Synthesis and characterization of a new bis-alanyl-appended porphyrin and its mononuclear Cu(II), Ni(II) and Zn(II) complexes. Crystal structure of the Ni(II) complex

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Abstract

A new multi-chelating ligand, *cis*-5,15-bis(*o*-[β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, *cis*-(ala)$_2$DPE, has been synthesized. Treatment of *cis*-(ala)$_2$DPE with methanol solutions of Ni(II), Cu(II) or Zn(II) leads to the formation of mononuclear metal complexes in which the metal has inserted into the porphyrin core. An X-ray structure determination was carried out for [*cis*-(ala)$_2$DPE]Ni(II)·$CHCl_3$·CH_3OH. Crystal data are as follows: monoclinic, $P2_1/n$, $a=14.195(5)$, $b=12.175(6)$, $c=28.071(1)$ Å, $\beta=98.97(3)°$, $R=0.085$, $R_w=0.089$.

Introduction

The importance of porphyrins and porphyrin derivatives is evident from the prominence of metalloporphyrins in many biological functions [1]. The use of synthetic metalloporphyrins to model the activities of natural systems has stimulated the preparation of a variety of functionalized porphyrins with specially designed cavities for selective substrate binding and/or ligating appendages for binding additional metals. A partial list of these porphyrins includes elegant molecules such as picket-fence porphyrins [2], pincer porphyrins [3], basket-handle porphyrins [4], gyroscope porphyrins [5], triple-decker porphyrins [6] and bis-pocket porphyrins [7]. In addition, a number of binucleating porphyrins have been prepared for use in modelling the active sites of multi-metal proteins [8–10]. The accessibility of multi-chelating porphyrin ligands should allow for the preparation of oligomeric metal complexes and capitalization of the chemistry that is unique to multi-metal systems. Of interest is the possibility of designing and preparing linear arrays of transition metals as a means of producing new materials with desired optical, magnetic or conductivity properties. However, the majority of the multi-chelating porphyrins such as those reported by Reed and co-workers [3], Elliot and Krebs [11], Gunter *et al.* [9] and Chang *et al.* [10] have sufficiently bulky appendages or have structures that limit these ligands to binding two metals. We have designed a more flexible ligand system in order to promote the formation of oligomeric complexes.

In this paper, we report the simple synthesis of a new multi-chelating ligand, *cis*-5,15-bis(*o*-[β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, *cis*-(ala)$_2$DPE. This ligand consists of two chemically distinct metal bonding sites — the porphyrin unit and the terminal amines of the alanyl groups. As a means of preparing molecular building blocks for multi-nuclear metal arrays, we have metallated the porphyrin core of this ligand to form mononuclear complexes with Ni(II), Cu(II) and Zn(II). A single crystal X-ray structure determination has been carried out for the nickel complex.

Experimental

Preparations

All reagents were of analytical grade. THF was freshly distilled from purple solutions containing sodium and benzophenone. 5,15-Bis(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin,

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$(NH_2)_2DPE$, was synthesized according to the method reported elsewhere [12].

cis-Bis(o-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (1)

The *cis* and *trans* mixture of bis(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, $(NH_2)_2DPE$, prepared by the Chang procedure [12], was converted to the *cis* isomer by following Lindsey's procedure with some modifications [13, 14]. A mechanically stirred mixture of toluene (1.5 l, dried over molecular sieves) and 300 g silica gel was heated at reflux for 2 h under nitrogen. A *cis/trans* mixture of $(NH_2)_2DPE$ (8.5 g) was added and heating at reflux was continued for 4–7 days. After cooling to room temperature, the slurry was poured into a 15 cm diameter coarse glass frit and rinsed with toluene until the washings were clear, to remove the *trans* isomer. *cis*-$(NH_2)_2DPE$ was eluted from the silica gel with benzene/ether (1:1) and isolated by removing the solvent under reduced pressure to yield 5.1 g (60%) of purple solid. Purity of the *cis* and *trans* isomers was checked by analytical TLC (SiO_2, CH_2Cl_2–CH_3OH; 98:2) and ^1H NMR spectroscopy. The ^1H NMR spectra agree well with literature values [12].

