Syntheses, characterization, and structural chemistry of biladien-*ac*-10-one and -*bc*-5-one metal complexes with 4N or (3N + O) co-ordination

Richard G. Khoury,[a] Mathias O. Senge,*,†,[a,b] John E. Colchester[c] and Kevin M. Smith *,[a]

[a] *Department of Chemistry, University of California, Davis, CA 95616, USA*

[b] *Institut für Organische Chemie (WE 02), Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany*

[c] *Zeneca Specialities, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, UK*

Transition-metal(II) complexes have been formed between Cu, Co, Pd, Hg, Cd, Zn and Ni and biladien-*bc*-5-ones or -*ac*-10-ones. All show spectroscopic and analytical data in accordance with the formation of 1:1 complexes. Reaction of 5- and 10-oxobiladienes with Cu^{II}, Co^{II}, Pd^{II}, Zn^{II}, Cd^{II} and Hg^{II} always gave complexes in which the metal is co-ordinated to the four pyrrole nitrogens (4N co-ordination) and led to a cyclic, helical conformation of the tetrapyrrole ligand. Reaction of biladien-*ac*-10-ones with Ni^{II} also gave the 4N-co-ordinated derivative. However, reaction of biladien-*bc*-5-ones with Ni^{II} gave two compounds, one being the 4N-co-ordinated complex and other a side product in which the metal is co-ordinated to three pyrrole nitrogens of the conjugated system and to the *meso*-oxygen atom of the oxobiladiene [(3N + O) co-ordination]. The latter co-ordination type was found to occur only when the C(19) position became substituted by nucleophiles such as OH or OMe leading to steric repulsion of the fourth pyrrole ring away from the metal. Single-crystal structure analyses were made for 10-oxobiladien-*ac* complexes with 4N co-ordination of Cu^{II}, Pd^{II}, Ni^{II} or Co^{II} and for 5-oxobiladien-*bc* complexes with 4N co-rdination of Pd^{II}, Co^{II} or Cu^{II}. These showed tetrahedrally distorted co-ordination geometries in the MN_4 unit. The molecular structures of two nickel complexes of 5-oxobiladien-*bc* derivatives with square-planar (3N + O) co-ordination have also been determined.

Owing to the important roles tetrapyrroles play in nature, much attention has been given to the chemistry and structural characterization of porphyrins and metalloporphyrins.[1,2] While many studies have been performed on the structural chemistry of linear tetrapyrroles and their smaller homologues[3] the situation is quite different for their metal complexes. Although a number of studies have appeared over the years which were concerned with the spectroscopic characterization of tetrapyrrole metal complexes related to naturally occurring bile pigments and related tetrapyrroles,[4,6] only a few definite structure determinations were reported. The spectroscopic data available pointed to the broad variability in the molecular geometry about the metal centre.

The first structural characterizations of pyrrole metal complexes were reported in the early seventies for dipyrromethene complexes. Depending on the metal, tetrahedral, distorted-tetrahedral and square-planar ML_2 complexes were reported (M = metal, L = ligand).[6] At the same time the molecular structures of the first linear tetrapyrrole metal complexes were characterized by the group of Dunitz during their studies on synthetic corrinoids related to vitamin B-12.[7] Complexes include nickel(II), palladium(II) and platinum(II) perchlorate salts of A/D-secocorrinoids[7a] and a nickel(II) complex of a C/D-secocorrinoid.[7b] Two zinc(II) complexes of a biliverdin were described by Fuhrhop and co-workers.[8] Both a monomeric hydrate complex (ML) with an almost planar core and a bis(helical) dimer (M_2L_2) with distorted tetrahedral geometry about the zinc ion were observed with 1-formyl-2,3,7,8,12,13,17,18-octaethylbiliverdin.[8b] The structure of a M_2L_2 tetrapyrrole complex, where $M = Zn^{II}$ and L = biladien-*ac*, was described by Sheldrick and Engel.[9] This complex contained two distorted-tetrahedral zinc ions and two quadridentate biladien-*ac* ligands. Interestingly, for the zinc(II) complex of a 1,19-dioxo-10-nor-bilin a polymeric structure was predicted on the basis of vapour-pressure osmometry.[10] The

nickel(II) complex of 2,3,7,8,12,13,17,18-octaethylbilin-1,19-dione, which showed a cyclic helical geometry with tetrahedral displacement of the pyrrole nitrogens from the NiN_4 plane, was described in 1977.[11]

Although much progress has been made in the intervening years with regard to tetrapyrrole structural chemistry[2,3] no detailed comparative structural analyses of linear tetrapyrrole metal complexes have so far been available. The only related structure published in recent years (2,3,7,8,12,13,17,18-octaethylbilin-1,19-dionato)copper(II), was obtained by Balch *et al.*[1,2] during studies on oxidative ring opening of metalloporphyrins.

In order to obtain detailed information on the molecular stereochemistry of metallobiladienes we have prepared a number of transition-metal(II) complexes of 5- and 10-oxobiladienes. Oxobiladienes have been shown to be useful starting materials for the synthesis of porphyrins and are easily prepared.[13] Besides being readily available we chose oxobiladienes to investigate whether the *meso* oxo function can be involved in co-ordination to the metal centres. We here report the synthesis of oxobiladiene metal complexes with $M = Cu^{II}$, Co^{II}, Ni^{II}, Pd^{II}, Cd^{II}, Zn^{II} or Hg^{II} and present spectroscopic and crystallographic data for the reaction products. Oxobiladienes were originally of interest to us in connection with macrocyclization reactions to accomplish a new synthetic route to oxochlorins; this route would obviously require that we obtain structural details on metallooxobiladienes in order to ascertain whether geometrical factors would enable cyclization reactions to be feasible. However, we subsequently showed that electrochemical[14a] and metal-promoted oxidative cyclization reactions[14b] failed to yield metallooxophlorins or other similar tetrapyrrole products.
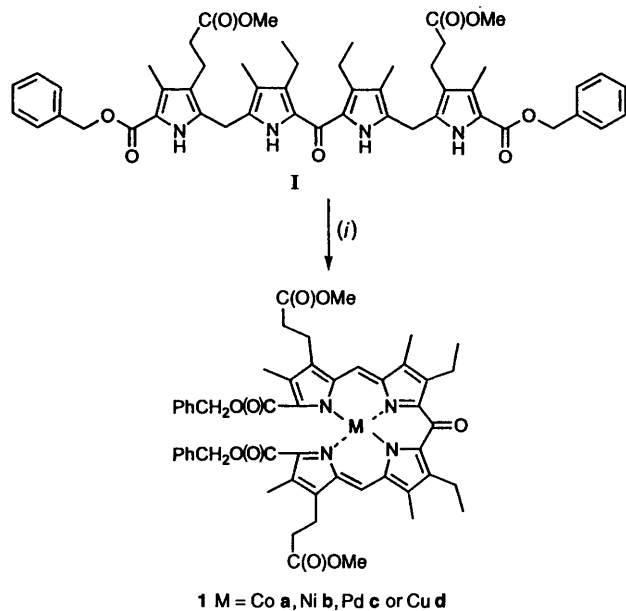
Results and Discussion

Syntheses

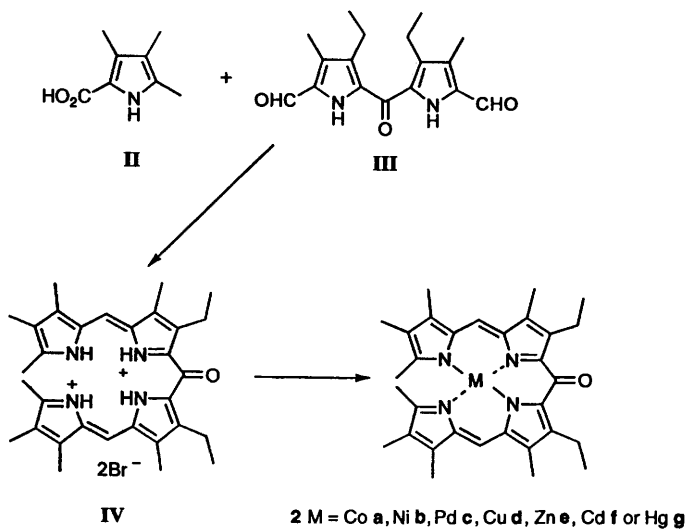For the synthesis of biladien-*ac*-10-ones and -*bc*-5-ones we

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† Address for correspondence is the German one.

employed the respective 5- and 10-oxobilanes, the syntheses of which have been described earlier.[13] The 1,19-di(benzyloxycarbonyl)oxobilanes utilized had substituent patterns, which upon cyclization, would have led to macrocycles of the mesoporphyrin IX, XI or XII type. For preparation of the desired metal complexes the oxobilanes were oxidized with bromine *in situ* to give the corresponding oxobiladiene dihydrobromides, which were used without further purification for metallation with the respective metal acetates or acetylacetonates in chloroform–methanol. Application of this method to the bilan-10-one I gave the corresponding metal complexes 1 with M = Co, Ni, Pd or Cu as the single products (Scheme 1). In a similar manner the bilan-5-ones V and VI could be converted into the corresponding metallobiladien-*bc*-5-ones 3 and 4 with M = Co, Pd, Cu or Ni (Schemes 3 and 4). In the case of Co, Pd and Cu again only a single product was formed during metallation. Metallation with nickel(II) acetate, however, yielded two different products (5 and 6), one being the expected metal complex (*e.g.* 2b) where the metal was chelated by the four pyrrole nitrogens the other being identified as a complex involving co-ordination of the *meso*-oxygen to the nickel (*e.g.* 5).

In order to prepare metal complexes with less complex side chains a new synthetic route to biladien-*ac*-10-ones was developed by condensation of 2 equivalents of pyrrole II with the bis(formylpyrrolyl)ketone III. The acid pyrrole was
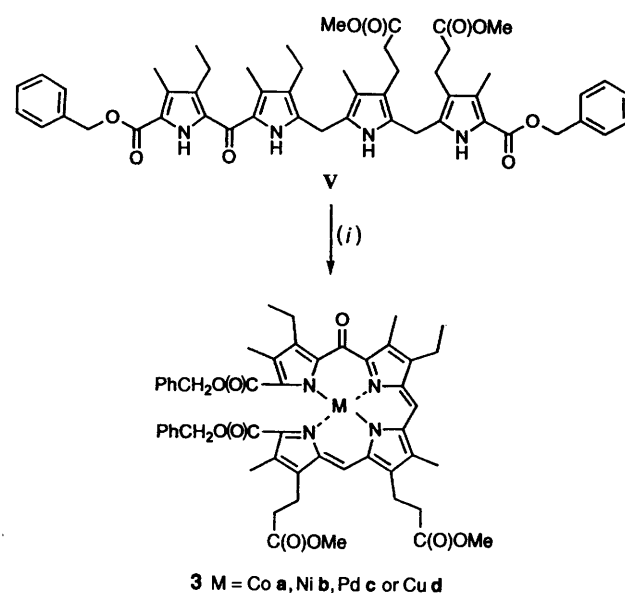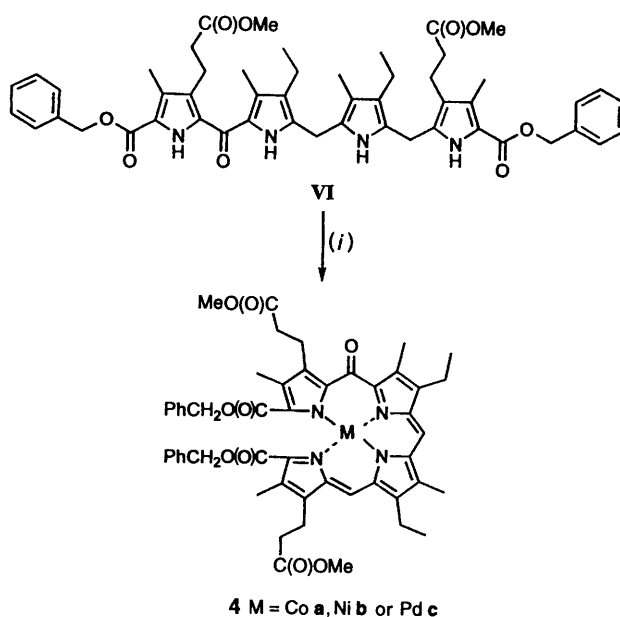
decarboxylated in trifluoroacetic acid and then condensed with the ketone in methanol (Scheme 2). Addition of diethyl ether at low temperature caused the product IV to precipitate in 85% yield. Although the synthesis of the biladien-*ac*-10-one IV is fairly direct and practical, the strategy followed can only be applied to the synthesis of symmetric oxobiladienes-*ac*. Metallation of IV with metal acetates in dry methanol and in the presence of sodium acetate proceeded smoothly and was completed after about 20 min of stirring. With the exception of the zinc and mercury complexes, the metal derivatives formed crystals and could then be easily isolated. The zinc and mercury derivatives required purification on alumina (grade III) using CH_2Cl_2 as the eluent. In all cases a single product was usually obtained after metallation.

