# Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name RSCPublishing

COMMUNICATION

# Heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes

Cite this: DOI: 10.1039/x0xx00000x

Ryojun Toyoda, Mizuho Tsuchiya, Ryota Sakamoto,* Ryota Matsuoka, Kuo-Hui Wu, Yohei Hattori and Hiroshi Nishihara

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

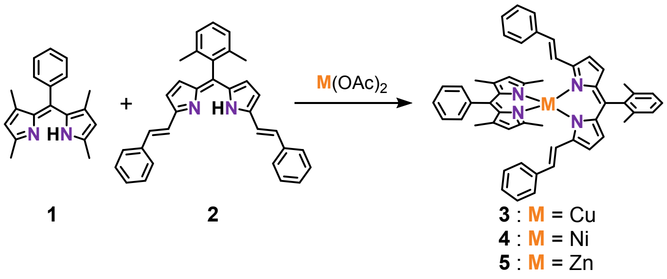
www.rsc.org/

**Heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes are synthesized. Their structures are determined by X-ray diffraction analysis, and their properties are investigated by using cyclic voltammetry, chronocoulometry, and UV/vis absorption spectroscopy.**

Dipyrrins are a family of organic ligand molecules that contain two pyrrole rings connected by a methine bridge, and thus possess a partial porphyrin structure. Dipyrrins and their complexes feature intense molar extinction coefficients for $\pi$-$\pi^*$ bands (~$10^5$ $M^{-1}$ $cm^{-1}$),[1] which enable them to collect visible light efficiently. For this reason, they are considered as promising candidates for pigment molecules for applications such as solar cells and chemosensors.[2] In addition, dipyrrins can form complexes with various metals (Zn, Cu, Ni, Pd, In, Ga, Fe, Co, and Ru) by chelating them with two pyrrole nitrogens.[3,4] In many cases, the complexation proceeds spontaneously under ambient conditions. These features mean that the motif is used in supramolecules, coordination polymers, and metal-organic frameworks.[5]

Bis(dipyrrinato)metal(II) and tris(dipyrrinato)metal(III) complexes reported thus far have mainly been homoleptic with a single type of dipyrrinato ligand:[3] a small number of heteroleptic complexes have been reported by Cohen,[6a] and Radecka,[6b,c] and Dolphin,[6d] where their asymmetry is trivial, such as introduction of different substituents on aryl groups at the meso position. In contrast, we have succeeded in creating heteroleptic bis(dipyrrinato)zinc(II) and tris(dipyrrinato)indium(III) complexes containing two types of dipyrrinato ligand with drastic differences in their electronic structures (i.e. a combination of plain ligands **1** and $\pi$-extended ligand **2**, scheme 1).[4,7] These $d^{10}$ homoleptic complexes exhibit brighter fluorescence than the corresponding homoleptic complexes.

Here, we report the synthesis, structure, and property of heteroleptic bis(dipyrrinato)metal(II) complexes employing copper(II) and nickel(II) ions as the central metals. Unlike zinc(II) ions, copper(II) and nickel(II) ions have vacant d-orbitals, with $d^9$ and $d^8$ configurations, respectively. We note that heteroleptic monodipyrrinato copper[8] and nickel[9] complexes have been reported, which contain non-dipyrrinato ligands as ancillary ligands, such as phosphine, acetylacetonate, dithiocarbamate, and so on.



**Scheme 1** Synthesis of heteroleptic bis(dipyrrinato) metal complexes. **3** : M = Cu(II), **4** : M = Ni(II), **5** : M = Zn(II).

Heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes (**3** and **4**) were synthesized with two types of dipyrrin ligands: plain ligand **1** and $\pi$-expanded ligand **2** (Scheme 1). As a reference, corresponding zinc(II) complex **5** was also prepared. Heteroleptic complexes **3**–**5** were synthesized by a method similar to our reported procedure.[4,7] A chloroform solution of dipyrrins **1** and **2**, and a methanol solution of each metal(II) acetate were mixed and stirred overnight (Scheme 1) at ambient temperatures. The crude heteroleptic complexes were separated and purified from the homoleptic complexes by gel permeation chromatography.

