

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### Synthesis and structural characterization of a Cu(II) complex with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT)

Ali Akbar Soudi<sup>a</sup>; Farzin Marandi<sup>a</sup>; Ali Morsali<sup>b</sup>; Rhett Kempe<sup>c</sup>; Ivonne Hertle<sup>c</sup>

<sup>a</sup> Department of Chemistry, Zanjan University, Zanjan, Iran <sup>b</sup> Department of Chemistry, School of Sciences, Tarbiat Modarres University, Tehran, Iran <sup>c</sup> Lehrstuhl Anorganische Chemie II, Universitaet Bayreuth, 95440 Bayreuth, Germany

**To cite this Article** Soudi, Ali Akbar , Marandi, Farzin , Morsali, Ali , Kempe, Rhett and Hertle, Ivonne(2005) 'Synthesis and structural characterization of a Cu(II) complex with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT)', Journal of Coordination Chemistry, 58: 17, 1631 – 1637

**To link to this Article:** DOI: 10.1080/00958970500262130

**URL:** <http://dx.doi.org/10.1080/00958970500262130>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Synthesis and structural characterization of a Cu(II) complex with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT)

ALI AKBAR SOUDI†, FARZIN MARANDI†, ALI MORSALI\*‡, RHETT KEMPE§ and IVONNE HERTLE§

†Department of Chemistry, Zanjan University,  
PO Box 45195-313, Zanjan, Iran

‡Department of Chemistry, School of Sciences,  
Tarbiat Modarres University, PO Box 14155-4838, Tehran, Iran

§Lehrstuhl Anorganische Chemie II, Universitaet Bayreuth,  
95440 Bayreuth, Germany

(Received 29 November 2004; revised 14 February 2005; in final form 2 July 2005)

Reaction between Cu(II) perchlorate and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT) ligand in ethanol produced  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$ . This compound has been characterized by UV/VIS, IR and CHN analysis. The structure of  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$  has been solved by X-ray crystallography. The coordination environment around the Cu(II) may be described as distorted octahedral in which two  $\text{ClO}_4^-$  anions in the complex are coordinated, occupying *trans* positions.

**Keywords:** 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine; X-ray crystal structure; Cu(II)

### 1. Introduction

Research on coordination chemistry of triazine-derived ligands has progressed very rapidly over the last two decades [1–14]. The 1,2,4-triazine compounds are well-known in natural materials and show interesting biological, pharmacological and medicinal properties. The 3,5,6-trisubstituted-1,2,4-triazines are a principal class of N-donor heterocyclic ligands. Some can be active as blood platelet aggregation inhibitors and others exhibit antiviral inhibitory activity, significant activity towards leukaemia and ovarian cancer, and anti-HIV activity [1–4]. In this work, we describe the synthesis and characterization of a new Cu(II) complex with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine ligand and the X-ray crystal structure analysis of  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$ . The general structure of the ligand can be found as PDPT in figure 1. This ligand is also interesting because of the different coordination modes.

\*Corresponding author. Email: morsali\_a@yahoo.com

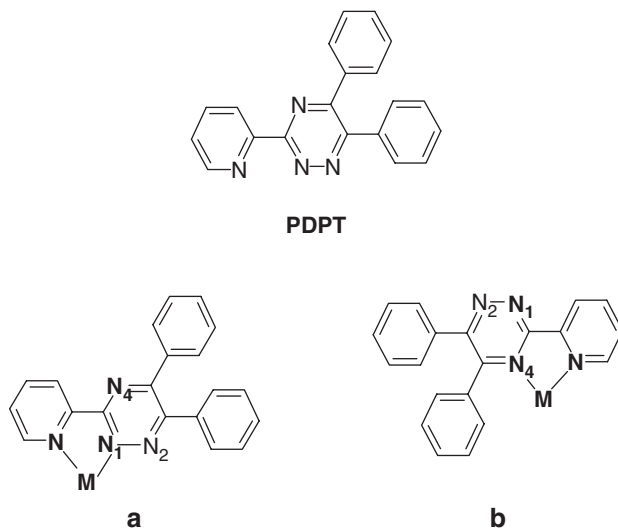


Figure 1. The general structure of the PDPT ligand and its modes of coordination.

The presence of a triazine nitrogen adjacent to the pyridyl group helps the PDPT ligand bind to a metal ion in a bidentate fashion forming one five-membered chelate ring either through N1-bonding (figure 1a) or through N3-bonding (figure 1b).

