

Synthesis, Spectroscopic Properties, and Structure of [Tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]metal Complexes

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A series of highly soluble [tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]metal complexes [MPc(OC₇H₁₅)₄] (M = Zn, Pd, Co) were prepared by cyclic tetramerization of 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile (**2**) in the presence of the corresponding metal salts and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol. For M = Zn and Pd, two major isomers with a C_{4h} and C_{2v} symmetry were isolated by column chromatography and characterized with various spectroscopic methods, while the cobalt analogue showed only the C_{4h} isomer. The (phthalocyaninato)manganese complex [MnClPc(OC₇H₁₅)₄] was also synthesized by metallation

of the metal-free phthalocyanine H₂Pc(OC₇H₁₅)₄ formed by treating **2** with CeCl₃ and DBU in *n*-pentanol. The structures of the C_{4h} isomers of the (phthalocyaninato)zinc and -cobalt complexes and the C₄ isomer of the manganese analogue were also established by X-ray diffraction analyses. The palladium counterpart formed a novel 1:1 inclusion complex with oxalic acid, the crystal structure of which was also determined.

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Introduction

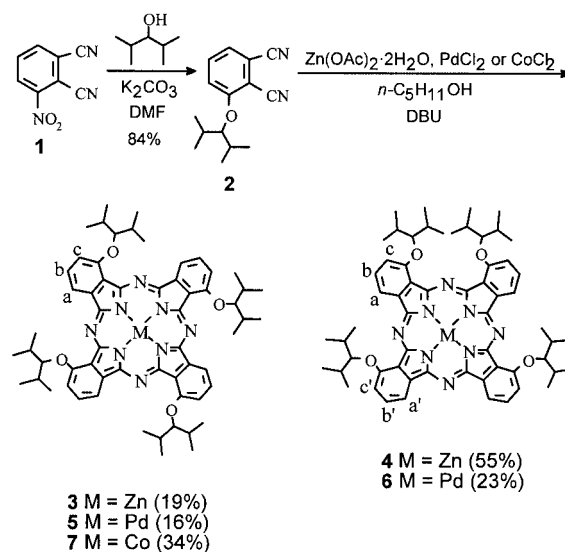
Phthalocyanines are traditional pigments that were discovered almost a century ago. They are a unique class of macrocyclic compounds, with intriguing physical and chemical properties that allow their use in many disciplines.^[1] Their well-documented functions as molecular opto-electronic materials,^[2] photosensitizers for photodynamic therapy,^[3] and catalysts for oxidative degradation of pollutants^[4] are still being actively exploited. For some of these applications, highly soluble and non-aggregated phthalocyanines are desirable. The former property facilitates the purification and the fabrication processes, while the latter assists in characterization and allows these materials to function properly; many properties of phthalocyanines change upon aggregation.^[5] As a result, a substantial number of phthalocyanines with sterically demanding substituents have been reported.^[6] We describe herein a series of (phthalocyaninato)metal complexes substituted with four 2,4-dimethyl-3-pentyloxy groups. These bulky and hydrophobic substituents not only enhance the solubility of phthalocyanines in organic solvents and reduce their tendency to aggregate, but also facilitate the separation of the isomers of tetra- α -substituted phthalocyanines. Phthalocy-

anines containing these substituents have been briefly reported for use as optical recording materials.^[7]

Results and Discussion

Synthetic Studies

In the synthesis of these (phthalocyaninato)metal complexes (Scheme 1) 3-nitrophthalonitrile (**1**) is treated with



Scheme 1. Preparation of [tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]zinc, -palladium, and -cobalt complexes

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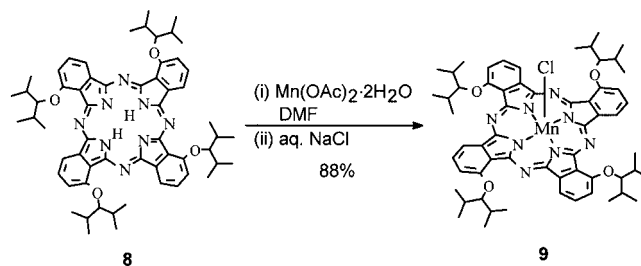
2,4-dimethyl-3-pentanol in the presence of K_2CO_3 in DMF to afford 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile (**2**). Cyclization of **2** with zinc(II) acetate or palladium(II) chloride in the presence of DBU in *n*-pentanol then furnishes the corresponding (phthalocyaninato)metal complexes. Only the C_{4h} and C_{2v} isomers could be isolated by column chromatography, while the D_{2h} and C_s isomers were not detected. For the (phthalocyaninato)zinc complexes, the C_{4h} isomer **3** was eluted first followed by the C_{2v} isomer **4**. Interestingly, this order was reversed for the palladium analogues **5** and **6**. These isomers are usually separated by medium- or high-pressure liquid chromatography,^[8] but their facile separation here may be attributed to the bulky 2,4-dimethyl-3-pentyloxy substituents at the α -positions. It is also noteworthy that for both the zinc and palladium analogues the C_{2v} isomer is produced in higher yield than the C_{4h} counterpart, which is supposed to be thermodynamically more stable. This cannot be explained by the alkoxide-induced sequential nucleophilic attack of phthalonitriles^[9] and the “template” mechanism proposed by Hanack et al.,^[8b] which will give predominantly the C_{4h} and C_s isomers, respectively. The reaction mechanism remains elusive but, as reported earlier,^[8b] the isomer distribution of tetra- α -substituted (phthalocyaninato)metal complexes depends on many factors, including the nature of the substituent, reaction conditions, and metal center. Further investigation is clearly required.

