Complexes of 2,4,4-Trimethyl-1,5,9-triazacyclododec-1-ene with Cobalt(II), Nickel(II), and Copper(II); *X*-Ray Structure Determination of Di-isothiocyanato(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)

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The preparations and properties of a number of complexes of Co^{II}, Ni^{II}, and Cu^{II} with 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, L, are reported. Reaction of bis(4-azaheptane-1,7-diamine)metal(II) complexes as their thiocyanate and perchlorate salts with acetone yields the products $[ML(NCS)_2]$ or $[(ML)(OH)_2][ClO_4]_2$ respectively. With Ni^{II}, and to a lesser extent Cu^{II}, the di-μ-hydroxo-dimer reacts with organic acids which form chelating anions to yield complexes [ML(X)]A (X = pentane-2,4-dionato, acetato, μ-oxalato, or 2-acetylphenolato; A = unco-ordinated perchlorate or thiocyanate ion). The complexes are five co-ordinate, except for $[\{NiL(NCS)\}_2C_2O_4]$ and [NiL(pd)(NCS)]. The structure of $[NiL(NCS)_2]$ has been determined by *X*-ray diffraction [space group *Pbca*, $a = 18.060(5)$, $b = 14.392(2)$, $c = 14.224(2)$ Å; $R = 0.068$, R' 0.057 for 1 126 reflections] and shows a distorted square-pyramidal arrangement about the nickel ion with a methyl group in the ' vacant ' octahedral site, 2.92 Å from the metal. *d–d* Spectra, i.r. spectra, and room-temperature magnetic susceptibilities are reported. The complexes $[(NiL)_2(OH)_2][ClO_4]_2$ and $[CuL(pd)][ClO_4]_2$ obey the Curie–Weiss law over the range 100—300 K, while $[(CuL)_2(OH)_2][ClO_4]_2$ shows appreciable antiferromagnetic spin coupling over this temperature range ($2J = -120$ cm^{-1}).

HOUSE and Curtis reported [1] a rapid reaction between bis(4-azaheptane-1,7-diamine)-nickel(II) and -copper(II) perchlorates (or tetrafluoroborates) and acetone to yield blue-green products of general formula $ML(OH)(ClO_4)$ [$L = C_{12}H_{25}N_3$, *i.e.* a ligand formed by condensation of one 4-azaheptane-1,7-diamine (4NH-hd) and two acetone residues with elimination of 2 molecules of water]. The products were stable in water, but were hydrolyzed by dilute acid releasing acetone.[1] Previously reported metal-ion–amine–acetone condensation products which yielded acetone on acid hydrolysis contained the acetone residues as *N*-isopropylideneamino-groups,[2,3] and on this basis the ligand L was assigned the linear bis(*N*-isopropylidene) structure $NH(CH_2CH_2CH_2N{=}CMe_2)_2$.

It was later observed that, when the nickel(II) complex was decomposed by reaction with cyanide, the carbonyl product isolated by steam distillation was 4-methylpent-3-en-2-one (mesityl oxide). This behaviour is characteristic of metal-ion–amine–acetone condensation products which contain the acetone residues as dimeric units, as β-aminoketone,[4] β-iminoalcohol,[5] or as β-aminoimino-bridging groups.[3] From the properties of the complexes the β-aminoimino-bridging group appeared probable, implying the presence of the macrocyclic ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene.

The complexes [ML(OH)]A (A = ClO_4 or BF_4) are formally four-co-ordinate. However, the magnetic moment of the copper complex was found to be low, and a methanol adduct having a magnetic moment well below the spin-only value was prepared,[1] implying the presence of spin pairing which could be achieved by formation of di-μ-hydroxo-bridges, $[LM(OH)_2ML]^{2+}$, analogous to many other dimeric complexes formed by Cu^{II}.[6] On the basis of this formulation the complexes are nominally five-co-ordinate, a relatively unusual co-ordination number for Ni^{II}.

In view of the likely presence of a novel triaza-macrocyclic ligand, and of five-co-ordination, the properties of the system were reinvestigated. The condensation reaction has been extended to the thiocyanate salts of the $[M(4NH\text{-}hd)_2]^{2+}$ complexes, yielding products $[ML(NCS)_2]$, and to include the cobalt(II) derivatives. An *X*-ray crystallographic study of $[NiL(NCS)_2]$ has confirmed the presence of the triaza-macrocyclic ligand L and of five-co-ordinate Ni^{II}. A number of derivatives of the ML moiety with a variety of additional ligands have been prepared from the perchlorate and thiocyanate salts of the hydroxo-complexes. Studies of the *d–d* spectra have confirmed the presence of five-co-ordinate structures in many cases, while temperature-variation studies of the susceptibility of some of the copper(II) derivatives have confirmed the presence of a spin-pairing mechanism. Analogous complexes of the 2,4,4,9-tetramethyl macrocycle, and of cyclic triamines formed by reduction of the imine groups of these macrocycles, will be reported separately.

DISCUSSION

The properties of analogous complexes of L with the metal ions Co^{II}, Ni^{II}, and Cu^{II} are generally very similar, and hence will be discussed together. A greater variety of complexes was obtained with Ni^{II} and the co-ordination stereochemistry is generally more unequivocally established; hence the nickel complexes are discussed first, followed by those of copper, and finally the few cobalt(II) complexes which could be prepared. The presence of the macrocyclic ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, L, is established by the *X*-ray crystallographic study of one complex (see below). Spectroscopic and magnetic properties are discussed separately.

Hydroxo-bridged Salts.—The preparation of a complex, now reformulated as ' $[NiL(OH)][ClO_4]$ ', by reaction of

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[1] D. A. House and N. F. Curtis, *J. Chem. Soc.* 1965, 5502.

[2] D. F. Cook and N. F. Curtis, *J.C.S. Dalton*, 1973, 1076.

[3] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

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

[5] J. W. L. Martin and N. F. Curtis, *J.C.S. Dalton*, 1975, 87.

[6] D. J. Hodgsen, *Progr. Inorg. Chem.*, 1975, **19**, 173.

$[Ni(4NH\text{-}hd)_2][ClO_4]_2$ with acetone, has been reported.[1] The complex shows a *d–d* spectrum indicative of five-co-ordination and, since most other co-ordination compounds of this macrocycle show a definite tendency to five-co-ordination, is assigned the di-μ-hydroxo-bridged structure $[(NiL)_2(OH)_2][ClO_4]_2$. The original report [1] mentions the formation of a green methanol adduct, which lost methanol to reform the blue starting material on drying. A stable green adduct is formed with *o*-chlorophenol.

Reaction of $[(NiL)_2(OH)_2][ClO_4]_2$ with the stoicheiometric amount of aqueous perchloric acid produced a blue solution which showed a *d–d* spectrum indicative of the NiN_3O_2 chromophore, and the presence of the five-co-ordinate diaqua-complex $[NiL(OH_2)_2]^{2+}$. Retention of five-co-ordination for this aqua-complex indicates the persistence of the co-ordination number for complexes of L.

Reaction of the dithiocyanato-complex $[NiL(NCS)_2]$ with sodium hydroxide (1 : >1.5) in methanol or acetone caused crystallization of a product $NiL(OH)(NCS)\cdot 0.75H_2O$.[*] The i.r. spectra of this complex and of $[(NiL)_2(OH)_2][ClO_4]_2$, apart from the anion bands, are closely similar, and the thiocyanate $\nu(C{\equiv}N)$ band at 2 044 cm^{-1} is indicative of ionic thiocyanate, so the complex is formulated as $[(NiL)_2(OH)_2][NCS]_2\cdot 1.5H_2O$. The occurrence of this complex with five-co-ordinate Ni^{II} and with unco-ordinated thiocyanate ion is a further indication of the reluctance of the NiL moiety to form six-co-ordinate complexes.

