

First example of a sixteen membered Jäger macrocycle having a 'Z' conformation

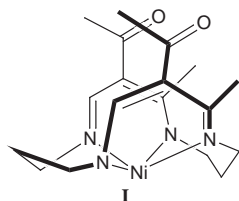
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The crystal structure of the first sixteen membered Jäger type macrocycle having a Z conformation rather than the expected saddle shaped geometry has been determined.

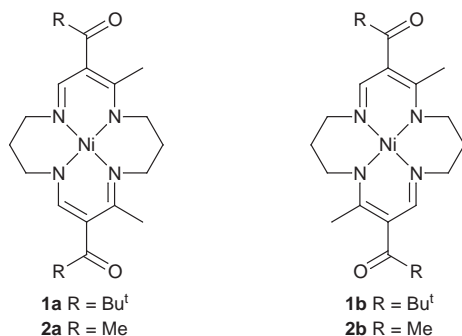
The family of tetraaza macrocycles first reported by Jäger¹ displays a fascinating interplay of structure–reactivity relationships and this has been exploited to interesting effect, in particular by Busch and Cairns, in the production of the so-called 'cyclidene' macrocyclic complexes² where examples have been used in reversible oxygen binding,³ as models for cytochrome P-450,⁴ and in supramolecular chemistry.⁵

The solid state structure of the Jäger macrocycles varies widely with ring size.⁶ The fourteen membered rings are planar, the fifteen membered rings adopt one of two possible geometries (either 'saddle shaped' or a Z conformation) while the sixteen membered ring, until now, has been found exclusively in the saddle shaped geometry (**1**). The saddle shape of the



sixteen membered species arises due to the conformations adopted by the two saturated six membered metallochelate rings present in the structure.⁶

As part of a study into the steric control of reactions of superstructured macrocycles⁷ we prepared a new example of a sixteen membered Jäger type complex, **1**, with neopentyl



substituents,[‡] and found that it exists as a 1:1 ratio of two isomers: the conventional species, with *cis* related ring methyl groups (**1a**) and an unusual *trans* isomer (**1b**). The complex was prepared by the general scheme described in the literature, except using neopentanoyl chloride as the acylation reagent.⁸ The isomers were separated using preparative TLC on neutral alumina, with CHCl₃–MeCN (10:1) as eluent and the isomeric nature of the two fractions was confirmed by mass spectrometry and by microanalysis. The slower moving isomer had a ¹H NMR spectrum consistent with those of saddle shaped (*cis*)

Jäger complexes, while both the ¹H and ¹³C NMR spectra of the other isomer indicated that it possessed higher symmetry.

Single crystals of each isomer were grown from CHCl₃–MeCN and the structures of **1a** (Fig. 1) and **1b** (Fig. 2) were determined. § Complex **1a** has the expected saddle shape and the most interesting feature of the structure is the disorder in the position of C(10), arising from the presence of both boat (22%) and chair (78%) conformations for the metallochelate ring containing this carbon atom. In **1b**, the ring methyl groups appear in a *trans* relationship, rather than the usual *cis*, and this causes the keto oxygen atoms also to adopt a *trans* relationship, to minimise steric repulsion between ring and acyl methyl groups. Further, also to avoid steric interaction with the ring methyls, both saturated metallochelate rings adopt a skewed conformation, forcing the molecule to adopt a structure that has one unsaturated chelate ring above and one below the Ni–N₄ plane, producing the unprecedented (for a sixteen membered ring) Z isomer. Notably this structure possesses a centre of inversion at the nickel centre and the NiN₄ unit is exactly planar. In both molecules there are intermolecular contacts between the keto oxygens and hydrogen atoms on the saturated portion of the macrocycle [in **1b**: O(1)⋯H(4) 2.534(3), in **1a**: O(1)⋯H(10B) 2.581(5), O(2)⋯H(3B) 2.589(4) and O(2)⋯H(5A) 2.359(4) Å].

Identification of the existence of **1b** opens the way for the production of new sixteen membered Jäger macrocyclic ligands with a radically different supramolecular structural motif from that of the *cis* isomer. For example the extended Z structure could be used as the basis for new polymeric systems, by bridging across the keto functions. Our work in this interesting area is continuing.

