Synthesis and Characterisation of the Nickel(II) and Copper(II) Complexes of New Quinquedentate (N_3O_2) Ligands and the Crystal Structure of Aqua[3,15-diacetyl-9-methyl-5,9,13-triazaheptadeca-3,14-diene-2,16-dionato-(2−)-$N^5N^9N^{13}O^2O^{16}$]nickel(II) Dihydrate *

James H. Cameron and Kevin J. McCullough
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS

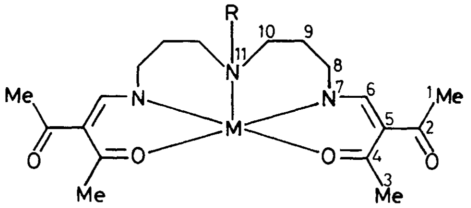
Nickel(II) and copper(II) complexes of two new multidentate ligands have been prepared and characterised. Although containing seven potential donor atoms, steric constraints dictate that the ligands behave as quinquedentate (N_3O_2) species. The nickel(II) complexes are isolated in both hydrated and anhydrous forms, each characterised by its colour and spectroscopic properties. In solution the copper complexes are five-co-ordinate, while the co-ordination number of the nickel(II) complexes depends on the nature of the solvent. In $CHCl_3$ the complexes are five-co-ordinate but in MeOH they are six-co-ordinate. The crystal structure of the trihydrate form of one of the complexes shows the nickel(II) ion to have a six-co-ordinate, pseudo-octahedral geometry, with one water molecule in the primary co-ordination sphere. This complex undergoes extremely facile dehydration to produce the five-co-ordinate, anhydrous form.

Over the last twenty years or so there has been considerable interest in the physical and chemical properties of complexes of various transition-metal ions with linear, potentially quinquedentate ligands.[1,2] Studies on such complexes have provided much interesting information concerning the magnetic, spectroscopic, and electronic properties of five-co-ordinate complexes. Some of the impetus for their study stemmed from the suggestion that complexes with this co-ordination environment would serve as models for some biological systems, providing co-ordinatively unsaturated materials able to bind a unidentate ligand to the metal ion, to realise the fully saturated co-ordination sphere.[3] A number of reports have been published concerning quinquedentate ligands of the Schiff-base type, derived from the triamines *N*-(3-aminopropyl)-1,3-propanediamine and *N*-(3-aminopropyl)-*N*-methyl-1,3-propanediamine.[4] A number of ligands have been prepared by the condensation of these amines with a variety of aldehydes[5] or ketones[6] and complexes derived from these ligands have been studied for a variety of purposes, for example cobalt(II) complexes as reversible binders of dioxygen[7] or as catalysts for the oxidation of organic substrates.[8] There are a large number of reports relating the physical, spectroscopic, and structural properties of such materials.

As part of a study of the chemistry of multidentate ligands derived from derivatives of 2,4-pentanedione, we have prepared two new multidentate ligands containing seven potential donor atoms (N_3O_4), (**1**) and (**2**). Due to steric constraints, the ligands can utilise only five of these donor atoms (N_3O_2), in forming complexes with both nickel(II) and copper(II) ions. In this paper we report the preparation, physical and spectroscopic properties of the new complexes (**3**)—(**6**). The *X*-ray crystal structure of the nickel(II) complex (**5**) is also reported.

Results and Discussion

Preparation of the Ligands (**1**) *and* (**2**).—The ligands are readily prepared in high yield by the reaction of 3-ethoxymethylidene-2,4-pentanedione (**7**)[9] with the appropriate triamine (**8**) or (**9**), in ethanol solution (Scheme). The ligands are rather more soluble in the reaction medium than others in their class but can be crystallised from solution upon cooling.



	M	R
(**1**)	2 x H	H
(**2**)	2 x H	Me
(**3**)	Ni	H
(**4**)	Cu	H
(**5**)	Ni	Me
(**6**)	Cu	Me

Spectroscopic analyses are consistent with the expected structures. For both ligands the ^1H n.m.r. spectrum, in $CDCl_3$ solution, contains a doublet at δ *ca.* 7.8, characteristic of the proton attached to C^6 which is coupled to the proton on the imine nitrogen atom. The other notable feature, common to both spectra, is the appearance of a signal with quartet fine structure, at δ *ca.* 3.5, due to the protons attached to C^8 which couple with the protons on C^9 and the imine nitrogen proton with, by coincidence, the same coupling constant (*J ca.* 6 Hz). Treating the n.m.r. sample with D_2O results in H/D exchange of the imine proton and causes these two n.m.r. signals to collapse to a singlet and a triplet respectively. For ligand (**2**) the N–CH_3 signal appears at δ 2.2 and the protons of C^{10} are shifted upfield by *ca.* 0.3, consistent with the change in the substituent on N^{11} from H [for (**1**)] to CH_3 [for (**2**)].

