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Polyhedron 22 (2003) 2215–2218

POLYHEDRON

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A synthetic study of metal complexes of coordinated neutral radicals based on an azaphenalenyl system

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Received 7 October 2002; accepted 13 December 2002

Abstract

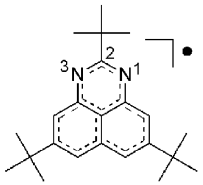
A new neutral radical ligand, 5,8-di-*tert*-butyl-2-(4′,6′-dimethylpyrimidine-2′-yl)-1,3-diazaphenalenyl (**2**), has been designed on the basis of 1,3-diazaphenalenyl system. As a study for the metal complexes of coordinated neutral radical **6**, we have synthesized the metal complex coordinated diazaphenalene **3** by a combination of $CoCl_2$ with 1,3-diazaphenalene **4**. The 1,3-diazaphenalene of the metal complex **3** in the crystal was planar and nearly coplanar with the pyrimidine ring, giving the first study on the structurally characterized metal complex based on the azaphenalene system. Preliminary magnetic susceptibility measurements have revealed that **3** is a spin-quartet in the ground state.

Keywords: 1,3-Diazaphenalenyl; 1,3-Diazaphenalene; Radical–metal complexes; X-ray structure analysis

1. Introduction

There has been much interest in the creation of exotic molecule-based magnetic materials, and one of the strategies is the construction of metal complexes of organic open-shell molecules [1]. A nitroxide family, radical anions of cyanocarbons such as TCNE, TCNQ, and semiquinone derivatives are widely used as major components of the radical ligands [2]. For further development of this field, creation of new stable radical ligands can afford the potential of materials challenges. Especially, the synthesis of the metal complexes with strong interaction between spin(s) on ligands and spin(s) on metal(s) are attracting much attention. Thus, we have designed the 1,3-diazaphenalenyl derivative with pyrimidine moiety **2** as a new neutral radical ligand. In this paper, we report on the synthesis of the cobalt complex of pyrimidine-substitued 1,3-diazaphenalene (**3**) as a study for the preparation of radical–metal complex.

1,3-Diazaphenalenyl is a typical example of the isoelectronic mode of heteroatomic modification for phenalenyl [3], and we have recently reported the synthesis and isolation of tri-*tert*-butylated 1,3-diazaphenalenyl derivative **1** [4,5]. The spin structure of **1** shows an extensively spin-delocalized and spin-polarized nature, which gives rise to an expectation of the strong



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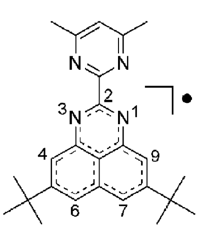

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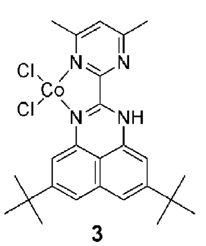

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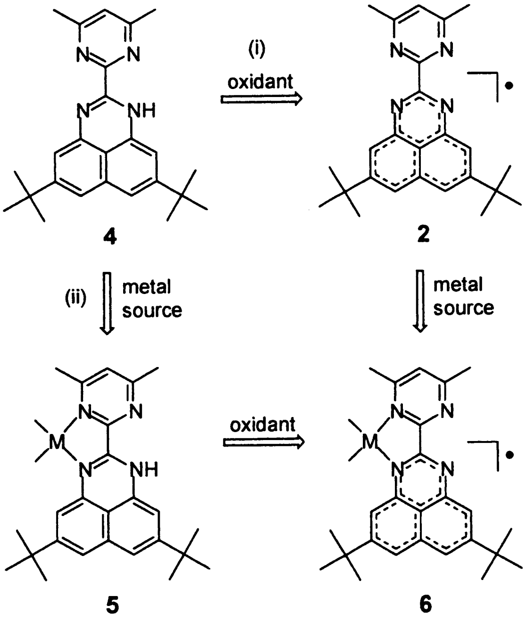
0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00176-1



Scheme 1.

spin–spin interaction between paramagnetic metal ion and the nitrogen atom(s) of the phenalenyl system in the metal complex **6**. For the preparation of the metal complexes of coordinated neutral radical **6**, following two routes are conceivable (Scheme 1): (i) oxidation of the 1,3-diazaphenalene derivative **4** to the neutral radical **2** followed by coordination with the metal sources, (ii) preparation of metal complex **5** with **4** and subsequent oxidation of 1,3-diazaphenalene moiety.

