Compartmental Ligands. Part 6.[1] Transition-metal Complexes of a Non-symmetric, Acyclic, Schiff Base derived from Heptane-2,4,6-trione, 1-(*o*-Hydroxyphenyl)butane-1,3-dione, and 1,2-Diaminoethane

Jean-Pierre Costes and David E. Fenton *
Department of Chemistry, The University, Sheffield S3 7HF

The preparation and metal complexing properties of a non-symmetric, acyclic, Schiff base derived from heptane-2,4,6-trione, 1-(*o*-hydroxyphenyl)butane-1,3-dione, and 1,2-diaminoethane are described. The ligand has available dissimilar, adjacent, donor sets (N_2O_2 and O_2O_2). Both mononuclear positional isomers are found for nickel(II) and copper(II) complexes; oxovanadium(IV), dioxouranium(VI), and cobalt(II) gave only the O_2O_2 isomer.

The literature is replete with examples of transition-metal complexes of salicylaldimine and β-ketoamine ligands derived from primary α,ω-diaminoalkanes.[2] The ligands have generally resulted from the condensation of two molecules of the keto-precursor with one molecule of diamine. Relatively few of the ligands reported have arisen from the condensation of the carbonyl function with only one end of the diamine and, until recently, no singly condensed Schiff-base derivatives of β-diketones had been studied.[3]

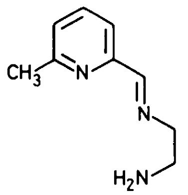
Metal complexes of such singly condensed ligands, hereafter referred to as ' half-units,' have been prepared by several routes. Partial hydrolysis of the quadridentate Schiff bases derived from 6-methylpyridine-2-carbaldehyde,[4] or thiophene-2-carbaldehyde,[5] and 1,2-diaminoethane in the presence of metal ions (Fe^{II} or Cu^{II}) led to the isolation of metal complexes of the terdentate ' half-units ' L^1 and L^2. The *X*-ray crystal structures of $[CuL^2{}_2(ClO_4)_2]$ and $[\{CuL^2Cl_2\}_2]$ confirm the nature of the ligand.[6] Similarly, partial hydrolysis of the quinquedentate Schiff base derived from 1,1,1-trifluoropentane-2,4-dione and 1,5-diamino-3-azapentane in the presence of copper(II), or nickel(II), hydroxide gave the metal complexes ML^3X (X = I or PF_6) after metathesis with NaI or NH_4PF_6.[3]

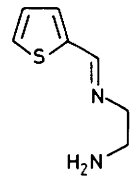
The reaction of $[M^{III}(salen)Cl]$ [M^{III} = Fe, Cr, or Co; salen = *NN'*-ethylenebis(salicylideneiminate)] with an excess of 1,2-diaminoethane resulted in the formation of $[M^{III}L^4{}_2Cl]\cdot H_2O$; this formulation was confirmed *via* the *X*-ray crystal structure of the iron(III) complex.[7]

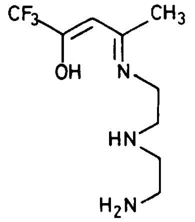
The single condensation of pentane-2,4-dione with 1,5-diamino-3-azapentane at dilution in acetone gave on addition of NaI, or NH_4PF_6, and adjustment to pH 5 using glacial ethanoic acid, the acid salts of HL^5. These were then used to prepare complexes of Ni^{II} and Cu^{II} with the ' half-unit '.[3] More recently the complex (*N*-salicylidenediethylenetriaminato)copper(II) hexafluorophosphate hydrate has been prepared from its components by a template procedure.[8]

