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Facile acid-promoted decarboxylation of a macrocyclic complex. Crystal structure of [6,14-diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-1(15),5,7,13-tetraen-2-olato]nickel(II)

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A new chiral tetradentate compound has been prepared from (*S*)-2,3-diaminopropanoic acid and 3-ethoxymethylenepentane-2,4-dione and the corresponding nickel(II) and palladium(II) complexes have been characterized. The racemic form of the nickel(II) complex underwent template-controlled ring closure with 1,3-diaminopropane to form a new 15-membered carboxylato-substituted macrocycle. In the presence of acid, this species underwent an unusual and facile oxidative-decarboxylation reaction to produce a new hydroxy-substituted macrocycle, the crystal structure of which has been determined.

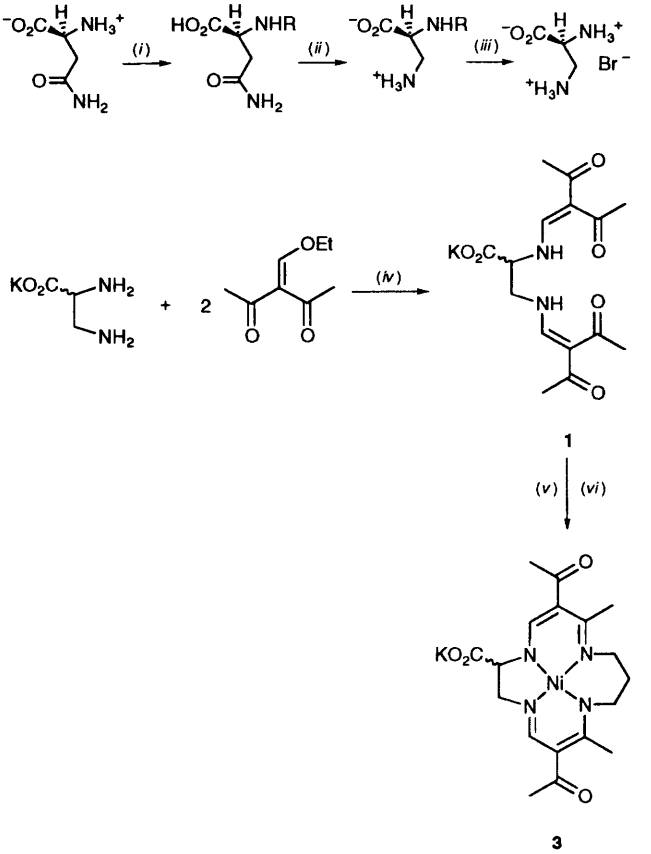
We have had a long-term interest in producing macrocycles of low symmetry in order to fine tune both the steric and electronic properties around metal centres.[1] We have had considerable success in modifying a range of different parent macrocycles to produce complexes with varied and useful peripheral functional groups, for example for the covalent attachment to synthetic polymer supports.[2] Recently we have extended our interests to include macrocycles bearing chiral functional groups, with the ultimate objective of inducing stereoselectivity into the reactions of complexes.[3]

There have of course been a wide range of studies on the preparation and reactions of compounds containing chiral centres and these have been put to good effect, for example in oxidation[4] and reduction[5] catalysis, or in substrate hydrolysis.[6] Owing to the ready availability and the useful functionality of chiral amino acids, the preparation of compounds using amino acid precursors is a rapidly growing field, and there are numerous recent examples of species derived from this source.[7] The well known kinetic and thermodynamic stability of macrocyclic systems[8] makes them attractive candidates as platforms for the location of chirality adjacent to the metal centres of complexes.