The i.r. spectra of the two ligands are very similar. Both have

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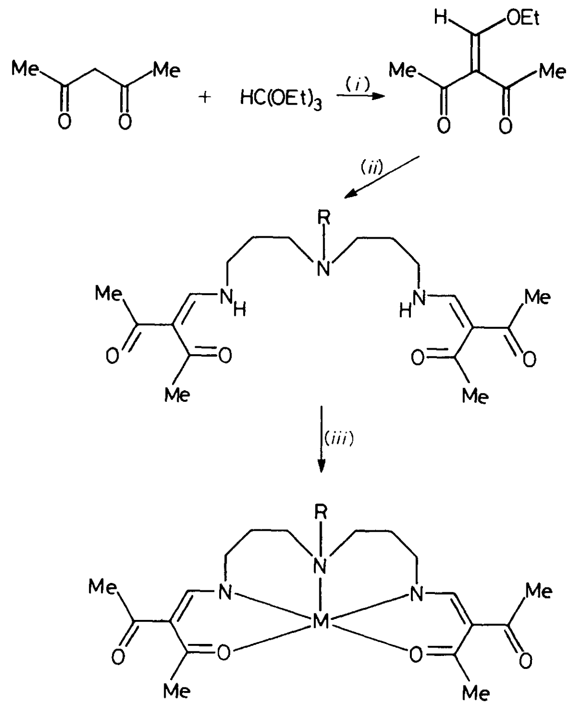
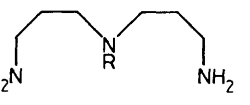
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: B.M. ≈ 9.27 × 10^{-24} J T^{-1}, cal = 4.184 J.



Scheme. (*i*) $(MeCO)_2O$; (*ii*) $NR(CH_2CH_2CH_2NH_2)_2$; (*iii*) $M(O_2CMe)_2$



(8) R = H

(9) R = Me

bands at 3 180 cm^{-1}, assigned to the N^7–H stretching vibration. A sharp band in the spectrum of (**1**) at 3 282 cm^{-1} is assigned to the N^{11}-H vibration. This is consistent with the secondary amine N–H stretching frequency found for an analogous ligand, derived from 2-hydroxyacetophenone and the same triamine.[3]

Although in principle the secondary amine of the triamine, (**8**) could react with 3-ethoxymethylidene-2,4-pentanedione (**7**) to produce the trisubstituted product, there was no evidence for formation of this species. Presumably the greater steric bulk surrounding the secondary amine of (**8**) inhibits the ability of N^{11} to react with (**7**).

Preparation of Complexes (**3**)—(**6**).—The ligands are readily metallated by treating a methanol solution of the ligand with a solution of the hydrated metal acetate, followed by 2 equivalents of base. It is notable that the new complexes are much less susceptible to hydrolysis than corresponding complexes derived from Schiff base condensation of (**8**) or (**9**) with non-aromatic aldehydes or ketones.[4] Complexes (**3**), (**4**) and (**6**) are isolated by reducing the volume of the solvent and allowing the products to crystallise. Complex (**5**) is isolated by adding an equivalent volume of water to the solution whereupon the product crystallises as the pale blue trihydrate. Upon drying at 60 °C for several hours this material undergoes an extremely facile loss of water to produce the dark green, anhydrous complex. The hydrate is regenerated by dissolving the green material in methanol and adding water.

Physical Properties of the Complexes.—*Infra-red spectra.* The i.r. spectra of the complexes are largely unremarkable but two key regions are useful in characterisation of the structure of the products.

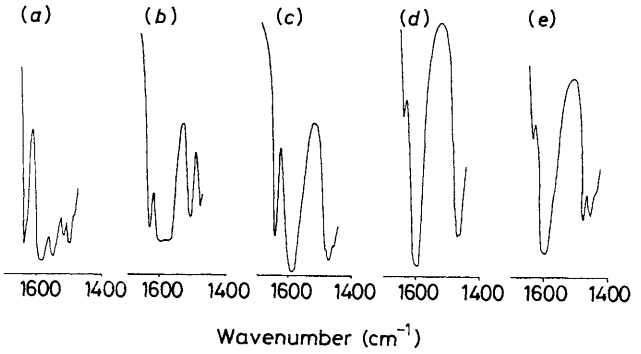


Figure 1. Infra-red spectra of complexes in the region 1 700—1 400 cm^{-1}: (*a*) (**3**), (*b*) (**4**), (*c*) (**5**) (trihydrate), (*d*) (**5**), and (*e*) (**6**). Nujol mulls between NaCl plates

Nickel(II) *complexes.* The purple complex (**3**) has a sharp band, at 3 238 cm^{-1}, assigned to ν(N–H) of the secondary amine. The shift in the position of this band relative to its position in the free ligand (3 282 cm^{-1}) strongly suggests that the secondary amine nitrogen atom is co-ordinated to the nickel(II) ion. There is a second, weaker, sharp band, at 3 638 cm^{-1}. This is tentatively assigned as a combination band of ν(N–H) and ν(N–Ni). A band at 1 640 cm^{-1} is assigned as ν(C–O) of the free acetyl group, with the co-ordinated acetyl group having a band at 1 585 cm^{-1} (Figure 1). The purple form (**3**) is converted into the blue hydrate by adding water to a methanol solution of the complex, followed by slow evaporation of the solvent. The i.r. spectrum of the hydrate is virtually identical to that of the purple form, except for the disappearance of the band at 3 638 cm^{-1} and appearance of a broad band due to H_2O, at 3 380 cm^{-1}.

The spectrum of complex (**5**) depends upon the conditions under which the solid is isolated. The pale blue trihydrate complex has a very broad, intense, asymmetric band in the region 3 100—3 550 cm^{-1}. A darker blue material, crystallised from methanol, has a sharp band at 3 460 cm^{-1} and broad bands at 3 330 and 3 240 cm^{-1}. This is assigned as a mixed H_2O—MeOH solvate. The green form of (**5**), prepared by gentle warming of the trihydrate, has no bands above 3 000 cm^{-1}.

