

Synthesis and Crystal Structures of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) Metal Complexes with NNO Functionalized Ligands

Yoon Jung Jang, Uk Lee,[†] and Bon Kweon Koo^{*}

Department of Chemistry, Catholic University of Daegu, Gyeongsan 712-702, Korea. *E-mail: bkkoo@cu.ac.kr

[†]Department of Chemistry, Pukyong National University, Pusan 608-737, Korea

Received February 24, 2005

Some new metal(II) complexes, $M^{II}L_2$ [$M = \text{Mn}$ (**1**), Co (**2**), Ni (**3**), Cu (**4**), and Zn (**5**)] of 2-acetylpyridine benzoylhydrazone ligand (HL) containing trifunctional NNO-donor system have been synthesized and crystallographically characterized for the complex **1** and **5**. The complexes consist of two ligands to give six-coordinate, which are bonded to the metal atom on a meridional plane through acetylpyridine ring nitrogen, azomethine nitrogen, and benzoyl oxygen atoms, respectively. The coordination geometry for other complexes was identified on the basis of the physicochemical data by elemental analyses, FAB-MS, IR, ^1H NMR, and electronic spectral measurements. The resulting data indicated that the complexes are accordance with the above formulation.

Key Words : Metal(II) complexes, Trifunctional NNO-donor ligand, Crystal structures

Introduction

Schiff base ligands have been widely used for the preparation of transition metal complexes.¹ Particularly tridentate ONO/S, NNO/S, and PNO/S functionalized ligands have recently attracted considerable interest.² But, surprisingly NNO-chelating ligands have, to our knowledge, been little published.³ The tautomerism of these ligands as well as the well known transition metal chelating properties allow various structural possibilities⁴ for the corresponding metal complexes. In addition, the versatile applications of Schiff base ligand complexes in the field of biological⁵ and industrial processes⁶ prompted us to synthesize the tridentate NNO-Schiff base ligand complexes. As part of our studies on transition metal complexes with these ligands, we have described the synthesis and spectroscopic and electrochemical properties for the Mn(II/III/IV),⁷ V(IV),⁸ and Mo(V/VI)⁹ metal complexes. Pelagatti, P, etc.¹⁰ recently reported the synthesis of Schiff base ligands involving three different HNNO acyl hydrazones and its palladium(II) complexes of the type $[\text{Pd}(\text{NNO})\text{Cl}]$. Also, other first-row transition metal(II) complexes, $[\text{M}(\text{PCAH})_2]$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and $\text{PCAH} = 2\text{-pyridine-carbaldehyde (4'-aminobenzoyl) hydrazone}$), $[\text{Mn}(\text{pybzhz})_2]$ ($\text{pybzhz} = \text{pyridine benzoyl hydrazone}$), and $[\{\text{Cu}(\text{APB})\text{Cl}\}_2\text{-(EtOH)}]$ ($\text{APB} = \text{acetylpyridine benzoyl hydrozone}$), with the nitrogen and oxygen donor system have been reported.¹¹ In this paper we further report the preparation of some

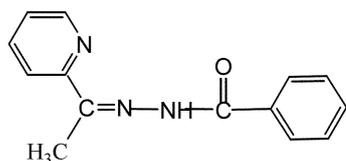
corresponding transition metals Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of 2-acetyl pyridine benzoylhydrazone ligand (HL) containing trifunctional NNO donor system.

Experimental Section

Materials and measurements. The ligand 2-acetylpyridine benzoylhydrazone was prepared as described in the literature.¹⁰ $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ as precursors and 2-acetylpyridine and benzoyl hydrazine were purchased from Aldrich Chemical Co. All other chemicals and solvents were obtained from commercial sources and used as received.

Carbon, hydrogen, nitrogen, and sulfur analyses were carried out using a Carlo Erba Model EA-1106 CHNS/O Analyzer. Positive-ion FAB mass spectra were obtained using a JEOL JMS 700 high resolution mass spectrometer in a *m*-nitrobenzyl alcohol matrix. Melting point determinations were carried out with a Laboratory Devices Inc. Mel-Temp II. Molar conductivities were determined in DMSO at 25 °C with a YSI Model 31 conductivity bridge. The IR spectra were recorded as KBr disk using a Mattson Polaris FT-IR spectrophotometer in the range 500-4,000 cm^{-1} . UV/Vis spectra were obtained in DMSO, using a Milton Roy Spectronic Genesys 2 spectrophotometer. ^1H NMR spectra of CDCl_3 solutions were obtained on a Varian Gemini-200 spectrometer. Chemical shifts are in ppm relative to internal Me_4Si .

