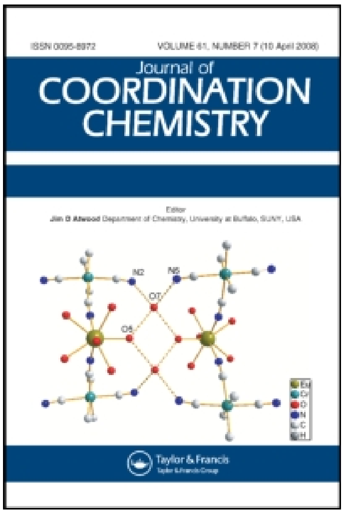

Journal of Coordination Chemistry

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

Synthesis and spectroscopic studies of mixed-ligand complexes of lead(II) hexafluoroacetylacetonate including the crystal structure of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$

Farzin Marandi[a]; Suchada Chantrapromma[b]; Hoong-Kun Fun[c]
[a] Department of Science, Payame Noor University, Zanjan, Iran [b] Faculty of Science, Department of Chemistry, Prince of Songkhla University, Hat-Yai, Songkhla 90112, Thailand [c] X-ray Crystallography Unit, School of Physics, Universiti Sains, Malaysia, 11800 USM Penang, Malaysia

To cite this Article Marandi, Farzin , Chantrapromma, Suchada and Fun, Hoong-Kun(2009) 'Synthesis and spectroscopic studies of mixed-ligand complexes of lead(II) hexafluoroacetylacetonate including the crystal structure of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$', Journal of Coordination Chemistry, 62: 2, 249 — 256
To link to this Article: DOI: 10.1080/00958970802203774
URL: http://dx.doi.org/10.1080/00958970802203774

Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 249–256

Taylor & Francis
Taylor & Francis Group

Synthesis and spectroscopic studies of mixed-ligand complexes of lead(II) hexafluoroacetylacetonate including the crystal structure of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$

FARZIN MARANDI*†, SUCHADA CHANTRAPROMMA‡ and
HOONG-KUN FUN§

†Department of Science, Payame Noor University, Zanjan, Iran
‡Faculty of Science, Department of Chemistry, Prince of Songkhla University,
Hat-Yai, Songkhla 90112, Thailand
§X-ray Crystallography Unit, School of Physics, Universiti Sains, Malaysia,
11800 USM Penang, Malaysia

(*Received 7 January 2008; in final form 19 March 2008*)

Four new mixed-ligand complexes of lead(II) hexafluoroacetylacetonate (hfa) were synthesized and characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy. The single-crystal structure of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$ (**1**) shows the complex to be a dimeric unit as a result of nitrate bridging. The coordination number of Pb(II) is eight with four N-donors from a "phen" and four O-donors from the hexafluoroacetylacetonate and nitrate ligands. This dimeric complex is the first fluorine β-diketonate and nitrate mixed-ligand lead(II) complex that has been characterized by X-ray structural analysis. The supramolecular features in this complex are controlled by weak directional intermolecular interactions and aromatic π–π stacking interactions.

Keywords: Spectroscopic studies; Crystal structure; Lead(II) complex; Intermolecular interactions

1. Introduction

Metal-organic supramolecular chemistry has developed rapidly to produce new materials with interesting structural features and potential applications [1, 2]. By self-assembly of well-designed organic ligands and metal ions under appropriate conditions, a variety of novel metallosupramolecular architectures have been achieved. Hydrogen bonds also have been used to organize coordination compounds in hydrogen-bonded networks; π–π interactions have been less studied in design and synthesis of coordination compounds [1, 2]. Shimoni and Glusker, however, have pointed out that although C–H$\cdots$F–C interactions are weak as compared to C–H$\cdots$O–C interactions, their contribution cannot be ignored in determining molecular packing in crystals [3]. A number of studies have been carried out to explore the different modes of interactions involving the C–F group [4]. Row *et al.* have investigated the

---

*Corresponding author. Email: fmarandi2004@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802203774

interactions of organic fluorine in different chemical environments and have demonstrated that fluorine provides different types ($F \cdots F$, $C–H \cdots F$, and $C–F \cdots \pi$) of directional interactions to build structures in a number of organic compounds [5].

