Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 360 (2007) 3123–3126

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Note

Presence of edge-to-face aromatic interaction in bis[1,2-bis(4-alkylphenyl)ethanedione dioximato]nickel(II) complexes and evaluation of the fastener effect

Yuji Soneta *, Tatsuo Moritaka, Kazuo Miyamura

Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

Received 24 October 2006; received in revised form 8 February 2007; accepted 13 February 2007
Available online 21 February 2007

Abstract

Bis[1,2-bis(4-methylphenyl)ethanedione dioximato]nickel(II), $[Ni\{(C_1)_2dpg\}_2]$ (**1**), was found to exhibit shift in diffuse reflectance spectra from the corresponding non-methyl species. Characterization by X-ray crystal structural analysis on **1** and bis[1,2-bis(4-*n*-hexylphenyl)ethanedione dioximato]nickel(II), $[Ni\{(C_6)_2dpg\}_2]$ (**2**), revealed the presence of the edge-to-face aromatic interactions caused by the electron-donating effect of the methyl and hexyl groups. The $Ni(dpg)_2$ units of complex **2** stack (staggered by 90°) at alternate intervals of 3.151 Å and 3.253 Å. Thus, the shift in the d–p transition of **2** was found to contain 43% of the effect of the edge-to-face aromatic interaction, together with 57% of the reported fastener effect.

Keywords: Nickel complex; X-ray crystal structure; Edge-to-face; Fastener effect

1. Introduction

It is well known that d^8 transition metal complexes with dioxime as a ligand have square planar configuration and stack face to face to form one-dimensional columnar structure consisting of linear metal chains perpendicular to the molecular plane [1,2]. These complexes exhibit piezochromism in the nd_{z^2}–$(n+1)p_z$ transition of the metal in the visible region [3,4]. The d–p transition is very sensitive to the one-dimensional metal to metal stacking distance, so the complex is used as a pressure indicator. Ohta et al. have introduced long-chain-substituents into these core complexes, and obtained discotic columnar liquid crystals with such a unique chromism [5]. These columnar liquid crystals can self-organize to show more preferable function than the unsubstituted non-mesogenic core complexes. For example, bis[1,2-bis(3,4-di-*n*-alkoxyphenyl)ethanedione dioximato]nickel(II) (*n*-alkoxy = n-$C_8H_{17}O$, n-$C_{12}H_{25}O$) exhibit columnar mesophases and exhibit thermochromism. These properties originate not from the individual molecules but from their supramolecular structure. Furthermore, liquid crystalline compounds are also well known to dramatically change their supramolecular structure upon slight modification of the molecular structure. In this paper, the structural and spectral changes of the bis[1,2-bis(4-alkylphenyl)ethanedione dioximato]nickel(II) complex brought about by the introduction of four methyl groups (**1**) and hexyl groups (**2**) are reported (Chart 1).

2. Experimental

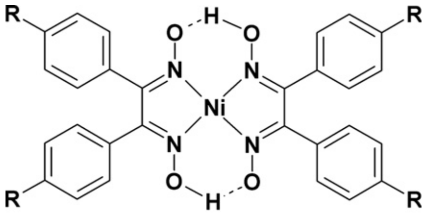
2.1. Preparation of $[Ni\{(C_1)_2dpg\}_2]$ (1) and $[Ni\{(C_6)_2dpg\}_2]$ (2)

Hydroxylamine hydrochloride (3.83 g, 55.1 mmol) and 85% potassium hydroxide (3.83 g, 58.0 mmol) were added to 91 ml of ethanol and the mixture was stirred vigorously for ca. 1 h, and then filtered to remove the resulting precipitate of potassium chloride. 4,4′-Dimethylbenzil (0.20 g,

---

* Corresponding author. Tel.: +81 3 5228 8256.
E-mail address: j1304705@ed.kagu.tus.ac.jp (Y. Soneta).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.02.013



R=H [Ni(dpg)$_2$]
R=CH$_3$ [Ni{(C$_1$)$_2$dpg}$_2$]
R=C$_6$H$_{13}$ [Ni{(C$_6$)$_2$dpg}$_2$]

Chart 1.

