# The observation of isocyano cobalt(III)-Schiff base complexes

Zhong Yu, Takayoshi Kuroda-Sowa*, Akihiro Okamoto, Atsuhiro Nabei, Takashi Okubo, Masahiko Maekawa

*Department of Chemistry, School of Science and Engineering, Kinki University,*

*Higashi-Osaka, Osaka 577-8502, Japan.*

* Corresponding author. Tel.: +816 6721 2332; fax: +816 6723 2721
E-mail address: kuroda@chem.kindai.ac.jp
(Received  February 1, 2013)

**Abstract**

Two isocyano-coordinated cobalt(III)-Schiff base complexes, [Co(L1)(CH$_3$OH)(NC)]·CH$_2$Cl$_2$ (**1**) and [Co(L2)(H$_2$O)(NC)]·CH$_2$Cl$_2$ (**2**) (H$_2$L1 = *N,N*-disalicylidene-2,3-naphthalenediimine, H$_2$L2 = *N,N*-bis(3-methoxysalicylaldehyde)-1,2-phenylene-diimine), were synthesized from the reaction of TCNQ and corresponding planar cobalt(II) complexes **3** and **4**, respectively. The single-crystal X-ray diffraction analysis of the crystals clearly shows the coordination of CN$^-$ moiety to the Co(III) complex. The characterization of products by the FT-IR and $^{13}$C NMR measurements indicate the coexistence of two isomers, isocyano and cyano complexes, both in the solid state and in solution. The DFT calculations on the isomerization reaction ($\Delta H_{iso}$: -42.6 kJ mol$^{-1}$, $E_a$: 121.3 kJ mol$^{-1}$) indicate the difficulty of the reaction at room temperature, which is in accordance with the observation of the two isomers.

Key words: Cobalt Schiff base complex; Isocyano group; DFT calculation; X-ray crystal structures

# Introduction

The extensive researches on cyano compounds have been conducted in organic and organometallic chemistry owing to their unique bonding capabilities and potential applications in design of new molecular materials,[1, 2] catalysis [3, 4] and medicines.[5] In contrast to many advances made toward research on organic isocyanide-cyanide isomerization,[6, 7] the reports on the isomerization in metal-organic complexes are relatively rare.

It is generally acknowledged that the common mode of cyano binding to metals and metalloids is monohapto via carbon due to greater configurational stability.[1] Binding through nitrogen is usually presented in those linkage mode, such as Cr(III) [8] and Ru(II) [9] isocyano complexes. Although the isocyano species can be isolated in favorable cases, the isocyano-cyano rearrangement is a common occurrence and further prompted by heating or laser irradiation.[10]

For the cobalt complexes, the transient intermediates [Co$^{III}$(CN)$_5$NC]$^{3-}$ [11, 12] is converted to the corresponding cyano species and [Co$^{III}$(NC) (H$_2$O) (dmgH)$_2$] [13] (dmgH$_2$ = dimethylglyoxime) is proved to rearrange to the cyano isomer. The only reports on isolated cobalt(III)-isocyano complexes are cis-α-[Co(NC)$_2$(trien)]ClO$_4$ and cis-β-[Co(NC)$_2$(trien)]ClO$_4$ (trien = triethylenetetramine).[14] Although the ease of formation and stability of these two diisocyano species can be understood in terms of Jörgensen's concept of symbiosis,[1, 15] the relevant mechanism and exemplification are still insufficient.

Herein we report on a particular coexistence of isocyano-cyano at room temperature in a new Co$^{III}$-N$_2$(CN/NC)O$_3$ system, where the cobalt(III) is six-coordinated with a N$_2$O$_2$ tetradentate Schiff base ligand, one oxygen atom of solvent molecule and one cyano/isocyano group. The syntheses, crystal structures and spectroscopic properties were

investigated, and the studies were supported by DFT calculations.