10-Oxobiladiene-*ac* metal complexes

Structures. As a typical example of the metal complexes the palladium structure 1c is shown in Fig. 1. Structural data were also obtained for the corresponding complexes of Cu, Ni and Co, 1d, 1b and 1a. Selected bond lengths for this and other structures are compiled in Table 1. All metal complexes were of the ML type and M_2L_2 complexes were not formed in contrast

1 M = Co **a**, Ni **b**, Pd **c** or Cu **d**

Scheme 1 (*i*) (*a*) Br$_2$, tetrahydrofuran (thf), HBr; (*b*) [M(acac)$_2$] (acac = acetylacetonate), CHCl$_3$, MeOH

IV

2 M = Co **a**, Ni **b**, Pd **c**, Cu **d**, Zn **e**, Cd **f** or Hg **g**

Scheme 2

3 M = Co **a**, Ni **b**, Pd **c** or Cu **d**

Scheme 3 (*i*) (*a*) Br$_2$, thf, HBr; (*b*) [M(acac)$_2$], CHCl$_3$, MeOH

4 M = Co **a**, Ni **b** or Pd **c**

Scheme 4 (*i*) (*a*) Br$_2$, thf, HBr; (*b*) [M(acac)$_2$], CHCl$_3$, MeOH

5

6

Fig. 2 Side view of the macrocycle skeleton of complex **1d**. Hydrogen atoms and side-chain atoms have been omitted for clarity
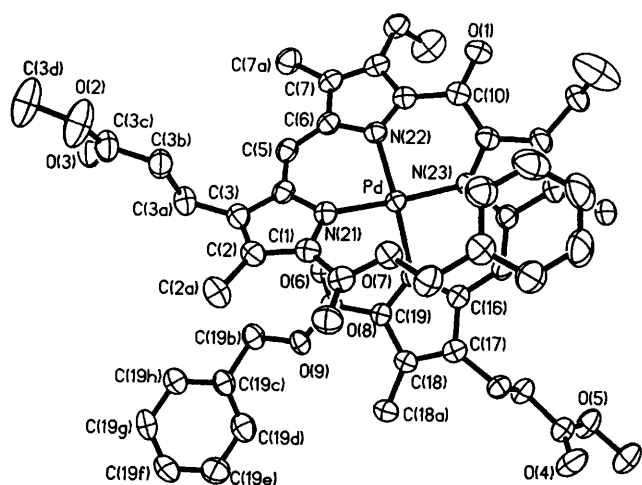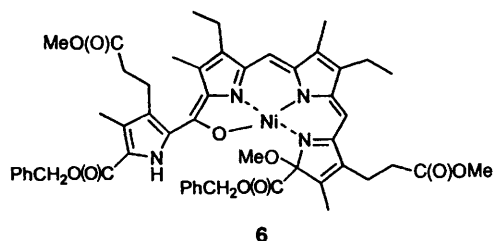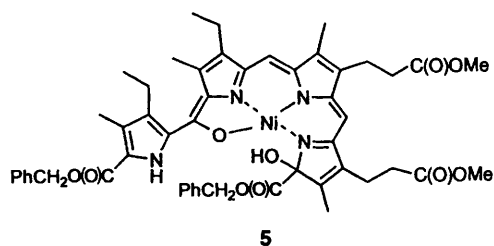

Fig. 1 Crystal structure and numbering scheme of complex **1c**. Ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity

Fig. 3 Crystal structure and numbering scheme of complex **1b**, form A. Details as in Fig. 1

to a zinc(II) biliverdin complex.[9] The general structural characteristics of the biladiene-*ac* ligand system in the different metal complexes are rather similar and agreed with those found for related systems.[15] The keto character of the *meso*-oxo function was clearly evidenced by C–O bond lengths in the order of 1.237–1.254 Å. The bis(dipyrrin) character, *i.e.* separation of the tetrapyrrole system into two dipyrrin halves separated by the *meso*-carbonyl group at C(10), is evidenced by the elongated C(9)–C(10) and C(10)–C(11) bond lengths. The C_a–C_m–C_a angles at C(10) are widened ($\approx 120°$) compared to those of *meso* groups involving conjugated groups of the dipyrromethene units at C(5) or C(15) (124–127°). The metal complexes are characterized by a helical conformation of the tetrapyrrole ligand co-ordinated *via* the four pyrrole nitrogens. The helical conformation is brought about by the steric interactions of the benzyl ester substituents at positions C(1) and C(19). These substituents lead to large separations between pyrrole rings I and IV as is illustrated in Fig. 2 for the complex **1d** [*e.g.* a C(1)···C(19) separation of 3.290 Å, see Table 3]. In contrast, a 1,19-di(ethoxycarbonyl)-2,3,7,8,12,13,17,18-octamethylbiladiene-*ac* dihydrobromide exhibited a quite different structure. There, the two dipyrrin units were folded away from each other and formed a dihedral angle of 107°.[16] A number of other biladiene-*ac* structures are known. However, these free-base structures are related to the naturally occurring bilirubins and show a ridge-tile conformation.[15]

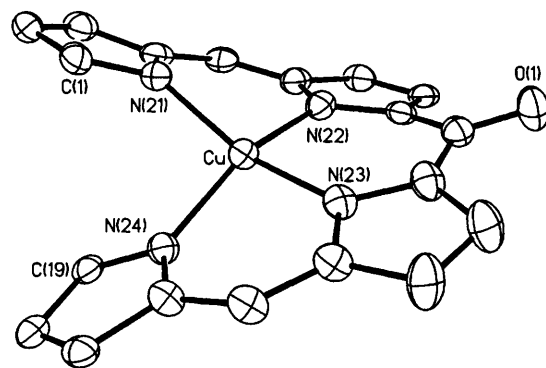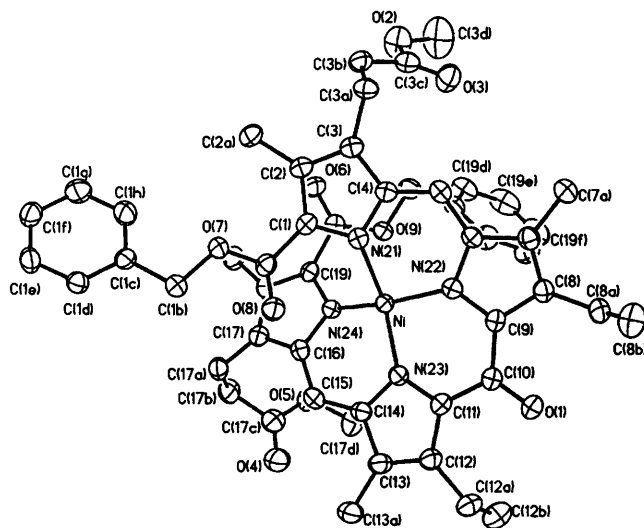The overall geometries of all metal complexes **1** are rather

similar. This is true not only for the monoclinic isostructural series (M = Cu, Pd or Co) but also for the respective nickel complex **1b** which crystallized in two different triclinic modifications (Fig. 3). Generally the two propionic methyl ester groups at C(3) and C(17) are extended away from the central part of the molecule and the two benzyl ester groups at C(1) and C(19) are similarly extended in opposite directions. However, in the latter case this leads to the orientation of one benzyl ester group over the face of the tetrapyrrole unit. Owing to the break in conjugation at C(10) the two dipyrrin units are not coplanar. Pyrroles II and III are tilted against each other by 18.8–25.1° (Table 3). Notably the individual dipyrrin units are not fully planar either, and the angles between rings I and II or III and IV range from 4.7 to 25.7°, respectively. With the exception of **1b** (form B) the largest bend in the tetrapyrrole unit is invariably found at C(10), where the *meso*-carbonyl group is located.

The co-ordination about the metal centres is tetrahedrally distorted in all cases. This is evidenced by the large deviations from planarity for the pyrrole nitrogens and the angles between the two N–M–N planes (Table 3) which increased in the order **1c** < **1a** < **1b** < **1d**. This is in agreement with the relative tendency of these metal(II) ions to retain square-planar co-ordination geometries. The observed co-ordination patterns are a result of the opposing forces of crystal-field stabilization energy and steric interactions, which favour planar and tetrahedrally distorted geometries, respectively. The ideal square-planar metal co-ordination is made impossible here by the helical conformation of the ligand system; due to the substituents at C(1) and C(19) a more planar co-ordination about the metal would have been only possible with major

distortions from planarity of the tetrapyrrole skeleton and loss of π-delocalization energy. Nevertheless, some distortion occurs in the two dipyrrin halves of the ligands as evidenced by the interpyrrole ring angles in Table 3. Thus, the pitch of the helices, often characterized by the C(1) ••• C(19) distances, is not as good a measure of the distortion in the metal chelate as is the degree of tetrahedral distortion in the MN_4 unit.

Compared to a bis(dipyrrin)[6b] and a bis(semicorrin) copper(II) complex,[17] for which crystal structures are available, the tetrahedral distortion in the MN_4 units is smaller in 1d since the tetrapyrrole system cannot distort as much as two individual dipyrrin units can rotate against each other. This is reflected in the relevant Cu–N bond lengths. The average Cu–N bond length in 1d is 1.963(4) Å, compared to 1.99(4) Å in the bis(dipyrrin) copper(II) complex.[6b] The relationship between Cu–N bond length and tetrahedral distortion has been shown for a number of copper(II) complexes with 4N ligands.[18] This is also reflected in the non-equivalence of the individual Cu–N bond lengths in 1d. Bonds to pyrrole rings II and III [average 1.952(4) Å] which are less out-of-plane are shorter than those to rings I and IV [average 1.975(4) Å]. Similar differences are found in the other metal complexes. Nevertheless, the Cu–N bond lengths found in 1d are slightly shorter than those found in copper(II) porphyrins with a square-planar metal co-ordination.[2b,19]

Similar trends are observed in the other metal complexes. Complex 1c shows the smallest degree of tetrahedral distortion and exhibits an average Pd–N bond length of 2.011(3) Å. This is slightly larger than in square-planar PdN_4 complexes [1.991–2.004(2) Å][20] and shorter than in a bis(dipyrrin) palladium(II) complex [2.028(10) Å],[6c] which was more distorted. The Pd–N bond lengths are comparable with those found in palladium(II) porphyrins, which show mostly square-planar co-ordination.[2b,19a,21] The Pd–N bond lengths of 2.01 Å were found in the structure of a palladium(II) secocorrinoid, which was also tetrahedrally distorted.[7a] Complex 1a shows an average Co–N bond length of 1.892(3) Å. Comparative data are 1.888(2) and 2.004(3) Å for almost square-planar[22] and pseudo-tetrahedral[23] CoN_4 complexes, respectively. Cobalt(II) porphyrins generally exhibit slightly longer Co–N bond lengths.[2b,24] Complex 1b exhibits an average Ni–N bond length of 1.892(3) Å, again shorter than Ni–N bond lengths found in porphyrins,[2b,25] and intermediate between those of other NiN_4 complexes with square-planar or distorted geometry.[26] These Ni–N bond lengths are directly comparable to those found in a nickel(II) A/D secocorrinoid (1.88 Å).[7a] Notably, the structure of a nickel(II) 5,15-dimethyl-5,15-dihydroporphyrin exhibits Ni–N bond lengths of 1.908(5) Å.[27] That structure can also be considered as a bis(dipyrrin) complex, albeit with much less possibility for tetrahedral distortion. The nickel complex of 2,3,7,8,12,13,17,18-octaethylbilin-1,19-dione, which exhibits a similar conformation to that of 1b, showed Ni–N bond lengths of 1.886(7) Å,[11] while a nickel(II) bis(dipyrrin) with larger distortion of the NiN_4 co-ordination sphere exhibited Ni–N bond lengths of 1.953(8) Å.[6c]

The complexes 1a, 1c and 1d form part of an isostructural series. These molecules pack in the crystal by formation of dimer-like structures which are related to each other by close contacts between the meso-carbonyl oxygen O(1) and the methylene group at C(3). The observed CH_2 ••• O=C contacts are of the order of 2.4–2.5 Å. Additionally π aggregation involving overlap of the pyrroles containing N(22) was found. The separation between neighbouring pyrrole II units is 3.5–3.6 Å. The unsolvated modification of 1b (form A) formed sheet-like structures in the crystal. Notable are close contacts between aromatic protons from the benzyl ester groups with carbonyl oxygens of the benzyl esters in neighbouring molecules. Similar aggregates were found in the solvated modification of 1b (form B). Here, interactions between aromatic protons and carbonyl oxygens from propionic methyl ester groups and between

methylene groups from propionic ester groups and the meso-carbonyl oxygen atom are found.

The structural trends observed in complexes 1 are retained in 2 and the overall structural characteristics in both series are comparable. A top view of the molecular structure of 2b and a side view of 2c are shown in Figs. 4 and 5, respectively. Of the three complexes studied crystallographically, the palladium complex shows the smallest degree of distortion in the MN_4 unit and the copper complex the largest. The M–N bond lengths are comparable to those found in 1, while the degree of distortion is slightly larger in 2 (Table 3). This might be due to the slightly higher steric demand of the sp^3-hybridized methyl group at C(1) and C(19) in 2 compared to the sp^2 carbonyl in 1.

