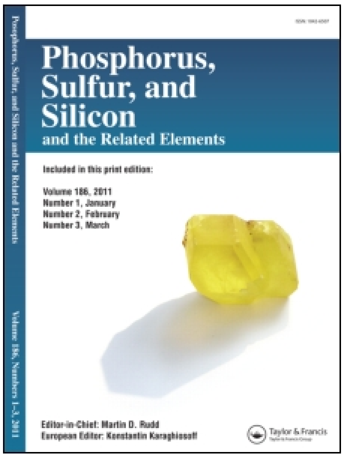


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of 2-Mercapto-1-cyclohexylimidazole-Based Zinc(II) and Cadmium(II) Bromide Complexes: The Crystal Structure of [Zn(Hmim$^{<i>chexyl</i>}$)$_2$(Br)$_2$] with N-H...Br Intermolecular Hydrogen Bonding Interactions

Mohamed M. Ibrahim[ab]; Salih S. Al-Juaid[c]; Q. Mohsen[b]
[a] Chemistry Department, Faculty of Science, Kafrelsheik University, Kafrelsheik, Egypt [b] Chemistry Department, Faculty of Science, Taif University, Taif, Saudi Arabia [c] Chemistry Department, Faculty of Science, King Abd Al Aziz University, Jeddah, Saudi Arabia

To cite this Article Ibrahim, Mohamed M. , Al-Juaid, Salih S. and Mohsen, Q.(2009) 'Synthesis and Characterization of 2-Mercapto-1-cyclohexylimidazole-Based Zinc(II) and Cadmium(II) Bromide Complexes: The Crystal Structure of [Zn(Hmim$^{<i>chexyl</i>}$)$_2$(Br)$_2$] with N-H...Br Intermolecular Hydrogen Bonding Interactions', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 9, 2324 — 2332

To link to this Article: DOI: 10.1080/10426500802454136

URL: http://dx.doi.org/10.1080/10426500802454136

Phosphorus, Sulfur, and Silicon, 184:2324–2332, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802454136

Synthesis and Characterization of 2-Mercapto-1-cyclohexylimidazole–Based Zinc(II) and Cadmium(II) Bromide Complexes: The Crystal Structure of [Zn(Hmim^{chexyl})$_2$(Br)$_2$] with N–H· · ·Br Intermolecular Hydrogen Bonding Interactions

Mohamed M. Ibrahim,[1,2] **Salih S. Al-Juaid,**[3] **and Q. Mohsen**[2]
[1]Chemistry Department, Faculty of Science, Kafrelsheik University, Kafrelsheik, Egypt
[2]Chemistry Department, Faculty of Science, Taif University, Taif, Saudi Arabia
[3]Chemistry Department, Faculty of Science, King Abd Al Aziz University, Jeddah, Saudi Arabia

Reactions of the ligand 2-mercapto-1-cyclohexylimidazole (Hmim^{chexyl}) with both zinc(II) and cadmium(II) bromides in ethanol solutions afforded 2:1 complexes of the type [M(Hmim^{chexyl})$_2$(Br)$_2$] (M = Zn ***1****, and Cd* ***2****) with an MBr$_2$S$_2$ configurations. Spectroscopic evidence (FT-IR and ^{1}H-^{13}C NMR) confirms that the exocyclic thione sulfur atoms are the donors in both complexes. Complex 1 crystallizes in a monoclinic system, space group C2/c, a = 16.180(3), b = 10.817(5), c = 13.602(3); α = 90, β = 106.754(17), γ = 90; Z = 4; R1 = 0.0229, wR2 = 0.0554. The coordination geometry about the zinc(II) atom is distorted tetrahedral with average Zn-S and Zn-Br bond lengths of 3.3418(8) and 2.4017(6) Å, respectively. The bromide ions form intermolecular N–H· · ·Br hydrogen bonding with the thione NH groups of the ligand molecule.*

Keywords Cadmium(II) complex; crystal structure; hydrogen bonding; mercaptoimidazole; zinc(II) complex

INTRODUCTION

The interaction of heterocyclic thiones with transition metals has attracted much attention in bioinorganic chemistry, because of their

Received 11 July 2008; accepted 13 August 2008.

