Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2018; **22**: 1–7
DOI: 10.1142/S108842461850013X

Synthesis and properties of a trinuclear copper(II) complex of a ligand with phthalocyanine and Schiff-base coordination sites

Makoto Handa[a,*◊], Kenichi Kanagawa[a], Natsumi Yano[a], Haruki Yairi[a], Airi Okuno[a], Minoru Mitsumi[b] and Yusuke Kataoka[a]

[a] *Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan*
[b] *Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-ku, Okayama 700-0005, Japan*

Dedicated to Professor Kazuchika Ohta on the occasion of his retirement

Received 29 November 2017
Accepted 5 January 2018

ABSTRACT: A trinuclear copper(II) phthalocyanine complex was synthesized by chelate coordination of the peripherally introduced Schiff-base nitrogen and phenoxide oxygen on the Cu(pc) core to a copper(II) ion. The magnetic, spectral and electrochemical properties were compared with those of the precursor mononuclear Cu(pc) complex with the NO chelate coordination site and a mononuclear Schiff-base copper(II) complex corresponding to the central bis-chelated unit of the title trinuclear complex. A stronger aggregating nature of the trinuclear complex compared with the precursor mononuclear Cu(pc) complex was confirmed by the spectral change of the Q band feature coming from the coordination to the copper(II) ion in dichloromethane. Two successive pc-ring reduction waves were not observed for the trinuclear complex in dichloromethane containing TBP(PF_6), alternatively showing an irreversible wave in the reduction side. The central bis-chelated copper(II) ion was considered to play an important role for the redox behavior of the trinuclear complex.

KEYWORDS: trinuclear copper(II) phthalocyanine, peripheral Schiff-base coordination site, spectral properties, magnetic properties, electrochemical properties.

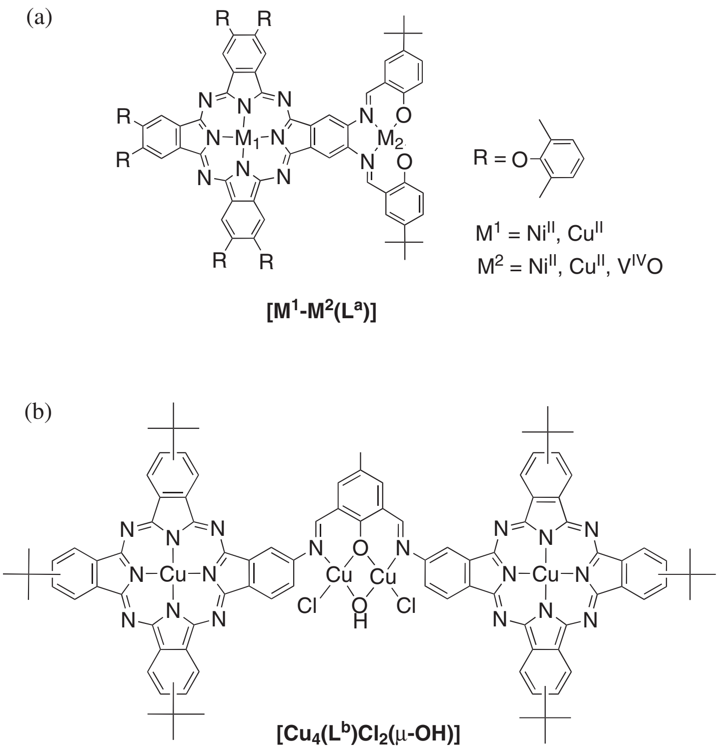
INTRODUCTION

Much interest has been devoted to phthalocyanines and their metal complexes ([M(pc)]) for their unique properties based on the extended π-system within the ligands [1–4]. The strong absorption in the near-infrared region (650–700 nm) observed for them, called the Q band, is the reason why they show remarkable blue or green colors, leading to their longtime use as dyes and pigments. Recently, they have been also applied as nonlinear optics (NLO), optical storage devices, chemical sensors, electrochromic devices, photosensitizers in photodynamic therapy (PDT), *etc*. [5–9]. Schiff-base complexes have attracted many chemists for their interesting electrochemical, catalytic and magnetic properties [10–19]. If metallophthalocyanine ([Mpc]) and Schiff-base complexes are combined within a molecule, new interesting properties could be produced by the combination. Based on such a concept, we have been engaged in synthesizing pc-Schiff-base conjugated complexes and reported dinuclear complexes ([M1–$M^2(L^a)$], $M^1 = Ni^{II}, Cu^{II}$; $M^2 = Ni^{II}, Cu^{II}, V^{IV}O$) [20, 21] and tetranuclear complexes ([$Cu_4(L^b)Cl_2(\mu\text{-}OH)$]) [22], structures of which are shown in Scheme 1. In this study, we synthesized a trinuclear copper(II) complex

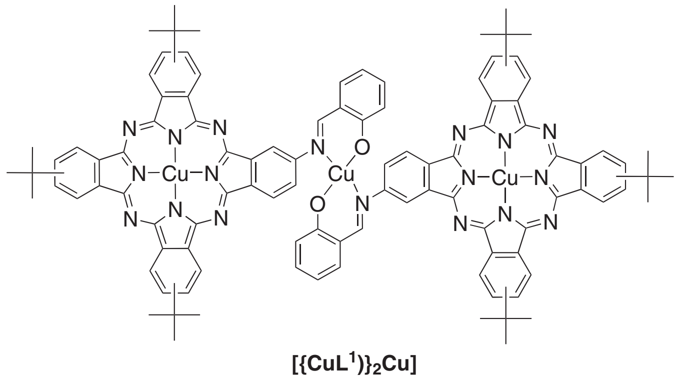
---

[◊] SPP full member in good standing.