With the exception of the meso-carbonyl group, no oxygen atoms are present in complexes 2 and crystal packings quite different from those described for 1 were found. All three compounds 2b–2d formed rather similar crystal structures, the last two being isostructural. The closely packed structures have intermolecular contacts involving methyl side chains and the metal centres of the order of 3.7 Å.

Spectroscopy. The NMR spectra of complexes 1b and 1c indicated a rather symmetric structure in solution. Only one proton signal was observed for the meso-H and β-pyrrole substituents. Similarly, 1b exhibited a singlet at δ 4.85 for the benzyl protons of the $PhCH_2O(O)C$-groups at C(1) and C(19) indicating a similar conformation for both ester groups, presumably extended away from the metal chelate system. A different situation was encountered in 1c where the benzyl signals were found as a complex multiplet (δ 4.66–4.92). This indicates diastereotopic CH_2 protons, presumably due to the fact that the structurally enforced helicity in the complexes introduced prochirality in the benzylic methylenes.

Similar results were found with the proton NMR spectra of
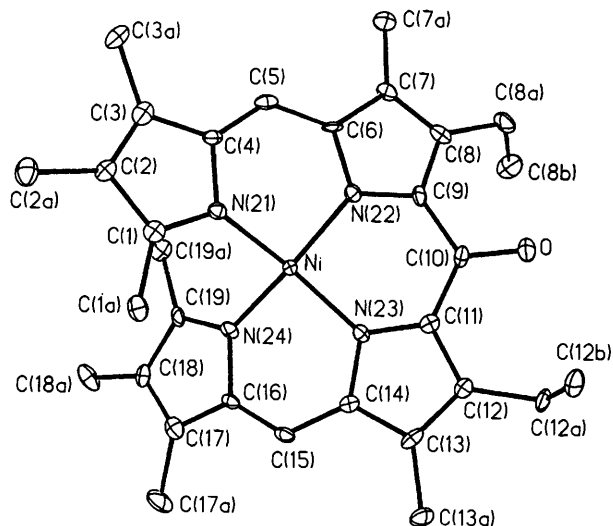

Fig. 4 Crystal structure and numbering scheme of complex 2b. Hydrogen atoms have been omitted for clarity
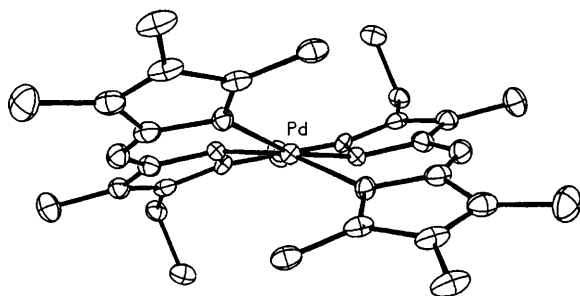

Fig. 5 Side view of the molecular structure of complex 2c. Hydrogen atoms have been omitted for clarity
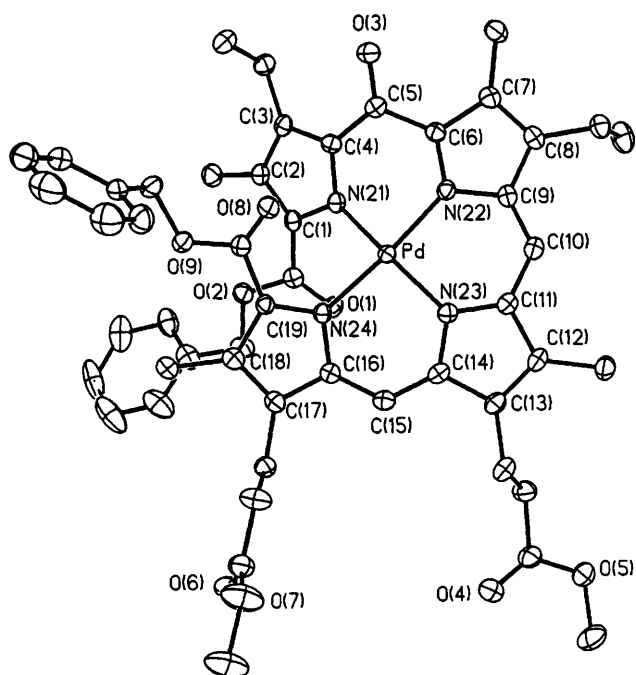
Fig. 6 Crystal structure and numbering scheme of complex **3c**. Details as in Fig. 1
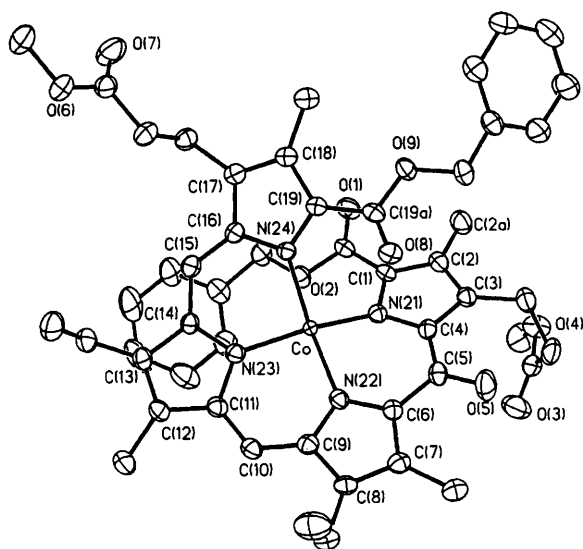

Fig. 7 Crystal structure and numbering scheme of complex **4a**. Details as in Fig. 1

complexes **2b**, **2c** and **2e–2g**. The spectra exhibited singlets for the meso-protons and the methyl groups and one ABX_3 system (ethyl groups with diastereotopic CH_2 protons). Both atrop-isomers were isolated for the cadmium complex **2f**, which were stable in solution showing no interconversion. One had an A_2X_3 system (ethyl CH_2) while the other had one ABX_3 system (ethyl groups with diastereotopic CH_2 protons). At room temperature the metal diethyloctamethylbiladien-ac-10-ones are locked into one conformation indicating a rigid structure for these molecules. The diastereotopicity of the ethyl CH_2 protons encountered in the ^1H NMR spectrum was maintained at high temperatures (375 K) for the nickel and cadmium complexes **2** indicating a restriction in their conformational flexibility.

The electronic absorption spectra of the metallobiladien-ac-10-ones are characterized by a main absorption band around 450 nm, along with one or two lower-intensity bands around 550 and 670 nm. The overall spectral type is that expected for a bis(dipyrrin) metal complex, since the 10-keto group effectively separates the tetrapyrrole into two dipyrrin units.[28] Falk and
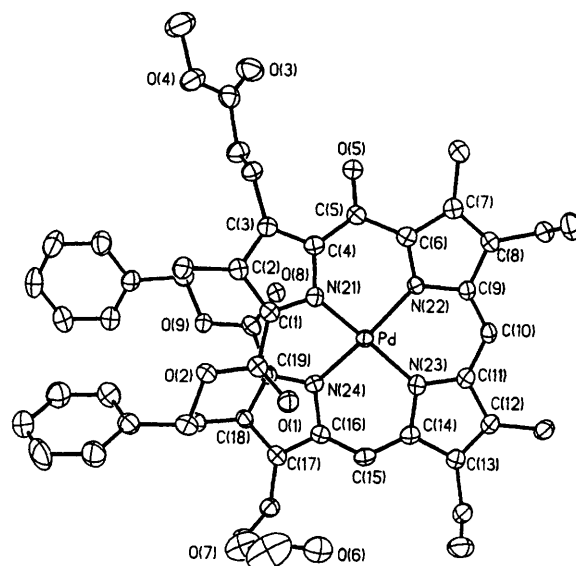

Fig. 8 Crystal structure of complex **4c**. Details as in Fig. 1

co-workers[28] have shown that the spectra of bis(dipyrrin) metal complexes depend strongly on the relative geometry of the dipyrrin units. In most cases the angles between the two dipyrrin units in **1** or **2** are rather similar and are in the range 27–36° (e.g. 35.9 in **2b**, 32.7° in **2c**, 36.2° in **2d**). The observed differences in the individual UV/VIS spectra have thus to be due to either metal effects or different conformations in solution. The difficulty of predicting the exact solution conformation prevents a detailed interpretation of the spectra.

5-Oxobiladiene-bc metal complexes with 4N co-ordination

Structures. Metal complexes were formed with two different biladien-bc-5-ones. As a typical example the structure of the palladium complex **3c** is shown in Fig. 6. Overall, the structures are similar to those observed for the chelates of biladien-ac-10-ones. However, a closer inspection reveals significant differences in the conformation of the tetrapyrrole ligand. The meso-carbonyl group at C(5) separates the ligand system into a pyrrole and a tripyrrin unit, clearly evidenced by the respective geometrical parameters of the ligand (Table 3). These are similar to those found in a 4,5-dimethoxybilin-bc-1,19-dione[29] and an etiotripyrrinone aldehyde.[30] Interruption of the conjugation at C(5) allows larger tilts of pyrrole ring I against the rest of the molecule; this is shown by the larger pyrrole tilt angles for ring I versus II. Both in **3c** and **3d** the steric hindrance induced by the substituents at C(1) and C(19) leads to larger tilt angles between rings IV and III compared to ring II versus III. Although the conformational properties of the biladiene-bc ligands in **1** or **2** are quite different from those of the biladienes-ac in **3** and **4**, the degree of tetrahedral distortion of the metal co-ordination is about the same with both ligand types. For example, the angles between the planes N(21)–Cu–N(22) and N(23)–Cu–N(24) are 33.7, 34.2 and 34.2° in **1d**, **2d** and **3d**, respectively while the corresponding Cu–N bond lengths are on average 1.963(4), 1.955(3) and 1.973(3) Å. Similar trends are observed in the N–M–N bond angles.

The molecular packing of complex **3c** is characterized by the formation of dimers in the crystal which are held together by an intricate network of aromatic and aliphatic C–H···O interactions of the type described for complexes **1**. The hydrogen–oxygen contacts are in the order of 2.6 Å. Close intermolecular contacts in the structure of **3d** involved aromatic C–H ester carbonyl interactions [H(1b)···O(1) 2.6 Å] and the metal centre and alkyl side chain [Cu···C(8a) 3.716 Å].

Switching of the substituent pattern of the tetrapyrrole ligand from type **3** to type **4** did not lead to major changes in the

Table 1 Selected bond lengths (Å) and angles (°) for the macrocycle atoms of the metallooxobiladienes