0.86 mmol) was added to the filtrate and the mixture was refluxed with stirring under a nitrogen atmosphere for 14 h. Nickel(II) chloride hexahydrate (0.43 g, 1.8 mmol) dissolved in a small amount of ethane-1,2-diol was added to the hot reaction mixture, and immediately neutralized with glacial acetic acid. After further refluxing for 4 h, the reaction mixture was cooled to room temperature and the resulting precipitate collected by filtration and dissolved in chloroform. The organic layer was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. The crude product of **1** was purified by recrystallization from chloroform and ethanol to give crystals suitable for X-ray analysis. **2** was prepared by the similar procedure using 4,4′-dihexylbenzil (0.32 g, 0.86 mmol) instead of 4,4′-dimethylbenzil. Yield, 0.025 g (10%). *Anal.* Calc. for $C_{32}H_{30}N_4NiO_4$ (**1**): C, 64.47; H, 5.09; N, 9.44. Found: C, 64.37; H, 5.01; N, 9.19%. Yield, 0.030 g (8%). *Anal.* Calc. for $C_{52}H_{70}N_4NiO_4$ (**2**): C, 71.47; H, 8.07; N, 6.41 Found: C, 71.50; H, 8.07; N, 6.36%.

2.2. Measurements

The UV–Vis and diffuse reflectance spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer. The DSC measurements were performed by DSC220C (Seiko Instruments). The elemental analysis were performed with a Perkin–Elmer 2400II CHN Analyzer.

2.3. X-ray crystallography

Single crystals of **1** and **2** were mounted on a glass capillary, transferred to a Bruker AXS SMART diffractometer equipped with a CCD area detector and Mo Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved and refined with SHELX-97 [6] using the direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. *Crystal data* for $C_{32}H_{30}N_4NiO_4$ (**1**), $M = 593.31$; $a = 18.0498(14)$ Å, $b = 24.7133(18)$ Å, $c = 6.6870(5)$ Å; $V = 2982.9(4)$ Å^3, Orthorhombic, space group *Pccn*, $Z = 4$, $T = 297(2)$ K, $D_{calc} = 1.321$ Mg/m^3, $\mu = 0.693$ mm^{-1}, 18627 reflections measured, 3435 unique ($R_{int} = 0.0726$), GOF (on F^2) = 0.939, final R_1 $(I > 2\sigma) = 0.0424$, $wR_2(I > 2\sigma) = 0.0979$, R_1 (all data) = 0.0717, wR_2 (all data) = 0.1196. For **2**: $C_{52}H_{70}N_4NiO_4$, $M = 873.83$; $a = 27.427(3)$ Å, $b = 27.427$ (3) Å, $c = 6.4041$ (10) Å, $V = 4817.6(11)$ Å^3, Tetragonal, space group $I\bar{4}$, $Z = 4$, $T = 173(2)$ K, $D_{calc} = 1.205$ Mg/m^3, $\mu = 0.450$ mm^{-1}, 15484 reflections measured, 5541 unique ($R_{int} = 0.0662$), GOF (on F^2) = 1.010, final R_1 $(I > 2\sigma) = 0.0487$, wR_2 $(I > 2\sigma) = 0.1327$, R_1 (all data) = 0.0609, wR_2 (all data) = 0.1431. Selected bond lengths and angles are shown in Table 1.

Table 1
Selected bond lengths (Å) and angles (°) in **1** and **2**

Compound **1**			
Ni1–N1	1.864(2)	N1–Ni1–N2	97.93(8)
Ni1–N2	1.868(2)	N1–Ni1–N2^a	82.17(8)
N1–O2	1.340(2)	N1–Ni1–N1^a	176.50(11)
O1–N2	1.338(2)	N2^a–Ni1–N2	176.52(11)
N1–C1	1.305(3)	C1–N1–O2	119.7(2)
N2–C2	1.300(3)	C2–N2–O1	120.9(2)
C1–C2^a	1.488(3)	C1–N1–Ni1	117.25(16)
		C2–N2–Ni1	116.82(16)
		O1–N2–Ni1	121.76(14)
		O2–N1–Ni1	122.44(14)
Compound **2**			
Ni1–N1	1.8670(19)	N2–Ni1–N1	98.05(8)
Ni1–N2	1.8604(18)	N2^b–Ni1–N1	81.97(8)
N1–O1	1.331(3)	N1–Ni1–N1^b	178.7(2)
N2–O2	1.333(3)	N2–Ni1–N2^b	177.9(2)
N1–C1	1.296(3)	C1–N1–O1	120.0(2)
N2–C14	1.300(3)	C14–N2–O2	120.67(19)
C1–C14^b	1.472(3)	C1–N1–Ni1	117.10(16)
		C14–N2–Ni1	116.80(16)
		O1–N1–Ni1	122.64(15)
		O2–N2–Ni1	122.32(15)

Symmetry operation: $^a -x + 1/2, -y + 3/2, z$; $^b -x + 2, -y + 1, z$.

