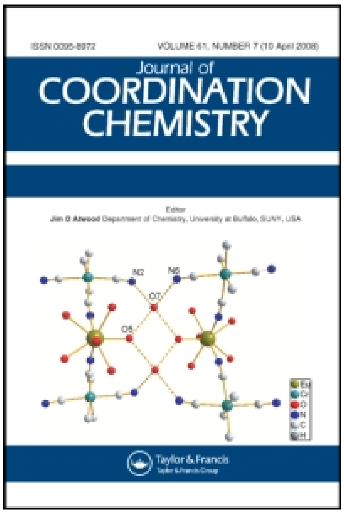


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

$\mathrm{Zn^{II}}$ and $\mathrm{Hg^{II}}$ complexes of 2,2'-diamino-4,4'-bis(1,3-thiazole) (DABTZ), spectroscopic, thermal and structural studies

Hamideh Ahankar[a]; Syavash Taheri[a]; Ali Morsali[b]; Ali Ramazai[c]; Long-guan Zhu[d]
[a] Department of Science, Abhar Azad University, Abhar, Zanjan, Iran [b] Department of Chemistry, School of Sciences, Tarbiat Modares University, Tehran, Iran [c] Department of Chemistry, Zanjan University, Zanjan, Iran [d] Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China

To cite this Article Ahankar, Hamideh , Taheri, Syavash , Morsali, Ali , Ramazai, Ali and Zhu, Long-guan(2006) '$\mathrm{Zn^{II}}$ and $\mathrm{Hg^{II}}$ complexes of 2,2'-diamino-4,4'-bis(1,3-thiazole) (DABTZ), spectroscopic, thermal and structural studies', Journal of Coordination Chemistry, 59: 18, 2039 — 2045

To link to this Article: DOI: 10.1080/00958970600737973

URL: http://dx.doi.org/10.1080/00958970600737973

Journal of Coordination Chemistry
Vol. 59, No. 18, 15 December 2006, 2039–2045

Taylor & Francis
Taylor & Francis Group

Zn^{II} and Hg^{II} complexes of 2,2′-diamino-4,4′-bis(1,3-thiazole) (DABTZ), spectroscopic, thermal and structural studies

HAMIDEH AHANKAR†, SYAVASH TAHERI†,
ALI MORSALI*‡, ALI RAMAZAI§ and LONG-GUAN ZHU¶

†Department of Science, Abhar Azad University, P.O. Box 22, Abhar, Zanjan, Iran
‡Department of Chemistry, School of Sciences, Tarbiat Modares University,
P.O. Box 14155-4838, Tehran, Iran
§Department of Chemistry, Zanjan University, P.O. Box 45195-313, Zanjan, Iran
¶Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China

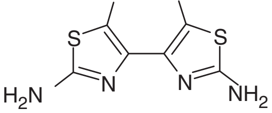
(*Received 7 December 2005*)

New zinc(II) and mercury(II) complexes of 2,2′-diamino-4,4′-bis(1,3-thiazole) (DABTZ), $[M(DABTZ)(CH_3COO)_2]$, have been synthesized and characterized by elemental analysis, IR-, ^1H NMR-, ^{13}C NMR spectroscopy and studied by thermal analysis and X-ray crystallography. The structural characterization of the $[Zn(DABTZ)(CH_3COO)_2]$ complex shows the complex to be a monomer and the Zn coordinated by two nitrogen atoms of the "DABTZ" ligand and four oxygen atoms of the acetate anions.

Keywords: Zinc; Mercury; Crystal Structure; 2,2′-diamino-4,4′-bis(1,3-thiazole)

1. Introduction

The effects of cobalt(II) and nickel(II) complexes with 2,2′-diamino-4,4′-bis (1,3-thiazole) on DNA synthesis of sarcoma 180 tumour cells has been investigated by the technique of isotopic liquid scintillation. The results indicated that complexes show ability to inhibit DNA synthesis of tumour cells [1]. In recent reports a series of different metal complexes of 4,4′-bithiazole ligands have been reported [2–9]. The 2,2′-diamino-4,4′-bis(1,3-thiazole) (DABTZ) contains the amine groups that can change both the electronic and steric properties of the ligand and the metal complexes.