Preparations. $[\text{MnL}_2]$ (1**):** To a well-stirred white suspension of 2-acetylpyridine benzoylhydrazone (2.0 mmol, 0.479 g) in methanol (25 mL) was added $\text{Mn}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol, 0.245 g) solid. The resulting mixture was refluxed for 2 h, during which a redish-brown solid appeared. After the product was allowed



NNO-donor (HL)

to stand at room temperature overnight, the solid was collected by filtration, washed with cool methanol, diethyl ether, and dried *in vacuo*. Yield: 0.441 g (83%). mp 290–292 °C. Anal. Calcd. for $C_{28}H_{24}N_6O_2Mn$: C, 63.28; H, 4.55; N, 15.81. Found: C, 63.32; H, 4.56; N, 16.01. FAB-MS, m/z: $[M]^+$, 531; $[M-L]^+$, 293. Λ_M (Mho $cm^2 mol^{-1}$): 1.0. UV/vis. (nm, log ϵ): 378 (4.56), 288 (4.18), 258 (4.27). Significant infrared bands (cm^{-1}): 1587, 1500, 1459, 1360, 1159, 1051, 714.

Other metal(II) complexes **2–5** were prepared in a fashion similar to that adopted for **1**, using an appropriate metal(II) acetates instead of manganese acetate.

[CoL₂] (2): redish-brown solid. Yield: 0.325 g (61%). mp 300–302 °C. Anal. Calcd. for $C_{28}H_{24}N_6O_2Co$: C, 62.81; H, 4.52; N, 15.69. Found: C, 62.79; H, 4.64; N, 15.57. FAB-MS, m/z: $[M]^+$, 535; $[M-L]^+$, 297. Λ_M (Mho $cm^2 mol^{-1}$): 2.1. UV/vis. (nm, log ϵ): 704 (1.96), 372 (4.49), 258 (4.31). Significant infrared bands (cm^{-1}): 1588, 1486, 1362, 1154, 1055, 894, 701.

[NiL₂] (3): redish-brown solid. Yield: 0.400 g (74%). mp 298 °C (dec.). Anal. Calcd. for $C_{28}H_{24}N_6O_2Ni$: C, 62.83; H, 4.52; N, 15.70. Found: C, 62.65; H, 4.64; N, 15.34. FAB-MS, m/z: $[M]^+$, 535; $[M-H]^+$, 534; $[M-H-L]^+$, 296. Λ_M (Mho $cm^2 mol^{-1}$): 2.1. UV/vis. (nm, log ϵ): 848 (1.58), 392 (4.96), 308 (4.68), 260 (4.469). Significant infrared bands (cm^{-1}): 1595, 1495, 1360, 1293, 1160, 1063, 904, 776, 708, 687.

[CuL₂] (4): green solid. Yield: 0.325 g (60%). mp 262

°C (dec.). Anal. Calcd. for $C_{28}H_{24}N_6O_2Cu$: C, 62.27; H, 4.48; N, 15.56. Found: C, 61.93; H, 4.53; N, 15.45. FAB-MS, m/z: $[M]^+$, 540; $[M-L]^+$, 302. Λ_M (Mho $cm^2 mol^{-1}$): 3.2. UV/vis. (nm, log ϵ): 714 (1.79), 384 (4.60), 264 (4.39). 246 (4.21). Significant infrared bands (cm^{-1}): 1585, 1498, 1356, 1291, 1158, 1054, 902, 775, 700.

[ZnL₂] (5): yellow solid. Yield: 0.400 g (74%). mp 355–357 °C. Anal. Calcd. for $C_{28}H_{24}N_6O_2Zn$: C, 62.06; H, 4.46; N, 15.51. Found: C, 62.13; H, 4.49; N, 15.62. FAB-MS, m/z: $[M]^+$, 542; $[M-H]^+$, 541; $[M-L-2H]^+$, 302. Λ_M (Mho $cm^2 mol^{-1}$): 2.1. UV/vis. (nm, log ϵ): 378 (4.61), 258 (4.22). Significant infrared bands (cm^{-1}): 1583, 1503, 1460, 1358, 1293, 1167, 1056, 716. ¹H NMR (in CDCl₃, ppm): 7.18–8.36 (br, ArH). 2.84 (s, -CH₃).