*Correspondence to: Makoto Handa, email: handam@riko.shimane-u.ac.jp, tel.: +81-852-32-6418, fax: +81 852-32-6429.



Scheme 1. Chemical structures of [M^1–M^2(L^a)] (a) and [Cu_4(L^b)Cl_2(μ-OH)] (b)



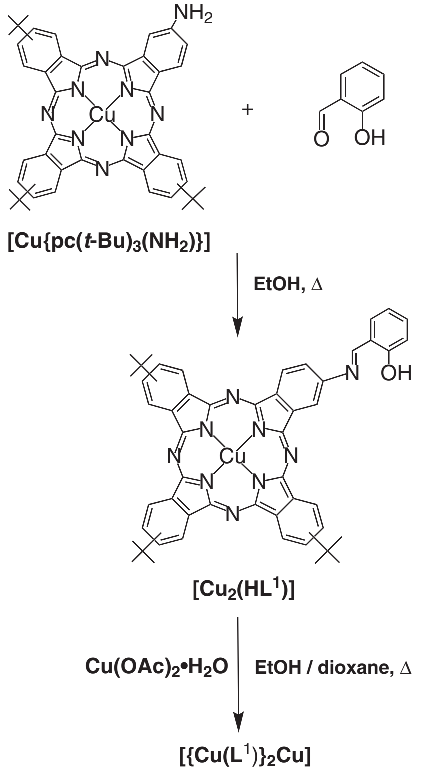
Scheme 2. Chemical structure of [{Cu(L^1)}$_2$Cu] (**2**)

of a fused ligand having phthalocyanine and Schiff-base coordination sites (H_3L^1). The chelate coordination of NO donor atoms of a peripherally introduced Schiff-base site onto the pc ring of a copper(II) complex [Cu(HL^1)] (**1**) to a copper(II) ion gave the objective trinuclear complex [{Cu(L^1)}$_2$Cu] (**2**), the structure of which is shown in Scheme 2. Further, we prepared a mononuclear copper(II) complex of a Schiff-base ligand *N*-(4-methylphenyl)salicylaldimine (HL^2), because the copper(II) complex [Cu(L^2)$_2$] (**3**) corresponds to the central part of the trinuclear copper(II) complex **2**. Here, we report on the syntheses and magnetic, spectroscopic, and electrochemical properties of the complexes **1**–**3** as well as the crystal structure of **3**.

RESULTS AND DISCUSSION

The synthetic procedure from [Cu{pc(*t*-Bu)$_3$(NH_2)}] to the title trinuclear complex [{Cu(L^1)}$_2$Cu] (**2**) through the mononuclear complex [Cu(HL^1)] (**1**) is illustrated in Scheme 3. The peripheral amino group on the pc ring of [Cu{pc(*t*-Bu)$_3$(NH_2)}] reacts with carbonyl group of salicylaldehyde to give the coordinating site consisting of Schiff-base nitrogen (N) and phenoxide oxygen (O) atoms. The NO chelate coordination to copper(II) ion produced the trinuclear complex. In order to investigate the NO chelate coordinated copper(II) site, a mononuclear complex [Cu(L^2)$_2$] (**3**) was prepared and its crystal structure determined. The crystal structure is drawn in Fig. 1. Selected bond distances and angles are given in Table S1 (see Supporting information). The crystallographical inversion center exists at the central copper atom of the mononuclear unit, hence giving the bond angles of O1–Cu1–O1′ = 180° and N1–Cu1–N1′ = 180°. The coordination geometry around the copper(II) ion adopts a square planar geometry, and two NO chelate ligands (*L^2*) coordinate to the copper(II) ion with the *trans* arrangement. The Cu–O and Cu–N bond distances are 1.886 (1) and 2.015 (2) Å, respectively, which are comparable to those for the copper(II) complexes with the NO type Schiff-base ligands derived from condensation of aniline and salicylaldehyde derivatives [23–36]. It seems to be usual that N_2O_2-tetra-coordinated copper(II) complexes with Schiff-base ligands adopt *trans* square planar, distorted square planar or tetrahedral geometry. However, a *cis* arrangement of the copper(II) complex with the same ligand as the present study (L^2)$^-$ has been reported for [Cu(L^2)]•DMF [31]. In [Cu(L^2)]•DMF, the copper(II) ion has a distorted square planar structure with a dihedral angle of 40.5(1)° between two CuNO coordination planes, where Cu–N = 1.965 (3) Å and Cu–O = 1.903 (2) and 1.895 (2) Å. DMF exists as a crystal solvent in the crystal, showing intermolecular hydrogen bonds with the Cu-complex unit. Although there have been discussions on the *trans*–*cis* isomerism concerning the copper(II)-Schiff-base complexes obtained by NO bidentate coordination, to our knowledge, the ligand HL^2 is the first example to give both *cis* and *trans* isomers structurally determined by X-ray structure analysis.

