# Preparation of 11-(2′-Dimethylaminoethyl)-1,4,7-trimethyl-1,4,7,11-tetra-azacyclotetradecane, and Characterisation of its Nickel(II), Copper(II), and Zinc(II) Complexes †

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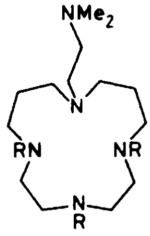
The new 14-membered, pendant-arm macrocyclic ligand, 11-(2′-dimethylaminoethyl)-1,4,7-trimethyl-1,4,7,11-tetra-azacyclotetradecane ($L^2$), and some of its complexes with $Cu^{II}$, $Ni^{II}$, and $Zn^{II}$ (M) of general formula $[M(L^2)]X_2$ ($X = ClO_4^-$ or $NO_3^-$) have been isolated. The five-co-ordinate complex $[Cu(L^2)][ClO_4]_2$ undergoes reversible protonation of the pendant arm to give $[Cu(HL^2)][ClO_4]_3$. The complex $[Ni(L^2)][ClO_4]_2$ is also five-co-ordinate but attempted selective protonation leads to complete dissociation of ($L^2$) from the $Ni^{2+}$ ion. The $^{13}C$ n.m.r. spectrum of $[Zn(L^2)][NO_3]_2$ reveals the presence of two species in aqueous solution, one symmetric and the other asymmetric.

Following earlier investigations into the synthesis and complexation reactions of functionalised macrocyclic ligands,[1–3] we have recently reported the preparation of two new 14-membered macrocycles containing a pendant arm which is capable of further co-ordination to a centrally placed metal ion.[4,5] Here we report the N-methylation of one of these ligands ($L^1$; R = H) to give the new pendant-arm macrocycle 11-(2′-dimethylaminoethyl)-1,4,7-trimethyl-1,4,7,11-tetra-azacyclotetradecane ($L^2$; R = Me), and the characterisation of its complexes with $Cu^{II}$, $Ni^{II}$, and $Zn^{II}$.



| | R |
|---|---|
| $L^1$ | H |
| $L^2$ | Me |

## Results and Discussion

The synthesis of ligand ($L^2$; R = Me) in high yield from 11-(2′-dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane [4] proceeds as described using a mixture of formic acid and formaldehyde as methylating agent. Although this method works with simple 14- and 16-membered tetra-aza macrocycles,[6] previously we showed that it is unsuitable for the related C-substituted macrocycles.[7]

Complexation of $L^2$ with $Ni(ClO_4)_2$ leads to the formation of a pale green, high-spin, five-co-ordinate complex $[Ni(L^2)][ClO_4]_2$ ($\mu_{eff.}$ = 3.43 B.M.; Table 1). Unlike previous nickel(II) complexes of this type,[4] attempted selective protonation of the pendant arm leads only to decomposition. This indicates that the structure is analogous to *trans*-I-$[Ni(L')]^{2+}$ (L′ = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) in which all four substituents project from the same side of the macrocycle, since this structure is known to be substitution labile in acidic solution. The acid lability of the *trans*-I-form is ascribed to the metal residing above the plane of the four macrocyclic nitrogen donors so as to reduce steric interactions from the four NMe groups.[8] In the case of ligand $L^2$ this steric interaction would be even more pronounced and would lead to the nickel(II) ion being even more removed from the macrocyclic nitrogen donors thus giving a distorted trigonal bipyramidal geometry analogous to that previously observed.[4] Protonation of the pendant arm would further weaken this structure and accelerate dissociation. The zinc(II) complex is also acid labile.

In contrast to these results, the copper(II) complex, $[Cu(L^2)][ClO_4]_2$, undergoes reversible protonation of the pendant-arm $^-NMe_2$ group to give a square-planar species [equation (1)]. This geometry change is from trigonal bipyramidal

$$\underset{\text{(blue)}}{[Cu(L^2)][ClO_4]_2} + HClO_4 \rightleftharpoons \underset{\text{(purple)}}{[Cu(HL^2)][ClO_4]_3} \qquad (1)$$

to square planar and is accompanied by a colour change from blue to purple.

Reaction of $L^2$ with $Zn(NO_3)_2{\cdot}6H_2O$ results in the formation of $[Zn(L^2)][NO_3]_2$. The $^{13}C$ n.m.r. spectrum (Figure) of this complex reveals the presence of two species, one symmetric, the other asymmetric. This deduction is based on the total number of resonances observed. The resonances at *ca.* 20 p.p.m. which arise from the central carbon atoms of the macrocyclic propyl units clearly show the presence of two species. For an asymmetric species two such resonances of equal intensity would be expected, while for a symmetric species only one would be observed. This is the case for $[Zn(L^2)][NO_3]_2$ where two equal-intensity resonances are observed at $\delta$ 20.7 and 20.9 p.p.m., while the third resonance for a symmetric species is evident at $\delta$ 20.3 p.p.m. The other resonances (Table 2) confirm this conclusion. It is likely that the symmetric species has all four substituents on the same side of the macrocycle, whereas the asymmetric species has only substituents at positions 1, 4, and 7 on the same side, as was previously observed for ($L^1$; R = H).[4,5]

## Experimental

All chemicals used were of the highest available purity. Carbon-13 n.m.r. spectra were recorded at 22.68 MHz with 1,4-

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† *Non-S.I. Units employed:* B.M. ≈ $9.27 \times 10^{-24}$ A m², mmHg ≈ 134 Pa.

