# Metal Ion Complexes of 5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. Part I. Some Nickel(II) and Copper(II) Compounds

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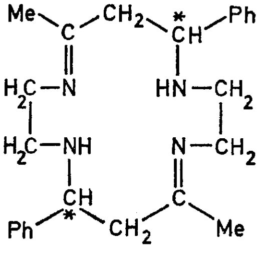
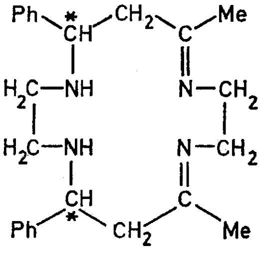
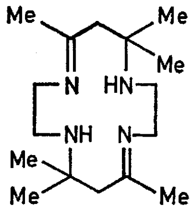
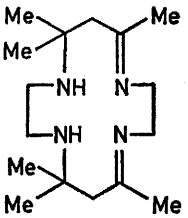
Preparations and properties of nickel(II) and copper(II) complexes of the tetra-aza macrocycle (**1**) formed by reaction of benzylideneacetone with diaminoethane are reported. Stereochemical evidence favouring assignment of the structure 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene for (**1**), present in the *trans-trans-meso*-configuration, is presented. Compounds with two configurations of the cation $[\mathrm{Ni}(\mathbf{1})]^{2+}$ arising from the chiral co-ordinated secondary amino-groups were isolated. The β (*N-meso*) configuration is optimum for planar *bcde*-co-ordination and singlet ground-state square-planar salts $[\mathrm{Ni}(\beta\mathbf{1})]X_2$, X = $ClO_4^-$, $BF_4^-$, $I^-$, and $0{\cdot}5ZnCl_4^{2-}$ and *trans*-octahedral triplet ground-state compounds *trans*-$[\mathrm{Ni}(\beta\mathbf{1})X_2]$, X = $Cl^-$, $NCS^-$, $CH_3CO_2^-$, or $NO_3^-$ and *trans*-$[\mathrm{Ni}(\beta\mathbf{1})(NH_3)(H_2O)](ClO_4)_2$ were prepared. The α (*N-rac*) configuration is optimum for folded *abcd*-co-ordination and triplet ground-state compounds with chelates occupying the *ef* co-ordination sites, $[\mathrm{Ni}(\alpha\mathbf{1})\mathrm{en}](ClO_4)_2$, $[\mathrm{Ni}(\alpha\mathbf{1})\mathrm{acac}]ClO_4$, and $[\{\mathrm{Ni}(\alpha\mathbf{1})\}_2C_2O_4](ClO_4)_2$ were prepared. Treatment of these compounds with acid removed the chelate by protonation while preserving the α configuration to give square planar salts $[\mathrm{Ni}(\alpha\mathbf{1})](ClO_4)_2$ and $[\mathrm{Ni}(\alpha\mathbf{1})]ZnCl_4$, metastable with respect to their β configurational isomers. The co-ordination stereochemistry of (**1**) is discussed and $^1H$ n.m.r., i.r., and *d–d* electronic spectra are reported. It is concluded that the metastability of the α configuration of (**1**) in planar co-ordination arises from strain introduced by the presence of a phenyl group as an axial substituent on one six-membered chelate ring. The compounds $[\mathrm{Cu}(\beta\mathbf{1})]X_2$, X = $ClO_4^-$, $NO_3^-$, or $NCS^-$ and $[\mathrm{Cu}(\beta\mathbf{1})]Cl_2,4H_2O$ are assigned tetragonal structures. The i.r. spectra of the perchlorate and nitrate indicate weak metal–anion interactions.

THE reaction of diaminoethane with benzylideneacetone to yield a tetra-aza macrocycle has been reported by Hideg and Lloyd.[1] The structure of the product of this reaction has not been unambiguously established, it could be 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (**1a**) or the geometrical isomer with one of the benzylideneacetone bridging groups 'reversed,' to give the 4,14-diene (**1b**). Related 1,4,8,11-tetra-azacyclotetradeca-4,11-dienes are formed by reactions between diaminoethane and mesityl oxide or acetone (**2**),[2] or ethyl methyl ketone,[3] and between 1,2-diaminopropane and acetone,[4] although in these cases the reacting diamines were monoprotonated, and the macrocycles crystallised as diprotonated salts. However, complexes of geometrically isomeric 4,14-dienes are formed by reaction of tris(diaminoethane)-nickel(II) or copper(II) with acetone (**3**),[5,6] or ethyl methyl ketone [3] and a related tetra-azahexadeca-5,16-diene complex results from reaction of 1,3-diaminopropane hydrochloride, methyl vinyl ketone, and a nickel(II) salt.[7] The pair of chiral carbon centres (marked * in formulae) present for (**1a**) (or **1b**) and *cis-* or *trans*-configurations of the imino-groups provide further possible sources of isomerism. The related reactions of salts of diaminoethane with ethyl methyl ketone, and of 1,2-diaminopropane with acetone yield exclusively the *C-meso* macrocycles.[3,4]


(**1a**)


(**1b**)


(**2**)


(**3**)

The most probable course of the reaction between diaminoethane and benzylideneacetone to yield (**1**) is considered to be a Michael addition to form a β-amino-ketone, followed by dimerisation by amine–carbonyl condensation, which would yield the 4,11-diene, probably in the *C-meso*-configuration. Hideg and Lloyd, however, favour the *cis*-structure (**1b**), formed by a different mechanism.[1] The product of the reaction, obtained in 80% yield,† appears to be homogeneous (as indicated by physical properties such as m.p. and i.r. and $^1H$ n.m.r. spectra) and attempts to separate it, or its complexes with metal-ions, into isomeric components were unsuccessful. When the imine functions of (**1**) were reduced using sodium borohydride, only three

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† An 80% yield of (**1**) was reported by Hideg and Lloyd, but higher overall yields of (**1**) were obtained by reacting the residues with nickel acetate and isolating $[\mathrm{Ni}(\beta\mathbf{1})](ClO_4)_2$.

[1] K. Hideg and D. Lloyd, *Chem. Comm.*, 1970, 929; *J. Chem. Soc.* (*C*), 1971, 3441.

[2] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

[3] N. F. Curtis, to be published.

[4] N. F. Curtis, T. N. Waters, D. A. Swann, and I. E. Maxwell, *J. Amer. Chem. Soc.*, 1969, **91**, 4588; N. F. Curtis, *J.C.S. Dalton*, 1973, 863.

[5] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.* (*A*), 1966, 1015.

[6] N. F. Curtis, *J.C.S. Dalton*, 1972, 1357.

