

The Syntheses, Properties and Crystal and Molecular Structures of the Copper(II) and Nickel(II) Complexes of the Non-symmetric Schiff Bases, Derived from 1,2-Diaminoethane, Pentane-2,4-dione and 2-Pyrrollecarboxaldehyde

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Abstract

The synthesis of a non-symmetric Schiff base derived from 1,2-diaminoethane, pentane-2,4-dione and 2-pyrrollecarboxaldehyde is described and the copper(II) and nickel(II) complexes are reported. The crystal structure of the nickel(II) complex is monoclinic, $R = 0.0368$, 1451 reflections: the crystal structure of the copper(II) complex is isomorphous, ($R = 0.0387$, 1239 reflections). In both structures, the metals adopt square-planar coordination geometries and long intermolecular contacts lead to weak oligomerisation. The EPR spectra of the copper(II) complex is discussed and related to the structure.

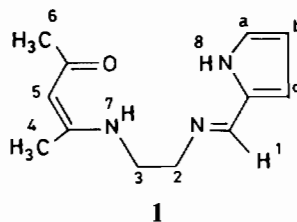
Introduction

There has been recent interest in the design, synthesis and application of non-symmetric Schiff base ligands. This has been stimulated partly by an awareness that in many metalloproteins the metals are contained in non-symmetrical environments and also by an interest in the potential modification of the properties of complexes derived from ligands having present non-symmetrically derived mixed donor sets. We have recently presented results concerning the derivation of non-symmetric tetradentate and compartmental Schiff bases and their complexes, and of their singly condensed 'half-unit' precursors [1, 2]. Included in that work was a brief review of this class of ligands [2].

In this paper we report the synthesis of the non-symmetric Schiff base (1) and of its copper(II) and nickel(II) complexes, together with the

properties and crystal and molecular structures of the complexes.

The structures of symmetric mononuclear Schiff base complexes such as $M(\text{acen})$, (2) [3] show a square planar metal environment and there is a 6,5,6-chelate ring arrangement around the central metal atom. The symmetric Schiff base (3) would provide a 5,5,5-chelate ring environment for a metal complex if mononuclear, but has been shown to give a binuclear copper(II) complex in which both ends of the Schiff base act as bis(bidentate) ligands [4]. It was therefore of interest to determine the structure of metal complexes of the non-symmetric Schiff base, (1), in which the intermediate 6,5,5-chelate ring system prevailed, in order to confirm both the structure, and the discrete nature, of the non-symmetric systems. Such compounds have been suggested as useful probes for the study of low symmetry complexes related to the low symmetry sites found in metalloproteins [5].



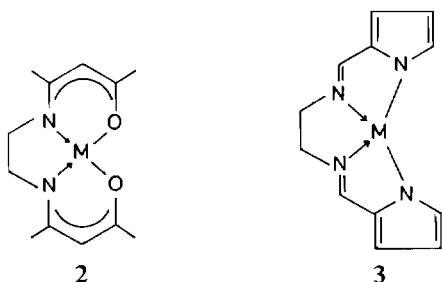
Results and Discussion

The non-symmetric ligand (1) was prepared by reaction of the 'half-unit' 7-amino-4-methyl-5-aza-hept-3-ene-2-one, [1] with 2-pyrrollecarboxaldehyde in stoichiometric ratio in methanol. The ligand was recovered as a yellow oil and characterised by ^1H NMR and MS. The

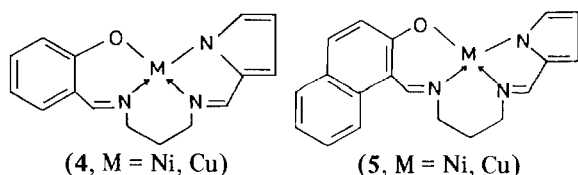
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MS gave a parent peak at 219 a.m.u. corresponding to (1), and no evidence for either of the two symmetrical tetradentate species which could arise through rearrangement reactions (214 a.m.u. and 224 a.m.u.). The ^1H NMR, run in CDCl_3 , gave signals at 1.89 (s, 3H, CH_3^4), 1.99 (s, 3H, CH_3^6), 3.47 (q, 2H, CH_2^3), 3.67 (t, 2H, CH_2^2), 4.94 (s, 1H, CH^5), 6.21 (t, 1H, H^b), 6.50 (d, 1H, H^a), 6.87 (d, 1H, H^c), 8.08 (s, 1H, H^1) and 10.00 (bd, 2H, H^7 and H^8) p.p.m. The yellow oil was then used, without further purification, to prepare the metal complexes. It was also possible to prepare these complexes by an in situ reaction in which the oil was not recovered, and in which triethylamine and the required metal salt were added to the reaction mixture.