Figure 2 shows temperature dependence of molar magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) for the complex **2**. The moment (per a trinuclear molecule; $\mu_{eff} = (8\chi_M \bullet T)^{1/2}$) is 3.43 μ_B at 300 K, which is rather close to the spin-only value (μ_{eff} = 3.00 μ_B) for magnetically independent three unpaired electrons



Scheme 3. Synthetic procedure from [Cu{Pc(*t*-Bu)$_3$(NH$_2$)}] to [{Cu(L^1)}$_2$Cu] (**2**)

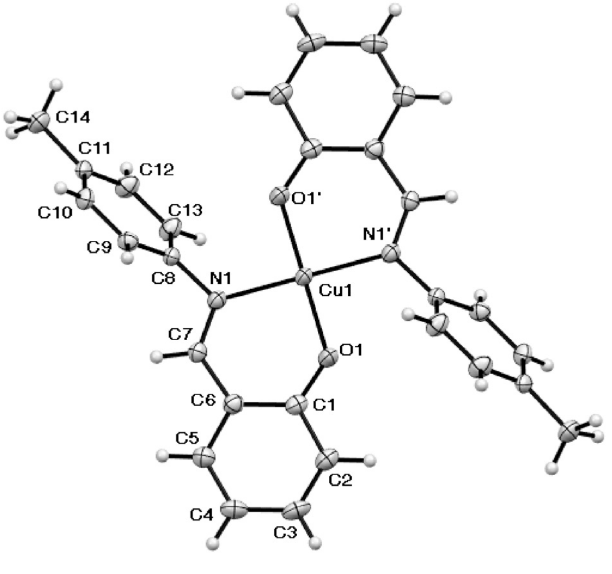


Fig. 1. ORTEP view of [Cu(L^2)$_2$] (**3**) with 50% probability displacement ellipsoids. Prime refers to the equivalent position (-x, -y, -z)

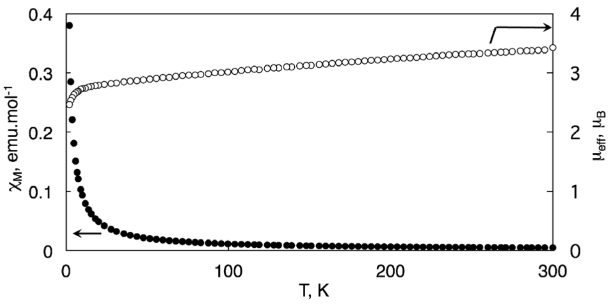
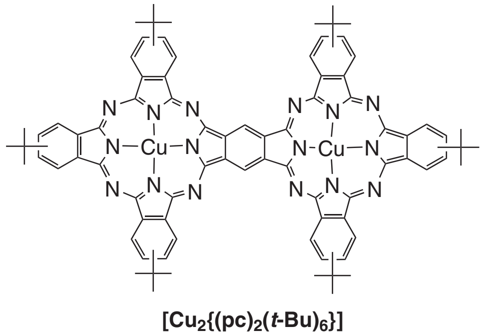


Fig. 2. Temperature dependences of magnetic susceptibility and moment of **2**



Scheme 4. Chemical structure of [Cu$_2${(pc)$_2$(*t*-Bu)$_6$}]

(S = 1/2 for each Cu(II) ion). The moment decreases slightly with the decrease of temperature to *ca*. 10 K. The decrease becomes steep below 10 K, which was considered to originate from an inter- or intra-molecular interaction between Cu(II) centers. The mononuclear Schiff base complex **3** does not show such decrease in the low temperature region, as shown for Fig. S1 (see Supporting information). A tetranuclear copper(II) complex [Cu$_4$(L^b)Cl$_2$(μ-OH)] (Scheme 1(b)) was reported to demonstrate a negligible interaction through an imino nitrogen and a benzene ring of the pc ligand between Cu^{II}(pc) and central dinuclear Cu^{II} units. The entire temperature-dependent magnetic moment behavior of **2** is similar to a dinuclear complex [Cu$_2${(pc)$_2$(*t*-Bu)$_6$}] (Scheme 4), which did not display any important interaction through the common benzene ring, but showed a weak interaction due to the aggregation nature due to the enlarged π-conjugate system [37].