	1d	1c	1b[a]	1a	2b	2c	2d	3d	3c	4c	4a
M–N(21)	1.967(4)	2.022(3)	1.901(3)	1.900(10)	1.888(3)	2.018(5)	1.972(3)	1.947(2)	2.010(3)	2.020(4)	1.965(3)
M–N(22)	1.956(4)	1.994(3)	1.882(3)	1.894(9)	1.877(3)	1.998(5)	1.937(3)	1.971(3)	1.989(3)	2.000(4)	1.944(3)
M–N(23)	1.948(4)	2.004(3)	1.890(3)	1.889(11)	1.885(3)	b	b	1.948(2)	2.000(3)	2.009(4)	1.948(3)
M–N(24)	1.982(4)	2.024(3)	1.895(3)	1.893(10)	1.890(3)	b	b	2.024(3)	2.033(3)	2.022(4)	1.973(3)
N(21)–C(1)	1.355(6)	1.356(5)	1.364(4)	1.355(15)	1.351(4)	1.398(8)	1.335(4)	1.360(5)	1.370(4)	1.354(7)	1.365(5)
N(21)–C(4)	1.383(6)	1.381(4)	1.376(6)	1.381(15)	1.421(5)	1.331(8)	1.400(4)	1.372(5)	1.363(5)	1.367(6)	1.368(5)
N(22)–C(6)	1.385(6)	1.390(5)	1.386(6)	1.399(16)	1.401(5)	1.391(8)	1.378(4)	1.335(4)	1.333(5)	1.337(6)	1.341(5)
N(22)–C(9)	1.343(6)	1.330(4)	1.362(4)	1.348(16)	1.362(4)	1.368(7)	1.363(4)	1.394(4)	1.400(5)	1.401(7)	1.389(5)
N(23)–C(11)	1.363(7)	1.354(5)	1.357(4)	1.365(17)	1.355(5)	b	b	1.370(4)	1.363(5)	1.354(7)	1.374(5)
N(23)–C(14)	1.384(6)	1.381(4)	1.385(5)	1.380(15)	1.384(5)	b	b	1.364(5)	1.371(5)	1.381(6)	1.367(5)
N(24)–C(16)	1.390(6)	1.386(4)	1.383(5)	1.392(15)	1.405(5)	b	b	1.398(4)	1.376(5)	1.389(6)	1.400(5)
N(24)–C(19)	1.332(6)	1.339(4)	1.360(5)	1.353(17)	1.339(5)	b	b	1.337(4)	1.341(6)	1.356(7)	1.332(5)
C(1)–C(2)	1.424(8)	1.415(5)	1.427(6)	1.416(18)	1.441(5)	1.442(9)	1.433(5)	1.414(4)	1.406(6)	1.408(7)	1.394(5)
C(2)–C(3)	1.373(7)	1.374(5)	1.376(6)	1.386(16)	1.361(6)	1.376(10)	1.365(5)	1.391(6)	1.393(5)	1.382(7)	1.383(5)
C(3)–C(4)	1.430(8)	1.419(5)	1.435(4)	1.417(18)	1.426(5)	1.439(9)	1.448(4)	1.409(4)	1.421(5)	1.421(7)	1.417(5)
C(4)–C(5)	1.386(7)	1.393(5)	1.379(5)	1.367(16)	1.353(5)	1.365(9)	1.360(5)	1.456(6)	1.446(5)	1.437(7)	1.450(5)
C(5)–C(6)	1.380(7)	1.387(5)	1.397(5)	1.370(18)	1.397(5)	1.398(9)	1.408(4)	1.493(4)	1.499(6)	1.479(7)	1.480(5)
C(6)–C(7)	1.440(7)	1.441(5)	1.435(5)	1.448(17)	1.422(5)	1.412(9)	1.419(4)	1.451(5)	1.449(5)	1.446(7)	1.441(5)
C(7)–C(8)	1.364(8)	1.355(5)	1.372(6)	1.337(19)	1.375(5)	1.400(9)	1.377(5)	1.361(4)	1.369(6)	1.363(7)	1.359(5)
C(8)–C(9)	1.438(6)	1.440(5)	1.424(6)	1.431(16)	1.425(6)	1.419(9)	1.424(4)	1.443(5)	1.442(5)	1.445(6)	1.444(5)
C(9)–C(10)	1.476(7)	1.487(5)	1.468(6)	1.435(18)	1.463(5)	1.471(7)	1.469(4)	1.370(4)	1.368(6)	1.362(7)	1.374(5)
C(10)–C(11)	1.460(7)	1.463(5)	1.465(5)	1.452(17)	1.451(5)	1.471(7)	1.469(4)	1.408(5)	1.400(5)	1.407(6)	1.400(5)
C(11)–C(12)	1.424(8)	1.428(5)	1.423(6)	1.401(19)	1.426(6)	b	b	1.437(4)	1.438(6)	1.437(7)	1.435(5)
C(12)–C(13)	1.382(8)	1.372(5)	1.374(5)	1.399(18)	1.386(5)	b	b	1.371(5)	1.363(5)	1.365(7)	1.364(5)
C(13)–C(14)	1.422(8)	1.428(6)	1.433(6)	1.428(20)	1.414(5)	b	b	1.443(4)	1.442(6)	1.432(7)	1.438(5)
C(14)–C(15)	1.388(7)	1.396(5)	1.387(5)	1.396(17)	1.416(5)	b	b	1.393(5)	1.390(5)	1.386(7)	1.409(5)
C(15)–C(16)	1.378(7)	1.382(5)	1.379(6)	1.361(18)	1.362(6)	b	b	1.380(4)	1.384(6)	1.377(7)	1.375(5)
C(16)–C(17)	1.434(7)	1.442(5)	1.432(5)	1.440(16)	1.432(5)	b	b	1.442(5)	1.434(5)	1.426(7)	1.441(5)
C(17)–C(18)	1.371(7)	1.375(5)	1.386(7)	1.365(18)	1.373(6)	b	b	1.364(5)	1.374(7)	1.372(7)	1.377(5)
C(18)–C(19)	1.433(7)	1.430(4)	1.416(5)	1.426(16)	1.439(5)	b	b	1.439(5)	1.432(5)	1.434(6)	1.434(5)
C_m–O	1.237(6)	1.239(5)	1.236(4)	1.254(16)	1.257(4)	1.246(10)	1.237(5)	1.231(5)	1.236(5)	1.233(5)	1.239(5)
N(21)–M–N(22)	90.2(2)	89.6(1)	92.2(1)	91.6(4)	92.6(1)	90.7(3)	91.5(2)	89.5(1)	87.2(1)	88.8(2)	90.3(1)
N(21)–M–N(23)	159.7(2)	167.0(1)	161.0(2)	163.6(4)	158.7(2)	163.2(2)	155.6(1)	156.9(1)	163.8(2)	166.0(1)	157.1(1)
N(22)–M–N(23)	90.8(2)	90.4(1)	92.6(1)	91.0(4)	92.2(1)	90.6(3)	91.6(1)	91.1(1)	91.7(1)	90.6(2)	91.9(1)
N(21)–M–N(24)	90.8(2)	93.2(1)	91.2(1)	91.2(4)	92.0(1)	b	b	98.1(1)	94.0(1)	93.8(2)	99.0(1)
N(22)–M–N(24)	152.7(2)	162.3(1)	158.2(2)	157.7(4)	156.9(2)	b	b	154.5(1)	169.2(2)	167.8(1)	151.7(1)
N(23)–M–N(24)	91.5(2)	90.7(1)	91.1(1)	92.6(4)	91.7(1)	b	b	91.2(1)	90.0(1)	89.8(2)	89.8(1)
M–N(21)–C(1)	128.7(3)	129.4(2)	127.3(3)	128.6(8)	128.2(3)	129.0(4)	129.7(2)	124.6(2)	125.7(2)	128.1(3)	125.8(2)
M–N(21)–C(4)	121.9(3)	123.1(2)	125.6(2)	124.5(8)	125.1(2)	123.6(4)	122.0(2)	126.6(2)	125.3(2)	123.3(3)	124.1(2)
C(1)–N(21)–C(4)	106.0(4)	106.2(3)	105.7(3)	105.9(10)	106.5(3)	107.4(5)	107.1(3)	105.9(2)	107.0(3)	106.8(4)	105.5(3)
M–N(22)–C(6)	122.4(3)	120.9(2)	122.9(2)	121.1(8)	122.0(2)	121.0(4)	121.7(2)	126.6(2)	126.4(3)	125.8(3)	125.8(2)
M–N(22)–C(9)	128.5(3)	127.2(3)	127.7(3)	129.5(8)	127.3(2)	126.5(4)	127.5(2)	127.0(2)	126.1(2)	126.4(3)	126.0(2)
C(6)–N(22)–C(9)	106.5(4)	106.8(3)	105.6(3)	106.6(9)	105.3(3)	106.3(5)	106.6(3)	106.4(3)	107.0(3)	107.1(4)	106.4(3)
M–N(23)–C(11)	129.0(3)	127.7(2)	129.5(3)	130.0(8)	128.6(2)	b	b	128.4(2)	126.0(2)	127.2(3)	127.1(2)
M–N(23)–C(14)	124.8(3)	123.9(2)	122.9(2)	124.0(9)	121.6(2)	b	b	124.9(2)	124.5(2)	124.2(3)	126.2(2)
C(11)–N(23)–C(14)	105.7(4)	106.2(3)	105.9(3)	104.4(10)	106.2(3)	b	b	106.0(2)	107.2(3)	106.2(4)	106.1(3)
M–N(24)–C(16)	122.8(3)	123.9(2)	124.8(3)	124.8(8)	124.9(3)	b	b	120.2(2)	123.6(3)	123.9(3)	124.2(2)
M–N(24)–C(19)	129.9(3)	129.7(2)	127.6(3)	129.5(8)	128.5(3)	b	b	131.4(2)	128.9(3)	130.0(3)	129.0(2)
C(16)–N(24)–C(19)	105.5(4)	106.1(3)	105.6(3)	105.4(10)	106.5(3)	b	b	105.1(3)	106.4(3)	105.6(4)	105.7(3)
N(21)–C(1)–C(2)	111.2(4)	110.8(3)	111.3(4)	110.6(10)	110.5(3)	110.7(5)	111.1(3)	111.0(3)	110.3(3)	110.6(4)	111.5(3)
C(1)–C(2)–C(3)	106.1(4)	106.5(3)	106.0(3)	107.0(11)	106.6(3)	106.6(5)	106.7(3)	106.1(3)	106.4(3)	106.5(4)	106.4(3)
C(2)–C(3)–C(4)	107.0(5)	106.8(3)	106.8(4)	105.6(11)	108.4(3)	106.6(6)	106.9(3)	106.4(3)	106.6(3)	106.5(4)	106.3(3)
N(21)–C(4)–C(3)	109.6(4)	109.6(3)	110.0(3)	110.6(10)	108.0(3)	108.5(5)	108.2(3)	110.6(3)	109.6(3)	109.5(4)	110.3(3)
N(21)–C(4)–C(5)	123.4(5)	122.1(3)	121.6(3)	121.7(11)	121.1(3)	122.4(6)	122.8(3)	122.7(3)	122.3(4)	124.8(5)	123.3(3)
C(3)–C(4)–C(5)	127.0(5)	127.9(3)	128.3(4)	127.5(11)	130.7(4)	128.2(6)	128.8(3)	126.7(3)	127.4(3)	125.3(4)	126.4(3)
C(4)–C(5)–C(6)	126.5(5)	127.6(3)	125.4(4)	125.7(11)	126.8(4)	128.8(6)	127.9(3)	119.3(3)	119.5(4)	120.2(4)	122.2(3)
N(22)–C(6)–C(5)	122.9(4)	124.2(3)	123.8(3)	124.2(11)	122.2(3)	126.8(6)	122.2(3)	124.2(3)	124.0(3)	124.6(4)	122.9(3)
N(22)–C(6)–C(7)	109.2(4)	108.6(3)	109.7(3)	107.6(11)	109.7(3)	109.8(5)	109.6(3)	111.5(3)	111.0(4)	110.6(4)	111.2(3)
C(5)–C(6)–C(7)	127.8(5)	127.2(3)	126.5(4)	128.2(12)	128.0(4)	126.8(6)	128.0(3)	124.3(3)	125.0(3)	124.8(4)	125.9(3)
C(6)–C(7)–C(8)	106.9(4)	107.3(3)	107.0(4)	107.9(10)	107.3(3)	107.1(6)	107.2(3)	105.7(3)	106.1(3)	106.7(4)	106.3(3)
C(7)–C(8)–C(9)	106.3(4)	106.2(3)	106.2(3)	107.1(10)	106.3(3)	106.1(5)	106.4(3)	107.5(3)	107.2(4)	107.0(4)	107.0(3)
N(22)–C(9)–C(8)	111.0(4)	111.2(3)	111.5(3)	110.6(10)	111.4(3)	110.8(5)	110.2(3)	109.0(3)	108.5(3)	108.4(4)	109.1(3)
N(22)–C(9)–C(10)	121.9(4)	123.5(3)	122.8(3)	120.7(10)	121.8(3)	122.9(5)	122.1(3)	123.7(3)	123.8(3)	124.3(4)	123.3(3)
C(8)–C(9)–C(10)	127.0(4)	125.2(3)	125.7(3)	128.7(11)	126.5(3)	126.3(6)	127.5(3)	127.3(3)	127.6(4)	127.0(5)	127.6(3)
C(9)–C(10)–C(11)	120.9(4)	120.1(3)	120.2(3)	122.3(12)	119.3(3)	121.3(7)	120.9(4)	126.5(3)	127.6(4)	127.1(5)	126.6(3)
N(23)–C(11)–C(10)	122.8(5)	124.0(3)	122.4(4)	120.3(11)	123.2(2)	b	b	122.8(3)	124.3(4)	123.9(4)	121.8(3)
N(23)–C(11)–C(12)	111.2(4)	110.6(3)	111.2(3)	113.2(11)	110.7(3)	b	b	110.6(3)	109.7(3)	110.7(4)	110.0(3)
C(10)–C(11)–C(12)	125.7(5)	125.4(3)	126.4(3)	126.3(12)	126.0(3)	b	b	126.6(3)	125.9(4)	125.3(5)	127.6(3)
C(11)–C(12)–C(13)	106.1(5)	106.7(3)	106.6(3)	105.3(12)	106.2(3)	b	b	106.5(3)	106.9(4)	106.4(5)	107.0(3)
C(12)–C(13)–C(14)	106.9(5)	106.5(3)	106.5(4)	106.7(4)	106.7(4)	b	b	106.3(3)	106.9(3)	106.9(4)	106.4(3)
N(23)–C(14)–C(13)	110.1(4)	109.9(3)	109.8(3)	110.6(11)	110.1(3)	b	b	110.6(3)	109.2(3)	109.8(4)	110.4(3)
N(23)–C(14)–C(15)	123.3(5)	124.7(3)	123.9(4)	124.9(12)	122.3(4)	b	b	122.9(3)	124.8(4)	123.7(4)	122.7(3)
C(13)–C(14)–C(15)	126.5(5)	125.4(3)	126.2(4)	124.3(12)	127.2(4)	b	b	126.1(3)	126.0(4)	126.5(4)	126.6(3)
C(14)–C(15)–C(16)	127.4(4)	127.7(3)	125.3(4)	124.3(11)	125.8(4)	b	b	127.3(3)	127.1(4)	128.1(4)	125.9(3)
N(24)–C(16)–C(15)	122.8(4)	123.1(3)	120.8(3)	123.0(10)	121.2(3)	b	b	124.3(3)	123.5(3)	123.1(4)	123.3(3)
N(24)–C(16)–C(17)	109.3(4)	109.2(3)	109.8(4)	108.9(10)	108.8(3)	b	b	109.7(3)	109.4(4)	109.7(4)	109.1(3)