In this work we sought to prepare macrocyclic complexes derived from the amino acid (*S*)-asparagine, following the template method[9] of ring closure. For convenience, the template reaction is carried out using complexes of nickel(II), but the metal ion can subsequently be replaced readily by more redox-active metals, such as iron or cobalt.[10]

Results and Discussion

The synthetic pathway used is outlined in Scheme 1. The chiral diamine (*S*)-2,3-diaminopropanoic acid was prepared in three steps *via* the Hoffman degradation of L-asparagine monohydrate, using literature procedures.[11] The diamine was isolated in its zwitterion form as the monohydrobromide salt in reasonable overall yield (45%) provided the concentration of bromine used in the degradation step was carefully controlled. If an excess of bromine was used, or if the rate of addition of protected asparagine was slow, then a substantial amount of toluene-*p*-sulfonamide was isolated from the reaction mixture rather than the desired product, suggesting that an alternative degradation pathway is possible, resulting in cleavage of the protected amino group. The optical rotation of the chiral diamine was in good agreement with the literature value and

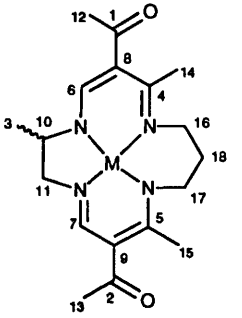


Scheme 1 R = 4-$MeC_6H_4SO_2$. (*i*) $NaHCO_3$, 4-$MeC_6H_4SO_2Cl$, 20 °C, 48 h; (*ii*) Br_2, NaOH, < 5 °C; (*iii*) HBr, $MeCO_2H$, 80 °C, 5 h; (*iv*) $KOBu^t$, EtOH, 20 °C, 15 min; (*v*) $Ni(O_2CMe)_2{\cdot}4H_2O$, MeOH, NaOH, 50 °C, 1 h; (*vi*) $H_2N(CH_2)_3NH_2$, 140 °C, 16 h

the NMR spectra of the product and the various intermediates were also satisfactory.

The chiral diamine was used in macrocycle formation, adopting a modification of the procedure of Jäger.[12] Deprotonation of the diamino salt and reaction with 3-ethoxymethylenepentane-2,4-dione produced, in 50% yield, the tetradentate acyclic compound, **1**, as the potassium salt. The ^1H NMR spectrum of **1** (Table 1) showed clearly the

Table 1 NMR data, in D_2O solution



(*a*) ^{13}C δ

Compound	$C^{1,2}$	C^3	$C^{4,5}$	$C^{6,7}$	$C^{8,9}$	C^{10}	C^{11}	C^{12-15}	$C^{16,17}$	C^{18}
1	201.3, 201.2	172.9	198.8,[a] 198.8[a]	162.4, 160.7	111.0,[a] 111.0[a]	64.2	52.5	30.4, 30.3, 25.8,[a] 25.8[a]		
2	199.0, 198.8	175.9	188.2,[a] 188.2[a]	161.9, 160.3	113.8,[a] 113.8[a]	71.6	62.4	27.8,[a] 27.8,[a] 27.8,[a] 27.8[a]		
3	196.2, 196.0	177.5	168.0, 167.8	158.7, 158.1	113.3, 113.1	br	62.5	25.8, 25.7, 18.0,[a] 18.0[c]	45.9, 45.7	25.7[a]
4[b]	193.6, 193.1		168.0, 167.8	158.2, 156.5	113.4,[a] 113.4[a]	89.6	69.1	*c*, *c*, 18.5, 18.3	46.5, 46.2	*c*

(*b*) ^1H δ(*J*/Hz)