DABTZ

---

*Corresponding author. Email: morsali_a@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970600737973

Numerous zinc(II), cadmium(II) and mercury(II) complexes with nitrogen or oxygen donor ligands have been synthesized and studied [10–12]. Some of these complexes are structural models for the active sites in enzymes [11]. In relation to work on different metal ions we became interested in "DABTZ" complexes with new homoleptic d^{10} complexes. In this article, we report the syntheses and characterization of coordination compounds formed between the "DABTZ" ligand and zinc(II) acetate and mercury(II) acetate [M(DABTZ)(CH_3COO)$_2$].

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 analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

2.2. *Preparation of 2,2′-diamino-4,4′-bis(1,3-thiazole) (DABTZ)*

The 2,2′-diamino-4,4′-bis(1,3-thiazole) ligand was prepared from 1,4-dibromobutane-2,3-dione and thiourea by method of Erlenmeyer and Üeberwasser [13].

2.3. *Preparation of [Zn(DABTZ)(CH_3COO)$_2$]*

The complex was prepared by dissolving zinc(II) acetate (0.50 mmol 0.107 g) in distillated water (10 mL) and adding an ethanolic solution of 2,2′-diamino-4,4′-bis(1,3-thiazole) (DABTZ) (0.099 g, 0.5 mmol). The resulting solution was stirred for 2 h at room temperature and then allowed to stand for 10 d at room temperature (ca. 25°C). Red crystals precipitated which were filtered off, washed with acetone and ether and dried in air (m.p. 210°C). Yield: 0.105 g, 55%. $C_{10}H_{12}N_4O_4S_2Zn$: Calcd C 31.43, H 3.14, N 14.67; Found C 31.55, H 2.90, N 14.50. – IR (KBr) selected bonds: $\nu = 712$(m), 970(w), 1410(vs), 1562(vs), 1600(vs), 2960(w), 3085(w), 3180(m) and 3210(m) cm^{-1}. –^{1}H NMR ([D$_6$]-DMSO): $\delta = 1.70$ (s, 3H), 6.50 (s, 1H), and 7.20 (s, 2H) ppm. ^{13}C-{^{1}H} NMR ([D$_6$]-DMSO): $\delta = 22.60$, 102.70, 146.15, 169.66, and 179.35 ppm.

2.4. *Preparation of [Hg(DABTZ)(CH_3COO)$_2$]*

The complex [Hg(DABT)(CH_3COO)$_2$] was prepared similarly. Reactant materials: DABTZ, mercury(II) acetate (1 : 1). White crystals, m.p. 220°C, Yield: 0.103 g, 40%. $C_{10}H_{12}N_4O_4S_2Hg$: Calcd C 23.26, H 2.32, N 10.85; Found C 22.90, H 2.50, N 10.50. – IR (KBr) selected bonds: $\nu = 710$(m), 972(w), 1412(vs), 1565(vs), 1606(vs), 2950(w), 3080(w), 3180(m) and 3212(m) cm^{-1}. – ^{1}H NMR ([D$_6$]-DMSO): $\delta = 1.71$ (s, 3H), 6.55 (s, 1H), and 7.24 (s, 2H) ppm. ^{13}C-{^{1}H} NMR ([D$_6$]-DMSO): $\delta = 22.60$, 102.75, 146.11, 169.65, and 179.40 ppm.

Table 1. Crystal data and structure refinement for [Zn(DABTZ)($CH_3COO)_2$].