	1d	1c	1b[a]	1a	2b	2c	2d	3d	3c	4c	4a
C(15)–C(16)–C(17)	127.5(4)	126.7(3)	129.0(4)	126.5(11)	129.4(3)	b	b	126.0(3)	126.7(3)	126.4(4)	127.3(3)
C(16)–C(17)–C(18)	107.6(4)	106.8(3)	106.9(4)	107.9(10)	107.2(3)	b	b	106.9(3)	107.1(3)	107.5(4)	107.1(3)
C(17)–C(18)–C(19)	104.7(4)	105.7(3)	105.7(3)	105.3(11)	106.3(3)	b	b	105.6(3)	105.4(4)	105.6(4)	105.3(3)
N(24)–C(19)–C(18)	113.0(4)	112.0(3)	112.0(4)	112.5(11)	111.1(3)	b	b	112.6(3)	111.6(4)	111.6(4)	112.8(3)
C$_a$–C$_m$–O^a	119.6(5)	120.0(3)	120.0(4)	118.9(12)	120.3(3)	119.3(4)	119.6(2)	120.3(4)	120.2(4)	119.8(5)	119.0(3)

^{a} Average of geometrically equivalent positions. ^{b} Generated by symmetry operation: $-x, y, -z + \frac{1}{2}$.

structure of the metal complexes. The molecular structures of **4a** and **4c** are shown in Figs. 7 and 8, respectively. A comparison of **3c** and **4c** shows rather similar degrees of tetrahedral distortion and M–N bond lengths. The molecules show some differences in the conformation of the side-chain esters. The relative conformation of the benzyl ester chains in **4a** resembles more the situation found in **1c** or **1b**, while their conformation in **4c** is similar to that found in **3c**. Notable differences are found in a comparison of the structures of **1a** and **4a**. The degree of tetrahedral distortion in the latter is much larger (angle between MN$_2$ planes 36.3°) than in the former (27.4°). This is mirrored in longer Co–N bond lengths in **4a** [1.958(3) Å] compared to **1a** [1.892(10) Å].

Compound **4a** showed molecular packing similar to that described for **3d**; however, no unusually short intermolecular contacts were observed. The molecules of **4c** packed by formation of a network connected by a number of C–H ··· O interactions involving both ester oxygen atoms and the carbonyl oxygen at C(5) (range 2.4–2.55 Å).

Spectroscopy. Proton NMR spectra of the nickel and palladium complexes **3** and **4** indicated solution structures rather similar to those found in the solid state. Different signals were observed for all proton groups, including those of the benzene rings or the methyl ester groups. As was observed for some biladien-ac-10-one complexes **1**, the benzyl protons in **3b**, **4b**, **3c** and **4c** were found to be diastereotopic due to prochirality introduced by the enforced helical conformations in these compounds. Signals for these protons were usually found as multiplets around δ 4.4–4.9. The 500 MHz NMR spectra showed the multiplets to consist of four sets of doublets with J = 12.5 Hz in line with two different AX systems. Differences between the spectra of the nickel and palladium complexes are found for the meso-proton signals. While for the palladium complexes both meso-proton signals were found close together around δ 7.2–7.4, a larger separation was found for the nickel complexes **3b** and **4b**. Here one meso-H signal was observed around δ 7.4 and the other around δ 6.4.

The 5-keto group effectively separates the tetrapyrrole system into a pyrrole and a tripyrrin system. Thus, electronic absorption spectra characteristic for the latter fragment were expected and found. No significant differences were found between spectra of complexes **3** and **4**. However, two different types of spectra were found for different metal complexes in either series. The complexes of Cu and Pd exhibited spectra with two main bands centred around 400 and 760 nm. The long-wavelength band is shifted bathochromically by about 200 nm when compared to those of non-metallated tripyrrin systems.[3] In contrast, the spectra of the complexes of Ni and Co exhibit a main absorption band around 350 nm and six overlapping bands of similar intensity in the region 400–750 nm, indicating substantial differences in their structural characteristics when compared with the complexes of Cu and Pd.

5-Oxobiladiene-bc metal complexes with (3N + O) co-ordination

Two molecules with quite different structures (Table 2) were obtained from the metallation of the ligand system in **3** and **4**
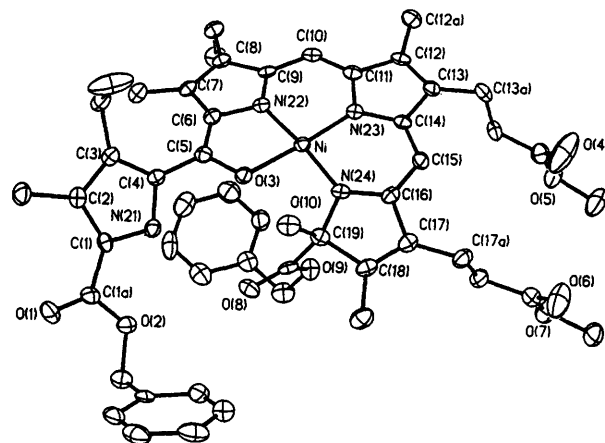

Fig. 9 Crystal structure and numbering scheme of complex **5**. Details as in Fig. 1
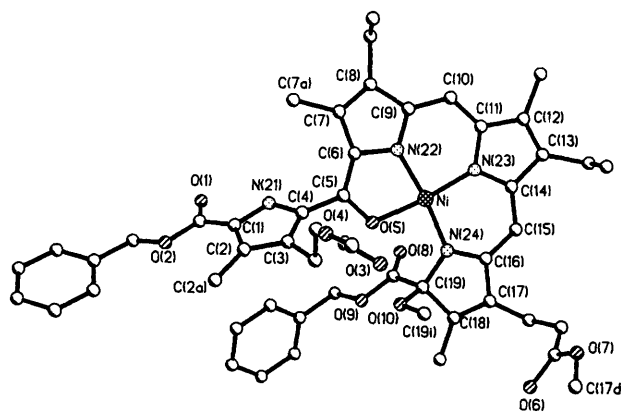
Fig. 10 Crystal structure and numbering scheme of complex **6**. Details as in Fig. 1

with nickel(II) acetate. Not only do the nickel complexes **5** (Fig. 9) and **6** (Fig. 10) show coordination to three pyrrole nitrogens and the meso-oxygen atom, but nucleophilic attack had also occurred in the ligand system at C(19). In **5** a hydroxyl group and in **6** a methoxyl group have been added leading to an sp^3-hybridized carbon centre in pyrrole IV. Similar substitution reactions at terminal C$_a$ positions have been described in the literature.[29] Introduction of these groups is possibly responsible for the observed metal co-ordination pattern. The presence of two substituents at C(19) increases the steric demand in its vicinity to such a degree that MN$_4$ co-ordination with the large benzyl ester group at C(1) is no longer possible. The only way co-ordinatively to saturate the metal atom lies in involvement of the meso-carbonyl oxygen which also requires rotation of the pyrrole I unit away from the rest of the remaining tripyrrin part. This is evidenced by the large tilt angles (50.9° in **5** and 57.4° in **6**) between pyrroles I and II. A similar co-ordination of the nickel centre to three pyrrole nitrogens and one oxygen atom was proposed for a 19-ethoxy-2,2,7,8,12,13,18,19-octamethyl-2,3,17,18-tetrahydrobilatriene-3,17-diene by Gossauer and Inhoffen.[31] However, in that case the oxo function involved in

Table 2 Selected bond lengths (Å) and bond angles (°) of compounds **5** and **6**

	6	**5**		**6**	**5**
Ni–N(22)	1.827(7)	1.816(3)	C(5)–O(5)	1.301(11)	1.318(4)
Ni–N(23)	1.862(5)	1.848(3)	C(6)–C(7)	1.425(12)	1.440(5)
Ni–N(24)	1.845(7)	1.848(3)	C(7)–C(8)	1.333(9)	1.382(5)
Ni–O(5)	1.886(4)	1.888(3)	C(8)–C(9)	1.442(14)	1.448(5)
N(21)–C(1)	1.366(7)	1.374(5)	C(9)–C(10)	1.404(11)	1.411(5)
N(21)–C(4)	1.361(14)	1.357(5)	C(10)–C(11)	1.369(15)	1.369(5)
N(22)–C(6)	1.395(10)	1.387(5)	C(11)–C(12)	1.451(14)	1.468(5)
N(22)–C(9)	1.350(9)	1.338(4)	C(12)–C(13)	1.324(19)	1.353(5)
N(23)–C(11)	1.402(11)	1.396(4)	C(13)–C(14)	1.437(11)	1.459(5)
N(23)–C(14)	1.362(13)	1.371(5)	C(14)–C(15)	1.415(13)	1.383(5)
N(24)–C(16)	1.343(10)	1.337(5)	C(15)–C(16)	1.361(10)	1.398(5)
N(24)–C(19)	1.465(8)	1.474(5)	C(16)–C(17)	1.465(11)	1.473(5)
C(1)–C(2)	1.385(14)	1.391(5)	C(17)–C(18)	1.312(11)	1.335(6)
C(2)–C(3)	1.422(12)	1.409(5)	C(18)–C(19)	1.532(12)	1.517(5)
C(3)–C(4)	1.380(10)	1.395(5)	C(19)–C(19a)	1.533(15)	1.549(6)
C(4)–C(5)	1.452(9)	1.459(5)	C(19)–O(10)	1.410(8)	1.406(5)
C(5)–C(6)	1.390(9)	1.386(5)	O(10)–C(19i)	1.372(16)	—
N(21)–Ni–N(22)	90.9(3)	91.3(1)	C(5)–C(6)–C(7)	143.2(7)	140.2(4)
N(22)–Ni–N(24)	173.1(3)	173.9(1)	C(6)–C(7)–C(8)	108.8(8)	106.0(3)
N(23)–Ni–N(24)	94.9(3)	94.4(1)	C(7)–C(8)–C(9)	108.3(8)	107.9(3)
N(22)–Ni–O(5)	83.2(2)	83.4(1)	N(22)–C(9)–C(8)	107.0(6)	108.3(3)
N(23)–Ni–O(5)	173.9(3)	174.6(1)	N(22)–C(9)–C(10)	118.9(9)	119.6(3)
N(24)–Ni–O(5)	91.1(2)	90.9(1)	C(8)–(9)–C(10)	133.9(7)	132.2(3)
Ni–N(22)–C(6)	115.5(4)	115.6(2)	C(9)–C(10)–C(11)	123.5(7)	122.7(3)
Ni–N(22)–C(9)	134.8(6)	134.0(3)	N(23)–C(11)–C(10)	125.0(7)	124.9(3)
Ni–N(23)–C(11)	126.6(6)	126.8(2)	N(23)–C(11)–C(12)	106.5(9)	108.6(3)
Ni–N(23)–C(14)	126.4(5)	126.3(2)	C(10)–C(11)–C(12)	128.5(8)	126.4(3)
Ni–N(24)–C(16)	127.4(4)	128.0(2)	C(11)–C(12)–C(13)	109.7(8)	107.5(3)
Ni–N(24)–C(19)	123.7(6)	123.6(2)	C(12)–C(13)–C(14)	106.4(10)	107.1(3)
Ni–O(5)–C(5)	114.1(4)	113.8(2)	N(23)–C(14)–C(13)	110.4(9)	110.0(3)
C(1)–N(21)–C(4)	110.0(7)	109.4(3)	N(23)–C(14)–C(15)	122.0(6)	124.2(3)
C(6)–N(22)–C(9)	109.8(7)	109.4(3)	C(13)–C(14)–C(15)	127.5(9)	125.8(3)
C(11)–N(23)–C(14)	106.9(6)	106.9(3)	C(14)–C(15)–C(16)	125.5(9)	123.4(3)
C(16)–N(24)–C(19)	107.7(6)	108.2(3)	N(24)–C(16)–C(15)	123.4(8)	123.5(3)
N(21)–C(1)–C(2)	108.3(8)	107.9(3)	N(24)–C(16)–C(17)	111.3(6)	110.6(3)
C(1)–C(2)–C(3)	106.1(6)	107.3(3)	C(15)–C(16)–C(17)	125.1(8)	125.9(3)
C(2)–C(3)–C(4)	108.0(9)	106.9(3)	C(16)–C(17)–C(18)	107.8(8)	108.4(3)
N(21)–C(4)–C(3)	107.5(6)	108.5(3)	C(17)–C(18)–C(19)	109.3(7)	108.4(3)
N(21)–C(4)–C(5)	123.4(7)	119.4(3)	N(24)–C(19)–C(18)	103.7(6)	104.4(3)
C(3)–C(4)–C(5)	129.1(10)	131.7(4)	N(24)–C(19)–C(19a)	108.0(6)	110.3(3)
C(4)–C(5)–C(6)	127.0(8)	128.4(3)	C(18)–C(19)–C(19a)	108.9(8)	109.9(3)
C(4)–C(5)–O(5)	116.4(6)	115.9(3)	N(24)–C(19)–O(10)	115.1(7)	113.2(3)
C(6)–C(5)–O(5)	116.6(6)	115.6(3)	C(18)–C(19)–O(10)	111.7(6)	110.7(3)
N(22)–C(6)–C(5)	110.6(7)	111.3(3)	C(19a)–C(19)–O(10)	109.2(6)	108.4(3)
N(22)–C(6)–C(7)	106.1(5)	108.4(3)	C(19)–O(10)–C(19i)	115.0(6)	