3. Results and discussion

3.1. UV–Vis absorption and diffuse reflectance spectra

The UV–Vis spectra of both complexes [Ni{(C$_1$)$_2$dpg}$_2$]{bis[1,2-bis(4-methylphenyl)ethanedione dioximato]nickel(II)} (**1**) and [Ni{(C$_6$)$_2$dpg}$_2$]{bis[1,2-bis(4-*n*-hexylphenyl)ethanedione dioximato]nickel(II)} (**2**) measured in chloroform exhibited an intense absorption band at 275 nm ($\varepsilon = 4.1 \times 10^4$ l mol^{-1} cm^{-1}) ascribed to the π–π^* transition of intra-ligand, and the absorption bands at 413 nm ($\varepsilon = 1.3 \times 10^4$ l mol^{-1} cm^{-1}) ascribed to the absorption of MLCT (metal to ligand charge transfer), and the absorption band at 367 nm ($\varepsilon = 1.0 \times 10^4$ l mol^{-1} cm^{-1}) could not be assigned [7]. These absorption peaks exhibited shifts to longer wavelength by the introduction of the alkyl groups, but no apparent change was visible by the difference in alkyl groups. In the solid phase, however, an additional sharp absorption peak occurs near 515 nm, which does not have an obvious counterpart in solution [8]. This peak was ascribed to d–p transition which is sensitive to the one-dimensional metal to metal stacking distance. This

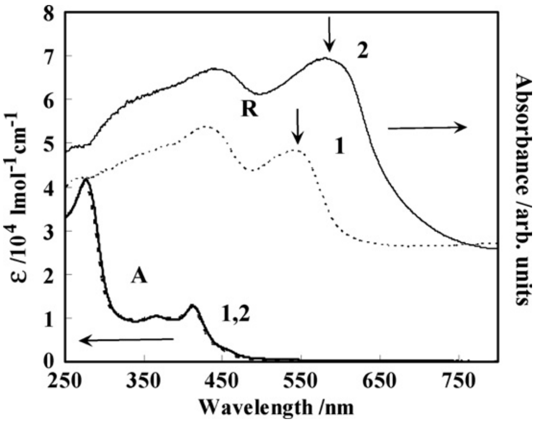


Fig. 1. Diffuse reflectance spectra (R) and absorption spectra in chloroform (A) of **1** and **2** are represented. The d–p transition peaks were indicated by arrows.

additional absorption of complexes **1** and **2** appeared at 542 and 582 nm, respectively as shown in Fig. 1, and they shifted to longer wavelength compared with that of [Ni(dpg)$_2$]. In the previous report, the shift of the absorption band was reported as dependent on the length of the Ni–Ni bonds due to the fastener effect of the long alkyl or alkoxy chains [5]. However, the methyl substituent in **1** is too short to attain fastener effect. Therefore, the stacking configurations of these complexes are investigated by the X-ray crystal structural analysis.

3.2. X-ray crystal structure

Fig. 2 shows the crystal structures of complexes **1** and **2**. In complex **1**, the Ni–N distances of 1.864(2) and 1.868(2) Å are close to the normally observed value of *ca.* 1.85 Å observed in several four-coordinate Ni(II) complexes. The N–C distances of 1.305(3) and 1.300(3) Å and the N–O distances of 1.340(2) and 1.338(2) Å in coordinating glyoxime ligand are comparable with those in non-alkylated species, [Ni(dmg)$_2$]{bis(dimethylglyoximato)nickel(II)} [9]. The benzene rings are tilted 47.3° and 44.5° from the chelate plane. In complex **2**, the Ni–N (1.8604(18), 1.8670(19) Å), N–C (1.296(3), 1.300(3) Å), N–O (1.331(3), 1.333(3) Å) and O–O (2.437 Å) distances are not significantly different from those of complex **1**.