Absorption spectra of **1** and **2** measured in dichloromethane are displayed in Figs 3 and 4, respectively. Complexes **1** and **2** show the Q band peaks both at 682 and 681 nm, respectively, where the molar extinction coefficient (ε/M^{-1}·cm^{-1}) is calculated to be the value per a Cu(pc) unit for **2**. It is well-known that the Q band is blue-shifted and appears as a broad band when the phthalocyanine molecules aggregate in a face to face mode [4, 38]. Although complex **1** shows the aggregating nature because the shoulder band at the shorter wavelength region comes to be remarkable in accordance with the decrease in the Q band intensity (ε /M^{-1}·cm^{-1}) when the concentration is increased from 2.0 × 10^{-6} M to 2.5 × 10^{-5} M, the aggregating nature is stronger for **2**, showing a much weaker Q band intensity with a stronger shoulder band compared with those of **1**.

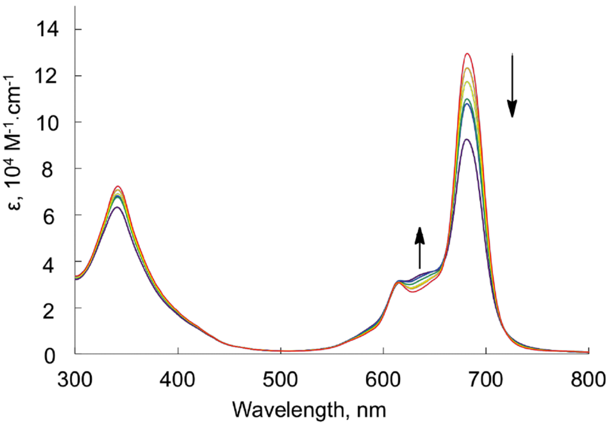


Fig. 3. Absorption spectra of **1**, which were measured in dichloromethane at the concentrations of 2.0×10^{-6} (—), 4.0×10^{-6} (—), 6.0×10^{-6} (—), 1×10^{-5} (—), 1.25×10^{-5} (—) and 2.5×10^{-5} M (—)

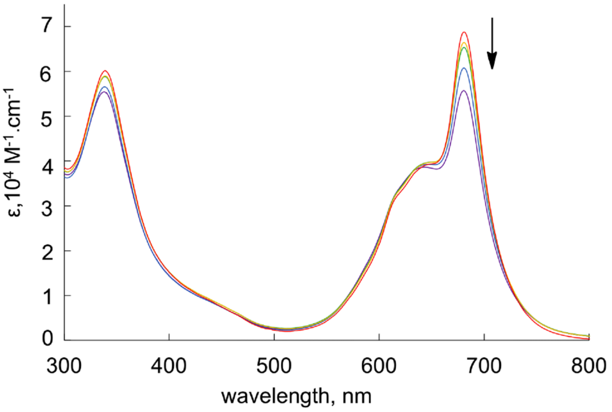


Fig. 4. Absorption spectra of **2**, which were measured in dichloromethane at the concentrations of 2.0×10^{-6} (—), 4.0×10^{-6} (—), 6.0×10^{-6} (—), 1×10^{-5} (—), 1.25×10^{-5} (—) and 2.5×10^{-5} M (—)

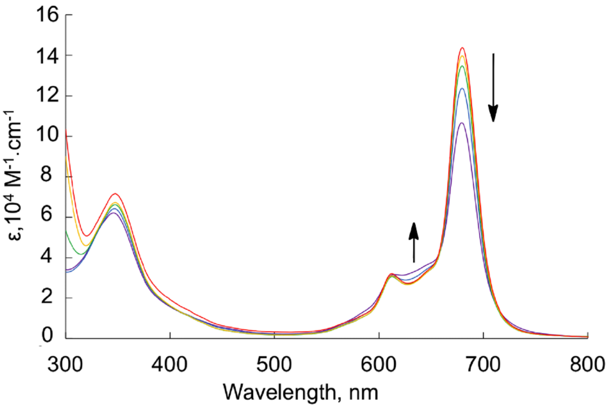


Fig. 5. Absorption spectra of **2**, which were measured in DMF at the concentrations of 1.0×10^{-6} (—), 1.25×10^{-6} (—), 2.5×10^{-6} (—), 5.0×10^{-6} (—) and 1.0×10^{-5} M (—)