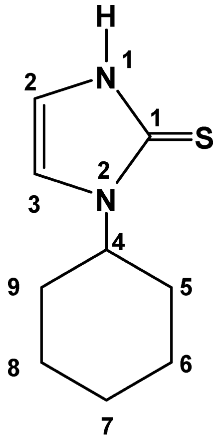
Mohamed M. Ibrahim is currently on leave, Chemistry Department, Faculty of Education, Kafrelsheikh University, Kafrelsheikh 33516, Egypt.

Address correspondence to Mohamed M. Ibrahim, Chemistry Department, Faculty of Science, Taif University, Taif, Saudi Arabia. E-mail: ibrahim652001@yahoo.com

usefulness as structural models for the active site of metalloproteins[1] as well as intermediates in the preparation of pharmaceutical products.[2] The chemical interest of the imidazoline-2-thiones lies in the fact that they are potentially ambidentate or multifunctional donors with the exocyclic S and heterocyclic N atoms available for coordination, and their biological interest arises from their structural analogy to thiolated nucleosides. In view of this, a series of metal complexes, including Cu(I), Ag(I), Cd(II), and Zn(II) ions with a range of heterocyclic thiones such as 1-methylimidazoline-2(3H)-thione (Hmimt) and imidazolidine-2-thione (Imt),[3] has been synthesized and characterized. Our investigations in this area have been concerned with zinc(II) model complexes[4,5] and, recently, a wide variety of thione- and thiolate-based zinc(II) complexes with either monomeric four-coordinate or dimeric pseudo-four-coordinated geometry have been prepared and characterized.[4–6] We report herein the synthesis and characterization of the monomeric thione-based zinc and cadmium complexes $[M(Hmim^{chexyl})_2(Br)_2]$ (M = Zn **1** and Cd **2**). The molecular structure of **1** is also reported.

RESULTS AND DISCUSSION

The reaction of the ligand 2-mercapto-1-cyclohexylimidazole (Scheme 1) with both zinc(II) and cadmium bromides in 2:1 molar ratio in hot ethanol readily produced the crystalline complexes $[Zn(Hmim^{chexyl})_2(Br)_2]$ **1** and $[Cd(Hmim^{chexyl})_2(Br)_2]$ **2** in good yield. The elemental analysis of both complexes confirmed their stoichiometry, and their physical properties are in accordance with the proposed



SCHEME 1 Structure of 2-mercapto-1-cyclohexylimidazole.

structures. In order to establish the mode of coordination in both complexes, we have examined their IR and ^{13}C NMR spectra, and also determined the crystal structure of one of these complexes.

IR and ^{13}C NMR Spectra

The IR spectra of complexes **1** and **2** show similarities due to the absence of ν (SH) band at $\sim$2500 cm^{-1} and the presence of ν (NH) band in the range of 3176–3170 cm^{-1}, as well as shifts to lower frequency in the ν (C=S) absorption to 515 cm^{-1}. This clearly indicates that the ligand is coordinated via the thione sulfur atoms in both complexes.[7] These shifts may result from (i) changes in the electronic state where the C=S bond loses some of its double bond character when the ligand coordinates via the thione sulfur and (ii) hydrogen bond effects, where it is a common feature of 1-methylimidazoline-2(3H)-thione complexes in which the thioamide proton (N(1)-H) of the molecule acts as an effective H-bond donor atom.[8] All of the thioamide bands are shifted to some degree, but the most significant change is that observed in the thioamide IV bands, which have the largest shift to lower frequency.[9] The thioamide IV band is affected with the bands in the free ligand (759 and 730 cm^{-1}), which are replaced by a sharp band at 741 and 673 cm^{-1} for zinc complex **1** and 744 and 681 cm^{-1} for cadmium complex **2**.