Compound	$H^{6,7}$	H^{10}	H^{11a}	H^{11b}	H^{12-15}	$H^{16,17}$	H^{18}	OH
1	7.78 (s, 2 H)	4.25 (dd, 1 H) (J = 9.3, 4.1)	4.07 (dd, 1 H) (J = 13.7, 4.1)	3.60 (dd, 1 H) (J = 13.7, 9.3)	2.33 (s, 3 H), 2.30 (s, 3 H), 2.10 (s, 6 H)			
2a	7.62 (s, 1 H), 7.55 (s, 1 H)	3.74 (br, 1 H)	3.74 (br, 1 H)	3.46 (br, 1 H)	2.27 (s, 3 H), 2.23 (s, 3 H), 2.15 (s, 6 H)			
2a[d]	7.60 (s, 1 H), 7.55 (s, 1 H)	3.60 (m, 1 H)	*c*	*c*	2.22 (s, 3 H), 2.30 (s, 3 H), 2.19 (s, 3 H), 2.17 (s, 3 H)			
2b[d]	8.04 (s, 1 H), 8.01 (s, 1 H)	4.52 (d, 1 H)	4.0 (m, 2 H)		2.35 (s, 3 H), 2.30 (s, 3 H), 2.28 (s, 6 H)			
3	7.65 (s, 1 H), 7.67 (s, 1 H)		3.3–3.85 (m, 3 H)		2.29 (s, 3 H), 2.25 (s, 3 H), 2.23 (s, 3 H), 2.20 (s, 3 H)	3.3–3.85 (m, 4 H)	1.9 (br, 2 H)	
4[e]	7.68 (s, 1 H), 7.47 (s, 1 H)	4.55 (br, 1 H)	3.45 (dd, 1 H)	3.02 (d, 1 H)	2.41 (s, 3 H), 2.40 (s, 3 H) 2.36 (s, 3 H), 2.33 (s, 3 H)	3.70 (m, 4 H)	1.84 (m, 2 H)	4.0 (br, 1 H)
4[b]	7.83 (s, 1 H), 7.65 (s, 1 H)	4.71 (dd, 1 H) (J = 3.5, 4.8)	3.36 (ddd, 1 H) (J = 12.6, 4.8, 1.1)	3.03 (ddd, 1 H) (J = 12.6, 3.5, 0.8)	2.38 (s, 3 H), 2.37 (s, 3 H), 2.19 (s, 3 H), 2.18 (s, 3 H)	3.61 (m, 4 H)	1.90 (m, 1 H)	3.88 (br, 1 H)

[a] Overlapping signal. [b] In acetone solution. [c] Obscured by solvent signals. [d] In Me_2SO solution. [e] In $CDCl_3$ solution.

asymmetric structure, with the three aliphatic protons derived from the diamino group appearing as a series of doublet of doublets between δ 3.5 and 4.3, and there were separate signals for the two methyls of the acetyl groups hydrogen bonded to the NH functions. The ^{13}C NMR spectrum confirmed the asymmetry of the structure, with separate signals for the methine carbon atoms C(6) and C(7), and also for keto carbons C(4) and C(5) (Table 1).

The nickel(II) and palladium(II) complexes of **1** were prepared as a red and a yellow solid respectively, **2a** and **2b**, and **2a** was characterized by ^1H and ^{13}C NMR spectroscopy and by microanalysis. The colour and diamagnetism of the complexes confirmed their structure as square planar. The ^1H NMR spectrum of **2a** was solvent dependent: in $(CD_3)_2SO$ solution the signals were sharp, with separate resonances for each methine proton and for each of the four methyl groups, showing the lack of symmetry in the complex (Table 1); in D_2O solution the signals were much broader but still showed the asymmetry of the structure, although now only three methyl signals (relative intensity 1:1:2) were observed. The ^{13}C NMR spectrum had broadened peaks for both the carboxylate group and in particular the adjacent carbon atom, C(10), implying some fluxionality in this part of the molecule (Table 1). A solution of **2a** in Me_2SO displayed an $[\alpha]_{589}$ of +5.8°. The ^1H NMR spectrum of the palladium(II) complex in $(CD_3)_2SO$ solution strongly resembled that of **2a**, except that several of the resonances were shifted appreciably downfield. This was most noticeable for the proton attached to C(10) which was shifted by 0.92 ppm, from δ 3.60 to 4.52 (Table 1).