Initially we believed that the new type of structural isomer was being formed during the addition of the neopentyl group,

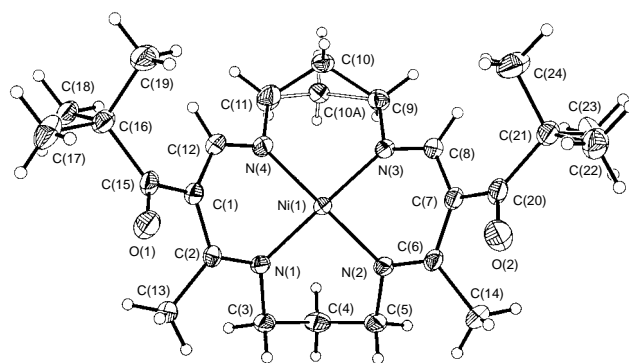


Fig. 1 Perspective view of compound **1a**; probability displacement ellipsoids are drawn at the 40% level. Selected bond lengths (Å) and angles (°) for **1a**: Ni(1)–N(4) 1.876(3), Ni(1)–N(3) 1.883(2), Ni(1)–N(2) 1.894(2), Ni(1)–N(1) 1.895(2), N(1)–C(2) 1.312(4), N(1)–C(3) 1.480(4), N(2)–C(6) 1.312(4), N(2)–C(5) 1.478(4), N(3)–C(8) 1.305(4), N(3)–C(9) 1.474(4), N(4)–C(12) 1.301(4), N(4)–C(11) 1.474(4); N(4)–Ni(1)–N(3) 92.22(11), N(4)–Ni(1)–N(2) 175.67(12), N(3)–Ni(1)–N(2) 88.09(10), N(4)–Ni(1)–N(1) 88.45(11), N(3)–Ni(1)–N(1) 174.90(11), N(2)–Ni(1)–N(1) 90.87(10), C(2)–N(1)–C(3) 118.2(3), C(6)–N(2)–C(5) 119.0(3), C(8)–N(3)–C(9) 117.2(3), C(12)–N(4)–C(11) 118.0(3).

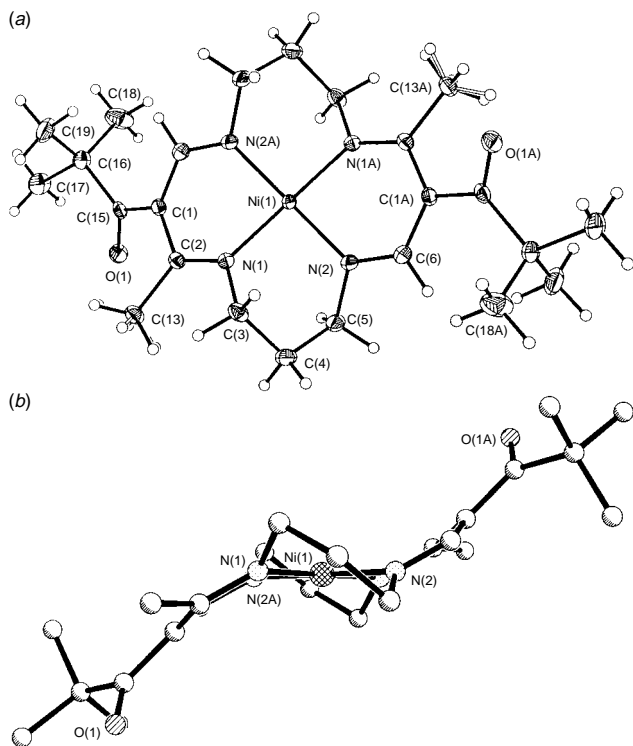


Fig. 2 (a) Perspective view of compound **1b**; probability displacement ellipsoids are drawn at the 40% level. Selected bond lengths (Å) and angles (°) for **1b**: Ni(1)–N(2) 1.874(2), Ni(1)–N(2A) 1.874(2), Ni(1)–N(1) 1.895(2), Ni(1)–N(1A) 1.895(2), N(1)–C(2) 1.308(3), N(1)–C(3) 1.479(3), N(2)–C(6) 1.296(4), N(2)–C(5) 1.469(3); N(2)–Ni(1)–N(2A) 180.0, N(2)–Ni(1)–N(1) 91.08(10), N(2A)–Ni(1)–N(1) 88.92(10), N(2)–Ni(1)–N(1A) 88.92(10), N(2A)–Ni(1)–N(1A) 91.08(10), N(1)–Ni(1)–N(1A) 180.0, C(2)–N(1)–C(3) 121.2(2), C(2)–N(1)–Ni(1) 126.6(2), C(3)–N(1)–Ni(1) 112.2(2), C(6)–N(2)–C(5) 118.1(2), C(6)–N(2)–Ni(1) 122.9(2), C(5)–N(2)–Ni(1) 118.7(2). Symmetry transformations used to generate equivalent atoms: A $-x, -y, -z + 1$. (b) Side view of **1b**, emphasising the Z conformation.