The cobalt counterpart **7**, prepared similarly using $CoCl_2$ as the metal salt, was unstable on silica gel: the blue color faded gradually during chromatography. Preliminary purification could, however, be achieved by flash chromatography through a short column packed with neutral alumina. Further purification by recrystallization led to the pure C_{4h} isomer **7**, which was confirmed by single-crystal X-ray analysis. Other constitutional isomers, which were probably also formed during the reaction, could neither be isolated nor detected by 1H NMR spectroscopy due to the paramagnetic cobalt(II) center.

Our recently reported cerium-promoted method to prepare metal-free phthalocyanines afforded high yields of 1,8,15,22-tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyanine (**8**),^[10] which can be used to prepare (phthalocyaninato)metal complexes. Thus, while treatment of the dinitrile **2** with $Mn(OAc)_2 \cdot 2H_2O$ and DBU in *n*-pentanol yielded a dark brown solution which did not show the typical phthalocyanines' Q-band absorption, compound **8** could be metallated with $Mn(OAc)_2 \cdot 2H_2O$ in DMF to give the (phthalocyaninato)manganese(III) complex **9** in 88% yield (Scheme 2). The manganese(II) ion was oxidized during the reaction and the axial chloro ligand came from the brine used during the workup procedure. Similar results were also observed during the preparation of (chloro)(porphyrinato)manganese(III) complexes.^[11]

Spectroscopic Properties

The C_{4h} and C_{2v} isomers of the (phthalocyaninato)zinc and -palladium complexes could be distinguished readily by 1H NMR spectroscopy. The rather broad signals for the



Scheme 2. Preparation of (phthalocyaninato)manganese complex **9**

zinc analogues **3** and **4** in $CDCl_3$ were sharpened upon addition of a drop of $[D_5]pyridine$ to give well-resolved spectra, due to the relief of aggregation by the axial coordination of the zinc(II) center by pyridine.^[12] The spectra for the palladium analogues **5** and **6** were well resolved even in the absence of $[D_5]pyridine$. Figure 1 (b) shows the 1H NMR spectrum of **5** in $CDCl_3$, in which all the signals can be assigned unambiguously. The spectrum shows a doublet at $\delta = 9.05$ ppm, an overlapping doublet of doublets (or virtual triplet) at $\delta = 8.03$ ppm, and a doublet at $\delta = 7.68$ ppm for the three sets of ring protons. The four equivalent 2,4-dimethyl-3-pentyloxy groups resonate at $\delta = 4.67$ (t, OCH), 2.54–2.64 (m, CH), 1.48 (d, Me), and 1.19 ppm (d, Me). All these signals are split for compound **6** [Figure 1 (a)], which clearly confirms its C_{2v} symmetry.

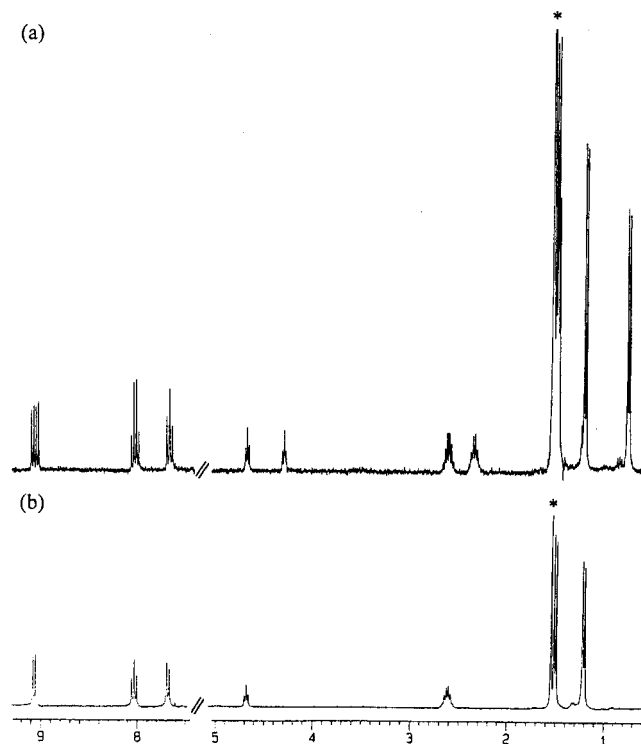


Figure 1. 1H NMR spectra of **6** (a) and **5** (b) in $CDCl_3$; * water signal

The (phthalocyaninato)metal complexes **3–7** and **9** gave typical UV/Vis absorptions of phthalocyanines (Table 1). The absorption data of the C_{4h} and C_{2v} isomers of the (phthalocyaninato)zinc and -palladium complexes do not

Table 1. UV/Vis data for (phthalocyaninato)metal complexes **3**–**7** and **9** in CHCl₃

