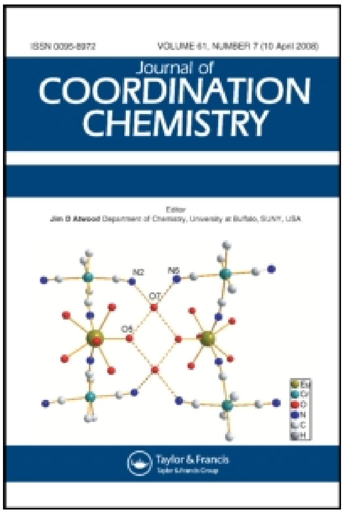

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectra, crystal structure and thermal properties of a polymeric 1-D cobalt(II) cyanato complex with hexamethylenetetramine

Mohamed A. S. Goher[a]; Mohamed R. Saber[b]; Rania G. Mohamed[b]; Afaf K. Hafez[a]; Franz A. Mautner[c]
[a] Faculty of Science, Department of Chemistry, Alexandria University, Ibrahimia, 21321 Alexandria, Egypt [b] Faculty of Science, Department of Chemistry, Fayoum University, Fayoum, Egypt [c] Institut fuer Physikalische und Theoretische Chemie, Technische Universitaet Graz, Rechbauerstr. 12, A-8010 Graz, Austria

To cite this Article Goher, Mohamed A. S. , Saber, Mohamed R. , Mohamed, Rania G. , Hafez, Afaf K. and Mautner, Franz A.(2009) 'Synthesis, spectra, crystal structure and thermal properties of a polymeric 1-D cobalt(II) cyanato complex with hexamethylenetetramine', Journal of Coordination Chemistry, 62: 2, 234 — 241

To link to this Article: DOI: 10.1080/00958970802247656

URL: http://dx.doi.org/10.1080/00958970802247656

Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 234–241

Synthesis, spectra, crystal structure and thermal properties of a polymeric 1-D cobalt(II) cyanato complex with hexamethylenetetramine

MOHAMED A. S. GOHER†[1], MOHAMED R. SABER‡, RANIA G. MOHAMED‡,
AFAF K. HAFEZ† and FRANZ A. MAUTNER*§

†Faculty of Science, Department of Chemistry, Alexandria University,
P.O. Box 426 Ibrahimia, 21321 Alexandria, Egypt
‡Faculty of Science, Department of Chemistry, Fayoum University, Fayoum, Egypt
§Institut fuer Physikalische und Theoretische Chemie, Technische Universitaet Graz,
Rechbauerstr. 12, A-8010 Graz, Austria

(*Received 23 September 2007; in final form 15 April 2008*)

A new cobalt(II) cyanato complex, $[Co(NCO)_2(H_2O)_2(hmt)]$ (**I**) where hmt is hexamethylenetetramine, has been synthesized and structurally characterized. The electronic spectra of the solid compound suggest octahedral cobalt and IR spectra revealed monodentate N-cyanato groups and aqua ligands, while hmt is a bridging N,N'-bidentate leading to a 1-D infinite polymeric chain. The structure has been confirmed from single crystal X-ray diffraction. Crystal data for **I** : Fw 319.20, $a = 9.234(2)$, $b = 11.252(2)$, $c = 12.576(3)$ Å, $\beta = 107.75(3)^\circ$, $V = 1244.5(4)$ Å^3, $Z = 4$, $T = 100$ K. Crystal system : monoclinic, space group : C2/c. Hydrogen bonds of the type O–H $\cdots$ O and O–H $\cdots$ N between aqua molecules and O atom of the terminal N-cyanato groups or an N atom of hmt ligands consolidate and extend the structure to a 3-D network. The thermal properties of **I** are reported.

Keywords: Cobalt(II) complex; Hexamethylenetetramine complex; Cyanato; X-ray structure; Thermal analysis

1. Introduction

The design and synthesis of supramolecular architecture analogous to important materials such as zeolites using the principle of crystal engineering are of much current interest [1]. The crystal engineering of coordination polymers is usually achieved by using bi- or multidentate ligands to bind the metal centers. The coordinating ligands are two types : neutral organic e.g. 4,4′-bipyridine, pyrazine etc. [2–4] and anionic e.g. azide, thiocyanate [5–7] or polyaromatic acid anions [8, 9] to build up one-, two-, or three-dimensional archictectural frameworks. The polycyclic tertiary amine, hexamethylenetetramine (hmt) is a potentially tetradentate neutral ligand and can connect through two, three or all four of its tertiary nitrogens to provide a variety of

---

*Corresponding author. Email: mautner@ptc.tu-graz.ac.at

[1] Deceased.