N-t-butoxycarbonyl-β-alanine (BOC-β-alanine)

This compound was prepared following a modified literature method [15]. BOC-ON (2-(t-butoxycarbonyloxyimino)-2-phenylacetonitrile) (30.0 g, 0.12 mol) dissolved in 66 ml 1,4-dioxane was added to a stirred solution of β-alanine (9.87 g, 0.11 mol) and triethylamine (24 ml) followed by a subsequent addition of 66 ml H_2O. After stirring the reaction mixture for 2.5 h, 80 ml saturated NaCl and 20 ml ethyl acetate were added. The aqueous layer was separated and washed several times with ethyl acetate. When the water solution became clear, it was acidified with 1 N HCl to pH 1 and was extracted with CH_2Cl_2 (4×10 ml). The CH_2Cl_2 fractions were combined and evaporated to yield a viscous oil. After addition of 20 ml hexane, the flask was cooled to −30 °C. The precipitate was filtered and dried under vacuum at ambient temperature to yield 20.4 g (88%) of white solid. ^1H NMR ($CDCl_3$): 6.30(s, 1H, OH), 5.08(s, 1H, NH), 3.36(t, 2H, CH_2), 2.54(t, 2H, CH_2), 1.41(s, 9H, t-butyl).

cis-Bis(o-[N-t-butoxycarbonyl-β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (2)

The method used to attach amino acid side chains to *cis*-$(NH_2)_2DPE$ is based on the strategy described by Rose and co-workers [16]. Under nitrogen, *N*-methyl piperidine (1.98 g, 20 mmol) and isobutylchloroformate (2.10 g, 15.4 mmol) were added to a cold (−30 °C) solution of *N*-t-butoxycarbonyl-β-alanine (3.78 g, 20 mmol) dissolved in 300 ml THF. *cis*-$(NH_2)_2DPE$ (1.32 g, 4 mmol) in 200 ml THF (cooled to −30 °C) was added to this solution through a cannula. The reaction mixture was stirred at −30 °C for 1 h and the temperature was slowly increased to ambient temperature over 10 h. The solution was filtered and the residues were washed with THF. The combined filtrates were evaporated to dryness, redissolved in 200 ml CH_2Cl_2 and washed successively with H_2O, 1% $NaHCO_3$, H_2O, 0.1 N HCl and H_2O. After drying the organic layer over $MgSO_4$ and filtering, the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (30×4 cm) eluting with CH_2Cl_2/ether (95:5 to 90:10). Removal of the solvent under reduced pressure yielded 1.8 g of purple solid (90%). Trace amounts of free BOC-β-alanine were always present in the final product, but were readily removed in the subsequent deprotection step. UV–Vis ($CHCl_3$): 408 (soret), 508, 542, 574, 626 nm. FAB-MS (MH^+): Found 1003.4; Calc. 1003.0. IR (nujol mull): $\nu_{CO} = 1680$ and 1710 cm^{-1}. ^1H NMR ($CDCl_3$): −2.49(s, 2H, $NH_{pyrrole}$), 1.19(s, 18H, t-butyl), 1.45(s, free BOC-β-alanine), 1.49(t, 4H, $-CH_2CH_2-$), 1.77(t, 12H, CH_2CH_3), 2.52(s, 12H, CH_3), 2.85(t, 4H, $-CH_2CH_2-$), 4.04(q, 8H, CH_2CH_3), 4.87(s, 2H, NHBOC), 6.84(s, 2H, NH aryl), 7.53(t, 2H, aryl), 7.85(m, 4H, aryl), 8.75(d, 2H, aryl), 10.27(s, 2H, *meso*-H).

cis-5,15-Bis(o-[β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (3)

The BOC-protected porphyrin, **2**, (0.5 g, 0.50 mmol) was dissolved in 40 ml 1:1 CH_2Cl_2/trifluoroacetic acid (TFA) and the resulting green solution was stirred at ambient temperature for 1 h. After removing the solvent under reduced pressure, the resulting solid was washed with diethyl ether until no green color in the washing was evident. The residues were dissolved in a minimum of acetone and poured into 400 ml of 1:1 CH_2Cl_2/water. The solution was neutralized to pH 7 with 1% $NaHCO_3$ and extracted with CH_2Cl_2. After removing the solvent under reduced pressure, the crude product was purified by chromatography on a 35×4 cm silica gel column eluting successively with 95:5, 90:10 to 80:20 CH_2Cl_2/MeOH solvent mixtures. The second band, a dark, slow moving component (90:10 to 80:20 fractions) was collected and evaporated to dryness to yield 0.2 g of purple solid (50%). UV–Vis ($CHCl_3$): 408 (soret), 510, 544, 575, 625 nm. FAB-MS (MH^+): Found 803.2; Calc. 803.0. IR (nujol mull): $\nu_{CO} = 1680$ cm^{-1}. ^1H NMR ($CDCl_3$): −2.48(s, 2H, $NH_{pyrrole}$), −1.35(s, 4H, NH_2), 9.48(s, 2H, NH aryl), 1.63(t, 8H, $-CH_2CH_2-$), 1.78(t, 12H, $-CH_2CH_3$), 2.55(s, 12H, CH_3), 4.02(q, 8H, CH_2CH_3), 7.49(t, 2H, aryl), 7.73(m, 4H, aryl), 8.76(d, 2H, aryl), 10.22(s, 2H, *meso*-H).