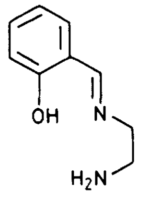
The ligand HL^6 was prepared by reaction of 2-hydroxybenzaldehyde with an excess of 1,3-diaminopropane but not isolated due to separation problems.[9] The nickel(II) complex, $[NiL^6{}_2]$, was isolated and characterised, as were the nickel(II) complexes of the corresponding ' half-units ' derived from 1,4-diaminobutane and 2,5-diamino-2,5-dimethylhexane. The suggestion was made that the metal could be removed from the complex using dimethylglyoxime as a precipitant and the free ligand then used to prepare non-symmetric ligands. This suggestion was later taken up and L^6 used in the preparation of complexes of Cu^{II} and Ni^{II} with the Schiff bases HL^7 and HL^8.[10]

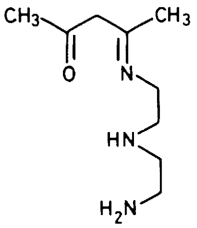
Metal complexes of non-symmetric Schiff bases had previously been prepared by mixing together stoicheiometric

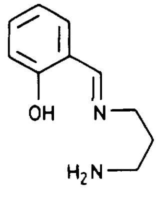

L^1

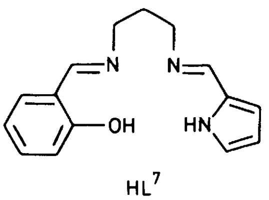

L^2

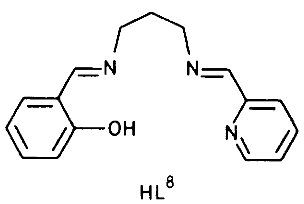

HL^3

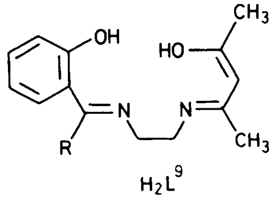

HL^4

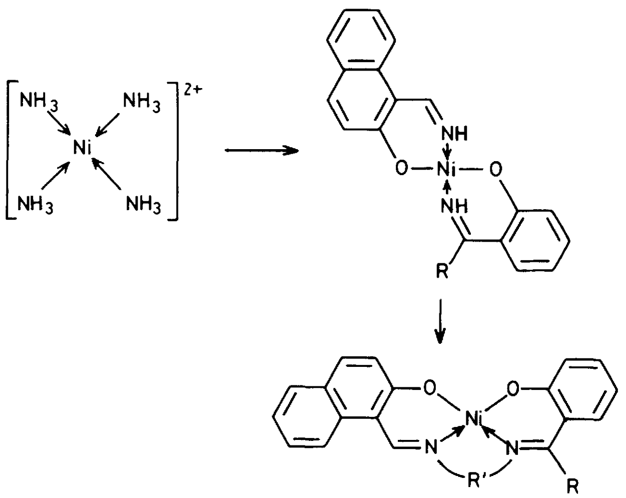

HL^5


HL^6

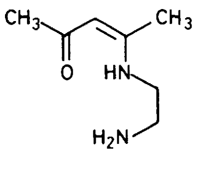

HL^7


HL^8

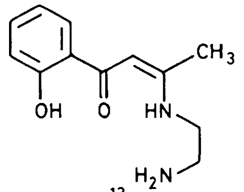

H_2L^9



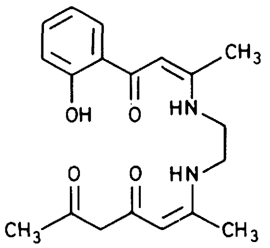
Scheme 1. R = H or CH_3; R′ = $(CH_2)_3$, $(CH_2)_6$, or *o*-phenylene