Lead can form a range of mono, di and polynuclear complexes which display interesting structural features as a consequence of the large radius, different coordination numbers and the possible occurrence of a stereochemically active lone pair of electrons [6]. In complexes of lead(II), the coordination sphere is generally determined by a number of factors, including lone pair-bond pair repulsions (of comparable influence) so that seemingly minor differences in ligands or in the crystal array can have quite remarkable effects upon coordination stereochemistry.

In an effort to explore weak interactions in complexes, lead(II) complexes with β-diketonate and neutral diimine chelating ligands have been synthesized and determined by X-ray crystal structure [7]. We report here on the preparation and crystal structure of the first fluorine β-diketonate and nitrate mixed-ligand lead(II) complex that was characterized by X-ray structural analysis.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Elemental analyses were conducted using a Heraeus CHN-O-Rapid analyzer. Solution ^{1}H NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz using d_6-dimethylsulfoxide as solvent.

2.2. *Preparation of [Pb_2(phen)$_4$(hfa)$_2$(μ-NO_3)$_2$] (1)*

A solution of Hhfa (1 mmol, 0.208 g), NaOH (1 mol L^{-1}, 1 mL) and 1,10-phenanthroline (2 mmol, 0.360 g) in CH_3CN (20 mL) was mixed with a solution of $Pb(NO_3)_2$ (1 mmol, 0.331 g) in 1 : 1 water/CH_3CN (15 mL). The clear solution formed was allowed to evaporate slowly at room temperature to provide crystals suitable for structure determination. Found: C, 41.32; H, 2.10; N, 8.64. Calculated for $C_{29}H_{17}F_6N_5O_5Pb$: C, 41.59; H, 2.03; N, 8.37%. IR (cm^{-1}): 763m, 1018m, 1149s, 1280vs, 1380vs, 1473s, 1533s, 1596m, 1615s, 1735w, 1765w, 3055w. ^{1}H NMR (d6-dmso, δ): 9.25 (Py–H), 8.65 (Py–H), 7.95 (Py–H), 7.70 (Py–H), 6.10 (s, =CH–). ^{13}C NMR (d6-dmso, δ): 83.93, 124.81, 127.60, 130.00, 138.70, 145.21, 150.41, 171.53, 172.85 ppm.

2.3. *Preparation of [Pb(2,2′-bpy)$_2$(hfa)(μ-NO_3)] (2)*

Complex **2** was synthesized in the same way as **1** using 2,2′-bipyridine in place of 1,10-phenanthroline. Found: C, 38.32; H, 2.30; N, 8.94. Calculated for $C_{25}H_{17}F_6N_5O_5Pb$: C, 38.07; H, 2.16; N, 8.88%. IR (cm^{-1}): 763 m, 1018 m, 1149s, 12650s, 1375vs, 1485s, 1530s, 1587 m, 1625s, 1720w, 1755w, 3065w. ^{1}H NMR (d6-dmso, δ): 8.75 (Py–H), 8.50 (Py–H), 7.95 (Py–H), 7.50 (Py–H), 6.00 (s, =CH–). ^{13}C NMR (d6-dmso, δ): 84.88, 121.41, 124.90, 138.30, 149.80, 155.52, 170.62, 173.26 ppm.

2.4. *Preparation of [Pb(phen)$_2$(hfa)(NCS)] (3)*

A solution of Hhfa (1 mmol, 0.208 g), NaOH (1 mol L^{-1}, 1 mL) and 1,10-phenanthroline (2 mmol, 0.360 g) in CH_3CN (20 mL) was mixed with a solution of $Pb(NO_3)_2$ (1 mmol, 0.331 g) and KSCN (2 mmol, 0.194 g) in 1 : 1 water/CH_3CN (15 mL). The clear solution formed was allowed to evaporate slowly at room temperature to provide crystals suitable for structure determination. Found: C, 43.52; H, 2.20; N, 8.44. Calculated for $C_{30}H_{17}F_6N_5O_2SPb$: C, 43.27; H, 2.04; N, 8.41%. IR (cm^{-1}): 765m, 779m, 1025m, 1155s, 1270s, 1480s, 1525s, 1590m, 1630s, 2045s, 3044w. ^{1}H NMR (d6-dmso, δ): 9.15 (Py–H), 8.67 (Py–H), 7.93 (Py–H), 7.77 (Py–H), 6.04 (s, = CH–). ^{13}C NMR (d6-dmso, δ): 83.55, 125.00, 127.43, 131.22, 132.15, 138.40, 145.00, 150.22, 171.25, 172.55 ppm.

