Compartmental Ligands. Part 8.[1] Metal Complexes of Ligands derived from 2,3-Dihydro-2-hydroxy-4*H*-1-benzopyran-4-one and α,ω-Diamines: Crystal and Molecular Structures † of Two Mononuclear Nickel(II) and One Mononuclear Copper(II) Complexes

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Compartmental Schiff-base ligands have been prepared from 2,3-dihydro-2-hydroxy-4*H*-1-benzopyran-4-one and alkane-α,ω-diamines. Mononuclear copper(II), nickel(II), cobalt(II), and dioxouranium(VI) complexes have been prepared and the site occupancy established: the nickel(II) and cobalt(II) are N_2O_2, the dioxouranium(VI) is O_2O_2, and positional isomers are available for copper(II). Homobinuclear copper(II), nickel(II), and oxovanadium(IV) complexes were prepared, as were heterobinuclear complexes containing copper(II) and dioxouranium(VI), and nickel(II) and dioxouranium(VI). Three-dimensional *X*-ray crystal structure analyses have been carried out on {3,3′-(ethane-1,2-diyldi-imino)bis[1-(*o*-hydroxyphenyl)-prop-2-enonato]-(*N*,*N*′,*O*¹*O*¹′)}nickel(II), (8a; M = Ni), {3,3′-(propane-1,3-diyldi-imino)bis[1-(*o*-hydroxyphenyl)prop-2-enonato](*N*,*N*′,*O*¹,*O*¹′)}copper(II), (8b; M = Cu), and the related complex {3,3′-(ethane-1,2-diyldi-imino)bis[1-(*o*-hydroxyphenyl)but-2-enonato](*N*,*N*′,*O*¹,*O*¹′)}nickel(II), (10). Two crystallographically independent molecules were found for (10). Complex (8a; M = Ni) has $Z = 8$ in a monoclinic cell with space group $C2/c$ (no. 15, C^6_{2h}), and dimensions $a = 23.373(13)$, $b = 7.800(1)$, $c = 20.819(6)$ Å, $\beta = 110.14(4)°$; $R = 0.1341$ for 603 reflections. Complex (8b; M = Cu) has $Z = 8$ in a monoclinic cell with space group $C2/c$ (no. 15, C^6_{2h}) and dimensions $a = 23.098(18)$, $b = 9.525(5)$, $c = 18.046(8)$ Å, $\beta = 104.15(5)°$; $R = 0.1063$ for 891 reflections. Complex (10) has $Z = 16$ in a monoclinic cell with space group $B2_1/c$ (a non-standard setting of $P2_1/c$, no. 14, C^5_{2h}) and dimensions $a = 26.11(4)$, $b = 7.797(4)$, $c = 38.42(6)$ Å, $\beta = 93.656(8)°$; $R = 0.0376$ for 4 344 reflections.

The Claisen condensation has been extensively used to prepare β-diketones from ketones and carboxylic esters. 2-Hydroxyaryl-β-diketones can cyclise to give chromones, although generally this process requires the presence of acids. The reaction of 2-hydroxyacetophenone with carboxylic esters and sodium has been used to synthesise 2-hydroxyaryl-β-diketones (1a) and (1b).[2,3] When ethyl methanoate was used in this reaction the product recovered was designated as 1-(*o*-hydroxyphenyl)propane-1,3-dione, (2).[4] However, close inspection of the n.m.r. and i.r. spectra showed that it is more correctly assigned as 2,3-dihydro-2-hydroxy-4*H*-1-benzopyran-4-one, (3).[5] Such ring-chain isomeric transformations involving hydroxycarbonyl compounds are well established,[6] and the above example clearly illustrates the possibility of prevalent ring-form stability. This is attributable to an enhancement of the electrophilic properties of the carbonyl group.[7]

The compound (3) readily gives the corresponding chromone, 4*H*-1-benzopyran-4-one, on treatment with acid and water; the chromone may also be isolated from the mother-liquor of the reaction.[4]

The reaction of (3) with 1,2-diaminoethane in ethanol gave the acyclic Schiff base (4), having m.p. 178—179 °C and $M = 352$.[8] If this reaction was carried out in the absence of ethanol a different product having m.p. 196—197 °C and $M = 296$ was obtained. This product has now been identified as (5) which results from a cleavage of the chromone to give first 2-hydroxyacetophenone and then the Schiff base.[9]

In this paper we report the synthesis of compartmental Schiff bases derived from the reaction of (3) with 1,2-diaminoethane and 1,3-diaminopropane [ligands (4) and (6)] and their metal complexation properties. Mono- and bi-nuclear complexes have been prepared for both ligands and the crystal and molecular structures of a nickel(II) complex of (4) and a copper(II) complex of (6) have been determined. The structure of a nickel(II) complex of the related ligand (7) is also reported.

Results and Discussion

The Schiff Bases.—The ligands (4) and (6) were prepared by condensation of (3) with 1,2-diaminoethane and 1,3-diaminopropane respectively in refluxing ethanol. The ^1H n.m.r. spectrum of (4) run in $CDCl_3$ shows signals at 3.45 (m, 4 H, CH_2), 5.75 (d, 2 H, $-CH=$), 6.80 and 7.35 (m, 8 H, aromatic), 7.60 (d, 2 H, $=CH-NH-$), 9.90 (br, 2 H, N-H-O), and 13.80 p.p.m. (s, 2 H, C_6H_4OH). This shows that the compound is present as the enamine tautomer; the signals at 5.75 and 7.60 p.p.m. are assigned according to Nog *et al.*[10] and have $J = 8.8$ Hz. The ^1H n.m.r. spectrum of (6) run in $CDCl_3$ gave signals at 2.15 (m, 2 H, $CH_2-CH_2-CH_2$), 3.41 (m, 4 H, $CH_2-CH_2-CH_2$), 5.75 (d, 2 H, $-CH=$), 6.79, 6.92, and 7.34 (m, 8 H, aromatic), 7.61 (d, 2 H, $=CH-NH-$), 9.95 (d, br, 2 H, NHO), and 13.36 p.p.m. (s, 2 H, C_6H_4OH), again indicating the presence of only the enamine form. If the spectrum is run in $[^2H_6]$acetone then a slow growth of a second set of signals of low intensity occurs, but the enamine form remains predominant. This suggests the presence of a tautomerism and parallels the behaviour of related acyclic compartmental Schiff bases.[11] The mass spectra show parent ion peaks at $m/e = 352$ and 366 respectively.