Single-crystal X-ray diffraction analysis elucidated the structure of copper(II) and nickel(II) complexes **3** and **4** (Fig. 1 and Tables S1 and S2†).[10] Their crystal structures (Fig. 1) show that they are heteroleptic and contain two different dipyrrinato ligands. The four nitrogen atoms on the two dipyrrinato ligands coordinate to the metal center, and the dihedral angles for the two planes, N(1)-M-N(2) and N(3)-M-N(4), in **3** and **4** are 86.02° and 86.18°, respectively. Therefore, the metal center adopts tetrahedral coordination spheres. Although copper(II) and nickel(II) complexes favor square planar coordination spheres,[12] steric repulsion between the methyl and styryl groups at the $\alpha$ position of the dipyrrinato ligand is severe, thus planar structures are not favored in these complexes. In fact, those with methyl groups at the $\alpha$

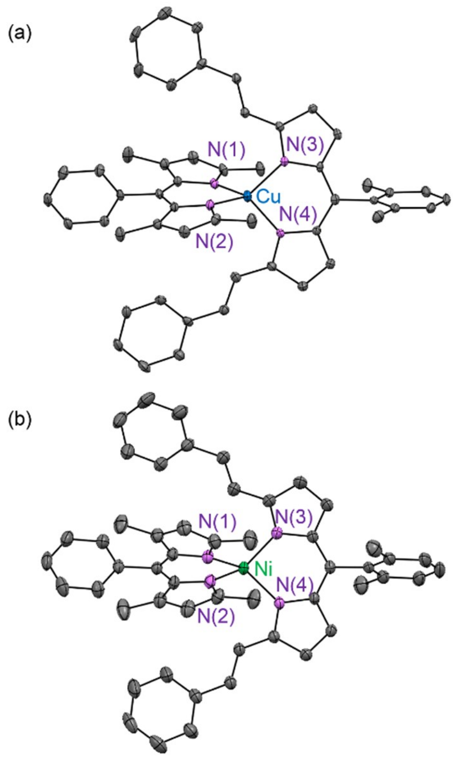


**Fig. 1** Crystal structures of (a) **3** and (b) **4** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. C : gray, N : purple, Cu : blue, Ni : green.

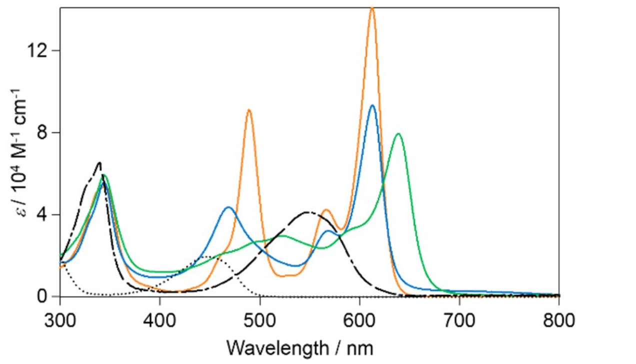


**Fig. 2** UV/Vis absorption spectra of **1** (black, dotted line), **2** (black, dashed dotted line), **3** (blue, solid line), **4** (green, solid line), **5** (orange, solid line).

position were reported to possess dihedral angles with 70.5° for a Cu complex,[6d] and 78.5° and 76.3° for Ni ones.[6d,11] The distances between the metal center and the pyrrole nitrogen span 1.930–1.958 Å for **3** and 1.935–1.958 Å for **4**, which are values typical of dipyrrinato copper(II) and nickel(II) complexes (1.949–1.985 and 1.948–1.967 Å, respectively).[6d,11,13]

UV/Vis absorption spectra of complexes **3**–**5** in toluene and ligands **1** and **2** are shown in Fig. 2, and the maximal absorption wavelength and molar extinction coefficient of each band are presented in Table 1. The chief absorption bands of **3**–**5** are derived from the π-π* transitions localized on the dipyrrinato ligands. The peaks at shorter wavelengths (**3**: 469 nm, **4**: 522 nm, **5**: 489 nm) originate from plain ligand **1**, whereas those at longer wavelengths (**3**: 613 nm, **4**: 639nm, **5**: 612 nm) stem from π-extended ligand **2**. These π-π* bands are red-shifted and sharper compared with those of free ligands **1** and **2**, which is a spectroscopic change typical of the complexation between a dipyrrin ligand and a metal ion.[14] The peaks at around 344 nm correspond to the transition from the ground state to the second excited state ($S_2 \leftarrow S_0$) of π-extended ligand **2**.[1,15] Both copper-centered **4** and nickel-centered **5** were non-emissive in fluid solutions at room temperature.