2.5. *Preparation of [Pb(2,2′-bpy)$_2$(hfa)(NCS)] (4)*

Complex **4** was synthesized in the same way as **3** using 2,2′-bipyridine in place of 1,10-phenanthroline. Found: C, 39.42; H, 2.11; N, 8.69. Calculated for $C_{26}H_{17}F_6N_5O_2SPb$: C, 39.79; H, 2.17; N, 8.93%. IR (cm^{-1}): 765m, 779m, 1022m, 1157s, 1253s, 1483s, 1543s, 1589m, 1735w, 1640s, 2040s, 3050w. ^{1}H NMR (d6-dmso, δ): 8.68 (Py–H), 8.55 (Py–H), 7.93 (Py–H), 7.50 (Py–H), 6.00 (s, = CH–). ^{13}C NMR (d6-dmso, δ): 84.73, 84.88, 121.21, 124.50, 135.44, 137.30, 149.20, 155.12, 170.82, 173.16 ppm.

2.6. *Crystallography*

Crystallographic data were collected at 100 K with the Oxford Cyrosystem Cobra low temperature attachment. The data were collected using a Bruker Apex2 CCD diffractometer with graphite monochromated Mo-Kα radiation at a detector distance of 5 cm and with APEX2 software [8]. The collected data were reduced using SAINT [8] and empirical absorption corrections were performed using SADABS [8]. The structures were solved by direct methods and refined by least-squares using the SHELXTL software package [9]. Materials for publication were prepared using SHELXTL [9] and ORTEPIII [10].

3. Results and discussion

3.1. *Spectroscopic studies*

IR spectra display characteristic absorption bands for "phen," "2,2′-bpy," "hfa," nitrate, and thiocyanate. The relatively weak absorption bands at 3065 and 3040 cm^{-1} are C–H modes involving the aromatic ring hydrogen atoms. The absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to aromatic ring vibrations of "phen" or "2,2′-bpy." The absorption bands with variable intensity in the frequency range 1100–1350 cm^{-1} correspond to C–F vibrations of "hfa" anion. Strong bands in the >1600 cm^{-1} regions were assigned to stretching modes of C=O of "hfa" ligands [11]. In general, IR absorption bands in the region 1300–1500 cm^{-1} are due to NO_3^- stretching vibrations. The combination band ($\upsilon_1 + \upsilon_4$) of NO_3^- appears to split into weak bands in the region 1700–1800 cm^{-1}. The width of the splitting parameter in $cm^{-1}(\Delta\upsilon)$ obtained from these weak bands is a good criterion for ascertaining the coordination of NO_3^-, *i.e*. the splitting for bidentate coordination is more than 25 cm^{-1}, for monodentate less than approximately 25 cm^{-1}, and there is no splitting for ionic (not coordinated) bonds [12]. $\Delta\upsilon$ values for **1** and **2** are rather large, which shows bidentate coordination of NO_3^-. The characteristic bands of the thiocyanate of **3** and **4** show one very strong and sharp band at 2045 and 2040 cm^{-1} due to the υ(CN) mode, in addition to medium to strong bands at 779 and 765 cm^{-1} related to υ(CS). Bridging N,S-thiocyanato groups are expected to exhibit two υ(CN) bands above and below 2000 cm^{-1}, as well as two υ(CS) bands [13]. However, the appearance of a single υ(CN) around 2000 cm^{-1} is not uncommon and has been reported in many μ(N,S)-thiocyanato complexes [14].