Compound	B-band	LMCT	$\lambda_{\max}$ [nm] (log ϵ) Vibronic band(s)	Q-band
Zn[Pc(OC ₇ H ₁₅) ₄] (3)	322 (4.54)	—	638 (4.37)	711 (5.13)
Zn[Pc(OC ₇ H ₁₅) ₄] (4)	323 (4.59)	—	638 (4.41)	709 (5.14)
Pd[Pc(OC ₇ H ₁₅) ₄] (5)	314 (4.31)	—	623 (4.36)	694 (5.10)
Pd[Pc(OC ₇ H ₁₅) ₄] (6)	314 (4.44)	—	625 (4.46)	696 (5.19)
Co[Pc(OC ₇ H ₁₅) ₄] (7)	313 (3.86)	—	631 (3.66)	702 (4.31)
MnCl[Pc(OC ₇ H ₁₅) ₄] (9)	337 (4.18)	550 (3.85)	693 (3.93)	775 (4.67)

show significant differences. The Q-band position, however, is highly dependent on the metal center in the order Pd^{II} < Co^{II} < Zn^{II} << Mn^{III}. The (phthalocyaninato)manganese complex **9** is brown instead of the characteristic blue-green as a result of the very long Q-band absorption (775 nm), which appears to be the longest wavelength recorded for (phthalocyaninato)metal complexes. This remarkably large red-shift may be attributed to the effects of metal center and the electron-donating alkoxy substituents introduced at the α -positions. A characteristic ligand-to-metal charge-transfer (LMCT) band at 550 nm was also seen for **9**.^[13]

Having four bulky 2,4-dimethyl-3-pentyloxy substituents, these phthalocyanines are expected to be relatively non-aggregated in solutions. This was confirmed by variable-concentration UV/Vis studies of compounds **3**, **5**, and **9** in CHCl₃. For these three compounds, plots of the Q-band absorbance versus concentration (from 2×10^{-7} to 3×10^{-5} mol·dm⁻³) gave perfect straight lines, showing that the compounds strictly follow the Lambert–Beer law. This indicates that the compounds exist mainly in monomeric form under the conditions employed. The zinc complexes **3** and **4**, however, are slightly aggregated at higher concentrations (ca. 10^{-3} mol·dm⁻³) as shown by NMR studies (see above).

Structural Studies

Both the zinc and cobalt phthalocyanines **3** and **7** co-crystallize with a water molecule, which may come from the solvents used for recrystallization. In the molecular structure of **3** the zinc atom is disordered about the inversion center relating the two halves of the molecule (Figure 2). The oxygen atom of water occupies a site with half occupancy, giving the shortest Zn–O distance at 2.034 Å, which may be regarded as axial ligation.^[14] The corresponding Co–O distance in **7** (2.494 Å), however, is significantly longer than typical Co–OH₂ bonds in (aquo)cobalt(II) complexes (ca. 2.1–2.2 Å).^[15]

Both **3** and **7** crystallize in the monoclinic system with two molecules per unit cell. The phthalocyanine rings are arranged in a herringbone manner^[16] along the crystallographic *b* axis with a stacking angle of 54.1 (**3**) or 59.7° (**7**) and an interplanar distance of 6.98 (**3**) or 7.40 Å (**7**) (Figure 3). This arrangement is similar to that of the metal-free analogue **8**^[10a] and the unsubstituted phthalocyanine.^[17] Due to the bulky 2,4-dimethyl-3-pentyloxy substituents, which act as spacers, the interplanar distances for these substituted phthalocyanines are much larger than that of the unsubstituted counterpart (3.31 Å).

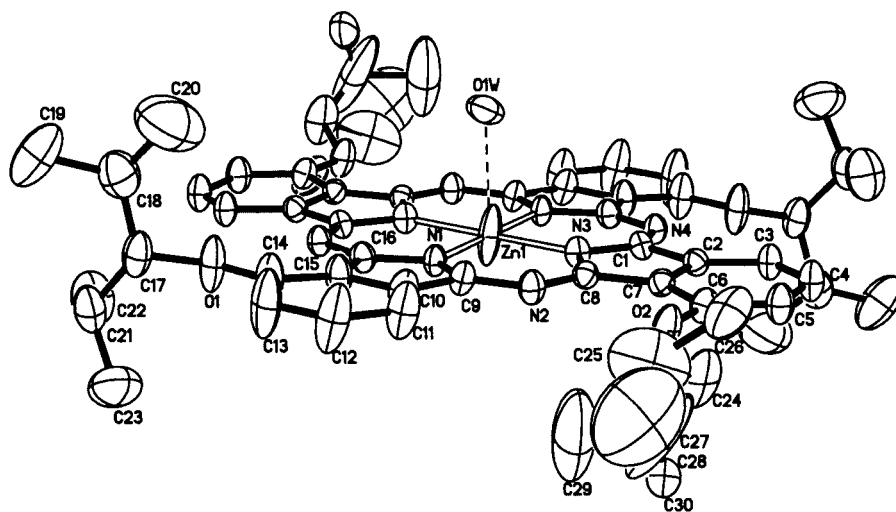


Figure 2. Molecular structure of **3** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms; the zinc atom is disordered with the shortest Zn–OH₂ distance at 2.034 Å