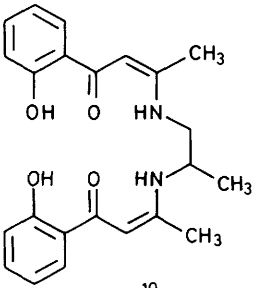
HL^{12}



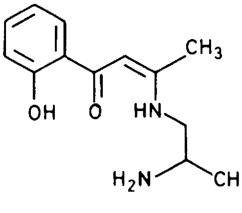
H_2L^{13}



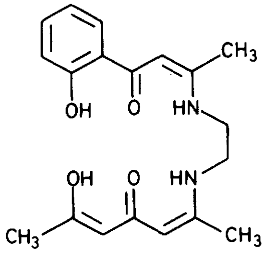
H_4L^{14}



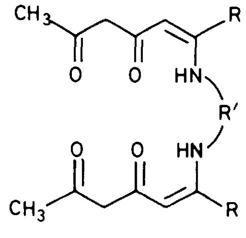
H_4L^{10}



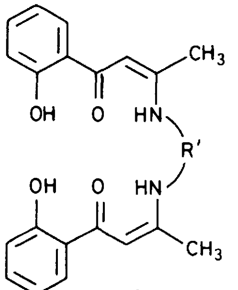
H_2L^{11}



H_4L^{14a}



H_4L^{15}



H_4L^{16}

amounts of the components and separating out the symmetric and non-symmetric products either by crystallisation or chromatography. In this way the derivatives of H_2L^9 (R = H, CH_3, C_2H_5, or n-C_3H_7) with Cu^{II},[11,12] of H_2L^9 (R = H, CH_3, or C_6H_5) with Ni^{II} and Pd^{II},[13] and of H_2L^9 (R = H) with Zn^{II} and Cd^{II} [12] had been prepared. Variations on this theme have recently been presented.[14] The nickel(II) complexes of non-symmetric Schiff bases derived from 2-hydroxy-1-naphthaldehyde and either 2-hydroxybenzaldehyde (HL) or *o*-hydroxyacetophenone (HL′) have been prepared by first forming a mixed imine complex by reaction of the carbonyl compounds with *trans*-$[Ni(H_2O)_2(NH_3)_4][NO_3]_2$. The mixed-ligand complex is then treated with a diamine and undergoes transimination to the non-symmetric species (Scheme 1). In an alternative approach the mixed carbonyl complex [Ni(L–L′)] was treated with diamine to yield the corresponding non-symmetric complex [Ni(L–R′–L′)].

Two reports of free Schiff bases derived from single condensations of β-diketones and primary α,ω-alkanediamines have recently appeared.[15,16] 1-(*o*-Hydroxyphenyl)-butane-1,3-dione reacts readily with α,ω-alkanediamines to give a series of compartmental ligands such as H_4L^{10}.[17] The reaction of the butanedione with 1,2-diaminopropane gave [15] also the ‘ half-unit ’ H_2L^{11} and this reaction was attributed, in part, to a steric interaction between proximal methyl groups inhibiting the formation of the compartmental ligand. The formulation H_2L^{11} has been proven in the *X*-ray crystal structure of $[\{Cu(HL^{11})(O_2CMe)\}_2]$.[18]

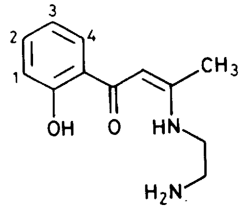
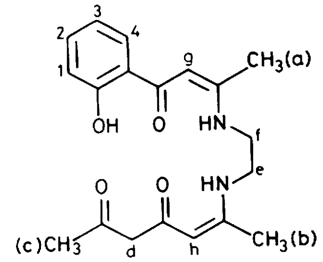
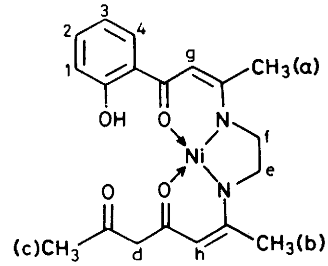
The reaction of pentane-2,4-dione with 1,2-diaminoethane generally yields the quadridentate Schiff base *NN*′-ethylenebis(acetylacetoneimine).[19] However if the reaction is carried out with a 1 : 1 ratio of the reagents in carbon tetrachloride or chloroform and under dilute conditions the ‘ half-unit ’ HL^{12} is formed.[16] The ligand HL^{12} has been used to prepare non-symmetric Schiff bases of type H_2L^9 (R = H or CH_3). The nickel(II) and cobalt(III) complexes derived from these ligands were also prepared and characterised.[20]

We report in this paper application of the above technique to the synthesis of H_2L^{13} by single condensation of 1,2-diaminoethane and 1-(*o*-hydroxyphenyl)butane-1,3-dione, and its conversion into the non-symmetric Schiff base H_4L^{14} by reaction with heptane-2,4,6-trione. The donor-site preferences and metal complexation properties of H_4L^{14} are also discussed.