The final step of Jager's scheme, ring closure to form the macrocyclic structure, is generally of variable yield and care must be taken to optimize the conditions for macrocycle formation. To avoid waste of the chiral complex, the racemic analogue of **2a** was prepared using commercially available 2,3-diaminopropanoic acid, and this racemic **2a** was used to optimize the cyclization conditions. Previous experience with related systems indicated that formation of five- was favoured over six-membered metallochelate rings in the cyclization step.[13] However, under the forcing conditions of the ring-closure reactions (high temperature and a large excess of diamine) macrocycle formation using 1,2-diamino-ethane or -propane occurred with 'diamine exchange' where the 2,3-diaminopropanoic acid group was eliminated from the structure. Ring closure with 1,3-diaminopropane produced macrocycle **3** as a red solid and the ^1H and ^{13}C NMR spectra of the crude product were in good agreement with the proposed structure. Although rather broad, the ^1H NMR spectrum in D_2O solution displayed the asymmetry of the structure with two closely placed singlets for the protons of C(6) and C(7) and a separate signal for each of the four methyl groups (Table 1). Peaks corresponding to the methylene groups of the expected product were present at δ 3.3–3.85 and at 1.9 in the correct intensity ratio. The ^{13}C NMR spectrum was particularly useful in demonstrating the asymmetry of the structure, with a separate signal appearing for each carbon atom, except that no signal was observed for C(10) and the signals for the acetyl methyl groups overlapped at δ 18.0 (Table 1). The broadening of the signal for C(10) which was observed for **2a** was now so great that the signal was lost in the baseline. Measurement of the magnetic properties of **3** both in the solid state and in solution indicated a small degree of paramagnetism, which accounts for the broadening observed in the ^1H NMR spectrum. The observed paramagnetism is ascribed to the presence of an equilibrium involving co-ordination of the carboxylate group to an axial site of the metal centre, producing a small amount of six-co-ordinate paramagnetic material, although the equilibrium favours the four-co-ordinate diamagnetic complex.

In a routine effort to purify the macrocycle, complex **3** was subjected to chromatography on a silica column. The product **4** was a bright pinkish red, diamagnetic material soluble in chloroform rather than water and the ^1H NMR spectrum showed that it was an asymmetrically substituted macrocycle, different from the starting material (Table 1). The signals due the protons of C(6) and C(7) appeared as two well resolved singlets of equal intensity and there were four separate methyl signals, but the major change was in the appearance of the signals of the protons attached to C(10) and C(11). The proton of C(10) was shifted downfield to δ 4.55, implying the presence of a strongly electronegative group on C(10). This signal became sharper after the sample was treated with D_2O and a broad feature at δ 4.0 (1 H), assigned to the proton of a hydroxyl group, disappeared. The 400 MHz ^1H NMR spectrum, in $(CD_3)_2CO$ solution, revealed a small coupling (*ca.* 1 Hz) between the protons attached to C(10) and C(11) and the hydroxyl proton which could not be resolved in the 200 MHz spectrum, and the ^{13}C NMR spectrum at 100 MHz confirmed the asymmetric structure, with separate signals for C(1) and C(2), C(4) and C(5), and C(6) and C(7) (Table 1). The crystal structure of the product confirmed it to be the macrocycle where the carboxy group of **3** had been replaced by a hydroxyl group. The details of the structure are discussed below.

It was of interest to explore further the nature of the facile reaction transforming the carboxylate-substituted macrocycle into the corresponding hydroxy species. The reaction is acid promoted, with the silica column used in the attempted purification of **3** being sufficiently acidic to effect the process. On a larger scale, treatment of the carboxylate macrocycle with dilute mineral acid caused the visible evolution of a gas, which was identified from its infrared spectrum as CO_2.

At first sight, this appeared to be a very unusual decarboxylation reaction, since transformation of a carboxylate into a hydroxyl group is normally carried out under oxidizing conditions,[14] but in this case no obvious oxidant was present. Aerial oxidation was eliminated as a possibility by carrying out the reaction on a vacuum line and employing freeze–pump–thaw cycles to remove any O_2 from the system, prior to addition of acid. The hydroxyl group must originate from the solvent water, but a simple nucleophilic displacement of CO_2 would require the concomitant loss of a hydride ion, an unlikely process under these conditions. The only feasible oxidant was the nickel(II) complex itself and thus the reaction appears to be a form of disproportionation of the macrocycle. In agreement with this, it was noticed that the amount of CO_2 evolved in the vacuum-line reactions was approximately 50% of that calculated, based on the amount of carboxy macrocycle used, and the isolated yield of the hydroxy macrocycle was also never more than 50%. Despite repeated efforts, it proved impossible to isolate and characterize any other products from the reaction mixture, however it was noted that the residue appeared to contain metallic nickel. We propose that while half of the macrocycles decarboxylate, the other half of the available nickel(II) is reduced to nickel metal which then dissociates from the ligand. The free macrocycle thus produced then hydrolyses in the acidic medium. The role of the acid in the decarboxylation reaction is to make the nickel(II) complex a better oxidant by protonating the carboxylate group. Unfortunately, attempts to confirm this hypothesis using electrochemistry were inconclusive. However, addition of 1 equivalent of potassium peroxodisulfate to a sample of **3**, without the addition of acid, resulted in the release of a much greater amount of CO_2, and the recovery of **4** in 87% yield, strongly supporting the oxidative mechanism.