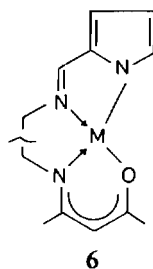
The complexes were isolated as violet needles (Cu) and as yellow needles (Ni). The IR spectra indicated that two types of imine bond were present, one which was purely $\text{C}=\text{N}$ and one with partial double bond character, $\text{C}=\text{N}$. The corresponding bands were found at 1590 cm^{-1} ($\text{C}=\text{O} + \text{C}=\text{N} + \text{C}=\text{C}$) and 1515 cm^{-1} ($\text{C}=\text{N}$) for the nickel(II) complex, and $1600 + 1590\text{ cm}^{-1}$ ($\text{C}=\text{O} + \text{C}=\text{N} + \text{C}=\text{C}$) and 1510 cm^{-1} ($\text{C}=\text{N}$) for the copper(II) complex. In the symmetric analogues (2) and (3) the $\text{C}=\text{N}$ bands are found *ca.* 1515 cm^{-1} (in (2)), [6] and the $\text{C}=\text{N}$ bands are found *ca.* 1590 cm^{-1} (in (3)) [7].



The DRS spectra showed for the Ni(II) complex a band at $25,500\text{ cm}^{-1}$, with shoulders at $28,500$ and $19,800\text{ cm}^{-1}$, and for the Cu(II) complex, bands at $26,700$ and $19,000\text{ cm}^{-1}$. These bands are comparable to those found in the visible spectra of the related species (4) [8] and (5), [9] which were attributed to square-planar, or distorted square-planar metal environments. Both of these species have trimethylene bridges present, and this could account for the differences in absolute values found as our complexes are ethylene-bridged.



The MS of the complexes show parent peaks corresponding to the molecular weight of the complex (275 a.m.u. (Ni) and 280 a.m.u. (Cu)). The fragmentation shows a symmetrical cleavage of the ligand (6) and it is possible, *e.g.* to detect peaks corresponding to the pyrrole half plus Ni(II)



(164 a.m.u.) and to the acac half plus Ni(II) (169 a.m.u.). A similar process is seen in the copper complex with peaks at 169 and 174 a.m.u. respectively.

The ^1H NMR of the nickel(II) complex was run in CDCl_3 and showed signals at 1.91 (s, 3H, $\text{CH}_3^{4,6}$); 1.92 (s, 3H, $\text{CH}_3^{6,4}$); 3.29 (t, 2H, CH_2^3); 3.52 (t, 2H, CH_2^2); 5.00 (s, 1H, CH^5); 6.10 (t, 1H, H^b); 6.54 (d, 1H, H^a); 6.70 (s, 1H, H^c) and 7.40 (s, 1H, CH^1) p.p.m. Signals due to $-\text{OH}$ and $-\text{NH}$ were not detected.

The EPR spectra of the copper(II) complex run as powdered samples were uninformative, even at low temperature (120 K), since they exhibit a slightly asymmetric derivative at $g = 2.061$. Frozen toluene solutions gave spectra which essentially consist of a feature typical of that expected for a monomeric copper(II) species (Fig. 1). At low temperature and using a high instrument gain three 'half-field' (*ca.* 1500G) lines were detected with an average spacing of 95G, which is practically half the value