**Table 1** Maximal absorption wavelengths ($\lambda_{abs}$) and molar extinction coefficients ($\varepsilon_{max}$) of **1-5**

| | $\lambda_{abs}$ (nm) | $\varepsilon_{max}$ ($10^4$ $M^{-1}cm^{-1}$) |
|---|---|---|
| **1** | 447 | 1.93 |
| **2** | 340, 548 | 6.52, 4.11 |
| **3** | 344, 469, 569, 613 | 5.56, 4.35, 3.20, 9.34 |
| **4** | 344, 522, 639 | 5.91, 2.96, 7.95 |
| **5** | 344, 489, 567, 612 | 5.35, 9.11, 4.23, 14.1 |

The electrochemical properties of the three complexes were investigated by cyclic voltammetry (Fig. 3, Table 2). In the voltammogram of zinc complex **5**, there are two oxidation peaks at $E_{1/2}$ = 0.25 and 0.50 V vs ferrocenium/ferrocene ($Fc^+$/Fc). The redox wave at the negative potential corresponds to a one-electron oxidation of π-extended ligand **2**, whereas that at the positive potential is derived from plain ligand **1**. A one-electron reduction from π-extended ligand

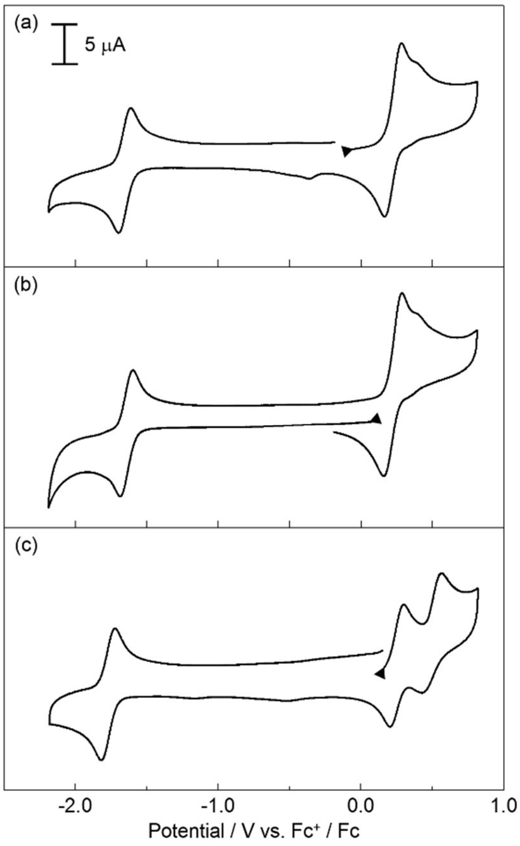


**Fig. 3** Cyclic voltammograms of (a) **3**, (b) **4**, (c) **5**. The triangles indicate the starting points of the potential sweep.

**Table 2** Redox potentials of **3**-**5** in dichloromethane solution (0.5 mM)

| | $E_{\mathrm{red}}$ (V)[a] | $E_{\mathrm{ox}}$ (V)[b] |
|---|---|---|
| **3** | -1.65[c] | 0.28[d] |
| **4** | -1.64[c] | 0.29[d] |
| **5** | -1.77[c] | 0.25[c], 0.50[c] |

[a] Reduction potential vs ferrocenium/ferrocene ($Fc^+/Fc$). [b] Oxidation potential vs $Fc^+/Fc$. [c] Half-wave potential ($E_{1/2}$) . [d] Anodic peak potential ($E_{\mathrm{pa}}$).

**2** is observed at $E_{1/2} = -1.77$ V, whereas that of **1** did not appear in the range of the potential window. The large positive shift in the reduction potential in **2** compared with **1** arises from the strong electron withdrawing effect of the styryl group. Copper and nickel complexes **3** and **4** also show a one-electron single reduction peak at $E_{1/2} = -1.65$ and −1.64 V, respectively, attributed to the reduction of ligand **2**. However, for the oxidation, a single redox wave is visible around 0.3 V. To gain insight into how many electrons are associated with the oxidation process, chronocoulometry was conducted for the oxidation and reduction of nickel complex **4** (Fig. S1†).[16] It gave a ratio of 2 : 1 for the number of electrons involved in the oxidation and reduction processes. Therefore, the oxidation of **4** is a two-electron process. The same conclusion may be drawn for copper complex **3**, judging from the similarity in the shape of the voltammograms. Frequently, structural alternations associated with a redox reaction induce a change in the redox potential.[17] As discussed in the single-crystal X-ray diffraction section, the copper and nickel centers adopt the enforced tetrahedral coordination sphere (Fig. 1). Thus, it is expected that after the first oxidation, complexes **3** and **4** undergo structural changes, which induce negative shifts in the second oxidation, and coalescence between the first and second oxidation waves.