The Schiff-base ligands have been found to react readily

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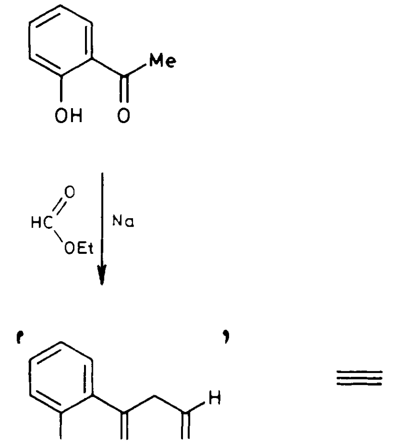
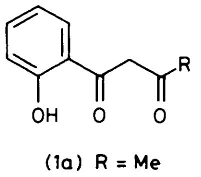
† *Supplementary data available* (No. SUP 23878, 64 pp.): H-atom co-ordinates, thermal parameters, structure factors, full details of planar fragments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

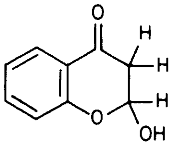
Non-S.I. unit employed: B.M. = 9.274×10^{-24} J T^{-1}.



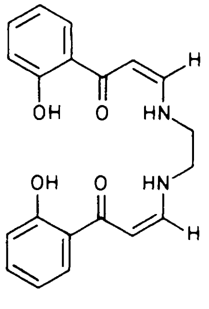
(2)



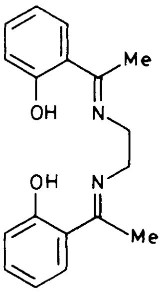
(1a) R = Me
(1b) R = Et



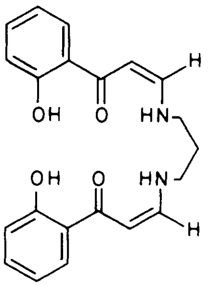
(3)



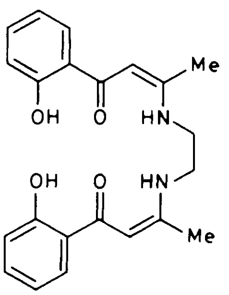
(4)



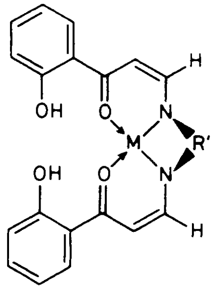
(5)



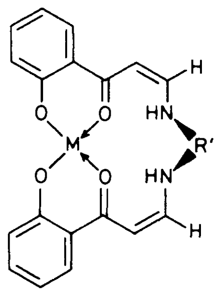
(6)



(7)



(8a) R' = CH_2CH_2
(8b) R' = $CH_2CH_2CH_2$



(9a) R' = CH_2CH_2
(9b) R' = $CH_2CH_2CH_2$

with metal salts to give mono-, homobi-, and heterobi-nuclear complexes.

Mononuclear Metal Complexes.—The mononuclear metal complexes derived from (4) parallel the mononuclear metal complexes of (7) in their selectivity patterns. It appears that modification of the ligand by changing the nature of the alkyl substituent of the Schiff-base compartment has no apparent influence on co-ordination selectivity, as we have further observed similar results in introducing Et and CH_2Ph groups at this position.[12]

The positional isomers (8a; M = Cu) and (9a; M = Cu) have been isolated. Reaction of copper(II) ethanoate with (4) in methanol gave the green O_2O_2 complex, whereas reaction in $CHCl_3$-MeOH gave the brown N_2O_2 complex. The electronic spectrum of the N_2O_2 isomer in $CHCl_3$ shows a peak at 548 nm directly comparable with that found for the analogous copper(II) complex of (7); [13] this suggests a square-planar environment for the metal. The green O_2O_2 isomer is insoluble in $CHCl_3$; the diffuse reflectance spectrum (d.r.s.) shows a peak at 620 nm closely similar to that found for the corresponding complex of (7).[13] The i.r. spectra of the positional isomers are different; (8a; M = Cu) does not show the ν(C=N) present in the O_2O_2 isomer at 1 620 cm^{-1} but gives a band at 1 540 cm^{-1} assigned to a metal-co-ordinated imine.

A single species (8b; M = Cu) was isolated from the reaction of copper(II) ethanoate with (6). The spectral data for the brown complex parallel those for (8a; M = Cu), and the assignment of an N_2O_2 occupancy is confirmed by the *X*-ray crystal structure determination.

For (8a; M = Ni) the spectral and magnetic data suggest a square-planar N_2O_2 occupancy. The complex is diamagnetic and the electronic spectrum in $CHCl_3$ shows a band at 562 nm comparable with that found for the Ni^{II} complex of (7).[13] This assignment is confirmed by the *X*-ray crystal structure.

The dioxouranium(VI) complexes [9a; M = $UO_2(H_2O)$] and (9b; M = UO_2) are proposed as having an O_2O_2 occupancy. The i.r. spectra show bands at *ca.* 3 050 cm^{-1} (phenolic OH) and *ca.* 1 620 cm^{-1} (C=N) and the visible spectrum (d.r.s.) of [9a; M = $UO_2(H_2O)$] gave a band at 374 nm. These values are directly comparable with those for complexes of (7).[13] It is interesting to note that whilst [9a; M = $UO_2(H_2O)$] has present a water of co-ordination, to give a preferred seven-co-ordinated uranium atom, (9b; M = UO_2) has no accompanying solvent. This could arise from the increased flexibility of the ligand caused by the extended bridge giving a better annular co-ordination of the central metal and diminishing the opportunity for solvent approach.

[8a; M = $Co(H_2O)$] was prepared as a bright red powder by the reaction of cobalt(II) ethanoate with the ligand in $CHCl_3$-EtOH under dinitrogen. The i.r. spectrum shows bands at 1 590, 1 520, and 1 500 cm^{-1} which may be assigned to ν(C=O), ν(C=C), and ν(C=N) respectively and a phenolic C–O is detected at 1 280 cm^{-1}. However, a broad peak obscures the position of the possible phenolic –OH, or imine NH bands. The magnetic moment is anomalous, 3.43 B.M. at room temperature, but this behaviour has been detected in related Schiff-base macrocyclic complexes.[14] We have not yet been able to grow crystals of this complex and site assignment is made on chemical grounds. The complex was found to absorb dioxygen when dissolved in Me_2SO; the stoicheiometry of the reaction indicated a product with composition (8a; M = Co) : O_2 of 2 : 1. By analogy with the known behaviour of cobalt(II) complexes with dioxygen [15] this suggests that, unless a site-exchange reaction has occurred on oxygenation, the cobalt(II) is located in the inner Schiff-base-like compartment.