2. Experimental

2.1. Material and methods

All chemicals were reagent grade and used without further purification. 1,8-Diamino-3,6-di-*tert*-butylnaphthalene (**7**) [3] and 4,6-dimethyl-2-pyrimidinecarboxaldehyde (**8**) [6] were prepared by the reference methods. All reactions requiring anhydrous conditions were performed under an argon atmosphere. Toluene was dried and distilled over CaH_2 under an argon atmosphere prior to use. Xylene (mixture of isomers) was dried by the filtration through the Alumina Super I (ICN Biomedicals) column. Recycle preparative gel permeation chromatography (GPC) was performed using tandemly connected two polystyrene gel columns (JAIGEL 1H, Japan Analytical Industry) with $CHCl_3$ as eluant. ^1H NMR spectra were recorded on a JEOL EX-270 spectrometer with Me_4Si as an internal standard. Infrared spectra were recorded using KBr plates or $Cl_2C{=}CCl_2$ solution on Perkin Elmer 1600 series FT-IR. Electronic spectra were recorded using KBr plates on Shimadzu UV-3100PC. EI MS spectra were recorded at 70 eV on a Shimadzu QP-5000. M.p. were recorded with a Yanaco micro m.p. apparatus and were uncorrected. X-ray crystallographic measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254}. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots became clearly visible.

2.2. Synthesis of 5,8-di-tert-butyl-2-(4′,6′-dimethylpyrimidine-2′-yl)-1,3-diazaphenalene (4)

Diaminonaphthalene **7** (228 mg, 0.85 mmol) was placed in a 50-ml Schlenk tube equipped with a reflux condenser and mixed with xylene (10 ml), dimethylpyrimidinecarboxaldehyde **8** (126 mg, 0.93 mmol) and 5% Pd/C (55 mg). This mixture was refluxed at 160 °C (bath temperature) for 3 h. After being cooled to room temperature, this reaction mixture was subjected to the Na_2SO_4 and celite column to remove the catalyst and water, and rinsed with CH_2Cl_2. The filtrates were concentrated under reduced pressure. The resulting crude products were subjected to GPC with $CHCl_3$ as eluant, to give the diazaphenalene **4** (316 mg, 96%) as a reddish orange powder. M.p. 285–287 °C; $R_f = 0.63$ (silica gel, 1:1 ethyl acetate–MeOH); ^1H NMR ($CDCl_3$) δ 1.32 (18H, s), 2.64 (6H, s), 6.38 (1H, d, $J = 1.6$ Hz), 7.02 (1H, d, $J = 1.6$ Hz), 7.10 (1H, d, $J = 1.6$ Hz), 7.15 (1H, s), 7.18 (1H, d, 1.6 Hz), 9.30 (1H, s); EI MS *m/z* 386 (M^+, 100%); IR (KBr) 3318, 2966 cm^{-1}; IR ($Cl_2C{=}CCl_2$) 3384, 2964 cm^{-1}; UV (KBr) 466, 352, 236 nm.

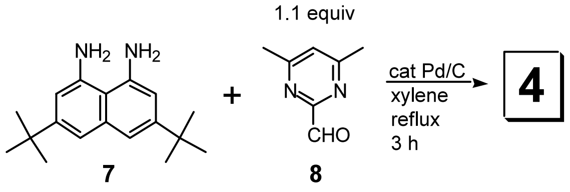
2.3. Synthesis of $CoCl_2$ complex of 5,8-di-tert-butyl-2-(4′,6′-dimethylpyrimidine-2′-yl)-1,3-diazaphenalene (3)