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802247656

polymers of interesting topologies; different topological motifs with different dimensionality involving metal centers are already reported [10–12]. Although many metals, including Mn(II) [13], Fe(II) [14], Co(II) [15], Ni(II) [10, 11], Cu(II) [16], Cu(I) [17], Zn(II) [12], Cd(II) [10], etc. complexes with hmt have been reported, almost all are metal halides, thiocyanate, phthalate, very few azides, and one example with selenocyanate [18]; to the best of our knowledge, no single example of metal(II) cyanato complexes with hmt has been mentioned in the literature.

As we have been interested in metal pseudo halide complexes, including cyanato derivatives [19], we prepared the first metal(II) cyanato complex with hmt, and here report the characterization of $[Co(NCO)_2(H_2O)_2(hmt)]_n$, with a neutral spacer and an anionic ligand. In the polymeric chain, Co(II) is in an octahedral environment surrounded by a bridging hmt neutral ligand, and cyanate and water as terminal ligands. System stability is enhanced through different types of hydrogen bonds such as O–H $\cdots$ N and O–H $\cdots$ O inter-chain hydrogen bonds [11a, 15b, 18].

2. Experimental

Hexamethylenetetramine was purchased from Aldrich, and the other chemicals are of analytical grade quality.

2.1. *Preparation of the complex*

2.1.1. $[Co(hmt)(NCO)_2(H_2O)_2]_n$ (I). An aqueous mixture of $CoSO_4 \cdot 7H_2O$ (0.562 g, 2 mmol) and hmt (0.14 g, 1 mmol) was stirred for ca. 20 min. To this mixture an aqueous solution of KNCO (0.324 g, 4 mmol) was added dropwise with continuous stirring. The final mixture was allowed to stand for one or two days to deposit good quality crystals of the complex. The crystals were collected by vacuum filtration and dried in vacuum. The yield was 50%. The analytical data are (%) : Found: C, 29.61; H, 5.43; N, 26.07; Co, 18.88 (%). Calculated for $C_8H_{16}N_6O_4Co$: C, 30.10; H, 5.06; N, 26.30; Co, 18.47.

2.2. *Physical measurements*

The IR spectral data for free ligand and **I** were obtained as KBr pellets using a Mattson Satalite FT-IR spectrophotometer. Thermal studies (TGA and DTA) of **I** were performed at a heating rate of $10^\circ C\,min^{-1}$ using a Perkin-Elmer Thermogravimetric Analyzer TGA7 in a dynamic atmosphere of nitrogen (flow rate $80\,mL\,min^{-1}$). The experimental procedures and instruments used for different physical measurements are as described previously [20].

2.3. *X-ray crystallography*

The X-ray single-crystal data were collected on a Bruker-AXS SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å).

Table 1. Crystallographic data and processing parameters.

Compound	$[Co(NCO)_2(H_2O)_2(hmt)]_n$
Empirical formula	$C_8H_{16}CoN_6O_4$
Formula weight	319.20
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell (Å, °)	
a	9.234(2)
b	11.252(2)
c	12.576(3)
β	107.75(3)
V (Å^3)	1244.5(4)
Z	4
Temperature (K)	100(2)
Absorption coefficient (mm^{-1})	1.401
D_{Calcd} (Mg m^{-3})	1.704
Crystal size (mm^3)	0.30 × 0.22 × 0.13
θ range for data collection (°)	2.94–26.35
Reflections collected	4094
Independent reflections (R_{int})	1254/0.0547
Parameters	95
Goodness-of-Fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0369$, $wR_2 = 0.0929$
R indices (all data)	$R_1 = 0.0389$, $wR_2 = 0.0956$
Residual extrema (e Å^{-3})	0.386/−0.656

The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in table 1. Lorentz-polarization and absorption corrections were made using the SADABS computer program [21]. The structure was solved by Direct Methods using the SHELXS-86 computer program and refined by full-matrix least-squares methods on F^2 using the SHELXL-93 program incorporated in the SHELXTL/PC V 5.03 [22] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints.