Complementary information is obtained by assignment of ^{1}H and ^{13}C NMR spectral features of the ligand and its complexes in DMSO-d_6. The ^{1}H NMR signals of the thioimidazolyl and cyclohexyl protons of both complexes are shifted downfield compared to their positions in the spectra of the free ligand, suggesting that in DMSO the ligand signals remain coordinated to both zinc(II) and cadmium(II) ions. The absence of the weak SH signal of the thiol form of the ligand and the complexes confirms that the coordination of the ligand in the solid state takes place only through the sulfur atom. The ^{13}C NMR resonance of the carbon atom attached to the thione sulfur atom (C1) is highly shifted by $\sim$3–4 ppm upfield upon complexation, and is thus the most sensitive to coordination. The ethylenic carbon atoms (C2-C3) are shifted downfield but to less extent (0.5–0.6 ppm). The cyclohexyl carbon atoms show much smaller chemical shifts. This observation has been further confirmed[10] for the complexation of thiourea (TU) with MCl_2 (M = Zn, Cd, and Hg), forming complexes of the formula $[M(TU)_2Cl_2]$. The ^{13}C NMR chemical shifts between free and bound TU also show a similar trend. The relatively significant upfield shifts exhibited by the thione carbon atoms (C1) in both complexes, together with the vibrational spectral evidence, are indicative of thione coordination.

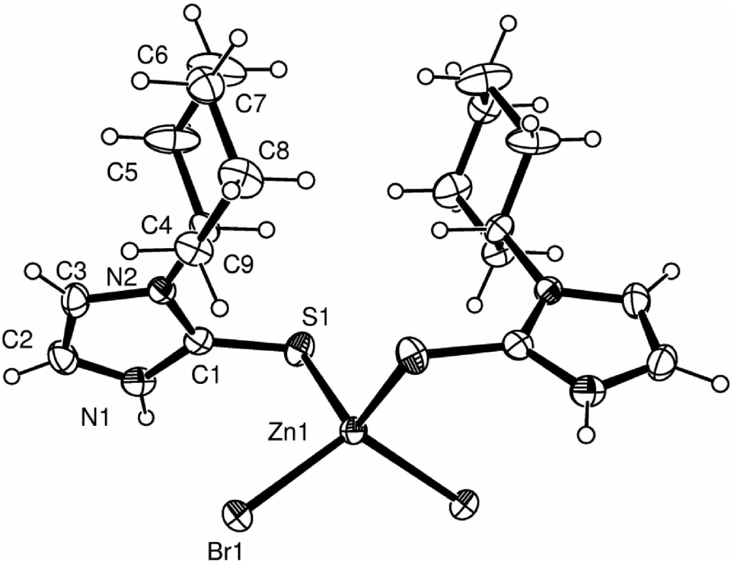


FIGURE 1 ORTEP drawing of the molecular structure of [Zn(Hmim^{chexyl})$_2$Br$_2$] **1**. Ellipsoids are depicted at 50% probability level.

X-Ray Crystal Structure of Complex 1

Complex **1** crystallizes as a monomer in a monoclinic crystal system in the space group C2/c (Table I). An ORTEP representation of the molecular structure of **1** is shown in Figure 1 and selected bond lengths (Å) and angles (°) are included in (Table II). In complex **1**, the zinc(II) ion is bound to the two sulfur atoms of the two imidazolidine thione ligand molecules, in addition to the two bromine ions. The four coordinate complexes have a distorted tetrahedral geometry. The bond angles are in the range 104.29(2)–116.13(3) degrees. The average Zn-S and Zn-Br bond lengths are 2.3418(8) and 2.4017(6) Å, respectively. These observed bond distances are in the same range as those found in the complexes of [Cd(Imt)$_2$Cl$_2$][11] and [Cd(thiou)$_2$Cl$_2$].[12] In complex **1**, the ligand molecules have their S(1)C(1)N(1)N(2) moieties essentially planar and have similar bond distances: S(1)-C(1) 1.713(3) Å, N(1)-C(1) 1.348(3) Å, and N(2)-C(1) 1.344(4) Å. The bond distances reported for the free imidazolinethiole molecule are *d*(S-C): 1.688(4) A, d(N-C): 1.330(3) Å, and 1.329(4) Å.[13] Intermolecular hydrogen bonding interactions take place between the N-bonded hydrogen atoms and the bromine ions. These are believed to be the main factor at the origin of the distortion of this compound.