[7] J. F. Meyers and C. H. L. Kennard, *Chem. Comm.*, 1972, 77.

isomeric amines were isolated, as expected for any one of the possible isomeric formulations. The isolation of these cyclic tetra-amines and the preparation of their complexes with metal-ions will be described subsequently.

## *Nickel*(II) *Complexes*

The macrocycle (**1**) reacts rapidly with a variety of nickel(II) salts in methanol to form the cation $[Ni(\mathbf{1})]^{2+}$, present in the β-configuration of the chiral nitrogen centres (below).* When poorly co-ordinating anions are present, square-planar, singlet ground-state salts are formed, *e.g.* $[Ni(\beta\mathbf{1})](ClO_4)_2$ or $[Ni(\beta\mathbf{1})]ZnCl_4$ (most compounds are hydrated, but this will be neglected in the discussion, details are in the Experimental section). When unidentate anions with a greater tendency to co-ordinate to nickel(II) are present, triplet ground state, *trans*-octahedral compounds are formed, *trans*-$[Ni(\beta\mathbf{1})X_2]$, $X = Cl^-$, $NCS^-$, $NO_3^-$, and $CH_3CO_2^-$. The cation $[Ni(\beta\mathbf{1})]^{2+}$ shows little tendency to co-ordinate neutral ligands, but does crystallise from concentrated aqueous ammonia as *trans*-$[Ni(\beta\mathbf{1})(NH_3)(H_2O)](ClO_4)_2$ and a pale green adduct crystallised when ether was added to a methyl cyanide solution of $[Ni(\beta\mathbf{1})](ClO_4)_2$ (this slowly reverted to the simple perchlorate on exposure to the atmosphere). $[Ni(\beta\mathbf{1})](ClO_4)_2$ reacts with diaminoethane, or acetylacetone plus base, in appropriate solvents, to yield the chelated derivatives *cis*-$[Ni(\alpha\mathbf{1})en](ClO_4)_2$ and *cis*-$[Ni(\alpha\mathbf{1})acac]ClO_4$, respectively, which reacted with oxalic acid to yield *cis*-$[\{Ni(\alpha\mathbf{1})\}_2C_2O_4](ClO_4)_2$, with bridging-bi-chelate oxalate. These chelate compounds must contain the macrocycle in folded *abcd* co-ordination to accommodate the chelate in *cis* co-ordination sites. The macrocycle is present in the α nitrogen configuration, which is optimum for folded co-ordination. Treatment with acid removes the chelate by protonation and preserves the nitrogen configuration, to give the metastable square planar salts $[Ni(\alpha\mathbf{1})](ClO_4)$ and $[Ni(\alpha\mathbf{1})]ZnCl_4$. These are stable in the solid, in aprotic solvents, or in strongly acid protic solvents, but the cation isomerises slowly in neutral or rapidly in basic solution to the β configuration which is stable in planar co-ordination. The configurations of the compounds are discussed in more detail, below.

The nickel(II) complexes of (**1**) are very resistant to substitution and (**1**) is displaced only by cyanide. The co-ordinated di-imine is very resistant to acid hydrolysis, but is slowly hydrolysed under basic conditions, solutions become turbid on standing and an odour of benzaldehyde develops.

*Infrared Spectra.*—The i.r. spectra of the complexes of (**1**) show bands assignable to (**1**) [in particular ν(NH), *ca.* 3200 $cm^{-1}$; δ(NH), *ca.* 1490 $cm^{-1}$; ν(C:N), *ca.* 1660 $cm^{-1}$ and aromatic bands near 1600 $cm^{-1}$ and in the region 700—780 $cm^{-1}$]. The ν(NH) absorption is generally displaced to lower frequency by 100—150 $cm^{-1}$ compared with (**1**) (a single, sharp band at 3316 $cm^{-1}$), except for the acetylacetone derivative, where ν(NH) is at the same frequency as for (**1**). Many of the compounds are hydrated and the i.r. spectra indicate hydrogen bonding by the water. For $[Ni(\beta\mathbf{1})Cl_2],4H_2O$ both ν(OH) and ν(NH) are broadened and lowered in frequency, suggesting that the secondary amine groups are involved in the hydrogen bonding interaction, while for $[Ni(\beta\mathbf{1})(NO_3)_2],3H_2O$, ν(OH) is broadened and lowered in frequency, but ν(NH) remains sharp and unshifted, suggesting that in this case the interaction is between the water and the anions.

The spectrum of the thiocyanato-compound is indicative of *N*-co-ordinated thiocyanate, which is normal for thiocyanate co-ordinated to nickel(II).[10] †

The bands assigned to the acetate ion of $[Ni(\beta\mathbf{1})(CH_3CO_2)_2]$ are similar in frequency to those of other nickel(II) tetramine compounds assigned structures with *trans*-unidentate co-ordinated acetate.‡ [11,12]

The i.r. spectrum of $[Ni(\beta\mathbf{1})(NO_3)_2],3H_2O$ is indicative of the presence of unidentate co-ordinated nitrate ions, the $\nu_3$ mode of the nitrate ion being split into two components, separation *ca.* 90 $cm^{-1}$, as observed for other nickel(II) tetra-amine compounds assigned structures with *trans* unidentate co-ordinated nitrate.[13,14] §

The compound $[Ni(\beta\mathbf{1})(NH_3)(H_2O)](ClO_4)_2$ shows bands indicative of co-ordinated ammonia.[12] Analysis shows the presence of only one mole of ammonia, so it is presumed that the water molecule occupies the sixth co-ordination site.||

The diaminoethane and acetylacetonato-compounds have i.r. spectra with bands typical of the normal chelates.[12] The acetylacetonate shows a doublet ν(C:N), while for all the other compounds this band is a singlet.¶

The spectrum of the compound $[\{Ni(\alpha\mathbf{1})\}_2C_2O_2](ClO_4)_2$ shows bands assignable to the oxalate ion $ very similar to those of $[\{Ni(\alpha\mathbf{2})\}_2C_2O_4](ClO_4)_2$,[15] and of

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* The nitrogen configuration optimum for folded co-ordination is designated α, and that optimum for planar co-ordination is designated β. This is consistent with the terminology adopted for the complexes of (**2**)[6] and also for complexes of related cyclic tetramines.[8,9]

† ν(CS), 815; ν(C:N), 2100vs, sp; 2080s,sh $cm^{-1}$.

‡ $\nu_{as}$(OCO), 1573vs,br; $\nu_s$(OCO), 1393s,sp; δ(OCO), 647s,sp $cm^{-1}$.

