* **2000**, *39*, 1621–1624; b) M. Leirer, G. Knör, A. Vogler, *Inorg. Chim. Acta* **1999**, *288*, 150–153; c) O. F. Danzeisen, M. Goanta, H. W. Rotter, G. Thiele, *Inorg. Chim. Acta* **1999**, *287*, 218–222.

[15] P. Majundar, S.-M. Peng, S. Goswami, *J. Chem. Soc. Dalton Trans.* **1998**, 1569–1574.

[16] K. D. Benkstein, J. T. Hupp, C. L. Stern, *Angew. Chem.* **2000**, *112*, 3013–3015; *Angew. Chem. Int. Ed.* **2000**, *39*, 2891–2893.

[17] a) M. A. Martinez-Lorente, F. Dahan, Y. Sanakis, V. Petrouleas, A. Bousseksou, J.-P. Tuchagues, *Inorg. Chem.* **1995**, *34*, 5346–5357; b) D. Boinnnard, P. Cassoux, V. Petrouleas, J.-M. Savariault, J.-P. Tuchagues, *Inorg. Chem.* **1990**, *29*, 4114–4122.

[18] M. Tadokoro, K. Sato, D. Shiomi, T. Takui, K. Itoh, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1997**, *306*, 49–56.

[19] Crystal data for **1**: $C_{114}H_{118}Cl_4Co_5N_{24}O_{11}$, $M_r = 2436.77\ \mathrm{g\,mol^{-1}}$, monoclinic, space group $C2/c$, $a = 32.4150(5)$, $b = 18.8240(7)$, $c = 20.4850$ Å, $\beta = 127.8221(13)°$, $V = 9873.6(6)$ Å^3; $Z = 4$; $\rho_{calc} = 1.639\ \mathrm{g\,cm^{-3}}$; $2\theta_{max} = 42°$; $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å; $T = 293(2)$ K; 36176 reflections, of which 5266 are unique, and of which 3503 were included in the refinement ($I > 4\sigma$); solution by direct methods (SIR97, A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119) and refinement on F^2 by full-matrix least squares procedure (SHELXL-97, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **1997**); 356 parameters; all C, N, H and disordered solvent atoms were refined isotropically; H atoms from the monoprotronated Hbbiz ligands were found after successive Fourier transform cycles and refined with the restriction of maintaining a constant distance to the N atom they are bonded; all other H atoms were included in their calculated positions, except in disordered solvent molecules; disordered solvent molecules were assigned partial occupancy

factors, and their positions restrained to maintain typical distances and shapes for toluene or methanol molecules; final values R $(F) = 0.0592$, R_w $(F^2) = 0.1423$.

[20] a) H. Kimagai, M. Ohba, K. Inoue, H. Okawa, *Chem. Lett.* **2002**, 1006 – 1007.

[21] M. C. Rezende, C. A. Marques, E. L. Dall'Oglio, C. Zucco, *Liebigs Ann.* **1997**, 925 – 929.