Crystal structure determination of 1 and 5. X-ray quality crystals of both complexes, **1** and **5** were obtained by slow diffusion of ethyl ether into a saturated dichloromethane solution (1 : 2) of the redish brown and yellowish white powder, respectively. Data were collected on a STOE STADIA¹² four-circle diffractometer using graphite monochromatized Mo-K α radiation by ω -2 θ scan. Unit cell parameters were determined by least-squares fit of 25 (**1**) and 35 (**5**) reflections having θ values in the ranges of 9.6–10.3 (**1**) and 9.6–10.4 (**5**), respectively. Intensities of three check reflections were measured after every 1 h during the data collection to monitor the crystal stability for both complexes and there was no significant change in the intensities of the check reflections. The structures were

Table 1. Crystal data and structure refinement for complexes **1** and **5**

	Complex 1	Complex 5
Empirical formula	$C_{28}H_{24}N_6O_2Mn$	$C_{28}H_{24}N_6O_2Zn$
Fw	531.47	541.90
Temp (K)	298(2)	298(2)
λ (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
a (Å)	22.865(3)	22.659(5)
b (Å)	10.199(2)	10.183(2)
c (Å)	12.102(2)	11.925(2)
β (°)	116.62(1)	115.11(2)
V (Å ³)	2523.0(8)	2491.5(9)
Z	4	4
D _{calc} (Mg/m ³)	1.399	1.445
μ (mm ⁻¹)	0.561	1.024
F (000)	1100	1120
Crystal size (mm)	0.56 × 0.31 × 0.13	0.65 × 0.25 × 0.10
Theta range	1.99–27.45°	1.99–27.46°
Index ranges	$h = -29 \rightarrow 26, k = 0 \rightarrow 13, l = 0 \rightarrow 15$	$h = -29 \rightarrow 26, k = 0 \rightarrow 13, l = 0 \rightarrow 15$
Reflections / unique	2888/2887 [R _{int} = 0.0000]	2860/2860 [R _{int} = 0.0000]
Completeness to theta	100.0%	100.0%
Data / restraints / parameters	2887/0/168	2860/0/168
R [$I > 2\sigma(I)$]	$R_1 = 0.0588, wR_2 = 0.0657$	$R_1 = 0.0578, wR_2 = 0.1047$
R (all data)	$R_1 = 0.1000, wR_2 = 0.0707$	$R_1 = 0.1036, wR_2 = 0.1329$
G.O.F. on F ²	1.934	1.061
Largest diff. peak and hole	0.540 and -0.300 eÅ ⁻³	0.456 and -0.443 eÅ ⁻³

solved by direct method¹³ and refined on F^2 by full-matrix least-squares procedures.¹⁴ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using riding model, but not refined. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indices, R and wR .

Results and Discussion

The reactions of appropriate metal(II) acetate with the Schiff base ligand derived from 2-acetylpyridine and benzoylhydrazone acting as tridentate ligand in methanol solution gave a monomeric transition-metal(II) complexes, **1-5** of $M^{\text{II}}L_2$ type ($M = \text{Mn, Co, Ni, Cu, Zn}$ and $L = 2$ -acetylpyridine benzoylhydrazone), respectively. The formulations were in accordance with the data of elemental analysis and physicochemical measurements. Positive-ion FAB mass spectra of the complexes showed a molecular ion

peak $[M]^+$ and the fragmentation corresponding to the loss of the ligand $[M-L]^+$ ($[M-H-L]^+$ for **3** and $[M-L-2H]^+$ for **5**), respectively (See Experimental section). The molar conductances of the complexes **1-5** determined at a concentration of $ca. 1 \times 10^{-3}$ M in DMSO show small values in the range 1.0-3.2 Mho $\text{cm}^2 \text{mol}^{-1}$, respectively, indicating that the complexes are non-electrolytes.¹⁵ The complexes are soluble in dichloromethane, dimethyl formamide, and dimethyl sulfoxide, but are not soluble in common organic solvents.