Nickel and copper porphyrin complexes

To a stirred solution of *cis*-$(ala)_2$DPE (0.20 g, 0.25 mmol) in 10 ml $CHCl_3$/MeOH (9:1) was added a solution of the respective metal acetate (0.25 mmol) in 5 ml MeOH with stirring. The resulting reaction mixture was heated at reflux for 4 h. After evaporating the solvent to dryness, 230 ml water and 20 ml 1 N HCl were added to the flask and the suspension was stirred for 4 h, before extracting the suspension with CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered, and concentrated to 2 ml. The solution was layered with 8 ml of n-hexane and cooled to 12 °C for 4 h. The precipitated solid was filtered, washed with n-hexane and dried *in vacuo* at ambient temperature.

[cis-(Ala)$_2$DPE]Ni(II). Yield: 0.18 g, 84.1% of red solid. UV–Vis ($CHCl_3$): 408 (soret), 530, 566 nm. FAB-MS (MH^+): Found 859.2; Calc. 858.9. ^{1}H NMR (CD_2Cl_2): 5.69(s, 2H, NH), 7.01(s, 4H, NH_2), 1.28(t, 4H, $-CH_2CH_2-$), 2.77(t, 4H, $-CH_2CH_2-$), 1.59(t, 12H, CH_2CH_3), 2.19(s, 12H, CH_3), 3.67(q, 8H, CH_2CH_3), 7.56(t, 2H, aryl), 7.69(t, 2H, aryl), 8.33(d, 4H, aryl), 9.39(s, 2H, *meso*-H).

[cis-(Ala)$_2$DPE]Cu(II). Yield: 0.16 g, 74.4% of brown solid. UV–Vis ($CHCl_3$): 410 (soret), 534, 570 nm. FAB-MS (MH^+): Found 864.3; Calc. 864.5.

[cis-(Ala)$_2$DPE]Zn(II)

Zinc acetate (0.056 g, 0.25 mmol) in 5 ml methanol was added to a stirred solution of *cis*-$(ala)_2$DPE (0.20 g, 0.25 mmol) in 10 ml $CHCl_3$/MeOH (9:1) and the mixture was heated at reflux for 4 h. After evaporating the solvent to dryness, 4 ml toluene and 6 ml n-hexane were added to the flask and the mixture was cooled to 12 °C for 4 h. The resulting light red solid was filtered, washed with n-hexane and dried *in vacuo* at ambient temperature to yield 0.14 g of product (67%). UV–Vis ($CHCl_3$): 420 (soret), 546, 582 nm. FAB-MS (MH^+): Found 866.4; Calc. 866.4. ^{1}H NMR ($CDCl_3$): 7.09(s, 2H, NH), 2.95(s, 4H, NH_2), 1.03(t, 4H, $-CH_2CH_2-$), 1.42(t, 4H, $-CH_2CH_2-$), 1.73(t, 12H, CH_2CH_3), 2.46(s, 12H, CH_3), 3.97(q, 8H, CH_2CH_3), 7.69(t, 2H, aryl), 7.84(t, 2H, aryl), 8.08(d, 4H, aryl), 10.10(s, 2H, *meso*-H).

Measurements

Visible spectra were recorded at room temperature on a HP 8452A diode array spectrophotometer using chloroform as solvent. IR spectra were run as nujol mulls on a IBM IR-98 Fourier transform infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Nicolet NIC 300 spectrometer using $CDCl_3$ as solvent. Chemical shifts δ (in ppm) are reported relative to $CDCl_3$ (7.24 ppm). FAB mass spectra were obtained on a Kratos MS-50 spectrometer. Magnetic susceptibility measurements were carried out on a Quantum Design superconducting quantum interference device. Diamagnetic corrections for the ligand and the copper complex were computed using Pascal's constants [17]. The susceptibility was corrected for the temperature independent paramagnetism term using 60×10^{-6} c.g.s. for the copper complex.