To our knowledge this is the first example of a nickel(II) complex taking part in such an oxidative decarboxylation reaction but there has been recent literature precedent for similar reactions involving cobalt(III),[15] copper(III)[16] and copper(II)[17] complexes.

A single crystal of complex **4**, grown from acetone solution, was subjected to X-ray crystallographic analysis. Atomic fractional coordinates and important geometrical parameters

Table 2 Atomic coordinates ($\times 10^4$) for complex **4**

Atom	*x*	*y*	*z*
Ni	511(1)	280(1)	1764(1)
N(1)	−935(2)	1019(2)	2287(2)
N(2)	183(2)	−722(2)	2688(1)
N(3)	1836(2)	−411(2)	1108(2)
N(4)	1078(2)	1250(2)	953(2)
C(1)	879(3)	2125(2)	1134(2)
C(2)	81(3)	2505(2)	1927(2)
C(3)	−888(3)	1919(2)	2455(2)
C(4)	−2172(3)	458(2)	2574(2)
C(5)	−1819(3)	−67(2)	3601(2)
C(6)	−272(3)	−383(2)	3708(2)
C(7)	413(3)	−1605(2)	2545(2)
C(8)	1103(3)	−1934(2)	1642(2)
C(9)	1882(3)	−1314(2)	1060(2)
C(10)	2812(3)	139(2)	501(2)
C(11)	1950(3)	965(2)	95(2)
C(12)	−1863(4)	2349(2)	3209(2)
C(13)	125(4)	−2305(2)	3397(2)
C(14)	252(3)	3484(2)	2152(2)
C(15)	937(4)	4120(2)	1393(3)
O(1)	−145(3)	3853(2)	2967(2)
C(16)	1082(3)	−2901(2)	1314(2)
C(17)	2291(4)	−3277(2)	715(3)
O(2)	108(3)	−3439(2)	1487(2)
O(3)	3982(2)	458(2)	1150(2)