3. Results and discussion

The reaction between Co(II) ions, NCO^- ions and hmt in a molar ratio of 2 : 4 : 1 in aqueous media afforded **I**. This complex is insoluble in polar solvents like water, ethanol, acetone, etc. suggesting its polymeric nature and dissolves only in DMF and DMSO, hot methanol and hot ethanol with a drastic change of color to blue, suggesting a washing out of two ligands with the formation of a tetrahedral geometry around Co(II).

3.1. *IR and electronic spectra*

The solid state IR spectrum of **I** recorded in the range 400–4000 cm^{-1} is fully consistent with its structure. The spectrum exhibits the following absorption bands (values in cm^{-1}) : around 3504m,br, 3397s,br, 3283 s,br due to $\nu(OH_2)$, and ν(H-bonds); the broad band at $2919\,cm^{-1}$ reflects the frequency of methylene groups of hmt molecules. The spectrum also shows absorption bands at $1668\,cm^{-1}$ δ(OH), 1468 ms, and 1376 s due to $\delta(CH_2)$, and 1313s, 1242 vs, related to ν(CO). These absorption frequencies are consistent with similar complexes reported in the literature [12a, 23]. The very strong absorption frequency at $2215\,cm^{-1}$, due to ν_{as}(CN), revealed terminal cyanato ligand rather than bridging [24]. It has been observed [25] that δ(CN) of NCO is split by at most a few wavenumbers when the cyanate is terminal while it typically shows a splitting of 30–40 cm^{-1} when bridging. The appearance of only one strong peak at $610\,cm^{-1}$, related to this mode, revealed terminal cyanato ligand and confirms the result drawn from the asymmetric vibration frequency.

The electronic spectrum of the solid complex **I** mulled in Nujol shows two broad bands of moderate intensity around $18281\,cm^{-1}$ and around $12722\,cm^{-1}$. Those absorption bands may be tentatively assigned as d-d transitions of Co(II) in a weak octahedral field [26, 27], assigned as $^4T_{1g}(F)$–$^4T_{1g}(P)$ and $^4T_{1g}(F)$–$^4A_{2g}$, respectively.

3.2. *Structure of the* $[Co(NCO)_2(H_2O)_2(hmt)]_n$ *(I)*

The X-ray analysis of **I** shows that the structure consists of distorted octahedral Co(II), located at an inversion center, linked by two terminal NCO groups, two water molecules and two neutral hmt molecules. Nitrogens N(1A) and N(1B) of the terminal *N*-cyanato groups [Co(1)–N(1) = 2.056(2) Å] and the two oxygens O(2) and O(2A) of coordinated water [Co(1)–O(2) = 2.0929(14) Å] form the equatorial plane around cobalt and the trans axial positions are occupied by nitrogens N(2) and N(2A) from bridging hmt molecules [Co(1)–N(2) = 2.3433(15) Å] giving a CoN_4O_2 chromophore. The Co(II) centers are bridged by neutral hmt molecules in a μ-N,N' fashion leading to a 1-D infinite polymeric chain along [0, 0, 1], i.e. *c*-axis of the unit cell. A section of the polymeric chain together with a labeling scheme is shown in figure 1, and selected bond parameters are collected in table 2. The NCO groups are almost linear [N–C–O angle = 179.4(2)°], but show a distortion from linearity in connection with Co(II) [Co(1)–N(1)–C(1) angle = 165.5(2)°]. The intra-chain Co $\cdots$ Co distances are identical, 6.2880(15) Å. Each hmt is a neutral bidentate spacer linking adjacent cobalt centers in