In conclusion, heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes were synthesized, and their structural, optical, and electrochemical properties were examined. Our results contribute to the understanding of dipyrrin metal complex chemistry.

The authors acknowledge Grants-in-Aid from MEXT of Japan (Nos. 21108002, 24750054, 25107510, 26708005, 26107510, 26620039, areas 2406 [All Nippon Artificial Photosynthesis Project for Living Earth], 2506 [Science of Atomic Layers]). R.S. is grateful to Tokuyama Science Foundation, Ogasawara Foundation for the Promotion of Science & Engineering, The Kao Foundation for Arts and Sciences, The Asahi Glass Foundation, The Noguchi Institute, and Japan Association for Chemical Innovation, The MIKIYA Science and Technology Foundation, Yazaki Memorial Foundation for Science and Technology, Shorai Foundation for Science and Technology, The Kurata Memorial Hitachi Science and Technology Foundation, and Kumagai Foundation for Science and Technology for financial supports. M.T. and R.M. acknowledge JSPS fellowship for young scientists. M.T. is also grateful to Advanced Leading Graduate Course for Photon Science (ALPS). The authors acknowledge the Research Hub Advanced Nano Characterization (Graduate School of Engineering, The University of Tokyo) for the single crystal XRD study.

## Notes and references

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: sakamoto@chem.s.u-tokyo.ac.jp.

†Electronic Supplementary Information (ESI) available: Experimental methods; single-crystal XRD data for **3** and **4**, chronocoulometry for **4**. See DOI: 10.1039/c000000x/

1 G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184–1201.

2 (*a*) C. Y. Lee and J. T. Hupp, *Langmuir*, 2010, **26**, 3760–3765; (*b*) Y. Mei, P. a. Bentley and W. Wang, *Tetrahedron Lett.*, 2006, **47**, 2447–2449.

3 (*a*) T. E. Wood and A. Thompson, *Chem. Rev.*, 2007, **107**, 1831–1861; (*b*) S. A. Baudron, *Dalton Trans.*, 2013, **42**, 7498–7509.

4 S. Kusaka, R. Sakamoto and H. Nishihara, *Inorg. Chem.*, 2014, **53**, 3275–3277.

5 (*a*) V. Stavila, a a Talin and M. D. Allendorf, *Chem. Soc. Rev.*, 2014, **43**, 5994–6010; (*b*) R. Clérac, H. Miyasaka, M. Yamashita and C. Coulon, *J. Am. Chem. Soc.*, 2002, **124**, 12837–12844; (*c*) Y. Xu, X.-B. Yin, X.-W. He and Y.-K. Zhang, *Biosens. Bioelectron.*, 2014, **68**, 197–203.

6 (*a*) S. R. Halper, J. R. Stork and S. M. Cohen, *Dalton Trans.* 2007, 1067–1074. (*b*) I. Szymańska, M. Stobiecka, C. Orlewska, T. Rohand, D. Janssen, W. Dehaen and H. Radecka, *Langmuir*, 2008, **24**, 11239–11245. (*c*) I. Grabowska, W. Maes, T. H. Ngo, T. Rohand, W. Dehaen, J. Radecki and H. Radecka, *Int. J. Electrochem. Sci.*, 2014, **9**, 1232–1249. (*d*) Q. Miao, J.-Y. Shin, B. O. Patrick and D. Dolphin, *Chem. Commun.*, 2009, 2541–2543.