X-ray crystal structure determination

A single crystal of [*cis*-$(ala)_2$DPE]Ni(II)·$CHCl_3$·CH_3OH suitable for X-ray structure determination was grown by slow evaporation of $CHCl_3$/hexane/CH_3OH (3:2:1) solution of [*cis*-$(ala)_2$DPE]Ni(II) at −15 °C. A purple hexagonal crystal having approximate dimensions of $0.18\times0.20\times0.30$ mm was mounted on a glass fiber. A Rigaku AFC6R diffractometer with graphite monochromated Mo Kα radiation (=0.71069 Å) and a 12 KW rotating anode generator was used to collect the data. Intensities exhibited a pronounced tendency to decrease rapidly with scattering angle, and even with a high intensity source, it was difficult to obtain a large number of observed ($I>3.0\sigma(I)$) reflections. Based on systematic absences of $h0l$: $h+l\neq2n$, $0k0$: $k\neq2n$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14). The intensity data were collected at -80 ± 1 °C using the ω scan technique to maximum 2θ value of 55.1°. Pertinent crystallographic parameters are presented in Table 1. Three standard reflections were monitored every 150 reflections measured, and their intensities showed good stability of the complex throughout the data collection. Reflection data were corrected for Lorentz–polarization and absorption. The structure was solved by direct methods [18]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as fixed contributions at riding, idealized locations. Full-matrix least-squares refinement of positional and thermal parameters led to convergence with a final unweighted R factor of 0.085 and a weighted R factor of 0.089 for 604 variables refined against 3460 observed reflections. The maximum peak in the final electron density map was 0.71 $e^-/Å^3$. Neutral atom scattering factors were taken from Cromer and Waber [19]. Anomalous dispersion effects were included in F_{calc} [20]; the values for $\Delta f'$ and $\Delta f''$ were those of

TABLE 1. Crystallographic parameters

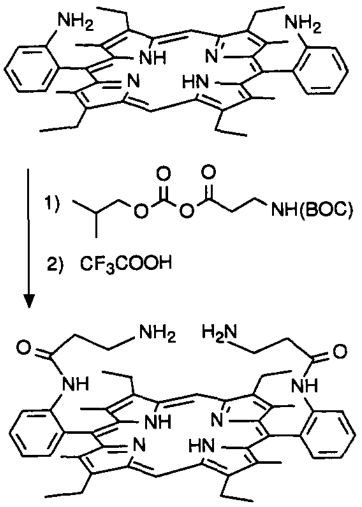
Empirical formula	$NiCl_3O_3N_8C_{52}H_{61}$
Formula weight (g mol^{-1})	1010.19
Crystal color, habit	purple, hexagonal
Crystal dimensions (mm)	0.18×0.20×0.30
Crystal system	monoclinic
No. reflections used for unit cell determination (2θ range)	15 (12.9–15.1°)
Omega scan peak width at half-height	0.48
Lattice parameters:	
a (Å)	14.195(5)
b (Å)	12.175(6)
c (Å)	28.07(1)
β (°)	98.97(3)
V (Å^3)	4792(3)
Space group	$P2_1/n$ (No. 14)
Z value	4
D_{calc} (g/cm^3)	1.367
$F(000)$	2040
μ(Mo Kα) (cm^{-1})	10.65
Diffractometer	Rigaku AFC6R
Radiation	Mo Kα (λ=0.71069 Å)
Temperature (°C)	−80
Take-off angle (°)	6.0
Detector aperture (mm)	6.0 horizontal 6.0 vertical
Scan type	ω
Scan rate (°/min)	16.0 (in omega) (2 rescans)
Scan width (°)	(1.29 + 0.30 tan θ)
$2\theta_{max}$ (°)	55.1
No. reflections measured	
total	12057
unique	11599 (R_{int} = 0.087)
Corrections	Lorentz–polarization absorption (transmission factors: 0.89–1.00)
Structure solution	direct methods
Refinement	full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
Anomalous dispersion	all non-hydrogen atoms
No. observations ($I > 3.00\sigma(I)$)	3460
No. variables	604
Reflection/parameter ratio	5.73
Residuals: R; R_w	0.085; 0.089
Goodness of fit indicator	2.46
Max. shift/error in final cycle	0.26
Max. peak in final difference map (e Å^{-3})	0.71
Min. peak in final difference map (e Å^{-3})	−0.59

Cromer [21]. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation [22].

Results and discussion

Synthesis of the ligand

The synthetic strategy for the preparation of the bis-alanyl-appended porphyrin ligand is depicted in Scheme 1. The key ligand precursor, bis(*o*-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, $(NH_2)_2DPE$, was obtained as a mixture of *cis* and *trans* isomers via the procedure given by Young and Chang [12]. Thermal atropisomerization of this mixture in a manner similar to that reported by Lindsey [13] and Elliott [14] allowed isolation of the pure *cis* isomer, **1**, in 60–80% yields. Attachment of ligating appendages to the *o*-amino substituents



Scheme 1.