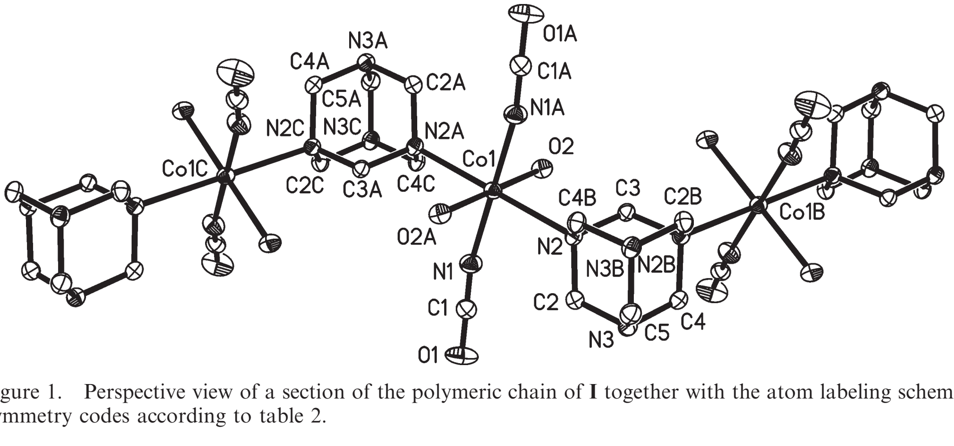

Figure 1. Perspective view of a section of the polymeric chain of **I** together with the atom labeling scheme. Symmetry codes according to table 2.

μ-N,N' fashion, while the cobalt centers are linear spacers to generate a 1-D zigzag chain. Thus, the hmt molecule connects two consecutive metal centers through only two out of its four nitrogen donor sites to link adjacent units.

In the asymmetric unit of **I** exists only one aqua oxygen atom O(2) which acts as donor atom to form: (a) a hydrogen bond of type O–H···N to a non-coordinated nitrogen atom N(3D) $[x-1/2, y+1/2, -z+1/2]$ of an adjacent hmt ligand molecule [O(2)···N(3D) distance = 2.785(3) Å; O(2)–H(21)···N(3D) angle = 167.8°]; and (b) a second hydrogen bond of type O–H···O to a non-coordinated oxygen atom O(1E) $[x-1/2, y+1/2, z]$ of a terminal cyanato group [O(2)···O(1E) distance = 2.769(3) Å; O(2)–H(22)···O(1E) angle = 161.4°] (table 3). As a consequence of the eight symmetry operations of the monoclinic C-centered space group C2/c, these two types of hydrogen bonds build up a rather complicated supramolecular 3-D network structure, which is described in the following way: along the [1, −1, 0] direction the polymeric chains of polyhedra are connected by hydrogen bonds to form a supramolecular 2-D layer (figure 2). The $[Co(NCO)_2(H_2O)_2(hmt)]$ polyhedron of Co(1) is involved in the following six "intra-sheet" donor–acceptor pairs (figures 1 and 2): O(1)–O(2) $[x+1/2, y-1/2, z]$; O(1A)–O(2) $[-x-1/2, -y+3/2, -z]$; O(2A)–O(1) $[-x+1/2, -y+3/2, -z]$; O(2)–O(1) $[-x+1, y, -z+1/2]$; N(3)–O(2) $[-x+1/2, y-1/2, -z+1/2]$ and N(3A)–O(2) $[-x, -y+2, -z]$; whereas additional 4 "inter-sheet" donor–acceptor pairs to parallel layers above and below the "parent" supramolecar sheet are formed: O(2)–N(3) $[-x+1/2, y+1/2, -z+1/2]$; O(2A)–N(3) $[x-1/2, -y+3/2, z-1/2]$; N(3B)–O(2) $[x-1/2, -y+5/2, z-1/2]$ and N(3C)–O(2) $[-x+1/2, -y+5/2, -z+1/2]$. The neighboring $[Co(NCO)_2(H_2O)_2(hmt)]$ polyhedron of Co(1B), which has a common hmt bridging ligand with the polyhedron of Co(1), however, is involved only in four "intra-sheet" O–N donor–acceptor pairs, whereas the remaining ones belong to "inter-sheeet" donor–acceptor pairs.

Thus, both un-coordinated N atoms of hmt are involved in inter-chain O–H···N hydrogen bonding making the hmt a good tetrahedral template, an important factor in establishing an ordered supramolecular structure formed by self-assembly.

Table 2. Selected bond lengths (Å) and angles (°) for **I**.

