

An Unstable Ligand-Unsupported Cu^I Dimer Stabilized in a Supramolecular Framework**

Shao-Liang Zheng,* Marc Messerschmidt, and Philip Coppens*

The attractive interactions that exist between d¹⁰ “closed-shell” elements of Group 11 have received extensive attention.^[1,2] The term “aurophilicity” has been coined to describe the Au^I–Au^I bonding interactions that are evident in many molecular and solid-state structures and have been attributed to correlation and relativistic effects.^[3] However, relativistic effects cannot be invoked for Cu^I⋯Cu^I interactions, which are generally referred to as “cuprophilicity”. These interactions are found in inorganic lattices, polynuclear compounds with bridging ligands^[2] or stabilized by electrostatic interactions,^[4] and polymeric systems, such as infinite ⋯Cu–ligand–Cu⋯ chains with short sideways Cu^I⋯Cu^I interactions.^[5] The existence of ligand-bridged Cu^I⋯Cu^I interactions is supported by spectral evidence^[6] and has been examined by a series of theoretical calculations, which have sometimes reached different conclusions.^[7] However, a recent comprehensive analysis^[8] has shown that only a small part of the intermolecular interaction energy is often gained in the ground state from the Cu^I⋯Cu^I interaction, whereas a large component results from Cu^I⋯ligand interactions, even in the case of ligand-unsupported Cu^I⋯Cu^I species.

Only a few examples of ligand-unsupported Cu^I aggregates have been described, most of which have been reported quite recently. These examples include the dimer of trimers based on a substituted pyrazolate,^[9] the dimer of dimers with a substituted phenanthroline/bipyridyl ligand,^[10] the infinite arrays of [Cu(*t*Bu)(CN)Li(OEt₂)₂], in which neighboring Cu^I dimers are connected through Li⁺ ions;^[11] the one- and three-dimensional infinite arrays of Cu^I ions in [Cu(NH₃)₂]Br and [Cu(NH₃)Cl], respectively;^[12] the one-dimensional chains of Cu^I atoms in [Cu(C₆F₆)(py)] (py = pyridine),^[13] and the [(CuCl₂)₂]²⁻ dimer cocrystallized with the monomeric [CuCl₃]⁻ ion and with amidinium cations.^[14] Except for the [(CuCl₂)₂]²⁻ dimer, all the ligand-unsupported Cu^I dimers (“dimer” refers to two Cu^I fragments with a short Cu^I⋯Cu^I distance) form one-dimensional infinite Cu^I⋯Cu^I or π–π-stacked chains.

[*] Dr. S.-L. Zheng, Dr. M. Messerschmidt, Prof. Dr. P. Coppens
Department of Chemistry
State University of New York at Buffalo
Buffalo, NY 14260–3000 (USA)
Fax: (+1) 716-645-6948
E-mail: coppens@buffalo.edu

[**] This work was supported by the Petroleum Research Fund of the American Chemical Society (PRF32638AC3) and the National Science Foundation (CHE0236317). The authors thank Dr. Irina Novozhilova and Dr. Anatoliy Volkov for help with the theoretical calculations.



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

Much stronger d^{10} metal–metal bonding with a possible formal metal–metal single bond has been predicted to exist in the electronically excited state of $[\text{Ag}(\text{CN})_2^-]_n$.^[15] The recently developed method of time-resolved (TR) diffraction allows experimental confirmation of such predictions.^[16] A recent TR diffraction experiment on trimeric $[\text{Cu}[\text{3,5}-(\text{CF}_3)_2\text{pyrazolate}]]_3$ at 17 K indeed shows a strong contraction of one of the intermolecular $\text{Cu}^{\cdot\cdot}\text{Cu}'$ distances in the one-dimensional infinite chains, thus leading to the formation of an excimer with a lifetime of 52 μs .^[17] The systematic luminescence investigations of a series of substituted Cu/pyrazolate trimers showed that the lifetime and wavelength of the luminescence emission were strongly dependent on the temperature and the wavelength of the excitation,^[18] thus suggesting the possible population of different excited states at different temperatures.