The preparation of blue-green $[(CuL)_2(OH)_2][ClO_4]_2$, similarly to the nickel(II) complex, has been reported, as well as the occurrence of a green methanol adduct with sub-normal magnetic moment.[1] A thiocyanate salt, $[(CuL)_2(OH)_2][NCS]_2\cdot H_2O$, was prepared similarly to the nickel(II) complex and has similar properties.

Reaction of a solution of cobalt(II) perchlorate with 4NH-hd (1 : 3) in acetone under nitrogen yielded a brown product $[(CoL)_2(OH)_2][ClO_4]_2\cdot 0.66H_2O$ formulated as for the nickel(II) and copper(II) complexes. The magnetic moment of the initial product, $\mu_{\text{eff.}} = 1.65$ B.M.,[†] may indicate an $S = \frac{1}{2}$ ground state or spin pairing *via* the hydroxo-bridges for $S = \frac{3}{2}$ Co^{II}. However, the moment decreased to zero over a period of weeks on exposure of the complex to the atmosphere, presumably because of oxidation to Co^{III}, so the matter was not pursued. Recrystallization from water, to which hydrogen peroxide had been added to ensure complete oxidation, yielded a red diamagnetic complex with a *d–d* spectrum typical of Co^{III}, and analyzing as $CoL(OH)_2(ClO_4)$. The complex is formulated as $[\{CoL(OH)\}_2(OH)_2][ClO_4]_2$, with one terminal and two bridging hydroxo-groups.

Thiocyanates.—The complexes $[Ni(4NH\text{-}hd)_2][NCS]_2$, '$[Cu_2(4NH\text{-}hd)_3][NCS]_2$', or cobalt(II) thiocyanate plus 2 mol of 4NH-hd reacted with acetone to yield deep blue, green, or purple products respectively of composition $ML(NCS)_2$, which all crystallized as acetone adducts. The nickel(II) and cobalt(II) complexes recrystallized from hot methanol as fractionally hydrated and anhydrous complexes, respectively. All the complexes crystallized from hot water, or from methanol containing base (or for copper, from all solvents except acetone), as anhydrous (or for the copper complex, fractionally hydrated) complexes, which differed from the first set of complexes in details of the i.r. spectra and *X*-ray diffraction patterns. In each case the original acetone adduct was reformed by recrystallization from acetone.

This isomerism is similar to that observed for many other macrocyclic ligands with co-ordinated secondary amino-groups, where it arises from restricted inversion at chiral nitrogen centres. An *X*-ray crystallographic study of the first mentioned unsolvated nickel complex showed that both NH groups of the macrocycle lay on the same side of the (flattened) macrocycle, and therefore the isomer has the configuration 5(*RS*),9(*RS*). The second isomer, formed by recrystallization from water or in the presence of base, and therefore the stable form, is assigned the configuration 5(*RS*),9(*SR*), with the NH groups on opposite sides of the molecular plane.[‡] By analogy with previous practice, the thermodynamically stable form is designated β and the metastable form α. Absence of an α–β designation indicates uncertainty of the configuration present. The crystallization of the α forms as acetone adducts appears to be a solubility effect. The complex α-$[NiL(NCS)_2]$ has a five-co-ordinate distorted square-pyramidal structure, and the *d–d* spectra of all the complexes are compatible with similar configurations.

The dithiocyanates all show two bands in the $\nu(C{\equiv}N)$ region, at energies typical of *N*-co-ordinated thiocyanate. The separation between the bands (*ca.* 20 cm^{-1}) is typical of those observed between the symmetrically and asymmetrically coupled $\nu(C{-}N)$ [7,8] modes for *cis*-di-isothiocyanato-complexes.

The nickel complex crystallized from dimethylformamide and dimethyl sulphoxide as 1 : 1 adducts, with retention of five-co-ordination.

Complexes with Other Additional Ligands.—The μ-hydroxo-nickel(II) and -copper(II) perchlorates react with a variety of organic acids the anions of which act as chelating ligands. Complexes $[ML(X)][ClO_4]$ [X = O_2CMe, pentane-2,4-dionate (pd), 2-acetylphenolate (ap) (Ni^{II} only), or μ-oxalate] were prepared and all had *d–d*

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[*] Many of the complexes occurred as hydrates or other adducts. The presence of the solvent was generally indicated by bands in the i.r. spectra, *e.g.* ν(OH) at *ca.* 3 600 cm^{-1} for hydrates, ν(C=O) at 1 705 cm^{-1} for acetone adducts, *etc.* The solvation number was calculated from the best fit to the analytical data, which often indicated fractional solvation, although the solvation numbers shown must be regarded as uncertain. The situation is complicated in a number of cases by the apparent occurrence of the unsolvated complex, plus a series of derivatives with varying solvation numbers (or with non-stoicheiometric solvation).

[†] Throughout this paper: $1\ \text{B.M.} \approx 9.27 \times 10^{-24}\ \text{A m}^2$.

[‡] The two chiral nitrogen centres are similar, although non-equivalent, and the isomers could be regarded as pseudo-*rac* and pseudo-*meso* forms. The metal atom is also a chiral centre.

[7] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1973.

[8] N. F. Curtis and Y. M. Curtis, *Austral. J. Chem.*, 1966, **19**, 1423.

and i.r. spectra compatible with five-co-ordinate formulations.

When $[(NiL)_2(OH)_2][NCS]_2$ was used as starting material, five-co-ordinate [NiL(ap)][NCS] and six-co-ordinate $[\{NiL(NCS)\}_2C_2O_4]$ were prepared. With pentane-2,4-dione (Hpd), the initially formed complex [NiL(pd)(NCS)] was six-co-ordinate, but this changed to a five-co-ordinate form, [NiL(pd)][NCS] on recrystallization, presumably with a change of nitrogen configuration. These five- and six-co-ordinate arrangements were assigned on the basis of the i.r. spectra (which indicated the presence of *N*-co-ordinated or ionic thiocyanate) and the *d–d* spectra (which were as expected for five- or six-co-ordination as appropriate).

Treatment of the μ-hydroxo-complexes with equimolar amounts of mineral acids (apart from $HClO_4$, see above) resulted in hydrolysis of the macrocycle. However, a complex $NiL(Cl)(ClO_4)$ {assigned a five-co-ordinate dimeric structure with chloride bridging, $[(NiL)_2Cl_2][ClO_4]_2$} was prepared by reaction of the acetato-complex with lithium chloride. Attempts to prepare similar complexes from $[(CuL)_2(OH)_2][NCS]_2$ or from $[(CoL)_2(OH)_2][ClO_4]_2$ were unsuccessful.

The complex $[Ni(4NH\text{-}hd)(en)][ClO_4]_2$ (en = ethylenediamine) reacted with acetone to yield a blue product which incorporated two acetone residues, condensed by elimination of two molecules of water. The product could be readily converted into derivatives of NiL, indicating the structure $[NiL(en)][ClO_4]_2$. The complex $Cu(4NH\text{-}hd)(en)(ClO_4)_2$ also reacted with acetone, but yielded a product without the cyclic ligand and containing *N*-isopropylideneamine groups.