The ^1H NMR spectra in DMSO of **1**–**4** at 7.50–9.50 ppm display four different aromatic protons of the "phen" or "2,2′-bpy" ligands. The methine, $=CH$, is a singlet at 6 ppm for all complexes. The ^{13}C NMR spectra (DMSO) of **1**, **3** and **2**, **4** has six and five distinct bands assigned to the aromatic carbons rings of the "phen" or "2,2′-bpy", respectively. Three distinct resonances at 85–180 ppm are assigned to carbons of "hfa" anions. The ^{13}C NMR spectra of **3** and **4** display a band at 132 ppm assigned to carbons of thiocyanate.

Because of the similarity of IR spectra and coordination mode of nitrate in **1** and **2**, **2** may be considered dinuclear, but **3** and **4** may be considered as coordination polymers. Given the high coordination numbers and the inherently relatively weak bonding interaction of a metal such as Pb [15] and comparison with reported structures [16], this is unsurprising.

3.2. *Crystal structure of [$Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2$] (1)*

Determination of the structure of the [$Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2$] (**1**) by X-ray crystallography (table 1) showed the complex (figure 1) to be dimeric. Each lead is chelated by four nitrogen atoms of two "phen" ligands with Pb–N distances of 2.611(3), 2.671(3), 2.671(3) and 2.673(3) Å (two chelating "phen" ligands have an angle of 69.97°) and four oxygen atoms of two hexafluoroacetylacetonates and two nitrates with Pb–O distances of 2.689(3), 2.727(3), 2.741(3) and 2.875(3) Å. The Pb atoms of dimeric units are linked *via* $Pb(\mu\text{-}NO_3)_2Pb$ (figure 1), a feature of many Pb(II) complex structures [17, 18] involving two nitrate-*O* atoms (a novel behavior of nitrate anion). The coordination number in this complex is eight (four of two "phen," two of "hfa" and two of nitrate anions). However, for Pb(II) complexes, a ′holodirected′ [19] coordination sphere has been identified based on Pb–O and Pb–N separations ranging from 2.605–2.873 Å; if other oxy-anions such as nitrate and perchlorate are assumed to be relatively weak donor ligands, Pb–O separations as great as 3.41 Å have been associated with bonding [17]. The range of Pb–X distances and the arrangement of ligands and anions in **1** indicate that the lone pair is inactive (table 2). The fluorine β-diketonate can be bidentate and bridging in lead(II) complexes [7], but in this compound "hfa" is bidentate. It is possible the presence of bridging nitrates and chelating ligands (two "phen" and "hfa") around Pb does not leave enough space for the bonding of "hfa" anions

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{29}H_{17}F_6N_5O_5Pb$
Formula weight	836.67
Temperature (K)	100.0(1)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.2950(5)
b	9.9310(5)
c	16.4819(9)
α	84.867(3)
β	79.842(2)
γ	66.327(3)
Volume (Å^3)	1371.26(13)
Z, calculated density (Mg m^{-3})	2, 2.026
Absorption coefficient (mm^{-1})	6.244
$F(000)$	804
Crystal size (mm^3)	$0.44 \times 0.26 \times 0.06$
θ range for data collection	1.26 to 37.14°
Limiting indices	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-27 \leq l \leq 27$
Reflections collected/unique	56308/13793 [$R_{(int)} = 0.0689$]
Data completeness	98.1%
Max. and min. transmission	0.7057 and 0.1711
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13793/0/415
Goodness-of-fit on F^2	0.995
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0387$, $wR_2 = 0.0908$
R indices (all data)	$R_1 = 0.0516$, $wR_2 = 0.0995$
Largest diff. peak and hole (e Å^{-3})	5.208 and −2.543