Empirical formula	$C_{10}H_{12}N_4O_4S_2Zn$
Formula weight	381.73
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2/c$
Unit cell dimensions (Å, °)	
a	7.3171(7)
b	8.8463(9)
c	13.2748(11)
β	122.7550(10)
Volume (Å^3)	722.64(12)
Z	2
Density (calculated) (Mg m^{-3})	1.754
Absorption coefficient (mm^{-1})	2.008
$F(000)$	388
Crystal size (mm^3)	0.28 × 0.20 × 0.10
Theta range for data collection (°)	2.90–26.40
Index ranges	$-8 \leq h \leq 8$
	$-10 \leq k \leq 10$
	$-16 \leq l \leq 16$
Reflections collected	1343
Independent reflections	1230 [$R(\text{int}) = 0.0268$]
Completeness to theta = 25.49°	99.7%
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.603 and 0.825
Data/restraints/parameters	1343/0/96
Goodness-of-fit on F^2	0.979
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0304$, $wR_2 = 0.0871$
R indices (all data)	$R_1 = 0.0336$, $wR_2 = 0.0903$
Largest diff. Peak, hole (eÅ^{-3})	0.449 and −0.567

2.5. *Crystallography*

Crystallographic measurements were made at 295(2) K using a Siemens R3 m V^{-1} diffractometer. The intensity data were collected within the range 2.90–26.40° using graphite monochromated Mo–K$_\alpha$ radiation. 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 [14–15].

Crystal data and structure refinements are given in table 1. 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, unit cell and perspective view of the packing are shown in figures 1–3.

3. Results and discussion

Reaction between 2,2′-diamino-4,4′-bis(1,3-thiazole) "DABTZ" and mixtures of aqueous zinc(II) acetate or mercury(II) acetate solutions provided crystalline [Zn(DABTZ)($CH_3COO)_2$] and [Hg(DABTZ)($CH_3COO)_2$], respectively. The IR spectra of these complexes exhibit absorption bands resulting from the skeletal vibrations of

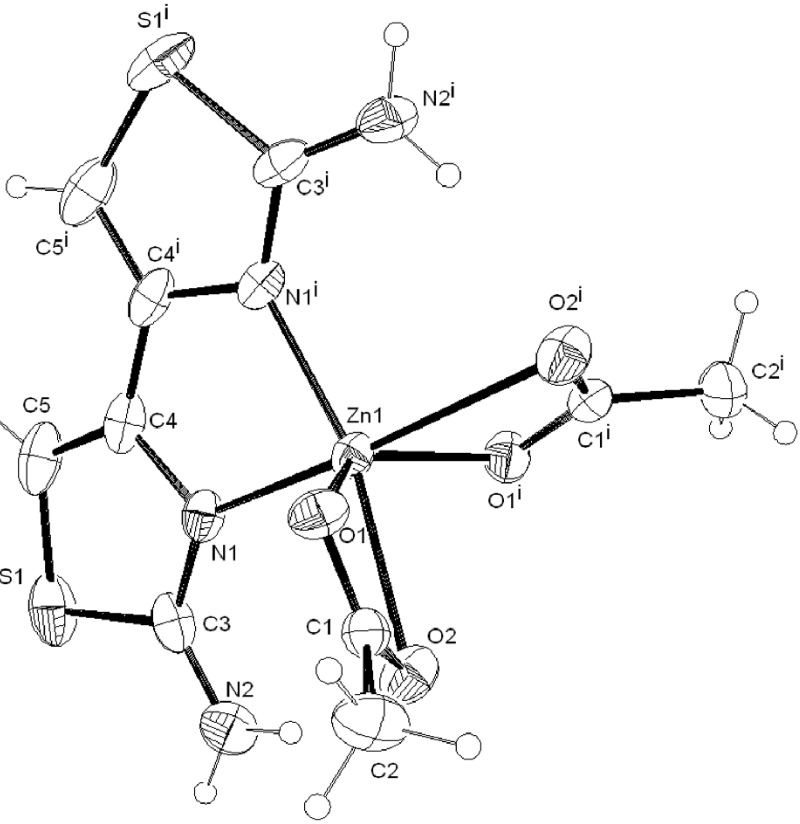


Figure 1. ORTEP diagram of [Zn(DABTZ)(CH_3COO)$_2$] with ellipsoids of 30% probability.