Infrared Spectra.—Infrared spectroscopic data are listed in Table 1 of Supplementary Publication No. SUP 22146 (12 pp.).* The spectra of all the derivatives of L show bands assignable to ν(NH), usually a doublet in the range 3 150—3 300 cm^{-1}, and to ν(C=N), a strong sharp band in the range 1 645—1 655 cm^{-1}.

The complexes assigned *N*-thiocyanato-structures show strong sharp ν(C≡N) bands at *ca.* 2 080 cm^{-1}, a doublet of separation *ca.* 20 cm^{-1} for the dithiocyanato-complexes and a singlet for the monothiocyanato-complexes. Complexes assigned structures with ionic thiocyanate showed a single band at *ca.* 2 050 cm^{-1}. The position of the ν(CS) band was more ambiguous because of the presence of other bands in the region, but the assignments are compatible with the structures proposed (weak bands at *ca.* 790 cm^{-1} for co-ordinated and at *ca.* 750 cm^{-1} for ionic thiocyanate).

The complexes assigned structures containing the chelates pd,[7] O_2CMe,[9] μ-C_2O_4,[10] ap,[7] and en [7] have i.r. bands similar to those of other complexes of these ligands. For the acetato-complexes the separation between the components of ν(OCO) is *ca.* 70 cm^{-1}, in the range for symmetrical bidentate co-ordination {*cf.* $[Ni(en)_2(O_2CMe)][ClO_4]$, 95 cm^{-1}; and 169 cm^{-1} for $[Cu(4NH\text{-}hd)(O_2CMe)][ClO_4]$ where the acetate acts as an asymmetric chelate with the weakly bound oxygen interacting with a second copper ion [11]}.

d–d Spectra.—The spectral data are shown in Table 1. The stereochemistry and *d–d* spectra of five-co-ordinate complexes of Co^{II}, Ni^{II}, and Cu^{II} have been reviewed.[12–14]

Five-co-ordinate nickel(II) *complexes*. The spectra of a number of $S = 1$ nickel(II) complexes with established five-co-ordinate structures have been reported. The geometries adopted generally show appreciable distortion from regular square-pyramidal or trigonal-bipyramidal arrangements, making details variable and band assignments difficult, but the spectra show some features in common which differentiate them from the spectra of six-co-ordinate complexes. In particular, for the five-co-ordinate complexes the lowest-energy band is in the 7 000—9 000 cm^{-1} region and the absorption coefficients are larger. The complexes assigned structures with NiN_5 and NiN_3O_2 chromophores have similar spectra, with three bands at *ca.* 7 000—8 000, 16 000—17 000, and 25 000—28 000 cm^{-1}, and weaker shoulders at *ca.* 10 000—11 000 and 12 000—14 000 cm^{-1}. The spectra generally resemble those published for five-co-ordinate $S = 1$ nickel(II) complexes. No bathochromic shift between NiN_5 and NiN_3O_2 is observed, comparable to that for the chromophores NiN_6 and NiN_4O_2. In general, the spectra are similar for the solids (reflectance) and for solutions in non-polar solvents such as acetone and in polar solvents such as water. This indicates that the five-co-ordination is retained in aqueous solution, which is somewhat unusual, and further shows the persistence of this arrangement for these complexes.

The complex $[(NiL)_2Cl_2][ClO_4]_2$, an NiN_3L_2 chromophore, has a spectrum similar to that of the other five-co-ordinate complexes of L but with the bands displaced to lower energy. The spectrum is similar for the solid and for the solution in methanol, but in water the bands are shifted to higher energy indicating aquation.

Six-co-ordinate nickel(II) *complexes*. Two complexes, $[NiL(pd)(NCS)]\cdot 0.5H_2O$ and $[\{NiL(NCS)\}_2C_2O_4][ClO_4]_2$, show reflectance spectra indicative of six-co-ordinate structures (also inferred from their i.r. spectra). The first complex on recrystallization changed to $[NiL(pd)][NCS]\cdot H_2O$ which is assigned a five-co-ordinate structure on the basis of both the i.r. and *d–d* spectrum. In water this complex slowly hydolyzes to form [Ni(4NH-hd)(pd)(NCS)], which has i.r. and *d–d* spectra indicative of a six-co-ordinate structure, and provides a useful comparison for these properties.

Five-co-ordinate copper(II) *complexes*. The spectra

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[9] N. F. Curtis, *J. Chem. Soc.*, 1963, 4109; *J. Chem. Soc. (A)*, 1968, 1584.

[10] N. F. Curtis, *J. Chem. Soc.*, *(A)*, 1968, 1580.

[11] B. W. Skelton, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 2133.

[12] R. Morassi, I. Bertini, and L. Scaconi, *Co-ordination Chem. Rev.*, 1973, **11**, 343.

[13] J. S. Wood, *Co-ordination Chem. Rev.*, 1967, **2**, 403.

[14] B. J. Hathaway and A. A. G. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1; E. D. McKenzie, *J. Chem. Soc. (A)*, 1970, 3095.

of five-co-ordinate copper(II) complexes are rather variable, being dependent on details of the co-ordination geometry.[14] However, for complexes of approximately square-pyramidal geometry the presence of two bands (or one band with a well defined shoulder) is general, and the derivatives of CuL show spectra of this type.

TABLE 1

d–d Absorption band maxima (10^3 cm^{-1}) from diffuse-reflectance spectra unless indicated otherwise [a]