Results and Discussion

Schiff Bases.—The potentially quadridentate Schiff base H_2L^{13} was prepared by the reaction of 1-(*o*-hydroxyphenyl)-

Table 1. N.m.r. spectra (p.p.m.)

	^1H ($CDCl_3$)	^{13}C-{^1H} ($CDCl_3$)
 H_2L^{13}	1.58 (br, 2 H, NH_2), 2.08 (s, 3 H, CH_3), 2.93 (t, 2 H, CH_2NH_2), 3.37 (q, 2 H, CH_2NH), 5.68 (s, 1 H, CH), 6.78 (t, 1 H, H^3), 6.89 (d, 1 H, H^1), 7.30 (t, 1 H, H^2), 7.61 (d, 1 H, H^4), 11.00 (br, 1 H, NH), and 13.48 (br, 1 H, OH)	20.02 (CH_3), 41.74 (CH_2NH_2), 46.41 (CH_2NH), 90.94 (CH), 118.06, 127.41, 133.17 (aromatic), 162.04 (COH), 165.6 (CN), and 190.02 (C=O)
 H_4L^{14}	1.95 [s, 3 H, CH_3 (c)], 2.07 [s, 3 H, CH_3 (a)], 2.23 [s, 3 H, CH_3 (b)], 3.38 [s, 2 H, CH_2 (d)], 3.52 [br, 4 H, CH_2 (e/f)], 5.02 [s, 1 H, CH (h)], 5.72 [s, 1 H, CH (g)], 6.80 (t, 1 H, H^3), 6.91 (d, 1 H, H^1), 7.33 (t, 1 H, H^2), 7.61 (d, 1 H, H^4), 9.98 (br, 2 H, NH), 13.30 (s, 1 H, OH)	18.74 [CH_3 (b)], 19.59 [CH_3 (a)], 30.27 [CH_3 (c)], 43.44, 43.81 [CH_2 (e, f)], 57.82 [CH_2 (d)], 91.55 [CH (g)], 96.16 [CH (h)], 118.12, 120.18, 127.58, 133.47 (aromatics), 162.04 (COH), 164.65, 165.51 (CN), 189.16, 190.62, and 204.03 (C=O)
 [Ni(H_2L^{14})](N_2O_2 site)	1.90 [s, 3 H, CH_3 (c)], 2.00 [s, 3 H, CH_3 (a)], 2.27 [s, 3 H, CH_3 (b)], 3.10 [s, 4 H, CH_2 (e/f)], 3.16 [s, 2 H, CH_2 (d)], 4.98 [s, 1 H, CH (h)], 5.66 [s, 1 H, CH (g)], 6.71 (t, 1 H, H^3), 6.83 (d, 1 H, H^1), 7.22 (t, 1 H, H^2), 7.43 (d, 1 H, H^4), and 11.29 (s, 1 H, OH)	

In both spectra of H_4L^{14} there are minor peaks at low intensity due to the presence of tautomers.