## 2. Experimental

### 2.1. Physical measurements

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- RAPID.

### 2.2. Preparation of [Cu(PDPT)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]

A blue solution of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (148 mg, 0.40 mmol) in EtOH (10 ml) was added dropwise to a refluxing yellow solution of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT) (248 mg, 0.80 mmol) in EtOH (40 ml). Halfway through the addition, a solid started to precipitate from the reaction mixture. After complete addition, the resulting blue-green suspension was refluxed for another hour and then allowed to cool to room temperature. The precipitate was filtered off and washed with EtOH. Drying *in vacuo* gave 335 mg (95%) of complex **1** as a turquoise microcrystalline solid. m.p. > 345°C dec. Anal. Calcd for C<sub>40</sub>H<sub>28</sub>Cl<sub>2</sub>CuN<sub>8</sub>O<sub>8</sub>: C 54.36, H 3.17, N 12.68. Found: C 54.40, H 3.28, N 12.86%. IR (KBr): m/cm<sup>-1</sup> = 3116, 1603, 1527, 1380, 1307, 1100, 1064, 783, 694, 624. UV/VIS/NIR (MeCN): λ<sub>max</sub>/nm (ε/L mol<sup>-1</sup> cm<sup>-1</sup>) = 310(33485), 240(24100), 669(100). Crystals of complex **1** suitable for single crystal X-ray structure analysis were obtained by addition of four parts of MeOH to a solution of complex in one part MeCN followed by slow evaporation.

### 2.3. Crystallography

Crystallographic measurements were made at 193(2)K using a STOE IPDS II diffractometer equipped with an Oxford Cryostream low temperature unit. The intensity data were collected (STOE X-Area program package) within the range  $1.44 \leq \theta \leq 25.73^\circ$  using graphite monochromated Mo-K $\alpha$  radiation. Intensities of 3553 unique reflections were obtained, from which 3213 with  $I > 2\sigma(I)$  were observed. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . Structure solution and refinement were accomplished using SIR97, SHELXL97 and WinGX [15, 16]. A numerical absorption correction was applied. Molecular plots were prepared using ORTEP III [17].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in figures 2 and 3.

## 3. Discussion

### 3.1. Synthesis

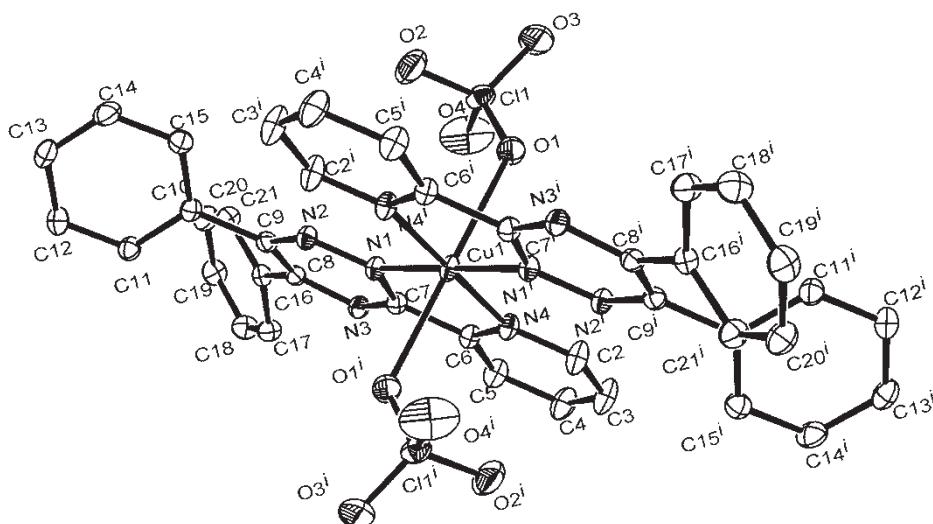
Reaction between PDPT and copper(II) perchlorate produced  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$ . The IR spectrum shows absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600  $\text{cm}^{-1}$  range and  $\nu(\text{ClO}_4)$  at ca. 1066–1100  $\text{cm}^{-1}$ . UV-Vis spectrum of  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$ , recorded from solution in MeCN,

Table 1. Crystal data and structure refinement for the  $[\text{Cu}(\text{DPT})_2(\text{ClO}_4)_2]$  complex.