Table 3 Bond lengths (Å) and angles (°) for complex **4**

Ni–N(4)	1.842(2)	Ni–N(3)	1.844(2)
Ni–N(1)	1.888(2)	Ni–N(2)	1.903(2)
N(1)–C(3)	1.316(3)	N(1)–C(4)	1.484(3)
N(2)–C(7)	1.308(3)	N(2)–C(6)	1.480(3)
N(3)–C(9)	1.306(3)	N(3)–C(10)	1.476(3)
N(4)–C(1)	1.298(3)	N(4)–C(11)	1.473(3)
C(1)–C(2)	1.414(4)	C(2)–C(3)	1.446(4)
C(2)–C(14)	1.448(4)	C(3)–C(12)	1.510(4)
C(4)–C(5)	1.520(4)	C(5)–C(6)	1.515(4)
C(7)–C(8)	1.442(3)	C(7)–C(13)	1.520(3)
C(8)–C(9)	1.403(3)	C(8)–C(16)	1.456(4)
C(10)–O(3)	1.394(3)	C(10)–C(11)	1.508(4)
C(14)–O(1)	1.247(3)	C(14)–C(15)	1.513(4)
C(16)–O(2)	1.232(3)	C(16)–C(17)	1.517(4)
N(4)–Ni–N(3)	85.52(9)	N(4)–Ni–N(1)	90.93(9)
N(3)–Ni–N(1)	173.78(9)	N(4)–Ni–N(2)	172.27(9)
N(3)–Ni–N(2)	90.99(9)	N(1)–Ni–N(2)	93.13(9)
C(3)–N(1)–C(4)	120.9(2)	C(3)–N(1)–Ni	126.8(2)
C(4)–N(1)–Ni	112.1(2)	C(7)–N(2)–C(6)	120.5(2)
C(7)–N(2)–Ni	128.1(2)	C(6)–N(2)–Ni	111.2(2)
C(9)–N(3)–C(10)	119.2(2)	C(9)–N(3)–Ni	125.9(2)
C(10)–N(3)–Ni	114.6(2)	C(1)–N(4)–C(11)	119.9(2)
C(1)–N(4)–Ni	125.9(2)	C(11)–N(4)–Ni	113.9(2)
N(4)–C(1)–C(2)	126.5(2)	C(1)–C(2)–C(3)	119.6(2)
C(1)–C(2)–C(14)	117.6(3)	C(3)–C(2)–C(14)	122.8(2)
N(1)–C(3)–C(2)	121.0(2)	N(1)–C(3)–C(12)	119.6(2)
C(2)–C(3)–C(12)	119.4(2)	N(1)–C(4)–C(5)	111.3(2)
C(6)–C(5)–C(4)	111.4(2)	N(2)–C(6)–C(5)	111.4(2)
N(2)–C(7)–C(8)	121.4(2)	N(2)–C(7)–C(13)	120.5(2)
C(8)–C(7)–C(13)	117.7(2)	C(9)–C(8)–C(7)	119.8(2)
C(9)–C(8)–C(16)	117.0(2)	C(7)–C(8)–C(16)	123.1(2)
N(3)–C(9)–C(8)	126.2(2)	O(3)–C(10)–N(3)	111.1(2)
O(3)–C(10)–C(11)	108.2(2)	N(3)–C(10)–C(11)	105.4(2)
N(4)–C(11)–C(10)	106.5(2)	O(1)–C(14)–C(2)	123.0(3)
O(1)–C(14)–C(15)	116.2(3)	C(2)–C(14)–C(15)	120.8(3)
O(2)–C(16)–C(8)	123.1(3)	O(2)–C(16)–C(17)	117.3(3)
C(8)–C(16)–C(17)	119.6(3)		

are listed in Tables 2 and 3, respectively. A perspective view of the molecule, indicating the numbering system used, is depicted in Fig 1. The structure consists of well ordered, discrete molecules of the complex. As expected from the spectroscopic data for complex **4**, a hydroxyl group is located in a pseudo-axial position at C(10) of the 15-membered macrocyclic ring.

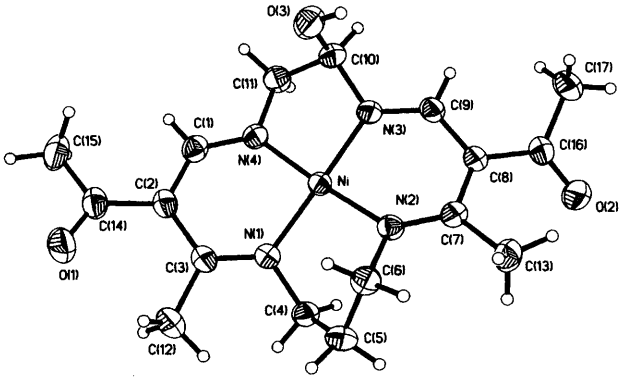


Fig. 1 Perspective view of a molecule of complex **4**, indicating the numbering scheme used (50% probability ellipsoids). Hydrogen-atom labels have been omitted for clarity

An intermolecular hydrogen-bonding contact is formed between the hydroxyl group hydrogen atom H(3A) and the carbonyl group oxygen atom O(1B) of an adjacent symmetry-related molecule [H(3A) · · · O(1A) 1.95 Å; symmetry operation $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$] (Fig. 2).

The nickel atom exists in a slightly disordered square-planar co-ordination geometry. The Ni–N(1) and Ni–N(2) bond distances are slightly longer than Ni–N(3) and Ni–N(4) [1.888(2) and 1.903(2) *versus* 1.844(2) and 1.842(2) Å]. There are also substantial angular variations at the nickel atom with the bond angles N(1)–Ni–N(2) and N(3)–Ni–N(4) deviating significantly from 90°. The remainder of the geometrical parameters lie within expected ranges. In general, if the presence of the hydroxyl group is ignored, the major structural features of complex **4** are in good agreement with those reported previously for the non-hydroxy fifteen-membered macrocycle.[18]

In a similar fashion to this species, **4** adopts a Z-shaped arrangement in which the the two unsaturated six-membered chelate rings are displaced on opposite sides of the NiN_4 plane and the saturated five- and six-membered chelate rings each have skew conformations. Mean deviations from the least-squares planes through atoms N(2)–C(7)–C(8)–C(9)–N(3) and N(4)–C(1)–C(2)–C(3)–N(1) were 0.044 and 0.038 Å, respectively, with the nickel atom being displaced by −0.517 and 0.559 Å from the respective planes.