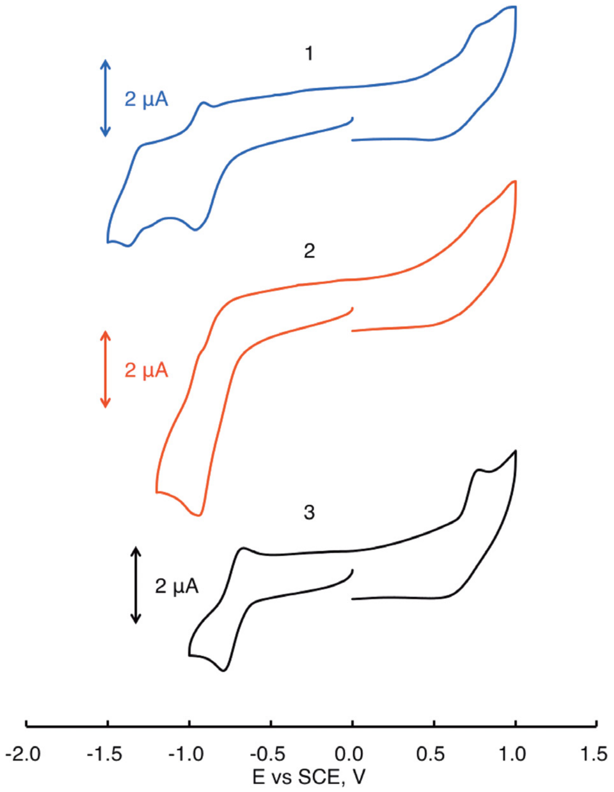


Fig. 6. Cyclic voltammograms of **1**, **2** and **3** in dichloromethane ([complex] = 1×10^{-4} M; [TBA(PF_6)] = 0.1 M; scan rate = 50 $mV \cdot s^{-1}$)

A similar phenomenon has been observed for the tetranuclear complex [$Cu_4(L^b)Cl_2(\mu\text{-}OH)$], which showed a stronger aggregating nature compered with the corresponding dinuclear complex [$Cu_2(HL^b)$]. The enlarged planarity of the complex molecule by the coordination of the Schiff-base sites to copper(II) ions was considered to be the plausible reason for the increased aggregating natures of **2** and [$Cu_4(L^b)Cl_2(\mu\text{-}OH)$]. Interestingly, the spectral feature of **2** changed in DMF (Fig. 5) (λ_{max} = 680 nm for the Q band) and became much similar to that of **1**, of which spectrum measured in DMF is given in Fig. S2 (λ_{max} = 682 nm for the Q band) (see Supporting information). The geometrical change around the central copper(II) ion in DMF from dichloromethane may be related to the observed spectral change.

Figure 6 displays cyclic voltammograms (CVs) measured in dichloromethane containing TBP(PF_6) (0.1 M) for **1**, **2** and **3**. There are redox couples ($E_{1/2}$ = -0.96 and -1.35 V *vs*. SCE) on the reduction side for **1**, which can be assigned to reduction at the pc ring because the copper(II) phthalocyanine with four *t*-butyl groups [Cu{pc(*t*-Bu)$_4$}] showed the corresponding redox couples, similarly at $E_{1/2}$ = -1.42 and -1.78 V *vs*. Fc^+/Fc [22], when taking $E_{1/2}$ (Fc^+/Fc) = *ca*. 0.45 V *vs*. SCE into account [39]. The broad wave in the oxidation side (*ca*. 0.7 V *vs*. SCE) was attributed to the oxidation of the aggregated pc rings [40, 41]. The redox behavior is nearly the same as

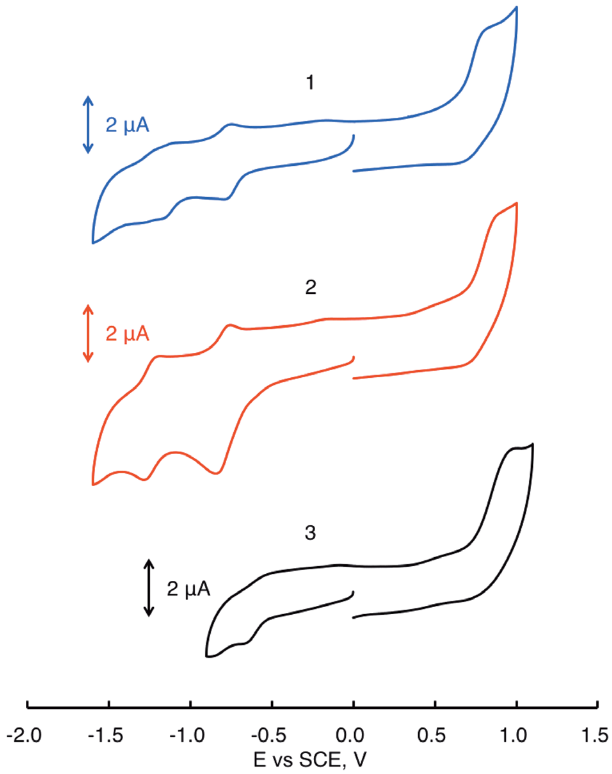


Fig. 7. Cyclic voltammograms of **1**, **2** and **3** in DMF ([complex] = 1×10^{-4} M; [TBA(PF_6)] = 0.1 M; scan rate = 50 mV · s^{-1})

those observed for [$Cu_4(L^b)Cl_2(\mu\text{-}OH)$] and [$Cu_2(HL^b)$] [22]. Complex **2** shows completely different behavior, with only an irreversible wave being found at *ca*. -0.95 V in the reduction side, although the mononuclear Schiff-base complex **3** shows a reversible or quasi-reversible wave at $E_{1/2}$ = -0.75 V *vs*. SCE. Further, **2** shows the redox couples at $E_{1/2}$ = -0.82 and -1.22 V *vs*. SCE similarly to **1** ($E_{1/2}$ = -0.78 and -1.14 V *vs*. SCE) when the CVs were measured in DMF containing TBP(PF_6) (0.1 M) (Fig. 7). The different redox behaviors of **2** observed in dichloromethane and DMF may be related to the fact that the copper(II) ion adopts different geometrical structures in dichloromethane and DMF as confirmed by their Q features in the absorption spectra. Complex **3** shows an irreversible reduction wave at *ca*. -0.6 V *vs*. SCE in DMF; the redox wave has been previously reported at a similar potential around -1.0 V *vs*. Ag/AgCl in DMF for the same, but *cis*-isomer complex [31].