The structures of the three distinct molecules are illustrated in Figures 1—3, in each case with the atom labelling used in the corresponding Tables. Bond lengths and angles (together

Table 1. Microanalytical data

Compound	Found (%)			Required (%)		
	C	H	N	C	H	N
(8a; M = Cu)	57.95	4.15	6.70	57.95	4.35	6.75
[9a; M = Cu(MeOH)]	53.40	4.40	6.35	53.65	4.45	6.25
(8a; M = Ni)	58.40	4.50	6.75	58.65	4.40	6.85
[9a; M = $UO_2(H_2O)$]	36.90	3.15	4.20	36.50	3.10	4.35
[8a; M = $Co(H_2O)$]	56.05	4.40	6.15	56.05	5.10	6.50
(8b; M = Cu)	58.90	4.65	6.55	58.50	4.65	6.60
(9b; M = UO_2)	39.70	3.40	4.10	39.75	3.15	4.40
(11a; M = M′ = Cu)	49.60	3.90	5.45	50.20	4.10	5.80
(11a; M = M′ = Ni)	51.35	3.55	6.85	51.50	3.45	6.00
(11a; M = M′ = VO)	47.35	4.00	5.85	48.00	3.60	5.60
(11a; M = UO_2, M′ = Ni)	35.35	2.90	2.90	35.30	2.95	4.10
[11a; M = UO_2(py), M′ = Ni]	39.35	2.75	5.40	39.70	2.80	5.55
[11a; M = UO_2(py), M′ = Cu]	39.20	2.90	5.50	39.35	3.00	5.50
[11a; M = $Cu(H_2O)$, M′ = Ni]	49.05	3.80	5.75	49.10	3.70	3.75
[11a; M = $Ni(py)_{1.5}$, M′ = Cu]	53.30	4.35	7.60	53.45	3.60	6.80
(11b; M = M′ = Cu)	51.45	3.75	5.70	51.20	3.65	5.70
[11b; M = UO_2(py),M′ = Cu]	39.65	3.10	4.85	40.25	2.95	5.40
[11b; M = $UO_2(py)_{1.5}$, M′ = Ni]	41.95	3.45	5.80	42.25	3.15	5.80

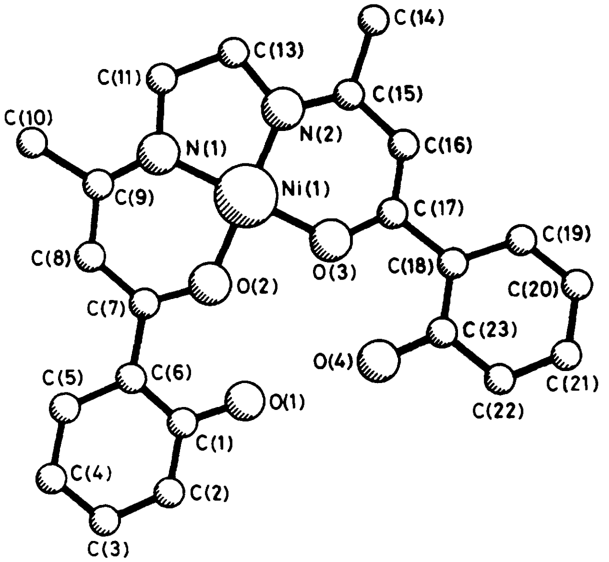


Figure 1. The molecular structure of (10) (molecule 1). Molecule 2 is similarly labelled with each atom carrying a prime superscript

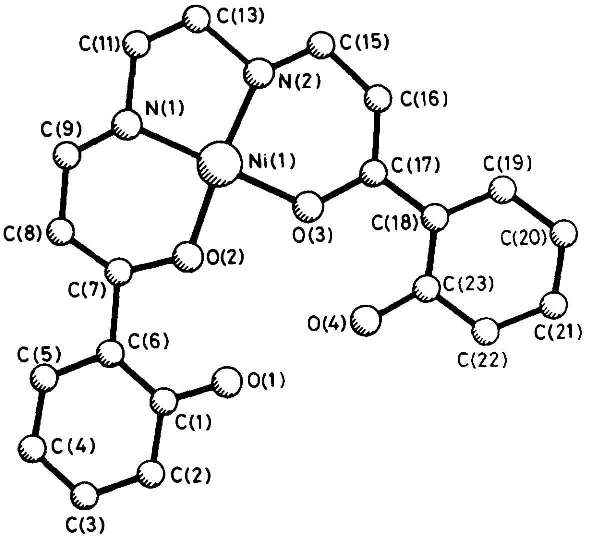
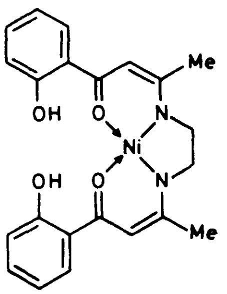


Figure 2. The molecular structure of (8a; M = Ni) with the atom labelling



(10)

with estimated standard deviations) are compared in Table 2 and details of planar fragments are summarised in Table 3.

In all four structures of the three compounds, the metal atom is co-ordinated in the inner (N_2O_2) compartment. In (10), there are two crystallographically independent molecules which differ only in conformation; in both, the co-ordination environment of the metal is essentially square-planar (particularly planar for molecule 1). The apparently lesser planarity in (8a; M = Ni) only reflects the much greater estimated standard deviations: however, in (8b; M = Cu), there is a substantial twist between the two *cis*-CuON planes, leading to a significant distortion in the direction of a tetrahedral geometry. It is tempting to ascribe this distortion to the presence of a 1,3-di-iminopropane bridge rather than a 1,2-di-iminoethane bridge. However, the absence of any such effect in a related vanadyl (O_2O_2) complex,[16] in which the perfectly coplanar heteroatoms define an inner compartment (N_2O_2) which is empty but in which the conformation of the skeleton indicates directed valence bonds on the imino-nitrogen atoms would be out-of-plane, suggests an alternative explanation. Since an undistorted square-planar geometry is impossible, it seems that the copper atom has a preference for

Table 2. Bond lengths (Å) and bond angles (°) with estimated standard deviations for the four molecules *