A MeCN (20 ml) solution of 1,3-diazaphenalene **4** (100 mg, 0.23 mmol) and a MeOH (5.0 ml) solution of $CoCl_2 \cdot 6H_2O$ (56 mg, 0.23 mmol) were combined in a 100-ml round-bottomed flask and evaporated under reduced pressure. The residue was dissolved in MeCN (10 ml) and CH_2Cl_2 (10 ml), and the resulting mixture was slowly evaporated by a flow of argon at room temperature. The generated crystal was obtained by the filtration, washed with hexane and MeOH, and dried in vacuo at room temperature for 2 h, to give the $CoCl_2$ complex **3** (59 mg, 49%) as a black crystal. The X-ray structure analysis was performed at room temperature: $C_{25}H_{30}N_4CoCl_2$, $M_r = 516.38$, crystal dimensions $0.30 \times 0.20 \times 0.05$ mm, black, Rigaku RAXIS-RAPID Imaging Plate diffractometer, Mo Kα radiation, $T =$ 23 °C, monoclinic, space group $P2_1/n$ (no. 14), $a = 15.856(1)$, $b = 10.3849(5)$, $c = 16.473(1)$ Å, $\beta = 104.527(2)°$, $V = 2624.9(3)$ Å^3, $Z = 2$, $\rho_{calc} = 0.65$ g cm^{-3}, 20957 reflections collected, 5835 unique intensities reflections observed [$I > 2.00\sigma$ (I)], $2\theta_{\max} = 54.7°$, structure solution with direct methods (SIR92) and refinement on F with 337 parameters, $R(R_w) = 0.072$ (0.192), S(GOF) = 0.93.

3. Results and discussion

3.1. *Synthesis of the pyrimidine derivative of 1,3-diazaphenalene (**4**)*

The precursor of the neutral radical and metal complex, dimethylpyrimidine substituted 1,3-diazaphenalene **4** was synthesized by the condensation of 1,8-diaminonaphthalene **7** with 2-pyrimidinecarboxaldehyde **8** followed by the dehydrogenation (Scheme 2) [7]. The product **4** was isolated as a reddish orange powder.



Scheme 2.

3.2. *$CoCl_2$ complex of 1,3-diazaphenalene (**3**)*

A $CoCl_2$ complex **3** was obtained by slow evaporation of the combined solution of $CoCl_2 \cdot 6H_2O$ and 1,3-diazaphenalene **4**. An X-ray structure analysis of **3** gives the first example of the structurally characterized metal