Supramolecular host matrices provide a well-defined environment in which the encapsulated luminescent guest molecules may occur in different states of aggregation and orientation relative to their environment, thus offering an attractive possibility for isolating photoactive molecular species in a dilute yet crystalline environment.^[19] For example, we have shown recently that the xanthone molecule occurs as a monomer and as a dimer in two crystalline resorcinarene-based inclusion complexes and results in significant variation of its spectral properties.^[20] On excitation, the xanthone dimer forms a phosphorescing excimer.^[21] Its geometry has been determined by TR diffraction methods.^[22]

The ligand-unsupported $[\{\text{Ag}(\text{NH}_3)_2\}_2]^{2+}$ ion has been trapped in a polymeric silver(I) hexamethylenetetramine coordination framework,^[23] thus suggesting that a favorable supramolecular system may give rise to a discrete ligand-unsupported Cu' dimer with the monodentate ammonia ligand. As part of our investigations of well-defined excimers in supramolecular environments,^[24] we isolated the analogous Cu' species in a supramolecular framework composed of tris(hydroxyphenyl)ethane anions (H_2THPE ; see the Supporting Information). This structure led to a solid with the composition $[\{\text{Cu}(\text{NH}_3)_2\}_2][\text{H}_2\text{THPE}]_2 \cdot 3.25\text{H}_2\text{O}$ (**1**), in which no photoactive molecules other than the Cu' dimer were present, thus simplifying a future TR diffraction analysis.

X-ray diffraction studies^[25] show that crystals of **1** contain two crystallographically independent H_2THPE anions connected by hydrogen-bonding interactions (Figure 1; see also the Supporting Information). The dimeric unit is further linked by hydrogen bonds to its center-of-symmetry related equivalent (symmetry code: $-x+2, -y, -z+1$) which extends into a two-dimensional wavy hydrogen-bonded layer ($\text{O}\cdots\text{O}$: 2.435(3)–2.593(4) Å; see the Supporting Information) parallel to the (011) plane. The wavy layer contains square-shaped channels (effective dimension: 2.1×2.1 Å), which constitute 4.8% of the crystal volume and run along the a axis.^[26] Adjacent hydrogen-bonded layers are juxtaposed along the b axis, so as to leave larger channels with an effective cross-section of 5.90 Å (again parallel to the a axis), and account for 17.6% of the crystal volume.

Each of the larger channels contains two crystallographically independent Cu' centers in proximity in each unit cell. Each Cu' center is ligated by two nitrogen atoms from