	(10)			
	Molecule 1	Molecule 2	(8a; M = Ni)	(8b; M = Cu)
M(1)–O(2)	1.860(3)	1.850(3)	1.86(4)	1.934(18)
M(1)–O(3)	1.859(3)	1.849(3)	1.87(4)	1.946(18)
M(1)–N(1)	1.862(4)	1.854(4)	1.88(4)	1.989(24)
M(1)–N(2)	1.846(4)	1.851(4)	1.89(4)	1.899(27)
O(1)–C(1)	1.353(6)	1.355(6)	1.32(6)	1.37(4)
C(1)–C(2)	1.389(6)	1.404(7)	1.40	1.44(5)
C(2)–C(3)	1.370(7)	1.363(8)	1.40	1.34(5)
C(3)–C(4)	1.393(8)	1.380(8)	1.40	1.32(5)
C(4)–C(5)	1.379(8)	1.385(8)	1.40	1.34(5)
C(5)–C(6)	1.394(7)	1.387(7)	1.40	1.45(5)
C(6)–C(1)	1.397(6)	1.404(7)	1.40	1.35(4)
C(6)–C(7)	1.489(6)	1.485(6)	1.58(5)	1.47(4)
O(2)–C(7)	1.310(5)	1.302(5)	1.32(5)	1.29(3)
C(7)–C(8)	1.369(6)	1.369(7)	1.34(7)	1.36(4)
C(8)–C(9)	1.420(7)	1.424(7)	1.47(8)	1.35(4)
C(9)–C(10)	1.519(7)	1.517(8)		
N(1)–C(9)	1.297(6)	1.296(6)	1.27(7)	1.32(4)
N(1)–C(11)	1.475(7)	1.468(7)	1.55(8)	1.53(4)
O(2)–M(1)–O(3)	83.89(13)	83.56(13)	83.2(16)	82.1(7)
O(2)–M(1)–N(1)	94.32(15)	94.49(14)	94.2(17)	92.3(9)
O(2)–M(1)–N(2)	178.18(15)	176.73(15)	172.8(17)	165.9(10)
O(3)–M(1)–N(1)	178.20(15)	177.81(15)	176.8(17)	165.6(9)
O(3)–M(1)–N(2)	94.31(15)	94.53(15)	91.5(17)	90.4(10)
N(1)–M(1)–N(2)	87.48(16)	87.38(16)	91.1(18)	97.6(11)
O(1)–C(1)–C(2)	116.2(4)	117.3(4)	116(3)	113(3)
O(1)–C(1)–C(6)	122.4(4)	122.6(4)	124(3)	123(3)
C(6)–C(1)–C(2)	121.4(4)	120.0(4)	120	123(3)
C(1)–C(2)–C(3)	119.9(4)	119.9(5)	120	117(3)
C(2)–C(3)–C(4)	120.2(5)	121.0(5)	120	122(4)
C(3)–C(4)–C(5)	119.4(5)	119.4(5)	120	121(3)
C(4)–C(5)–C(6)	122.0(5)	121.5(5)	120	122(3)
C(5)–C(6)–C(1)	117.1(4)	118.1(4)	120	114(3)
C(5)–C(6)–C(7)	121.5(4)	121.0(4)	117(3)	126(3)
C(1)–C(6)–C(7)	121.4(4)	120.9(4)	122(3)	120(3)
O(2)–C(7)–C(6)	115.2(4)	115.0(4)	109(3)	119(2)
O(2)–C(7)–C(8)	123.3(4)	123.9(4)	132(4)	119(3)
C(6)–C(7)–C(8)	121.4(4)	121.2(4)	118(4)	122(3)
M(1)–O(2)–C(7)	127.4(3)	126.6(3)	122(3)	131.6(17)
C(7)–C(8)–C(9)	124.7(4)	124.3(4)	119(5)	128(3)
N(1)–C(9)–C(8)	123.4(4)	122.8(4)	121(5)	130(3)
N(1)–C(9)–C(10)	120.7(4)	120.8(4)		
C(8)–C(9)–C(10)	115.9(4)	116.4(4)		
M(1)–N(1)–C(9)	126.8(3)	126.8(3)	130(4)	118.8(20)
M(1)–N(1)–C(11)	113.5(3)	112.3(3)	107(3)	121.2(18)
C(9)–N(1)–C(11)	119.6(4)	120.8(4)	123(4)	120(2)
N(1)–C(11)–C(13)	111.8(4)	112.9(5)	113(5)	
C(11)–C(13)	1.478(8)	1.424(9)	1.36(8)	
C(11)–C(12)				1.38(5)
C(12)–C(13)				1.38(5)
N(2)–C(13)	1.457(7)	1.460(8)	1.54(6)	1.49(5)
N(2)–C(15)	1.305(6)	1.301(6)	1.28(8)	1.31(5)
C(14)–C(15)	1.520(8)	1.507(7)		
C(15)–C(16)	1.422(7)	1.416(7)	1.46(8)	1.36(6)
C(16)–C(17)	1.346(7)	1.364(7)	1.41(7)	1.43(5)
O(3)–C(17)	1.317(5)	1.303(5)	1.40(6)	1.23(3)
C(17)–C(18)	1.488(6)	1.485(6)	1.44(6)	1.50(4)
C(23)–C(18)	1.384(7)	1.391(6)	1.40	1.37(4)
C(18)–C(19)	1.412(7)	1.408(7)	1.40	1.40(4)
C(19)–C(20)	1.381(8)	1.372(8)	1.40	1.36(5)
C(20)–C(21)	1.381(8)	1.384(8)	1.40	1.39(4)
C(21)–C(22)	1.366(8)	1.382(8)	1.40	1.37(4)
C(22)–C(23)	1.402(8)	1.393(7)	1.40	1.40(4)
O(4)–C(23)	1.351(6)	1.357(6)	1.32(5)	1.34(3)
N(1)–C(11)–C(12)				113(3)
C(11)–C(12)–C(13)				129(3)
N(2)–C(13)–C(12)				109(3)
N(2)–C(13)–C(11)	111.1(5)	112.5(5)	112(4)	
C(13)–N(2)–C(15)	118.5(4)	119.4(4)	116(4)	113(3)
M(1)–N(2)–C(13)	115.1(3)	113.5(3)	107(3)	123.8(22)
M(1)–N(2)–C(15)	126.3(3)	126.9(3)	137(4)	123.2(25)
C(14)–C(15)–C(16)	115.7(4)	116.7(4)		
N(2)–C(15)–C(14)	120.3(4)	121.1(4)		
N(2)–C(15)–C(16)	124.0(4)	122.2(4)	114(5)	130(4)
C(15)–C(16)–C(17)	124.6(5)	124.7(5)	130(5)	122(3)
M(1)–O(3)–C(17)	127.8(3)	126.3(3)	128(3)	131.9(17)
C(16)–C(17)–C(18)	121.8(4)	121.3(4)	123(4)	117(3)
O(3)–C(17)–C(16)	123.0(4)	124.2(4)	120(4)	121(3)
O(3)–C(17)–C(18)	115.1(4)	114.5(4)	117(4)	122(2)
C(17)–C(18)–C(23)	122.1(4)	120.9(4)	121(3)	118(2)
C(17)–C(18)–C(19)	121.1(4)	121.0(4)	119(3)	123(2)
C(23)–C(18)–C(19)	116.8(4)	118.1(4)	120	118(2)
C(18)–C(19)–C(20)	121.9(5)	121.2(5)	120	122(3)
C(19)–C(20)–C(21)	119.5(5)	119.5(6)	120	119(3)
C(20)–C(21)–C(22)	120.4(5)	120.9(5)	120	121(3)
C(21)–C(22)–C(23)	120.0(5)	119.4(5)	120	119(3)
C(22)–C(23)–C(18)	121.5(5)	120.7(4)	120	121(3)
O(4)–C(23)–C(18)	122.5(5)	122.4(4)	125(3)	124(2)
O(4)–C(23)–C(22)	116.0(5)	116.9(4)	115(3)	116(2)

* Values quoted without estimated standard deviations were constrained during refinement.