Co(1)–N(1)	2.056(2)	Co(1)–N(1A)	2.056(2)
Co(1)–O(2)	2.0929(14)	Co(1)–O(2A)	2.0929(14)
Co(1)–N(2)	2.3433(15)	Co(1)–N(2A)	2.3433(15)
Co(1)···Co(1C)	6.2880(15)	N(1)–C(1)	1.165(3)
C(1)–O(1)	1.213(3)	N(2)–C(4B)	1.485(2)
O(2)–H(21)	0.817	O(2)–H(22)	0.820
N(1)–Co(1)–O(2)	91.90(5)	N(1)–Co(1)–N(2)	90.11(7)
O(2)–Co(1)–N(2A)	75.77(12)	O(3)–Co(1)–O(3A)	139.55(14)
Co(1)–N(1)–C(1)	165.5(2)	N(1)–C(1)–O(1)	179.4(2)
H(21)–O(2)–H(22)	108.8		

Symmetry codes: (A) $-x, -y+2, -z$; (B) $-x, y, -z+1/2$; (C) $-x, y, -z+1/2$.

Table 3. Hydrogen bond system for **I**.

Donor–H···Acceptor	Symmetry code	Distance (Å)	Angle (°)
O(2)–H(21)···N(3)	$[x-1/2, y+1/2, 1/2-z]$	2.785(3)	167.8
O(2)–H(22)···O(1)	$[x-1/2, y+1/2, z]$	2.769(2)	161.4

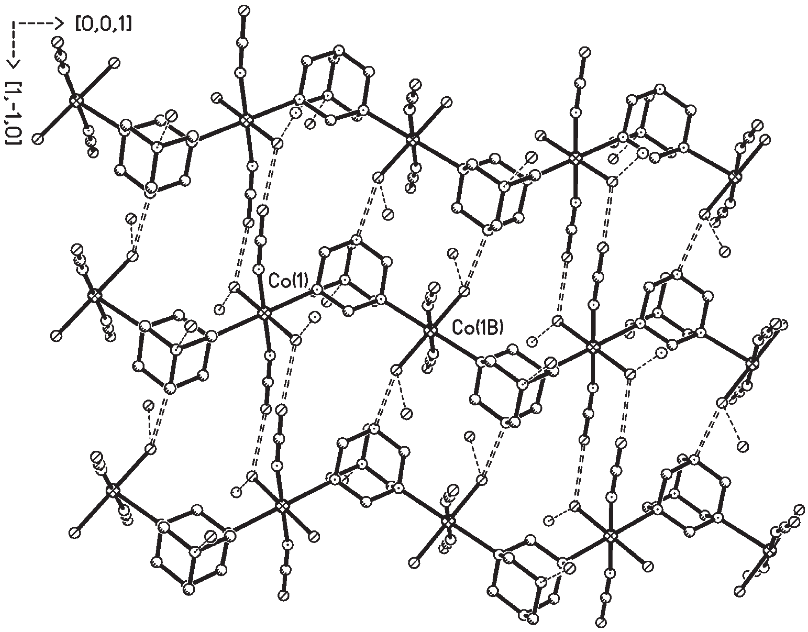

Figure 2. View onto the "parent" supramolecular sheet extending the polymeric chains of polyhedra of **I** along $[1, -1, 0]$. The intra-sheet hydrogen bonds are indicated by broken bonds and the inter-layer hydrogen bonds are represented by broken lines.

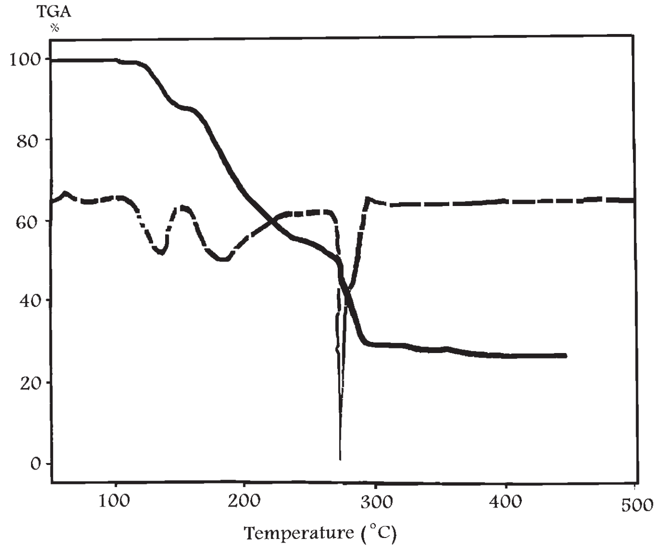

Figure 3. Thermal decomposition curves of **I**. TG (full line) weight (%) vs. temperature (°C); DTA (broken line) arb. units vs. temperature (°C).