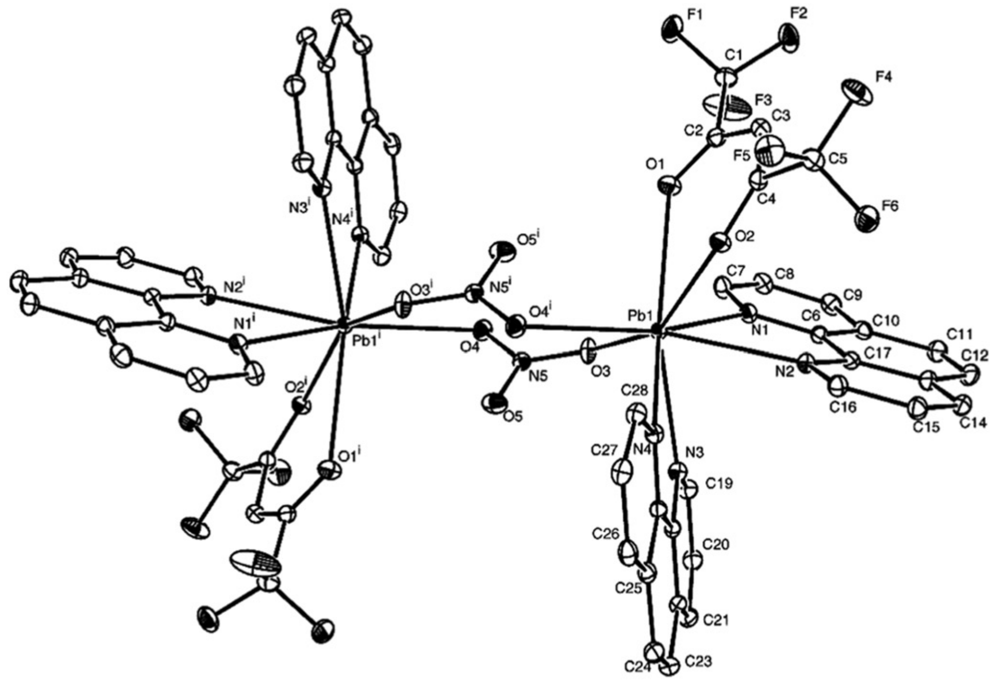

Figure 1. ORTEP diagram of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$.

of adjacent molecules. To the best of our knowledge, this dimeric complex is the first fluorine *β*-diketonate and nitrate mixed-ligand lead(II) complex that has been characterized by X-ray structural analysis.

Since the two phenanthroline ligands on each metal have different orientations (two chelating "phen" ligands have an angle of 69.97°), it is unsurprising, given the importance of *π–π* stacking and other inter-aromatic attractions in solid-state structures of numerous azaaromatic ligands [20, 21], to find that the lattice contains two arrays of parallel phenanthroline units. The packing diagram of this complex exhibits self-assembled structural topologies via two different *π–π* stacking [face-to-face with distance of 3.352 and 3.428 Å, slipped face-to-face with distance of 3.401 and 3.486 Å (figure 2)], appreciably shorter than the normal *π–π* stacking [22].

Table 2. Selected bond lengths (Å) and angles (°) for $[Pb_2(phen)_4(hfacac)_2(\mu\text{-}NO_3)_2]$.

Pb1–N3	2.611(3)	Pb1–O2	2.689(2)
Pb1–N1	2.671(3)	Pb1–O1	2.727(3)
Pb1–N2	2.671(3)	Pb1–O3	2.741(3)
Pb1–N4	2.673(3)	Pb1–O4^{i}	2.875(3)
N3–Pb1–N1	82.35(8)	O2–Pb1–O1	66.76(8)
N3–Pb1–N2	72.52(8)	N3–Pb1–O3	74.99(8)
N2–Pb1–O2	69.38(8)	N1–Pb1–O3	68.83(8)
N4–Pb1–O2	80.21(8)	O4^{i}–Pb1–O1	99.18(8)
N1–Pb1–O1	69.01(9)	O4^{i}–Pb1–O2	86.67(8)
N2–Pb1–O1	99.35(8)	O4^{i}–Pb1–O3	92.55(8)

i: $-x, -y, -z$.