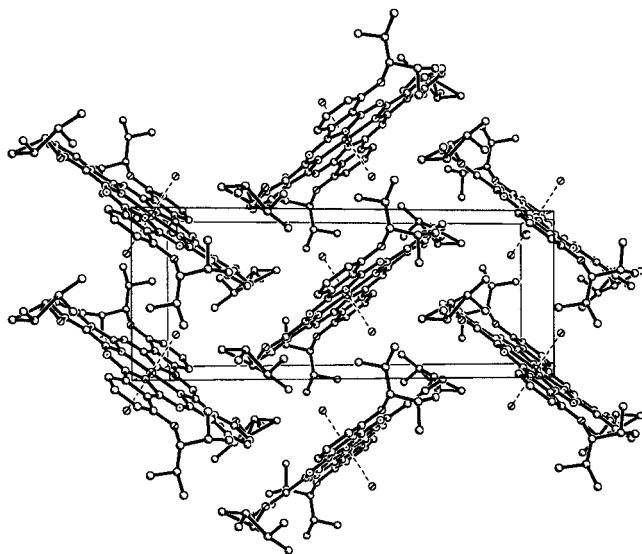


Figure 3. Packing of $3 \cdot \text{H}_2\text{O}$ viewed along the a axis; all hydrogen atoms omitted for clarity

In the (phthalocyaninato)manganese complex **9** the manganese center is coordinated by four isoindole nitrogen atoms of the phthalocyanine ring and one terminal chloro ligand, forming a slightly distorted square pyramid (Figure 4). In contrast to the zinc and cobalt analogues, in which the metal center lies in the isoindole N_4 plane, the manganese atom is displaced $0.291 \text{ \AA}$ above the N_4 plane towards the apical chloro ligand. The displacement is similar to that in $[\text{Mn}(\text{OESTAP})\text{Cl}]$ [$0.291 \text{ \AA}$; $\text{OESTAP} = 2,3,7,8,12,13,17,18$ -octakis(ethylsulfanyl)-*meso*-tetraazaporphyrinate],^[18] but is $0.03 \text{ \AA}$ longer than that in $[\text{Mn}(\text{TPP})\text{Cl}]$ ($\text{TPP} = \text{meso}$ -tetraphenylporphyrinate).^[19] The average $\text{Mn}-\text{N}(\text{isoindole})$ distance ($1.960 \text{ \AA}$) is also similar to the average $\text{Mn}-\text{N}(\text{pyrrole})$ distance of $[\text{Mn}(\text{OESTAP})\text{Cl}]$ ($1.951 \text{ \AA}$), but shorter than that in

$[\text{Mn}(\text{TPP})\text{Cl}]$ ($2.02 \text{ \AA}$). This is in agreement with the larger central cavity of the TPP ring. The $\text{Mn}-\text{Cl}$ distance in **9** ($2.343 \text{ \AA}$) is significantly shorter than that in $[\text{Mn}(\text{OESTAP})\text{Cl}]$ ($2.394 \text{ \AA}$) and $[\text{Mn}(\text{TPP})\text{Cl}]$ ($2.37 \text{ \AA}$). Due to the square-pyramidal structure and the C_4 disposition of the substituents, compound **9** can exhibit chirality. That the compound crystallizes in the orthorhombic system with a $P2_12_12_1$ space group shows that the crystal contains only one of the enantiomers, although a racemic mixture is expected to form during the reaction. This compound is thus a rare example of a structurally characterized manganese complex^[20] and phthalocyanine with a planar asymmetry.^[21]

We have recently reported a novel 1:1 inclusion complex of the metal-free phthalocyanine **8** and oxalic acid generated unexpectedly in a cerium-promoted cyclization reaction.^[10a] The crystal structure shows that the oxalic acid molecules are intercalated between the phthalocyanine rings and not be hydrogen-bonded in any conventional or unconventional manner. This is very unusual for molecules, such as oxalic acid, which have good hydrogen-bonding functionalities.^[22] To further explore this novel class of inclusion complexes, the (phthalocyaninato)palladium complex **5** was recrystallized in the presence of 1 equiv. of oxalic acid, giving the 1:1 inclusion complex $5 \cdot \text{C}_2\text{H}_2\text{O}_4$. The IR spectrum of $5 \cdot \text{C}_2\text{H}_2\text{O}_4$ (KBr) showed a strong band at 1671 cm^{-1} and a medium band at ca. 3400 cm^{-1} , which can be ascribed to the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ stretches, respectively, of the oxalic acid. Figure 5 depicts the packing of molecules in the lattice viewed along the crystallographic a and b axes, which shows that the guest species are not hydrogen-bonded and simply hang between the phthalocyanine rings. The polar oxalic acid preferentially resides in the more polar cavity between the phthalocyanine rings rather than in bulk CHCl_3 . The stacking angle is 54.3° and the interplanar distance is $7.13 \text{ \AA}$, which are similar to those of **3** and **7**. The oxalic acid