The remainder of the spectra of the blue samples are very similar, being characterised by a pronounced band at 1 630—1 640 cm^{-1}, assigned to the unco-ordinated C=O of the ligand (Figure 1). The green anhydrous sample has a very different i.r. spectrum, significantly showing a considerable reduction of intensity for the band at 1 640 cm^{-1}, which appears merely as a weak band on the shoulder of a more intense band of lower frequency (Figure 1). The change is presumably associated with a change in the geometry of the complex, from pseudo-octahedral to pseudo-trigonal bipyramidal. The green form is assigned a pseudo-trigonal bipyramidal geometry by analogy with the known structure of a green Schiff-base complex of nickel(II).[10] By extension of the above argument, the fact that the spectrum of (**3**) has a pronounced band at 1 640 cm^{-1} implies that this complex is six-co-ordinate. The nature of this sixth ligand to the Ni^{II} has not been established but it is postulated that it may be an oxygen donor, by intermolecular association *via* an acetyl oxygen atom.

Copper complexes. The i.r. spectrum of complex (**4**) contains a sharp band at 3 223 cm^{-1} due to ν(N–H) of the ligand. As for the nickel(II) complex of the same ligand (see above) this shift in the position of the secondary amine N–H stretching frequency, relative to the free ligand, implies that the nitrogen atom is co-ordinated to the copper(II) ion. The presence of a pronounced band at 1 632 cm^{-1} implies that the Cu^{II} is six-co-ordinated

Table 1. Electronic spectra and magnetic moment data

Complex^a	Colour	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})		μ^b/B.M.	Ref.
		MeOH	$CHCl_3$		
(**3**)	Purple	536 (13)	557 (57)	3.21	This work
(**5**) (trihydrate)	Blue	543 (24)	567 (64)	3.40	This work
(**5**)	Green	538 (28)	568 (60)	3.24	This work
[NiL^1]	Green		621 (40)	3.25	4
[NiL^2]	Green		621 (60)	3.25	4
[NiL^3]	Green		598 (69.5)	3.40	1
[NiL^4]	Green		605 (52)	3.25^c	3
(**4**)	Green	751 (310)	753 (292)	1.99	This work
(**6**)	Green	754 (303)	753 (303)	1.95 (1.85)^c	This work
[CuL^1]	Green		781 (162)	1.83	4
[CuL^2]	Green		769 (180)	1.86	4
[CuL^3]	Green		806 (213)	1.93	1
[CuL^4]	Green		685 (189)	1.90^c	3

^{a} L^1 = 4,14-Dimethyl-5,9,13-triazaheptadeca-3,14-diene-2,16-dionate(2 −), L^2 = 4,9,14-trimethyl-5,9,13-triazaheptadeca-3,14-diene-2,16-dionate(2 −), L^3 = 1,11-bis(2′-oxidophenyl)-2,6,10-triazaundeca-1,10-diene(2 −), and L^4 = 2,12-bis(2′-oxidophenyl)-3,7,11-triazatrideca-2,11-diene(2 −). ^{b} In the solid state. ^{c} In solution.

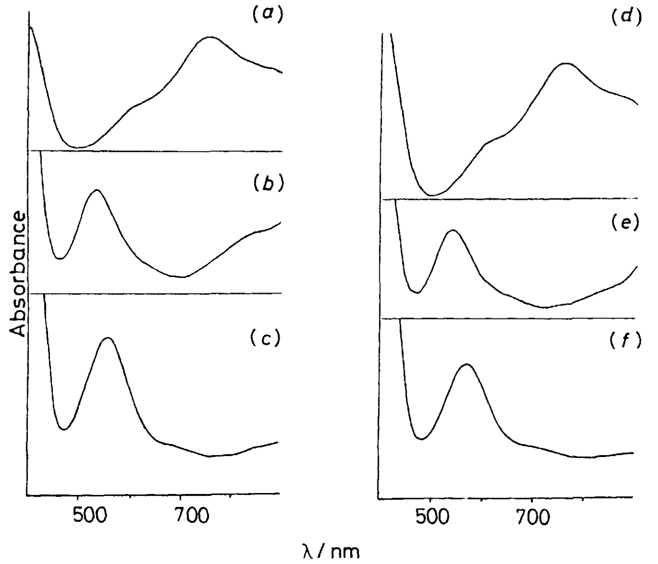


Figure 2. Electronic spectra of the complexes in the region 400—900 nm: (*a*) (**4**) in $CHCl_3$, (*b*) (**3**) in MeOH, (*c*) (**3**) in $CHCl_3$, (*d*) (**6**) in $CHCl_3$, (*e*) (**5**) in MeOH, and (*f*) (**5**) in $CHCl_3$

(Figure 1). As in the case of the nickel(II) complex of the same ligand, the nature of the sixth donor atom is not known.

In contrast, the spectrum of complex (**6**) contains no bands above 3 000 cm^{-1} and the band assigned to the free C=O group at 1 642 cm^{-1} is very weak (Figure 1). In fact the spectrum of (**6**) is almost identical to that of the anhydrous nickel(II) complex of the same ligand. This implies that (**6**) contains a five-co-ordinate copper(II) ion, presumably of pseudo-trigonal bipyramidal geometry.

Electronic spectra. Details of the electronic spectra of the complexes are listed in Table 1. In both methanol and chloroform solution the copper(II) complexes have remarkably similar spectra. In each case there is a broad, asymmetric band, $\lambda_{max.}$ *ca.* 750 nm, with shoulders at *ca.* 620 and 850 nm and the major band is of very similar intensity, with ε *ca.* 300 dm^3 mol^{-1} cm^{-1} (Figure 2). With regard to band position and intensity, the spectra are rather similar to those of Schiff-base complexes derived from reaction of a number of diketones, salicylaldehyde, or 2-hydroxyphenones with triamines (**8**) and (**9**).[3,4] Spectroscopic details on some of these complexes are included in the table for comparison.