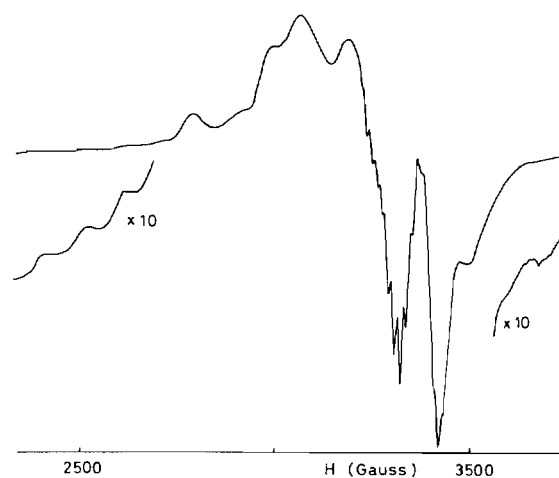


Fig. 1. High-field portion of the X-band (9.41 GHz) EPR spectrum of $\text{C}_{12}\text{H}_{15}\text{CuN}_3\text{O}$ in toluene at 120 K.

expected for a monomeric species. These low field components are attributed to $\Delta M_S = \pm 2$ transitions arising from dipolar interactions between copper(B) ions in a dimeric species which could exist in the frozen solution. Their weak intensity indicates that the proportion of copper(H) ions involved in such dimeric species is low. As a consequence observation of the related $\Delta M_S = \pm 1$ transitions proved difficult due to the dominant signals associated with the monomer. However four signals appear in the 2400-2730 G area with an average spacing of 98 G. Two other lines may be assigned to shoulders at 2980 and 3077 G. Considering that one component is likely to be masked by a parallel transition in the monomer at cu. 2790 G, the overall feature comprises seven lines as expected from the interaction with two copper nuclei. Due to zero-field splitting a second seven-line pattern should occur at higher field; these signals and the other features associated with the triplet spectrum are largely obscured by the monomer transition. However the weak signal at 3715 G is likely to be due to the highest field transition of the second seven-line pattern. This attribution yields $g_{\parallel} = 2.189$ and $D_{\parallel} = 345 \times 10^{-4} \text{ cm}^{-1}$. Tentatively a g_{\perp} value of ca. 2.045 may be estimated by considering that the two remaining signals at 3060 and 3510 G are the components of the perpendicular portion of the dimer spectrum.

For the monomeric species, consideration of the X- and Q-band spectra of liquid (295 K) and frozen (120 K) toluene solutions gives the following parameters: $g_{\text{iso}} = 2.090$, $A_{\text{iso}}(\text{Cu}) = 86 \times 10^{-4} \text{ cm}^{-1}$; $g_{\parallel} = 2.187$, $A_{\parallel}(\text{Cu}) = 196 \times 10^{-4} \text{ cm}^{-1}$, $A(\text{N}) = 14.4 \times 10^{-4} \text{ cm}^{-1}$; $g_{\perp} = 2.042$, $A(\text{Cu}) = 34 \times 10^{-4} \text{ cm}^{-1}$. These values are consistent with a square planar coordination. However it may be emphasized that the X-band spectrum, as well as the Q-band, shows only two g-values indicating that the effective ligand-field at the copper(H) ion is axial.

The main interest of this study is to provide evidence for the dimeric species in solution. However the dimer occurs only to a minor extent. Dimer formation from copper(H) Schiff-base complexes in inert solvents has been previously reported [10-12] and the EPR data have been analysed in terms of dipole-dipole coupled copper(H) ions in order to afford some structural information on the dimer species. In the present case the low concentration of the dimer does not allow a reliable attribution of all of the transitions in the triplet spectrum and therefore prevents the use of such a sophisticated analysis. However, if the magnetic interaction is assumed to be essentially of a dipolar nature, a crude estimation of the Cu-Cu distance may be obtained from the equation $R = (0.65 g_{\parallel}^2 / D_{\parallel})^{1/3}$ [13]. The resulting value, cu. 4.5 Å is reasonable and may be compared with the value observed in the solid state.

The X-ray crystal structure of the copper complex is illustrated in Fig. 2 with the atom labelling used in the corresponding Tables: the nickel complex is visually indistinguishable and is similarly labelled. Bond lengths and angles (together with estimated standard deviations) and a summary of the planar fragments are compared in Tables I and II.