Table 2. Major i.r. bands (cm^{-1}) and diffuse reflectance spectra (nm) for the Schiff bases and metal complexes

Compound	ν(NH)	ν(C=O)	ν(C–C), ν(C–N), ν(C–O)	Aromatic	Other	Diffuse reflectance
H_2L^{13}	3 300		1 600, 1 575, 1 545, 1 515	775	3 370 (OH, phenol)	
H_4L^{14}	3 070—3 030	1 700	1 600, 1 570, 1 545, 1 515	745	3 360 (OH, phenol)	
[Cu(H_2L^{14})] (N_2O_2)		1 710	1 595, 1 515	760	3 360 (OH, phenol)	625, 537
[Cu(H_2L^{14})]·H_2O (O_2O_2)	3 150		1 615, 1 600, 1 545, 1 520	750	3 400 (H_2O)	645
[Ni(H_2L^{14})] (N_2O_2)		1 700	1 590, 1 510	750	3 360 (OH, phenol)	568
[Ni(H_2L^{14})]·2H_2O (O_2O_2)	3 070		1 605, 1 595, 1 555, 1 510	740	3 400 (H_2O)	613
[Co(H_2L^{14})]·2H_2O (O_2O_2)	3 070		1 600, 1 555, 1 520	740	3 400 (H_2O)	598, 485
[VO(H_2L^{14})]·H_2O (O_2O_2)	3 050		1 625, 1 595, 1 555, 1 525	750	3 400 (H_2O), 990 (V=O)	
[UO_2(H_2L^{14})]·H_2O (O_2O_2)	3 080		1 630, 1 600, 1 555, 1 520	720	3 450 (H_2O), 905 (UO_2)	

butane-1,3-dione and 1,2-diaminoethane in 1 : 1 ratio in chloroform under dilute conditions and characterised by i.r., mass, ^1H and ^{13}C-{^1H} n.m.r. spectroscopy. The n.m.r. spectra showed that H_2L^{13} exists in the ene–amino-form, and the presence of i.r. bands ascribable to NH stretches together with the parent peak at *m/e* 220 in the mass spectrum confirmed that an intermolecular condensation to the diazepin did not occur.

The ' half-unit ' was used to prepare the non-symmetric compartmental ligand H_4L^{14} by reaction with an equimolar amount of heptane-2,4,6-trione. This Schiff base was characterised by i.r., mass, ^1H and ^{13}C-{^1H} n.m.r. spectroscopy. The i.r. showed a band at 1 700 cm^{-1} attributable to the carbonyl in the outer compartment of H_4L^{14} and bands in the region 3 070—3 030 cm^{-1} from the inner compartment NH ··· O groups. The ^1H n.m.r. further indicated that the base exists almost entirely as the keto-tautomer, although very weak signals assignable to the presence of the enol tautomer (H_4L^{14a}) were detected. The mass spectrum gave a peak of low relative abundance corresponding to the parent molecular ion and the breakdown pattern resembled that for the symmetric analogues.[21]

Mononuclear Metal Complexes.—Compartmental ligands such as H_4L^{15} and H_4L^{16} have available for metal co-ordination two adjacent, dissimilar donor sets, N_2O_2 and O_2O_2. This leads to the possibility of the formation of positional isomers unless a site is metal specific. The pattern of selectivity in symmetric compartmental ligands has been established using magnetic and spectroscopic data, and confirmed by *X*-ray structure determination where possible.[22] Nickel(II) has been shown to exhibit a strong preference for the N_2O_2 site, Cu^{II} gave positional isomers depending upon the nature of the ligand and conditions of reaction, and VO^{2+} and UO_2^{2+} were found to occupy the O_2O_2 site. Cobalt(II) and Fe^{II} have been found to occupy the outer site in H_4L^{15} ($R = CH_3$, $R' = CH_2CH_2$).

Mononuclear metal complexes of H_4L^{14} have been prepared and the site occupancy investigated. The pattern follows that for the symmetric ligands. Positional isomers are found for Cu^{II}; these are identified by using i.r. and diffuse reflectance spectroscopy. The N_2O_2 isomer shows a band at 1 710 cm^{-1} corresponding to the free carbonyl frequency and this band is absent in the O_2O_2 isomer. The diffuse reflectance spectra are comparable with those found for the positional isomers of the mononuclear copper(II) complexes of H_4L^{15} ($R = CH_3$, $R' = CH_2CH_2$) [21] and H_4L^{16} ($R' = CH_2CH_2$).[17] The mononuclearity is indicated further by the detection of P^+ at $m/e = 405$ in the mass spectra, with no evidence for peaks attributable to homobinuclear complex formation.