TABLE I Crystallographic Details of Complex 1

Identification code	**1**
Empirical formula	$C_{18}H_{28}Br_2N_4S_2$ Zn
Formula weight	589.75
Crystal size [mm]	0.40 × 0.30 × 0.20 mm^3
Crystal color	Colorless
Space group Crystal system	C2/c Monoclinic
Z	4
a [Å]	16.180(3)
b [Å]	10.817(3)
c [Å]	13.602(3)
Volume [$Å^3$]	2279.6(9)
d (calc.) [g/cm^3]	1.718
Absorption coefficient [mm^{-1}] F(000)	4.777 1184
Temperature [K]	160(2)
$\theta-$ range for data collection [°]	2.30 to 24.98
Index ranges	−19<=h<=10 −10<=k<=12 −15<=l<=16
Reflections collected	4209
Independent reflections	2005[R(int) = 0.0377]
Completeness to θ Max. and min. transmission	99.5 % 0.4483 and 0.2509
Refinment method Data/restraints/parameters	Full-matrix least-squares on F^2 2005/0/123
Goodness-of-fit	0.827
Final R indices [I>2σ (I)]	R1 = 0.0229, wR2 = 0.0554
R indices (all data)	R1 = 0.0376, wR2 = 0.0619
Largest diff. Peak [e.$Å^{-3}$] and hole	0.450 and –0.458

TABLE II Selected Bond Lengths (Å) and Bond Angles (°) of 1

Zn(1)?S(1)	2.3418(8)	C(1)—S(1)	1.713(3)
Zn(1)—S(1)#1	2.3418(8)	C(1)—N(1)	1.348(3)
Zn(1)—Br(1)	2.4017(6)	C(1)—N(2)	1.344(4)
Zn(1)—Br(1)#1	2.4017(6)		
b) bond angles (°)			
S(1)—Zn(1)—S(1)#1	116.13(5)	S(1)#1—Zn(1)—Br(1)	104.29(2)
S(1)—Zn(1)—Br(1)#1	104.29(2)	Br(1)#1—Zn(1)—Br(1)	117.20(9)
S(1)#1—Zn(1)—Br(1)#1	107.79(3)	C(1)—S(1)—Zn(1)	101.20(9)
S(1)—Zn(1)—Br(1)	107.79(2)	N(2)—C(1)—N(1)	106.10(2)
N(2)—C(1)—S(1)	128.90(2)	N(1)—C(1)—S(1)	124.90(2)

Symmetry transformations used to generate equivalent atoms:
#1-x,y,-z-5/2

TABLE III Selected Hydrogen Bonds Parameters of 1

D—H ···· A	d(D—H)	d(H ···· A)	d(D ···· A)	<(DHA)
N(1)—H(1) ···· Br(1)#2	0.88	2.58	3.418(2)	158.5

Symmetry transformations used to generate equivalent atoms: #2-x,y,-z-2

The effects of monodentate thione-sulfur coordination on the ^{13}C resonance signals of the coordinated ligands have been discussed above. On average, the C=S distance is increased from 1.685 Å, in the free ligand[14] to 1.713 Å in complex **1**. This is consistent with a partial reduction of π -character of the C=S bonds in the coordinated ligands and thus a decrease of the C=S distance relative to the main free ligand distance.[14] This indicates that the C=S bonds are double bonds, as in the free ligand.

The smaller Zn-S-C angles are associated with ligands involved in intermolecular hydrogen bonding (Table III). The ligands also twist about their respective Zn-S-C planed, with dihedral angles 88 degrees for a ligand with intermolecular hydrogen bonding. The hydrogen