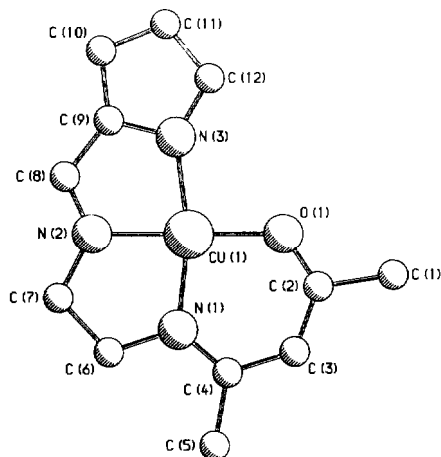


Fig. 2. The molecular structure of the copper complex with atom labelling; the nickel complex is isostructural and is similarly labelled.

TABLE I. Bond Lengths (Å) and Bond Angles ($^{\circ}$) with e.s.d.s for Both Isomorphous Complexes.

	(M = Cu)	(M = Ni)
M(1)-O(1)	1.899(4)	1.840(4)
M(1)-N(1)	1.934(5)	1.846(4)
M(1)-N(2)	1.935(5)	1.846(4)
M(1)-N(3)	1.964(5)	1.889(4)
O(1)-C(2)	1.282(8)	1.287(7)
C(1)-C(2)	1.505(10)	1.505(9)
C(2)-C(3)	1.376(9)	1.366(8)
C(3)-C(4)	1.411(9)	1.428(8)
C(4)-C(5)	1.495(10)	1.506(8)
N(1)-C(4)	1.318(8)	1.309(7)
N(1)-C(6)	1.476(8)	1.477(7)
C(6)-C(7)	1.499(10)	1.472(9)
N(2)-C(7)	1.460(9)	1.458(8)
N(2)-C(8)	1.275(8)	1.286(7)
C(8)-C(9)	1.419(9)	1.428(7)
N(3)-C(9)	1.381(8)	1.384(6)
C(9)-C(10)	1.391(9)	1.391(8)
C(10)-C(11)	1.391(10)	1.392(8)
C(11)-C(12)	1.390(9)	1.390(8)
N(3)-C(12)	1.347(8)	1.348(7)
O(1)-M(1)-N(1)	96.62(19)	97.65(17)
O(1)-M(1)-N(2)	177.50(20)	176.18(17)
O(1)-M(1)-N(3)	97.17(19)	92.80(16)
N(1)-M(1)-N(2)	84.09(20)	86.15(18)
N(1)-M(1)-N(3)	166.21(20)	169.51(18)

(continued overleaf)

TABLE I (continued)

	(M = Cu)	(M = Ni)
N(2)-M(1)-N(3)	82.14(20)	83.40(18)
M(1)-O(1)-C(2)	123.0(4)	123.6(3)
O(1)-C(2)-C(1)	114.5(6)	113.5(5)
O(1)-C(2)-C(3)	126.8(6)	126.3(5)
C(1)-C(2)-C(3)	118.8(6)	120.2(5)
C(2)-C(3)-C(4)	127.3(6)	125.1(5)
C(3)-C(4)-C(5)	117.4(6)	117.0(5)
N(1)-C(4)-C(3)	122.1(6)	121.5(5)
N(1)-C(4)-C(5)	120.5(6)	121.5(5)
M(1)-N(1)-C(4)	124.1(4)	125.7(4)
M(1)-N(1)-C(6)	114.6(4)	114.3(3)
C(4)-N(1)-C(6)	121.3(5)	119.9(4)
N(1)-C(6)-C(7)	112.7(6)	111.7(5)
N(2)-C(7)-C(6)	110.1(6)	109.1(5)
M(1)-N(2)-C(7)	116.8(4)	116.7(4)
M(1)-N(2)-C(8)	115.6(4)	117.3(4)
C(7)-N(2)-C(8)	127.6(6)	125.9(5)
N(2)-C(8)-C(9)	116.3(6)	114.3(5)
N(3)-C(9)-C(8)	114.7(5)	112.3(4)
N(3)-C(9)-C(10)	109.8(5)	110.4(5)
C(8)-C(9)-C(10)	135.5(6)	137.2(5)
C(9)-C(10)-C(11)	106.3(6)	105.2(5)
C(10)-C(11)-C(12)	106.8(6)	108.1(5)
N(3)-C(12)-C(11)	110.6(5)	109.8(5)
M(1)-N(3)-C(9)	111.3(4)	112.7(3)
M(1)-N(3)-C(12)	142.2(4)	140.8(4)
C(9)-N(3)-C(12)	106.5(5)	106.5(4)
Intermolecular contacts (Å)		
M(1)···M(1)[-x, -y, -z]	3.657	3.561
M(1)···M(1)[1-x, -y, -z]	3.973	3.999
M(1)···N(1)[-x, -y, -z]	3.462	3.592
M(1)···N(1)[1-x, -y, -z] > 4.0		3.834
M(1)···N(2)[1-x, -y, -z]	3.661	3.913