NiN_5 chromophore					
α-[$NiL(NCS)_2$]·$0.5Me_2CO$	7.4	11.8	13.3(sh)	17.0	26.3
α-[$NiL(NCS)_2$]·$0.25H_2O$	6.3(sh), 7.4	12.9br		16.8	26.1
	[b] 7.4 (37)	11.0 (12)	12.6 (11.5)	16.7 (51)	26.0 (127)
β-[$NiL(NCS)_2$]	7.2	10.6(sh)	13.0	16.7	26.0
[$NiL(NCS)_2$]·dmf	7.6	11.4(sh)		16.6	24.0br
[$NiL(NCS)_2$]·dmso [c]	7.6	10.7(sh)		16.5	25.6
[NiL(en)][ClO_4]$_2$	7.3	11.5(sh)		16.6	25.1
NiN_3O_2 chromophore					
[$(NiL)_2(OH)_2$][ClO_4]$_2$	7.4			16.4	26.4
	[b] 7.4 (20)			16.6 (35)	26.8 (80)
	[d] 7.6 (20)	11.0(sh)	13.0(sh)	16.4 (32)	26.3 (64)
	[e] 8.0 (17)	11.0(sh)	13.0(sh)	16.2 (37)	26.0 (60)
[$(NiL)_2(OH)_2$][ClO_4]$_2$·C_6H_4-(OH)Cl	6.0	7.1	11.4	16.1	26.1
[$(NiL)_2(OH)_2$][NCS]$_2$	7.0	11.2	13.2	16.3	26.6
[$NiL(O_2CMe)$][ClO_4]	7.1	10.4(sh)		16.2	26.5
	[f] 7.7 (18)	10.9(sh)	12.8 (10)	16.2 (40)	26.2 (95)
[$(NiL)_2C_2O_4$][ClO_4]$_2$·H_2O	7.4		13.0(sh)	16.6	26.5
	[d] 7.8 (14)	12.9 (6)	12.9 (6)	16.5 (35)	26.8 (69)
[NiL(pd)][ClO_4]·$0.5H_2O$	6.2(sh), 7.0	11.4		17.0	28.2
	[f] 7.6 (25)	11.5(sh)	13.2 (18.5)	17.2 (49)	27.4(sh)
[NiL(ap)][ClO_4]·$0.5H_2O$	6.7	8.1	12.4	17.0	25.4
	[f] 6.9 (8.2)	11.2(sh)	12.6(sh)	16.8 (113)	25.6 (4 610)
[NiL(ap)][NCS]·$0.5H_2O$	7.2	11.4(sh)		16.2	25.6
NiN_3Cl_2 chromophore					
[$(NiL)_2Cl_2$][ClO_4]$_2$	7.8	10.0(sh)		15.4	24.4
NiN_4O_2 chromophore					
[NiL(pd)(NCS)]·$0.5H_2O$		10.2		16.8	28.3
[$\{NiL(NCS)\}_2C_2O_4$]		10.3		17.2	27.6
CoN_5 chromophore					
α-[$CoL(NCS)_2$]	5.3	9.7	17.3	18.3	21.7
α-[$CoL(NCS)_2$]·$0.5Me_2CO$	5.4	9.1	17.1	18.6	21.8
β-[$CoL(NCS)_2$]	5.3, 7.3	9.0	17.1	18.4	21.5
CuN_5 chromophore					
[$CuL(NCS)_2$]		9.0		16.0	
		[b] 9.1 (50)		14.3 (162)	
CuN_3O_2 chromophore					
[$(CuL)_2(OH)_2$][ClO_4]$_2$		10.6			
		[g] 9.4 (54)	15.6 (138)		27.4 (1 300)
[$(CuL)_2(OH)_2$][NCS]$_2$·H_2O		9.7(sh)	15.0	16.2	
[$CuL(O_2CMe)$][ClO_4]		8.3	14.2	15.7(sh)	
		[f] 8.7 (58)	14.4 (99)		
[$(CuL)_2C_2O_4$][ClO_4]$_2$·$2H_2O$		8.9	14.4	15.6(sh)	
		[f] 9.0 (69)	14.5 (166)		
		[d] 8.7 (55)	14.4 (126)		
[CuL(pd)][ClO_4]		9.8		16.3	
		[f] 9.8 (49)		15.6 (138)	
		[d] 9.4 (91)		15.3 (196)	

[a] For solution spectra, molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] In dimethylformamide (dmf). [c] dmso = Dimethyl sulphoxide. [d] In water. [e] In water containing 2 mol equivalents of $HClO_4$. [f] In acetone. [g] In dichloromethane.

Dimeric copper(II) complexes with antiferromagnetic spin coupling generally have a moderately strong absorption band in the near u.v., which has been assigned to a charge-transfer transition from the non-bonding π orbitals of the oxygen bridging atoms to unfilled metal *d* orbitals. This band is present for the solids, and for solutions in non-polar solvents, but is generally absent from spectra of solutions in polar solvents. The complex [$(CuL)_2(OH)_2$][ClO_4]$_2$, which shows antiferromagnetic spin coupling, exhibits a band at 27 400 cm^{-1} (ε 1 320 dm^3 mol^{-1} cm^{-1}) in dichloromethane, which is absent from the spectrum in water and from the spectra of the other copper(II) derivatives of L, and is assigned to the charge-transfer transition.

Five-co-ordinate cobalt(II) *complexes*. The spectra of a number of complexes of $S = \frac{3}{2}$ Co^{II} with established five-co-ordination have been reported, but none has the CoN_5 chromophore in square-pyramidal geometry. However, the reflectance spectrum of α-[$CoL(NCS)_2$] (maxima at 5.3, 9.7, 17.3, 18.3, and 21.7 × 10^3 cm^{-1}) shows similarities with the reported spectra.

Magnetic Susceptibilities.—The room-temperature magnetic susceptibilities and effective magnetic moments of derivatives of L are listed in Table 2 of SUP 22146. In general, the complexes have values of *ca.* 3.3 B.M. for Ni^{II}, 1.9 B.M. for Cu^{II}, and 4.6 B.M. for Co^{II}. (The case of $[(CoL)_2(OH)_2][ClO_4]_2$ is discussed above.) The dimeric complexes have the possibility of spin pairing by superexchange *via* the bridge atoms. This is generally negligible at room temperature for Ni^{II} (and the dimeric NiL complexes show normal room-temperature moments), but can be appreciable for copper(II) dimers. The complex $[(CuL)_2(OH)_2][ClO_4]_2$ has a sub-normal moment at room temperature, and the susceptibility was measured over the range 100—300 K for this complex, for the nickel(II) analogue, and for $[CuL(pd)][ClO_4]$ for comparison. For the last two complexes, linear Curie–Weiss plots were obtained with $\theta = 59.5 \pm 0.5$ K and $\mu = 3.22$ B.M., and $\theta = 7.5 \pm 0.5$ K and $\mu = 2.04$ B.M., respectively.* The temperature dependence of the magnetic susceptibility of a number of dimeric nickel(II) complexes has been measured, and they generally show little deviation from Curie-law behaviour above 100 K, although antiferromagnetic or ferromagnetic coupling may become appreciable at lower temperatures. For $[(CuL)_2(OH)_2][ClO_4]_2$ the susceptibility data were fitted to the Bleaney–Bowers relation with $2J = -120$ cm^{-1}, $g = -2.1$, and $N\alpha = -60 \times 10^{-6}$ c.g.s. units (Figure 1). The susceptibility data for the three complexes over the temperature range studied are in Table 3 of SUP 22146. The temperature dependence of the susceptibilities of the μ-oxalato-compounds will be published. The Cu^{II} compound shows appreciable spin-pairing.

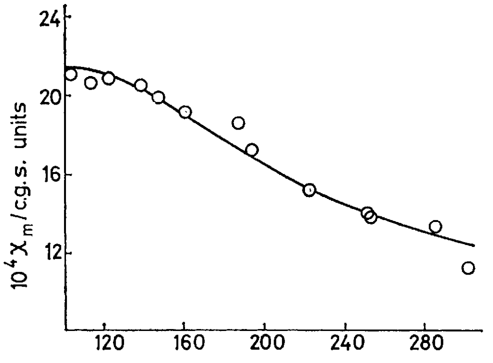


FIGURE 1 Temperature variation of the molar magnetic susceptibility of $[(CuL)_2(OH)_2][ClO_4]_2$. The full line was calculated from the Bleaney–Bowers relation with $2J = -120$ cm^{-1}, $g = 2.1$, and $N\alpha = -60 \times 10^{-6}$ c.g.s. units

Discussion of the Structure of α-$[NiL(NCS)_2]$.—The unit cell contains eight discrete $NiL(NCS)_2$ molecules with no significant intermolecular interactions. Atom positions, bond lengths, and bond angles are listed in Tables 2, 3, and 4 respectively. An ORTEP diagram of the molecule is shown in Figure 2, and a stereoscopic projection of the molecular arrangement within the unit cell is in Figure 3. The crystallographic atom numbering is shown in Figure 2, and in formula (I).