Description of crystal structures. Complexes **1** and **5** display essentially similar coordination geometry. Ortep representations of the complexes are shown in Figure 1 and selected interatomic parameters are listed in Table 2 and 3, respectively.

The structure of **1** consists of two trifunctional Schiff base ligands, in which the Mn(II) ion located on the twofold symmetry axis. Two molecules of the tridentate ligand

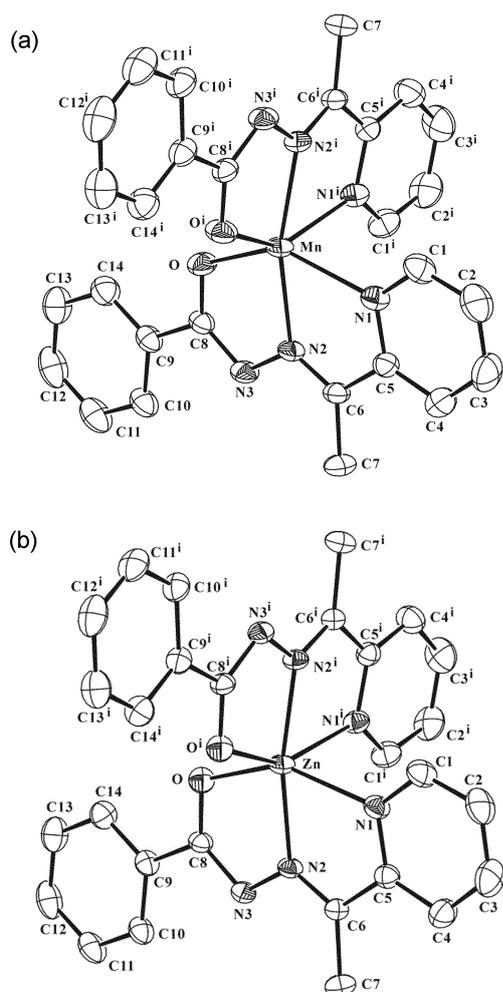


Figure 1. Ortep III¹⁶ drawings of (a) MnL_2 , **1** and (b) ZnL_2 , **5**. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity. Symmetry code: (i) $-x, y, 3/2-z$.

Table 2. Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Mn-O	2.142(2)	Mn-O ⁱ	2.142(2)
Mn-N1	2.321(2)	Mn-N2	2.185(2)
Mn-N1 ⁱ	2.321(2)	Mn-N2 ⁱ	2.185(2)
N1-C5	1.354(3)	C5-C6	1.483(4)
C6-N2	1.287(3)	N2-N3	1.378(3)
N3-C8	1.333(3)	C8-O	1.274(3)
Bond angles			
O-Mn-O ⁱ	102.61(12)	O-Mn-N2	72.27(8)
O ⁱ -Mn-N2	117.83(8)	O-Mn-N2 ⁱ	117.83(8)
O ⁱ -Mn-N2 ⁱ	72.27(8)	N2-Mn-N2 ⁱ	165.08(13)
O-Mn-N1	143.01(7)	O ⁱ -Mn-N1	95.73(8)
N2-Mn-N1	70.77(8)	N2 ⁱ -Mn-N1	98.20(8)
O-Mn-N1 ⁱ	95.73(8)	O ⁱ -Mn-N1 ⁱ	143.01(7)
N2-Mn-N1 ⁱ	98.20(8)	N2 ⁱ -Mn-N1 ⁱ	70.77(8)
N1-Mn-N1 ⁱ	88.10(12)		