The absence of a free carbonyl frequency in the i.r. spectra of the complexes of VO^{2+}, UO_2^{2+}, and Co^{II} with H_4L^{14} indicates an outer-site occupancy. The uranyl complex has a molecule of water; it is suggested that this is to allow the metal to achieve its preferred seven-co-ordination as has been observed in related complexes.[22] The Co^{II} is dihydrated and so six-co-ordinated as is the case in the symmetric analogues [23] and cobalt(II) complexes of β-diketonates.[24] The mononuclearity of the vanadium(IV) complex is confirmed by P^+ at $m/e = 409$, and for the cobalt(II) complex there is a trace of the homobinuclear complex indicated by a peak at m/e 458 as well as P^+ at $m/e = 401$.

The reaction of nickel(II) ethanoate with H_4L^{14} in a $CHCl_3$–EtOH solvent mixture gave an inner-site occupancy as indicated by the free carbonyl stretch at 1 700 cm^{-1} and a diffuse reflectance spectrum comparable to those for the symmetric complexes.[17,21] However, on changing the reaction conditions it was possible to prepare the second positional isomer. The ligand was dissolved in acetone and an aqueous solution of $LiOH \cdot H_2O$ added. An aqueous solution of nickel(II) ethanoate, or chloride, was then added and the O_2O_2-occupied nickel(II) complex of H_4L^{14} recovered.* The absence of a free carbonyl frequency is indicative of an outer occupancy and the diffuse reflectance spectrum resembles those for bis(pentane-2,4-dionato)nickel(II) complexes.[24] Both complexes show P^+ at $m/e = 400$ in the mass spectrum and traces of the homobinuclear species are indicated by $m/e = 456$. Further evidence for the site occupancy comes from the ^1H n.m.r. spectra. No defined spectrum is recorded for the O_2O_2 complex; the Ni^{II} is six-co-ordinate, two molecules of water being present, and therefore paramagnetic. A clear spectrum is recorded for the N_2O_2 complex in which the Ni^{II} is square coplanar and diamagnetic.

It is believed that the LiOH preferentially deprotonates the outer chamber hydroxyl groups thus facilitating incorporation of the Ni^{II} in this site. In the absence of LiOH only the inner-occupied isomer is produced. No evidence has yet been found for site exchange in this system.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. Infrared spectra were recorded using a Perkin-Elmer 297 spectrometer using KBr discs, powder diffuse reflectance spectra using a Cary 14 spectrophotometer. Proton n.m.r. spectra were run on a Perkin-Elmer R34 spectrometer, $^{13}C-\{^1H\}$ n.m.r. spectra on a JEOL PFT-100 FT spectrometer at 25.15 MHz. Mass spectra were obtained using a Kratos MS 25 mass spectrometer.

Heptane-2,4,6-trione and 1-(*o*-hydroxyphenyl)butane-1,3-dione were prepared by literature methods.[26,27] Table 1 lists the ^1H and $^{13}C-\{^1H\}$ spectra and Table 2 gives the principal i.r. and diffuse reflectance peaks.

The 1 : 1 *Condensation of* 1-(o-*Hydroxyphenyl*)*butane*-1,3-*dione and* 1,2-*Diaminoethane to give Ligand* H_2L^{13}.—1,2-Diaminoethane (1 g) was dissolved in $CHCl_3$ (50 cm^3) and a solution of 1-(*o*-hydroxyphenyl)butane-1,3-dione (3 g) in $CHCl_3$ (50 cm^3) was added slowly, with stirring, over 18 h. The solvent was removed by rotary evaporation to leave a sticky yellow solid which was redissolved in the minimum amount of $CHCl_3$. On addition of heptane the yellow 1 : 1 condensation product was precipitated in good yield, m.p. 75 °C (Found: C, 64.3; H, 6.9; N, 12.5%; P^+ at $m/e = 220$. $C_{12}H_{16}N_2O_2$ requires C, 65.4; H, 7.3; N, 12.7%; $M = 220$).