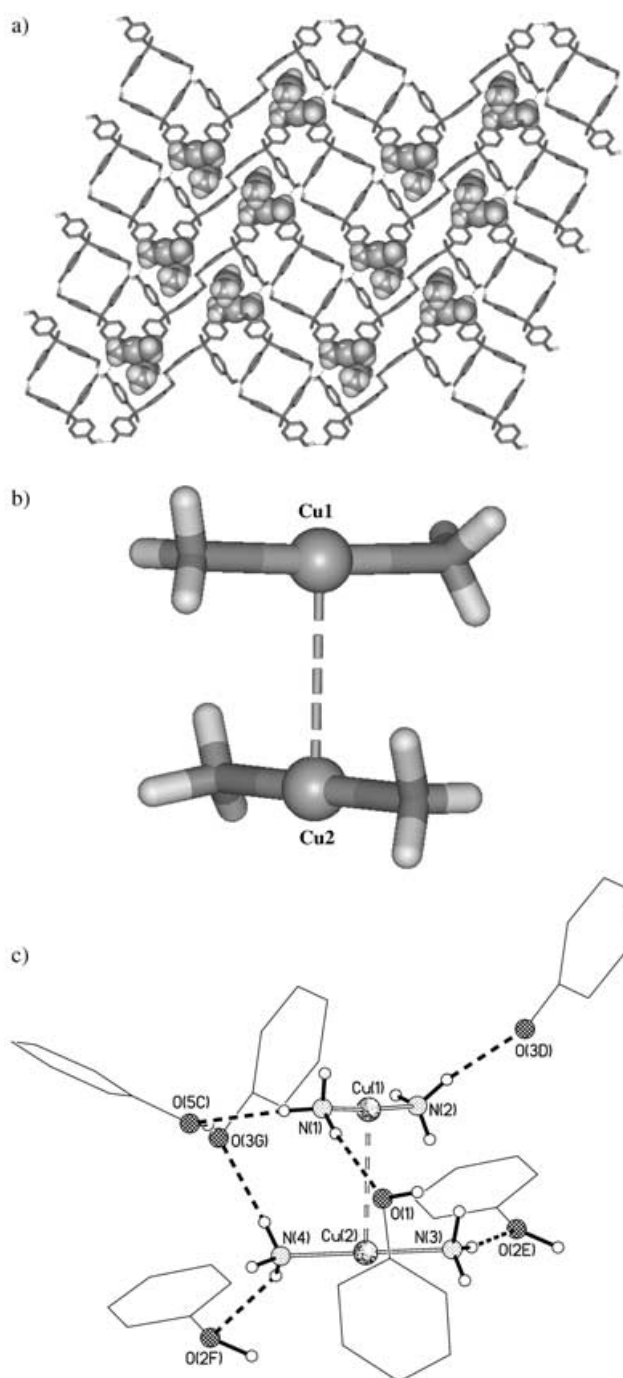


Figure 1. a) Three-dimensional supramolecular architecture of **1** viewed along the a axis, b) discrete dimeric $[\{\text{Cu}(\text{NH}_3)_2\}_2]^{2+}$ species in **1**, and c) the $[\{\text{Cu}(\text{NH}_3)_2\}_2]^{2+}$ species trapped in the supramolecular framework (selected distances [Å]: N(1)–O(5C) 2.968(4), N(1)–O(1) 3.185(4), N(2)–O(3D) 2.850(3), N(3)–O(2E) 2.996(4), N(4)–O(2F) 3.258(4), N(4)–O(3G) 2.889(4); see the Supporting Information. The water molecules included in the lattice are omitted for clarity.)

ammonia (Cu–N: 1.886(3)–1.892(3) Å, N–Cu–N: 176.3(1) and 177.3(2)°; see the Supporting Information). The Cu' centers are separated by only 3.0248 Å with N–Cu–Cu–N torsion angles of 73.2(2) and 77.6(2)° for the two cations, respectively (see the Supporting Information). As the $\text{Cu}'\cdots\text{Cu}'$ distance is within the range reported for ligand-

unsupported Cu^I...Cu^I separations (2.71–3.60 Å),^[9–14] the complex can be described as a novel dimeric $[[\text{Cu}(\text{NH}_3)_2]_2]^{2+}$ species. The ammonia ligands act as donors in hydrogen-bonding interactions with the oxygen atoms of the hydroxy groups in the adjacent H₂THPE anions (N...O: 2.850(3)–3.258(4) Å; Figure 1c), so that the supramolecular framework provides support and allows the dimeric $[[\text{Cu}(\text{NH}_3)_2]_2]^{2+}$ species to exist. One fully ordered water molecule is clathrated in each larger channel to fill the gap left between the Cu^I dimers. The water molecules form hydrogen-bonding interactions with the oxygen atom of the hydroxy group (O(1W)-H...O: 2.772(1) Å) of the host network. The smaller square-shaped channels are occupied by disordered water molecules.

The molecular dilution of the $[[\text{Cu}(\text{NH}_3)_2]_2]^{2+}$ species trapped in the supramolecular framework is pronounced: its concentration is 1.75 mol L⁻¹ for **1**, relative to 7.35 mol L⁻¹ for two $[\text{Cu}(\text{NH}_3)_2]^+$ ions in $[\text{Cu}(\text{NH}_3)_2]\text{Br}$ crystals.^[12] The Cu^I...Cu^I distance is slightly longer than that found in the one-dimensional infinite $[\text{Cu}(\text{NH}_3)_2]^+$ chains (2.93 Å) in $[\text{Cu}(\text{NH}_3)_2]\text{Br}$.^[12]