was accomplished with mixed anhydrides of *N*-t-butoxycarbonyl (BOC) protected amino acids. Thus, *cis*-5,15-bis(*o*-[*N*-t-butoxycarbonyl-β-alanylamido]-phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-porphyrin (**2**) was prepared by treating *cis*-$(NH_2)_2$DPE with the mixed anhydride derived from *N*-BOC-β-alanine and isobutylchloroformate. Removal of the BOC protecting groups with CH_2Cl_2/TFA led to the formation of the desired binucleating ligand *cis*-5,15-bis(*o*-[β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, *cis*-(ala)$_2$DPE (**3**). The solid state IR spectrum of **3** exhibits an amide carbonyl stretch at 1680 cm^{-1}. The ^{1}H NMR spectrum of **3** readily demonstrates the presence of the β-alanyl groups attached to the *o*-aminophenyl substituents. Both sets of methylene protons of the alanyl fragment coincidentally resonate at 1.63 ppm. The amide proton signal is at 9.48 ppm and the terminal amine protons appear at −1.35 ppm. The high-field shift of the terminal amine proton signal indicates that the appended alanyl groups spend a significant time in the shielding porphyrin ring current. The assignments of the amide-NH and terminal-NH_2 resonances have been confirmed by observing the disappearance of these signals in a D_2O-exchanged sample. A particularly useful area in the NMR spectra of these types of compounds is the *meso*-proton region, which is typically well-separated from other signals. The chemical shift of the *meso* proton can be diagnostic of the type of complex, while the number of signals in this region gives an indication of the purity of the sample. In the free-base ligand, the *meso* proton appears at 10.22 ppm. The UV–Vis spectrum of *cis*-(ala)$_2$DPE exhibits a Soret band at 408 nm and four visible bands at 510, 544, 575 and 625 nm.

Metal complexes

Treatment of *cis*-(ala)$_2$DPE (**3**) in $CHCl_3$ with freshly prepared methanolic solutions of Ni(II), Cu(II) or Zn(II) ions afforded metallated complexes. After 4 h of heating at reflux, UV–Vis spectra of the reaction mixtures showed that the four Q bands of the free ligand collapsed to a two-band pattern. This clearly indicated that a metal has inserted into the porphyrin core of the ligand. In the case of [*cis*-(ala)$_2$DPE]Cu(II) and [*cis*-(ala)$_2$DPE]Ni(II), it was necessary to hydrolyze the crude product with aqueous HCl to remove any possibility of formation of species of higher nuclearity [23]. In contrast, [*cis*-(ala)$_2$DPE]Zn(II) did not require an acid work-up as mononuclear complexes were always isolated under the reaction conditions employed. FAB mass spectra of the complexes exhibit the expected molecular ion peaks for mononuclear metal complexes. Further evidence for the insertion of Zn and Ni into the porphyrin core is derived from ^{1}H NMR. In both of these cases, the internal pyrrole NH proton resonances are no longer present in the NMR spectra of the isolated complexes and indicate that the pyrrole nitrogens are coordinated to metal ions. The purity of the diamagnetic metal complexes is readily ascertained by the presence of a single *meso*-proton resonance in the NMR spectrum. In [*cis*-(ala)$_2$DPE]Ni(II), this signal appears at 9.39 ppm. For the corresponding Zn complex, it occurs at 10.10 ppm. The copper(II) complex is paramagnetic with a magnetic moment of 2.22 BM at ambient tem-

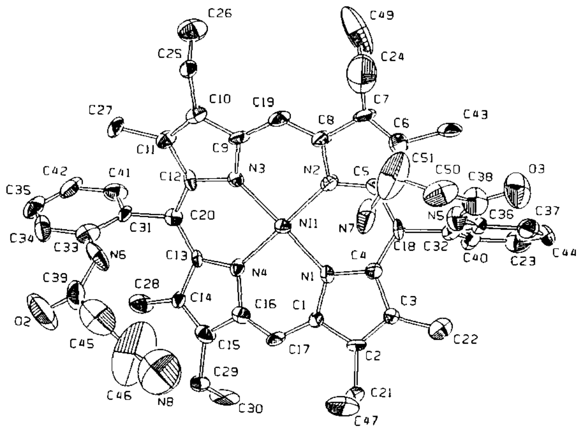


Fig. 1. Molecular structure and atom numbering scheme for [*cis*-(ala)$_2$DPE]Ni(II). Note that the atom numbering scheme is unrelated to the numbering rules used for systematic nomenclature of the ligand. Hydrogen atoms and solvate molecules have been omitted for clarity.