While electronic spectra of copper(II) complexes are widely regarded as being poor indicators of geometry, it has been suggested that trigonal bipyramidal Cu^{II} will absorb in the range 800—850 nm and square pyramidal Cu^{II} in the range 670—550 nm.[11] This suggests that, in solution, the new complexes adopt the distorted trigonal bipyramidal geometry which has been observed for copper(II) complexes of other quinquedentate ligands.

It is worthy of note that while i.r. spectroscopic evidence suggests that there appears to be a difference in the co-ordination geometry of (**4**) and (**6**) in the solid state, in solution both complexes appear to be five-co-ordinate.

The electronic spectra of the nickel(II) complexes are solvent dependent (Table 1). With methanol as solvent, both (**3**) and (**5**) display spectra which are consistent with the nickel(II) ion being six-co-ordinate ($\lambda_{max.}$ *ca.* 540 nm, ε *ca.* 20 dm^3 mol^{-1} cm^{-1}) (Figure 2). Both spectra give clear evidence for a broad asymmetric peak of somewhat lower intensity, extending into the near-i.r. region of the spectrum. These bands are assigned, respectively, as being related to the $^3T_{1g}(F) \longleftarrow {}^3A_{2g}$ and the $^3T_{2g} \longleftarrow {}^3A_{2g}$ transitions predicted for an octahedral geometry. The third expected transition presumably is masked by intense ligand transitions at shorter wavelength.

In solution in chloroform the spectra are similar to those of some Schiff-base complexes of Ni^{II} which have been assigned five-co-ordinate structures, intermediate between trigonal bipyramidal and square planar geometries.[4] The spectra display only one band in the region 900—400 nm, of significantly higher intensity than the major peak in methanol solution ($\lambda_{max.}$ *ca.* 560 nm, ε *ca.* 60 dm^3 mol^{-1} cm^{-1}) (Figure 2). This behaviour is very similar to that observed for the single-crystal spectra of a Schiff-base nickel(II) complex, which is known to have a distorted trigonal bipyramidal structure in the solid state.[10] Both the hydrated and anhydrous forms of complex (**5**) produce the same spectrum when dissolved in chloroform, consistent with the weakly bound water molecule of the hydrate being dissociated when the complex is in solution.

Magnetic properties. The magnetic moments of the complexes in the solid state were determined using a Gouy balance and the results are included in Table 1. The nickel(II) complexes have magnetic moments in the range 3.2—3.4 B.M., consistent with the behaviour expected for a high-spin, five- or six-co-ordinate species. The copper(II) complexes have magnetic moments of *ca.*

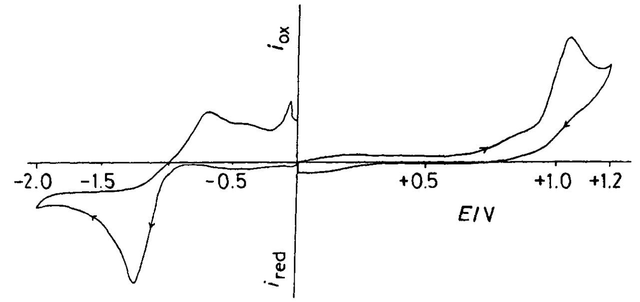


Figure 3. Cyclic voltammograms of complex (**4**) in dimethyl sulphoxide solution. Platinum working electrode, s.c.e. reference electrode. Starting potential, 0 V. Scan rate, 50 mV s^{-1}. Electrolyte, 0.1 mol dm^{-3} $LiClO_4$

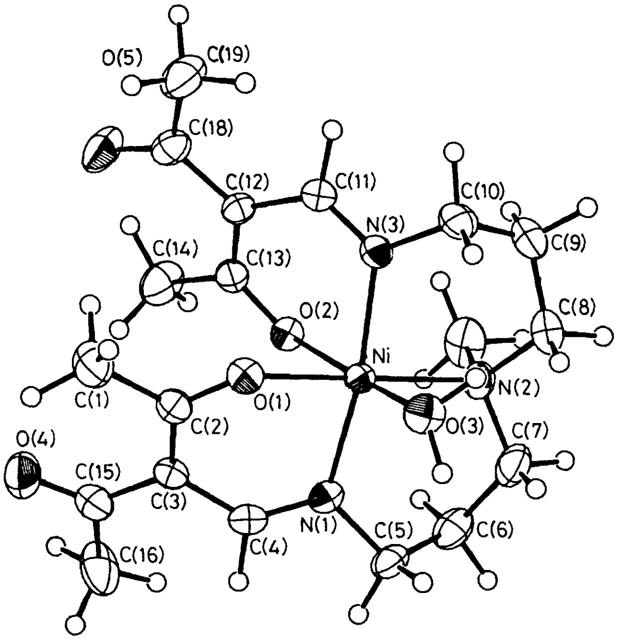


Figure 4. The molecular structure of complex (**5**) in the solid state (C. K. Johnson, ORTEP, Report ORNL-5183, Oak Ridge National Laboratory, Tenessee, 1976). Hydrogen atom labels have been omitted for clarity

1.95 B.M. This falls within the range expected for a species having a single unpaired electron and precludes any copper(II)–copper(II) interaction. The magnetic moment of complex (**6**), in $CDCl_3$ solution was determined using Evans' method[12] to be 1.85 B.M.