7 S. Kusaka, R. Sakamoto, Y. Kitagawa, M. Okumura and H. Nishihara, *Chem. Asian J.*, 2012, **7**, 907–910.

8 (a) X. Liu, H. Nan, W. Sun, Q. Zhang, M. Zhan, L. Zou, Z. Xie, X. Li, C. Lu and Y. Cheng, *Dalton Trans.*, 2012, **41**, 10199–10210. (b) S. R. Halper, M. R. Malachowski, H. M. Delaney and S. M. Cohen, *Inorg. Chem.*, 2004, **43**, 1242–1249. (*c*) D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 331–338. (*d*) T. E. Hewat, L. J. Yellowlees and N. Robertson, *Dalton Trans.*, 2014, **43**, 4127–4136. (e) R. K. Gupta, R. Pandey, A. Kumar, K. V. Ramanujachary, S. E. Lofland and D. S. Pandey, *Inorg. Chim. Acta*, 2014, **409**, 518–527. (f) A. Béziau, S. A. Baudron and M. W. Hosseini, *Dalton Trans.*, 2012, **41**, 7227–7234. (g) D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 331–338. (h) B. Kilduff, D. Pogozhev, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 11231–11239. (i) S. A. Baudron, D. Salazar-Mendoza and M. W. Hosseini, *CrystEngComm*, 2009, **11**, 1245–1254. (j) S. R. Halper and S. M. Cohen, *Inorg. Chem.*, 2005, **44**, 4139–4141. (k) L. Do, S. R. Halper and S. M. Cohen, *Chem. Commun.*, 2004, 2662–2663.

9 (a) R. K. Gupta, R. Pandey, R. Singh, N. Srivastava, B. Maiti, S. Saha, P. Li, Q. Xu and D. S. Pandey *Inorg. Chem.*, 2012, **51**, 8916−8930. (b) V. Kumar, V. Singh, A. N. Gupta, S. K. Singh, M. G. B. Drew and N. Singh, *Polyhedron*, 2015, **89**, 304–312. (c) S. K. Singh, V. Kumar, M. G. B. Drew and N. Singh, *Inorg. Chem. Commun.*, 2013, **37**, 151–154. (d) A. Béziau, S. A. Baudron, G. Rogez and M. W. Hosseini, *Inorg. Chem.*, 2015, **54**, 2032–2039. (e) R. K. Gupta, M. Dubey, P. Z. Li, Q. Xu and D. S. Pandey, *Inorg. Chem.*, 2015, **54**, 2500–2511.

10 CCDC 1047911 (**3**), and 1047912 (**4**) contain the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

11 F. A. Cotton, B. G. DeBoer and J. R. Pipal, *Inorg. Chem.*, 1970, **9**, 783–788.

12 C. Brückner, V. Karunaratne, S. J. Rettig and D. Dolphin, *Can. J. Chem.*, 1996, **74**, 2182–2193.

13 D. Salazar-Mendoza, S. A. Baudron and M. W. Hosseini, *Chem. Commun.*, 2007, **62**, 2252–2254.

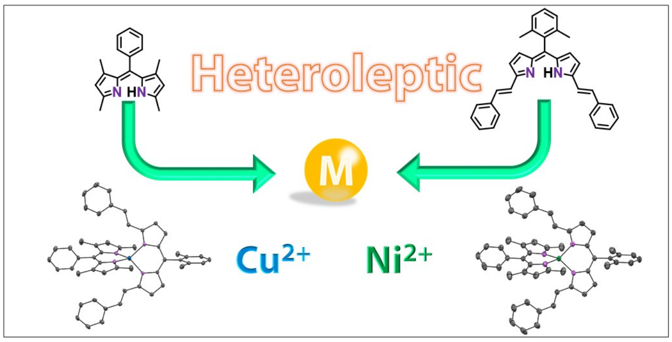
14 (*a*) K. Servaty, E. Cauët, F. Thomas, J. Lambermont, P. Gerbaux, J. De Winter, M. Ovaere, L. Volker, N. Vaeck, L. Van Meervelt, W. Dehaen, C. Moucheron and A. Kirsch-De Mesmaeker, *Dalton Trans.*, 2013, **42**, 14188–14199; (*b*) L. Yang, Y. Zhang, G. Yang, Q. Chen and J. S. Ma, *Dye. Pigment.*, 2004, **62**, 27–33.

15 M. Tsuchiya, R. Sakamoto, S. Kusaka, Y. Kitagawa, M. Okumura and H. Nishihara, *Chem. Commun.*, 2014, **50**, 5881–5883.

16 A. J. Bard, L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, ed. D. Harris, E. Swain, C. Robey and E. Aiello, Wiley, Hoboken, 2nd edn., 2000, ch. 5, pp. 210–216.

17 D. H. Evans, *Chem. Rev.*, 2008, **108**, 2113–2144.

Graphical abstract



Abstract for WEB: Heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes are synthesized for the first time, and the structural and photochemical, and electrochemical properties are disclosed.