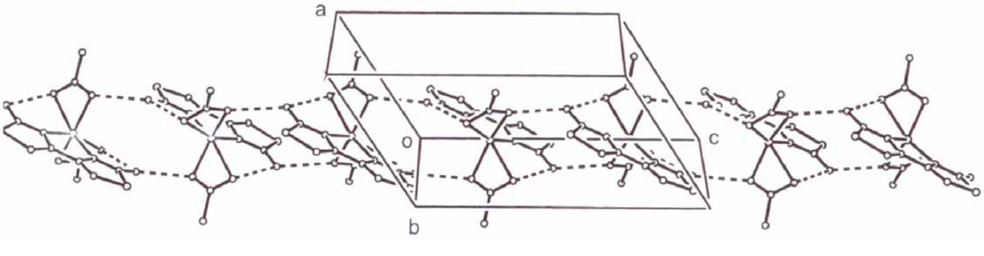


Figure 2. The unit cell of the [Zn(DABTZ)(CH_3COO)$_2$] and showing the hydrogen bonding.

aromatic rings in the 1400–1615 cm^{-1} range. The relatively weak bands at around 2950 and 3080 cm^{-1} are assigned to the $\nu(CH_3)$ mode of the acetate group and the ν(CH) mode of the DABTZ aromatic rings, respectively. The broad absorption band at 3180 and 3210 cm^{-1} are assigned to the $\nu(–NH_2)$ modes. The broad band is perhaps attributable to $\nu(N–H \cdots X)$, indicating the presence of hydrogen bonds, which has been confirmed by the crystal structure determination of this complex. The characteristic

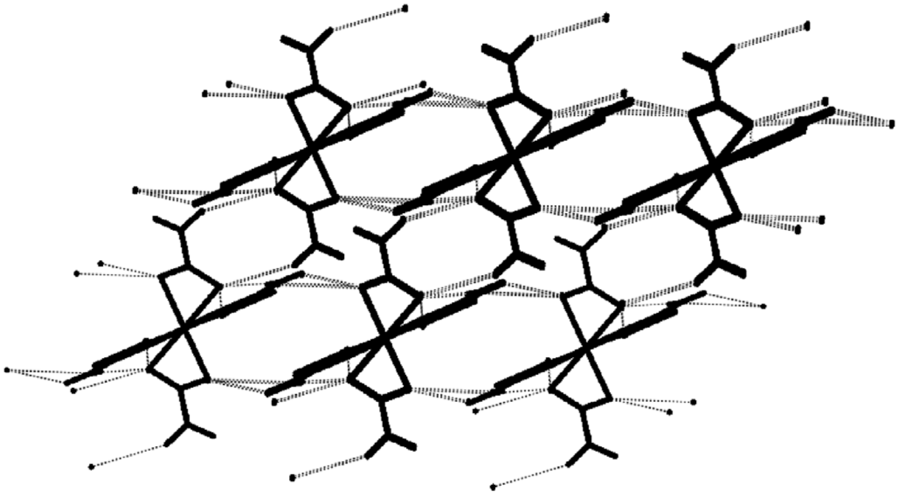


Figure 3. Showing of the hydrogen bonding and π–π stacking interactions in the packing of [Zn(DABTZ)($CH_3COO)_2$].

bands of the carboxylate group in [Zn(DABTZ)($CH_3COO)_2$] appear around 1562 for $\upsilon_{as(C–O)}$ and 1410 for $\upsilon_{sym(C–O)}$, and in [Hg(DABTZ)($CH_3COO)_2$] around 1565 for $\upsilon_{as(C–O)}$ and 1412 cm^{-1} for $\upsilon_{sym(C–O)}$. The $\Delta\upsilon$ value (υ_{as}–υ_{sym}) of 152 cm^{-1} for [Zn(DABTZ)($CH_3COO)_2$] is similar to the value of $\Delta\upsilon = 143\,cm^{-1}$ for [Hg(DABTZ)($CH_3COO)_2$], indicating that the carboxylate group is coordinating with Zn(II) and Hg(II) in the same bidentate manner [16–20], as also unambiguously confirmed by the crystal structure of the Zn complex. The ^1H NMR spectra of DMSO solutions of the two complexes display two distinct absorption bands at 6.50(s, 2H) and 7.20(s, 4H) ppm which have been assigned to the aromatic and amino protons, respectively. The band at 1.70 (s, 6H) is assigned to the methyl protons of the acetate anions of both complexes. The ^{13}C NMR spectra of the DMSO solutions of the two complexes display three distinct absorption bands at 102.75, 146.10, and 169.65 ppm assigned to the aromatic carbon atoms. Two other resonances at 22.60 ($^{13}CH_3$–COO) and 179.40 (CH_3–^{13}COO) are assigned to the carbon atoms of acetate anions.