§ $(\nu_1 + \nu_3)$, 2403m, 2320sh; $(\nu_1 + \nu_4)$, 1756w; $\nu_3$, 1412m, 1321s,br; $\nu_2$, 825m,sp $cm^{-1}$; $\nu_4$ obscured by aromatic bands.

|| ν(OH), 3580m,sp, 3450; $\nu(NH_3)$, 3343m, 3266m; ν(NH), 3185w,sp; $\delta(NH_3) + \delta(H_2O)$, 1622m,br; $\delta_s(NH_3)$, 1263m,br $cm^{-1}$).

¶ $[Ni(\alpha\mathbf{1})en](ClO_4)_2,2H_2O$; ν(OH), 3570m,br, 3535m,br; $\nu(NH_2)$, 3341s, 3287s; ν(NH), 3181; $\delta(NH_2)$, 1604m $cm^{-1}$. $[Ni(\alpha\mathbf{1})acac]ClO_4,0{\cdot}5H_2O$: ν(OH), 3614m,sp, 3535w,sp; ν(NH), 3316w,sp; ν(C:N), 1677s,sp, 1665s,sp; (acac), 1599s, 1514s, 1407s,br $cm^{-1}$.

$ $\nu_{as}$(OCO), 1645vs; $\nu_s$(OCO), 1370m; δ(OCO), 793m $cm^{-1}$.

[8] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

[9] N. F. Curtis and G. W. Reader, *J. Chem. Soc.* (*A*), 1971, 1771.

[10] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407; N. F. Curtis and Y. M. Curtis, *Austral. J. Chem.*, 1966, **19**, 1423.

[11] N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1579.

[12] K. Nakomoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, 1963.

[13] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.

[14] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[15] N. F. Curtis, *J. Chem. Soc.*, 1963, 4109.

$[\{Ni(en)_2\}_2C_2O_4](NO_3)_2$,[16] which has been shown to have a structure in which the oxalate ion acts as a bridging group, forming five-membered chelate rings with two nickel(II) ions.[17]

The aromatic band near 800 $cm^{-1}$ gives some support to the suggestion (below) that the two phenyl substituents are in equivalent sites for the β configuration, and in non-equivalent sites for the planar α configuration. This band is a singlet for the β perchlorate (775 $cm^{-1}$) and tetrachlorozincate (772 $cm^{-1}$), but a doublet for the α analogues (765, 773; 770, 780 $cm^{-1}$ respectively). Lowered site symmetry could also cause a splitting of this band, and although it is a singlet for the other *trans* compounds, it is a doublet for the thiocyanate (775, 785 $cm^{-1}$).

The isomeric perchlorates show marked differences in the frequencies of the ν(NH) band: $[Ni(\alpha\mathbf{1})](ClO_4)_2,0\cdot5H_2O$, 3204 $cm^{-1}$; $[Ni(\beta\mathbf{1})](ClO_4)_2$, 3161 $cm^{-1}$ and a smaller difference in the position of the ν(C:N) band: α-form, 1656 $cm^{-1}$; β-form, 1646 $cm^{-1}$.

TABLE 1

Nickel(II) *d–d* spectra of singlet ground-state compounds [a]

| | |
|---|---|
| $[Ni(\beta\mathbf{1})](BF_4)_2,0\cdot5H_2O$ [b] | 22·5 (105) |
| $[Ni(\beta\mathbf{1})](ClO_4)_2$ [c] | 21·3 |
| $[Ni(\beta\mathbf{1})]I_2,0\cdot5H_2O$ [c] | 20·4 |
| $[Ni(\alpha\mathbf{1})](ClO_4)_2,0\cdot5H_2O$ [d] | 23·0 (116) |
| $[Ni(\alpha\mathbf{1})](ClO_4)_2,0\cdot5H_2O$ [c] | 20·8 |

[a] Band maximum in $10^3$ $cm^{-1}$, molar extinction coefficients in parentheses. [b] In acetone. A solution in methyl cyanide showed in addition weak bands at 10 300 and 14 800 $cm^{-1}$, possibly due to the presence of a small amount of a triplet ground state methyl cyanide adduct (see ref. 11 for analogous case). [c] Diffuse reflectance spectrum. [d] In *ca.* 0·5M methanolic perchloric acid.

*Nickel Ion* d–d *Spectra.*—Solution and reflectance spectra of singlet ground-state (Table 1) and triplet ground-state (Table 2) compounds are listed. The triplet ground-state compounds with unidentate additional ligands all show four band spectra indicative of the *trans*-configuration.[13,18] When soluble, the triplet ground-state compounds have spectra in acetone or methyl cyanide similar to those of the solids, but in water or methanol of the $[Ni(\beta\mathbf{1})]^{2+}$ ion, indicating dissociation.

TABLE 2

Nickel(II) *d–d* spectra [a] and magnetic susceptibilities of triplet ground-state compounds

| Compound | $\nu_1$ [b] | $\nu_2$ | $10^6\chi_g(T/K)$ | $\mu_{eff}$/B.M. [c] |
|---|---|---|---|---|
| $[Ni(\beta\mathbf{1})(NCS)_2]0\cdot5H_2O$ | 10·5, 14·7 | 19·8 | 6·713 (297·2) | $3\cdot0_3$ |
| $[Ni(\beta\mathbf{1})C_2O_4]4H_2O$ | 10·2, 14·5 | 18·8 | 6·203 (299·2) | $3\cdot0_9$ |
| $[Ni(\beta\mathbf{1})(OAc)_2]$ | 10·1, 15·1 | 19·9 | 6·948 (297·0) | $3\cdot0_8$ |
| $[Ni(\beta\mathbf{1})(NO_3)_2]3H_2O$ | 9·4, 15·6 | 20·1 | 6·362 (299·2) | $3\cdot0_9$ |
| $[Ni(\beta\mathbf{1})Cl_2]2H_2O$ | 9·3, 15·4 | 19·8 | | |
| $[Ni(\beta\mathbf{1})(NH_3)(H_2O)](ClO_4)_2$ | 9·8, 15·4sh | 20·0 | | |
| $[Ni(\alpha\mathbf{1})acac](ClO_4),0\cdot5H_2O$ | 11·3 | 19·0 | 6·068 (295·9) | $3\cdot0_9$ |
| $[\{Ni(\alpha\mathbf{1})\}_2C_2O_4](ClO_4)_2$ | 10·8 | 18·3 | | |
| $[Ni(\alpha\mathbf{1})en](ClO_4)_2,2H_2O$ | 10·6 | 18·5 | 4·553 (298·8) | $2\cdot9_0$ |
| $[Ni(\alpha\mathbf{2})acac]ClO_4$ [d] | 10·5 | 17·8 | | |
| $[\{Ni(\alpha\mathbf{2})\}_2C_2O_4)_2$ [d] | 10·8 | 17·9 | | |
| $[Ni(\beta\mathbf{2})(NCS)_2]$ [e] | 10·8, 12·5 | 15·5 | | |