Empirical formula	$\text{C}_{20}\text{H}_{14}\text{ClCu}_{0.50}\text{N}_4\text{O}_4$
Formula weight	441.57
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.181(2)$ Å; $\alpha = 80.97(2)^\circ$ $b = 8.786(2)$ Å; $\beta = 88.34(2)^\circ$ $c = 14.332(2)$ Å; $\gamma = 68.400(10)^\circ$
Volume	$945.5(3)$ Å <sup>3</sup>
Z	2
Density (calculated)	$1.551 \text{ Mg m}^{-3}$
Absorption coefficient	$0.786 \text{ mm}^{-1}$
$F(000)$	451
Crystal size	$0.2 \times 0.2 \times 0.1 \text{ mm}^3$
Theta range for data collection	$1.44$ to $25.73^\circ$
Index ranges	$-9 \leq h \leq 9$ , $-10 \leq k \leq 10$ , $-17 \leq l \leq 17$
Reflections collected	12493
Independent reflections	3553
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3553/0/324
Goodness-of-fit on $F^2$	1.047
Final R indices [for 3213 rfl. with $I > 2\sigma(I)$ ]	$R1 = 0.0307$ , $wR2 = 0.0807$
R indices (all data)	$R1 = 0.0346$ , $wR2 = 0.0824$
Largest diff. Peak and hole	0.366 and $-0.321 \text{ e Å}^{-3}$

Table 2. Selected bond lengths (Å) and angles (°) for the  $[\text{Cu}(\text{DPT})_2(\text{ClO}_4)_2]$  complex.

N4–Cu1	2.0683(16)	Cu1–N4 <sup>i</sup>	2.0095(14)
N1–Cu1	2.0095(14)	Cu1–N1 <sup>i</sup>	2.0683(16)
O1–Cu1	2.3816(16)	Cu1–O1 <sup>i</sup>	2.3816(16)
N1–Cu1–N1 <sup>i</sup>	180.0	N4–Cu1–N4 <sup>i</sup>	180.0
N1–Cu1–N4	79.27(6)	N1 <sup>i</sup> –Cu1–N4 <sup>i</sup>	79.27(6)
N1 <sup>i</sup> –Cu1–N4	100.73(6)	N1–Cu1–N4 <sup>i</sup>	100.73(6)
N1 <sup>i</sup> –Cu1–O1	83.80(6)	N1–Cu1–O1 <sup>i</sup>	83.80(6)
N1–Cu1–O1	96.20(6)	N1 <sup>i</sup> –Cu1–O1 <sup>i</sup>	96.20(6)
N4 <sup>i</sup> –Cu1–O1	85.29(6)	N4–Cu1–O1 <sup>i</sup>	85.29(6)
N4–Cu1–O1	94.71(6)	N4 <sup>i</sup> –Cu1–O1 <sup>i</sup>	94.71(6)
O1–Cu1–O1 <sup>i</sup>	180.0		

Symmetry operations: (i)  $-x, -y, -z$ .Figure 2. ORTEP plot of the molecule showing the atom-numbering of  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$ .

exhibits three main transitions. A single d–d band is centered at 669 nm ( $1000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The two next bands observed at 310 nm ( $33,485 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 240 nm ( $24,100 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) are due to ligand to metal charge transfer transitions. The results did not allow us to infer the geometry of the metal center in solution [18–21].

The structure of  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$  was confirmed by X-ray crystallography.

### 3.2. Crystal structure of $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$

Single X-ray crystal analysis reveals that  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$  crystallizes in triclinic space group  $P\bar{1}$ . The molecular structure of the complex (figure 1) consists of separate  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$  molecules. In the complex, the metal atom is coordinated to two 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazines (PDPT) via one triazine nitrogen and one pyridine nitrogen, and to two oxygen atoms of perchlorate.