The Ligand H_4L^{14}.—The ' half-unit', H_2L^{13} (1 g), was dissolved in $CHCl_3$ (50 cm^3) and added to heptane-2,4,6-trione (0.63 g) dissolved in EtOH (50 cm^3). The solution was heated on a steam-bath for 1 h. The ligand, H_4L^{14}, was recovered after cooling the solution for 2 d in a refrigerator, or by adding ether to the concentrated reaction solution as a precipitant, m.p. 112 °C (Found: C, 66.1; H, 6.6; N, 8.4%; P^+ at $m/e = 344$. $C_{19}H_{24}N_2O_4$ requires C, 66.3; H, 7.0; N, 8.1%; $M = 344$).

Metal Complexes of H_4L^{14}.—(*i*) $[Cu(H_2L^{14})]$ (N_2O_2 *site*). The ligand H_4L^{14} (0.344 g) was dissolved in MeOH (100 cm^3) and heated or a steam-bath to effect complete dissolution. Copper(II) ethanoate monohydrate (0.199 g) was dissolved in MeOH (100 cm^3) and this solution was added dropwise to that of the ligand. A purple colour appeared and the solution was heated to reduce the volume to *ca.* 30 cm^3. Crystals of the copper(II) complex appeared on refrigeration; these were filtered off and dried *in vacuo* (Found: C, 56.3; H, 5.6; N, 6.7%; P^+ at m/e 405. $C_{19}H_{22}CuN_2O_4$ requires C, 56.2; H, 5.4; N, 6.9%; $M = 405$).

(*ii*) $[Ni(H_2L^{14})]$(N_2O_2 *site*) *and* $[UO_2(H_2L^{14})] \cdot H_2O$ (O_2O_2 *site*). These complexes were prepared by application of Method A from ref. 17 [Found: C, 56.4; H, 5.5; N, 7.0%; P^+ at $m/e = 400$. $C_{19}H_{22}N_2NiO_4$ requires C, 56.9; H, 5.5; N, 7.0%; $M = 400$. Found: C, 36.9; H, 4.0; N, 4.5%. $C_{19}H_{24}N_2O_7U$ requires C, 36.2; H, 3.8; N, 4.4% (too involatile for mass measurement)].

(*iii*) $[Cu(H_2L^{14})] \cdot H_2O$ (O_2O_2 *site*). A solution of $LiOH \cdot H_2O$ (0.084 g) in water (10 cm^3) was added to a solution of H_4L^{14} (0.344 g) in acetone (50 cm^3) and stirred for 15 min. A solution of copper(II) ethanoate monohydrate (0.199 g) in water (50 cm^3) was added dropwise. A green precipitate appeared and the mixture was heated for 10 min on a steam-bath. The mixture was filtered whilst hot to give the complex in 70—75% yield [Found: C, 53.0; H, 4.9; N, 6.5%; P^+ at $m/e = 405$ ($P - H_2O$). $C_{19}H_{24}CuN_2O_5$ requires C, 53.8; H, 5.6; N, 6.6%; $M = 423$].