[a] Diffuse reflectance spectra, band maxima in $10^3$ $cm^{-1}$. [b] Assignments for $O_h$ symmetry $\nu_1$, ${}^3T_{1g}\leftarrow{}^3A_{2g}$; $\nu_2$, ${}^3T_{2g}\leftarrow{}^3A_{2g}$. The $\nu_3$ band, ${}^3T_{2g}(F)\leftarrow{}^3A_{2g}$, was generally not resolved from charge transfer, and ligand absorption, except for $Ni(\beta\mathbf{1})(OAc)_2$, 27 700 $cm^{-1}$. [c] Calculated assuming Curie law, with corrections for diamagnetism and for T.I.P. ($8N\beta^2/\Delta$, where Δ is taken as the energy of the $\nu_1$ transition. [d] From ref. 9. [e] From ref. 19.

Comparison of the data for the spectra of the analogous compounds of (**1**) and (**2**) (Table 2) shows that the effective ligand field strength of (**1**) is greater than that of (**2**) for the thiocyanates (β-planar) and acetylacetonates (α-folded), but is similar for the oxalates (α-folded).

*Magnetic Susceptibilities.*—The magnetic susceptibilities and moments at room temperature of some of the triplet ground-state compounds are shown in Table 2. The magnetic moments are within the normal range for 'octahedral' nickel(II).

*Proton Magnetic Resonance Spectra.*—Chemical shifts for the methyl and phenyl resonances are: (**1**); $\sigma_{Me}$, 1·80 (6H); $\sigma_{Ph}$, 7·26 (10H) in deuteriochloroform; $[Ni(\beta\mathbf{1})](ClO_4)_2$; $\sigma_{Me}$, 2·19 (6H); $\sigma_{Ph}$, 7·40 (10H unresolved); $[Ni(\alpha\mathbf{1})](ClO_4)_2,0\cdot5H_2O$; $\sigma_{Me}$, 2·12 (3H), 2·25 (3H); $\sigma_{Ph}$, 7·46 (5H unresolved), 7·55, 7·63, 7·67, 7·80 (3H, *o* and *p* protons); 8·67, 8·75 (2H, *m* protons) in deuteriotrifluoroacetic acid, in p.p.m. downfield from T.M.S. as internal standard at 100 MHz.

The spectrum of $[Ni(\beta\mathbf{1})]^{2+}$ shows single phenyl and methyl resonances, indicating that the substituents on the two six-membered chelate rings are in equivalent sites. The phenyl resonance of (**1**) is not greatly affected by co-ordination, but the methyl resonance is shifted downfield by *ca.* 0·4 p.p.m., presumably as a result of decreased electron density in the imine function resulting from formation of the co-ordinate bond by the nitrogen atom. The methyl resonance chemical shift for $[Ni(\beta\mathbf{1})]^{2+}$ is similar to that observed for nickel(II) complexes of (**2**), (**3**), and related macrocycles with a methyl group adjacent to a co-ordinated imine function.[19] The spectrum of $[Ni(\alpha\mathbf{1})]^{2+}$ shows a methyl doublet, and two distinct phenyl resonances, one unresolved, and the other with large 'across the ring' chemical shift differ-

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[16] N. F. Curtis, *J. Chem. Soc. (A)*, 1968, 1584.

[17] N. F. Curtis, I. R. N. McCormick, and T. N. Waters, *J.C.S. Dalton*, in the press.

[18] A. B. P. Lever, *Co-ordination Chem. Rev.*, 1968, **3**, 119.

[19] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 703; 1968, **90**, 6938.

ences and greater overall downfield shift. One methyl, and the unresolved phenyl resonance have chemical shifts similar to those for the $\beta$ isomer, and it is concluded that one of the six-membered chelate rings of the $\alpha$ isomer has a conformation which results in the substituents being in sites similar to those for the $\beta$ isomer. For the second six-membered chelate ring of the $\alpha$ isomer, the substituents are in sites differing from those of the $\beta$ isomer, and the phenyl protons in particular are subjected to some magnetic perturbation. Protons sited close to the metal, above the 'plane' of square planar $d^8$ complexes, are subject to large downfield chemical shifts,[20] as, *e.g.*, for the axial components of the *gem* dimethyl groups of the related cations $[\mathrm{Ni}(\mathbf{2})]^{2+}$ and $[\mathrm{Ni}(\mathbf{3})]^{2+}$.[19] It is therefore probable that the $\alpha$ configuration of (**1**) in planar co-ordination has a conformation which places one of the phenyl groups as an axial substituent of the six-membered chelate ring. The interpretation of this information in terms of the structure of (**1**), and configuration and conformation of its complexes is discussed below.

## *Copper*(II) *Compounds*

The macrocycle (**1**) reacts readily with copper salts in methanol to give compounds of the cation $[\mathrm{Cu}(\mathbf{1})]^{2+}$. The method of preparation of the copper complexes [basic solution arising from the basic character of (**1**)] ensured that the optimum $\beta$-configuration would be adopted. This was confirmed by the similarity of the *X*-ray powder diffraction patterns of $[\mathrm{Ni}(\beta\mathbf{1})](\mathrm{ClO_4})_2$ and $[\mathrm{Cu}(\mathbf{1})](\mathrm{ClO_4})_2$ which indicate that they are most probably isostructural.

Attempts to prepare nominally five-co-ordinate derivatives of the type $[\mathrm{Cu}(\mathbf{1})\mathrm{X}]\mathrm{Y}$, analogous to *e.g.* $[\mathrm{Cu}(1,3\text{-pn})_2\mathrm{NCS}]\mathrm{ClO_4}$ [21] by crystallising together equimolar amounts of *e.g.* $[\mathrm{Cu}(\mathbf{1})](\mathrm{NCS})_2$ and $[\mathrm{Cu}(\mathbf{1})](\mathrm{ClO_4})_2$ were unsuccessful; in each case the least soluble simple salt crystallised first, followed by the other. Compounds of this type, where $\mathrm{X} = \mathrm{Cl}^-$, $\mathrm{NCS}^-$, $\mathrm{CN}^-$, *etc.* and $\mathrm{Y} = \mathrm{ClO_4}^-$, $\mathrm{I}^-$, *etc.* are formed by related tetra-aza-macrocycles,[22] including cyclic tetra-amines formed by the reduction of (**1**).[23]

*Infrared Spectra.*—The i.r. spectra of the four compounds are nearly identical in the region 650—1000 cm$^{-1}$, with the exception of bands assigned to the anions [825 cm$^{-1}$, $\nu_2(\mathrm{NO_3}^-)$ and 751 cm$^{-1}$, $\nu$(CS) of $\mathrm{NCS}^-$] supporting assignment of the same configuration of (**1**). All the compounds show a single strong absorption *ca.* 1660 cm$^{-1}$ assigned to $\nu$(C:N); and a single band in the region 3140—3230 cm$^{-1}$, assigned to $\nu$(NH).