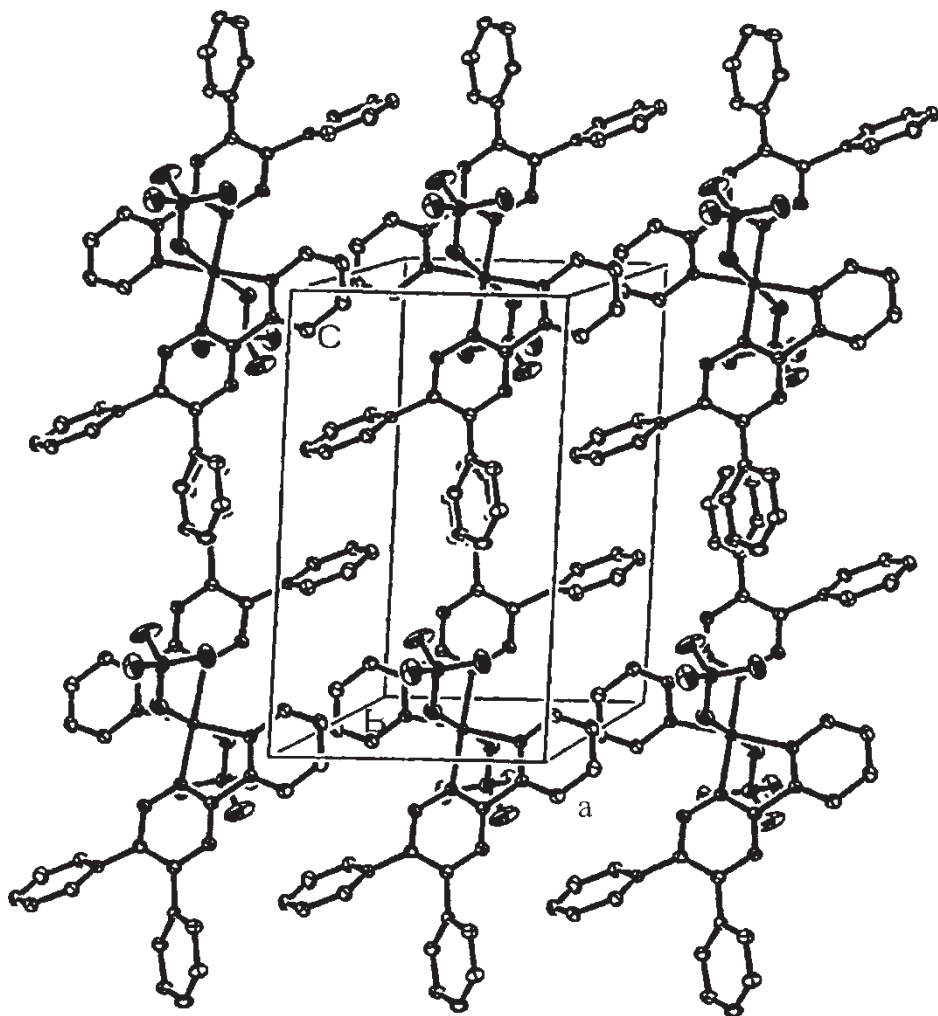


Figure 3. Unit cell and a view of [010] layer showing intermolecular  $\pi$ - $\pi$  stacking of the phenyl groups in the  $[\text{Cu}(\text{PDPT})_2(\text{ClO}_4)_2]$  molecules.

The PDPT is a bidentate ligand and, using only two donor nitrogen atoms, forms a five-membered metalocycle. In this complex, the triazine group of PDPT uses the nitrogen atom from position 1 and is coordinated as form **a** in figure 1, due to the steric effect of the phenyl group close to the nitrogen atom in position 4. The coordination number in this copper(II) complex is six with a  $\text{CuN}_4\text{O}_2$  chromophore and the coordination around Cu is a distorted octahedron. The N1, N1<sup>i</sup>, N4, N4<sup>i</sup> atoms of the PDPT ligands define the best equatorial tetragonal plane, while the O1 and O1<sup>i</sup> atoms of perchlorate anions occupy the axial positions [ $\text{O1}-\text{Cu1}-\text{O1}^i=180.0^\circ$ ]. The large distortion of the coordination polyhedron may be a consequence of the small bite angle [ $79.27(6)^\circ$ ] of the PDPT ligand. The  $\text{Cu}-\text{N}_{\text{py}}$  bond distances are 2.0683(16) and the two  $\text{Cu}-\text{N}_{\text{tz}}$  are 2.0095(14) Å. The two  $\text{Cu}-\text{O}_{\text{perchlorate}}$  distances are 2.3816(16) Å.