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* Application of this synthetic procedure to the reaction of nickel(II) ethanoate and H_4L^{16} ($R' = CH_2CH_2$) led to the isolation of the O_2O_2 isomer of the nickel complex.[25] Previously only the N_2O_2 isomer had been reported.[17]

This method has also been used for the preparation of $[Co(H_2L^{14})]\cdot 2H_2O$, $[Ni(H_2L^{14})]\cdot 2H_2O$, and $[VO(H_2L^{14})]\cdot H_2O$ (all O_2O_2 site). In the case of VO^{2+}, $VO(SO_4)$ was used. It was found that $NiCl_2\cdot 6H_2O$, $CoCl_2$, and $CuCl_2\cdot H_2O$ could be used as well as the corresponding ethanoates [Found: C, 51.0; H, 5.6; N, 6.1%; P^+ at $m/e = 401$ ($P - 2H_2O$). $C_{19}H_{26}CoN_2O_6$ requires C, 52.1; H, 5.9; N, 6.4%; $M = 437$. Found: C, 51.7; H, 5.9; N, 6.5%; P^+ at $m/e = 400$ ($P - 2H_2O$). $C_{19}H_{26}N_2NiO_6$ requires C, 52.2; H, 5.9; N, 6.4%; $M = 436$. Found: C, 52.7; H, 5.4; N, 6.7%; P^+ at $m/e = 409$ ($P - H_2O$). $C_{19}H_{24}N_2O_6V$ requires C, 53.4; H, 5.6; N, 6.6%; $M = 427$].

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References

1 Part 5, H. Adams, N. A. Bailey, D. E. Fenton, and M. S. Leal Gonzalez, *J. Chem. Soc., Dalton Trans.*, 1983, 1345.
2 R. H. Holm, G. W. Everett, jun., and A. Chakravorty, *Prog. Inorg. Chem.*, 1966, **7**, 83; R. H. Holm and M. J. O'Connor, *ibid.*, 1971, **14**, 241.
3 W. N. Wallis and S. C. Cummings, *Inorg. Chem.*, 1974, **13**, 991.
4 H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, 1960, **82**, 5013.
5 A. C. Braithwaite, C. E. F. Rickard, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1975, 2149.
6 P. G. Beckingsale, A. T. Morcom, C. E. F. Rickard, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1977, 2135.
7 A. P. Summerton, A. A. Diamantis, and M. R. Snow, *Inorg. Chim. Acta*, 1978, **27**, 123.
8 E. Rotondo and F. C. Priolo, *J. Chem. Soc., Dalton Trans.*, 1982, 1825.
9 R. C. Elder, *Aust. J. Chem.*, 1978, **31**, 35.
10 P. J. Burke and D. R. McMillin, *J. Chem. Soc., Dalton Trans.*, 1980, 1794.
11 H. A. Kuska, M. F. Farona, P. Pappas, and S. Potterton, *J. Coord. Chem.*, 1971, **1**, 259.
12 U. Doraswamy and P. K. Bhattacharya, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1665.
13 E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1980, **42**, 197.
14 R. P. Sharma and R. N. Prasad, *Synth. React. Inorg. Metal-Org. Chem.*, 1982, **12**, 347.
15 G. Bett, D. E. Fenton, and J. R. Tate, *Inorg. Chim. Acta*, 1981, **54**, L101.
16 J.-P. Costes and G. Cros, *C. R. Acad. Sci., Ser. 2*, 1982, **294**, 173.
17 D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato, and M. Vidali, *Inorg. Chim. Acta*, 1978, **27**, 9.
18 J. R. Tate, Ph.D. Thesis, University of Sheffield, 1982.
19 A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, 1955, **5**, 170.
20 J.-P. Costes, G. Cros, M.-H. Darbieu, and J.-P. Laurent, *Inorg. Chim. Acta*, 1982, **60**, 111.
21 D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.*, 1977, 2101.
22 U. Casellato, P. A. Vigato, D. E. Fenton, and M. Vidali, *Chem. Soc. Rev.*, 1979, **8**, 199.
23 D. E. Fenton and C. M. Spencer, unpublished work.
24 J. P. Fackler, jun., *Prog. Inorg. Chem.*, 1966, **7**, 361.
25 J.-P. Costes and D. E. Fenton, unpublished work.
26 J. R. Bethell and P. Maitland, *J. Chem. Soc.*, 1962, 2751.
27 G. Wittig, *Liebigs Ann. Chem.*, 1926, **446**, 173.

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