TABLE 2

Atomic co-ordinates for α-$[NiL(NCS)_2]$

Atom	x/a	y/b	z/c
Ni	0.070 7(1)	0.019 6(1)	0.198 4(1)
S(1)	0.360 1(2)	0.267 3(3)	0.002 8(3)
S(2)	0.173 0(2)	0.387 9(2)	0.261 9(3)
Ni(1)	0.175 2(5)	0.075 3(6)	0.191 8(6)
N(2)	0.571 (5)	0.779 (6)	0.329 4(6)
N(3)	0.031 9(5)	0.122 6(6)	0.115 5(6)
N(4)	0.404 8(5)	0.416 7(7)	0.109 9(7)
N(5)	0.033 0(6)	0.457 4(6)	0.281 4(7)
C(1)	0.122 8(8)	0.049 6(8)	0.387 2(8)
C(2)	0.368 4(7)	0.440 9(8)	0.371 3(9)
C(3)	0.106 4(7)	0.066 7(10)	0.496 2(8)
C(4)	0.193 1(6)	0.099 5(9)	0.363 6(8)
C(5)	0.215 5(7)	0.107 4(8)	0.260 3(9)
C(6)	0.288 6(7)	0.156 3(10)	0.246 7(9)
C(7)	0.204 6(7)	0.083 0(9)	0.091 3(7)
C(8)	0.159 7(8)	0.160 0(10)	0.042 0(9)
C(9)	0.077 3(8)	0.132 7(8)	0.024 4(7)
C(10)	0.023 2(7)	0.216 4(8)	0.163 4(9)
C(11)	0.484 3(7)	0.206 4(8)	0.240 0(10)
C(12)	0.040 4(6)	0.181 1(7)	0.338 3(9)
C(13)	0.383 1(6)	0.355 6(7)	0.064 5(7)
C(14)	0.092 8(7)	0.430 0(8)	0.273 8(8)

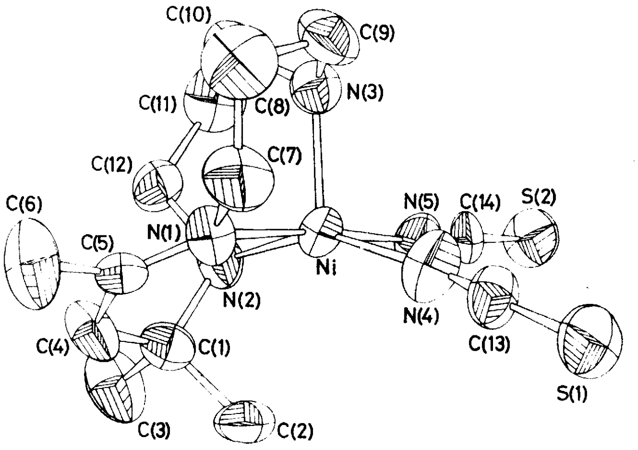
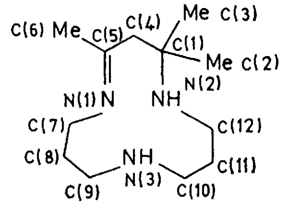


FIGURE 2 An ORTEP representation of the molecular structure of α-$[NiL(NCS)_2]$



(I)

Co-ordination about the nickel(II) *ions*. The nickel(II) ion is co-ordinated to the three nitrogen atoms of the macrocycle and to the nitrogen atoms of two thiocyanate ions. The two NH groups are on the same side of the (flattened) macrocycle, *i.e.* the configuration is 5(*RS*),-9(*RS*). The primary co-ordination sphere about the nickel(II) ion can be regarded as a distorted square pyramid, or less appropriately as a distorted trigonal

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* $\chi_m \propto (T + \theta)^{-1}$.

bipyramid. Viewed as a square pyramid, with N(3) apical, the interbasal angles are 89.5, 86.7, 88.2, and 93.3°, while the base–apex angles are 90.3, 100.8, 94.8, and 104.7° [sequentially N(1), N(2), N(5), and N(4) in each case]. The base shows a tetrahedral distortion, with the nickel ion displaced towards the apex [N(1)-NiN(5) 174.1, N(2)NiN(4) 154.3°]. As a trigonal bipyramid, with N(1) and N(5) apical, N(1)NiN(5) is 174.1°, and the intraequatorial angles are 100.8, 104.7, and 154.3° [sequentially N(2), N(3), and N(4)].

TABLE 3

Bond lengths (Å)

Ni–N(1)	2.05(1)	C(7)–C(8)	1.54(2)
Ni–N(2)	2.06(1)	C(8)–C(9)	1.56(2)
Ni–N(3)	2.02(1)	C(9)–N(3)	1.54(1)
Ni–N(4)	1.99(1)	N(3)–C(10)	1.52(1)
Ni–N(5)	2.10(1)	C(10)–C(11)	1.55(2)
N(2)–C(1)	1.50(1)	C(11)–C(12)	1.55(2)
C(1)–C(2)	1.59(2)	N(2)–C(12)	1.52(1)
C(1)–C(3)	1.60(1)	N(4)–C(13)	1.16(1)
C(1)–C(4)	1.50(2)	C(13)–S(1)	1.60(1)
C(4)–C(5)	1.53(2)	N(5)–C(14)	1.16(1)
C(5)–C(6)	1.51(2)	C(14)–S(2)	1.58(1)
N(1)–C(5)	1.30(1)	Ni–C(2)	2.92(1)
N(1)–C(7)	1.53(1)		

Conformation of the macrocycle. The macrocycle is co-ordinated facially, with the imine chelate ring in the basal plane of the square pyramid. The two saturated six-membered chelate rings adopt chair conformations, very flattened for the N(2)–N(3) case, with chelate angles (NMN) of 100.8 [N(2)–N(3) (exceptionally large)] and 90.3° [N(1)–N(3)]. The trimethyl imine chelate ring adopts its usual conformation with the imine group approximately planar, the imine methyl equatorial, and the *gem*-dimethyl groups equatorially–axially orientated, with a chelate angle of 89.5° (Table 5 and Figure 4).

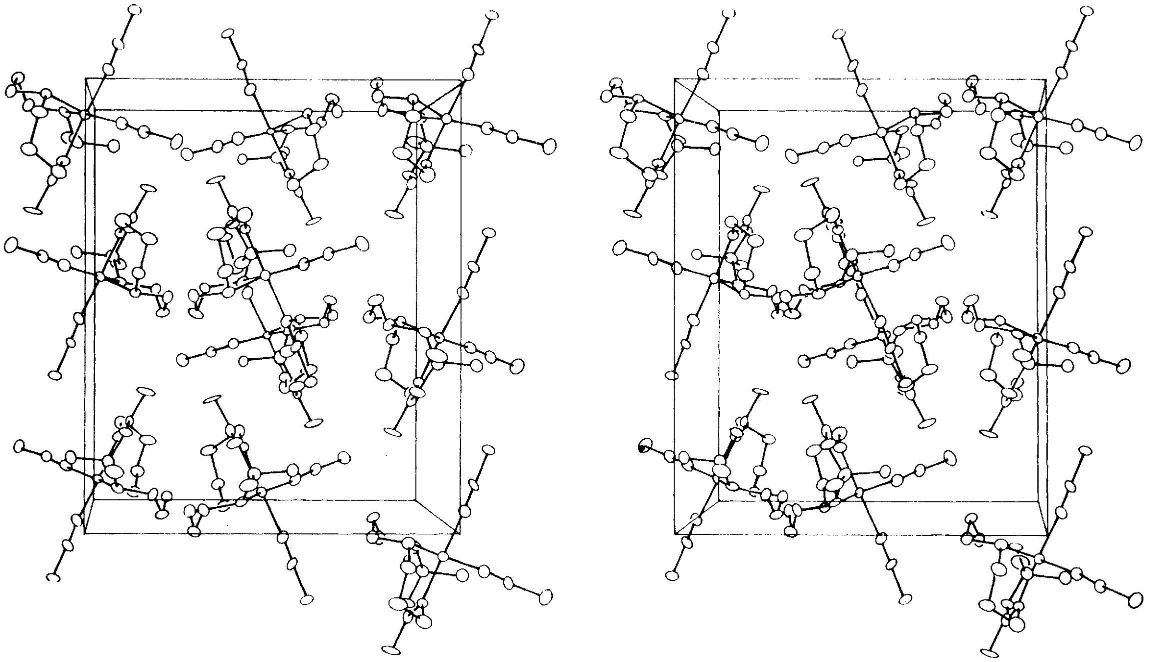

FIGURE 3 Stereoscopic projects of the molecular arrangement within the unit cell of α-[NiL(NCS)$_2$] as viewed down the *b* axis

