Construction of a New Versatile Hydrazonic Ligand and its Chemical and Structural Behaviour towards Metal Ions†

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The synthesis of a new hydrazonic ligand, 2,6-diacetylpyridine bis[2-(semicarbazono)propionylhydrazone] (H_4L), is reported together with the synthesis, X-ray structure analysis and the IR spectroscopic characterisation of the complexes $[\{Ni_2(H_2L)(OH_2)Cl\}_2Cl_2]\cdot 2dmf\cdot 5H_2O$ **1** (dmf = dimethylformamide), $[Co(H_4L)(OH_2)_2][NO_3]_2\cdot 2H_2O$ **2** and $[Zn(H_3L')(OH_2)_2][ClO_4]_2\cdot 1.5H_2O$ **3** [H_3L' = 2,6-diacetylpyridine semicarbazone 2-(semicarbazono)propionylhydrazone]. The interest of these structures pertains mainly to the cations. In **1** a tetranuclear complex is present with two non-equivalent nickel atoms, both of which exhibit distorted-octahedral co-ordination, and with the hydrazone acting as enneadentate donor. The structures of **2** and **3** consist of monomeric units in which the metal atom has a pentagonal–bipyramidal environment with two axial H_2O molecules and the hydrazone ligand forming the basal plane.

In order to isolate new bi- or poly-metallic, homo- and heteronuclear, complexes, which are of interest mainly in the field of electric and magnetic materials[1,2] we are projecting more flexible and polyfunctional ligands by modifying the nature and geometry of acylhydrazones previously examined as chelating agents in complexes with transition and main-group elements.[3–5] Accordingly, we have synthesised new polydentate hydrazides, $RC(O)NHN{=}C(R')C(O)NHNH_2$, by introducing additional hydrazonic or semicarbazonic groups *via* stepwise processes.[6]

This paper reports the synthesis of H_4L, the first of this series of new ligands, as well as the synthesis and the crystal and molecular structure of three complexes, namely $[\{Ni_2(H_2L)(OH_2)Cl\}_2]Cl_2\cdot 2dmf\cdot 5H_2O$ **1** {H_4L = 2,6-diacetylpyridine bis[2-(semicarbazano)propionylhydrazone], dmf = dimethylformamide}, $[Co(H_4L)(OH_2)_2][NO_3]_2\cdot 2H_2O$ **2** and $[Zn(H_3L')(OH_2)_2][ClO_4]_2\cdot 1.5H_2O$ **3** [H_3L' = 2,6-diacetylpyridine semicarbazone 2-(semicarbazono)propionylhydrazone].

Experimental

Preparations.—$H_2NC(O)NHN{=}C(CH_3)CO_2CH_3$. To an aqueous solution (70 cm^3) of semicarbazide hydrochloride (5.6 g), adjusted to pH 7 with an aqueous sodium hydroxide solution, was added an aqueous solution (50 cm^3) of methyl pyruvate (5.1 g, 1:1 molar ratio) at room temperature with stirring. A white product was immediately formed, which was then recrystallised from warm water (m.p. 198–200 °C). Yield 80% (Found: C, 37.45; H, 5.80; N, 26.55. $C_5H_9N_3O_3$ requires C, 37.75; H, 5.70; N, 26.40%).

$H_2NC(O)NHN{=}C(CH_3)C(O)NHNH_2$.—To an appropriate amount of hydrazine hydrate (2 g, 40%) an equimolar amount (14.7 g) of the above product was added dropwise and the mixture slowly heated at reflux for about 15 min. Absolute ethanol (80 cm^3) was then added to the suspension until the resulting solution was completely clear; it was refluxed for about 3 h, and a white product then isolated (yield 65%, m.p. 224–225 °C) after removal of solvent by distillation under vacuum. (Found: C, 30.05; H, 5.60; N, 44.25. $C_4H_9N_5O_2$ requires C, 30.20; H, 5.70; N, 44.00%).

2,6-Diacetylpyridine bis[2-(semicarbazono)propionylhydrazone](H_4L). To a boiling ethanol–water (50:50 v/v) solution (100 cm^3) of $H_2NC(O)NHN{=}C(CH_3)C(O)NHNH_2$ (6.4 g) was added an ethanolic solution (50 cm^3) of 2,6-diacetylpyridine (3.3 g, 2:1 molar ratio). The solution was then refluxed for about 30 min and a pale yellow solid collected by filtration (yield 85%, m.p. 245–246 °C). The compound is slightly soluble in ethanol and water (Found: C, 42.70; H, 5.80; N, 31.85. $C_{17}H_{27}N_{11}O_6$ (the dihydrate) requires C, 42.40; H, 5.65; N, 32.00%]. Mass spectrum: m/z 307 (3.6), 287 (8.0), 260 (2.4), 252 (7.2), 218 (4.0), 190 (2.4), 176 (96.0), 167 (32.0), 148 (100.0), 130 (37.6) and 106 (29.6%). ^1H NMR [$(CD_3)_2SO$]: δ 10.5 (2 H, s, amidic), 9.5 (2 H, s, amidic), 8.0 (2 H, m, pyridyl), 6.9 (4 H, m, NH_2), 2.5 (6 H, s, CH_3) and 2.0 (6 H, s, CH_3). Thermogravimetric analysis (TGA) in the range 30–400 °C revealed the complete loss of two water molecules below 100 °C; between 100 and *ca.* 320 °C the weight of the sample remained practically constant, then at *ca.* 330 °C an almost total decomposition occurred.