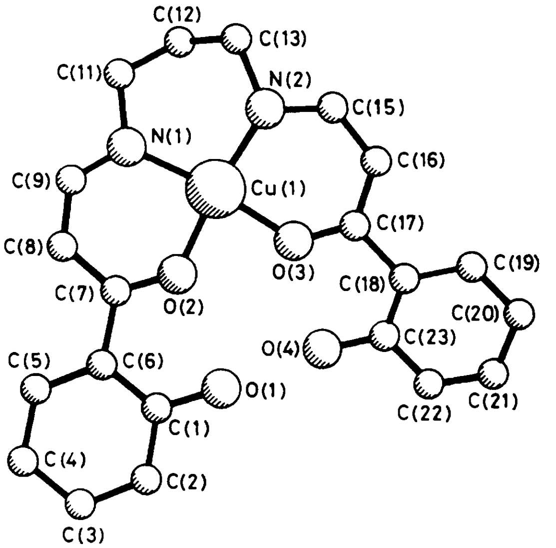


Figure 3. The molecular structure of (8b; M = Cu) with the atom labelling

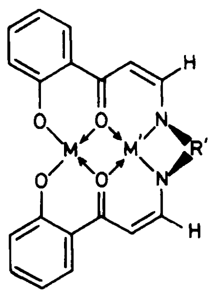
a tetrahedral distortion rather than a substantial out-of-plane displacement.

The two independent molecules of (10) exhibit small but distinct conformational differences; molecule 1 has a slightly ' stepped ' arrangement of the two iminoketone chelates about the nickel and the whole molecule, with the exception of the phenyl groups, is quite closely planar. Molecule 2 has a ' butterfly ' arrangement of the two chelate planes, with the nickel atom displaced in the same direction from each of the two planes. In (8a; M = Ni) one iminoketone chelate fragment appears to be buckled but the conformation is again stepped. Only in molecule 1 of (10) does the metal lie close to the plane of an iminoketone fragment; in all four molecules, the carbon–carbon bonds within the iminoketone fragments are unequal in length.

In (10) the carbon–carbon torsion angles in the 1,2-di-iminoethane fragments are much smaller than would be expected in the free diamine, reflecting the steric constraints consequent on the co-ordination of a metal atom in the inner site. The larger value found in (8a; M = Ni) and the short carbon–carbon bond length is probably a reflection of the high estimated standard deviations and may also indicate some disorder of the two carbon atoms. There is similar evidence of disorder of the carbon atoms in the 1,3-di-iminopropane fragment of (8b; M = Cu) but, in both cases, the quality of the data precluded the possibility of determining minor disorder components.

In all four molecules, the length of the carbon–carbon bond to the phenyl ring suggests little π-bond order and the phenyls are twisted in mutually opposite directions out of the mean molecular plane. The phenyl rings are each planar [constrained so in (8a; M = Ni)] and their substituents are approximately coplanar with them.

Both nickel complexes exhibit short intermolecular contacts to centrosymmetrically related molecules. In (10), the contacts occur on only one side of the molecular plane: $\mathrm{Ni(1)} \cdots \mathrm{Ni(1)}[-x,-y,-z]$ 3.72; $\mathrm{Ni(1)} \cdots \mathrm{N(2)}[-x,-y,-z]$ 3.56; $\mathrm{Ni(1')} \cdots \mathrm{O(3')}[-\frac{1}{2}-x,-1-y,\frac{1}{2}-z]$ 3.61 Å. In (8a; M = Ni), there are two unequal contacts, one on either side of the molecule: $\mathrm{Ni(1)} \cdots \mathrm{Ni(1)}[-x,-y,-z]$ 3.73; $\mathrm{Ni(1)} \cdots \mathrm{O(2)}[-x,-y,-z]$ 3.40; $\mathrm{Ni(1)} \cdots \mathrm{O(3)}[-x,1-y,-z]$ 3.69 Å. There are no such contacts in the crystal structure of (8b; M = Cu). All four independent molecules exhibit intramolecular hydrogen bonding between the phenolic hydroxyl groups and the co-ordinating oxygen atom on the same side of the outer compartment. Oxygen–oxygen distances are: 2.57, 2.51 Å for (10), molecule 1; 2.57, 2.57 Å for (10), molecule 2; 2.57, 2.54 Å for (8a; M = Ni); 2.53, 2.57 Å for (8b; M = Cu).



(11a) R′ = CH_2CH_2
(11b) R′ = $CH_2CH_2CH_2$

There has been some interest in defining the geometry of the nickel(II) site in (10) and related species as in the heterobinuclear complex [{$UO_2(Me_2SO)$}NiL][L = tetra-anion of (7)] where the nickel is in a highly distorted N_2O_2 environment and $UO_2(Me_2SO)$ is O_2O_2.[17] The origin of this distorted geometry was uncertain and it was suggested that the ligand distorts to accommodate the dioxouranium(VI) group and therefore the nickel atom cannot maintain a planar co-ordination geometry. The observation that in related mononuclear copper(II) complexes a marked tetrahedral distortion occurred [1] suggested that there might be an inherent twist in the ligand predisposing it towards a distorted geometry at the metal site. The structure of (11) shows a square-planar environment for the nickel(II) thus lending some support to the first proposition.

Homobinuclear Complexes.—The homobinuclear complexes (11a; M = M′ = Cu), (11a; M = M′ = Ni), (11a; M = M′ = VO), and (11b; M = M′ = Cu) were prepared.

The dicopper(II) complexes showed broad d.r.s. spectra with peaks based on 625 nm (11a; M = M′ = Cu) and 604 nm (11b, M = M′ = Cu); both complexes gave reduced magnetic moments at ambient temperature, 1.30 and 1.13 B.M. per Cu atom respectively. The i.r. spectra showed broad bands at *ca.* 1 600 cm^{-1} [ν(C=O) + ν(C=C)] and further prominent bands at 1 510 [ν(C=N)] and 1 300 cm^{-1} [$\nu(\mathrm{C{-}O})_{\mathrm{phenolic}}$]. The dinickel(II) complex (11a; M = M′ = Ni) interestingly had no molecules of solvation for the nickel(II) in the O_2O_2 compartment. This contrasts with several related nickel(II) complexes of Schiff bases derived from triketones,[11,18] but corresponds with the dinickel(II) complex derived from (7).[13] The d.r.s. is similar to that of the mononuclear species (573, 467 nm) and the magnetic moment (μ = 3.15 B.M.) per Ni is lower than that expected for a spin-only value. It is probable that the complex oligomerises in the solid state. Such behaviour has been observed in β-diketonates of nickel(II).[19]