Conclusion

Chiral (*S*)-2,3-diaminopropanoic acid can be used as a building block in the preparation of a new chiral tetradentate compound, which forms square-planar complexes with both nickel(II) and palladium(II). The racemic form of the nickel(II) complex undergoes ring closure with 1,3-diaminopropane to produce a new, unsymmetrically substituted macrocyclic complex. This species is acid sensitive and undergoes facile oxidative decarboxylation to generate the corresponding hydroxy-substituted macrocycle by a form of disproportionation reaction.

Experimental

All materials were reagent grade and solvents were purified and dried using standard methods. The NMR spectra were recorded on a Bruker WP200 spectrometer, operating at 200.13 (^{1}H) and 50.323 (^{13}C) MHz or a Bruker WH400 spectrometer, operating at 400.13 (^{1}H) or 100.62 (^{13}C) MHz. Chemical shifts are reported with respect to an external tetramethylsilane reference (positive to low field). Electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer and infrared spectra as KBr discs on Nicolet Impact 400 FTIR or Perkin-Elmer 983 spectrophotometers.

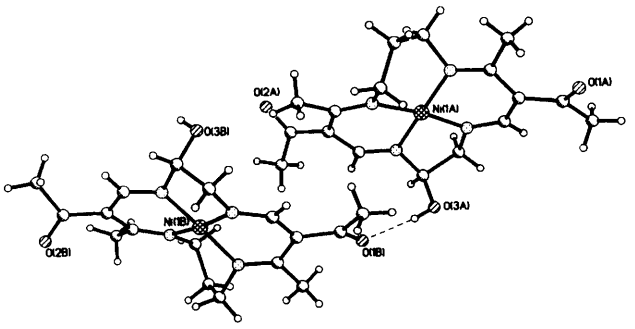


Fig. 2 Intermolecular hydrogen bonding between the hydroxyl group hydrogen atom, H(3A), and the carbonyl oxygen atom, O(1A), of two adjacent molecules of complex **4**

(*S*)-2,3-Diaminopropanoic acid was prepared as its hydrogen bromide salt following literature procedures.[11] 3-Ethoxymethylenepentane-2,4-dione was prepared by the literature method.[19]

Preparations

Potassium (*S*)-3,10-diacetyl-2,11-dioxo-5,8-diazadodeca-3,9-diene-6-carboxylate 1. To a suspension of (*S*)-2,3-diaminopropanoic acid hydrobromide (2.5 g, 17.8 mmol) in dry ethanol (30 cm^3) was added KOBu^t (3.99 g, 35.6 mmol). The mixture was filtered to remove KBr and the filtrate added to a solution of 3-ethoxymethylenepentane-2,4-dione (5.56 g, 35.6 mmol) in ethanol (25 cm^3). After stirring for *ca.* 15 min the white precipitate was filtered off. Yield 3.2 g, 50% (Found: C, 50.0; H, 5.4; N, 7.3. Calc. for $C_{15}H_{19}KN_2O_6$·0.5EtOH: C, 49.8; H, 5.7; N, 7.25%).

Complex 2a. To a warm solution of salt **1** (5 g, 13.7 mmol) in methanol (30 cm^3) were added 2 equivalents of sodium hydroxide pellets and a slurry of nickel(II) acetate tetrahydrate (3.42 g, 13.7 mmol) in methanol (20 cm^3), and the mixture was heated at reflux for 1 h. On cooling to room temperature and reducing the volume an orange-red precipitate appeared. Yield 3.74 g, 60%. FAB mass spectrum: *m/z* 404, $[M + H]^+$; 426, $[M + Na]^+$ and 442, $[M + K]^+$ (Found: C, 43.1; H, 4.95; N, 7.0. Calc. for $C_{15}H_{17}KN_2NiO_6$: C, 43.0; H, 4.1; N, 6.7%).