Table 3 Selected structural parameters of the metal complexes studied

Compound	MN_4 distortion ^{a}	$\Delta 4N^b$/Å	$\Delta(3N + O)^c$/Å	$\Delta 23^d$/Å	Angles (°) between pyrrole planes			Distances/Å	
					I–II	II–III	III–IV	C(1)···C(19)	C(1A)···C(19A)
1d	33.7	0.400	—	0.571	10.6	24.9	15.7	3.290	3.771
1a	27.4	0.319	—	0.524	13.7	23.9	15.8	3.065	3.769
1c	21.9	0.267	—	0.479	11.5	25.1	13.8	3.229	3.599
1b (form A)	28.6	0.272	—	0.518	4.7	18.8	16.0	2.941	3.771
1b (form B)	30.3	0.355	—	0.618	11.1	23.4	16.6	3.096	3.636
2b	31.0	0.292	—	0.665	13.2	23.3	23.0	3.265	3.914
2c	23.6	0.292	—	0.591	14.8	26.6	14.8	3.370	3.629
2d	34.2	0.412	—	0.673	13.4	25.7	13.4	3.392	3.792
3c	19.5	0.234	—	0.353	28.7	2.7	9.7	3.088	3.493
3d	34.2	0.410	—	0.520	21.5	7.2	13.6	3.265	3.743
4a	36.3	0.429	—	0.609	7.5	19.3	17.7	3.314	3.694
4c	18.6	0.228	—	0.357	13.3	3.8	14.0	3.146	3.361
5	2.3	0.176	0.015	0.181	50.9	9.5	4.7	5.732	5.348
6	4.1	0.082	0.043	0.237	57.4	1.1	12.1	6.796	6.522

^{a} Angle between the two MN_2 planes in the MN_4 unit; in complexes **5** and **6** the angle between the NiNO and NiN_2 plane. ^{b} Deviations of the four pyrrole nitrogens from their least-squares plane. ^{c} Deviations of the nitrogens and oxygens bonded to the metal centre from their least-squares plane. ^{d} Deviations of the 23 macrocycle atoms (pyrrole nitrogens and ring carbon atoms) from their least-squares plane.

the co-ordination was a β-pyrrole and co-ordination to the oxygen required rotation of a pyrrole unit by 180°.

In contrast to the metal complexes with 4N co-ordination the NiN_3O unit exhibits a square-planar co-ordination geometry

with only minute deviations from planarity (Table 3). The Ni–N bond distances in 5 [1.845(6) Å] and 6 [1.837(3) Å] are shorter than in the other nickel complexes with tetrahedral distortion described here. The Ni–N and Ni–O bond lengths agree well with those found in other NiN$_3$O complexes with square-planar co-ordination geometry.[32] Owing to the co-ordination to the nickel atom the C$_m$–O bond lengths are elongated [1.301(11) Å in 5 and 1.318(4) Å in 6].

With regard to the molecular packing in the crystal the most prominent feature of complexes 5 and 6 is the presence of the pyrrole hydrogen at N(21) in the pyrrole unit not involved in co-ordination. While one possible reason for the observation of the (3N + O) co-ordination is the presence of the hydroxyl or methoxyl substituent at C(19), analysis of the molecular packing reveals that the NH group in ring I is involved in hydrogen bonding which also prevents the utilization of this pyrrole unit for co-ordination. Thus, it is possible that the nucleophile is added after the (3N + O) co-ordination to the metal ion. Two different types of hydrogen bonds are formed in both nickel complexes. In the structure of 5 the molecules form parallel layers in which neighbouring tetrapyrrole units are connected by weak interactions [H(18a)···O(4) 2.543, H(17e)···O(5) 2.562 Å]. The propionic methyl ester groups of the molecules in neighbouring layers point towards each other. Thus bilayer-like structures are formed in the crystal. Notable is the intramolecular hydrogen bond between the NH in ring I and the hydroxyl group at C(19) [N(21)···O(8) 3.078, H(21a)···O(8) 2.279 Å]. This intramolecular hydrogen bond fixes pyrrole I in an orientation where the NH vector points to the same face as the meso-carbonyl group at C(5) [N(21)···O(3) 2.821 Å, torsion angle N(21)–C(4)–C(5)–O(3) 40.3°]. Quite a different situation was encountered in the crystal structure of 6. Here dimeric structures are formed in the crystal which are held together by two intermolecular hydrogen bonds between the pyrrole NH unit and ester carbonyl oxygens of the benzyl ester group at C(1) [N(21)···O(1) 2.784, H(21a)···O(1) 2.120 Å]. In contrast to the packing observed for 5 this requires that the pyrrole I unit is rotated away from the main metal co-ordination area and the N–H vector pointed in a direction opposite to that of the C(19)–C(10) vector [N(21)···O(5) 3.452 Å, torsion angle N(21)–C(4)–C(5)–O(5) −125.6°]. Additional stabilization of the molecular packing in 6 is provided by weak interactions between C–H and oxygen functionalities [H(3a)···O(3) 2.553, H(17e)···O(6) 2.446 Å] and close contacts involving the nickel centre are observed [Ni···H(13d) 2.879 Å]. Thus, two different types of hydrogen bonds give rise to two quite different orientations of the pyrrole unit part of the biladiene-bc with (3N + O) co-ordination. The two nickel complexes exhibited rather similar spectroscopic characteristics in solution, indicating they have similar solution structures.

Conclusion

This study has shown that both biladien-ac-10-one and biladien-bc-5-one typically form 1:1 metal complexes with a variety of transition metals. Normally, the metal centres are co-ordinated in a distorted tetrahedral fashion by the four pyrrole units and the tetrapyrrole ligand exhibits a helical conformation with significant deviations from planarity. The degree of tetrahedral distortion was largest for copper, nickel and cobalt complexes, while palladium complexes showed a smaller degree of distortion. The biladiene-ac and -bc ligand systems led to very similar degrees of tetrahedral distortion of the co-ordination for individual metals. Tetrahedral distortion of the MN$_4$ units was due to the substituents at C(1) and C(19) which made square-planar co-ordination of the metals sterically impossible. Different types of conformational distortion of the tetrapyrrolic ligand were observed for 5- and 10-oxo biladienes. In addition two nickel complexes of biladien-bc-5-one with co-

ordination of the metal to the meso-carbonyl oxygen and three pyrrole nitrogens were described. These showed square-planar NiN$_3$O co-ordination with rotation of the unco-ordinated pyrrole unit away from the residual tripyrrin unit. This co-ordination type was only observed when additional substituents were present at C(19) which led to increased steric bulk and prevented coordination of pyrrole I to the nickel atom and made the pyrrole NH available for inter- and intra-molecular hydrogen bonding.

Experimental

General

Melting points were measured on a Reichert-Thermovar apparatus and are uncorrected. Neutral alumina (Merck, usually Brockmann Grade III, i.e. deactivated with 6% water) was used for column chromatography. Analytical thin-layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thickness). Reactions were monitored by TLC and spectrophotometry. Elemental analyses were performed at Midwest Microlab, Indiana, USA. Electronic absorption spectra were measured in dichloromethane solution using a Hewlett-Packard 8450A or Zeiss Speccord P10 spectrophotometer, ^{1}H NMR spectra in CDCl$_3$ on a Bruker AM 500 or AM 270 spectrometer. Mass spectra were obtained with electron ionization using a Finnigan 3200 spectrometer [direct insertion probe, 70 eV (ca. 1.12 × 10^{-17} J), 50 mA, source temperature from 200 to 400 °C] at the Mass Spectrometry Facility, University of California, San Francisco.

Syntheses

The oxobilanes used as starting material were prepared according to literature procedures.[13] Unless otherwise stated, they were oxidized with bromine in tetrahydrofuran solution and crystallized as the hydrobromide salt of the corresponding oxobiladienes. The unco-ordinated oxobiladiene dihydrobromides were not further characterized but used immediately for metallation. Metallation was carried out by dissolving the oxobiladienes in chloroform and addition of the respective metal salts in the form of dichlorides or acetates dissolved in methanol. The solution was refluxed overnight, then poured into water and the products extracted with chloroform. The organic phase was washed repeatedly with water to remove excess of salts, and then dried over anhydrous Na$_2$SO$_4$. Compounds were purified by column chromatography (alumina grade III, elution with chloroform). Except for metallations with nickel(II) acetate (see text), only one major product fraction was obtained. Metal complexes of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethylbiladien-ac-10-one dihydrobromide IV were prepared by adding biladiene (150 mmol), metal diacetate (0.2 mmol) and sodium acetate (0.11 mmol) to dry methanol (50 cm^3). The mixture was stirred for 15 min under argon. The metallic purple crystals were filtered off, washed with cold methanol and dried under vacuum. All samples were recrystallized from methylene chloride–hexane.

[1,19-Di(benzyloxycarbonyl)-8,12-diethyl-3,17-di(2-methoxycarbonylethyl)-2,7,13,18-tetramethylbiladien-ac-10-onato]cobalt(II) 1a. Black crystals, yield 86%, m.p. 183–186 °C (Found: C, 66.4; H, 5.60; N, 6.20. C$_{51}$H$_{52}$CoN$_4$O$_9$ requires C, 66.3; H, 5.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 462 (41 800), 560 (sh, 15 900) and 660 (sh, 7200) m/z 923.9 (M$^+$).

Complex 15 (M = Ni). Black crystals, yield 95%, m.p. 191–192 °C (Found: C, 66.2; H, 5.50; N, 5.95. C$_{51}$H$_{52}$N$_4$NiO$_9$ requires C, 66.3; H, 5.65; N, 6.05%); λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 454 (45 500), 558 (13 400) and 680 (sh); δ$_H$(CDCl$_3$) 1.14 (6 H, t, J 7 Hz, 2 CH$_2$CH$_3$), 2.04 (6 H, s, 2 CH$_3$), 2.24 (6

Table 4 Summary of crystal data, data collection and refinement for the metal complexes

	1d	1c	1b, form A	1b, form B	1a	2b	2c
Formula	$C_{51}H_{52}CuN_4O_9$	$C_{51}H_{52}N_4O_9Pd$	$C_{51}H_{52}N_4NiO_9$	$C_{51}H_{52}N_4NiO_9 \cdot CH_2Cl_2$	$C_{51}H_{52}CoN_4O_9$	$C_{31}H_{36}N_4NiO \cdot CHCl_3$	$C_{31}H_{36}N_4OPd$
M	928.5	971.4	923.7	1008.6	923.9	658.7	587.04
Crystal	Block	Cube	Block	Cube	Cube	Parallelepiped	Parallelepiped
Colour	Dark blue	Black	Black	Brown	Black	Brown	Black
Crystal size/mm	0.86 × 0.61 × 0.39	1 × 0.95 × 0.8	1.1 × 0.75 × 0.68	0.42 × 0.42 × 0.4	0.18 × 0.18 × 0.18	0.5 × 0.1 × 0.05	0.4 × 0.15 × 0.08
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
$a/\text{Å}$	14.169(7)	14.291(10)	12.359(3)	13.360(4)	14.016(7)	11.324(2)	20.946(6)
$b/\text{Å}$	16.217(8)	16.356(12)	13.175(3)	13.383(8)	16.013(8)	11.675(2)	10.715(3)
$c/\text{Å}$	19.825(7)	19.655(12)	16.169(5)	15.552(9)	20.266(10)	12.076(3)	11.745(3)
$\alpha/°$			66.52(2)	103.92(5)		76.47(2)	
$\beta/°$	97.24(3)	96.51(5)	88.44(2)	94.63(4)	98.22(4)	84.22(2)	91.35(2)
$\gamma/°$			70.77(2)	115.03(4)		79.56(2)	
$U/\text{Å}^3$	4519(4)	4565(5)	2263.8(10)	2392(2)	4499(3)	1523.6(6)	2635(1)
Z	4	4	2	2	4	2	4
$D_c/\text{g cm}^{-3}$	1.365	1.413	1.355	1.400	1.364	1.436	1.480
μ/mm^{-1}	0.543	0.459	0.488	0.579	0.439	3.594	5.921
$2\theta_{max}/°$	55	55	55	55	50	115	114
Octants collected	$\pm h, +k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$	$\pm h, +l, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$
$F(000)$	1948	2016	972	1056	1940	688	1216
g or (a, b)	0.0004	0.0003	0.0020	0.0057	0.0005	0.0003	(0.0903, 14.9147)
Independent reflections	10 428	10 499	10 369	10 990	5901	4108	1784
Observed reflections	5660 [$F > 4\sigma(F)$]	7513 [$F > 5\sigma(F)$]	6913 [$F > 5\sigma(F)$]	6315 [$F > 4\sigma(F)$]	2662 [$F > 5\sigma(F)$]	3718 [$F > 4\sigma(F)$]	1615 [$F > 4\sigma(F)$]
No. parameters	588	586	586	613	286	370	169
Δ/σ	0.094	0.013	0.06	0.095	0.026	0.067	0.001
$\rho_{max}/\text{e Å}^{-3}$	0.79	0.82	0.72	1.21 (solvent)	0.7	0.63	2.31 (near Pd)
R^a	0.074	0.043	0.05	0.12	0.091	0.064	$R1 = 0.057^b$
R'^a	0.065	0.046	0.056	0.124	0.082	0.080	$wR2 = 0.140^b$
S	1.44	1.68	1.51	1.66	1.46	0.97	1.043