The reaction of oxovanadium(IV) ethanoate with (4) did not yield an isolable mononuclear species but gave a complex analysing as (11a; M = M′ = VO). This contrasts with the reaction of oxovanadium(IV) ethanoate with (7) in which a mononuclear species predominates, and the dinuclear complex was detected *via* the presence of a peak at the correct number in the mass spectrum.[20] A similar result was obtained from the corresponding Schiff base derived from heptane-2,4,6-trione and 1,2-diaminoethane.[16]

Table 3. Summary of planar fragments of the four molecules (M = Ni or Cu; all deviations in Å)

		(10)			
		Molecule 1	Molecule 2	(8a; M = Ni)	(8b; M = Cu)
Plane A [O(2), O(3), N(1), N(2)]					
R.m.s. deviations		0.004	0.013	0.025	0.199
Out-of-plane displacements	M(1)	0.001	−0.030	0.056	0.017
	O(1)	−0.883	−0.814	−0.748	0.665
	O(4)	0.328	0.987	0.569	−1.210
Plane B [M(1), O(2), N(1)]					
Out-of-plane displacements	C(7)	0.050	0.214	−0.046	0.090
	C(8)	0.045	0.296	−0.206	0.130
	C(9)	−0.003	0.158	−0.015	0.076
Plane C [M(1), O(3), N(2)]					
Out-of-plane displacements	C(15)	−0.022	0.214	0.115	0.187
	C(16)	−0.049	0.304	0.158	0.312
	C(17)	−0.022	0.158	0.080	0.226
Plane D [O(2), N(1), C(7)—C(9)]					
R.m.s. deviations		0.013	0.014	0.047	0.004
Out-of-plane displacements	M(1)	0.028	0.190	−0.120	0.092
Plane E [O(3), N(2), C(15—C(17)]					
R.m.s. deviations		0.005	0.015	0.011	0.011
Out-of-plane displacements	M(1)	−0.030	0.194	0.103	0.219
Plane F [C(1)—C(6)]					
R.m.s. deviations		0.007	0.013	0	0.011
Plane G [C(18)—C(23)]					
R.m.s. deviations		0.005	0.017	0	0.028
Selected angles (°) between planes					
	B–C	0.4	3.0	5.4	16.5
	B–D	1.4	8.6	4.6	3.9
	C–E	1.3	8.8	4.5	9.3
	D–F	22.8	25.6	18.4	3.3
	E–G	7.7	29.8	14.0	17.0
	D–E	0.3	20.2	5.5	19.8
	F–G	25.7	32.2	16.0	39.6
Torsion angles (°)					
	N(1)–C(11)–C(13)–N(2)	+10.9	−6.8	+36.7	
	N(1)–C(11)–C(12)–C(13)				−54.7
	C(11)–C(12)–C(13)–N(2)				+68.9

Heterobinuclear Complexes.—Heterobinuclear complexes containing copper(II) and nickel(II) were prepared by reaction of (8a; M = Cu) and nickel(II) ethanoate, and from (8a; M = Ni) and copper(II) ethanoate. The two routes gave different products which are assigned as the positional isomers (11a; M = Ni, M′ = Cu) and (11a; M = Cu, M′ = Ni). The d.r.s. vary only slightly, the former having bands at 605 and 455 nm and the latter having bands at 617 and 482 nm. The i.r. spectra are, however, very different and show prominent peaks at 1 608, 1 598, 1 500, 1 463, 1 448, 1 330, and 1 248 cm^{-1}, and 3 400, 1 598, 1 515, 1 445, and 1 300 cm^{-1} respectively. The magnetic moments are also very different: [11a; M = Ni(py)$_{1.5}$, M′ = Cu] (py = pyridine) has μ = 3.04 B.M., whereas that for [11a; M = Cu(H_2O), M′ = Ni] is 1.96 B.M. The latter is compatible with an inner, N_2O_2 compartmental occupancy by nickel(II), giving a square-planar and therefore diamagnetic metal atom. Such an environment has previously been found for the corresponding copper–nickel complex of (7).[21] The former suggests a contribution from the nickel(II) which is in the outer O_2O_2 compartment and not square planar (there are 1.5 moles of pyridine present in the molecule).

Complexes of (4) containing dioxouranium(VI), and copper(II) or nickel(II), were also prepared. Two routes were used: (9a; M = UO_2) was reacted with the corresponding metal ethanoate, or (8a; M = Ni or Cu) was reacted with dioxouranium(VI) ethanoate to yield (11a; M = UO_2, M′ = Ni or Cu). Both routes gave the same product in each case and so the added metal goes to the vacant site. The properties of these species are directly comparable to those of the corresponding complexes of (7),[13] and in each a molecule of pyridine is present, probably co-ordinated to the dioxouranium(VI) to give the uranium a preferred seven-co-ordinated environment. Similar heterobinuclear complexes were prepared using ligand (6).

Experimental

Details of physical measurements have been previously given.[1] 2,3-Dihydro-2-hydroxy-4*H*-1-benzopyran-4-one, (3), was synthesised according to the method of Kostka.[4] {3,3′-(Ethane-1,2-diyldi-imino)bis[1-(*o*-hydroxyphenyl)but-2-enonato]-*N*,*N*′,*O*^{1},*O*$^{1'}$} nickel(II) was prepared by the literature method.[13]

The Schiff Bases.—The reaction of (3) with alkane-α,ω-diamines was carried out according to literature procedures,[8] to give the ligands (4) and (6) [Found for (4): C, 68.25; H, 5.70; N, 7.80%; P^+ at *m/e* = 352. $C_{20}H_{20}N_2O_4$ requires C, 68.20; H, 5.70; N, 7.95%; M = 352], yield = 72% [Found for (6): C, 68.70; H, 5.80; N, 7.35%; P^+ at *m/e* = 366. $C_{21}H_{22}N_2O_4$ requires C, 68.85; H, 6.00; N, 7.65%; M = 366], yield = 70%.