There are  $\pi$ - $\pi$  stacking [22, 23] interactions between two phenyl rings belonging to adjacent chains in this complex, as shown in figure 3. The phenyl groups are almost parallel and separated by a distance of about 3.5 Å; close to that of the layers in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the  $\pi$ -stacking type, rather than edge-to-face or vertex-to-face types [24–27]. Projection of the structure perpendicular to the ring plane shows the overall form of ‘slipped’ stacking [27, 28], which can be rationalized qualitatively in terms of optimizing the attraction between atoms of opposite charges [29].

### Supplementary material

Crystallographic data for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-257057. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

### Acknowledgements

Support of this investigation by Zanjan and Tarbiat Modarres Universities is gratefully acknowledged. We also acknowledge financial support from the Fonds der Chemischen Industrie.

### References

- [1] Z. El-Gendy, J.M. Morsy, H.A. Allimony, W.R. Abdel-Monem Ali, R.M. Abdel-Rahman. *Pharmazie*, **56**, 376 (2001).
- [2] N.R. El-Brollosy. *Phosphorus, Sulfur Silicon*, **77**, 163 (2000).
- [3] C. Ross. *Phytochemistry*, **3**, 603 (1964).
- [4] R.M. Abdel-Rahman, J.M. Morsy, F. Hanafy, H.A. Amene. *Pharmazie*, **54**, 347 (1999).
- [5] S.T. Tomas, A. Titire, A. Popescu, E. Tomas, N. Cajal. *Rev. Roum. Virol.*, **42**, 71 (1991).
- [6] L.K. Mishra, Y. Jha, B.K. Sinha, R. Kant, R. Singh. *J. Indian Chem. Soc.*, **76**, 65 (1999).
- [7] M. Mashaly, H.A. Bayoumi, A. Taha. *Chem. Papers*, **53**, 299 (1999).
- [8] M. Mashaly, H.A. Bayoumi, A. Taha. *J. Serb. Chem. Soc.*, **64**, 621 (1999).
- [9] M. Ghassemzadeh, M. Bolourtchian, S. Chitsaz, B. Neumüller, M.M. Heravi. *Eur. J. Inorg. Chem.*, 1877 (2000).
- [10] A. Taha. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 205 (2001).
- [11] A. Zuiwertz, S. Tomas, A. Popescu, C. Cristescu, E. Tomas. *Rev. Roum. Med.-Virol.*, **39**, 217 (1988).
- [12] C.G. Palivan, H.M.N. Palivan, B.A. Goodman, C. Cristescu. *Appl. Magn. Reson.*, **15**, 477 (1998).
- [13] N.S. Oxtoby, A.J. Blake, N.R. Champness, C. Wilson. *Proc. Natl. Acad. Sci.*, **99**, 4905 (2002).
- [14] C. Janiak, L. Uehlin, H.-P. Wu, P. Klufers, H. Piotrowski, T.G. Scharmann. *J. Chem. Soc.*, 3121 (1999).
- [15] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).
- [16] L.J. Farrugia. *J. Appl. Cryst.*, **32**, 837 (1999).
- [17] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
- [18] D. Sutton. *Electronic Spectra of Transition Metal Complexes*, McGraw-Hill, London (1975).
- [19] G. Murphy, P. Nagle, B. Murphy, B. Harhaway. *J. Chem. Soc.*, 1642 (1997).
- [20] P.J. Cornelissen, J.H. van Diemen, L.R. Groeneveld, J.G. Haasnoot, A.L. Speck, J.H. Reedjick. *Inorg. Chem.*, **31**, 198 (1992).
- [21] J. Foley, S. Tyagi, B.J. Hathaway. *J. Chem. Soc.*, 1 (1984).

- [22] N.N. Greenwood, A. Earnshaw. *Chemistry of the Elements*, Pergamon Press, Oxford, p. 235 (1986).
- [23] R. Foster (Ed.). *Molecular Complexes*, Paul Elek (Scientific Books) Ltd, London (1973).
- [24] V. Russell, M.L. Scudder, I.G. Dance. *J. Chem. Soc.*, 789 (2001).
- [25] I.G. Dance, M.L. Scudder. *J. Chem. Soc.*, 3755 (1996).
- [26] C. Janiak. *J. Chem. Soc.*, 3885 (2000).
- [27] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, X.-Z. You. *New J. Chem.*, **24**, 1057 (2000).
- [28] T.M. Barclay, A.W. Cordes, J.R. Mingie, R.T. Oakley, K.E. Preuss. *Cryst. Eng.Comm.*, 80 (2000).
- [29] C.A. Hunter, J.K.M. Sanders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).