The nickel–macrocycle-nitrogen distances are shorter than usual for $S = 1$ nickel(II) amine complexes in octahedral co-ordination, with no significant difference between the imine and amine nitrogens [2.04(1) Å, mean]. There is a significant difference between the Ni–N bond lengths for the two thiocyanato-groups [1.99(1) and 2.10(1) Å] with Ni–N–C–S approximately linear.

TABLE 4

Bond angles (°)

N(1)–Ni–N(2)	89.5(3)	Ni–N(1)–C(5)	124.3(8)
N(1)–Ni–N(3)	90.3(4)	Ni–N(1)–C(7)	113.1(5)
N(1)–Ni–N(4)	93.3(4)	C(5)–N(1)–C(7)	118.6(9)
N(1)–Ni–N(5)	174.1(3)	N(1)–C(7)–C(8)	107.1(9)
N(2)–Ni–N(3)	100.8(4)	C(7)–C(8)–C(9)	113.1(11)
N(2)–Ni–N(4)	154.3(4)	C(8)–C(9)–N(3)	113.4(8)
N(2)–Ni–N(5)	86.7(2)	Ni–N(3)–C(9)	112.0(5)
N(3)–Ni–N(4)	104.7(4)	C(9)–N(3)–C(10)	110.4(7)
N(3)–Ni–N(5)	94.8(3)	Ni–N(3)–C(10)	115.2(5)
N(4)–Ni–N(5)	88.2(3)	N(3)–C(10)–C(11)	111.2(9)
Ni–N(2)–C(1)	106.9(7)	C(10)–C(11)–C(12)	111.3(9)
N(2)–C(1)–C(2)	105.6(10)	C(11)–C(12)–N(2)	107.4(9)
N(2)–C(1)–C(3)	110.6(9)	Ni–N(2)–C(12)	119.5(5)
N(2)–C(1)–C(4)	114.7(9)	C(12)–N(2)–C(1)	113.1(7)
C(2)–C(1)–C(3)	107.2(8)	Ni–N(4)–C(13)	172.1(8)
C(2)–C(1)–C(4)	110.8(12)	N(4)–C(13)–S(1)	175.0(9)
C(3)–C(1)–C(4)	107.7(8)	Ni–N(5)–C(14)	174.0(10)
C(1)–C(4)–C(5)	118.4(10)	N(5)–C(14)–S(2)	177.2(12)
C(4)–C(5)–C(6)	112.9(11)	C(2)–Ni–N(1)	81.0(9)
C(4)–C(5)–N(1)	123.1(11)	C(2)–Ni–N(2)	56.0(8)
C(6)–C(5)–N(1)	124.0(12)	C(2)–Ni–N(3)	155.0(10)

A feature of the structure is the presence of the methyl group C(2) close to the 'vacant' octahedral co-ordination site, 2.92 Å from the nickel(II) ion. The chemistry of this macrocycle co-ordinated to Co^{II}, Ni^{II}, and Cu^{II} is dominated by five-co-ordination, the persistence of which is indicated by the occurrence of five-co-ordinate thiocyanate salts and the retention of five-co-ordination in aqueous solution. The question arises as to whether the complexes adopt five-co-ordinate arrangements because the preferred ligand conformation has the methyl group blocking the sixth co-ordination site, or whether the square-pyramidal stereochemistry is a feature of the unsubstituted macrocycle, and the methyl substituent simply occupies the vacant spatial region below the metal ion. Models suggest that the macrocycle could readily adopt conformations which do not place the methyl group in this site, and for the β configuration there seems to be no compelling reason why the methyl group should be sited there at all. It can be noted that very similar co-ordination stereochemistry is shown by the cyclic triamine formed by reduction of the imine group of L, and by the 9-methyl derivative of L, to be discussed subsequently.

TABLE 5

Equations of least-squares planes in the form $ax + by + cz + d = 0$, and perpendicular distances (Å) from the planes in square brackets

Plane 1: N(1), Ni, N(2)

$$-0.372\,2x + 0.827\,0y - 0.421\,4z + 1.432\,3 = 0$$

[C(1) −1.13, C(2) −2.38, C(3) −1.46, C(4) −0.86, C(5) −0.30, C(6) −0.13, C(7) 0.50, C(12) 1.29]

Plane 2: N(1), Ni, N(3)

$$0.194\,5x - 0.552\,7y - 0.810\,4z + 2.194\,5 = 0$$

[C(5) −0.90, C(7) 1.20, C(8) 1.00, C(9) 1.13, C(10) −1.33]

Plane 3: N(2), Ni, N(3)

$$0.918\,9x + 0.390\,7y - 0.054\,8z - 1.128\,7 = 0$$

[C(1) 0.89, C(9) 0.88, C(10) 0.35, C(11) −0.43, C(12) 0.30]

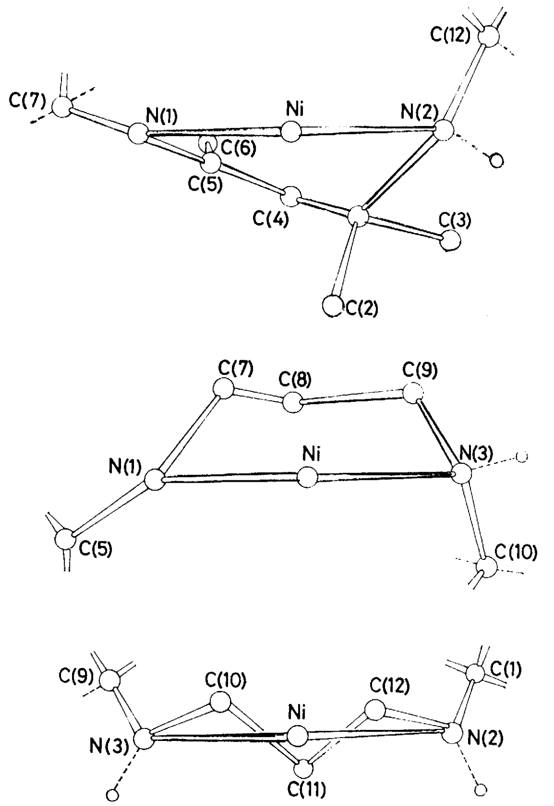

FIGURE 4 Conformation of chelate rings, represented as projections on a plane through the donor atoms, normal to the NiN_2 chelate plane

Studies of complexes of Ni^{II},[15,16] Cu^{II},[15,16] and Co^{II} [17] with a series of triaza-macrocycles of varying ring size have been made. Macrocycles having less than 12 ring members generally form six-co-ordinate nickel(II) complexes, while those with more than 12 generally form five-co-ordinate nickel(II) complexes. For 1,5,9-triazacyclododecane (L′), both five- and six-co-ordinate complexes were prepared, and, for example, $NiL'(NCS)_2$ was assigned a six-co-ordinate structure with bridging thiocyanate.[15] The change in preferred co-ordination number with ring size was attributed to a general stereochemical crowding effect by the increasing number of skeletal methylene groups.[15] The macrocycle L shows stereochemical behaviour similar to that of a larger unsubstituted macrocycle, and this can be attributed to a general stereochemical effect of the methyl substituents, rather than to any specific siting of these groups.