Table 4. Atomic positional parameters with estimated standard deviations for (10) (atoms carrying a prime superscript refer to molecule 2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni(1)	−0.041 66(2)	−0.185 71(8)	−0.012 99(1)
Ni(1′)	−0.215 10(2)	−0.265 90(8)	0.234 87(1)
O(1)	−0.154 54(12)	−0.326 8(5)	0.052 83(9)
O(2)	−0.103 89(11)	−0.166 2(4)	0.007 70(7)
O(3)	−0.019 29(11)	−0.284 0(4)	0.029 37(7)
O(4)	−0.050 24(13)	−0.319 6(6)	0.089 56(9)
O(1′)	−0.104 74(13)	−0.488 0(5)	0.304 17(9)
O(2′)	−0.150 32(10)	−0.307 2(4)	0.255 50(7)
O(3′)	−0.235 75(10)	−0.305 5(4)	0.279 28(7)
O(4′)	−0.195 21(11)	−0.256 9(5)	0.341 14(8)
N(1)	−0.066 01(15)	−0.085 5(5)	−0.054 82(9)
N(2)	0.020 88(14)	−0.209 3(5)	−0.032 35(9)
N(1′)	−0.191 96(14)	−0.223 4(5)	0.191 05(8)
N(2′)	−0.280 42(14)	−0.215 1(5)	0.216 14(9)
C(1)	−0.191 80(16)	−0.209 4(6)	0.045 38(11)
C(2)	−0.233 32(17)	−0.213 0(7)	0.066 24(11)
C(3)	−0.272 84(18)	−0.099 0(7)	0.060 31(13)
C(4)	−0.271 50(20)	0.020 5(8)	0.033 43(15)
C(5)	−0.230 41(19)	0.021 2(7)	0.012 58(13)
C(6)	−0.189 74(16)	−0.093 9(6)	0.017 70(11)
C(7)	−0.146 24(17)	−0.095 2(6)	−0.005 55(11)
C(8)	−0.151 42(18)	−0.029 8(6)	−0.038 64(11)
C(9)	−0.112 05(19)	−0.029 0(6)	−0.062 49(11)
C(10)	−0.126 61(23)	0.045 4(8)	−0.098 31(13)
C(11)	−0.027 73(21)	−0.081 2(7)	−0.081 42(12)
C(13)	0.023 57(23)	−0.135 1(8)	−0.067 00(14)
C(14)	0.111 14(21)	−0.288 6(8)	−0.036 78(15)
C(15)	0.062 19(17)	−0.278 4(7)	−0.017 47(13)
C(16)	0.065 20(18)	−0.347 7(7)	0.016 84(13)
C(17)	0.026 50(16)	−0.346 7(6)	0.038 38(12)
C(18)	0.033 23(17)	−0.412 0(6)	0.074 77(12)
C(19)	0.079 41(19)	−0.491 4(7)	0.087 25(15)
C(20)	0.087 25(21)	−0.545 2(8)	0.121 41(16)
C(21)	0.049 01(22)	−0.521 8(7)	0.144 20(14)
C(22)	0.003 45(21)	−0.447 9(8)	0.132 97(14)
C(23)	−0.004 27(18)	−0.392 3(7)	0.098 34(13)
C(1′)	−0.061 97(17)	−0.402 4(7)	0.295 97(12)
C(2′)	−0.017 55(19)	−0.424 8(7)	0.318 10(13)
C(3′)	0.026 06(19)	−0.337 0(8)	0.311 86(14)
C(4′)	0.027 56(19)	−0.227 1(9)	0.283 81(15)
C(5′)	−0.015 60(18)	−0.209 1(8)	0.261 21(13)
C(6′)	−0.060 70(16)	−0.296 6(6)	0.266 47(11)
C(7′)	−0.106 74(16)	−0.276 1(6)	0.242 07(11)
C(8′)	−0.102 32(18)	−0.228 5(7)	0.208 09(11)
C(9′)	−0.144 65(19)	−0.207 0(7)	0.183 20(11)
C(10′)	−0.131 74(23)	−0.161 8(9)	0.146 37(13)
C(11′)	−0.234 25(21)	−0.207 1(9)	0.164 19(12)
C(13′)	−0.283 09(23)	−0.191 1(11)	0.178 39(13)
C(14′)	−0.369 58(19)	−0.117 0(8)	0.215 16(14)
C(15′)	−0.321 04(17)	−0.186 8(6)	0.233 23(12)
C(16′)	−0.321 64(17)	−0.214 8(7)	0.269 61(12)
C(17′)	−0.281 16(16)	−0.275 7(6)	0.290 20(11)
C(18′)	−0.285 47(16)	−0.305 8(6)	0.328 06(11)
C(19′)	−0.332 78(19)	−0.350 2(8)	0.341 26(14)
C(20′)	−0.337 71(21)	−0.367 6(9)	0.376 41(15)
C(21′)	−0.295 52(21)	−0.339 7(8)	0.399 39(13)
C(22′)	−0.248 26(18)	−0.299 2(7)	0.387 35(12)
C(23′)	−0.243 04(16)	−0.287 9(6)	0.351 56(11)

Preparation of Mononuclear Complexes.—The following complexes were prepared according to procedure A for mononuclear complexes given in ref. 13; (8a; M = Cu), (8a; M = Ni), (8b; M = Cu), [9a; M = $UO_2(H_2O)$], and (9b; M = UO_2). [8a; M = $Co(H_2O)$] was prepared using this method but under a dinitrogen atmosphere. [9a; M = Cu(MeOH)] was prepared according to procedure B for mononuclear complexes given in ref. 13. Microanalyses are given in Table 1 and spectroscopic data in the text where relevant.

Preparation of Binuclear Complexes.—The following complexes were prepared according to procedure B for binuclear complexes given in ref. 13; (11a; M = M′ = Ni), (11a; M = M′ = VO), (11b; M = M′ = Cu), (11a; M = UO_2, M′ = Ni), [11a; M = UO_2(py), M′ = Ni], [11a; M = UO_2(py), M′ = Cu], [11a; M = $Cu(H_2O)$, M′ = Ni], [11b; M = UO_2(py), M′ = Cu], [11b; M = $UO_2(py)_{1.5}$, M′ = Ni]. The compound (11a; M = M′ = Cu) was prepared using procedure B for binuclear complexes from ref. 13. Microanalyses are given in Table 1 and spectroscopic data are given in the text where appropriate.

The dioxygen uptake experiments were carried out using a modification of the procedure of Appleton.[22]

Crystal Data for (10).—Complex (10) crystallises from chloroform as brown needles; crystal dimensions 0.27 × 0.55 × 0.26 mm. $C_{22}H_{22}N_2NiO_4$, $M = 437.13$, monoclinic, $a = 26.11(4)$, $b = 7.797(4)$, $c = 38.42(6)$ Å, $\beta = 93.656(8)°$, $U = 7\,805(18)$ Å^3, $D_m = 1.48$, $Z = 16$, $D_c = 1.488$ g cm^{-3}, $F(000) = 3\,648$, space group $B2_1/c$ (a non-standard setting of $P2_1/c$, no. 14, C^5_{2h}), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 10.27 cm^{-1}.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. 4 344 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions [C–H 0.97, O–H 0.92 Å; C–C–H(methyl) 111°]; their contributions were included in structure factor calculations ($B = 8.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at $R = 0.0376$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of the metal. Table 4 lists the atomic positional parameters with estimated standard deviations.