Table 4 *(continued)*

	2d	3d	3c	4a	4c	5	6
Formula	$C_{31}H_{36}CuN_4O$	$C_{51}H_{52}CuN_4O_9$	$C_{51}H_{52}N_4O_9Pd \cdot CH_2Cl_2$	$C_{51}H_{52}CoN_4O_9$	$C_{51}H_{52}N_4O_9Pd$	$C_{51}H_{54}N_4NiO_{10}$	$C_{52}H_{56}N_4NiO_{10}$
M	544.2	928.5	1056.3	923.9	971.4	941.7	955.7
Crystal	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped	Parallelepiped
Colour	Black	Brown	Black	Black	Black	Dark brown	Green
Crystal size/mm	0.5 × 0.16 × 0.15	1.2 × 0.2 × 0.2	0.8 × 0.16 × 0.15	0.80 × 0.42 × 0.16	0.8 × 0.65 × 0.34	0.88 × 0.28 × 0.24	0.33 × 0.18 × 0.17
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
a/Å	21.044(9)	10.451(3)	13.598(7)	13.736(4)	11.713(4)	25.190(6)	13.055(2)
b/Å	10.730(4)	14.529(6)	13.818(6)	16.364(8)	13.404(4)	8.481(2)	15.090(4)
c/Å	12.049(4)	16.916(6)	14.846(7)	20.046(8)	15.266(5)	21.615(5)	15.177(3)
α/°		111.13(3)	76.48(4)		87.60(3)		118.26(2)
β/°	93.28(3)	103.92(3)	66.47(4)	93.76(3)	72.84(2)	94.78(2)	110.20(2)
γ/°		97.51(3)	75.53(4)		87.53(3)		94.22(2)
U/Å³	2716(2)	2257(1)	2448(2)	4496(3)	2287(1)	4601(2)	2368(1)
Z	4	2	2	4	2	4	2
D_c/g cm⁻³	1.331	1.366	1.433	1.365	1.411	1.359	1.339
μ/mm⁻¹	0.835	0.547	0.559	0.445	0.468	0.483	1.115
$2\theta_{max}$/°	50	55	55	55	55	50	108.5
Octants collected	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$
$F(000)$	1148	974	1092	1940	1008	1984	1006
g (a, b)	(0.042, 5.1168)	0.0007	0.0003	0.0005	0.0001	0.0011	0.0318
Independent reflections	2390	10 356	11 241	10 324	10 521	8345	5780
Observed reflections	1946 [$F > 4\sigma(F)$]	7126 [$F > 4\sigma(F)$]	8810 [$F > 4\sigma(F)$]	6262 [$F > 5\sigma(F)$]	7987 [$F > 5\sigma(F)$]	5832 [$F > 4\sigma(F)$]	4277 [$F > 4\sigma(F)$]
No. parameters	169	586	598	586	586	595	599
Δ/σ	0.002	0.003	0.001	0.098	0.038	0.006	0.067
ρ_{max}/e Å⁻³	0.31	0.44	2.12 (solvent)	0.54	1.33 [near C(19)]	0.51	1.30
R^a	$R1 = 0.058^b$	0.055	0.052	0.051	0.057	0.052	0.100
R'^a	$wR2 = 0.107^b$	0.054	0.051	0.052	0.052	0.055	0.129
S	1.038	1.28	1.36	1.34	1.96	1.08	0.88

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + gF^2$. ^{b} (all data) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

H, s, 2 CH$_3$), 2.38–2.62 (4 H, m, 2 CH$_2$CH_2CO$_2$), 2.76–2.96 (4 H, m, 2 CH$_2$CH$_3$), 2.96–3.14 (4 H, m, 2 CH$_2$CH$_2$CO$_2$), 3.62 [6 H, s, 2 C(O)OCH$_3$], 4.85 [4 H, s, 2 C(O)OCH$_2$Ph], 7.10–7.28 (10 H, m, 2 C$_6$H$_5$) and 7.44 (2 H, s, 2 meso-H): m/z 922.8 (M$^+$).

Complex 1c (M = Pd). Black crystals, yield 91%; m.p. 187–189 °C (Found: C, 62.9; H, 5.40; N, 5.80. C$_{51}$H$_{52}$N$_4$O$_9$Pd requires C, 63.05; H, 5.40; N, 5.75%); λ$_{max}$/nm (ε/dm^3 mol^{-1}) cm^{-1} (CH$_2$Cl$_2$) 450 (39 700), 592 (13 500) and 680 (sh): δ$_H$(CDCl$_3$) 1.20 (6 H, t, J 6 Hz, 2 CH$_2$CH$_3$), 2.11 (6 H, s, 2 CH$_3$), 2.30 (6 H, s, 2 CH$_3$), 2.46–2.64 (4 H, m, 2 CH$_2$CH$_2$CO$_2$), 2.82–2.92 (4 H, m, 2 CH$_2$CH$_3$), 2.98–3.21 (4 H, m, 2 CH$_2$CH$_2$CO$_2$), 3.82 [6 H, s, 2 C(O)OCH$_3$], 4.66–4.92 [4 H, m, 2 C(O)OH$_2$Ph], 7.18–7.38 (10 H, m, 2 C$_6$H$_5$) and 7.48 (2 H, s, 2 meso-H): m/z 969.9 (M$^+$).

Complex 1d (M = Cu). Metallic blue crystals, yield 88%; m.p. 193–195 °C (Found: C, 65.7; H, 6.85; N, 6.20. C$_{51}$H$_{52}$CuN$_4$O$_9$ requires C, 65.95; H, 6.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1}cm^{-1}) (CH$_2$Cl$_2$) 456 (38 100), 500 (sh), 582 (17 400) and 666 (7000): m/z 927.4 (M$^+$).

Compound IV. 3,4,5-trimethylpyrrole-2-carboxylic acid **II** (300 mg, 1.95 mmol) was treated with trifluoroacetic acid (7 cm^3) for 2 min and bis(3-ethyl-5-formyl-4-methylpyrrol-2-yl) ketone **III** (240 mg, 0.80 mmol), dissolved in methanol (35 cm^3), added. The reaction mixture was placed in an ice-bath and 30% Br$_2$–acetic acid (8.0 cm^3) was added followed by diethyl ether (200 cm^3) after 10 min. The solution was placed in a refrigerator for 2 h. The purple crystals were filtered off, washed with ether, and dried under vacuum to yield compound **IV** (439 mg, 85%), m.p. 105–108 °C (Found: C, 57.75; H, 6.30; N, 8.55. C$_{31}$H$_{40}$Br$_2$N$_4$O requires C, 57.75; H, 6.60; N, 8.70%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 454 (46 400) and 522 (21 200): δ$_H$(CDCl$_3$) 1.39 (6 H, t, J 6.5, 2 CH$_2$CH$_3$), 1.91 (6 H, s, 2 CH$_3$), 2.24 (6 H, s, 2 CH$_3$), 2.35 (6 H, s, 2 CH$_3$), 2.48 (6 H, s, 2 CH$_3$), 2.64 (4 H, q, J 6.5 Hz, 2 CH$_2$CH$_3$), 7.48 (2 H, s, meso-H), 12.45 (2 H, br s, 2 NH) and 13.94 (2 H, br s, 2 NH): m/z 482.3 (M$^+$ – 2 HBr, 100), 460.1 (30) and 391.3 (15%).

(8,12-Diethyl-1,2,3,7,13,17,18,19-octamethylbiladien-ac-10-onato)cobalt(II) 2a. Metallic green crystals, 75 mg, 85%, m.p. > 300 °C (Found: C, 68.15; H, 6.70; N, 10.15. C$_{31}$H$_{36}$CoN$_4$O·0.5H$_2$O requires C, 67.85; H, 6.80; N, 10.2%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 474 (34 900), 636 (10 000) and 660 (8300): m/z 539.2 (M$^+$, 100) and 524.2 (12%).

Complex 2b (M = Ni). Metallic purple crystals, 80 mg, 72%, m.p. > 300 °C (Found: C, 66.7; H, 6.70; N, 9.70. C$_{31}$H$_{36}$N$_4$NiO· H$_2$O requires C, 66.8; H, 6.85; N, 10.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 448 (53 100): δ$_H$(CDCl$_3$) 1.15 (6 H, t, J 7.5, 2 CH$_2$CH$_3$), 1.67 (6 H, s, 2 CH$_3$), 1.76 (6 H, s, 2 CH$_3$), 2.13 (6 H, s, 2 CH$_3$), 2.28 (6 H, s, 2 CH$_3$), 2.87 (4 H, q, J 7.5 Hz, 2 CH$_2$CH$_3$) and 6.99 (2 H, s, 2 CH$_3$): m/z 538.2 (M$^+$, 100) and 269.1 (10%).

Complex 2c (M = Pd). Metallic purple crystals, 75 mg, 85%, m.p. > 300 °C (Found: C, 63.75; H, 6.35; N, 9.30. C$_{31}$H$_{36}$N$_4$OPd requires C, 63.45; H, 6.20; N, 9.55%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 430 (49 600) and 530 (16 500): δ$_H$(CDCl$_3$) 1.39 (6 H, t, J 7, 2 CH$_2$CH$_3$), 1.81 (6 H, s, 2 CH$_3$), 1.92 (6 H, s, 2 CH$_3$), 2.19 (6 H, s, 2 CH$_3$), 2.21 (6 H, s, 2 CH$_3$), 2.92 (4 H, m, J 7 Hz, 2 CH$_2$CH$_3$) and 6.90 (2 H, s, CH$_3$): m/z 586.2 (M$^+$, 100%).

Complex 2d (M = Cu). Metallic green crystals, 110 mg, 92%, m.p. > 300 °C (Found: C, 68.3; H, 6.80; N, 10.2. C$_{31}$H$_{36}$CuN$_4$O requires C, 68.4; H, 6.65; N, 10.3%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 408 (33 300) and 476 (35 600): m/z 543.2 (M$^+$, 100) and 317.1 (33%).

Complex 2e (M = Zn). Dark blue powder, 45 mg, 40%, m.p. > 300 °C (Found: C, 68.2; H, 6.80; N, 10.25. C$_{31}$H$_{36}$N$_4$OZn requires C, 68.2; H, 6.65; N, 10.25%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 454 (38 300): δ$_H$(CDCl$_3$) 1.22 (6 H, t, J 7, 2 CH$_2$CH$_3$), 1.49 (6 H, s, 2 CH$_3$), 1.74 (6 H, s, 2 CH$_3$), 2.04 (6 H, s, 2 CH$_3$), 2.11 (4 H, m, J 7 Hz, 2 CH$_2$CH$_3$), 2.13 (6 H, s, 2 CH$_3$) and 6.86 (2 H, s, 2 CH$_3$): m/z 544.2 (M$^+$, 100%).

Complex 2f (M = Cd). Metallic purple crystals, 80 mg, 87%, m.p. 217–220 °C (Found: C, 61.7; H, 5.95; N, 9.10. C$_{31}$H$_{36}$CdN$_4$O·0.5H$_2$O requires C, 61.85; H, 6.20; N, 9.30%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 406 (24 700) and 664 (9800): δ$_H$(CDCl$_3$) 1.55 (6 H, s, 2 CH$_3$), 1.85 (6 H, s, 2 CH$_3$), 1.94 (6 H, t, J 7, 2 CH$_2$CH$_3$), 2.15 (6 H, s, 2 CH$_3$), 2.25 (6 H, s, 2 CH$_3$), 2.86 (4 H, q, J 7 Hz, 2 CH$_2$CH$_3$) and 6.88 (2 H, s, 2 CH$_3$): m/z 594.1 (M$^+$, 100%).

Complex 2g (M = Hg). Red powder, 84 mg, 40%, m.p. 198–200 °C. λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 454 (42 500) and 550 (21 600): δ$_H$(CDCl$_3$) 1.13 (6 H, t, J 7.5, 2 CH$_2$CH$_3$), 2.09 (6 H, s, 2 CH$_3$), 2.16 (6 H, s, 2 CH$_3$), 2.21 (6 H, s, 2 CH$_3$), 2.30 (6 H, s, 2 CH$_3$), 2.66 (4 H, m, J 7 Hz, 2 CH$_2$CH$_3$) and 6.94 (2 H, s, 2 CH$_3$): m/z 682.1 (M$^+$, 100%).