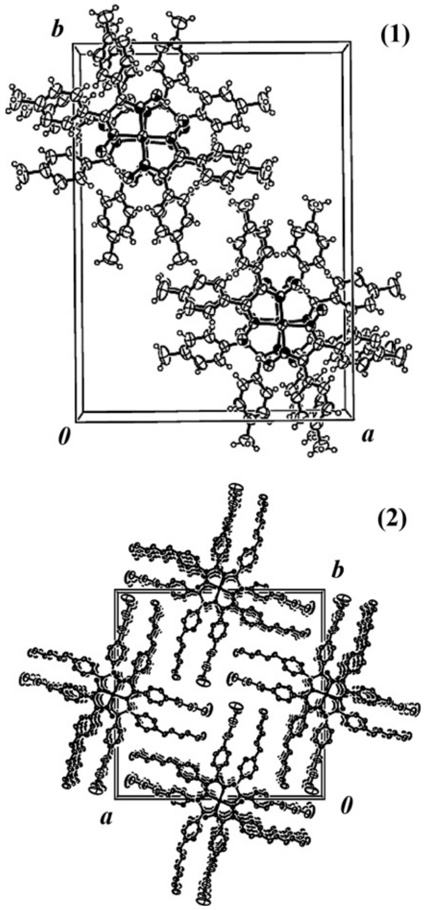


Fig. 2. Crystal structures of **1** and **2** viewed along *c*-axis. H atoms for **2** were omitted for clarity.

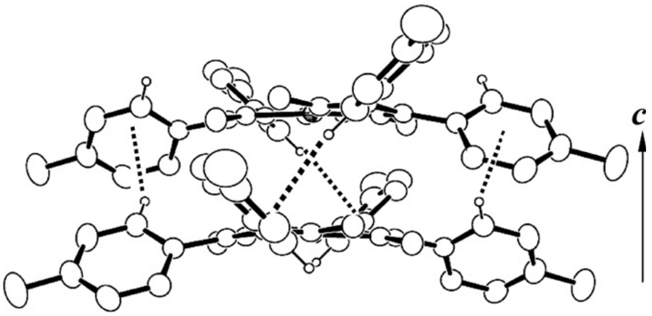


Fig. 3. Edge-to-face aromatic interaction of **1** viewed along *a*-axis.

The [Ni(dpg)$_2$] units of **1** stack (staggered by 90°) at intervals of 3.344 Å. The Ni–Ni distance in **1** is thus 0.20 Å shorter than that of [Ni(dpg)$_2$] (3.547 Å). When the geometric structure of **1** was compared with the non-substituted complex [Ni(dpg)$_2$], no apparent difference in molecular structure that leads to the decrease in Ni–Ni distance could be found. Itoh et al. reported the preparation of the diphenylglyoxime complex substituted with hydroxyl or amino group, and found that these crystal structures were strongly controlled by the hydrogen bond [10], but no such interactions with neighboring columns were observed in the crystal of **1**. However, the edge-to-face aromatic interactions reported elsewhere, especially in the field of structural biology, were present [11]. As is seen in Fig. 3, the edge-to-face distance between C–H and the plane of π-system was 2.751 and 2.810 Å shorter than the mean distance (*ca.* 2.86 Å) of the sp^2-CH$\cdots\pi$ reported by Suezawa et al. [12]. This is an evidence for the edge-to-face aromatic interaction. In the case of complex **1**, the Ni(dpg)$_2$ moieties attract each other by the edge-to-face aromatic interactions, may be due to increase in the electrostatic potential brought about by the introduction of the methyl groups, since the electron-donating groups (NH$_2$, OH and CH$_3$) and electron-withdrawing groups (NO$_2$ and CN) increase and decrease, respectively, the negative electrostatic potential on the π-electron system of the aromatic ring. No such interaction could be observed in the crystal structure of non-substituted [Ni(dpg)$_2$]. A similar situation can also be seen in **2**.

To investigate the mesomorphic properties of **2**, the phase transition temperatures and enthalpy changes were measured by DSC. When **2** was heated to 121.2 °C (6.8 kJ/mol), the crystalline phase transformed into a mesophase. On further heating, the mesophase changed into an isotropic liquid phase at 198.7 °C (12.25 kJ/mol). It is known that disk-like molecules substituted with four alkoxychains tend to show disk-like lamellar mesophases, while those with eight alkoxychains tend to show columnar phase [13]. However, Ohta et al. reported that the columnar mesophases are observed although the [Ni{(C$_{12}$)$_2$dpg}$_2$] complex has only four long chains and this behavior may be attributable to the dimerization by which a disk unit (dimer) can apparently possess eight long chains [5]. The structural feature of **2**, where the [Ni(dpg)$_2$] units of **2** stack (staggered by 90°) at intervals of 3.151 Å and 3.253 Å is consistent with this report. In **2**, one hexyl group adopted an all-trans conformation with a slight distortion. This distortion was due to the steric repulsion between the approached hexyl groups. This is an evidence for the fastener effect proposed by Ohta et al. [5]. However, the contribution of the fastener effect to the spectroscopic change in d–p transition is not as high as they predicted. Since the methyl substituted analogue **1** exhibited a shift of 970 cm^{-1}, the 43% of the peak shift, 2240 cm^{-1}, of hexyl-substituted analogue **2** should be attributed to the edge-to-face interaction and the rest (57%) to the fastener effect.