The $\nu$(NH) band for the perchlorate salt occurs at 3229 cm$^{-1}$ and is strong and sharp. Displacements to lower frequency for the thiocyanate (3190m,sp cm$^{-1}$) and especially the nitrate (3139m cm$^{-1}$) may indicate some form of intermolecular NH-anion hydrogen bonding. For the chloride hydrate, the lower than usual frequencies for $\nu$(OH) (3380 cm$^{-1}$) and $\nu$(NH) (3140 cm$^{-1}$) suggests the presence of hydrogen bonding involving the water and amino-groups. The compound probably has a structure similar to that found for other copper(II) tetra-amine halide hydrates, such as $\mathrm{Cu(en)_2Cl_2,2H_2O}$.[24,25]

For the compounds $\mathrm{Cu}(\mathbf{1})\mathrm{X}_2$, $\mathrm{X}^- = \mathrm{ClO_4}^-$, $\mathrm{NO_3}^-$, and $\mathrm{NCS}^-$ the i.r. spectra indicate the pressure of the anion in one environment, thus excluding structures of the type $[\mathrm{Cu}(\mathbf{1})\mathrm{X}]\mathrm{X}$. The bands assigned to the anions of $[\mathrm{Cu}(\mathbf{1})](\mathrm{NO_3})_2$ * and $[\mathrm{Cu}(\mathbf{1})](\mathrm{ClO_4})_2$ † show the $\nu_2(\mathrm{NO_3}^-)$ and $\nu_3(\mathrm{ClO_4}^-)$ modes as doublets, indicating lowered symmetry,[26-28] but the magnitudes of these splittings are less than normally observed for unidentate co-ordination to a divalent ion. The separation between the components of $\nu_2$ is 70 cm$^{-1}$ for $[\mathrm{Cu}(\mathbf{1})](\mathrm{NO_3})_2$ compared with 90 cm$^{-1}$ for $[\mathrm{Ni}(\mathbf{1})(\mathrm{NO_3})_2]$ (above) where the nitrate ion is in 'normal' co-ordination. Similar i.r. spectra have been reported for the anions of bis(diaminoethane)-copper(II) nitrate and perchlorate,[24-29] and *X*-ray structural studies have confirmed weak anion interactions in the tetragonal sites for these compounds.[30,31]

The i.r. spectrum of $[\mathrm{Cu}(\mathbf{1})](\mathrm{NCS})_2$ shows a single strong band at 2048 cm$^{-1}$ and a weak band at 751 cm$^{-1}$,‡ which suggests that the two thiocyanate ions are structurally equivalent, unlike square pyramidal [Cu(trien)SCN]SCN [32] or trigonal bipyramidal [Cu(tren)NCS]SCN,[33] which both show i.r. bands assignable to ionic and co-ordinated thiocyanate ions.[34,35] The spectra of $\mathrm{Cu(en)_2(SCN)_2}$ (2020, 730 cm$^{-1}$) [36] and

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* $\nu_2$: 825m,sp; $\nu_3$: 1314s, 1384s; $(\nu_1 + \nu_3)$: 2405w, *ca.* 2340w; $(\nu_1 + \nu_4)$: 1738v,br cm$^{-1}$. $\nu_1$ and $\nu_4$ obscured.

† $\nu_3$: 1058vs, 1092vs cm$^{-1}$.

‡ A further $\nu$(CS) band *could* be obscured by the aromatic band at 706 cm$^{-1}$.

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$Cu(1,3\text{-}pn)_2(SCN)_2$ (2062, 760 $cm^{-1}$) [37] both with tetragonal *S*-interaction structure [38,39] and Cu(*NN'-dimethylethylenediamine*)$_2$(NCS)$_2$ (2062, 746 $cm^{-1}$) [33]* with a tetragonal *N*-interaction structure [40] indicate that thiocyanate i.r. spectra are unreliable for diagnosis of weak *N*- or *S*-tetragonal site interactions of the type found for copper(II) tetra-amine dithiocyanates. However, in view of the definite indication of tetragonal site interactions for the perchlorate and nitrate, it seems reasonable to conclude that the thiocyanate ion, which is a better ligand, will also be interacting in the axial sites.

*Copper*(II) d–d *Spectra and Magnetic Susceptibilities*.—These are listed in Table 3 and are similar to those of tetragonal $[Cu(en)_2]X_2$ compounds,[24] and compounds with related tetra-aza macrocycles.[8,41]

TABLE 3

Copper-ion *d–d* spectra and magnetic susceptibilities

| Compound | Band max.[a] | $10^6\chi g$ [b] | $\mu_{eff}$ [c] |
|---|---|---|---|
| $[Cu(\mathbf{1})](ClO_4)_2$ | 19·7 | 1·786 | $1{\cdot}8_1$ |
| $[Cu(\mathbf{1})](NO_3)_2$ | 19·5 [d] | 1·999 | $1{\cdot}7_0$ |
| $[Cu(\mathbf{1})](NCS)_2$ | 18·5 | | |
| $[Cu(\mathbf{1})]Cl_2,4H_2O$ | 18·8, *ca.* 16·5sh [e] | 1·723 | $1{\cdot}7_1$ |

[a] Diffuse reflectance spectra in $10^3$ $cm^{-1}$. [b] At 296 K. [c] In B.M., calculated assuming Curie law, with corrections for diamagnetism (Pascals' constant) and for T.I.P. ($4N\beta^2/\Delta$, where $\Delta$ was taken as $1{\cdot}3 \times 10^4$ $cm^{-1}$). [d] 19 000 $cm^{-1}$ ($\varepsilon = 130$) in methanol solution. [e] 18 700 ($\varepsilon = 119$) in methanol solution.