Further inter-chain O–H $\cdots$ O hydrogen bonding is formed between coordinated water molecules of the Co(II) in one chain and the O atom from terminal *N*-cyanato ligands in an adjacent chain.

3.3. *Thermal properties*

The results of the thermal studies of **I** are given in figure 3, as TG and DTA curves. The TG curve revealed that the decomposition takes place through three steps with weight loss of 11.48%, 25.8% and 36.2%, respectively. The DTA curve shows these three steps as three endotherms with $T_{\max} = 133^\circ\text{C}$, 181.9°C and 272°C, respectively. The weight loss in the first step corresponds to loss of two water molecules (theor. = 11.32%). The dehydrated complex starts to decompose just above 150°C and the second step is completed around 220°C; the weight loss in this step corresponds to loss of two NCO groups (theor. = 26.4%). The final step suggests the degradation of the rest leading to the formation of a stable residue.

Supplementary material

Further details of the crystal structure investigation are available from the Cambridge Crystallographic Data Center, CCDC-657937, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

Acknowledgements

M. A. S. G. thanks the Swedish International Development Coorporation Agency under the Swedish Research Links program (Grant 348-2004-5473). M. R. S. thanks the Faculty of Science, Fayoum University, for assistance.

References

[1] (a) J.M. Lehn. *Supramolecular Chemistry*, VCH, Chapter 9 (1985); (b) R. Robson, B.F. Abrahms, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Lieu. *Supramolecular Archeticture*, American Chemical Society, Washington DC (1992); (c) P. Feng, X. Bu, G.D. Stucky. *Nature*, **388**, 735 (1997); (d) Y. Zhang, M. Nishiura, J. Li, W. Deng, T. Imamoto. *Inorg. Chem.*, **38**, 825 (1999).

[2] (a) H. Zhang, X. Wang, K. Zhang, B.K. Teo. *Coord. Chem. Rev.*, **183**, 157 (1999); (b) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *Chem. Commun.*, 631 (1997).

[3] (a) T.C.W. Mak. *Z. Kristallogr.*, **165**, 105 (1983); (b) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *J. Am. Chem. Soc.*, **117**, 12861 (1995).

[4] (a) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *Inorg. Chem.*, **36**, 1732 (1997); (b) J. Pickardt, G. Gong. *Z. Anorg. Allg. Chem.*, **602**, 183 (1994).

[5] (a) S.-L. Zhong, M.-L. Tong, R.-W. Fu, X.-M. Chen, S.W. Ng. *Inorg. Chem.*, **40**, 3562 (2001); (b) M.A.S. Goher, F.A. Mautner, M.A.M. Abu-Youssef, A.K. Hafez, A.M.A. Badr. *J. Chem. Soc., Dalton Trans.*, 3309 (2002); (c) N. Mondal, M.K. Saha, S. Mitra, V. Gramlich. *J. Chem. Soc., Dalton Trans.*, 3218 (2000).

[6] (a) S.A. Barnett, A.J. Blake, N.R. Champness, C. Wilson. *Chem. Commun.*, 1640 (2002); (b) M.A.S. Goher, F.A. Mautner, A.K. Hafez, A.M.A. Abu-Youssef, C. Gspan, A.M.A. Badr. *Polyhedron*, **22**, 975 (2003).

[7] M.A.S. Goher, F.A. Mautner, M.A.M. Abu-Youssef, A.K. Hafez, A.M.A. Badr, C. Gspan. *Polyhedron*, **22**, 3137 (2003).

[8] (a) F. Wiesbrock, H. Schmidbaur. *J. Chem. Soc., Dalton Trans.*, 3201 (2002); (b) O.R. Evans, W. Lin. *Inorg. Chem.*, **39**, 2189 (2000).

[9] C. Livage, C. Egger, M. Nogues, G. Ferey. *J. Mater. Chem.*, **8**, 2743 (1998).