## Results and Discussion

The recent interest on functional supramolecular systems based on salen/salophen scaffolds has attracted our attention to associate it with the linking and bridging function of the cyano species. The new complexes $[Co^{III}(L1)$ $(CH_3OH)$ $(CN/NC)] \cdot CH_2Cl_2$ ($H_2L1$ = $N,N$-disalicylidene-2,3-naphthalenediimine) (1) and $[Co^{III}(L2)(H_2O)(CN/NC)] \cdot CH_2Cl_2$ ($H_2L2$ = $N,N$-bis(3-methoxysalicylaldehyde)-1,2-phenyl enediimine) (2) were isolated from the reaction solutions of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and starting complex $[Co^{II}(L1)] \cdot CH_3OH \cdot CH_2Cl_2$ (3) or its analogue $[Co^{II}(L2)] \cdot H_2O \cdot CH_2Cl_2$ (4), respectively.[16]

The starting cobalt(II)-salophen complexes were isolated from the reaction solutions of CoCl₂·6H₂O with Schiff base ligand in diffusion method. Complex 3 shows a tetra-coordinated cobalt(II) planar geometry (Figure 1a), leaving the vacant axial positions for binding of the incoming TCNQ.

The single crystal X-ray analyses of 1 revealed that the TCNQ molecule is not found in the structure, where the six-coordinated cobalt(III) presents an almost regular octahedral geometry with tetradentate ligand bound in the equatorial plane and the axial sites bound by one cyano group and one oxygen atom of methanol (Figure 1b).

The axial-coordinated cyano group of 1 exhibits a disorder feature involving two orientations of cyano and isocyano in the determination of X-ray analysis, which can be regarded as the consequence of the coexistence of cyano and isocyano species in structure. In order to obtain a good refinement, the cyano group is treated as isocyano and cyano conformations, respectively.
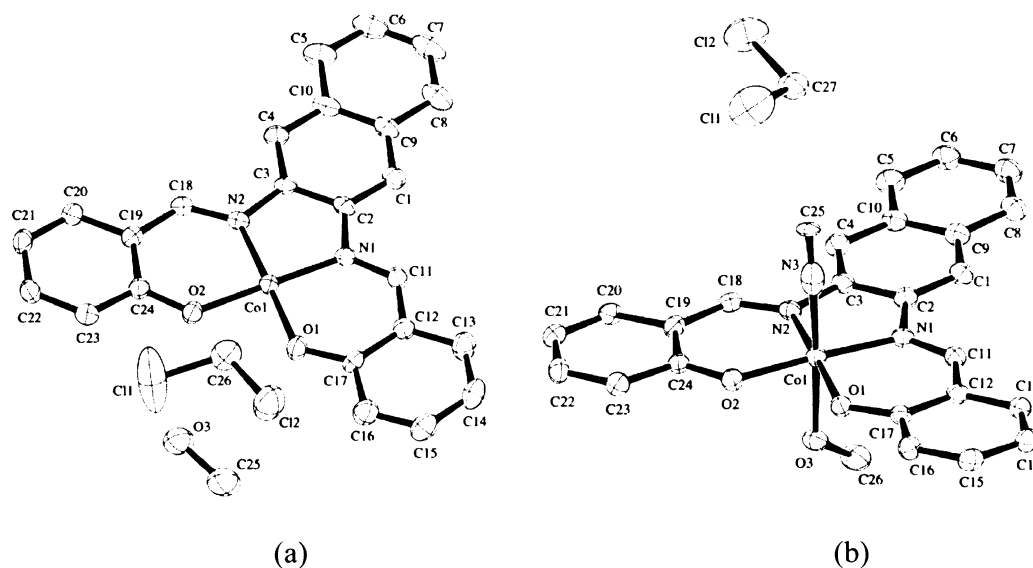


(a)                                           (b)

**Figure 1.** ORTEP drawings of the molecular structure with the atom numbering scheme for selected atoms. (a) Complex **3**, $[Co^{II}(L1)] \cdot CH_3OH \cdot CH_2Cl_2$. (b) Complex **1** in isocyano coordination, $[Co^{III}(L1)$ $(CH_3OH)$ $(NC)] \cdot CH_2Cl_2$. Hydrogen atoms are omitted for clarity.