EXPERIMENTAL

Syntheses of complexes

Copper(II) phthalocyanine with an amino group and three *t*-butyl groups ([Cu{pc(*t*-Bu)$_3$(NH_2)}]) was prepared according to the method described in the literature [42]. Salicylaldehyde and *p*-toluidine were purchased from Wako Pure Chemical Industries, Ltd. and used as being supplied.

[Cu(HL^1)] (1): [Cu{pc(*t*-Bu)$_3$(NH_2)}] (76 mg, 0.10 mmol) and salicylaldehyde (122 mg, 1.0 mmol) were dissolved in ethanol (10 mL) and refluxed for 16 h. After the solvent was removed by evaporation, the resultant solid was chromatographed on a silica gel column with a chloroform–toluene (25:1) solvent mixture as an eluent. The first fraction was collected and evaporated to remove the solvent. The obtained green powder was recrystallized using hexane (20 mL), collected again by the filtration, and dried under vacuum. The yield was 17.2 mg (20% based on [Cu{pc(*t*-Bu)$_3$(NH_2)}]). Anal. calcd. for $C_{51}H_{45}CuN_9O$: C, 70.94; H, 5.25; N, 14.60%. Found C, 70.68; H, 5.27; N, 14.35. HR-MS (ESI-TOF): *m/z* 863.3091 (calcd. for $[M+H]^+$ 863.3116).

[{Cu(L^1)}$_2$Cu] (2): To an ethanolic solution (60 mL) of copper(II) acetate was added a solution of **1** (34.6 mg, 0.04 mmol) dissolved in 1,4-dioxane (20 mL). The solution was refluxed for 3 h and followed by evaporation to a small portion (*ca*. 10 mL) and addition of hexane (20 mL). The green precipitate was collected by suction filtration, washed with ethanol, and dried under vacuum. The yield was 33.3 mg (93.8% based on **1**). Anal. calcd. for $C_{102}H_{88}Cu_3N_{18}O_2$: C, 68.50; H, 4.96; N, 14.10%. Found C, 67.88; H, 5.15; N, 13.76. HR-MS (ESI-TOF): *m/z* 1810.4817 (calcd. for $[M+Na]^+$ 1810.5126).

[Cu(L^2)$_2$] (3): *p*-Toluidine (213 mg, 2mmol) and salicylaldehyde (244 mg, 2 mmol) were mixed and refluxed with stirring for 30 min in methanol (40 mL). To the reaction solution, copper(II) acetate monohydrate (200 mg, 1 mmol) in methanol (25 mL) was added and refluxed further for 16 h. The resultant solution was evaporated to 20 mL and stored in refrigerator (at *ca*. 0 °C) to give a brown precipitate, which was collected by suction filtration, washed with a small amount of methanol, and dried under vacuum. The yield was 421 mg (87.0%). Anal. calcd. for $C_{28}H_{24}CuN_2O_2$: C, 69.48; H, 5.00; N, 5.79%. Found C, 69.32; H, 4.75; N, 5.85. Single crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from methanol.

Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanako CHN CORDER MT-6. Absorption spectra were measured in dichloromethane and DMF using a JASCO V-670 spectrophotometer. ESI-TOF mass spectra were taken on a Bruker micrOTOF system. Cyclic voltammograms were taken in dichloromethane and DMF solutions containing tetra-*n*-butylammonium hexafluorophosphate [TBA(PF_6)] on a BAS ALS-DY2325 Electrochemical Analyzer. A glassy carbon disk (1.5 mm radius), platinum wire, and saturated calomel electrodes were used as working, counter, and reference electrodes, respectively. Variable–temperature magnetic susceptibility measurements were

Table 1. Crystallographic data and structure refinement of $[Cu(L^2)_2]$ (**3**)

	Parameter values[a]
Empirical formula	$C_{28}H_{24}CuN_2O_2$
Formula mass	484.03
Temperature, T (K)	150
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.110 (4)
b (Å)	7.327 (2)
c (Å)	13.438 (4)
β (°)	111.062 (3)
Unit-cell volume, V (Å^3)	1112.7 (6)
Formula per unit cell, Z	2
Density, D_{calcd} (g cm^{-3})	1.445
Crystal size (mm)	0.160 × 0.100 × 0.030
Absorption coefficient, μ (mm^{-1})	1.010
θ range for data collection (°)	3.249–25.996
Reflections collected/unique	2096/1777
R indices $[I > 2\sigma(I)]$[b]	$R_1 = 0.0300$, $\omega R_2 = 0.0777$
Goodness-of-fit on F^2	1.073

[a] Standard deviations in parentheses; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $\omega R_2 = [\Sigma\omega(F_o^2-F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

carried out using a superconducting quantum interference device (SQUID) MPMSXL-5 from Quantum Design. The measured data were corrected for diamagnetic contributions [43].