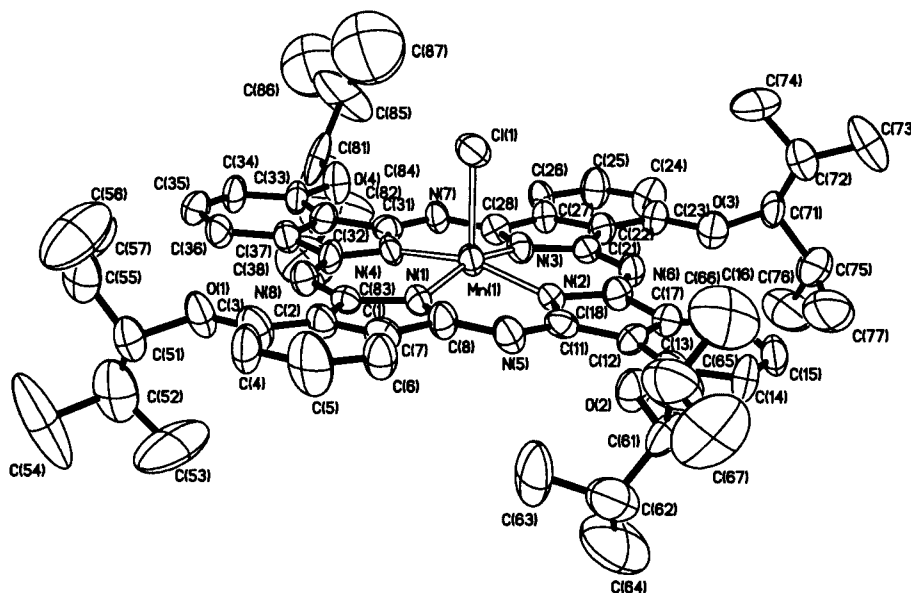


Figure 4. Molecular structure of **9** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms

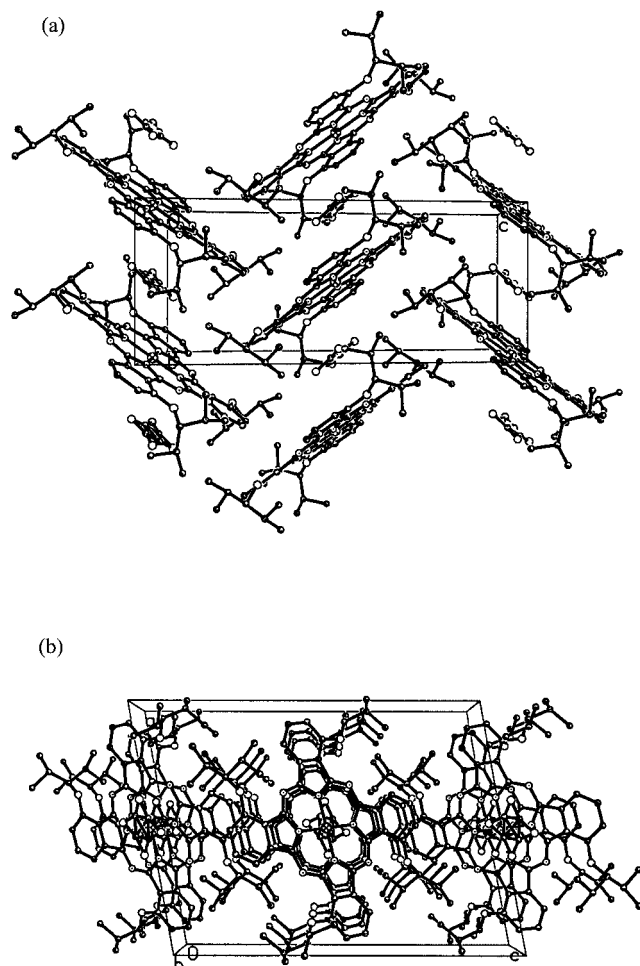


Figure 5. Crystal structure of $5 \cdot \text{C}_2\text{H}_2\text{O}_4$: views along the a (a) and b axis (b); all hydrogen atoms omitted for clarity

molecule is disordered (Figure 6). The average C–C, C=O, and C–O bond lengths are 1.569, 1.159, and 1.217 Å, respectively. The latter two are significantly shorter than the corresponding values for hydrogen-bonded oxalic acid (ca. 1.20 and 1.31 Å).^[23]

Conclusion

We have prepared and characterized a series of (phthalocyaninato)metal complexes substituted with four bulky 2,4-dimethyl-3-pentyloxy groups. The C_{4h} isomers of the (phthalocyaninato)zinc and -cobalt complexes and the C_4 isomer of the manganese analogue have been structurally characterized. The palladium counterpart forms a rare 1:1 inclusion complex, with oxalic acid, the structure of which has also been determined.