TABLE 2. Positional parameters and B_{eq} for $NiCl_3O_3N_8C_{52}H_{61}$

Atom	x	y	z	B_{eq}[a]
Ni(1)	0.2040(1)	0.2075(1)	0.52757(6)	2.12(7)
Cl(1)	0.0229(3)	0.2223(5)	0.8162(2)	7.7(3)
Cl(2)	0.0759(4)	0.0988(5)	0.7384(2)	10.9(4)
Cl(3)	−0.1046(4)	0.0689(6)	0.7642(2)	10.4(4)
O(1)	−0.091(2)	0.497(3)	0.643(1)	34(3)
O(2)	−0.2735(9)	0.389(1)	0.4198(5)	11(1)
O(3)	0.7130(8)	0.378(1)	0.6621(4)	6.9(7)
C(52)	−0.096(1)	0.391(2)	0.6863(8)	10(1)
N(1)	0.2293(7)	0.2352(9)	0.5960(3)	2.4(5)
N(2)	0.3386(7)	0.197(1)	0.5278(3)	2.9(5)
N(3)	0.1772(6)	0.199(1)	0.4584(3)	2.1(5)
N(4)	0.0693(6)	0.2029(9)	0.5281(3)	1.9(4)
N(5)	0.5567(8)	0.330(1)	0.6428(4)	3.4(6)
N(6)	−0.1254(8)	0.331(1)	0.4172(5)	4.3(7)
N(7)	0.438(1)	0.451(1)	0.5725(4)	5.5(7)
N(8)	−0.098(2)	0.545(2)	0.5439(8)	14(2)
C(1)	0.1647(9)	0.277(1)	0.6221(4)	2.7(6)
C(2)	0.2125(8)	0.306(1)	0.6698(4)	2.6(6)
C(3)	0.3016(8)	0.274(1)	0.6735(4)	2.3(6)
C(4)	0.3145(8)	0.231(1)	0.6271(4)	2.1(6)
C(5)	0.410(1)	0.176(1)	0.5656(5)	3.1(7)
C(6)	0.499(1)	0.154(1)	0.5483(5)	4.0(8)
C(7)	0.482(1)	0.178(2)	0.5014(5)	6(1)
C(8)	0.3830(8)	0.206(2)	0.4876(4)	4.2(7)
C(9)	0.2421(9)	0.220(1)	0.4277(4)	2.4(6)
C(10)	0.197(1)	0.226(1)	0.3794(4)	2.5(6)
C(11)	0.1048(9)	0.204(1)	0.3776(4)	2.4(6)
C(12)	0.0916(8)	0.185(1)	0.4271(4)	2.1(6)
C(13)	−0.0030(8)	0.163(1)	0.4934(4)	1.7(5)
C(14)	−0.0914(8)	0.150(1)	0.5129(4)	2.1(6)
C(15)	−0.0755(9)	0.192(1)	0.5569(5)	2.8(6)
C(16)	0.0225(8)	0.225(1)	0.5671(4)	2.1(6)
C(17)	0.0678(9)	0.272(1)	0.6082(4)	2.6(6)
C(18)	0.3980(8)	0.189(1)	0.6136(4)	2.1(6)
C(19)	0.3391(9)	0.222(1)	0.4414(4)	3.6(7)
C(20)	0.0064(9)	0.160(1)	0.4448(4)	1.9(6)
C(21)	0.164(1)	0.367(1)	0.7056(4)	3.8(8)
C(22)	0.376(1)	0.290(1)	0.7173(5)	4.2(7)
C(23)	0.542(1)	0.027(1)	0.7123(5)	4.0(8)
C(24)	0.572(2)	0.227(2)	0.4608(9)	12(2)
C(25)	0.2474(9)	0.247(1)	0.3372(4)	3.2(7)
C(26)	0.272(1)	0.144(1)	0.3134(5)	5.0(9)
C(27)	0.0311(9)	0.203(1)	0.3327(4)	4.0(7)
C(28)	−0.1807(9)	0.093(1)	0.4911(5)	3.5(7)
C(29)	−0.1450(8)	0.204(1)	0.5910(4)	2.8(6)
C(30)	−0.149(1)	0.105(2)	0.6230(5)	6(1)
C(31)	−0.0819(8)	0.139(1)	0.4085(4)	2.3(6)
C(32)	0.4779(9)	0.159(1)	0.6534(4)	2.5(6)
C(33)	−0.146(1)	0.227(1)	0.3954(5)	2.9(7)
C(34)	−0.223(1)	0.212(2)	0.3602(5)	4.2(8)
C(35)	−0.243(1)	0.110(2)	0.3411(5)	4.4(9)
C(36)	0.5558(9)	0.229(1)	0.6670(4)	2.8(7)
C(37)	0.627(1)	0.198(1)	0.7043(5)	3.6(7)
C(38)	0.631(1)	0.397(1)	0.6406(6)	4.7(9)
C(39)	−0.190(1)	0.405(2)	0.4295(6)	5(1)
C(40)	0.474(1)	0.063(1)	0.6758(5)	3.4(7)
C(41)	−0.101(1)	0.039(1)	0.3882(5)	3.0(7)
C(42)	−0.180(1)	0.020(1)	0.3542(5)	3.9(8)
C(43)	0.592(1)	0.112(1)	0.5753(5)	4.7(8)
C(44)	0.620(1)	0.097(1)	0.7259(5)	3.8(8)
C(45)	−0.149(1)	0.503(2)	0.4593(9)	7(1)
C(46)	−0.143(2)	0.465(2)	0.514(1)	16(2)
C(47)	0.165(1)	0.491(2)	0.7018(6)	6(1)
C(48)	−0.009(2)	0.148(3)	0.767(1)	27(3)
C(49)	0.560(1)	0.127(2)	0.451(1)	11(2)
C(50)	0.611(1)	0.492(2)	0.6071(6)	6(1)
C(51)	0.546(2)	0.473(2)	0.5605(7)	10(1)