Table 3. Selected bond lengths (Å) and angles (°) for complex **5**

Bond lengths			
Zn-O	2.105(3)	Zn-O1 ⁱ	2.105(3)
Zn-N1	2.275(3)	Zn-N2	2.064(3)
Zn-N1 ⁱ	2.275(3)	Zn-N2 ⁱ	2.064(3)
N1-C5	1.348(5)	C5-C6	1.475(5)
C6-N2	1.290(5)	N2-N3	1.370(4)
N3-C8	1.334(5)	C8-O	1.271(4)
Bond Angles			
O-Zn-O ⁱ	99.2(2)	O-Zn-N2	75.8(1)
O ⁱ -Zn-N2	112.4(1)	O-Zn-N2 ⁱ	112.4(1)
O ⁱ -Zn-N2 ⁱ	75.8(1)	N2-Zn-N2 ⁱ	168.1(2)
O-Zn-N1	149.4(1)	O ⁱ -Zn-N1	93.7(1)
N2-Zn-N1	73.6(1)	N2 ⁱ -Zn-N1	97.7(1)
O-Zn-N1 ⁱ	93.7(1)	O ⁱ -Zn-N1 ⁱ	149.4(1)
N2-Zn-N1 ⁱ	97.7(1)	N2 ⁱ -Zn-N1 ⁱ	73.6(1)
N1-Zn-N1 ⁱ	89.0(2)		

coordinate to the Mn(II) ion to form four five-membered chelate rings [Mn-N1-C5-C6-N2, Mn-N2-N3-C8-O, Mn-N1ⁱ-C5ⁱ-C6ⁱ-N2ⁱ, and Mn-N2ⁱ-N3ⁱ-C8ⁱ-Oⁱ]. The basal plane of the Mn octahedral is defined by the two oxygen and two acetylpyridine ring nitrogen donors, while the apical positions are occupied by each azomethine nitrogen atoms. This MnO₂N₄ coordination spheres are considerably distorted, which is probably due to the ligand rigidity.^{11d} The angles at the Mn center show large deviations (Table 2) from the ideal octahedral values of 90° and 180°. The mean deviation of plane OOⁱN1N1ⁱ from the least-square plane is 0.692(1) Å, in contrary to the planes, ON2N1N2ⁱ and OⁱN2N1ⁱN2ⁱ with mean deviation of 0.052(1) Å, respectively. The interplanar angles between these planes lie in the interval 86°-89°.

The tridentate ligands in the complex is almost planar. The maximum deviations from the least-squares mean planes through Mn-N1-C1-C2-C3-C4-C5-C6-N2-N3-C8-O (mean deviation 0.027(2) Å) are exhibited by C2 (-0.040(3) Å) and C6 (0.037(3) Å). The three individual rings, namely the acetylpyridine and the two five-membered chelate rings, are individually nearly planar with small dihedral angles (1.1(2)-1.7(2)°) between them. The pair of coordinating ligands are nearly orthogonal to each other with the dihedral angle 88.12(4)°.

The average bond distances for each of Mn-O and Mn-N in this coordination geometry are 2.142(2) and 2.253(2) Å. The values are similar to that of typical Mn(II) complexes.^{11a,17} Each distance 2.321(2) Å of Mn-N1 and Mn-N1ⁱ is slightly longer than 2.185(2) Å of Mn-N2 and Mn-N2ⁱ bonds, which can be related to greater *trans* influence of the oxo group on the each Mn-N1 and Mn-N1ⁱ bonds. The relatively short C8-N3 bond distances of 1.333(3) Å (normal single bond is 1.52 Å¹⁸), coupled with the lengthened C8-O distance of 1.274(3) Å which is typical of ketonic linkage (1.23 Å^{11d}), indicate that the ligands act as enol form.

In the complex **5**, the angles at the Zn(II) center shows small deviations from the ideal octahedral (Table 3) compared to the complex **1**. The maximum deviations from planarity of the tridentate ligand through Zn-N1-C1-C2-C3-C4-C5-C6-N2-N3-C8-O (mean deviation 0.021(3) Å) are exhibited by C6 (-0.029(4) Å) and N3 (0.032(3) Å). The dihedral angle between the two ligands is 85.01(7)°. The three rings, the acetylpyridine and the two five-membered chelate rings, are individually nearly planar with the dihedral angle of 1.23° between the ring Zn-N1-C5-C6-N2 and Zn-N2-N3-C8-O. The metal-ligand bond lengths are slightly shorter than their counterparts in **1** (Table 3).

Structural determination of the complexes **2-4** was not possible to grow diffraction quality crystals although all attempts.