Structural studies of complexes of other triaza-macrocycles, tribenzo[*b*,*f*,*j*]triazacyclododecine [18a] and 2-methyl-1,4,8,11-triazacyclononane [18b] have been reported. Macrocycles have also been prepared in cyclization reactions of 4NH-hd with 2,6-diacetylpyridine in the presence of metal ions to form complexes of tetra-aza-macrocycles, several of which have been structurally investigated.[19-21]

EXPERIMENTAL

Di-μ-hydroxo-bis[(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)] perchlorate, and the copper(II) analogue, were prepared by reaction of bis(4-azaheptane-1,7-diamine)-nickel(II) [or -copper(II)] perchlorate with acetone, as previously described.[1] Analytical data (C, H, metal, plus some N values) are shown in Table 4 of SUP 22146. Yields of the macrocycle condensation reactions, and of the metathetical interconversions, were generally *ca.* 70%.

Di-isothiocyanato(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II)–*Acetone* (2/1), *and Hydrate*, α-$[NiL(NCS)_2]\cdot0.5Me_2CO$, *and* α-$[NiL(NCS)_2]\cdot0.25H_2O$.—Bis(4-azaheptane-1,7-diamine)nickel(II) dithiocyanate was treated with acetone in a stoppered flask at room temperature for 3 d, or under reflux for 1 h, then allowed to react at room tem-

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[15] M. Nonoyama, *Transition Metal Chem.*, 1976, **1**, 70.

[16] M. Nonoyama, *Inorg. Chim. Acta*, 1976, **20**, 53.

[17] M. Nonoyama, *J. Inorg. Nuclear Chem.*, 1977, **39**, 550.

[18] (*a*) B. Fleischer and E. Klein, *Inorg. Chem.*, 1965, **4**, 637; R. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, 1970, **92**, 1929; (*b*) S. F. Mason and R. D. Peacock, *Inorg. Chim. Acta*, 1976, **10**, S. F. Mason and R. D. Peacock, *Inorg. Chim Acta*, 1976, **19**, 75; attributed to Y. Saito, personal communication.

[19] R. Dewar and E. B. Fleischer, *Nature*, 1969, **222**, 372.

[20] E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 1968, **11**, 2312.

[21] R. H. Prince, D. A. Stotter, and P. R. Wooley, *Inorg. Chim. Acta*, 1974, **9**, 51.

perature in a stoppered flask for 1 d. The deep blue platelets of the product were filtered off and recrystallized from hot acetone. (In some preparations the β isomer crystallized after *ca.* 1 d, but redissolved to deposit the product.) Slow recrystallization from hot methanol yielded the hydrate.

Methanol, Dimethylformamide, and Dimethyl Sulphoxide Adducts of β-$[\mathrm{NiL}][\mathrm{NCS}]_2$.—Recrystallization of the α isomer from hot water yielded indigo-blue cubic crystals of the β isomer. This complex crystallized as a 1 : 1 adduct from hot dimethylformamide and from hot dimethyl sulphoxide, and as a 2 : 1 adduct when α-$[\mathrm{NiL(NCS)_2}]\cdot0.5\mathrm{Me_2CO}$ was recrystallized from hot methanol containing an equimolar proportion of sodium hydroxide.

Di-μ-hydroxo-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II)] *Thiocyanate Hydrate*, $[\mathrm{(NiL)_2(OH)_2}][\mathrm{NCS}]_2\cdot1.5\mathrm{H_2O}$.—The dithiocyanato-complex (any form) was dissolved in hot methanol or acetone containing 2.2 mol equivalents of Na[OH], and filtered while hot. Light blue crystals of the product separated on cooling and were recrystallized from hot acetone.

Pentane-2,4-*dionato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *Perchlorate Hemihydrate*, $[\mathrm{NiL(pd)}][\mathrm{ClO_4}]\cdot0.5\mathrm{H_2O}$.—Pentane-2,4-dione (2.2 mol equivalents) was slowly added to a hot methanolic solution of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2$, the resulting solution was evaporated to small volume, and the blue product precipitated with propan-2-ol. Recrystallization was from hot methanol or water.

Isothiocyanato(*pentane*-2,4-*dionato*)(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *Hemihydrate*, $[\mathrm{NiL(pd)(NCS)}]\cdot0.5\mathrm{H_2O}$.—Pentane-2,4-dione (1.2 mol equivalents) was added to a hot methanolic suspension of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{NCS}]_2\cdot0.75\mathrm{H_2O}$ and the resulting solution was filtered and vacuum evaporated to leave a blue oil. This was dissolved in a little warm propan-2-ol and the product precipitated with diethyl ether. *Pentane*-2,4-*dionato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *thiocyanate monohydrate*, $[\mathrm{NiL(pd)}][\mathrm{NCS}]\cdot\mathrm{H_2O}$, crystallized when the complex was recrystallized from hot methanol–water (1 : 1).

Acetato(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)-*nickel*(II) *Perchlorate Hydrate*, $[\mathrm{NiL(O_2CMe)}][\mathrm{ClO_4}]\cdot\mathrm{H_2O}$.—Blue crystals of the product separated when diethyl ether was added to a methanol solution of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2$ containing 2.2 mol equivalents of acetic acid. The product was recrystallized from hot methanol or propan-2-ol.

Di-μ-chloro-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II)] *Perchlorate*, $[\mathrm{(NiL)_2Cl_2}][\mathrm{ClO_4}]_2$.—Acetic acid (2.1 mol equivalents) was added to a methanol solution of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2$, followed by an excess of lithium chloride. The solution was filtered and vacuum evaporated until crystallization occurred. The green product recrystallized as needles from hot ethanol.

μ-Oxalato-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)-*nickel*(II)] *Perchlorate*, $[\mathrm{(NiL)_2C_2O_4}][\mathrm{ClO_4}]_2$.—Oxalic acid (1.05 mol equivalents) was added to a hot methanol solution of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2$. The blue product crystallized on cooling and was recrystallized from hot methanol. *μ-Oxalato-bis*[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*-(II) *thiocyanate*, $[\mathrm{(NiL)_2C_2O_4}][\mathrm{NCS}]_2$, was prepared similarly by substituting a methanol suspension of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{NCS}]_2$ for the solution of the perchlorate.

(2-*Acetylphenolato*)(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *Perchlorate Hemihydrate*, $[\mathrm{NiL(ap)}][\mathrm{ClO_4}]\cdot0.5\mathrm{H_2O}$.—The deep green product crystallized when propan-2-ol was added to a solution of $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2$ in methanol to which had been added 2-acetylphenol (2.1 mol equivalents). Recrystallization was from hot ethanol.