Experimental Section

General Remarks: Reactions were performed under nitrogen. *n*-Pentanol and THF were distilled from sodium and sodium/benzophenone ketyl, respectively. DMF was predried with barium oxide and distilled under reduced pressure. Chromatographic purifi-

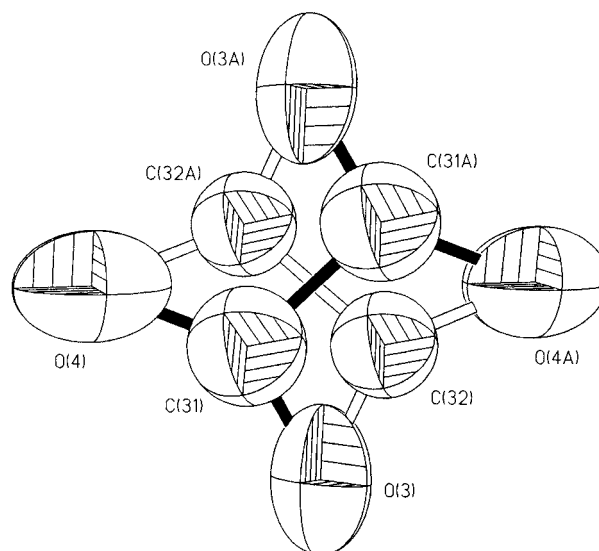


Figure 6. Molecular structure of the disordered oxalic acid in $5 \cdot \text{C}_2\text{H}_2\text{O}_4$; selected bond lengths [Å] and angles [°]: C(31)–C(31A) 1.566(10), C(31)–O(4) 1.142(16), C(31)–O(3) 1.204(18), C(32)–C(32A) 1.572(10), C(32)–O(4A) 1.176(16), C(32)–O(3) 1.229(18); O(4)–C(31)–O(3) 140.7(13), O(4)–C(31)–C(31A) 129(2), O(3)–C(31)–C(31A) 89.7(17), O(4A)–C(32)–O(3) 147.5(13), O(4A)–C(32)–C(32A) 125(2), O(3)–C(32)–C(32A) 87.7(16)

cations were performed on silica gel columns (Macherey–Nagel, 70–230 mesh) with the indicated eluents unless otherwise stated. Hexane used in chromatography was distilled from anhydrous CaCl_2 . All other reagents and solvents were of reagent grade and used as received. The preparation of the metal-free phthalocyanine **8** has been reported previously.^[10] ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 spectrometer (^1H : 300 MHz; ^{13}C : 75.4 MHz) in CDCl_3 solutions unless otherwise stated. Chemical shifts are relative to internal SiMe_4 ($\delta = 0$ ppm). IR spectra were measured with a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. UV/Vis spectra were taken with a Cary 5G UV/Vis/NIR spectrophotometer. Liquid secondary-ion (LSI) mass spectra were recorded with a Bruker APEX 47e Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by Medac Ltd., Brunel Science Centre, UK.

3-(2,4-Dimethyl-3-pentyloxy)phthalonitrile (2):^[24] A mixture of 3-nitrophthalonitrile (**1**) (2.0 g, 12 mmol), 2,4-dimethyl-3-pentanol (4.8 g, 41 mmol), and K_2CO_3 (12.6 g, 91 mmol) in DMF (20 mL) was heated at 65 °C for 2 d. The mixture was then poured into ice-cold water (200 mL) to give a light brown solid, which was filtered off and dissolved in CHCl_3 (20 mL). The resultant solution was dried with anhydrous MgSO_4 and then concentrated in vacuo. The residue was chromatographed with CHCl_3 as eluent to give the product as a white solid. Further purification was achieved by recrystallization with hexane to afford white shiny needles (2.4 g, 84%), m.p. 82–83 °C. $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$ (242.3): calcd. C 74.34, H 7.49, N 11.57; found C 74.43, H 7.28, N 11.62. ^1H NMR: $\delta = 7.50$ – 7.55 (m, 1 H, ArH), 7.21–7.24 (m, 2 H, ArH), 4.00 (t, $J = 6.0$ Hz, 1 H, OCH), 2.02–2.11 (m, 2 H, CH), 0.94 (d, $J = 6.9$ Hz, 6 H, Me), 0.88 (d, $J = 6.9$ Hz, 6 H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 163.3$, 134.3, 124.5, 117.8, 117.1, 115.4, 113.3, 105.0, 90.9, 30.5, 19.8, 17.4 ppm. IR (KBr): $\tilde{\nu} = 2225$ cm^{-1} (C≡N). HRMS (EI): m/z calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}$ [M^+] 242.1419, found 242.1435.

[Tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]zinc(II) (3 and 4): A mixture of the dinitrile **2** (100 mg, 0.41 mmol), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (32 mg, 0.15 mmol), and DBU (0.2 mL) in *n*-pentanol (3 mL) was heated at 160 °C for 8 h. The volatiles were then removed in vacuo and the residue was chromatographed with hexane/ethyl acetate (2:1) as eluent. A green band was collected and the solvents were evaporated to give a crude isomeric mixture of $[\text{ZnPc}(\text{OC}_7\text{H}_{15})_4]$, which was further purified by chromatography using CHCl_3 /ethyl acetate (10:1) as eluent. Two green bands were then followed which were collected separately to give the C_{4h} isomer **3** (20 mg, 19%) and the C_{2v} isomer **4** (59 mg, 55%), respectively. **3**: ^1H NMR (CDCl_3 with a drop of $[\text{D}_5]\text{pyridine}$): δ = 9.06 (d, J = 7.5 Hz, 4 H, Pc- H_a), 7.95 (t, J = 7.5 Hz, 4 H, Pc- H_b), 7.61 (d, J = 7.5 Hz, 4 H, Pc- H_c), 4.61 (t, J = 5.7 Hz, 4 H, OCH), 2.50–2.60 (m, 8 H, CH), 1.47 (d, J = 6.6 Hz, 24 H, Me), 1.14 (d, J = 6.6 Hz, 24 H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 with a drop of $[\text{D}_5]\text{pyridine}$): δ = 158.7, 153.8, 143.9, 142.0, 129.8, 125.8, 114.7, 113.6, 89.7, 31.2, 20.2, 18.4 ppm. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{73}\text{N}_8\text{O}_4\text{Zn}$ $[\text{MH}^+]$ 1033.5046, found 1033.5182. **4**: ^1H NMR (CDCl_3 with a drop of $[\text{D}_5]\text{pyridine}$): δ = 9.03–9.11 (m, 4 H, Pc- H_a and Pc- H_a'), 7.93–8.04 (m, 4 H, Pc- H_b and Pc- H_b'), 7.59–7.68 (m, 4 H, Pc- H_c and Pc- H_c'), 4.66 (t, J = 6.0 Hz, 2 H, OCH), 4.27 (t, J = 6.0 Hz, 2 H, OCH), 2.52–2.64 (m, 4 H, CH), 2.28–2.39 (m, 4 H, CH), 1.49–1.53 (m, 24 H, Me), 1.17 (d, J = 6.6 Hz, 12 H, Me), 0.73 (d, J = 6.6 Hz, 12 H, Me) ppm. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{73}\text{N}_8\text{O}_4\text{Zn}$ $[\text{MH}^+]$ 1033.5046, found 1033.5181.

[Tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]palladium(II) (5 and 6): A mixture of the dinitrile **2** (100 mg, 0.41 mmol), PdCl_2 (21 mg, 0.12 mmol), and DBU (0.2 mL) in *n*-pentanol (3 mL) was heated at 140 °C for 18 h. The volatiles were then removed in vacuo and the residue was subjected to chromatography using CHCl_3 as eluent. The crude product was chromatographed again with hexane/ CHCl_3 (2:1) as eluent to develop two green bands, which were collected and the solvents evaporated. The first band was found to be the C_{2v} isomer **6** (26 mg, 23%), while the second band was the C_{4h} isomer **5** (18 mg, 16%), which could be further purified by recrystallization from CHCl_3 /MeOH. **5**: $\text{C}_{61}\text{H}_{73}\text{Cl}_3\text{N}_8\text{O}_4\text{Pd}$ ($\text{5} \cdot \text{CHCl}_3$): calcd. C 61.39, H 6.17, N 9.40; found C 60.34, H 6.32, N 9.24. ^1H NMR: δ = 9.05 (d, J = 7.5 Hz, 4 H, Pc- H_a), 8.03 (dd, J = 7.5, 8.1 Hz, 4 H, Pc- H_b), 7.68 (d, J = 8.1 Hz, 4 H, Pc- H_c), 4.67 (t, J = 5.7 Hz, 4 H, OCH), 2.54–2.64 (m, 8 H, CH), 1.48 (d, J = 6.6 Hz, 24 H, Me), 1.19 (d, J = 6.6 Hz, 24 H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 158.6, 154.7, 143.1, 141.4, 130.6, 124.2, 114.7, 113.7, 89.5, 31.4, 20.4, 18.5. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{73}\text{N}_8\text{O}_4\text{Pd}$ $[\text{MH}^+]$ 1075.4783, found 1075.4870. **6**: ^1H NMR: δ = 9.09 (d, J = 7.5 Hz, 2 H, Pc- H_a or Pc- H_a'), 9.03 (d, J = 7.5 Hz, 2 H, Pc- H_a or Pc- H_a'), 7.98–8.06 (m, 4 H, Pc- H_b and Pc- H_b'), 7.64–7.69 (m, 4 H, Pc- H_c and Pc- H_c'), 4.69 (t, J = 5.7 Hz, 2 H, OCH), 4.31 (t, J = 5.7 Hz, 2 H, OCH), 2.57–2.68 (m, 4 H, CH), 2.30–2.41 (m, 4 H, CH), 1.49–1.52 (m, 24 H, Me), 1.22 (d, J = 6.6 Hz, 12 H, Me), 0.77 (d, J = 6.6 Hz, 12 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 160.0, 158.6, 154.0, 152.0, 143.2, 143.0, 140.0 (2 overlapping signals), 130.6, 130.4, 124.2 (2 overlapping signals), 117.0, 115.0, 114.4, 113.9, 94.2, 89.4, 31.4, 29.7, 20.4, 19.9, 18.4, 18.3 ppm. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{73}\text{N}_8\text{O}_4\text{Pd}$ $[\text{MH}^+]$ 1075.4783, found 1075.5037.

[1,8,15,22-Tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]cobalt(II) (7): A mixture of the dinitrile **2** (100 mg, 0.41 mmol), anhydrous CoCl_2 (13 mg, 0.10 mmol), and DBU (0.2 mL) in *n*-pentanol (3 mL) was heated under reflux overnight. The volatiles were then removed in vacuo and the residue was subjected to flash chromatography on neutral alumina using hexane/ethyl acetate (1:4) as

eluent. The crude product obtained was further purified by chromatography again using the same eluent to develop two blue bands. The first band was collected and the solvents were evaporated to give the C_{4h} isomer **7** as a green solid (35 mg, 34%), which could be recrystallized by layering MeOH onto a CHCl_3 solution. The second band contained about 5 mg of material, which could not be further purified by recrystallization because of its instability in solutions. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{72}\text{CoN}_8\text{O}_4$ $[\text{M}^+]$ 1027.5008, found 1027.4739.