Electrochemistry. The cyclic voltammogram of complex (**5**), in solution in methanol displays a peak at +0.63 V (*versus* a standard calomel electrode) and this is assigned to the Ni^{II}–Ni^{III} couple. The peak is pseudo-reversible; $\Delta E_p = 100$ mV. Complex (**3**), in the same solvent, displays a similar peak, at +0.57 V ($\Delta E_p = 80$ mV). This 60 mV shift in $E_{\frac{1}{2}}$ for the Ni^{II}–Ni^{III} couple is in the opposite sense to that predicted based upon the relative inductive effects of H and Me. That complex (**5**) is more difficult to oxidise may imply that the presence of the methyl substituent on the nitrogen atom induces greater steric strain in this complex which serves to reduce the metal–nitrogen interaction. This appears to be a general phenomenon for ligands of this type since electrochemical studies of the corresponding Schiff-base complexes with a family of substituted salicylaldehydes revealed cathodic shifts of 30–70 mV for the *N*-methyl-substituted nickel(II) complexes.[13] The new nickel(II) complexes are rather more difficult to oxidise than the salicylaldehyde-derived complexes. This reflects both the different donor abilities of the ligands and the differences in solvation of the complexes in the two solvents.

The electrochemistry of the two copper complexes was studied using dimethyl sulphoxide as solvent. For complex (**6**) a cyclic voltammogram of the region from 0 to −1.6 V displays a single cathodic peak, at −1.06 V, ascribed to the reduction of Cu^{2+} to Cu^{+}. The anodic peak associated with this reduction appears at −0.72 V. The poor reversibility of this process indicates that a chemical reaction follows the electrochemical reduction. Since the corresponding copper(I) complex is likely to be of low stability, the subsequent chemical reaction may be ligand dissociation from the complex. Complex (**4**) displays very similar electrochemistry, with the cathodic peak appearing at −1.23 V and associated anodic peak at −0.67 V (Figure 3). These results are in close agreement with a literature report of the electrochemistry of a copper(II) complex.[13]

A more detailed study of the electrochemistry of complex (**4**) reveals an anodic peak at +1.04 V which is ascribed to the oxidation of Cu^{2+} to Cu^{3+}. The cathodic peak associated with this oxidation appears at −0.4 V. This again indicates that a chemical reaction follows the initial electrochemical process. When complex (**4**) was subjected to large negative potentials (*ca.* −2 V) a number of new species were electrogenerated but these were not identified.

Crystal Structure of Complex (**5**).—A single crystal of complex (**5**), grown from methanol–water solution, was subjected to *X*-ray crystallographic analysis. The solid-state structure consists of well ordered molecules of the complex containing a nickel atom in a distorted octahedral co-ordination geometry, with the ligand acting as a N_3O_2 donor and a molecule of water occupying the sixth co-ordination site, together with two molecules of water as solvent of crystallisation. A perspective view of a molecule of (**5**), omitting the solvent of crystallisation for clarity, is depicted in Figure 4. Atomic fractional co-ordinates and important geometrical parameters are listed in Tables 2 and 3 respectively.

Although there are several crystalline complexes between Ni^{II} and quinquedentate ligands which give trigonal bipyramidal structures,[2,10] the above octahedral geometry is very similar to that reported previously for the complex derived from the Schiff-base ligand formed by condensation of 2-hydroxy-4′,5-dimethylbenzophenone with *N*-(2′-aminoethyl)-1,3-propanediamine (**10**).[6c] The nitrogen atoms of the present ligand adopt a meridional arrangement, coplanar with O(1), and the ligand oxygen atoms O(1) and O(2) are *cis* related [angle O(1)–Ni–O(2) 86.68(11)°]. Consequently, this conformation results in an approximately square pyramidal co-ordination for the ligand, leaving a free site which can readily accommodate a water molecule.

In general there are only minor variations between corresponding Ni–O and Ni–N bond distances in complexes (**5**) and (**10**), except for the Ni–O (water) distances. The Ni(1)–O(3) distance of 2.127(3) Å [*cf.* 2.286(2) Å in (**10**)], which is 0.035 Å longer than the mean Ni–O (ligand) distance, suggests that the co-ordinated water molecule is more tightly bound in (**5**) than in (**10**). Although there is significant angular distortion from normal octahedral geometry (in the range 0.5—9.5°), deviations from the three principal planes through the co-ordinating atoms and the central nickel atom are less than 0.1 Å.

The two non-co-ordinated water molecules, present as solvent of crystallisation, are involved in a series of intermolecular hydrogen-bonding contacts (Table 4). One of the water molecules links adjacent monomers of the complex by interactions of (*a*) oxygen atom O(6) with one of the hydrogens