[a] The equivalent isotropic temperature factor [24] is defined as follows: $B_{eq} = \frac{8\pi^2}{3} \sum_{i-1}^{3} \sum_{j-1}^{3} U_{ij} a_i{}^* a_j \overline{a_i} \cdot \overline{a_j}$.

perature as expected for magnetically dilute copper complexes.

X-ray structure of the Ni(II) complex

The molecular structure of [*cis*-(ala)$_2$DPE]Ni(II) is shown in Fig. 1 along with the atom numbering scheme. Table 2 presents a listing of fractional coordinates for non-hydrogen atoms and Table 3 gives selected bond distances and angles. The large thermal parameters associated with some of the atoms on the periphery of the molecule would explain the rapid fall-off in observed intensities. The average dihedral angle between the mean planes of adjacent pyrrole rings is 25.4° and indicates that the porphyrin core of this complex is ruffled in a manner similar to the S_4-ruffling of the tetragonal form of octaethylporphyrinato nickel(II), Ni(OEP). The average Ni–$N_{pyrrole}$ distance of 1.92 Å is at the lower limit for Ni–N distances in other Ni porphyrin structures [25–30]. The N–Ni–N bond angles range from 88.1(4) to 92.3(4)° and indicate that the Ni environment is square planar. An unusual difference in the ruffled porphyrin core of [*cis*-(ala)$_2$DPE]Ni(II) relative to that of the tetragonal form of Ni(OEP) involves the displacement of the *meso* carbons from the mean porphyrin plane. In Ni(OEP) these atoms are displaced alternately above and below the mean porphyrin plane by 0.51 Å. Although the *meso* carbons in [*cis*-(ala)$_2$DPE]Ni(II) are also positioned alternately above and below the mean porphyrin plane, one of the atoms, C_{20}, bearing a phenyl group, is only displaced 0.19 Å from the plane while the other three atoms show a more typical displacement averaging 0.55 Å. The smaller displacement of C_{20} does not appear to be due to any unusual nonbonding interactions involving the appended alanyl arm. There is clearly no intramolecular interappendage H-bonding as the two terminal nitrogen atoms, N_7 and N_8, are separated by 7.61 Å. This is in marked contrast to the structures of monometallic pincer porphyrins in which the orientation of the benzimidazole arms is influenced by intramolecular

TABLE 3. Selected intramolecular distances (Å) and bond angles (°) involving the non-hydrogen atoms[a]