Crystal Data for (8a; M = Ni).—The complex crystallises from ethanol–chloroform as red-brown needles; crystal dimensions 0.08 × 0.25 × 0.06 mm. $C_{20}H_{18}N_2NiO_4$, $M = 409.07$, monoclinic, $a = 23.373(13)$, $b = 7.800(1)$, $c = 20.819(6)$ Å, $\beta = 110.14(4)°$, $U = 3\,563(2)$ Å^3, $D_m = 1.55$, $Z = 8$, $D_c = 1.525$ g cm^{-3}, $F(000) = 1\,696$, space group $C2/c$ (no. 15, C^6_{2h}), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 11.20 cm^{-1}.

The data were collected ($3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer) and processed [603 independent reflections with $I/\sigma(I) > 2.0$, absorption corrections not applied] and the structure solved and refined ($R = 0.1341$) as for (10) above, with the exceptions that the geometries of the phenyl rings were constrained during refinement (D_{6h} symmetry, C–C 1.40 Å) and hydrogen atoms were not positioned; anisotropic thermal motion was allowed for the nickel atom only. Table 5 lists atomic positions and estimated standard deviations.

Table 5. Atomic positional parameters with estimated standard deviations for (8a; M = Ni) *

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni(1)	0.019 28(27)	0.232 5(12)	0.004 22(31)	C(8)	0.014 2(25)	0.070(8)	−0.141 5(27)
O(1)	−0.157 6(14)	0.242(8)	−0.137 9(15)	C(9)	0.073 8(22)	0.081(7)	−0.086 4(24)
O(2)	−0.045 4(15)	0.167(5)	−0.073 1(17)	C(11)	0.141 8(28)	0.181(8)	0.027 7(31)
O(3)	−0.043 1(16)	0.316(5)	0.032 9(18)	C(13)	0.140 6(20)	0.314(6)	0.069 5(22)
O(4)	−0.155 7(14)	0.271(6)	0.012 3(15)	C(15)	0.081 5(27)	0.398(9)	0.138 0(30)
N(1)	0.079 3(17)	0.152(5)	−0.029 8(19)	C(16)	0.021 7(21)	0.433(7)	0.142 1(23)
N(2)	0.079 5(17)	0.325(5)	0.082 1(19)	C(17)	−0.037 0(20)	0.401(7)	0.094 3(22)
C(1)	−0.154 4(16)	0.130(4)	−0.183 6(15)	C(18)	−0.091 9(12)	0.434(5)	0.108 8(19)
C(2)	−0.208 8(12)	0.095(4)	−0.237 3(18)	C(19)	−0.089 6(12)	0.550(5)	0.161 0(17)
C(3)	−0.208 8(12)	−0.017(5)	−0.289 8(14)	C(20)	−0.143 4(17)	0.599(4)	0.171 3(15)
C(4)	−0.154 5(16)	−0.094(4)	−0.288 7(15)	C(21)	−0.199 4(12)	0.533(5)	0.129 4(19)
C(5)	−0.100 0(12)	−0.060(4)	−0.235 1(18)	C(22)	−0.201 8(12)	0.417(5)	0.077 3(17)
C(6)	−0.100 0(12)	0.052(5)	−0.182 5(14)	C(23)	−0.148 0(17)	0.367(4)	0.066 9(15)
C(7)	−0.036 5(18)	0.097(6)	−0.126 6(19)				

* The estimated standard deviations for atoms C(1)—C(6) and C(18)—C(23), which comprise the phenyl rings (the geometries of which were constrained during refinement), were derived from the estimated standard deviations of the group parameters which were used to refine them.

Table 6. Atomic positional parameters with estimated standard deviations for (8b; M = Cu)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	−0.025 20(14)	0.228 8(4)	0.008 67(20)	C(8)	−0.010 3(14)	0.449(3)	−0.121 4(18)
O(1)	0.152 8(8)	0.283 8(27)	0.005 7(13)	C(9)	−0.066 3(13)	0.423(3)	−0.114 0(17)
O(2)	0.040 8(7)	0.312 0(20)	−0.024 1(10)	C(11)	−0.151 9(13)	0.321(3)	−0.074 4(17)
O(3)	0.038 9(7)	0.164 6(19)	0.093 2(10)	C(12)	−0.164 3(15)	0.236(4)	−0.018 2(19)
O(4)	0.140 7(8)	0.250 3(20)	0.172 0(11)	C(13)	−0.144 7(17)	0.101(4)	0.003 0(22)
N(1)	−0.084 9(10)	0.341(3)	−0.066 0(13)	C(15)	−0.062 8(18)	0.009(4)	0.092 2(22)
N(2)	−0.079 6(9)	0.106(3)	0.039 6(14)	C(16)	−0.008 2(17)	−0.019(4)	0.138 2(21)
C(1)	0.150 7(13)	0.370(3)	−0.055 3(17)	C(17)	0.043 1(11)	0.063(3)	0.136 1(15)
C(2)	0.208 6(14)	0.400(4)	−0.067 9(19)	C(18)	0.100 4(10)	0.027(3)	0.193 1(14)
C(3)	0.210 6(17)	0.484(4)	−0.126 8(21)	C(19)	0.111 5(14)	−0.103(3)	0.229 2(18)
C(4)	0.162 2(15)	0.544(4)	−0.170 1(19)	C(20)	0.164 3(14)	−0.132(4)	0.280 2(18)
C(5)	0.108 0(15)	0.520(4)	−0.157 8(19)	C(21)	0.207 4(13)	−0.028(3)	0.296 8(17)
C(6)	0.099 8(13)	0.429(3)	−0.096 7(16)	C(22)	0.200 5(12)	0.096(3)	0.257 4(17)
C(7)	0.042 2(12)	0.398(3)	−0.078 8(15)	C(23)	0.145 3(11)	0.125(3)	0.206 5(15)

Crystal Data for (8b; M = Cu).—The complex crystallises from ethanol–chloroform as thin, red-brown needles; crystal dimensions 0.105 × 0.41 × 0.045 mm. $C_{21}H_{20}CuN_2O_4$, M = 427.94, monoclinic, a = 23.098(18), b = 9.525(5), c = 18.046(8) Å, β = 104.15(5)°, U = 3 850(4) $Å^3$, D_m = 1.52, Z = 8, D_c = 1.477 g cm^{-3}, $F(000)$ = 1 768, space group $C2/c$ (no. 15, C^6_{2h}), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 11.64 cm^{-1}.

The data were collected ($3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer) and processed [891 independent reflections with $I/\sigma(I) > 2.0$] and the structure solved and refined (R = 0.1063) as for (10) above. Anisotropic thermal motion was allowed for nickel, oxygen, and nitrogen atoms only. The contributions of hydrogen atoms (C–H 0.94, O–H 0.93 Å, B = 10.0 $Å^2$) were included in structure factor calculations. Table 6 lists atomic positions and estimated standard deviations.

Scattering factors were taken from ref. 23; unit weights were used throughout the refinements. Computer programs formed part of the Sheffield *X*-ray system.

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