Table 2. Fractional co-ordinates of atoms with standard deviations

Atom	*x*	*y*	*z*
Ni	0.035 92(7)	0.100 34(2)	0.236 34(3)
O(1)	0.162 8(4)	0.010 69(14)	0.202 63(17)
C(1)	0.179 3(7)	−0.108 39(25)	0.184 5(3)
C(2)	0.087 1(6)	−0.040 81(21)	0.166 42(25)
C(3)	−0.075 8(6)	−0.035 47(20)	0.113 58(25)
C(4)	−0.141 8(6)	0.031 83(21)	0.087 0(3)
N(1)	−0.104 7(4)	0.090 31(16)	0.121 59(21)
C(5)	−0.179 0(6)	0.150 62(22)	0.074 4(3)
C(6)	−0.277 0(6)	0.199 09(24)	0.129 6(3)
C(7)	−0.151 5(7)	0.238 06(22)	0.194 9(3)
N(2)	−0.079 4(5)	0.197 68(17)	0.269 96(22)
C(8)	0.055 6(7)	0.243 94(23)	0.316 8(3)
C(9)	0.146 7(7)	0.216 03(23)	0.399 7(2)
C(10)	0.271 4(7)	0.155 60(23)	0.387 2(3)
N(3)	0.168 5(5)	0.095 71(17)	0.354 10(21)
C(11)	0.166 6(6)	0.042 62(21)	0.402 3(3)
C(12)	0.062 0(6)	−0.019 24(20)	0.386 95(25)
C(13)	−0.102 8(6)	−0.016 31(20)	0.335 69(25)
C(14)	−0.235 1(7)	−0.074 3(3)	0.330 9(4)
O(2)	−0.151 0(4)	0.036 22(13)	0.290 66(17)
C(15)	−0.173 4(6)	−0.094 43(24)	0.078 6(3)
C(16)	−0.352 2(8)	−0.083 3(3)	0.027 5(4)
O(4)	−0.125 1(5)	−0.154 84(17)	0.089 70(23)
C(17)	−0.226 5(7)	0.183 6(3)	0.325 3(3)
C(18)	0.129 3(6)	−0.081 16(23)	0.429 4(3)
C(19)	0.313 0(7)	−0.078 7(3)	0.479 1(4)
O(5)	0.052 3(5)	−0.137 78(16)	0.425 26(23)
O(3)	0.252 5(4)	0.153 99(15)	0.187 36(20)
O(6)	−0.265 6(5)	0.257 91(18)	0.552 46(22)
O(7)	−0.491 2(5)	0.049 97(22)	0.192 7(3)

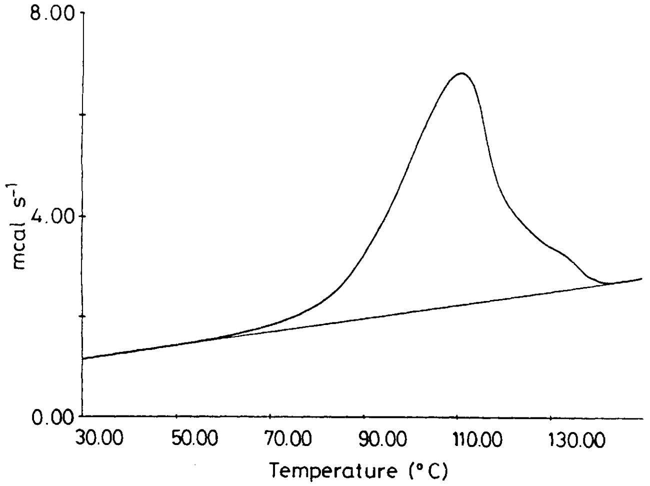


Figure 5. Differential scanning calorimeter trace for dehydration of complex (**5**). Scan rate 20 °C min^{-1}

Table 3. Derived geometrical parameters (distances in Å, angles in °) for complex (**5**)

Ni–O(1)	2.075(3)	N(2)–C(8)	1.497(6)
Ni–N(1)	2.017(3)	N(2)–C(17)	1.487(6)
Ni–N(2)	2.163(4)	C(8)–C(9)	1.517(7)
Ni–N(3)	2.025(3)	C(9)–C(10)	1.523(7)
Ni–O(2)	2.109(3)	C(10)–N(3)	1.465(6)
Ni–O(3)	2.127(3)	N(3)–C(11)	1.281(5)
O(1)–C(2)	1.261(5)	C(11)–C(12)	1.443(6)
C(1)–C(2)	1.499(7)	C(12)–C(13)	1.415(6)
C(2)–C(3)	1.418(6)	C(12)–C(18)	1.445(6)
C(3)–C(4)	1.446(6)	C(13)–C(14)	1.498(7)
C(3)–C(15)	1.441(6)	C(13)–O(2)	1.276(5)
C(4)–N(1)	1.279(5)	C(15)–C(16)	1.516(7)
N(1)–C(5)	1.469(6)	C(15)–O(4)	1.236(6)
C(5)–C(6)	1.513(7)	C(18)–C(19)	1.522(7)
C(6)–C(7)	1.530(7)	C(18)–O(5)	1.241(6)
C(7)–N(2)	1.479(6)		
O(1)–Ni–N(1)	84.57(12)	C(6)–C(7)–N(2)	115.6(4)
O(1)–Ni–N(2)	175.99(12)	Ni–N(2)–C(7)	113.2(3)
O(1)–Ni–N(3)	89.85(12)	Ni–N(2)–C(8)	112.2(3)
O(1)–Ni–O(2)	86.68(11)	Ni–N(2)–C(17)	108.3(3)
O(1)–Ni–O(3)	86.48(11)	C(7)–N(2)–C(8)	104.9(3)
N(1)–Ni–N(2)	96.58(13)	C(7)–N(2)–C(17)	109.1(4)
N(1)–Ni–N(3)	171.61(14)	C(8)–N(2)–C(17)	109.0(4)
N(1)–Ni–O(2)	89.55(12)	N(2)–C(8)–C(9)	116.2(4)
N(1)–Ni–O(3)	94.50(13)	C(8)–C(9)–C(10)	113.5(4)
N(2)–Ni–N(3)	89.41(13)	C(9)–C(10)–N(3)	110.4(4)
N(2)–Ni–O(2)	97.16(12)	Ni–N(3)–C(10)	119.3(3)
N(2)–Ni–O(3)	89.60(12)	Ni–N(3)–C(11)	123.2(3)
N(3)–Ni–O(2)	83.86(12)	C(10)–N(3)–C(11)	117.5(4)
N(3)–Ni–O(3)	91.40(13)	N(3)–C(11)–C(12)	127.3(4)
O(2)–Ni–O(3)	171.69(11)	C(11)–C(12)–C(13)	119.7(4)
Ni–O(1)–C(2)	125.7(3)	C(11)–C(12)–C(18)	117.0(4)
O(1)–C(2)–C(1)	115.3(4)	C(13)–C(12)–C(18)	123.2(4)
O(1)–C(2)–C(3)	122.4(4)	C(12)–C(13)–C(14)	122.6(4)
C(1)–C(2)–C(3)	122.2(4)	C(12)–C(13)–O(2)	122.6(4)
C(2)–C(3)–C(4)	119.3(4)	C(14)–C(13)–O(2)	114.8(4)
C(2)–C(3)–C(15)	123.1(4)	Ni–O(2)–C(13)	122.13(25)
C(4)–C(3)–C(15)	117.4(4)	C(3)–C(15)–C(16)	118.9(4)
C(3)–C(4)–N(1)	128.6(4)	C(3)–C(15)–O(4))	124.7(4)
Ni–N(1)–C(4)	122.9(3)	C(16)–C(15)–O(4)	116.3(4)
Ni–N(1)–C(5)	121.3(3)	C(12)–C(18)–C(19)	118.3(4)
C(4)–N(1)–C(5)	115.8(3)	C(12)–C(18)–O(5)	124.9(4)
N(1)–C(5)–C(6)	112.8(4)	C(19)–C(18)–O(5)	116.7(4)
C(5)–C(6)–C(7)	113.1(4)		