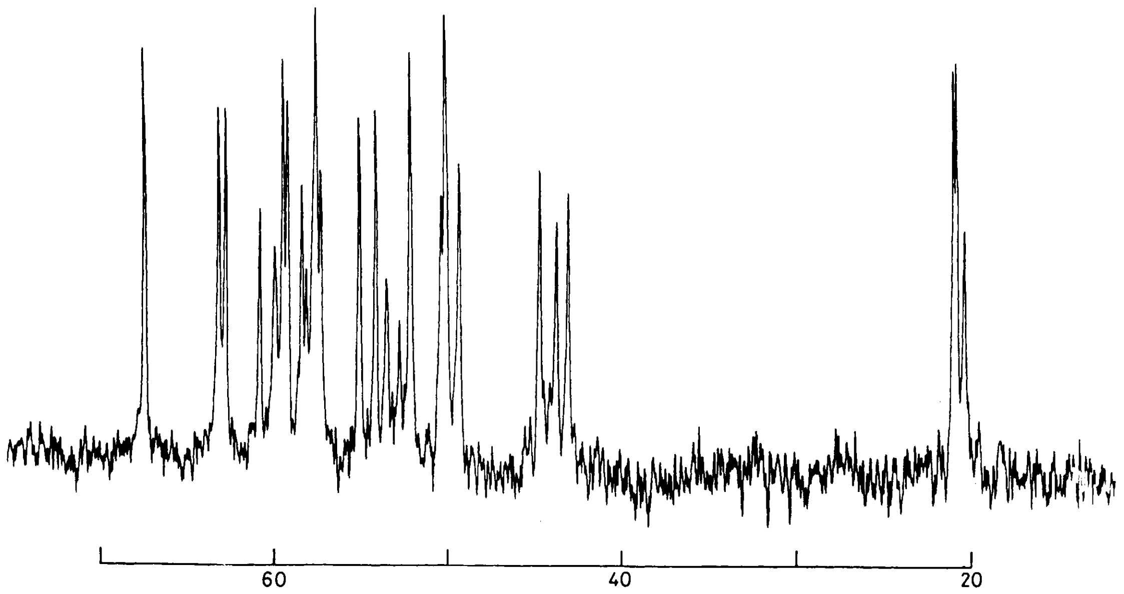

**Figure.** Carbon-13 n.m.r. spectrum of $[Zn(L^2)][NO_3]_2$ in $D_2O$

**Table 1.** Visible spectra and magnetic moments

| Complex | Magnetic moment, $\mu_{eff.}$/B.M. | Visible spectra [a] in $CH_3NO_2$ | Water |
|---|---|---|---|
| $[Cu(L^2)][ClO_4]_2$ | 2.21 | 700 (sh),<br>812 (353) | 700 (sh),<br>814 (337) |
| $[Cu(HL^2)][ClO_4]_3$ | 2.10 | 540 (sh),<br>635 (273) | 700 (130),[b]<br>952 (166) |
| $[Ni(L^2)][ClO_4]_2$ | 3.43 | 404 (92),<br>480 (sh),<br>679 (25.5),<br>1 150 (8) | 408 (82),<br>480 (sh),<br>684 (28),<br>1 150 (6) |

[a] λ/nm (ε/dm³ mol⁻¹ cm⁻¹). [b] The spectrum in water differs from that in $CH_3NO_2$ due to the equilibrium $[Cu(HL^2)]^{3+} + H_2O \rightleftharpoons [Cu(L^2)]^{2+} + H_3O^+$. Analogous behaviour was found in an earlier related study.[5]

**Table 2.** Carbon-13 n.m.r. data (δ/p.p.m.) for ($L^2$; R = Me), and two isomers of $[Zn(L^2)][NO_3]_2$ in $D_2O$ at 310 K (reference, 1,4-dioxane, δ 67.4; for each species, figures in parentheses represent the relative areas of the resonances)

| | $[Zn(L^2)][NO_3]_2$ | | |
|---|---|---|---|
| $L^2$ | Symmetric | Asymmetric | Assignment |
| 20.9(2) | 20.3(2) | 20.7(1), 20.9(1) | $C-CH_2-C$ |
| 43.7(1),<br>44.0(2), 45.0(2) | 43.1(2), 43.7(2),<br>50.1(1) * | 44.6(1), 49.3(1),<br>50.1(1),* 50.4(1),<br>52.1(1) * | $N-CH_3$ |
| 49.4(2), 50.0(2),<br>51.0(2), 52.7(1),<br>54.2(2), 56.2(1) | 52.1(1),* 52.7(1),<br>53.5(2), 58.1(2),<br>59.9(2), 60.7(2) | 54.1(1), 55.0(1),<br>57.2(1), 57.5(2),*<br>58.3(1), 59.1(1),*<br>59.4(1), 62.8(1),<br>63.2(1) | $N-CH_2-C$ |