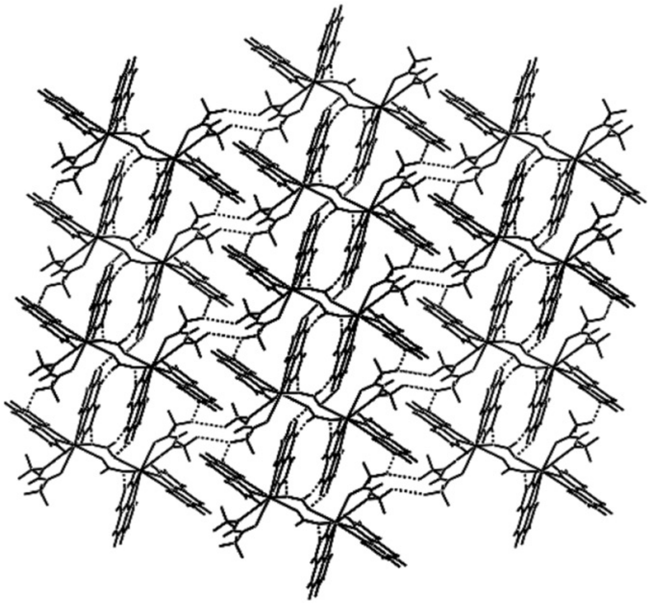

Figure 2. Packing of **1** to form 3D supramolecular layers *via* intermolecular interactions.

A search was made for weak directional intermolecular interactions in the crystal structure of **1**. There are C–F $\cdots\pi$ interactions (F1 $\cdots$ Cg (C19 $\cdots$ C28) with distance of 2.996 Å) [23], C–F $\cdots$ H–C interactions (F2 $\cdots$ H15–C15 with distance of 2.527 Å (H–C $\cdots$ F = 3.337 Å and ∠F $\cdots$ H–C = 145.87°), and C–H $\cdots$ O (nitrate) interaction (O3 $\cdots$ H27–C27 with distance of 2.483 Å (H–C $\cdots$ O = 3.411 Å and ∠O $\cdots$ H–C = 176°, O4 $\cdots$ H21–C21 with distance of 2.391 Å (H–C $\cdots$ O = 3.175 Å and ∠O $\cdots$ H–C = 141.76° and O5 $\cdots$ H24–C24 with distance of 2.499 Å (H–C $\cdots$ O = 3.406 Å and ∠O $\cdots$ H–C = 165.26°) [5b], values that suggest strong interactions within this class of weak non-covalent contacts [4, 24]. The four shortest F $\cdots$ F distances of 2.758(4) Å (F2 $\cdots$ F4), smaller than the sum of the van der Waals radii (2.94 Å) [25], indicate preferred packing of fluorines (figure 2).

The ability of weak interactions to control packing of molecular moieties to generate different patterns suggests their importance in crystal engineering. Such weak interactions are prolific in molecular assemblies providing both directionality and flexibility in the crystal structure. Further studies on the mapping of the charge density distributions followed by topological analysis of the regions in C–F $\cdots\pi$, C–F $\cdots$ H–C, C–H $\cdots$ O, F $\cdots$ F and $\pi\cdots\pi$ interactions are currently in progress.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-664357 for $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$. 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].

Acknowledgement

This work was supported by Payame Noor University. HKF would like to thank the Malaysian Government and Universiti Sains Malaysia for Scientific Advancement Grant Allocation (SAGA), grant no. 304/PFIZIK/653003/A118.

References

[1] (a) M.W. Hosseini. *Acc. Chem. Res.*, **38**, 313 (2005); (b) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (c) L. Carlucci, G. Ciani, D.M. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2003).
[2] (a) P.J. Steel. *Acc. Chem. Res.*, **38**, 243 (2005); (b) B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005); (c) L. Brammer. *Chem. Soc. Rev.*, **33**, 476 (2004).
[3] L. Shimoni, J.P. Glusker. *Struct. Chem.*, **5**, 383 (1994).
[4] K. Reichenbacher, H.I. Suss, J. Hulliger. *Chem. Soc. Rev.*, **34**, 22 (2005).
[5] (a) A.R. Choudhury, R.G. Bhat, T.N.G. Row, S. Chandrasekaran. *Cryst. Growth Des.*, **7**, 844 (2007); (b) D. Chopra, T.N.G. Row. *Cryst. Growth Des.*, **6**, 1267 (2006) and **5**, 1679 (2005).
[6] (a) C. Janiak. *J. Chem. Soc., Dalton Trans.*, 2781 (2003); (b) F. Marandi, B. Mirtamizdoust, A.A. Soudi, V.T. Yilmaz, C. Kazak. *Z. Anorg. Allg. Chem.*, **632**, 2380 (2006); (c) J.L. Song, J.G. Mao, Y.Q. Sun, A. Clearfield. *Eur. J. Inorg. Chem.*, **23**, 4218 (2003).