but this required a major rearrangement of the parent macrocycle which mechanistically seemed unlikely. Careful scrutiny of the reactions revealed that in fact both *cis* (**2a**) and *trans* (**2b**) forms of the parent sixteen membered complex were produced in the Schiff's base condensation reaction used to form this Jäger macrocycle from its acyclic precursor, and both **2a** and **2b** have now been structurally characterised.⁹ Prior to this work, the *trans* form had not been recognised as a product of the cyclisation reaction, and we believe that this is because it is usually the minor isomer and also it is rather more soluble than the *cis* isomer, hence previously only the *cis* form had been isolated and characterised. We have now carried out a detailed study of the conditions of the ring closure reaction and have found that it is possible to favour the formation of the *trans* isomer relative to the *cis*, and the details of this work, and the

X-ray structures of **2a** and **2b**, will be reported in a separate publication.⁹

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Notes and References

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‡ *Spectroscopic data*: for **1a**: ¹H NMR (CDCl₃, 200 MHz), δ 7.42 (s, 2 H), 3.10 (t, 4 H), 2.90 (s, 6 H), 2.10 (s, 6 H), 1.92 (m, 2 H) and 1.25 (s, 18 H); ¹³C NMR (CDCl₃, 50 MHz), δ 201.8, 167.6, 157.1, 113.8, 54.9, 50.0, 42.8, 30.7, 29.8, 29.5 and 20.2. For **1b**: ¹H NMR (CDCl₃, 400 MHz), δ 7.40 (s, 2 H), 3.00 (t, 4 H), 2.91 (t, 4 H), 2.30 (m, 4 H), 2.05 (s, 6 H) and 1.22 (s, 18 H); ¹³C NMR (CDCl₃, 100.6 MHz), δ 202.2, 166.7, 156.2, 114.2, 52.0, 48.7, 42.3, 29.1, 28.7 and 19.6.

§ For **1a** and **1b** intensity data were measured on a Siemens P4 diffractometer with Mo-Kα radiation, λ = 0.71073 Å, ω mode, θ range 2.0–25.00° at 160 K. Data collection and reduction were performed using the program XSCANS.¹⁰ Direct methods solution and refinements (full-matrix least squares on F²) were performed using SHELXTL/PC¹¹ Version 5.03.

Crystal data: for **1a**: red crystal (0.80 × 0.52 × 0.64 mm) from CHCl₃–MeCN coated with Nujol mounted on a glass fibre, C₂₄H₃₈N₄NiO₂·C₂H₃N, *M* = 514.34, monoclinic, space group *P*2₁/*n*, *a* = 10.1000(10), *b* = 10.5670(10), *c* = 25.414(3) Å, β = 90.950(10)°, *U* = 2712.0(5) Å³, *Z* = 4, *D*_c = 1.252 g cm⁻³, μ = 0.746 mm⁻¹. The structure was refined to *R*1 = 0.0501, *wR*2 = 0.1367 and goodness of fit 1.011 for 3988 unique observed [*I* > 2σ(*I*)] data and 317 parameters.

For **1b**: red crystal (0.6 × 0.4 × 0.25 mm) from CHCl₃–MeCN coated with Nujol mounted on a glass fibre, C₂₄H₃₈N₄NiO₂·2CHCl₃, *M* = 712.03, orthorhombic, space group *Pbca*, *a* = 15.721(2) *b* = 10.493(2), *c* = 19.668(3) Å, *U* = 3244.4(9) Å³, *Z* = 4, *D*_c = 1.458 g cm⁻³, μ = 1.123 mm⁻¹. The structure was refined to *R*1 = 0.0361, *wR*2 = 0.0801 and goodness of fit 1.021 for 2158 unique observed [*I* > 2σ(*I*)] data and 178 parameters. CCDC 182/913.

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