* Overlapping resonance; tentative assignment.

dioxane (δ = 67.4 p.p.m.) as reference, using a Bruker WH90 Fourier-transform spectrometer. Proton n.m.r. spectra were recorded with $SiMe_4$ (δ = 0) as reference using a 400-MHz Bruker WH400 Fourier-transform spectrometer. U.v.-visible spectra were recorded with a Shimadzu (model 365) spectrophotometer, i.r. spectra with a Perkin-Elmer (model 580B) spectrometer, and mass spectra with a Kratos (model MS80) instrument. 11-(2′-Dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane was prepared as previously described.[4]

*Ligand* $L^2$.—11-(2′-Dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane (0.25 g, 0.9 mmol) was dissolved in 98% formic acid (3 cm³) and formaldehyde (8 cm³ of a 40% aqueous solution) was added. After heating at 90 °C for 15 h the reaction mixture was cooled, basified to *ca.* pH 10 with 15% aqueous NaOH, and extracted with $CH_2Cl_2$ (5 × 10 cm³). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to leave a pale yellow oil. Distillation (Kügelröhr apparatus) gave 11-(2′-dimethylaminoethyl)-1,4,7-trimethyl-1,4,7,11-tetra-azacyclotetradecane (0.26 g, 0.8 mmol), b.p. 130—135 °C (0.01 mmHg) in *ca.* 90% yield. ¹H N.m.r. ($CDCl_3$): δ 1.59 (4 H, pentet), 2.21 (15 H, s), 2.37 (2 H, m), and 2.48 p.p.m. (18 H, m). I.r. (thin film): no N–H stretch. Mass spectrum (electron ionisation): $M^+$ at $m/z$ 313 (calc.: 313). The ¹³C n.m.r. data are in Table 2.

$[Cu(L^2)][ClO_4]_2$.—Ligand $L^2$ (0.1 g, 0.32 mmol) was dissolved in ethanol and added to an ethanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (120 mg, 0.32 mmol). The resulting blue precipitate was filtered off, washed with diethyl ether, and dried (170 mg, 0.28 mmol) in *ca.* 87% yield. Combustion analysis: found: C, 33.3; H, 6.85; N, 11.25, calc. for $C_{17}H_{39}Cl_2CuN_5O_8 \cdot 2H_2O$: C, 33.35; H, 7.00; N, 11.45%.

$[Cu(HL^2)][ClO_4]_3$.—The salt $[Cu(L^2)][ClO_4]_2$ (0.1 g, 0.16 mmol) was stirred in ethanol during cautious addition of 70% perchloric acid. The resulting purple precipitate was filtered off, washed with diethyl ether, and dried to give $[Cu(HL^2)][ClO_4]_3$ (95 mg, 0.13 mmol) in *ca.* 82% yield. Combustion analysis: found: C, 28.5; H, 6.65; N, 9.70, calc. for $C_{17}H_{40}Cl_3CuN_5O_{12} \cdot 2H_2O$: C, 28.65; H, 6.25; N, 9.85%.

$[Ni(L^2)][ClO_4]_2$.—Ligand $L^2$ (50 mg, 0.16 mmol) was dissolved in ethanol and added to an ethanolic solution of $[Ni(dmso)_6][ClO_4]_2$ (116 mg, 0.16 mmol) (dmso = dimethyl sulphoxide). The resulting pale green precipitate was filtered off, washed with ether, and dried *in vacuo* to give [Ni(L$^2$)][ClO$_4$]$_2$ (82 mg, 0.14 mmol) in *ca.* 90% yield. Combustion analysis: found: C, 34.5; H, 7.20; N, 11.9, calc. for $C_{17}H_{39}Cl_2N_5NiO_8\cdot H_2O$: C, 34.7; H, 7.05; N, 11.9%.

[Zn(L$^2$)][NO$_3$]$_2$.—The salt $Zn(NO_3)_2\cdot 6H_2O$ (47 mg, 0.16 mmol) was dissolved in ethanol and added to an ethanolic solution of ligand L$^2$ (40 mg, 0.16 mmol). The product was precipitated as a white solid by addition of diethyl ether. Filtration and drying *in vacuo* gave [Zn(L$^2$)][NO$_3$]$_2$ (71 mg, 0.14 mmol) in 88% yield. The $^{13}$C n.m.r. data are compared with those of the free ligand in Table 2, and show the presence of two species.

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