Complex 2b. A similar method was employed except that $K_2[PdCl_4]$ was dissolved in the minimum volume of water and added to a solution of the salt **1** in methanol. The solution turned dark red and after *ca.* 5 min the yellow precipitate was filtered off. A second crop was obtained by reducing the volume of the filtrate. Yield 60%.

Potassium [6,14-diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-1(15),5,7,13-tetraene-6-carboxylato]nickelate(II) 3. A slurry of complex **2a** (2.69 g, 6.42 mmol) in 1,3-diaminopropane (30 cm^3) was heated at reflux for *ca.* 16 h. On cooling the red precipitate formed was filtered off and washed thoroughly with diethyl ether. Yield 1.66 g, 56%.

[6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-1(15),5,7,13-tetraen-2-olato]nickel(II) 4. Macrocycle **3** (0.48 g, 1 mmol) was dissolved in water (100 cm^3) to give a dark red solution to which was added dropwise 1 mol dm^{-3} HCl until the pH reached 4. During addition of the acid a gas was evolved and the red solution was extracted with chloroform and the organic layer dried over anhydrous $MgSO_4$. Upon reducing the volume of the solution and addition of diethyl ether, the product precipitated as an orange solid (yield 0.1 g, 25%) (Found: C, 47.1; H, 6.9; N, 11.5. Calc. for $C_{17}H_{24}N_4NiO_3$·0.5Et_2O·3H_2O: C, 47.3; H, 7.1; N, 11.6%). The experiment was repeated using a vacuum line of known volume and the solvent was degassed by several freeze–pump–thaw cycles. Addition of acid *via* syringe through a septum resulted in the evolution of gas which was expanded into a gas cell and the infrared spectrum measured.

Crystallography

The crystal of complex **4** used for X-ray data collection (dimensions *ca.* 0.2 × 0.15 × 0.1 mm) was grown by slow evaporation from an acetone solution and mounted in a sealed Lindemann capillary tube.

Crystal data. $C_{17}H_{24}N_4NiO_3$, $M = 1391.11$, orange irregular polyhedra, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $a = 9.373(2)$, $b = 14.429(3)$, $c = 12.693(3)$ Å, $\beta = 94.79(3)°$, $U = 1710.6(6)$ Å^3, $Z = 4$, $D_c = 1.519$ g cm^{-3}, $F(000) = 824$, μ(Mo-Kα) = 1.159 mm^{-1}.

Data collection. The intensity data were collected on an Enraf-Nonius diffractometer fitted with a FAST area detector [150(2) K; θ 2.82–29.68°; $-13 \leqslant h \leqslant 12$, $-19 \leqslant k \leqslant 18$, $-11 \leqslant l \leqslant 17$] using graphite-monochromated Mo-Kα X-radiation (λ 0.710 69 Å) and ω scans.[20] Of the 4250 unique data [R(int) = 0.0432] measured, 2552 had $I > 2\sigma(I)$. The data were corrected for Lorentz-polarization effects, and for absorption (DIFABS[21]).

Structure solution and refinement. The approximate position of the Ni atom was determined by Patterson methods (SHELXS 86[22]) with the remaining non-hydrogen atoms being subsequently located from a Fourier-difference map phased on the refined nickel position. The structure was refined by full-matrix least-squares methods on F^2 (SHELXTL[23]) using all unique data and anisotropic thermal parameters for all the non-hydrogen atoms. All hydrogen atoms were located on Fourier-difference maps and included in the refinement process at idealized positions with isotropic thermal parameters of 1.5 times U_{iso} of the bonded heavy atom. At convergence, the discrepancy factors R and R' [$I > 2\sigma(I)$] were 0.0343 and 0.0901, respectively. The weighting scheme, $w^{-1} = [\sigma^2(F_o^2) + (0.052P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, was found to give satisfactory analyses of variance. The final Fourier-difference map was essentially featureless (general noise level less than ± 0.3 e Å^{-3}) with the largest difference peak and hole of 0.642 and -0.499 e Å^{-3}.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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