Table 4. Intermolecular hydrogen-bonding contacts

	Distance (Å)	Symmetry operation
H(3A) ··· O(6)	1.793(10)	$\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
H(6A) ··· O(4)	2.050(10)	$-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
H(7B) ··· O(2)	2.050(10)	x, y, z
H(7A) ··· O(1)	2.495(10)	$-1 - x, y, z$
H(7A) ··· O(3)	2.567(10)	$-1 - x, y, z$

H(3A) of the co-ordinated water molecule, and (*b*) one of its hydrogens H(6A) with a non-co-ordinated ligand oxygen atom, O(4), thereby forming infinite polymeric chains which are weakly cross-linked by interactions between the remaining water molecule and ligand oxygen atoms in monomers translationally related along the short *a* axis.

Thermochemistry.—Thermogravimetric analysis of complex (**5**) indicates a weight loss of 11.3% in the region 323—393 K (heating rate 10 K s^{-1}). This is in good agreement with the calculated weight loss for complete dehydration of the trihydrate of 11.34%. Despite the loss of the three water molecules from different environments in the structure (see above) the weight loss appears as one smooth curve, implying that there is no major difference between the energies required for loss of any particular water molecule. This is confirmed by differential scanning calorimetry (d.s.c.). The d.s.c. trace shows a large asymmetric endotherm around 383 K, corresponding to the loss of the water molecules from the structure (Figure 5). Individual steps are not resolved. The tail of the endotherm has a small shoulder around 398 K which is tentatively assigned to the energy required for structural rearrangement for the now five-co-ordinate complex, from square pyramidal toward trigonal bipyramidal geometry.

Conclusion

Nickel(II) and copper(II) complexes of two new quinquedentate ligands have been prepared and characterised. Infra-red spectroscopic data imply that the complexes of ligand (**1**) are both six-co-ordinate in the solid state. The copper(II) complex and the anhydrous nickel(II) complex of ligand (**2**) are both five-co-ordinate while the trihydrate nickel(II) complex, (**5**), is six-co-ordinate. The *X*-ray crystal structure of this trihydrate complex confirms that the ligand, (**2**), behaves as a N_3O_2 donor, with the sixth co-ordination site being occupied by a weakly bound water molecule. The blue complex, (**5**), undergoes facile dehydration to the green anhydrous form. Neither thermal gravimetric analysis nor d.s.c. differentiates the loss of water molecules from different environments in the structure of the complex.

The copper(II) complexes are five-co-ordinate in both methanol and chloroform solution while the nickel(II) complexes show solvent-dependent spectroscopic behaviour. In chloroform solution both are five-co-ordinate but in methanol solution the spectra are indicative of six-co-ordinate geometry.

Attempts to ring close complex (**3**) to form a quinquedentate macrocyclic complex, using either 1,3-propanediamine or 1,2-ethanediamine, were unsuccessful. Further work on the chemical modification of these ligands is continuing.

Experimental

3-Ethoxymethylidene-2,4-pentanedione (**7**) was prepared by the literature procedure.[9]

3,15-*Diacetyl*-5,9,13-*triazaheptadeca*-3,14-*diene*-2,16-*dione* (**1**).—A solution of compound (**7**) (20 g, 0.126 mol) in ethanol (50 cm^3) was cooled in an ice-bath and a solution of *N*-(3-aminopropyl)-1,3-propanediamine (7.5 g, 0.064 mol) in ethanol (30 cm^3) was added dropwise with stirring over a period of about 30 min. After addition was complete, the pale yellow reaction mixture was stirred for a further 20 min at 0 °C and then stored in a freezer overnight. The off-white solid product was collected by filtration. A second crop of product was obtained by reducing the volume of the filtrate and cooling. Typically the second crop had a pronounced yellow coloration but it was identical spectroscopically to the first crop. Combined yield 17.5 g (78%). δ_H(60 MHz, $CDCl_3$) 1.70 (m, 5 H, 2 × $CH_2CH_2CH_2$ and NH), 2.20 (s, 6 H, 2 × CH_3), 2.40 (s, 6 H, 2 × CH_3), 2.68 (t, 4 H, J = 6.5, 2 × $N^1CH_2CH_2$), 3.45 (q, 4 H, J = 6.5, 2 × $CH_2CH_2N^7$), 7.80 (d, 2 H, J = 14 Hz, CH), and 10.90 (br, 2 H, N^7H).