Spectral properties. The IR spectrum of the ligand has several prominent bands appearing at 3173 and 1655 cm⁻¹ due to ν_{N-H} and ν_{C=O} stretching modes, respectively. Both these bands are disappeared on complexation and a new ν_{C=O} band at 1051-1063 cm⁻¹ is appeared. In addition, ¹H NMR of free ligand showed the bands at 10.91, 7.43-8.64,

and 2.48 ppm associated with the δ(N-H), δ(ArH), and δ(C(CH₃)=N) resonances, respectively. On complexation for **5**, the NH proton resonance at 10.91 ppm of free ligand is disappeared, and the resonance for the aromatic and azomethine methyl proton are observed at 7.18-8.36 and 2.84 ppm, respectively. This fact suggests that the Schiff base acts as monobasic tridentate ligands with acetylpyridine nitrogen, azomethine nitrogen, and oxygen donor atoms in the enol form by tautomerism. However, ¹H NMR spectra for the complexes **1-4** were not helpful for identification of functional group due to paramagnetic electron configuration.

Absorption spectra were obtained in DMSO and the resulting data are given in the Experimental section. The manganese complex **1** and the zinc complex **5** show no prominent absorption in the visible region because Mn^{II} of high-spin d⁵ electronic configuration has no spin-allowed d-d transition and Zn^{II} of d¹⁰ electronic configuration has no d-d transition.¹⁹ The complexes **2-4** exhibited one weak and broad peak at 704, 848, and 714 nm, which are assigned to d-d transition bands of Co^{II}(d⁷), Ni^{II}(d⁸), and Cu^{II}(d⁹) having octahedral coordination environment, respectively.²⁰ In all metal complexes, a strong band in the range 372-392 nm and two or more moderately intense bands in the range 224-308 nm are observed. The intense band near 382 nm may be associated with a charge transfer transition.^{20c,21} The last bands below 308 nm are seen for free ligand (224-302 nm) and thence can be attributed to intraligand transition band.

Conclusions

A number of new metal(II) complexes, M^{II}L₂ (M = Mn, Co, Ni, Cu, and Zn) with the trifunctional NNO-donor atoms have been synthesized and characterized. Crystal structure analyses of complexes **1** and **5** revealed that each unit cell consists of two Schiff base ligands. The ligands behave as monobasic NNO tridentate, bonding to metal(II) through the acetylpyridine ring nitrogen, azomethine nitrogen, and benzoyl oxygen to form a distorted octahedral structure.

Supporting information available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-255027 (**1**) and 255028 (**5**)). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

References

- (a) McCleverty, J. A.; Meyer, T. J. *Comprehensive Coordination Chemistry II*; Molina, H. R.; Mederos, A., Eds.; Elsevier: London, The United Kingdom, 2004; Vol. 31.
- (a) Stelzig, L.; Kotte, S.; Krebs, B. *J. Chem. Soc. Dalton Trans.* **1998**, 2921. (b) Rana, A.; Dinda, R.; Sengupta, P.; Ghosh, S.; Falvello, L. R. *Polyhedron* **2002**, *21*, 1023. (c) Bustos, C.; Burckhardt, O.; Schreiber, R.; Carrillo, D.; Arif, A. M.; Cowley, A. H.; Nunn, C. M. *Inorg. Chem.* **1990**, *29*, 3996. (d) Rana, A.;