[7] (a) F. Marandi, A. Morsali, A.A. Soudi. *Z. Anorg. Allg. Chem.*, **633**, 661 (2007); (b) F. Marandi, N. Asghari, M. Ghorbanloo, A.A. Soudi, P. Mayer. *Z. Anorg. Allg. Chem.*, **633**, 536 (2007); (c) F. Marandi, P. McArdle, B. Mirtamizdoust, A.A. Soudi. *J. Coord. Chem.*, **60**, 891 (2007); (d) J.M. Harrowfield, F. Marandi, A.A. Soudi. *Inorg. Chim. Acta*, **358**, 4099 (2005); (e) J.M. Harrowfield, S. Maghaminia, A.A. Soudi. *Inorg. Chem.*, **43**, 1810 (2004); (f) F. Marandi, N. Asghari, M. Ghorbanloo, P. McArdle. *J. Coord. Chem.*, **61**, 1545 (2008).

[8] Bruker. *APEX2 Version 1.27, SAINT Version 7.12a and SADABS Version 2004/1*, Bruker AXS Inc., Madison, Wisconsin, USA (2005).

[9] G.M. Sheldrick. *SHELXTL Version 5.1*, Bruker AXS: Madison, WI, USA (1998).

[10] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).

[11] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, John Wiley & Sons, New York (1986).

[12] Y. Fukuda, A. Nakao, K. Hayashi. *J. Chem. Soc., Dalton Trans.*, 527 (2002).

[13] M.A.S. Goher, F.A. Mautner, A.K. Hafez, M.A.M. Abu-Youssef, C. Gspan, A.M.-A. Badr. *Polyhedron*, **22**, 975 (2003).

[14] B. Chand, U. Ray, G. Mostafa, T.-H. Lu, C. Sinha. *Polyhedron*, **23**, 1669 (2004).

[15] P. Schwerdtfeger, G.A. Heath, P. Dolg, M.A. Bennett. *J. Am. Chem. Soc.*, **114**, 7518 (1992).

[16] (a) A.R. Mahjoub, A. Morsali. *Polyhedron*, **21**, 197 (2002); (b) A. Morsali, X.-M. Che. *J. Coord. Chem.*, **57**, 1233 (2004); (c) A. Morsali, M. Payeghadr, S. Salehi, M. Moradi. *J. Coord. Chem.*, **56**, 761 (2003).

[17] A.A. Soudi, F. Marandi, A. Ramazani, E. Ahmadi, A. Morsali. *C. R. Chimie*, **8**, 157 (2005).

[18] A.K. Hall, J.M. Harrowfield, A. Morsali, A.A. Soudi, A. Yanovsky. *CrystEngCommun*, **2**, 82 (2000).

[19] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).

[20] (a) V. Russell, M. Scudder, I.G. Dance. *J. Chem. Soc.*, *Dalton Trans.*, **6**, 789 (2001); (b) M. Scudder, I.G. Dance. *J. Chem. Soc.*, *Dalton Trans.*, 3755 (1996); (c) M. Scudder, I.G. Dance. *Chem. Eur. J.*, **2**, 481 (1996).

[21] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2001).

[22] (a) T. Dorn, C. Janiak, K. Abu-Shandi. *CrystEngComm.*, **7**, 633 (2005); (b) S. Banerjee, A. Ghosh, B. Wu, P.-G. Lassahn, C. Janiak. *Polyhedron*, **24**, 593 (2005); (c) S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak, A. Ghosh. *Inorg. Chim. Acta*, **358**, 535 (2005).

[23] A.R. Choudhury, T.N.G. Row. *Cryst. Growth Des.*, **4**, 47 (2004).

[24] D.L. Reger, R.F. Semeniuc, V. Rassolov, M.D. Smith. *Inorg. Chem.*, **43**, 537 (2004).

[25] R.S. Rowland, R. Taylor. *J. Phys. Chem.*, **100**, 738 (1996).