The metal coordination polyhedra are essentially square-planar; the small loss of coplanarity in the copper complex is wholly associated with atom N(2). The metal-to-ligand bond lengths are up to 0.09 Å shorter in the case of the nickel complex, due to the absence of an anti-bonding electron in the $d_{x^2-y^2}$ orbital in that d^8 complex.

The pyrrole rings and the imino-ketone chelate fragments are all essentially planar with only small out-of-plane deviations of the metal atoms and of other substituents. The geometries around the nitrogen atoms and around the trigonal carbon atoms C(2), C(4), C(9) are all planar and all ligand bond lengths are unexceptionable. The very large external angles at N(3) and C(9) and the deviation of N(1)-M(1)-N(3) from 180° reflect the residual strain in the ligand that results from coordination to the metal. The torsion angle about C(6)-C(7) is, as usual, much reduced from the free ligand value.

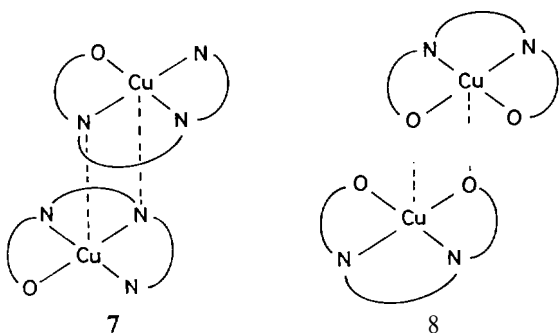
TABLE II. Summary of Planar Fragments of Both Complexes (M = Cu or Ni; Deviations from Planes in Å).

	(M = Cu)	(M = Ni)
Plane A [O(1), N(1)-N(3)]		
r.m.s. deviation (Å)	0.023	0.011
deviations of atoms M(1)	-0.017	-0.004
Plane B [M(1), O(1), N(1)]		
deviations of atoms		
N(2)	0.081	-0.012
N(3)	-0.003	0.030
C(2)	0.045	0.026
C(3)	0.095	0.084
C(4)	0.056	0.041
Plane C [M(1), N(2), N(3)]		
deviations of atoms		
O(1)	0.080	-0.014
N(1)	-0.022	0.032
Plane D [M(1), N(1), N(2)]		
deviations of atoms		
O(1)	0.079	-0.012
N(3)	-0.023	0.032
C(6)	-0.119	-0.107
C(7)	0.082	0.106
Plane E [O(1), N(1), C(2)-C(4)]		
r.m.s. deviation (Å)	0.007	0.011
deviations of atoms		
M(1)	0.061	0.050
C(1)	-0.071	-0.070
C(5)	-0.043	-0.056
Plane F [N(3), C(9)-C(12)]		
r.m.s. deviation (Å)	0.004	0.003
deviations of atoms		
M(1)	0.041	0.061
N(2)	0.086	0.101
C(8)	0.035	0.060
Angle between planes (°)		
B - C	2.4	1.0
B - E	2.7	2.2
C - F	1.9	2.3
Torsion angle: N(1)-C(6)-C(7)-N(2) + 14.7° + 15.3°		

Both crystal structures exhibit long intermolecular contacts to centrosymmetrically related molecules. In the nickel complex, the interaction is one-sided, tending towards a weak dimerisation in which the short nickel-nickel contact (3.56 Å) is the most significant. In the copper complex, a small re-adjustment has resulted in a much shorter Cu···N(1') contact and an increased copper-copper distance; and a different nitrogen atom (N(2'')) of a second centrosymmetrically related molecule has filled the other octahedral position, giving rise to weak polymerisation. This relative slippage of the molecular planes accounts for the small differences in cell constants (in b, c, β), but it is noteworthy that the a-axis, to which the molecular planes are

approximately perpendicular, is identical in length in the two crystal structures.