(2-*Acetylphenolato*)*isothiocyanato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *Hemihydrate*, $[\mathrm{NiL(ap)(NCS)}]\cdot0.5\mathrm{H_2O}$.—2-Acetylphenol (2.1 mol equivalents) was added to a hot methanol suspension of $[\mathrm{(NiL)(OH)_2}][\mathrm{NCS}]_2$, and the solution filtered. The product was precipitated by propan-2-ol, filtered off, and washed with ethanol.

Di-μ-hydroxo-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II)] *Perchlorate* o-*Chlorophenol* (1/1), $[\mathrm{(NiL)_2(OH)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{C_6H_4(OH)Cl}$.—Green crystals of the product crystallized when the perchlorate salt was recrystallized from hot methanol containing *o*-chlorophenol (1.5 mol equivalents).

Ethylenediamine(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*nickel*(II) *Perchlorate*, $[\mathrm{NiL(en)}][\mathrm{ClO_4}]_2$.—4-Azaheptane-1,7-diamine(ethylenediamine)nickel(II) perchlorate, $[\mathrm{Ni(4NH\text{-}hd)(en)}][\mathrm{ClO_4}]_2$, was dissolved in acetone. Violet crystals which separated over *ca.* 3 d were filtered off, washed with ethanol, and recrystallized from hot methyl cyanide–propan-2-ol. Attempts to prepare analogous complexes by substituting propane-1,3-diamine for en were unsuccessful.

Di-isothiocyanato(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*copper*(II)—*Acetone* (2/1) α-$[\mathrm{CuL(NCS)_2}]\cdot0.5\mathrm{Me_2CO}$.—The green product crystallizes over a period of weeks when (4-azaheptane-1,7-diamine)di-isothiocyanatocopper(II) reacts with acetone. The reaction is more rapid in the presence of amine, *e.g.* 0.5 molar proportions. *Di-isothiocyanato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*copper*-(II)-*water* (4/1), β-$[\mathrm{CuL(NCS)_2}]\cdot0.25\mathrm{H_2O}$, was obtained as a green product when the α isomer was recrystallized from methanol or water.

Di-μ-hydroxo-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*copper*(II)] *Thiocyanate Hydrate*, $[\mathrm{(CuL)_2(OH)_2}][\mathrm{NCS}]_2\cdot\mathrm{H_2O}$.—A warm methanol solution of Na[OH] was added to an acetone solution of (4-azaheptane-1,7-diamine)di-isothiocyanatocopper(II), in equimolar proportions. The resulting solution was left in a stoppered flask for 3 d, when the blue-green product was filtered off and washed with acetone.

Pentane-2,4-*dionato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*copper*(II) *Perchlorate*, $[\mathrm{CuL(pd)}][\mathrm{ClO_4}]$.—The blue product, prepared as for the nickel(II) analogue, was recrystallized from hot ethanol. *μ-Oxalato-bis*[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*copper*(II)] *perchlorate*, $[\mathrm{(CuL)_2C_2O_4}][\mathrm{ClO_4}]_2$, was similarly prepared as a blue product by substituting oxalic acid (1.5 mol equivalents) for pentane-2,4-dione, and was recrystallized from hot methanol.

Acetato(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)-*copper*(II) *Perchlorate*, $[\mathrm{CuL(O_2CMe)}][\mathrm{ClO_4}]$.—Acetic anhydride (3 mol equivalents) in methanol was added to a solution of $[\mathrm{(CuL)_2(OH)_2}][\mathrm{ClO_4}]_2$ in methanol. The solution was filtered, evaporated to small volume, and the blue product precipitated with propan-2-ol. Recrystallization was from hot ethanol. This complex decomposed over a period of weeks when exposed to the atmosphere.

Di-μ-hydroxo-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*cobalt*(II)] *Perchlorate Hydrate*, $[\mathrm{(CoL)_2(OH)_2}][\mathrm{ClO_4}]_2\cdot0.66\mathrm{H_2O}$.—An acetone solution of cobalt(II) perchlorate hydrate was added dropwise with stirring, under nitrogen, to a warm (*ca.* 30 °C) acetone solution containing 4NH-hd

(3 mol equivalents). The flask was stoppered under nitrogen and maintained at 30 °C for *ca.* 1 h, when much of the brown crystalline product had separated. The yield was improved by allowing the mixture to stand for *ca.* 2 d. The crystals were filtered off and washed well with acetone.

Di-isothiocyanato(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*cobalt*(II) *and its Acetone Adduct*, α-[CoL(NCS)$_2$] *and* α-[CoL(NCS)$_2$]·0.33Me$_2$CO.—These complexes were prepared as for the perchlorate, using cobalt(II) thiocyanate and the amine (2.1 mol equivalents). The purple acetone adduct was recrystallized from hot acetone, under nitrogen. The unsolvated complex was obtained by recrystallization from hot methanol, under nitrogen. It is slowly oxidized to Co^{III} over a period of weeks on exposure to the air. *Di-isothiocyanato*(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)-*cobalt*(II), β-[CoL(NCS)$_2$], was prepared by recrystallization of the α isomer from hot water, under nitrogen.

Di-μ-hydroxo-bis[(2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*)*cobalt*(III)], [(CoL)$_2$(OH)$_2$][ClO$_4$]$_2$.—Red crystals of the product formed when an aqueous solution of the cobalt(II) complex, to which sodium perchlorate and a few drops of hydrogen peroxide had been added, was evaporated. The complex is diamagnetic and has a *d–d* spectrum typical of octahedral cobalt(III) complexes.

(4-*Azaheptane*-1,7-*diamine*)*isothiocyanato*(*pentane*-2,4-*dionato*)*nickel*(II), [Ni(4NH-hd)(pd)(NCS)].—The diamine and pentane-2,4-dione were successively added to an ethanol solution of nickel(II) thiocyanate (1.1 : 1.1 : 1 molar proportions) and the blue product recrystallized from hot methanol or water.

X-*Ray Structural Determination of Di-isothiocyanato*-{5(RS),9(RS)-2,4,4-*trimethyl*-1,5,9-*triazacyclododec*-1-*ene*}-*nickel*(II), α-[NiL(NCS)$_2$].—Crystals suitable for analysis were obtained by very slow cooling of a hot methanolic solution. The crystal used was an approximately rectangular parallelopiped (0. 16 × 0.06 × 0.15 mm).

Crystal data. $M = 386.2$, Orthorhombic, $a = 18.060(5)$, $b = 14.392(2)$, $c = 14.224(2)$ Å (standard deviations from a least-squares fit to diffractometer parameters of 12 reflections), $U = 3\,697.1$ Å^3, $F(000) = 1\,632$, $D_m = 1.40$, $Z = 8$, $D_c = 1.39$ g cm^{-3}, space group *Pbca*, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 12.7$ cm^{-1}.

Intensity data were collected using a Hilger and Watts four-circle diffractometer. Absorption corrections were applied to the 1 126 reflections observed at the $\geqslant \sigma(F^2)$ level used for the solution and refinement of the structure. Structure-factor data and thermal parameters are listed in Tables 5 and 6 of SUP 22146.

Solution and refinement of the structure. The structure was solved by conventional heavy-atom Patterson and Fourier methods, and refined by a full-matrix least-squares process. Atomic-scattering factors from ref. 22 were used, with the quantity $\Sigma w(F_o - F_c)^2$, where $w = 4F_o{}^2/\sigma(F_c{}^2)$, being minimized. Anisotropic temperature factors for all the non-hydrogen atoms were successively introduced during the refinement which converged to give R 0.068 and R' 0.057.

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[22] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.