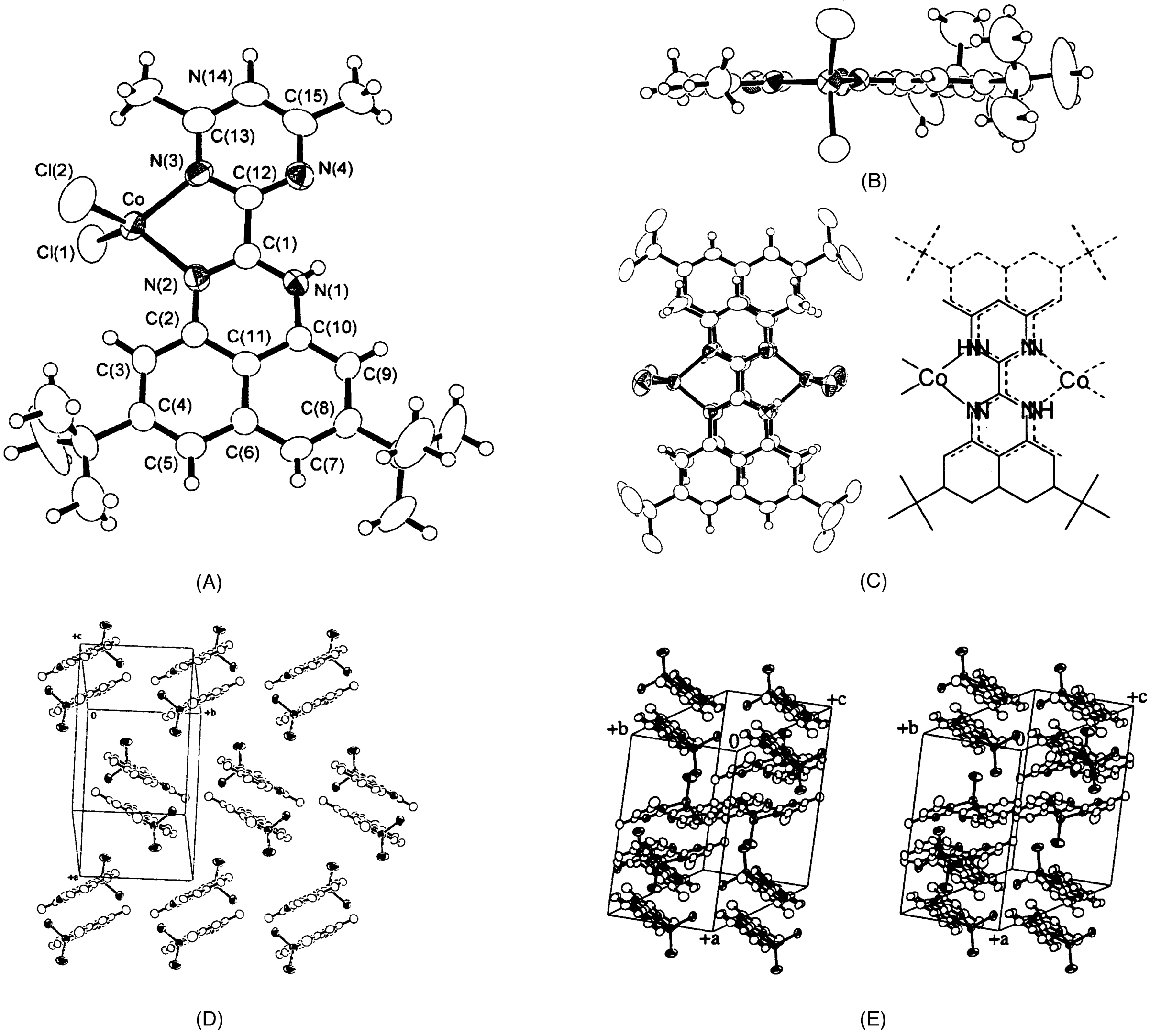


Fig. 1. ORTEP views of **3**, (A) molecular structure, (B) side view, (C) the dimer structure and a schematic representation (the protons of *tert*-butyl groups are omitted for clarity), (D) the herringbone structure and (E) stereo view of crystal packing. The *tert*-butyl groups and protons are omitted for clarity in D and E.

Table 1
Selected bond lengths and angles of the $CoCl_2$ complex **3**

	Lengths (Å)		Angles (°)
Co–N(2)	2.020(4)	N(2)–Co–N(3)	81.0(1)
Co–N(3)	2.069(4)	N(2)–Co–Cl(1)	111.9(1)
Co–Cl(1)	2.222(2)	N(2)–Co–Cl(2)	120.1(1)
Co–Cl(2)	2.195(2)	N(3)–Co–Cl(1)	106.8(1)
C(1)–N(1)	1.331(6)	N(3)–Co–Cl(2)	115.1(1)
C(1)–N(2)	1.312(6)	Cl(1)–Co–Cl(2)	116.19(7)

complex based on an azaphenalene system [8]. The molecular structure of **3** is shown in Fig. 1. The chelate complexation of 1,3-diazaphenalene derivative **4** to $CoCl_2$ affords tetrahedral four-coordinate complex. The selected bond lengths and angles are summarized in Table 1. The 1,3-diazaphenalene ring of **3** is planar and nearly coplanar with the pyrimidine ring, forming dihedral angles of 0.8° [N(1)–C(1)–C(12)–N(4)] and 2.3° [N(2)–C(1)–C(12)–N(3)] (Fig. 1(B)). The metal complex **3** forms the dimer structure in the crystal (Fig. 1(C–E)). The pyrimidine ring of **3** overlaps with the ring system contained nitrogen atoms of the other molecule in the dimer (Fig. 1(C)). The distances of the dimeric pair of **3** range from 3.48 to 3.70 Å. The dimer packing mode is a herringbone structure (Fig. 1(D and E)). Preliminary magnetic susceptibility measurements by a SQUID magnetometer have revealed that Co(II) of **3** is a ground-state quartet as expected from a nearly tetrahedral symmetry for the Co(II) site.

4. Summary

We have succeeded in the synthesis of the metal complex of 1,3-diazaphenalene–$CoCl_2$ (**3**) as a study for the preparation of radical–metal complex. An X-ray structure analysis of **3** gives the first study on the structurally characterized metal complex based on an azaphenalene system. A close study of the magnetic properties of **3** is underway. Attempts for the preparation and isolation of the metal complexes of coordinated neutral radical **6** are in progress.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Area ‘Delocalized π-Electronic Systems’ (No. 297) and other Grants from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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