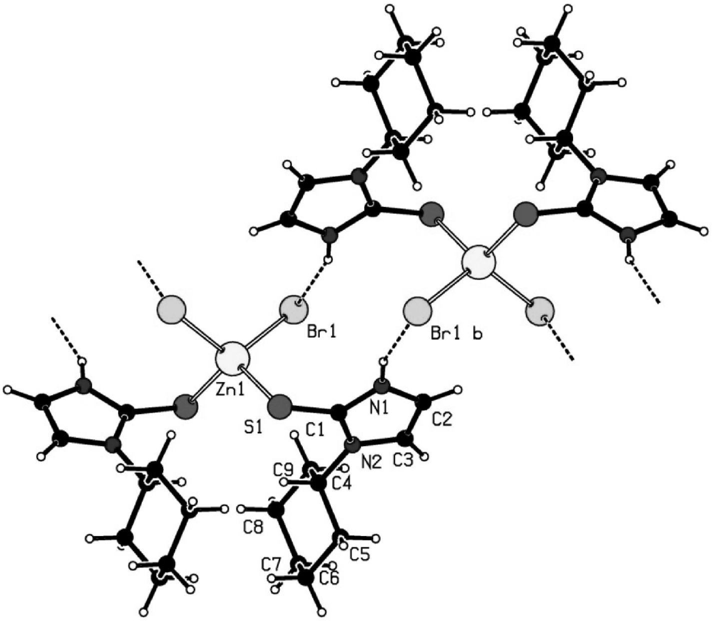


FIGURE 2 Part of the polymeric chain formed by N–H···Br intermolecular hydrogen bonding interaction.

bonding interactions are between thioamide NH groups and bromide ions (N(3)$\cdots$Br(1) 3.418(2) Å, N–H$\cdots$Br 158.5 degrees). A part of the polymeric chain formed by N–H$\cdots$Br intermolecular hydrogen bonding interaction is shown in Figure 2. These interactions link molecules together into chains.

CONCLUSION

Two new monomeric zinc(II) and cadmium(II) bromides complexes of the type [M(mim^{cyclohexyl})$_2$(Br)$_2$] (M = Zn **1**, and Cd **2**), derived from the ligand 2-mercapto-1-cyclohexylimidazole Tim^{cyclohexyl}, have been synthesized and characterized. The molecular structure of zinc(II) complex **1** has been determined and the coordination geometry about the zinc(II) atom is distorted tetrahedral. The bromide ions form intermolecular N–HBr hydrogen bonding with thione NH groups of the ligand molecule.

SUPPLEMENTARY MATERIAL

X-ray crystal data of zinc(II) complex **1** in CIF format has been deposited with the Cambridge Crystallographic Data Center and is available upon request.

EXPERIMENTAL

Materials and Physical Measurements

Infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vector22 FT-IR spectrophotometer from KBr pellets.^{1}H and ^{13}C NMR spectra were obtained using a Mercury-300 BB NMR300 and Gemini-200 NMR spectrophotometer.

Syntheses

Synthesis of 2-Mercapto-1-cyclohexylimidazole, Hmim^{chexyl}

The ligand 2-mercapto-1-cyclohexylimidazole was prepared from bromoacetaldehyde diethylacetal and cyclohexylamine according to the established procedure [4a,6]. Anal. For $C_9H_{14}N_2S$ (182.22): Calcd. C, 59.32; H, 7.74; N, 15.38; S, 17.56; Found C, 59.86; H, 7.73; N, 15.45; S, 17.49. ^{1}H NMR (DMSO), 298 K, TMS): $\delta = 1.17$–1.56 [p, 4H, CH_2(6,8)], 1.73–1.85 [q, 4H, CH_2(5,9)], 1.91 [m, 2H, CH_2(7], 4.66 [m, 1H, CH(4)], 6.71 [d, 1H, H^3-thioimidazole], 6.73 [d, 1H, H^2-thioimidazole], and 10.75 ppm [b, 1H, NH]. ^{13}C NMR (DMSO ,298 K, TMS): $\delta = 25.7$ [C(6,8)], 25.8 [C(5,9)], 32.2 [C(7)], 65.9 [C(4)], 114.5 [C^3(thioimidazole)], 114.7 [C^2(thioimidazole)], and 161.2 ppm [C^1 =S]. I R (KBr): ν (cm^{-1}):

3091 [s, br, NH], 1572 [s, -C=C- + C=N], 1425 [s, Thioamide I], 1288 [m, Thioamide II], 1097 [m, thioamide III], 759 and 730 [s, Thioamide IV], 676 [m, δ (C=S)], and 525 [s, π (C=S)].