- Dinda, R.; Ghosh, S.; Blake, A. *Polyhedron* **2003**, *22*, 3075. (e) Costamagna, J.; Vargas, J.; Latorre, R.; Alvarado, A.; Mena, G. *Coord. Chem. Rev.* **1992**, *119*, 67.
3. (a) Tandon, S. S.; Chander, S.; Thompson, L. K. *Inorg. Chim. Acta* **2000**, *300-302*, 683. (b) Oshio, H.; Toriumi, M. Y.; Takashima, Y. *Inorg. Chem.* **1991**, *30*, 4252. (c) Nazir, H.; Yildiz, M.; Yilmaz, H.; Tahir, M. N.; Ulku, D. *J. Mol. Struct.* **2000**, *524*, 241.
4. Jeffery, J. C.; Thornton, P.; Ward, M. D. *Inorg. Chem.* **1994**, *33*, 3612.
5. (a) Dutta, S. K.; Tiekink, E. R. T.; Chaudhury, M. *Polyhedron* **1997**, *16*, 1863. (b) Scovill, J. P. *Phosphorus, Sulfur, and Silicon* **1991**, *60*, 15. (c) Pessoa, J. C.; Tomaz, I.; Henriques, R. T. *Inorg. Chim. Acta* **2003**, *356*, 121.
6. (a) Ando, R.; Yagyu, T.; Maeda, M. *Inorg. Chim. Acta* **2004**, *357*, 2237. (b) Ando, R.; Mori, S.; Hayashi, M.; Yagyu, T.; Maeda, M. *Inorg. Chim. Acta* **2004**, *357*, 1177.
7. (a) Mo, S. J.; Lim, W. T.; Koo, B. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 1175. (b) Mo, S. J.; Koo, B. K. *Bull. Korean Chem. Soc.* **1999**, *20*, 1225. (c) Lee, U.; Koo, B. K. *Bull. Korean Chem. Soc.* **2002**, *23*, 613.
8. Koo, B. K.; Jang, Y. J.; Lee, U. *Bull. Korean Chem. Soc.* **2003**, *24*, 1014.
9. (a) Jang, Y. J.; Mo, S. J.; Koo, B. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 1124. (b) Mo, S. J.; Koo, B. K. *Bull. Korean Chem. Soc.* **1999**, *20*, 1105. (c) Kim, D. W.; Lee, U. *Bull. Korean Chem. Soc.* **2004**, *25*, 1071.
10. Pelagatti, P.; Carcelli, M.; Pelizzi, C.; Costa, M. *Inorg. Chim. Acta* **2003**, *342*, 323.
11. (a) Naskar, S.; Biswas, S.; Mishra, D.; Adhikary, B.; Falvello, L. R.; Soler, T.; Schwalbe, C. H.; Chattopadhyay, S. K. *Inorg. Chim. Acta* **2004**, *357*, 4257. (b) Karunakar, G. V. *et al. J. Coord. Chem.* **2000**, *50*, 51. (c) Armstrong, C. M. *et al. Eur. J. Inorg. Chem.* **2003**, 1145. (d) Patole, J.; Sandbhor, U.; Padhye, S.; Deobagkar, D. N.; Anson, C. E.; Powell, A. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 51.
12. *STOE STAD14, X-RED & X-SHAPE*, X-ray structure evaluation package; STOE-Cie GmbH: Hilpertstrase 10, D64295, Darmstadt, Germany, 1996.
13. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
14. Sheldrick, G. M. *SHELXS97-2 and SHELXL97-2*; University of Gottingen: Gottingen, Germany, 1997.
15. Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
16. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
17. Fegy, K.; Sanz, N.; Luneau, D.; Belorizky, E.; Rey, P. *Inorg. Chem.* **1998**, *37*, 4518.
18. Dutta, S.; Basy, P.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4031.
19. Yamami, M.; Tanaka, M.; Sakiyama, H.; Koga, T.; Kobayashi, K.; Miyasaka, H.; Ohba, M.; Okawa, H. *J. Chem. Soc. Dalton Trans.* **1997**, 4595.
20. (a) Patra, A. K.; Mukherjee, R. *Inorg. Chem.* **1999**, *38*, 1388. (b) Ray, M. S.; Bhattacharya, R.; Chaudhuri, S.; Righi, L.; Bocelli, G.; Mukhopadhyay, G.; Ghosh, A. *Polyhedron* **2003**, *22*, 617. (c) Dey, M.; Rao, C. P.; Saarenketo, P. K.; Rissanen, K. *Inorg. Chem. Commun.* **2002**, *5*, 924. (d) Yang, C. T.; Vittal, J. J. *Inorg. Chim. Acta* **2003**, *344*, 65.
21. (a) Dung, N. H.; Viosat, B.; Busnot, A.; Gonzalez Perez, J. M.; Gonzalez Garcia, S.; Gutierrez, J. N. *Inorg. Chem.* **1987**, *26*, 2365. (b) Sorrell, T. N.; Allen, W. E.; White, P. S. *Inorg. Chem.* **1995**, *34*, 952. (c) Asada, H.; Hayashi, K.; Negoro, S.; Fujiwara, M.; Matsushita, T. *Inorg. Chem. Commun.* **2003**, *6*, 193. (d) Saha, N.; Mukherjee, N. *Polyhedron* **1984**, *3*, 1135.
-