## DISCUSSION

The product of the diaminoethane–benzylideneacetone reaction could have the structures (**1a**) or (**1b**), in each case present in the *C-meso* or *C-rac* configuration and with *cis*- or *trans*-configuration of the imino-groups. As a stereochemical necessity, the formation of compounds of (**1**) in which the nitrogen atoms occupy *bcde*- or *abcd*-octahedral co-ordination sites determines that the imino-groups have the *trans*-configuration [as observed for complexes of (**2**) and (**3**)]. The two secondary amino groups become chiral centres when co-ordinated, leading to three possible configurations for each of the previous structures. For related secondary amino-complexes, such as those of (**2**), the nitrogen configurations are interconvertible in solution, the inversion reaction being rapid in base, effectively inhibited in strongly acidic or aprotic solvents,[5,19] and the same behaviour would be expected for the complexes of (**1**). For (**1**), nickel(II) complexes were prepared with two nitrogen configurations, designated α and β. The β configuration is stable in singlet ground-state, square-planar salts and triplet ground-state *trans*-octahedral complexes with unidentate 'additional' ligands. The α configuration is stable for octahedral complexes with a chelate occupying the two 'additional' co-ordination sites, but is metastable in planar co-ordination.

In planar *bcde* co-ordination the 4,11-diene (**1a** or **2**) and the 4,14-diene (**1b** or **3**) macrocycles can co-ordinate with either the *N-rac* or *N-meso* configurations. Structures of *N-rac*-$[Ni(\mathbf{2})](ClO_4)_2$ [42] (and its *C-rac-N-rac*-3,10-dimethyl derivative [43]), *N-rac*-$[Ni(\mathbf{2})](CNS)_2,H_2O$,[43a] *N-rac*-$[Ni(\mathbf{3})](ClO_4)_2$,[44] and *trans-N-meso*-$[Co(\mathbf{3})(CN)_2]ClO_4$ [45] have been reported. These all have the six-membered chelate rings in a similar half-chair conformation. This conformation also occurs for other compounds with the same chelate ring,[46] and is in agreement with that predicted by strain energy minimisation calculations.[42] For this conformation of the chelate ring, the phenyl groups of (**1a**) or (**1b**) are equatorial substituents for *trans* NH,CH groups and axial substituents for these groups *cis*. The axial-equatorial substituent sites are reversed for the more strained half-boat conformation.

In folded *abcd* co-ordination the 4,11-diene macrocycle (**1a** or **2**) can occur in two conformations, both with the *N-rac* configuration (*i.e.* with both NH groups on the same side of the flattened macrocycle), which appear, from models, to be relatively unstrained. The first is related to the conformation found for the cyclic tetra-amine complexes *cis*-$[Co(cyclam)Cl_2]Cl$,[47] *cis*-[Ni(tet*b*)OAc]ClO$_4$, [48] and *cis*-[Ni(tet*a*)acac]ClO$_4$ [49,†] with distortions introduced by the planar imino-groups. This has twofold symmetry with both six-membered chelate rings in the half-chair conformation, and with the bridging methylene groups of the five-membered chelate ring at the amino-groups on the *bd*-fold line as axial substituents of the six-membered chelate rings. For (**1a**), the phenyl groups are equatorial substituents of the chelate rings for *cis* NH,CH groups. With a bulky chelate such as acetylacetone occupying the remaining *ef* co-ordination sites, conformations which have the phenyl groups as axial substituents appear to be impossibly crowded.

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* Assuming that the dihydrate (i.r. spectra) is structurally the same as the anhydrous compound (structural determination).

† Cyclam = 1,4,8,11-tetra-azacyclotetradecane, tet*a* and tet*b* are the *C-meso* and *C-rac* isomers, respectively, of the hexamethyl-cyclam formed by reduction of (**2**).

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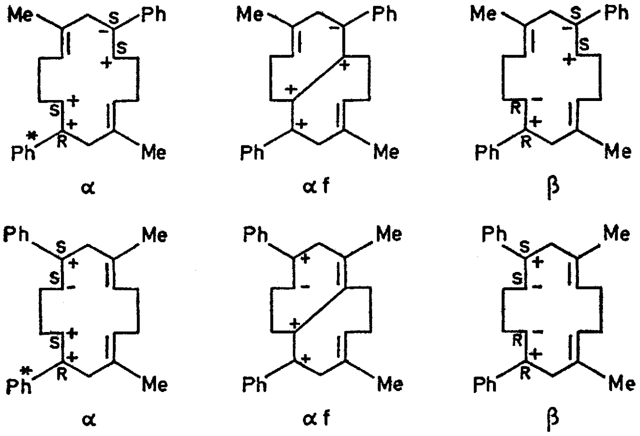
The second conformation has one of the six-membered chelate rings in a half-boat conformation with the fold line methylene group of this chelate ring as an ' equatorial ' substituent. For this chelate ring the phenyl group for (**1a**) is an ' equatorial ' substituent for *trans* CH,NH groups.

For the 4,14-diene system (**1b** or **3**) the presence of a planar imino-group at the fold line restricts the macrocycle to a conformation of the second type, again with the *N-rac* configuration (*i.e.* with the NH groups on opposite sides of the flattened macrocycle). Strain in models increases sharply as the *ac* fold angle is reduced below *ca.* 110°.

From the $^1$H n.m.r. evidence it was concluded that in planar co-ordination, for the β configuration the six-membered chelate rings were equivalent, while for the α configuration the six-membered chelate rings were non-equivalent, with one of the phenyl groups probably occupying an axial site.

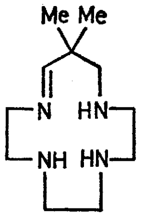


Configurations of co-ordinated *C-meso*-(**1a**) (upper) and *C-meso*-(**1b**) (lower). A + sign at a chiral centre indicates that the hydrogen atom is above the plane of the flattened macrocycle, a − sign that it is below. Configurations are also shown using the *RS* nomenclature. Co-ordination with the macrocycle folded *abcd* is represented by the symbol *f*, with the *bd* fold line shown. In each case in folded co-ordination the upper six-membered chelate ring adopts the half-boat conformation, and the lower one the half-chair conformation (the second conformation described in the text). Phenyl groups * for the α, planar, configuration are axial substituents if the six-membered chelate ring adopts the half-chair conformation normal for planar co-ordination

This information can be reconciled with the *C-meso*-(**1a**) or the *C-meso*-(**1b**) structures with α = *N-rac* and β = *N-meso* in both cases (Figure). The assignment would require the β configuration of (**1b**) to have the *N-meso* configuration, while only the *N-rac* configuration is observed for $[\mathrm{Ni}(\mathbf{3})]^{2+}$.[5,23] However, *trans*-$[\mathrm{Co}(\mathbf{3})(\mathrm{CN})_2]\mathrm{ClO}_4$ has the *N-meso* configuration,[24] so the energy difference in planar co-ordination cannot be excessive.