Synthesis of [Zn(Hmim^{chexyl})$_2$(Br)$_2$] 1

A warm solution of $ZnBr_2$ (90 mg, 0.4 mmol) in 10 mL of ethanol was added to a warm solution of Hmim^{chexyl} (103 mg, 0.8 mmol) in 10 mL ethanol. The resulting mixed solution was stirred for 10 h at room temperature. The volume of the solution was reduced to 10 mL in vacuo, and the precipitate was filtered off and dried. A single colorless crystal suitable for X-ray crystallography was obtained by slow evaporation of methanolic solution of the complex. Yield 406 mg (86%). Anal. For $C_{18}H_{28}N_4S_2Br_2Zn$ (588.48): Calcd. C, 36.71; H, 4.79; N, 9.52; S, 10.87; Found C, 35.24; H, 4.71; N, 9.43; S, 10.62. ^{1}H NMR (DMSO), 298 K, TMS): δ = 1.25–1.64 [p, 8H, CH_2(6,8)], 1.83–1.97 [q, 8H, CH_2(5,9)], 1.94 [m, 4H, CH_2(7], 4.72 [m, 2H, CH(4)], 6.87 [d, 2H, H^3-thioimidazole], 6.11 [d, 2H, H^2-thioimidazole], and 11.11 ppm [b, 2H, NH]. ^{13}C NMR (DMSO ,298 K, TMS): δ = 26.0 [C(6,8)], 26.2 [C(5,9)], 32.2 [C(7)], 66.9 [C(4)], 115.7 [C^3(thioimidazole)], 115.9 [C^2(thioimidazole)], and 164.3 ppm [C^1 =S]. I R (KBr): ν (cm^{-1}): 3176 [s, br, NH], 1575 [s, -C=C- + C=N], 1458 [s, Thioamide I], 1289 [m, Thioamide II], 1107 [m, thioamide III], 731 and 673 [s, Thioamide IV], 667 [m, δ (C=S)], and 513 [s, π (C=S)].

Synthesis of [Cd(Hmim^{chexyl})$_2$(Br)$_2$] 2

The same procedure was employed to synthesize this complex, using $CdBr_2$ (0.051 g, 0.19 mmol). A white powder was obtained. Yield 418 mg (82%). Anal. For $C_{18}H_{28}N_4S_2Br_2Cd$ (635.86): Calcd. C, 33.99; H, 4.44; N, 8.81; S, 10.07; Found C, 34.62; H, 4.39; N, 8.63; S, 10. ^{1}H NMR (DMSO), 298 K, TMS): δ = 1.22–1.63 [p, 8H, CH_2(6,8)], 1.81–1.94 [q, 8H, CH_2(5,9)], 1.92 [m, 4H, CH_2(7], 4.70 [m, 2H, CH(4)], 6.82 [d, 2H, H^3-thioimidazole], 6.88 [d, 2H, H^2-thioimidazole], and 10.89 ppm [b, 2H, NH]. ^{13}C NMR (DMSO ,298 K, TMS): δ = 25.9 [C(6,8)], 25.9 [C(5,9)], 32.2 [C(7)], 66.9 [C(4)], 115.7 [C^3(thioimidazole)], 115.8 [C^2(thioimidazole)], and 165.1 ppm [C^1 =S]. I R (KBr): ν (cm^{-1}): 3170 [s, br, NH], 1571 [s, -C=C- + C=N], 1430 [s, thioamide I], 1298 [m, thioamide II], 1100 [m, thioamide III], 744 and 681 [s, Thioamide IV], 669 [m, δ (C=S)], and 511 [s, π (C=S)].

X-Ray Crystallography

The crystallographic data sets (Table I) were obtained at 160 K with a Bruker AXS Smart CCD diffractometer equipped with graphite-monochromated Mo Kα radiation with radiation wavelength of 0.71073 Å. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 689635. Lorentz polarization corrections were performed by SAINT.[15] Empirical absorption corrections were made by using the SADABS program.[16] The structures were solved with direct methods and refined anisotropically using the SHELTX 97.[17]

REFERENCES

[1] (a) E.S. Raper, *Coord. Chem. Rev.*, **153,** 199 (1996); (b) H. Fleischer, *Coord. Chem. Rev.*, **213,** 181 (2001); (c) S. Ahmed, A. A. Isab, S. Ali, and A. R. Al-Arfaj, *Polyhedron*, **25,** 1633 (2006).