The crystalline samples of complexes 2 and 4, moderate quality for X-ray diffraction study, were obtained by similar method. Disorder feature and structural treatment of complex 2 were similar with 1.

The cobalt-donors octahedron in complex 1 is distorted with average bond distances close to those reported in six-coordinated cobalt(III) species.[17, 18] The cobalt(III) center deviates slightly from the basal plane defined by ligand with 0.008 Å which is smaller than the value of 0.063 Å in complex 3 (Figure 1b), indicating the effects of axial coordination on metal center. In complex 1, extended aromatic rings of ligand participate in the π-π interactions (3.438(3) Å) with overlapped molecules, making the supramolecular crystal structure more stable. The dichloromethane is located in the lattice as the inclusion solvent molecule. Based on the structural analyses, it is reasonable to believe that the axial-coordinated cyano/isocyano group derives from a decomposition process of TCNQ during the reaction with cobalt(II)-salophen starting complexes. As a pronounced electron acceptor, TCNQ readily oxidizes cobalt(II) center to cobalt(III) and gets an electron to form an

anion-radical salt $[Co^{III}(L)]^+ \cdot TCNQ^{\cdot -}$. A consideration of the reaction operated in the presence of $H_2O$ allows a $H_2O$-induced

decomposition process of $TCNQ^{\cdot -}$ and resulting product $CN^-$ anion in solution.[19, 20] And then $CN^-$ anion coordinates to the free axial site of $[Co^{III}(L)]^+$ to generate the apprehensible mixed product of 1 including cyano and isocyano species, i.e. $[Co^{III}(L1)$ $(CH_3OH)$ $(CN)]$ and $[Co^{III}(L1)$ $(CH_3OH)$ $(NC)]$. The similar reaction process takes place on complex 2.

Complexes 1 and 2 have been characterized by FT-IR spectral analyses. Comparing with the single band observed in $[Co^{III}(CN)$ $(H_2O)$ $(dmgH)_2]$ $(v(CN) = 2186$ $cm^{-1})$ or $[Co^{III}(NC)$ $(H_2O)$ $(dmgH)_2]$ $(v(NC) = 2136$ $cm^{-1})$ [10], respectively, the both characteristic bands corresponding to cyano and isocyano groups were presented in complex 1 (2188 and 2135 $cm^{-1}$) or 2 (2188 and 2140 $cm^{-1}$), suggesting the coexistence of cyano and isocyano species in these cobalt(III)-Schiff base systems. Lower $v(NC)$ for isocyano-cobalt species in comparison to cyano isomer can be attributed to lesser σ-antibonding donor ability of isocyano group.[10] Whereas in cyano-cobalt species, the greater bond strengths in the $CN^-$ ligand causes the higher $v(NC)$.

The trans axial donors of cobalt center, such as amine and aniline ligands, is proved to enhance electron transfer interaction, which can be easily observed in lower cayno stretching frequencies than free cyanide ion (up 2200 $cm^{-1}$) in IR spectra.[21, 22] In complexes 1, 2 and $[Co^{III}(CN)$ $(H_2O)$ $(dmgH)_2]$, although the axial-coordinated $CH_3OH$ or $H_2O$ solvent molecules are expected to have similar effects as amine and aniline, the IR spectrum show no much decrease on wavenumbers, which indicate the sensitivity of cyano stretching vibrations to the bonding of different ligands.[10]