The compounds of (**1**) with the macrocycle in folded co-ordination which have been prepared with nickel(II) or cobalt(III) have properties similar to those of analogous derivatives of (**2**). Attempts to prepare compounds with (**3**) in folded co-ordination have been unsuccessful. This may simply be a reflection of the fact that all attempts to prepare triplet ground-state octahedral derivatives of $[\mathrm{Ni}(\mathbf{3})]^{2+}$ have been unsuccessful, presumably because of interactions involving the *gem*-dimethyl group (below), while little work has been done on the cobalt(III)–(**3**) system. However models suggest that the 4,14-diene macrocycle (**1b**) would be much more strained than the 4,11-diene (**1a**) for *ac* fold-angles approaching 90°, and the ready preparation of folded derivatives of (**1**) is taken as strong evidence in favour of the *C-meso*-4,11-diene structure (**1a**).

The nickel(II) compounds of (**1**) differ from those of (**2**) and (**3**) in the ease of formation of triplet ground-state, octahedrally co-ordinated compounds. For $[\mathrm{Ni}(\mathbf{2})]^{2+}$, singlet ground-state square planar salts are normal, exceptions being metastable $[\mathrm{Ni}(\beta\mathbf{2})(\mathrm{NCS})_2]$ (formed by recrystallising the stable singlet ground-state form $[\mathrm{Ni}(\beta\mathbf{2})](\mathrm{NCS})_2$ from chloroform, and which reverts to the stable form on exposure to the air)[19] and the ' folded ' derivatives $[\{\mathrm{Ni}(\alpha\mathbf{2})\}_2\mathrm{C}_2\mathrm{O}_4](\mathrm{ClO}_4)_2$[15] and $[\mathrm{Ni}(\alpha\mathbf{2})\mathrm{acac}]\mathrm{ClO}_4$.[3] For $[\mathrm{Ni}(\mathbf{1})]^{2+}$ on the other hand *trans* octahedral compounds are formed with a variety of co-ordinated anions, including relatively poor ligands such as nitrate, and with ammonia–water and methyl cyanide. *cis*-Octahedral compounds are formed with the chelating anions oxalate and acetylacetonate and also with diaminoethane (attempts to isolate a diaminoethane compound of $[\mathrm{Ni}(\mathbf{2})]^{2+}$ were unsuccessful). This difference is probably a consequence of repulsions between the axial methyl substituents present on the six-membered chelate rings of (**2**)[42–45] and the ' additional ' ligands. The chemistry of (**1**) with nickel(II) more closely resembles that of the thirteen membered macrocycle (**4**) than that of (**2**).[9] The feature which (**1**) and (**4**) have in common, the absence of axial substituents on the carbon atoms adjacent to the secondary amino-groups of the six-membered chelate ring, apparently is more important than the difference in macrocycle ring size.



(**4**)

The apparent ligand field strength in octahedral co-ordination with nickel(II) [and also with cobalt(III)] is less for (**2**) than for (**1**). Replacement of the *gem*-methyl groups of (**2**) by the phenyl groups of (**1**) would be expected to cause a decrease in base strength, and hence donor ability.[50] The apparent reversal of ligand field strength and base strength for (**1**) and (**2**) is probably another consequence of repulsions between the axial methyl groups of (**2**) and the ' additional ' ligands.

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[50] Chem. Soc. Special Publications Nos. 17 and 25.

## EXPERIMENTAL

The ligand (**1**) was prepared by the method of Hideg and Lloyd,[1] and recrystallised from cyclohexane or light petroleum.

(β-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate*, $[Ni(\beta\mathbf{1})](ClO_4)_2$.—Nickel perchlorate hexahydrate (0·73 g) and the ligand (**1**) (0·76 g, equimolar proportions) were warmed together in methanol (30 ml) on a steam-bath until the reactants completely dissolved, some orange product crystallising as the reaction proceeded. Propan-2-ol (10 ml) was added, and the methanol evaporated. The orange *product* was filtered from the cold solution and recrystallised from hot methanol–propan-2-ol (Found: C, 45·9; H, 5·2; Ni, 9·3. $C_{24}H_{32}Cl_2N_4NiO_8$ requires C, 45·4; H, 5·1; Ni, 9·3%).

The orange *tetrafluoroborate hemihydrate*, mauve *di-isothiocyanato-hemihydrate*, purple *dinitrato trihydrate*, *diacetato-* and *dichloro-dihydrate* compounds were prepared and recrystallised analogously to the perchlorate. $[Ni(\beta\mathbf{1})](BF_4)_2,0{\cdot}5H_2O$ (Found: C, 46·7; H, 5·4; Ni, 9·3. $C_{48}H_{66}B_4F_{16}N_8Ni_2O$ requires C, 46·6; H, 5·4; Ni, 9·4%). $[Ni(\beta\mathbf{1})(NCS)_2]0{\cdot}5H_2O$ (Found: C, 55·8; H, 5·9; Ni, 10·3. $C_{52}H_{66}N_{12}Ni_2OS_4$ requires C, 55·7; H, 5·9; Ni, 10·3%). $[Ni(\beta\mathbf{1})(NO_3)_2],3H_2O$ (Found: C, 46·7; H, 5·9; Ni, 10·0. $C_{24}H_{38}N_6NiO_9$ requires C, 47·0; H, 6·2; Ni, 9·6%). $[Ni(\beta\mathbf{1})(OAc)_2]$ (Found: C, 59·9; H, 6·9; Ni, 10·6. $C_{28}H_{38}N_4NiO_4$ requires C, 60·1; H, 6·9; Ni, 10·5%). $[Ni(\beta\mathbf{1})Cl_2],2H_2O$ (Found: C, 53·3; H, 6·7; Ni, 10·6. $C_{24}H_{36}Cl_2N_4NiO_2$ requires C, 53·2; H, 6·7; Ni, 10·8%).

(β-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Tetrachlorozincate Hemihydrate*, $[Ni(\beta\mathbf{1})]ZnCl_4,0{\cdot}5H_2O$.—A hot concentrated solution of zinc chloride plus lithium chloride (*ca.* 1 : 2 mol ratio) in methanol containing a few drops of hydrochloric acid was added to a hot concentrated methanolic solution of the dichloro-complex (previous preparation). The product was filtered from the cold solution and recrystallised by dissolving in the minimum volume of boiling water, filtering, and adding a few drops of the $ZnCl_2$–LiCl solution. The orange *product* was filtered from the cold solution and washed with ethanol (Found: C, 44·3; H, 5·1; Ni, 9·2. $C_{48}H_{66}Cl_8N_8Ni_2OZn_2$ requires C, 44·2; H, 5·1; Ni, 9·0%).