Results of TGA show one main weight loss step, which appeared from 280 to 320°C in [Zn(DABTZ)($CH_3COO)_2$] and 320 to 480°C in [Hg(DABTZ)($CH_3COO)_2$], during which the compound decomposed. The final products are ZnO and HgO with total weight loss of 78.2%, 58.06%, respectively, close to the calculated values of 78.3%, 58.2%.

An ORTEP diagram of [Zn(DABTZ)($CH_3COO)_2$] is given in figure 1. The selected bond distances and angles around Zn(II) are shown in table 2. Each zinc is octahedrally chelated by two nitrogen atoms of one DABTZ ligand with Zn–N distances of 2.051(2) Å and four oxygen atoms of the acetate anion with Zn–O distances of 2.0270(18) and 2.443(2) Å. The average internal dihedral angle of 4.62° between the thiazole rings of the DABTZ ligand shows a twisted structure of the ligand in the complex. The complex is linked by inter-molecular hydrogen bonding (figure 2 and table 3). The amine protons of "DABTZ" act as hydrogen-bond donors with oxygen atoms of acetate anions as hydrogen-bond acceptors. The distances of two parallel

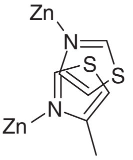
Table 2. Bond lengths (Å) and angles (°) for [Zn(DABTZ)$(CH_3COO)_2$].

Zn1–O1	2.0270(18)	O1–Zn1–O1^i	133.11(12)
Zn1–O1^i	2.0270(18)	O1–Zn1–N1^i	108.27(8)
Zn1–N1	2.051(2)	O1^i–Zn1–N1^i	107.22(8)
Zn1–N1^i	2.051(2)	O1–Zn1–N1	107.22(8)
Zn1–O2	2.443(2)	N1–Zn1–N1^i	80.01(13)
Zn1–O2^i	2.443(2)	O1–Zn1–O2	56.74(7)
		O1–Zn1–O2^i	90.50(8)
		N1–Zn1–O2^i	162.28(8)
		N1–Zn1–O2	94.96(8)
		O1^i–Zn1–O2^i	56.74(7)
		N1^i–Zn1–O2^i	94.96(8)

i: $-x, y, -z+(1/2)$.

Table 3. H-bonds in the structure of [Zn(DABTZ)$(CH_3COO)_2$].

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	DHA (°)
N2–H2D···O2	2.973(3)	0.86	2.17	155.6
N2–H2E···O1[x, $2-y$, $1/2+-z$]	2.819(3)	0.86	2.07	145.2



Scheme 1. Showing π–π stacking in the 2n (DABTZ) $(CH_3COO)_2$.

edges, which belong to bithiazole rings of adjacent molecules are only 3.883 Å, indicating edge-to-edge π–π stacking interactions [21], which further stabilize this packing system. Projection of the structure perpendicular to the ring plane shows the overall form of "slipped" stacking (scheme 1) [22–24].

Thus, two factors, hydrogen bonding and π–π stacking control the packing of the complexes. Consequently, the hydrogen bonding and π–π stacking interactions grow the structure into a hybrid two-dimensional network (figure 3).