3,15-*Diacetyl*-9-*methyl*-5,9,13-*triazaheptadeca*-3,14-*diene*-2,16-*dione* (**2**).—This compound was prepared in the manner described for compound (**1**). Yield 65%. δ_H(60 MHz, $CDCl_3$) 1.80 (qnt, 4 H, J = 6, $CH_2CH_2CH_2$), 2.20 (s, 3 H, N–CH_3), 2.27 (s, 6 H, 2 × CH_3), 2.35 (m, 4 H, 2 × CH_2NCH_3), 2.48 (s, 6 H, 2 × CH_3), 3.50 (q, 4 H, J = 6, 2 × $CH_2CH_2N^7$), 7.85 (d, 2 H, J = 13.5 Hz, CH), and 10.90 (br, 2 H, NH).

Nickel(II) *and Copper*(II) *Complexes of Ligands* (**1**) *and* (**2**).—These four complexes (**3**)—(**6**) were prepared by similar methods and the procedure is given for only one example.

[3,15-*Diacetyl*-5,9,13-*triazaheptadeca*-3,14-*diene*-2,16-*dionato*(2–)-$N^5N^9N^{13}O^2O^{16}$]*nickel*(II) (**3**).—Ligand (**1**) (1 g, 2.85 mmol) was dissolved in methanol (25 cm^3) and to this was added $Ni(O_2CMe)_2 \cdot 4H_2O$ (0.71 g, 2.85 mmol). The solution became purple in colour. Sodium hydroxide pellets (0.23 g, 5.70 mmol) were added and the mixture was stirred at *ca.* 50 °C for 30 min. On standing overnight purple crystals of the product appeared and were collected by filtration. A second crop of product was isolated as a purple powder by reducing the volume of the filtrate. Combined yield 0.87 g (75%) (Found: C, 52.85; H, 7.2; N, 10.5. Calc. for $C_{18}H_{27}N_3NiO_4$: C, 53.0; H, 6.6; N, 10.3%).

Analytical Data for Other Complexes.—Complex (**4**) (Found: Cu, 14.8. Calc. for $C_{18}H_{27}CuN_3O_4$: Cu, 15.4), (**5**) (Found: C, 46.05; H, 7.25; N, 8.4; Ni, 11.4. Calc. for $C_{19}H_{29}N_3NiO_4 \cdot 4H_2O \cdot 0.5MeOH$: C, 45.9; H, 7.65; N, 8.2; Ni, 11.5), and (**6**) (Found: Cu, 15.3. Calc. for $C_{19}H_{29}CuN_3O_4$: 14.4%).

Instrumentation.—Proton n.m.r. spectra were run on a Perkin-Elmer R-12 instrument at 60 MHz using $CDCl_3$ as solvent and hexamethyldisiloxane (hmds) as internal standard, i.r. spectra on a Perkin-Elmer 580 spectrophotometer, as Nujol mulls between rock salt flats, and electronic spectra as solutions using a Shimadzu UV-160 spectrophotometer with quartz cells (path length 1 cm). Electrochemistry was performed using a Thomson potentiostat and miniscan, linked to a Linseis XY recorder and platinum working electrodes, with tetrabutylammonium tetrafluoroborate as the electrolyte. Potentials are reported with respect to a saturated calomel reference electrode (s.c.e). Magnetic moments on solid samples were determined using a Gouy balance (Newport Instruments). Diamagnetic corrections were made using Pascal's constants. The solution magnetic moment was determined by Evans' method, using a Bruker WH-200 spectrometer, operating at 200 MHz. Solutions, in $CDCl_3$, were contained in coaxial tubes (Wilmad Glass Co.) with hmds as the reference standard.

Crystallography.—Crystal data for complex (**5**). $C_{19}H_{29}N_3NiO_4 \cdot 3H_2O$, light blue prisms, M = 476.2, monoclinic, space group $P2_1/n$ (non-standard setting of no. 14), a = 7.485(3), b = 19.428(3), c = 15.719(4) Å, β = 95.00(3)°, U = 2 277.2 $Å^3$, Z = 4, D_c = 1.389 g cm^{-3}, λ = 0.710 693 Å, μ(Mo-K_α) = 8.95 cm^{-1}, F(000) = 1 016, data crystal *ca.* 0.40 × 0.40 × 0.20 mm.

Structure solution and refinement. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using ω-2θ scanning and graphite-monochromated Mo-K_α *X*-radiation over the region $1.5 < \theta < 25°$. The 2 076 observed intensities with $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects, and for absorption (DIFABS).[14] The position of the Ni atom was located on a Patterson map (SHELXS 86)[15] with the remainder of the structure being located subsequently on a series of difference Fourier maps. The structure was refined using full-matrix least-squares techniques (SHELX 76)[16] with anisotropic thermal parameters for all of the non-hydrogen atoms. All of the hydrogen atoms were located on a difference Fourier map and included in the refinement process on idealised positions (C–H 0.95 Å) with a fixed isotropic thermal parameter (U_{iso} = 0.10 $Å^2$). The water molecules were treated as idealised rigid groups (O–H 0.985 Å and H–O–H 104.7°). At convergence, the conventional and weighted R factors $[w^{-1} = \sigma^2(F) + 0.000\,386\,(F^2)]$ were 0.040 and 0.052 respectively. The final difference Fourier map contained no features greater than ± 0.41 e $Å^{-3}$. Miscellaneous crystallographic calculations and compilation of tables were carried out using the program CALC.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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