(β-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Iodide Hemihydrate* $[Ni(\beta\mathbf{1})]I_2,0{\cdot}5H_2O$.—As for the preparation of the diacetato-complex, with the addition of sodium iodide (0·75 g). The *product* was brown in colour (Found: C, 41·0; H, 4·9; Ni, 8·4. $C_{48}H_{66}I_4N_8Ni_2O$ requires C, 41·2; H, 4·8; Ni, 8·4%).

trans-*Aquoammino*(β-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate*, $[Ni(\beta\mathbf{1})(H_2O)(NH_3)](ClO_4)_2$.—The perchlorate salt of $[Ni(\beta\mathbf{1})]^{2+}$ (0·5 g) was warmed with concentrated aqueous ammonia (15 ml, '880') until all the starting material had dissolved. The purple-brown *product* which crystallised as the reaction proceeded was filtered off from the cold solution and washed with ethanol (Found: C, 43·0; H, 5·7; N, 10·3; Ni, 8·7. $C_{24}H_{37}Cl_2N_5NiO_9$ requires C, 43·1; H, 5·7; N, 10·5; Ni, 8·8%).

cis-*Acetylacetonato*(α-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate Hemihydrate*, $[Ni(\alpha\mathbf{1})acac]ClO_4,0{\cdot}5H_2O$.—The perchlorate salt of $[Ni(\beta\mathbf{1})]^{2+}$ (1 g) anhydrous potassium carbonate (2 g), acetylacetone (0·5 ml), and acetone (30 ml) were placed in a stoppered container and occasionally agitated until all the $[Ni(\beta\mathbf{1})](ClO_4)_2$ had dissolved (1—2 days). The potassium carbonate was filtered off, diethyl ether added to the purple filtrate until turbid, and the solution allowed to stand while the purple *product* crystallised. This was filtered off and recrystallised from acetone–ether as before (Found: C, 54·0; H, 6·2; Ni, 9·3. $C_{58}H_{76}Cl_2N_8Ni_2O_{13}$ requires C, 54·1; H, 6·0; Ni, 9·4%).

(α-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate Hemihydrate*, $[Ni(\alpha\mathbf{1})](ClO_4)_2,0{\cdot}5H_2O$.—The acetylacetonato-derivative (previous preparation, 0·5 g) was warmed gently in methanol (20 ml) containing perchloric acid (1·5 ml of 60%) until all the solid dissolved. The solution was filtered, and the orange *product* which crystallised when the solution cooled was filtered off and washed with ethanol containing a few drops of perchloric acid (Found: C, 45·1; H, 5·6; Ni, 9·2. $C_{48}H_{66}Cl_4N_8Ni_2O_{17}$ requires C, 44·9; H, 5·2; Ni, 9·1%).

cis-*Diaminoethane*(α-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate Dihydrate*, $[Ni(\alpha\mathbf{1})en](ClO_4)_2,2H_2O$.—Diaminoethane (0·2 g) and $[Ni(\beta\mathbf{1})](ClO_4)_2$ were warmed in methanol (10 ml) until all the solid dissolved to give a purple solution. Diethyl ether was added until turbid and the solution allowed to stand while the purple *product* crystallised. This was filtered off and washed with ether (Found: C, 42·3; H, 5·9; N, 11·8; Ni, 7·9. $C_{26}H_{44}Cl_2N_4NiO_{10}$ requires C, 42·7; H, 6·1; N, 11·5; Ni, 8·0%).

μ-*Oxalato-bis*[(α-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II)] *Perchlorate, Bis*(*methyl cyanide*). $[\{Ni(\alpha\mathbf{1})\}_2C_2O_4](ClO_4)_2,2CH_3CN$.—A small excess of oxalic acid was added to a solution of the acetylacetonate in acetone. The blue-violet precipitate was filtered off after 24 h and recrystallised from methyl cyanide–ether (Found: C, 52·1; H, 6·0; N, 11·0; Ni, 9·2. $C_{54}H_{70}Cl_2N_{10}Ni_2O_{12}$ requires C, 52·3; H, 5·7; N, 11·3; Ni, 9·5%).

(α-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Tetrachlorozincate Hydrate*, $[Ni(\alpha\mathbf{1})]ZnCl_4,H_2O$.—A solution of zinc chloride containing a few drops of concentrated hydrochloric acid was added to an acetone solution of the acetylacetonate. The orange precipitate was filtered off and washed with ethanol (Found: C, 43·8; H, 5·0; Ni, 8·8. $C_{24}H_{34}Cl_4N_4NiOZn$ requires C, 43·7; H, 5·2; Ni, 8·9%).

(5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Perchlorate*, $[Cu(\mathbf{1})](ClO_4)_2$.—Copper(II) perchlorate tetrahydrate (0·69 g) and the ligand (**1**) (0·76 g, equimolar proportions) were warmed in methanol (30 ml). The maroon coloured *product* which crystallised as the reaction proceeded was filtered off from the cold solution and recrystallised from hot methanol (Found: C, 45·1; H, 5·0; Cu, 10·1. $C_{24}H_{32}N_4Cl_2CuN_4O_8$ requires C, 45·1; H, 5·0; Cu, 10·0%).

(5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Nitrate*, $[Cu(\mathbf{1})](NO_3)_2$.—As for the previous preparation, substituting copper nitrate trihydrate (0·49 g) for the perchlorate. The *product* was deep purple coloured (Found: C, 51·2; H, 5·7; Cu, 11·2. $C_{24}H_{32}CuN_6O_6$ requires C, 51·1; H, 6·0; Cu, 11·3%).

(5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Chloride Tetrahydrate*, $[Cu(\mathbf{1})]Cl_2,4H_2O$.—Copper(II) chloride dihydrate (0·35 g) and (**1**) (0·76 g) were warmed in methanol until the solids dissolved. Propan-2-ol (10 ml) was added and the methanol removed using a rotary evaporator. The pale maroon-coloured *product* was filtered off from the cold solution and recrystallised from hot methanol–propan-2-ol (Found: C, 49·3; H, 6·2; Cu, 11·0. $C_{24}H_{40}Cl_2CuN_4O_4$ requires C, 49·4; H, 6·8; Cu, 10·9%).

(5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Thiocyanate*, [Cu(1)](NCS)$_2$.—Copper(II) acetate hydrate (0·40 g) (1) (0·76 g) and sodium thiocyanate dihydrate (0·90 g) were reacted together in methanol (30 ml) and the deep purple *product* isolated and recrystallised as for the chloride (Found: C, 55·9; H, 5·8; Cu, 11·9. $C_{26}H_{32}CuN_6S_2$ requires C, 56·1; H, 5·8; Cu, 11·9%).

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