It is interesting to discuss ligand stoichiometry of zinc(II) salts in their complexes with "DABTZ". Attempts to isolate 1 : 2 adducts, [Zn$(DABTZ)_2(CH_3COO)_2$] and 1 : 1 adducts, [Zn(DABTZ)(CH_3COO)](ClO_4) and Zn(DABTZ)$(ClO_4)_2$, were not successful; each time the 1 : 1 adduct [Zn(DABTZ)$(CH_3COO)_2$] and the 1 : 2 adducts [Zn$(DABTZ)_2(CH_3COO)$](ClO_4) [8] and Zn$(DABTZ)_2(ClO_4)_2$ [7] were isolated. This may be consistent with acetate being a stronger ligand than perchlorate, resulting in the acetate anion coordinating to zinc(II) preventing formation of 1 : 2 adducts with two acetate anions.

Supplementary material

Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.

CCDC-289460. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Support of this investigation by Islamic Azad of Abhar and Tarbiat Modarres Universities is gratefully acknowledged.

References

[1] Y.-N. Tian, P. Yang, H.-F. Wang. *Polyhedron*, **15**, 2771 (1996).
[2] A.R. Mahjoub, A. Morsali. *Polyhedron*, **21**, 1223 (2002).
[3] A.R. Mahjoub, A. Morsali. *Chem. Lett.*, 1234 (2000).
[4] A. Morsali, A. Tadjarodi, R. Mohammadi, A.R. Mahjoub. *Z. Kristallogr. NCS*, **216**, 379 (2001).
[5] A. Morsali, A.R Mahjoub. *J. Coord. Chem.*, **56**, 779 (2003).
[6] S.A.A. Torabi, F. Jamali, G.A. Koutsantonis, A. Morali, B.W. Skelton, A. White. *Aust. J. Chem.*, **56**, 949 (2003).
[7] A. Morsali, M. Payheghader, M.R. Poorheravi, F. Jamali. *Z. Anorg. Allg. Chem.*, **629**, 1627 (2003).
[8] J. Abedini, A. Morsali. *Z. Naturforsch.*, **60b**, 951 (2005).
[9] J. Abedini, A. Morsali, R. Kempe, I. Hertle. *J. Coord. Chem.*, **58**, 1719 (2005).
[10] N.J. Brownless, D.A. Edwards, M.F. Mahon. *Inorg. Chim. Acta*, **287**, 89 (1999).
[11] C. Kirchner, B. Krebs. *Inorg. Chem.*, **26**, 3569 (1987).
[12] B.H. Ye, F. Xue, G.Q. Xue, L.N. Ji, T.C.W. Mak. *Polyhedron*, **18**, 1785 (1999).
[13] H. Erlenmeyer, H. Üeberwasser. *Helv. Chim. Acta*, **23**, 1268 (1940).
[14] G. Ferguson, C. Glidewell, E.S. Lavender. *Acta Crystallogr.*, **55B**, 591 (1999).
[15] G.M. Sheldrick (1998b), SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA.
[16] X.-M. Chen, Z.-T. Xu, X.-L. Yu, T.C.W. Mak. *Polyhedron*, **13**, 2079 (1994).
[17] X.-M. Chen, T.C.W. Mak. *Inorg. Chim. Acta*, **189**, 3 (1991).
[18] V.T. Yilmaz, S. Hamamci, O. Andac, K. Guven. *Z. Anorg. Allg. Chem.*, **629**, 172 (2003).
[19] S. Sen, S. Mitra, P. Kundu, M.K. Saha, C. Kruger. *J. Bruckmann Polyhedron.*, **16**, 2475 (1997).
[20] A.V.R. Warrier, R.S. Krishnan. *Spectrochim. Acta*, **24A**, 1243 (1971).
[21] C.A. Hunter, J.K.M. Sanders. *J. Am. Chem. Soc.*, **112**, 5525 (1990).
[22] C. Janiak. *J. Chem., Soc. Dalton Trans.*, 3885 (2000).
[23] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, X.-Z. You. *New J. Chem.*, **24**, 1057 (2000).
[24] T.M. Barclay, A.W. Cordes, J.R. Mingie, R.T. Oakley, K.E. Preuss. *Cryst. Eng. Commun.*, 80 (2000).