[1,19-Di(benzyloxycarbonyl)-3,8-diethyl-13,17-di(2-methoxycarbonylethyl)-2,7,12,18-tetramethylbiladien-bc-5-onato]cobalt(II) 3a. Black crystals, yield 75%, m.p. 193 °C (Found: C, 66.5; H, 5.75; N, 6.25. C$_{51}$H$_{52}$CoN$_4$O$_9$ requires C, 66.3; H, 5.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) (10 700), 492 (12 200), 540 (sh), 590 (sh), 618 (14 100) and 682 (11 100): m/z 924.2 (M$^+$, 100%).

Complex 3b (M = Ni). Brown crystals, yield 60%, m.p. 139 °C (Found: C, 66.55; H, 6.10; N, 5.75. C$_{51}$H$_{52}$N$_4$NiO$_9$ requires C, 66.3; H, 5.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) (8500), 428 (9300), 488 (10 600), 592 (12 000), 616 (12 100) and 682 (9900): δ$_H$(CDCl$_3$) 1.08 (3 H, t, J 7.5, CH$_2$CH$_3$), 1.30 (3 H, t, J 7.5, CH$_2$CH$_3$), 2.29 (3 H, s, CH$_3$), 2.33 (3 H, s, CH$_3$), 2.52 (3 H, s, CH$_3$), 2.77 (3 H, s, CH$_3$), 2.85–3.05 (6 H, m, CH$_2$CH$_2$CO$_2$ and 2 CH$_2$CH$_3$), 3.20 (2 H, t, J 7.5 Hz, CH$_2$CH$_2$CO$_2$), 3.65 [3 H, s, C(O)OCH$_3$], 3.70 [3 H, s, C(O)OCH$_3$], 4.45–4.75 [4 H, m, 2 C(O)OCH$_2$Ph], 6.35 (1 H, s, meso-H), 6.68–7.15 (10 H, m, 2 C$_6$H$_5$) and 7.35 (1 H, s, meso-H): m/z 923.4 (M$^+$, 100%).

Complex 3c (M = Pd). Black crystals, yield 82%, m.p. 198 °C (Found: C, 63.1; H, 5.45; N, 5.80. C$_{51}$H$_{52}$N$_4$O$_9$Pd requires C, 63.05; H, 5.40; N, 5.75%). λ$_{max}$/nm (ε/dm^{3}mol^{-1}cm^{-1}) (CH$_2$Cl$_2$) 392 (32 000), 450 (sh), 610 (9500) and 760 (11 900): δ$_H$(CDCl$_3$) 1.21 (3 H, t, J 7, CH$_2$CH$_3$), 1.26 (3 H, t, J 7, CH$_2$CH$_3$), 2.05 (3 H, s, CH$_3$), 2.19 (3 H, s, CH$_3$), 2.37 (3 H, s, CH$_3$), 2.39 (3 H, s, CH$_3$), 2.58 (2 H, t, J 7.5, CH$_2$CH$_2$CO$_2$), 2.60 (2 H, t, J 7.5, CH$_2$CH$_2$CO$_2$), 2.74 (4 H, q, J 7.5, CH$_2$CH$_3$), 2.88 (4 H, q, J 7.5 Hz, CH$_2$CH$_3$), 3.05 (4 H, m, 2 CH$_2$CH$_2$CO$_2$), 3.62 [3 H, s, C(O)OCH$_3$], 3.64 [3 H, s, C(O)OCH$_3$], 4.82–4.99 [4 H, m, 2 C(O)OCH$_2$Ph], 7.10–7.32 (10 H, m, 2 C$_6$H$_5$), 7.35 (1 H, s, meso-H) and 7.44 (1 H, s, meso-H): m/z 971.8 (M$^+$, 100%).

Complex 3d (M = Cu). Brown crystals, yield 87%, m.p. 116–118 °C (Found: C, 65.9; H, 5.70; N, 6.00. C$_{51}$H$_{52}$CuN$_4$O$_9$ requires C, 65.95; H, 5.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 391 (40 400), 460 (sh), 700 (sh) and 768 (26 400): m/z 927.9 (M$^+$, 100%).

[1,19-Di(benzyloxycarbonyl)-8,13-diethyl-3,17-di(2-methoxycarbonylethyl)-2,7,12,18-tetramethylbiladien-bc-5-onato]cobalt(II) 4a. Black crystals, yield 86%; m.p. 187 °C (Found: C, 66.35; H, 5.65; N, 6.00. C$_{51}$H$_{52}$CoN$_4$O$_9$ requires C, 66.3; H, 5.65; N, 6.05%). λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 400

(10 200), 428 (11 500), 492 (12 500), 588 (13 400), 622 (13 200) and 686 (11 700): m/z 924.1 (M^+, 100%).

Complex 4c (M = Pd). Black crystals, yield 77%; m.p. 212 °C (Found: C, 63.0; H, 5.40; N, 5.75. $C_{51}H_{52}N_4O_9Pd$ requires C, 63.05; H, 5.40; N, 5.75%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 394 (31 800), 460 (sh), 612 (9200) and 768 (11 600): δ_H(CDCl$_3$) 1.22 (3 H, t, J 7.5, CH$_2$CH_3), 1.24 (3 H, t, J 7.5 Hz, CH$_2$CH_3), 2.02 (3 H, s, CH$_3$), 2.18 (3 H, s, CH$_3$), 2.34 (3 H, s, CH$_3$), 2.37 (3 H, s, CH$_3$), 2.49–2.60 (2 H, m, CH$_2$CH_2CO$_2$), 2.63–2.82 (6 H, m, CH$_2$CH_2CO$_2$ + 2 CH_2CH$_3$), 2.92–3.12 (2 H, m, CH$_2$CH$_2$CO$_2$), 3.31–3.5 (2 H, m, CH_2CH$_2$CO$_2$), 3.67 [3 H, s, C(O)OCH$_3$], 3.69 [3 H, s, C(O)OCH$_3$], 4.74–4.99 [4 H, m, 2 C(O)OCH_2Ph], 7.20 (1 H, s, meso-H), 7.21–7.36 (10 H, m, 2 C$_6$H$_5$), and 7.34 (1 H, s, meso-H): m/z 971.1 (M^+, 100%).

Complex 4b (M = Ni). Black crystals, yield 64%; m.p. 126–128 °C (Found: C, 66.4; H, 5.75; N, 6.10. $C_{51}H_{52}N_4NiO_9$ requires C, 66.3; H, 5.65; N, 6.05%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 404 (10 100), 428 (10 900), 498 (11 600), 500 (sh, 12 300), 610 (12 900) and 688 (10 600): δ_H(CDCl$_3$) 1.34 (3 H, t, J 7.5, CH$_2$CH_3), 1.37 (3 H, t, J 7.5 Hz, CH$_2$CH_3), 2.32 (3 H, s, CH$_3$), 2.37 (3 H, s, CH$_3$), 2.54 (3 H, s, CH$_3$), 2.72 (3 H, s, CH$_3$), 2.57–2.69 (2 H, m, CH$_2$CH_2CO$_2$), 2.83–3.04 (6 H, m, CH$_2$CH_2CO$_2$ + 2 CH_2CH$_3$), 3.13–3.39 (2 H, m, CH_2CH$_2$CO$_2$), 3.66 [3 H, s, C(O)OCH$_3$], 3.69 [3 H, s, C(O)OCH$_3$], 4.46–4.79 [4 H, m, 2 C(O)OCH_2Ph], 6.43 (1 H, s, meso-H), 6.67–7.21 (10 H, m, 2 C$_6$H$_5$) and 7.38 (1 H, s, meso-H): m/z 923.8 (M^+, 100%).

1,19-Di(benzyloxycarbonyl)-3,8-diethyl-19-hydroxy-13,17-di(2-methoxycarbonylethyl)-2,7,12,18-tetramethylbiladien-bc-5-onato]nickel(II) 5. Side product from metallation of compound **V** with nickel(II) acetate, dark brown crystals, yield 22%; m.p. 128 °C (Found: C, 65.35; H, 5.85; N, 5.60. $C_{51}H_{54}N_4NiO_{10}$ requires C, 65.05; H, 5.80; N, 5.95%): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 357 (18 200), 428 (8800), 485 (sh), 565 (sh), 606 (11 800) and 686 (7000): δ_H(CDCl$_3$) 1.30 (3 H, t, J 7.5, CH$_2$CH_3), 1.38 (3 H, t, J 7.5 Hz, CH$_2$CH_3), 2.29 (3 H, s, CH$_3$), 2.34 (3 H, s, CH$_3$), 2.51 (3 H, s, CH$_3$), 2.69 (3 H, s, CH$_3$), 2.55–2.67 (2 H, m, CH$_2$CH_2CO$_2$), 2.82–3.10 (6 H, m, CH$_2$CH_2CO$_2$ + 2 CH_2CH$_3$), 3.08–3.35 (2 H, m, CH_2CH$_2$CO$_2$), 3.64 [3 H, s, C(O)OCH$_3$], 3.68 [3 H, s, C(O)OCH$_3$], 4.45–4.78 [4 H, m, 2 C(O)OCH_2Ph], 6.40 (1 H, s, meso-H), 6.63–7.18 (10 H, m, 2 C$_6$H$_5$), 7.36 (1 H, s, meso-H) and 9.04 (1 H, s, NH): m/z 941.9 (M^+, 100%).

[1,19-Di(benzyloxycarbonyl)-8,13-diethyl-19-methoxy-3,17-di(2-methoxycarbonylethyl)-2,7,12,18-tetramethylbiladien-bc-5-onato]nickel(II) 6. Side product from metallation of compound **VI** with nickel(II) acetate, metallic green crystals, yield 18%; m.p. 121–124 °C (Found: C, 65.6; H, 6.05; N, 5.95. $C_{52}H_{56}N_4NiO_{10}$ requires C, 65.35; H, 5.90; N, 5.85%): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH$_2$Cl$_2$) 352 (9500), 426 (9900), 484 (sh), 566 (sh), 604 (14 400) and 689 (8100): m/z 955.1 (M^+, 100%).

Crystallography

X-Ray-quality crystals were grown by slow diffusion of hexane into a concentrated solution of the complexes in dichloromethane. The crystals were removed from the solution and covered with a layer of hydrocarbon oil (Paraton N®). A suitable single crystal was selected, attached to a glass fibre, and immediately placed in the low-temperature nitrogen stream as described by Hope.[33] Data sets for compounds **1d**, **1c**, **1b** (forms A and B), **1a**, **2d**, **3d**, **3c**, **4c**, **4a** and **5** were collected at 130 K with the use of a Siemens R3m/V diffractometer (Mo-Kα radiation, λ = 0.710 69 Å) equipped with a graphite monochromator and a locally modified Enraf-Nonius Universal low-temperature device. The data set for compound **6** was collected at 126 K using a Siemens P4 diffractometer with an attached Siemens rotating anode (Cu-Kα radiation, λ = 1.541 78 Å) and equipped with a locally modified Siemens low-temperature device. The data sets for **2b** and **2c** were collected at 130 K using a Syntex P2$_1$ (graphite-monochromated Cu-Kα radiation, λ = 1.541 78 Å). Crystallographic programs used for the structure solutions and refinements were those of SHELXTL PLUS[34] installed on a Micro Vax station 3200. Scattering factors were used as supplied with SHELXTL PLUS. The intensities were corrected for Lorentz-polarization, and absorption effects;[35] extinction was disregarded. All data collections showed only statistical variation in intensity.

The crystal structures of complexes **1c**, **1b** (forms A and B), **2b–2d**, **3d**, **3c**, **4c**, **5** and **6** were solved by Patterson syntheses followed by subsequent structure expansion, while those of **1a**, **1d** and **4a** were solved with direct methods. If necessary, missing side-chain atoms were located on a difference map in several Fourier-difference cycles. Most refinements were carried out by full-matrix least squares on $|F|$. The function minimized was $\Sigma w(F_o - F_c)^2$. The structures of **2c** and **2d** were refined against $|F^2|$ using the program XL[36] for refinement and XABS2 for absorption corrections.[37] Hydrogen atoms were included at calculated positions and refined by using a riding model (C–H 0.96, N–H 0.9 Å). If not otherwise stated, all non-hydrogen atoms were refined with anisotropic thermal parameters. The structure of **1b**, form B, showed unusually high thermal parameters for the pyrrole nitrogen atoms and refined badly. Data for it are listed in the supplementary material only. The limited crystal quality and a low-intensity data set obtained for **1a** allowed refinement of only the Co and N atoms with anisotropic thermal parameters. In the structure of **3c** the solvate molecule of CH$_2$Cl$_2$ was not refined with anisotropic thermal parameters. The refinement of **6** gave relatively high estimated standard deviations (e.s.d.s) for some side-chain atoms and the ethyl group at C(13) was connected to the macrocycle by an unreasonably long distance (1.831 Å). All attempts to find a better model for this side chain failed. No hydrogen atoms were included in the refinement for it. Details of the crystal data, data collection and refinement are given in Table 4.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/188.

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