Molecular-orbital calculations were performed with the X-ray geometry of the $[[\text{Cu}(\text{NH}_3)_2]_2]^{2+}$ dimer to gain insight into the Cu^I...Cu^I interactions in the dimer. An intermolecular perturbation theory (IMPT)^[27] calculation indicates that the Cu^I dimer with the geometry found in crystals of **1** is less stable by 309.1 kJ mol⁻¹ than the isolated monomers.^[28] Variation of the Cu^I...Cu^I distance shows no local minimum with the observed configuration (see the Supporting Information), thus suggesting that such a dimer is unlikely to occur in solution. Nevertheless, it can be stabilized in the supramolecular environment, as is evident from the crystal structure of **1**. Bimolecular Cu^I...Cu^I aggregates that have like charges have been calculated to be repulsive.^[8] In the ground state, often only a small part of the intermolecular interaction energy gained results from the direct Cu^I...Cu^I interaction, whereas a large component of this energy results from Cu^I...ligand interactions. In accordance with the calculations reported by Carvajal et al., the IMPT calculations show that the electrostatic repulsion, which is purely Coulombic in origin, is dominant in the current case (311.8 kJ mol⁻¹; see the Supporting Information). Nevertheless, the orbital interactions, including induction, charge transfer, and dispersion, are stabilized by -27.2 kJ mol⁻¹ and so fall into the range of cuprophilic interactions estimated from spectroscopic or theoretical studies.^[6–8] The results of the DFT calculations indicate that the HOMO-1 (HOMO = highest occupied molecular orbital) is a Cu^I...Cu^I σ bonding molecular orbital, the HOMO is a Cu^I...Cu^I σ antibonding molecular orbital, and the lowest unoccupied molecular orbital (LUMO) has Cu^I...Cu^I bonding character with 4d, 5s, and 5p contributions from the Cu^I center (Figure 2). The Mayer bond order^[17,29] of the Cu^I...Cu^I interaction is calculated to be 0.187 (see the Supporting Information), which is in agreement with the IMPT analysis and shows the orbital interactions to be weakly attractive.

Optimization of the excited triplet state results in a shorter Cu^I...Cu^I distance of 2.6 Å (see the Supporting Information), which indicates a much stronger metal–metal