Atom	Distance	Atom	Distance
Ni(1)–N(1)	1.93(1)	C(9)–C(10)	1.41(2)
Ni(1)–N(2)	1.91(1)	C(9)–C(19)	1.37(2)
Ni(1)–N(3)	1.922(9)	C(10)–C(11)	1.33(2)
Ni(1)–N(4)	1.914(9)	C(10)–C(25)	1.50(2)
Cl(1)–C(48)	1.65(2)	C(11)–C(12)	1.45(2)
Cl(2)–C(48)	1.65(2)	C(11)–C(27)	1.51(2)
Cl(3)–C(48)	1.66(2)	C(12)–C(20)	1.41(1)
O(1)–C(52)	1.80(4)	C(13)–C(14)	1.45(2)
O(2)–C(39)	1.19(2)	C(13)–C(20)	1.39(1)
O(3)–C(38)	1.25(2)	C(14)–C(15)	1.32(2)
N(1)–C(1)	1.36(1)	C(14)–C(28)	1.49(2)
N(1)–C(4)	1.38(1)	C(15)–C(16)	1.43(2)
N(2)–C(5)	1.37(2)	C(15)–C(29)	1.48(2)
N(2)–C(8)	1.38(1)	C(16)–C(17)	1.36(2)
N(3)–C(9)	1.38(1)	C(18)–C(32)	1.51(2)
N(3)–C(12)	1.40(1)	C(20)–C(31)	1.51(2)
N(4)–C(13)	1.39(1)	C(21)–C(47)	1.51(2)
N(4)–C(16)	1.39(1)	C(23)–C(40)	1.37(2)
N(5)–C(36)	1.41(2)	C(23)–C(44)	1.39(2)
N(5)–C(38)	1.34(2)	C(24)–C(49)	1.25(3)
N(6)–C(33)	1.41(2)	C(25)–C(26)	1.48(2)
N(6)–C(39)	1.37(2)	C(29)–C(30)	1.51(2)
N(7)–C(51)	1.64(3)	C(31)–C(33)	1.41(2)
N(8)–C(46)	1.38(3)	C(31)–C(41)	1.36(2)
C(1)–C(2)	1.45(2)	C(32)–C(36)	1.40(2)
C(1)–C(17)	1.37(2)	C(32)–C(40)	1.33(2)
C(2)–C(3)	1.31(2)	C(33)–C(34)	1.37(2)
C(2)–C(21)	1.50(2)	C(34)–C(35)	1.36(2)
C(3)–C(4)	1.44(2)	C(35)–C(42)	1.42(2)
C(3)–C(22)	1.50(2)	C(36)–C(37)	1.39(2)
C(4)–C(18)	1.39(2)	C(37)–C(44)	1.38(2)
C(5)–C(6)	1.45(2)	C(38)–C(50)	1.49(2)
C(5)–C(18)	1.45(2)	C(39)–C(45)	1.52(2)
C(6)–C(7)	1.33(2)	C(41)–C(42)	1.37(2)
C(6)–C(43)	1.52(2)	C(45)–C(46)	1.59(3)
C(7)–C(8)	1.44(2)	C(50)–C(51)	1.50(2)
C(8)–C(19)	1.36(2)		

Atom	Angle	Atom	Angle
N(1)–Ni(1)–N(2)	88.7(4)	C(1)–C(2)–C(3)	108(1)
N(1)–Ni(1)–N(4)	91.7(4)	C(2)–C(3)–C(4)	107(1)
N(2)–Ni(1)–N(3)	92.3(4)	N(1)–C(4)–C(3)	110(1)
N(3)–Ni(1)–N(4)	88.1(4)	C(1)–C(17)–C(16)	126(1)
Ni(1)–N(1)–C(1)	124.5(8)	C(4)–C(18)–C(5)	123(1)
Ni(1)–N(1)–C(4)	129.3(8)	C(4)–C(18)–C(32)	117(1)
C(1)–N(1)–C(4)	106(1)	C(8)–C(19)–C(9)	124(1)
Ni(1)–N(2)–C(5)	129.0(8)	C(12)–C(20)–C(13)	124(1)
Ni(1)–N(2)–C(8)	125.1(8)	C(18)–C(32)–C(36)	122(1)
Ni(1)–N(3)–C(9)	125.1(8)	N(5)–C(36)–C(32)	118(1)
Ni(1)–N(3)–C(12)	131.2(8)	N(5)–C(36)–C(37)	123(1)
Ni(1)–N(4)–C(13)	129.4(8)	N(5)–C(38)–C(50)	116(1)
Ni(1)–N(4)–C(16)	126.9(8)	C(38)–C(50)–C(51)	117(2)
C(36)–N(5)–C(38)	129(1)	N(7)–C(51)–C(50)	109(2)
N(1)–C(1)–C(2)	109(1)		

[a] e.s.d.s. in the least significant figure are given in parentheses.

H-bonding with an adjacent pivalamido group [3]. However, H-bonding does occur between the terminal amine (N$_7$) and the amido group (N$_5$) of the same appendage. The N$_7$–N$_5$ distance is 2.80 Å. The distance between the terminal amine, N$_8$, and the amide, N$_6$, of the other arm is 4.38 Å. A key feature to note is that the insertion of Ni into the porphyrin core has not caused atropisomerization of the alanyl appendages. Thus the chelating ability of the terminal amines is retained and further metallation is possible.

Conclusions

The attachment of ligating appendages to porphyrins to form multi-chelating ligands is a relatively straightforward procedure using amino acid peptide coupling methods. It should be possible to vary the length of these ligating appendages by choosing amino acids with different numbers of methylene units between the amine and carbonyl group. The initial studies reported here indicate that molecular building blocks for multi-chelating arrays can be readily prepared and structurally characterized by X-ray crystallography. The extension of this study to form trinuclear complexes will be reported elsewhere [23].

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