[10] (a) J. Pickardt, G. Gong. *Z. Naturforsch.*, **B48**, 23 (1993); (b) J. Pickardt, G. Gong. *Z. Anorg. Allg. Chem.*, **602**, 183 (1994); (c) J. Pickardt, G. Gong, S. Wischnack, C. Steinkopff. *Z. Naturforsch.*, **B49**, 325 (1994).

[11] (a) J. Chakraborty, B. Samanta, A.S. Batsanov, J. Ribas, M.S. El Fallah, S. Mitra. *Struct. Chem.*, **17**, 401 (2006); (b) B.-H. Liu, S.-H. Yu, S.-F. Chen, C.-Y. Wu. *J. Phys. Chem. B*, **110**, 4039 (2006).

[12] (a) Y. Zhang, J. Li, M. Nishiura, T. Imamoto. *J. Mol. Struct.*, **523**, 257 (2000); (b) Q. Liu, Y.-Z. Li, Y. Song, H. Liu, Z. Xu. *J. Solid State Chem.*, **177**, 4701 (2004).

[13] (a) Q. Liu, X. Sun, J.-Z. Zou, Z. Xu, K.-B. Yu. *J. Coord. Chem.*, **55**, 1021 (2002); (b) Q. Liu, B. Li, X. Sun, Z. Xu, K. Yu. *Acta Crystallogr.*, **E57**, m151 (2001).

[14] H.-L. Zhu, D.-S. Xia, Q.-F. Zeng, Z.-G. Wang, D.-Q. Wang. *Acta Crystallogr.*, **E59**, m1020 (2003).

[15] (a) D. Chopra, P. Dagur, A.S. Prakash, T.N.G. Row, M.S. Hegde. *J. Cryst. Growth*, **275**, e2049 (2005); (b) J. Chakraborty, B. Samanta, G. Rosair, V. Gramlich, M.S. El Fallah, J. Ribas, T. Matsushita, S. Mitra. *Polyhedron*, **25**, 3006 (2005).

[16] K.-Y. Choi, M.-H. Kim, M.J. Kim. *Transition Met. Chem.*, **29**, 904 (2004).

[17] P.M. Graham, R.D. Pike, M. Sabat, R.D. Baily, W.T. Pennington. *Inorg. Chem.*, **39**, 5121 (2000).

[18] A.K. Ghosh, D. Ghoshal, G.B. Drew, G. Mostafa, N.R. Chaudhuri. *Struct. Chem.*, **17**, 85 (2006).

[19] (a) F.A. Mautner, M.A.S. Goher, N.A. Al-Salem. *Polyhedron*, **16**, 2877 (1997); (b) M.A.S. Goher, F.A. Mautner. *J. Chem. Soc., Dalton Trans*., 1923 (1999); (c) M.A.S. Goher. *Can. J. Chem.*, **53**, 2657 (1975); (d) T.C.W. Mak, M.A.S. Goher, A.K. Hafez. *Inorg. Chim. Acta*, **146**, 103 (1988).

[20] M.A.S. Goher, A. Escuer, F.A. Mautner, N.A. Al-Salem. *Polyhedron*, **21**, 1871 (2002).

[21] R.H. Blessing. *Acta Crystallogr.*, **A51**, 33 (1995); SADABS: Bruker AXS (1998).

[22] (a) G.M. Sheldrick. *SHELXS-86: Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen, Germany (1986); (b) G.M. Sheldrick. *SHELXL-93: Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany (1993); (c) *SHELXTL 5.03 (PC-Version), Program Library for the Solution and Molecular Graphics*, Siemens Analytical Instruments Division, Madison, WI (1995).

[23] S. Banerjee, M.G.B. Drew, A. Ghosh. *Polyhedron*, **22**, 2933 (2003).

[24] D. Forster, G.M.L. Goodgame. *J. Chem. Soc.*, 1286 (1965).

[25] R.A. Baily, S.L. Kozak, T.M. Michelsen, W.N. Mills. *Coord. Chem. Res.*, **6**, 407 (1971).

[26] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd edn, Elsevier, New York (1984).

[27] M. Linhart, M. Weigel. *Z. Anorg. Allg. Chem.*, **66**, 226 (1951).