The $^{13}C$ NMR spectra analyses prove further the existence of cyano and isocyano groups in complexes. As shown in Figure 2, the $^{13}C$ NMR signals of complex 2 agree with the structure proposed (13 signals at the δ 30.7-159.2 ppm). The signals at δ 30.7 and 54.9, with the both 0.5 of relative intensities, are assigned respectively to the cyano and isocyano
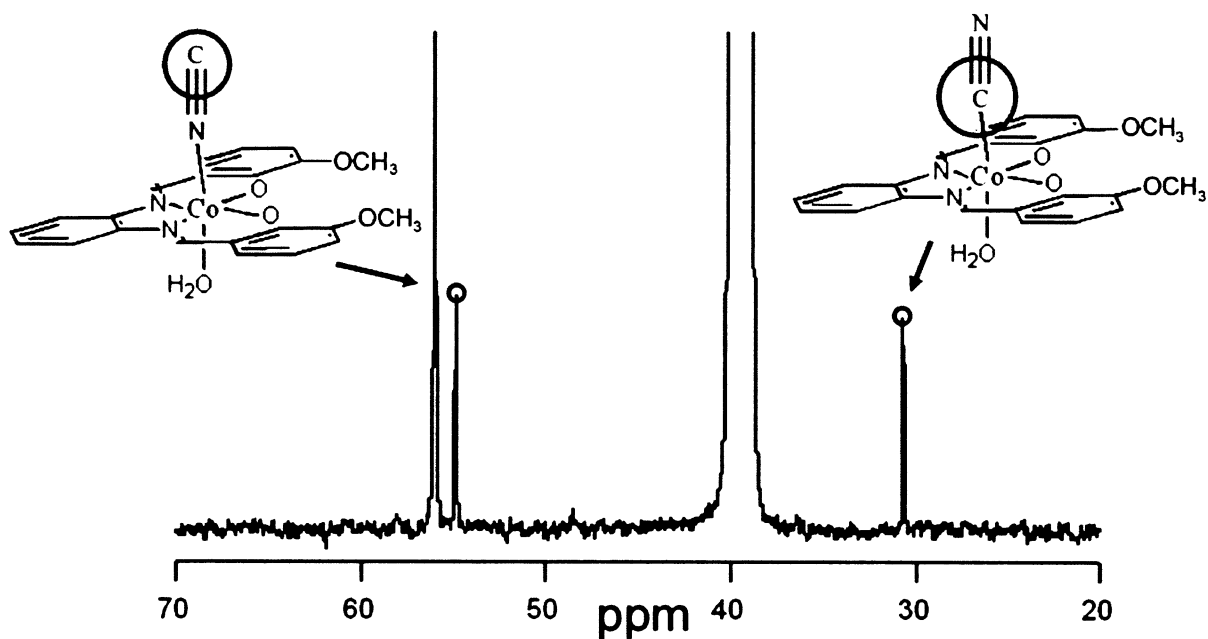
**Figure 2.** $^{13}$C NMR spectra of complex **2**, [Co$^{III}$(L2)(H$_2$O)(CN/NC)]·CH$_2$Cl$_2$.

groups. The chemical shift of methoxy carbon is located at δ 56.0 ppm. The remaining 10 carbon signals (δ 113.9-159.2 ppm) of ligand component in **2** are in agreement with the values found for ligand H$_2$L2 molecule (δ 115.4-164.3 ppm), which is also supported by those observed in similar salophen ligand (δ 115-168.1 ppm).[23] The relative intensity of these ligand component peaks were found to be approximately equal to 1.0.

The spectral analyses of FT-IR and $^{13}$C NMR determine the coexistence of cyano and isocyano species in cobalt(III)-Schiff base systems, which indicate that the coordination of CN$^-$ to the free axial sites of [Co$^{III}$(L)]$^+$ has both possibilities of the formation of cyano and isocyano complexes. It is generally believed that N-bonded CN$^-$ mode is a transient existence [13, 24, 25] and a π-back bonding effect is usually allowed to take into account in cyano-cobalt species due to involved in a

transfer of electron density from cobalt center into the carbon-centered member of the cyanide π*-antibonding orbital for more stabilization, i.e. Co→C≡N. Therefore, the isomerization of isocyano to cyano is a common occurrence, e.g. in Hg(CN)$_2$, [Co(CN)(NH$_3$)$_5$]Cl$_2$ and Cs$_2$K[Cr(CN)$_6$],[1] although the conversion does not appear to be extremely rapid in the solid state.

Nevertheless for cobalt(III) system, the isocyano to cyano isomerization still seems to be complicated.[11, 12, 26] In complexes **1** and **2**, the quantitative conversion from isocyano to cyano species has not been observed, suggesting the chemical stability of the both species at room temperature.