The structural data indicate that the dimeric form in solution is likely to be held by Cu-N interactions (7). The EPR spectra of (4, M = Cu) [5] and (5, M = Cu) [6] have been interpreted in terms of dimer formation in frozen xylene solution, and for (4, M = Cu) a monomer-dimer distribution is found in frozen chloroform solution -in this case the solvent can hydrogen bond to



the complex. These species however are proposed as being linked through a Cu-O bridge, as is found in related crystal structures (8) [14]. Our work indicates that in the absence of X-ray structural information giving the precise nature of any dimeric interactions, caution might be exercised in EPR interpretations.

Experimental

Microanalysis were carried out by the University of Sheffield Microanalytical Service. Physical measurements (IR, DRS, MS, NMR) were carried out as detailed in reference 2. EPR spectra were obtained using a Bruker 200 TT spectrometer.

The Synthesis of (I)

To a solution of 7-amino-4-methyl-5-aza-hept-3-ene-2-one (2 g; 1.4×10^{-2} mol) in ethanol (30 cm^3) was added 2-pyrrolecarboxaldehyde (1.35 g; 1.4×10^{-2} mol). The solution was warmed on a steam bath for 1.5 min. After cooling, the solvent was removed to leave a yellow oil which was characterised by MS, IR and ^1H NMR and used without further purification.

The Synthesis of (6) (M = Cu, Ni)

A solution of 7-amino-4-methyl-5-aza-hept-3-ene-2-one (1.42 g; 1×10^{-3} mol) and 2-pyrrolecarboxaldehyde (0.95 g; 1×10^{-3} mol) in ethanol (30 cm^3) was heated on a steam bath for 15 min and then cooled. After cooling two equivalents of triethylamine (*ca.* 2.5 cm^3) were added with stirring followed by a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

(2.2 g; 8×10^{-4} mol) dissolved in ethanol (50 cm^3). After heating this mixture for a few minutes an orange precipitate appeared. On cooling this precipitate was isolated and recrystallised from CH_2Cl_2 or toluene.

The copper(B) complex was similarly prepared, but in the absence of triethylamine. Analyses: (6) (M = Ni); $\text{C}_{12}\text{H}_{15}\text{N}_3\text{NiO}$ requires C, 52.2; H, 5.4; N, 15.2% (Found: C, 52.5; H, 5.6; N, 15.3%). (6) (M = Cu); $\text{C}_{12}\text{H}_{15}\text{N}_3\text{CuO}$ requires C, 51.3; H, 5.2; N, 15.0% (Found: C, 51.0; H, 5.2; N, 15.0%).

Crystal Data for (6) (M = Cu)

$\text{C}_{12}\text{H}_{15}\text{CuN}_3\text{O}$, M = 280.81, crystallises from CH_2Cl_2 as violet platy needles; crystal dimensions $0.36 \times 0.18 \times 0.10$ mm. Monoclinic, $a = 7.180(3)$, $b = 11.888(7)$, $c = 14.769(9)$ Å, $\beta = 103.03(4)^\circ$, $U = 1228.1(12)$ Å³, $D_m = 1.53$, $D_c = 1.519$ g cm⁻³, $Z = 4$; space group $P2_1/c$ (C_{2h}^5 , No. 14), Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 17.68$ cm⁻¹, $F(000) = 580$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet/Syntex R3m diffractometer by the ω -scan method. 1239 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and placed in calculated positions (C-H 0.97 Å, C-C-H(methyl) 111°); their contributions were included in structure factor calculations ($B = 8.0$ Å²) but no refinement of positional parameters was permitted. Refinement converged at R 0.0387 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of the metal. Table III lists the atomic positional parameters with estimated standard deviations.