X-ray diffraction data of complex **3** was collected at 150 K on a RIGAKU Saturn 724 CCD system equipped with Mo rotating-anode X-ray generator with Monochromated Mo Kα radiation (λ = 0.71075 Å) and were processed with using CrystalClear-SM 2.0 program (RIGAKU). The structure of complex **3** was solved by the direct method (SIR-2011) and refined using the full-matrix least-squares technique F^2 with SHELXL2014 equipped in the CrystalStructure 4.2.5 software (RIGAKU). Non-hydrogen atoms were refined with anisotropic displacement, and almost all of the hydrogen atoms were located through a difference Fourier map and refined with isotropic thermal parameters. Crystal data as well as the details of data collection and refinement for complex **3** are summarized in Table 1 and can be obtained as a CIF file from Cambridge Crystallographic Data Center (CCDC). The deposition number of complex **3** is CCDC-1587713.

CONCLUSION

A trinuclear copper(II) phthalocyanine complex (**2**) was synthesized by chelate coordination of the peripherally introduced Schiff-base nitrogen and phenoxide oxygen on the {Cu(pc)(*t*-Bu_3)} core to a copper(II) ion. The magnetic and spectral properties were compared with those of the precursor mononuclear Cu(pc) complex with the NO chelate coordination site (**1**) and the mononuclear Schiff-base copper(II) complex (**3**) corresponding to the central bis-chelated unit of the trinuclear complex. A stronger aggregating nature of the trinuclear complex compared with the precursor mononuclear complex was confirmed by the spectral change of the Q band feature coming from the coordination to the copper(II) ion in dichloromethane. Further, two successive pc-ring reduction waves were not found for the trinuclear complex in dichloromethane containing TBP(PF_6), alternatively showing an irreversible wave in the reduction side. It was considered that the central bis-chelated copper(II) ion should play an important role for the redox behavior. However, it is still unknown why only the present trinuclear complex showed the behavior whereas the tetranuclear copper(II) complex of a pc-Schiff-base fused ligand with a hydroxide- and phenoxido-copper(II) binuclear core $[Cu_4(L^b)Cl_2(\mu\text{-OH})]$ did not show such a behavior. The trinuclear complex with a redox inactive metal ion at the central coordinated unit could give the useful information. Efforts to prepare the hetero-metal complexes such as Cu–Zn–Cu and Zn–Zn–Zn combinations are being made in our laboratory.

Acknowledgments

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 15K17897 and 16K05722 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan). The authors are grateful to Dr. Michiko Egawa (Shimane University) for her measurements of elemental analyses and Prof. Masahiro Mikuriya (Kwansei Gakuin University) for his helpful discussion.

Supporting information

Selected bond distance and angles of **3** (Table S1), temperature dependences of magnetic susceptibility and moment of **3** (Fig. S1) and absorption spectra of **1** in DMF (Fig. S2) are given in the supplementary material. This material is available free of charge *via* Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-1587713. Copies can be obtained on request, free of charge, *via* the internet at http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