The density functional theory (DFT) calculations[27] based on the theoretical model of an intramolecular transition state contribute to our understanding of this coexistence phenomenon. The isomerization of complex **1**
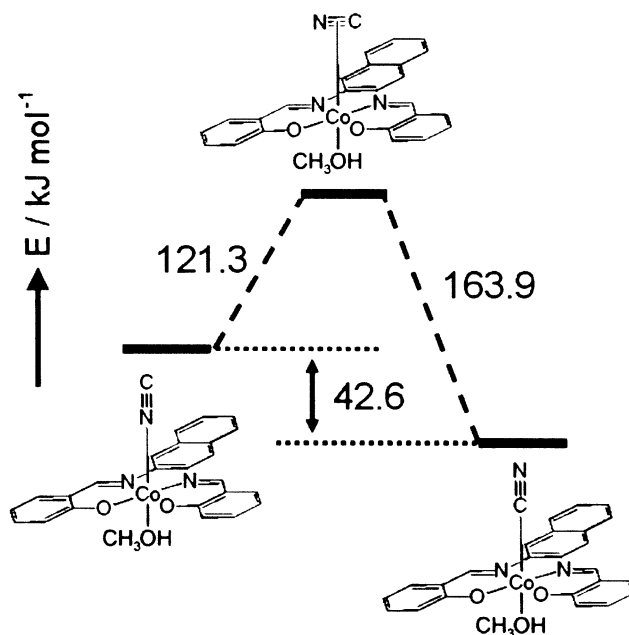
**Figure 3.** Calculated isomerization of [Co$^{III}$(L1)(CH$_3$OH)(NC)] to [Co$^{III}$(L1)(CH$_3$OH)(CN)] (B3LYP/LanL2DZ).

was modeled as an intramolecular reaction employing DFT calculations by means of the B3LYP functional.[28-30] The LANL2DZ basis set[31-33] implemented in the Gaussian 03 program[34] was chosen in the geometry optimization and normal modes calculations.

As presented in Figure 3, DFT calculations yield a reaction enthalpy of $\Delta H_{iso}$(298K) = – 42.6 kJ mol$^{-1}$ and an activation energy of $E_a$ = 121.3 kJ mol$^{-1}$, which can be compared with those calculated values in K[(CF$_3$)$_3$BNC] ($E_a$ = 155.7 kJ mol$^{-1}$) [35] or (CH$_3$)$_3$SiNC ($E_a$ = 108.5 kJ mol$^{-1}$).[36] The great values of energy barrier ($E_a$) between two isomer configurations are thought to be the possible causes of the appreciable coexistence of cyano and isocyano complexes, which obstruct the bulk conversion of isocyano to cyano species at room temperature.

In conclusion, two cobalt(III)-Schiff base complexes with axial-coordinated

cyano/isocyano groups were synthesized by a reaction involved the starting material cobalt(II)-salophen complexes and TCNQ. The CN$^-$ anion derived from H$_2$O-induced decomposition of TCNQ was reasonably believed to coordinate to cobalt center to generate both of cyano and isocyano species.

The coexistence of cyano and isocyano were determined by IR and $^{13}$C NMR spectrum analyses. DFT calculation was employed to yield the isomerization enthalpy and activation energy, which are thought to be the causes of the appreciable coexistence of cyano and isocyano complexes, which obstruct the bulk conversion of isocyano to cyano species at room temperature.

## Experimental

The Schiff base ligands (H$_2$L1 and H$_2$L2) were prepared according to standard literature

procedures.[37, 38]

The starting material of complex **3** was obtained as follows. To a solution of H₂L1 (73.4 mg, 0.2 mmol) in dichloromethane (10 ml) was added a methanol solution (10 ml) containing $CoCl_2 \cdot 6H_2O$ (47.7 mg, 0.2 mmol) with stirring at room temperature. Black precipitate of **3** were isolated by filtration and dried in vacuum. Yield: 68.1 mg, 63%. Anal. Calcd for $C_{26}H_{22}N_2O_3CoCl_2$, **3**: C, 57.80; H, 4.10; N, 5.18. Found: C, 57.76; H, 4.31; N, 5.11 %. IR (KBr, cm⁻¹): 1604(s), 1580(S), 1530(S), 1458(S), 1443(S), 1339(m), 1196(m), 1155(m), 754(m). The black crystals of **3** suitable for X-ray diffraction analysis were obtained by layering the methanol solution containing Co(II) ion over the ligand solution for one week at room temperature.