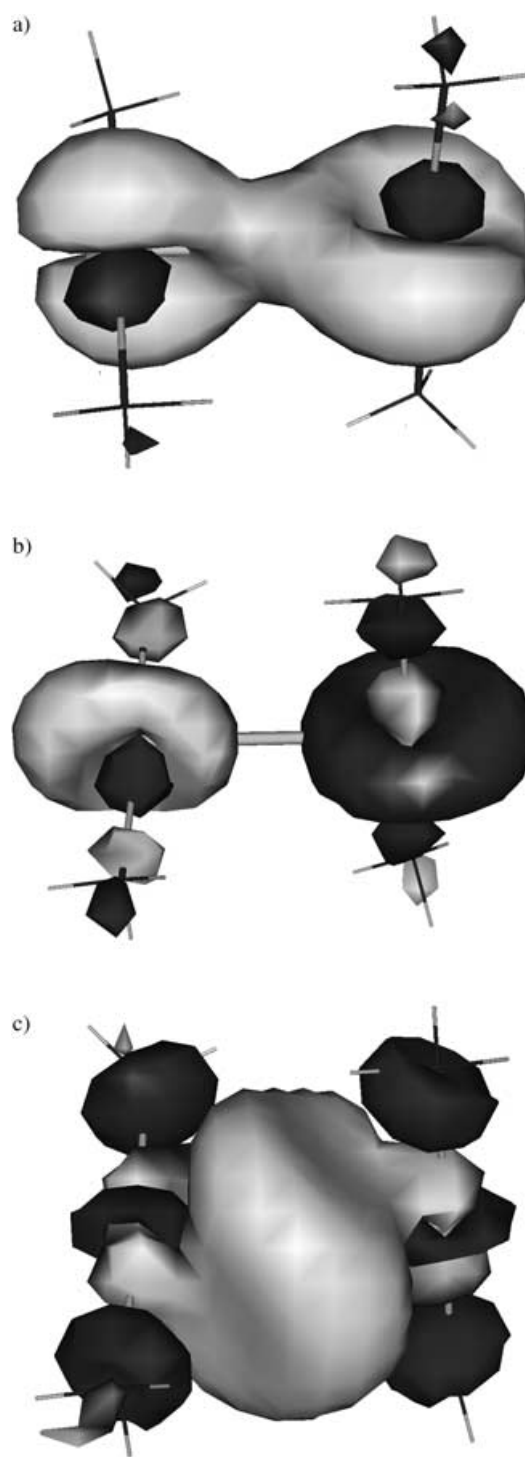


Figure 2. Contour plots (isosurfaces at ± 0.04 au) of the frontier molecular orbitals of the $[[\text{Cu}(\text{NH}_3)_2]_2]^{2+}$ species: a) HOMO-1, b) HOMO, and c) LUMO.

bonding interaction on population of the Cu^I...Cu^I bonding LUMO (Figure 2). Emission measurements show an intense photoluminescence at 17 K with emission at 495 nm and a lifetime of approximately 4.2 μs, thus indicating that crystals of **1** may be suitable for TR diffraction studies.^[19]

In summary, a ligand-unsupported Cu^I dimer that is unstable by itself is stabilized in the cavities of a supramolec-

ular framework to give **1**, thus offering the opportunity for systematic studies of the ground state of a Cu^I dimer with weak cuprophilicity and of its excited state by the use of TR diffraction methods. Analysis of the isolated dimeric species eliminates effects that occur in infinite chains of species linked through Cu^I...Cu^I interactions and provides the background needed for analysis of more complicated systems.

Experimental Section

1: Freshly prepared Cu(OH)₂ (0.5 mmol), H₃THPE (0.5 mmol), aqueous ammonia (25%, 2.0 mL), and toluene (2 mL) were sealed in a 6-mL pyrex glass tube. The tube was maintained at 160 °C for 40 h and then cooled to room temperature over 2 days. Pale-yellow needle-shaped crystals appeared during the cooling period.

CCDC-267412 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).

Received: March 31, 2005

Keywords: copper · density functional calculations · host–guest systems · metal–metal interactions