4. Conclusion

Bis[1,2-bis(4-alkylphenyl)ethanedione dioximato] nickel (II) {alkyl = methyl; [Ni{(C$_1$)$_2$dpg}$_2$] (**1**) and alkyl = *n*-hexyl; [Ni{(C$_6$)$_2$dpg}$_2$] (**2**)} have been prepared and analyzed by diffuse reflectance spectra. The absorption peaks ascribed to d–p transition exhibited shifts to longer wavelength by the introduction of the alkyl groups compared with that of no substituted [Ni(dpg)$_2$] in solid state. Therefore, the stacking configurations of these complexes were investigated by the X-ray crystal structural analysis. The [Ni(dpg)$_2$] units of **1** stacked (staggered by 90°) at intervals of 3.344 Å, and the Ni–Ni distance in **1** was 0.20 Å shorter than that of [Ni(dpg)$_2$] (3.547 Å). In the case of complex **1**, the Ni(dpg)$_2$ moieties attracted each other by the edge-to-face aromatic interactions, may be due to increase in the electrostatic potential brought about by the introduction of the methyl groups. The [Ni(dpg)$_2$] units of **2** stacked (staggered by 90°) at intervals of 3.151 Å and 3.253 Å. In the case of **2**, the Ni(dpg)$_2$ moieties attracted each other by the edge-to-face aromatic interactions and fastener effect. Therefore, the evaluation of the edge-to-face interaction and fastener effect could be calculated by the spectral shift.

Appendix A. Supplementary material

CCDC 615018 and 615019 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.02.013.

References

[1] L.E. Godycki, R.E. Rundle, Acta Crystallogr. 6 (1953) 487.

[2] M.S. Hussain, B.E.V. Salinas, E.O. Schlemper, Acta Crystallogr. B 35 (1979) 628.

[3] J.C. Zahner, H.G. Drickamer, J. Chem. Phys. 33 (1965) 1625.

[4] M. Tkacz, H.G. Drickamer, J. Chem. Phys. 85 (1986) 184.

[5] (a) K. Ohta, H. Hasebe, M. Moriya, T. Fujimoto, I. Yamamoto, Mol. Cryst. Liq. Crystallogr. 208 (1991) 43;
(b) K. Ohta, H. Hasebe, M. Moriya, T. Fujimoto, I. Yamamoto, J. Mater. Chem. 1 (1991) 831;
(c) K. Ohta, M. Moriya, M. Ikejima, H. Hasebe, T. Fujimoto, I. Yamamoto, Bull. Chem. Soc. Jpn. 66 (1993) 3553;
(d) K. Ohta, M. Moriya, M. Ikejima, H. Hasebe, T. Fujimoto, I. Yamamoto, Bull. Chem. Soc. Jpn. 66 (1993) 3559;
(e) K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto, N. Kobayashi, J. Mater. Chem. 8 (1998) 1979;
(f) K. Ohta, Y. Inagaki-Oka, H. Hasebe, I. Yamamoto, Polyhedron 19 (2000) 267.

[6] G. M. Sheldrick, SHELXS-97 and SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.

[7] Y. Ohashi, I. Hanazaki, S. Nagakura, Inorg. Chem. 9 (1970) 2551.

[8] C.V. Banks, D.W. Barnum, J. Am. Chem. Soc. 80 (1958) 4767.

[9] D.E. Williams, G. Wohlauer, R.E. Rundle, J. Am. Chem. Soc. 81 (1959) 755.

[10] T. Itoh, K. Iijima, J. Toyoda, K. Nakasuji, Mol. Crystallogr.. Liq. Crystallogr. 285 (1996) 287.

[11] E. Kim, S. Paliwal, C.S. Wilcox, J. Am. Chem. Soc. 120 (1998) 11192.

[12] H. Suezawa, T. Yoshida, Y. Umezawa, S. Tsuboyama, M. Nishio, Eur. J. Inorg. Chem. (2002) 3148.

[13] (a) K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto, K. Matsuzaki, Mol. Crystallogr. Liq. Crystallogr. 140 (1986) 131;
(b) Y. Shimizu, M. Miya, A. Nagata, K. Ohta, A. Matsumura, I. Yamamoto, S. Kusabayashi, Chem. Lett. (1991) 25;
(c) K. Ohta, Y. Morizumi, H. Ema, T. Fujimoto, I. Yamamoto, Mol. Crystallogr. Liq. Crystallogr. 208 (1991) 55.