The brown single crystals of complex **1** suitable for X-ray analysis were obtained by layering the methanol solution (10 ml) of **3** (108.1 mg, 0.2 mmol) over a dichloromethane (10 ml) solution of TCNQ (40.4 mg, 0.2 mmol) in one week at room temperature. Yield: 57.8 mg, 51%. Anal. Calcd for $C_{27}H_{22}N_3O_3CoCl_2$, **1**: C, 57.26; H, 3.92; N, 7.42. Found: C, 57.21; H, 4.03; N, 7.47%. IR (KBr, cm⁻¹): 2188(m), 2135(m), 1605(s), 1582(S), 1525(S), 1438(S), 1456(S), 1340(m), 1196(m), 1151(m), 754(m).

## X-ray analyses

Crystal data for **1** (isocyano mode): $C_{27}H_{22}N_3O_3CoCl_2$, $M_r$ = 566.33, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 11.073(5) Å, $b$ = 11.324(4) Å, $c$ = 11.605(4) Å, $\alpha$ = 119.182(16)°, $\beta$ = 91.15(2)°, $\gamma$ = 103.75(2)°, $V$ = 1218.2(8) Å³, $Z$ = 2, $F(000)$ = 580, $T$ = 110.1K, $Dc$ = 1.544 g cm⁻³, $\mu$(Mo-K$\alpha$) = 9.60 cm⁻¹. For **3**: $C_{26}H_{22}Cl_2CoN_2O_3$, $M_r$ = 540.31, monoclinic, space group $Cc$ (no. 9), $a$ = 21.094(1) Å, $b$ =

15.063(8) Å, $c$ = 7.352(4) Å, $\alpha$ = 90.000(0)°, $\beta$ = 97.316(7)°, $\gamma$ = 90.000(0)°, $V$ = 2317(2) Å³, $Z$ = 4, $F(000)$ = 1108, $T$ = 170.1K, $Dc$ = 1.549 g cm⁻³, $\mu$(Mo-K$\alpha$) = 10.04 cm⁻¹. Data collections were performed on RIGAKU/MSC Mercury CCD diffractometer (Mo-K$\alpha$, $\lambda$ = 0.71070 Å) with θ-ranges of 3.2 < θ < 27.5° at 170.1 K and 3.0< θ < 27.5° at 110.1 K. The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least squares (SHELXL-97), giving for **1** a final $R_1$ value of 0.0642 for 326 parameters and 4645 unique reflections with $I > 2\sigma(I)$ and $wR_2$ of 0.1744 for all 5520 reflections and for **3** a final $R_1$ value of 0.0389 for 308 parameters and 2607 unique reflections with $I > 2\sigma(I)$ and $wR_2$ of 0.0933 for all 2643 reflections.

The refinements for cyano species of **1** were carried out, giving the similar $R_1$ value of 0.0623 and $wR_2$ of 0.1701.

CCDC 711776 and 711775 contain the supplementary crystallographic data for complexes **1** (isocyano mode) and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## References

[1] Fehlhammer, W. P.; Fritz, M. *Chem. Rev.*, **1993**, 93, 1243–1280.

[2] Schelter, E. J.; Prosvirin, A. V.; Reiff, W. M.; Dunbar, K. R. *Angew. Chem., Int. Ed.*, **2004**, 43, 4912-4915.

[3] Tanabiki, M. et al, *Organometallics* **2004**, 23, 3976-3981.

[4] Singleton, E.; Oosthuizen, H. E., *Adv. Organomet. Chem.* **1983**, 22, 209-310.