Chloro[1,8,15,22-tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]manganese(III) (9): A mixture of the metal-free phthalocyanine **8** (50 mg, 0.05 mmol) and $\text{Mn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (10 mg, 0.05 mmol) in DMF (3 mL) was heated at 60 °C for 4 h. Water (10 mL) was then added and the resulting mixture was washed with hexane (3×15 mL) to remove unchanged **8**. The obtained brown aqueous layer was mixed with saturated brine (5 mL), and the mixture was then extracted with CHCl_3 (3×15 mL). The combined reddish-brown extracts were dried with anhydrous MgSO_4 and the solvents evaporated in vacuo to give a brown residue, which was purified by column chromatography on neutral alumina using hexane/ethyl acetate (4:1) as eluent. The crude product was further purified by recrystallization from hexane/THF to give brown needles (48 mg, 88%). $\text{C}_{64}\text{H}_{80}\text{ClMnN}_8\text{O}_5$ ($\text{9} \cdot \text{THF}$): calcd. C 67.93, H 7.13, N 9.91; found C 67.84, H 7.03, N 9.77. HRMS (LSI): m/z calcd. for $\text{C}_{60}\text{H}_{72}\text{MnN}_8\text{O}_4$ $[\text{M}^+ - \text{Cl}]$ 1023.5057, found 1023.4670.

X-ray Crystallographic Analyses of $3 \cdot \text{H}_2\text{O}$, $5 \cdot \text{C}_2\text{H}_2\text{O}_4$, $7 \cdot \text{H}_2\text{O}$ and $9 \cdot \text{H}_2\text{O} \cdot \text{THF}$: Single crystals of $3 \cdot \text{H}_2\text{O}$ and $7 \cdot \text{H}_2\text{O}$ were obtained by layering MeOH onto a CHCl_3 solution of **3** or **7**. By adding oxalic acid in the MeOH layer, single crystals of $5 \cdot \text{C}_2\text{H}_2\text{O}_4$ were obtained similarly. Single crystals of $9 \cdot \text{H}_2\text{O} \cdot \text{THF}$ were obtained by layering hexane onto a THF solution of **9**. Crystal data and details of data collection and structure refinement are given in Table 2. Data collection for all these compounds was performed with a Bruker SMART CCD diffractometer with Mo- K_α radiation (λ = 0.71073 Å) in a sealed tube at 293 K, using an ω -scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all of the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. The following software was employed: SMART to collect frames of data, index reflections, and determine the lattice constants; SAINT-PLUS to integrate the intensity of reflections and for scaling;^[25] SADABS for absorption correction;^[26] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.^[27] CCDC-212501 to -212504 contain the supplementary crystallographic data for $3 \cdot \text{H}_2\text{O}$, $5 \cdot \text{C}_2\text{H}_2\text{O}_4$, $7 \cdot \text{H}_2\text{O}$ and $9 \cdot \text{H}_2\text{O} \cdot \text{THF}$, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 2. Crystallographic data for (phthalocyaninato)metal complexes **3**, **5**, **7**, and **9**

	3·H ₂ O	5·C ₂ H ₂ O ₄	7·H ₂ O	9·H ₂ O·THF
Empirical formula	C ₆₀ H ₇₄ N ₈ O ₅ Zn	C ₆₂ H ₇₄ N ₈ O ₈ Pd	C ₆₀ H ₇₄ CoN ₈ O ₅	C ₆₄ H ₈₂ ClMnN ₈ O ₆
Formula mass	1052.64	1165.69	1046.20	1149.77
Crystal size [mm]	0.22 × 0.18 × 0.14	0.34 × 0.32 × 0.20	0.42 × 0.23 × 0.20	0.35 × 0.19 × 0.17
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	16.024(4)	15.8995(8)	16.015(3)	13.470(3)
<i>b</i> [Å]	8.619(2)	8.7861(4)	8.5760(10)	31.079(6)
<i>c</i> [Å]	21.726(5)	21.5407(10)	21.708(3)	16.002(3)
β [°]	99.661(5)	100.3590(10)	99.493(4)	90
<i>V</i> [Å ³]	2958.0(12)	2960.1(2)	2940.6(8)	6699(2)
<i>Z</i>	2	2	2	4
<i>F</i> (000)	1120	1224	1114	2448
<i>D</i> _{calcd.} [mg m ^{−3}]	1.182	1.308	1.182	1.140
μ [mm ^{−1}]	0.468	0.374	0.345	0.289
θ range [°]	2.11–25.00	1.92–25.00	2.11–25.00	1.31–25.00
Reflections	15498	16002	15482	36485
Unique reflections	5200 (<i>R</i> _{int} = 0.0915)	5213 (<i>R</i> _{int} = 0.0306)	5167 (<i>R</i> _{int} = 0.0857)	11769 (<i>R</i> _{int} = 0.2925)
Parameters	377	367	326	715
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0917	0.0382	0.1096	0.1087
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.2460	0.1050	0.2991	0.2473
Goodness of fit	0.918	1.005	1.049	0.913

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