- [1] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, *24*, 391–400.
- [2] a) P. D. Harvey, *Coord. Chem. Rev.* **1996**, *153*, 175–198; b) P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563–594; c) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636.
- [3] P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512–4557; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456, and references therein.
- [4] J. M. Poble, M. Benard, *Chem. Commun.* **1998**, *11*, 1179–1180.
- [5] For example, see: a) K. Jin, X. Huang, L. Pang, J. Li, A. Appel, S. Wherland, *Chem. Commun.* **2002**, 2872–2873; b) X.-C. Huang, J.-P. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 13218–13219.
- [6] a) C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *Angew. Chem.* **2000**, *112*, 4250–4254; *Angew. Chem. Int. Ed.* **2000**, *39*, 4084–4088; b) D. L. Phillips, C.-M. Che, K.-H. Leung, Z. Mao, M.-C. Tse, *Coord. Chem. Rev.* DOI: 10.1016/j.ccr.2004.09.015, and references therein.
- [7] For example, see: a) F. A. Cotton, X. Feng, M. Matusz, R. Poli, *J. Am. Chem. Soc.* **1988**, *110*, 7077–7083; b) H. L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* **2001**, *7*, 5333–5342; c) L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006–1013; d) E. O'Grady, N. Kaltsoyannis, *Phys. Chem. Chem. Phys.* **2004**, *6*, 680–687.
- [8] M. A. Carvajal, S. Alvarez, J. J. Novoa, *Chem. Eur. J.* **2004**, *10*, 2117–2132.
- [9] a) K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 2942–2943; b) M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, J. Trotter, *Can. J. Chem.* **1990**, *68*, 1444–1449; c) H. V. R. Dias, S. A. Polach, Z. Wang, *J. Fluorine Chem.* **2000**, *103*, 163–169; d) H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072–12073.
- [10] a) X.-M. Zhang, M.-L. Tong, M.-L. Gong, H.-K. Lee, L. Luo, K.-F. Li, Y.-X. Tong, X.-M. Chen, *Chem. Eur. J.* **2002**, *8*, 3187–3194; b) J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Ling, X.-M. Chen, *Chem. Eur. J.* **2005**, *11*, 552–561.
- [11] G. Boche, F. Bosold, M. Marsch, K. Harms, *Angew. Chem.* **1998**, *110*, 1779–1781; *Angew. Chem. Int. Ed.* **1998**, *37*, 1684–1686.
- [12] G. Margraf, J. W. Bats, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* **2003**, 956–957.
- [13] A. Sundararaman, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Chem. Commun.* **2005**, 1708–1710.
- [14] R. D. Kön, G. Seifert, Z. Pan, M. F. Mahon, G. Kociok-Kön, *Angew. Chem.* **2003**, *115*, 818–821; *Angew. Chem. Int. Ed.* **2003**, *42*, 793–796.
- [15] a) M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **1998**, *120*, 7696–7705; b) H. H. Patterson, S. M. Kanan, M. A. Omary, *Coord. Chem. Rev.* **2000**, *208*, 227–241, and references therein.
- [16] P. Coppens, O. Gerlits, I. I. Vorontsov, A. Yu. Kovalevsky, Y.-S. Chen, T. Graber, I. V. Novozhilova, *Chem. Commun.* **2004**, 2144–2145; P. Coppens, I. I. Vorontsov, T. Graber, M. Gembecky, A. Yu. Kovalevsky, *Acta Crystallogr. A* **2005**, *61*, 162–172, and references therein.
- [17] P. Coppens, I. I. Vorontsov, A. Yu. Kovalevsky, Y.-S. Chen, T. Graber, I. V. Novozhilova, *Phys. Rev. Lett.* **2005**, *94*, 193003.
- [18] a) H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072–12073; b) H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary, M. A. Omary, *J. Am. Chem. Soc.* **2005**, *127*, 7489–7501.
- [19] P. Coppens, B.-Q. Ma, O. Gerlits, Y. Zhang, P. Kulshrestha, *CrystEngComm* **2002**, *4*, 302–309.
- [20] S.-L. Zheng, P. Coppens, *Chem. Eur. J.* **2005**, *11*, 3583–3590.
- [21] N. N. Barashkov, T. V. Sakhno, R. N. Nurmukhanmetov, O. V. Khakel', *Uspekhi Khimii* **1993**, *62*, 579–593; *Russ. Chem. Rev.* **1993**, *62*, 539–552, and references therein.
- [22] S.-L. Zheng, M. Gembecky, I. Vorontsov, T. Graber, M. Messerschmidt, P. Dominiak, P. Coppens, unpublished results.
- [23] S.-L. Zheng, M.-L. Tong, X.-M. Chen, S. W. Ng, *J. Chem. Soc. Dalton Trans.* **2002**, 360–364.
- [24] S.-L. Zheng, P. Coppens, *Cryst. Growth Des.*, submitted.
- [25] Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 6.8426(3)$, $b = 12.0173(5)$, $c = 23.859(1)$ Å, $\alpha = 78.507(1)$, $\beta = 89.118(1)$, $\gamma = 79.825(1)^\circ$, $U = 1892.0(1)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.517$ g cm⁻³, $\text{Mo}_{\text{K}\alpha} = 0.71073$ Å, $R_1 = 0.0437$, $wR_2 = 0.1262$, GOF = 1.050 (see the Supporting Information).
- [26] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2003**.
- [27] a) I. C. Hayes, A. J. Stone, *Mol. Phys.* **1984**, *53*, 83–105; b) A. J. Stone, *The Theory of Intermolecular Forces*, Clarendon, Oxford, **1996**.
- [28] Similar values of 305.7 and 242.1 kJ mol⁻¹ are obtained with MP2 BSSE correlation calculations in GAUSSIAN03 and with DFT calculations in Amsterdam Density Functional Program (ADF), respectively.
- [29] a) I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270–274; b) I. Mayer, *Int. J. Quantum Chem.* **1984**, *26*, 151–154; c) A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095–2108.