[5] Sharma, V.; Piwnica-Worms, D., *Chem. Rev.* **1999**, 99, 2545-2560.

[6] Ruechardt, C. et al, *Angew. Chem. Int. Ed.* **1991**, 30, 893-901.

[7] Mikhailova, O. I. et al, *Russ. J. Org. Chem.* **2008**, 44, 1451-1463.

[8] Birk, J. P.; Espenson, J. H., *J. Am. Chem. Soc.* **1968**, 90, 1153-1162.

[9] Isied, S. S.; Taube, H., *Inorg. Chem.* **1975**, 14, 2561-2562.

[10] Alvarez, S.; Lopez, C., *Inorg. Chim. Acta* **1982**, 64, L99-L100.

[11] Halpern, J.; Nakamura, S., *J. Am. Chem. Soc.* **1965**, 87, 3002-3003.

[12] Spreer, L. O. et al, *J. Am. Chem. Soc.* **1977**, 99, 7894-7898.

[13] Griffith, W. P. et al, *Inorg. Chim. Acta* **1990**, 175, 161-162.

[14] Kuroda, K.; Gentile, P. S., *Inorg. Nucl. Chem. Lett.* **1967**, 3, 151-156.

[15] Jørgensen, C. K., *Inorg. Chem.* **1964**, 3, 1201-1202.

[16] Nabei, et al, *Acta Crystallogr. Sect. E* **2009**, *E65*, m188-m189.

[17] Summers, M. F. et al, *J. Am. Chem. Soc.* **1984**, 106, 4478-4485.

[18] Weil, M.; Khalaji, A. D., *Anal. Sci.: X-Ray Struct. Anal. Online* **2008**, 24, x19-x20.

[19] Mizoguchi, K. et al, *J. Polym. Sci., Polym. Chem. Ed.* **1978**, 16, 3259-3274.

[20] Grossel, M. C. et al, *Chem. Mater.* **2000**, 12, 2319-2323.

[21] Appelt, R.; Vahrenkamp, H., *Inorg. Chim. Acta* **2003**, 350, 387-398.

[22] Vafazadeh, R.; Ardakani, M. H., *Bull. Korean Chem. Soc.* **2006**, 27, 1685-1688.

[23] Alvarez, R. et al, *Trans. Met. Chem.* **2002**, 27, 213-217.

[24] Griffith, W. P., *Coord. Chem. Rev.* **1975**, 17, 177-247.

[25] Alvarez, S.; Lopez, C., *Inorg. Chim. Acta* **1982**, 63, 57-62.

[26] Jackson, W. G.; Rahman, A. F. M. M., *Inorg. Chem.* **1990**, 29, 3247-3250.

[27] Kohn, W.; Sham, L. J., *Phys. Rev.* **1965**, 140, A1133.

[28] Becke, A. D., *Phys. Rev. A* **1988**, 38, 3098.

[29] Becke, A. D., *J. Chem. Phys.* **1993**, 98, 5648-5652.

[30] Lee, C. et al, *Phys. Rev. B* **1988**, 37, 785.

[31] Hay, P. J.; Willard, R. W., *J. Chem. Phys.* **1985**, 82, 270-283.

[32] Willard, R. W.; Hay, P. J., *J. Chem. Phys.* **1985**, 82, 284-298.

[33] Hay, P. J.; Willard, R. W., *J. Chem. Phys.* **1985**, 82, 299-310.

[34] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.;

Pople, J. A., Gaussian 03, Revision C.02 (Wallingford CT: Gaussian, 2004)

[35] Finze, M. et al, *J. Am. Chem. Soc.* **2005**, 127, 10712-10722.

[36] Booth, M. R.; Frankiss, S. G., *Spectrochimica Acta Part A: Molecular Spectroscopy* **1970**, 26, 859-869.

[37] Rohrbach, D. F. et al, *Inorg. Chem.* **1979**, 18, 2536-2542.

[38] Nabei, A. et al, *Inorg. Chim. Acta* **2008**, 361, 3489-3493.