[2] (a) D. Katiyar, V. K. Tiwari, R. P. Tripathi, A. Srivastava, V. Chaturvedi, R. Srivastava, and B. S. Srivastava, *Bioorg. Med. Chem.*, **11**, 4369 (2003); (b) K. H. Scheit and E. Gartner, *Biochim. Biophys. Acta*, **182,** 10 (1969).

[3] A. Beheshti, W. Clegg, N. R. Brooks, and F. Sharafi, *Polyhedron,* **24,** 435 (2005).

[4] (a) M. M. Ibrahim, M. Shu, and H. Vahrenkamp, *Eur. J. Inorg. Chem.*, 1388 (2005); (b) M. M. Ibrahim, G. He, J. Seebacher, B. Benkmil, and H. Vahrenkamp, *Eur. J. Inorg. Chem.*, 4070 (2005); (c) M. M. Ibrahim, C. P. Olmo, T. Tekeste, J. Seebacher, G. He, J. A. M. Calvo, K. Böhmerle, G. Steinfeld, H. Brombacher, and H. Vahrenkamp, *Inorg. Chem.*, **45,** 7493 (2006); (d) M. M. Ibrahim, *Inorg. Chem. Commun.*, **9,** 1215 (2006).

[5] (a) M. M. Ibrahim, J. Seebacher, G. Steinfeld, and H. Vahrenkamp, *Inorg. Chem.*, **44,** 8531 (2005); (b) M. Rombach, J. Seebacher, M. Ji, G. Zhang, G. He, M. M. Ibrahim, B. Benkmil, and H. Vahrenkamp, *Inorg. Chem.*, **45,** 4571 (2006); (c) M. M. Ibrahim, *Inorg. Chim. Acta,* **359,** 4235 (2006); (d) M. M. Ibrahim and H. Vahrenkamp, *Z. Anorg. Allg. Chem.*, **632,** 1083 (2006).

[6] (a) R. G. Jones, E. C. Kornfeld, K. C. McLaughlin, and R. C. Anderson, *J. Am. Chem. Soc.*, **71,** 4000 (1949); (b) J. Kister, G. Assef, G. Mille, and J. Metzger, *Can. J. Chem.*, **57,** 813 (1979).

[7] SAINT, V6.02, Bruker AXS, Madison, WI (1999).

[8] G. M. Sheldrick, SADABS, *Area-Detector Absorption Correction,* Göttingen, Germany (1996).

[9] G. M. Sheldrick, Program SHELXS, *Program for Crystal Structure Determination,* Göttingen, Germany (1997).

[10] R. Shunmugam and D. Sathyanarayana, *J. Coord. Chem.*, **12,** 151 (1983).

[11] E. S. Raper and J. L. Books, *J. Inorg. Nucl. Chem.*, **39,** 2163 (1977).

[12] (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* 3rd ed. (Chapman and Hall, London, 1975); (b) E. S. Raper and P. H. Crackett, *Inorg. Chim. Acta,* **50,** 159 (1981).

[13] A. A. Isab and M. I. M. Wazeer, *J. Coord. Chem.*, **58,** 529 (2005).

[14] A. R. Al-Arfaj, J. H. Reibenspies, A. A. Isab, and M. S. Hussain, *Acta Crystallogr., Sect. C,* **54,** 51 (1998).

[15] C. Marcos, J. M. Alia, V. Adovasio, M. Prieto, and S. Garcia-Granda, *Acta Crystallogr., Sect. C,* **54,** 1225 (1998).

[16] L. P. Battaglia, A. B. Corradi, and M. Nardelli, *Croat. Chem. Acta,* **57,** 545 (1984).

[17] E. S. Raper, J. R. Creighton, R. E. Oughtred, and I. W. Nowell, *Acta Crystallogr., Sect. B,* **39,** 393 (1983).