REFERENCES

1. Moser FH and Thomas AL. *The Phthalocyanines*, Vols. I, II. CRC Press: Boca Raton, 1983.
2. Leznoff CC and Lever ABP. *Phthalocyanines–Properties and Applications*, Vols. 1–4. VCH Publishers Inc.: New York, 1989–1996.
3. Jiang J. *Functional Phthalocyanine Molecular Materials*, Springer-Verlag: Berlin, Heidelberg, 2010.
4. Isago H. *Optical Spectra of Phthalocyanines and Related Compounds*, Springer: Japan. 2015.
5. DeRosa MC and Crutchley RJ. *Coord. Chem Rev*. 2002; **223–234**: 351–371.
6. de la Torre G, Glaessens CG and Torres T. *Chem. Commun.* 2007: 2000–2015.
7. Claessens CG, Hahn U and Torres T. *Chem. Rec*. 2008; **8**: 75–97.
8. Bian YZ and Jiang J. In *50 Years of Structure and Bonding–The Aniversary Volume*, Mingos DMP (Ed.) Springer-Verlag: Switzerland, 2016; pp. 159–199.
9. Lu H and Kobayashi N. *Chem. Rev*. 2016; **116**: 6184–6261.
10. Sinn E and Harris CM. *Coord. Chem. Rev*. 1969; **4**: 391–422.
11. Garnovskii AD, Nivorozhkin AL and Minkin VI. *Coord. Chem. Rev*. 1993; **126**: 1–69.
12. Yamada S. *Coord. Chem. Rev*. 1999; **190–192**: 537–555.
13. Vigato PA, Tamburini S and Beltolo L. *Coord. Chem. Rev.* 2007; **251**: 1311–1492.
14. Miyasaka H, Saitoh A and Abe S. *Coord. Chem. Rev.* 2007; **251**: 2622–2664.
15. Gupta KC and Sutar AK. *Coord. Chem. Rev.* 2008; **252**: 1420–1450.
16. Pradeep CP and Das SK. *Coord. Chem. Rev.* 2013; **257**: 1699–1715.
17. Cavey EL and Pilkington M. *Coord. Chem. Rev.* 2015; **296**: 125–152.
18. Zoubi WA and Ko YG. *J. Organomet. Chem.* 2016; **822**: 173–188.
19. Das P and Linert W. *Coord. Chem. Rev.* 2016; **311**: 1–23.
20. Ikeue T, Fukahori T, Sugimori T and Handa M. In *New Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry*, Melnik M, Segl'a P and Tatarko M. (Eds.), *Slovak University of Technology Press*: Blatislava, 2011; 183–189.
21. Ikeue T, Fukahori T, Mitsumune T, Ueda K, Fujii K, Kurahashi S, Koikawa M, Sugimori T, Hiromitsu I, Yoshino K, Mikuriya M and Handa M. *Inorg. Chim. Acta* 2014; **409**: 433–440.
22. Handa M, Murakoshi K, Nishikawa A, Yahata K, Shiomi K, Hiromitsu I, Sugimori T, Sogabe K, Isa K, Nakata M and Kasuga K. *Bull. Chem. Soc. Jpn*. 2007; **80**: 1949–1954.
23. Fernández JM, Lembrino-Canales JJ and Villena-I R. *Monatsh. Chem*. 1994; **125**: 275–284.
24. Fernández-G JM, del Rocío Patino-Maya M, Tascano RA, Velasco L, Otero-López M and Aguilar-Martínez M. *Polyhedron* 1997; **16**: 4371–4378.
25. Elerman Y and Geselle M. *Acta Cryst. Sect. C.* 1997; **53**: 549–551.
26. Fernández-G JM, Hernández-Ortega S, Cetina-Rosado R, Macías-Ruvalcaba N and Aguilar-Martínez M. *Polyhedron* 1998; **17**: 2425–2432.
27. Elerman Y, Elmali A and Özbey S. *Acta Cryst. Sect. C.* 1998; **54**: 1072–1074.
28. Aguilar-Martínez M, Saloma-Aguilar R, Macías-Ruvalcaba N, Cetina-Rosado R, Navarrete-Vázquez A, Gómez-Vidales V, Zentella-Dehesa A. Toscano RA, Hernandez-Ortega S and Fernández-G JM. *J. Chem. Soc., Dalton Trans.* 2001; 2346–2352.
29. Ünver H and Durlu TN. *J. Chem. Crystallogr.* **2002**; 31: 479–483.
30. Ünver H. *J. Mol. Struct.* 2002; **641**: 35–40.
31. Yildrim LT, Emregul KC, Kurtaran R and Atakol O. *Cryst. Res. Technol.* 2002; **37**: 1344–1351.
32. Kasumov VT, Bulut A, Köksal F, Aslanoglu M, Ucar I and Kazak C. *Polyhedron* 2006; **25**: 1133–1141.
33. Sundaravel K, Suresh E and Palaniandavar M. *Inorg. Chim. Acta* 2009; **362**: 199–207.
34. Zhu P, Wang H, Wang Y, Chen Y and Wei Q. *Acta Cryst. Sect. E.* 2010; **66**: m1076.
35. Ahmad JU, Räisänen MT, Nieger M, Sundberg MR, Figiel PJ, Leskelä M and Repo T. *Polyhedron* 2012; **38**: 205–212.
36. Chamayou AC, Makhloufi G, Nafie LA, Janiak C and Lüdeke S. *Inorg. Chem.* 2015; **54**: 2193–2203.
37. Handa M, Kataoka N, Ito Y, Tonomura T, Hiromitsu I, Sugimori T, Sogabe K and Kasuga K, *Bull. Chem. Soc. Jpn.* 2004; **77**: 1647–1648.
38. Stillman MJ and Nyokong T. In *Phthalocyanines–Properties and Applications*, Leznoff CC and Lever ABP. (Eds.) VCH: New York, 1989; Chap. 3, pp. 133–290.
39. Stawyer DT, Sobkowiak A and Robert JL, Jr. In *Electrochemistry for Chemists, 2nd Ed.,* John Wiley & Sons, Inc.: New York, 1995; Chap. 13.
40. Lever ABP, Milaeva ER and Speier G. In *Phthalocyanines–Properties and Applications*, Vol. 3. Leznoff CC and Lever ABP. (Eds.), VCH: New York, 1993; Chap. 1. pp. 1–70.
41. Mu P, Nakao T, Handa M, Kasuga K and Sogabe K. *Bull. Chem. Soc. Jpn.* 1991; **64**: 3202–3204.
42. Kudrevich SV, Ali H and van Lier JE. *J. Chem. Soc. Perkin Trans*. 1994; 2767.
43. Kahn O. In *Moleclar Magnetism*, VCH: Yew York, 1993; Chap. 1.