Crystal Data for (6) (M = Ni)

$\text{C}_{12}\text{H}_{15}\text{N}_3\text{NiO}$, M = 275.97, crystallises from CH_2Cl_2 as yellow needles; crystal dimensions $0.424 \times 0.15 \times 0.087$ mm. Monoclinic, $a = 7.184(6)$, $b = 11.510(18)$, $c = 15.223(24)$ Å, $\beta = 106.94(4)^\circ$, $U = 1204(3)$ Å³, $D_m = 1.51$, $D_c = 1.523$ g cm⁻³, $Z = 4$; space group $P2_1/c$ (C_{2h}^5 , No. 14), Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 16.04$ cm⁻¹, $F(000) = 576$.

The data were collected ($6.5 < 2\theta < 50^\circ$ on a Stoe Stadi-2 diffractometer) and processed (145 independent reflections, absorption corrections applied) and the structure solved and refined (R 0.0368) as for the analogous copper complex above. The crystal structures are isomorphous. Table IV lists atomic positional parameters and estimated standard deviations.

TABLE III. Atomic Positional Parameters with e.s.d.s for the Copper Complex.

	x/a	y/b	z/c
Cu(1)	0.25466(10)	0.03348(6)	0.03525(5)
O(1)	0.2098(6)	0.1908(3)	0.0365(3)
N(1)	0.1752(6)	0.0141(4)	-0.0979(3)
N(2)	0.3123(7)	-0.1256(4)	0.0352(4)
N(3)	0.3461(7)	0.0141(4)	0.1700(3)
C(1)	0.1231(12)	0.3720(6)	-0.0211(5)
C(2)	0.1518(9)	0.2489(6)	-0.0377(4)
C(3)	0.1129(9)	0.2096(6)	-0.1276(4)
C(4)	0.1211(8)	0.0972(6)	-0.1571(4)
C(5)	0.0632(10)	0.0745(7)	-0.2592(4)
C(6)	0.1798(10)	-0.1032(6)	-0.1300(5)
C(7)	0.2850(11)	-0.1802(6)	-0.0554(5)
C(8)	0.3730(9)	-0.1699(5)	0.1150(5)
C(9)	0.3956(8)	-0.0964(5)	0.1923(4)
C(10)	0.4646(9)	-0.1066(6)	0.2878(4)
C(11)	0.4538(10)	0.0002(6)	0.3249(4)
C(12)	0.3817(9)	0.0715(5)	0.2507(4)

TABLE IV. Atomic Positional Parameters with e.s.d.s for the Nickel Complex.

	x/a	y/b	z/c
Ni(1)	0.25518(9)	0.02676(5)	0.03436(4)
O(1)	0.2187(5)	0.1848(3)	0.0375(2)
N(1)	0.1921(5)	0.0106(4)	-0.0916(3)
N(2)	0.2946(5)	-0.1319(3)	0.0395(3)
N(3)	0.3313(5)	0.0141(3)	0.1637(3)
C(1)	0.1450(10)	0.3753(5)	-0.0141(4)
C(2)	0.1685(8)	0.2491(5)	-0.0346(4)
C(3)	0.1382(8)	0.2131(5)	-0.1232(4)
C(4)	0.1456(7)	0.0953(5)	-0.1514(3)
C(5)	0.0953(9)	0.0726(6)	-0.2531(4)
C(6)	0.1881(9)	-0.1108(5)	-0.1235(4)
C(7)	0.2770(10)	-0.1907(5)	-0.0473(4)
C(8)	0.3483(7)	-0.1790(5)	0.1196(4)
C(9)	0.3713(7)	-0.0991(4)	0.1938(4)
C(10)	0.4323(8)	-0.1031(5)	0.2893(4)
C(11)	0.4289(8)	0.0117(5)	0.3175(3)
C(12)	0.3653(7)	0.0807(5)	0.2395(3)

Tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters, ob-

served structure amplitudes and calculated structure factors and full details of planar fragments are available from the authors. Scattering factors were taken from reference 15; unit weights were used throughout the refinements; computer programs formed part of the Sheffield X-ray system.

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