$[\{Ni_2(H_2L)(OH_2)Cl\}_2]Cl_2\cdot 2dmf\cdot 5H_2O$ **1**. To a warm solution of H_4L (0.5 g) in ethanol–dimethylformamide (100 cm^3, 80:20 v/v) was added an ethanolic solution (20 cm^3) of nickel(II) chloride hexahydrate (0.6 g; a small excess of the metal was used with respect to a 2:1 metal:ligand molar ratio). From the yellow-green solution after some hours red-brown crystals were isolated (yield 60%) (Found: C, 30.90; H, 4.70; N, 21.95. $C_{40}H_{70}Cl_4N_{24}Ni_4O_{17}$ requires C, 31.30; H, 4.60; N, 21.90%). A dimethyl sulphoxide solution of the complex shows an absorption at about 530 nm.

$[Co(H_4L)(OH_2)_2][NO_3]_2\cdot 2H_2O$ **2**. To a boiling methanolic solution (50 cm^3) of H_4L (0.5 g) a methanolic solution (20 cm^3) of cobalt(II) nitrate hexahydrate (0.3 g, 1:1 molar ratio) was added under a nitrogen atmosphere. The solution was refluxed for about 1 h and then allowed to stand at room temperature. After slow evaporation of the solvent orange crystals were isolated (yield 75%). The compound was obtained also when a 2:1 metal:ligand molar ratio was used (Found: C, 28.95; H, 4.50; N, 26.35. $C_{17}H_{31}CoN_{13}O_{14}$ requires C, 29.15; H, 4.45; N, 26.00%).

$[Zn(H_3L')(OH_2)_2][ClO_4]_2\cdot 1.5H_2O$ **3**. A procedure similar

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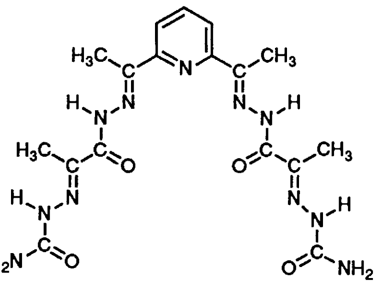
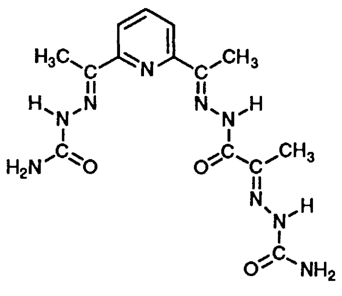
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



H_4L



H_3L'

to that described for the cobalt complex was employed, using zinc perchlorate hexahydrate (0.4 g, 1:1 or 2:1 metal:ligand molar ratio). After slow evaporation of the methanol, yellow crystals were isolated (yield 80%). The analytical data are consistent with the formula established by X-ray analysis (Found: C, 24.65; H, 4.15; N, 18.10. $C_{14}H_{26}Cl_2N_9O_{14.5}Zn$ requires C, 24.40; H, 3.80; N, 18.30%).

Measurements.—Elemental C, H and N analyses were carried out on Perkin-Elmer model 240 automatic equipment. Infrared spectra (4000–200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer, mass spectra on a Varian CH-5 spectrometer [70 eV (*ca.* 1.12×10^{-17} J)] ^1H NMR spectra on a Varian EM-360 instrument and electronic spectra (900–400 nm) in dimethyl sulphoxide solution on a JASCO 505 spectrophotometer. The thermogravimetric analysis was made with a Perkin-Elmer Delta series TGA 7 thermobalance from 30 to 400 °C at a rate of 20 °C min^{-1}.

X-Ray Crystallography.—Unit-cell determination and data collection were carried out at ambient temperature on a Siemens AED single-crystal diffractometer equipped with a IBM PS2/30 personal computer; Cu-Kα radiation was used for the nickel and zinc compounds and Mo-Kα radiation for the cobalt compound. Thirty reflections with θ 17–30° for compound **1**, 10–16° for **2** and 14–39° for **3** were located by a random search procedure and subsequently centred. These reflections were used as a basis for the indexing. The cell parameters and the orientation matrix obtained were refined by least squares. The crystal data and experimental conditions are summarised in Table 1. The reflections were measured using a modified version[7] of the Lehmann and Larsen procedure.[8] One quadrant of data was collected for all the three structures. One standard reflection was measured every 50 reflections to monitor for any decomposition during the X-ray analysis. Its intensity remained essentially constant throughout the data collection for both the cobalt and zinc compounds, whereas in the case of the nickel compound it decayed significantly (this was allowed for by appropriate scaling). The measured intensities were corrected for Lorentz and polarisation effects. A correction for absorption was also applied by using the pseudo-empirical method of Walker and Stuart.[9]

The three structures were solved by a combination of direct methods and heavy-atom techniques and refined by full-matrix least squares based upon F until convergence. The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ and a weighting scheme of the type $w = k/[\sigma^2(F_o) + gF_o^2)$ was used during the final stages. Because of the limited amount of data, not all of the non-hydrogen atoms were allowed to vary anisotropically; in particular, only atoms heavier than nitrogen in the nickel complex cation and carbon in the cobalt complex cation were refined anisotropically, whereas in the zinc compound all atoms except the oxygens of the perchlorate anions and the half-populated water molecule were assigned anisotropic thermal parameters. In each case a remarkable difficulty was encountered in growing crystals of size suitable for X-ray analysis. So, the small sample size and the limited scattering ability and, as far as the nickel crystal is concerned, also the gradual decomposition by X-ray irradiation, could account for the somewhat disappointing R values. In the case of the zinc compound we note that a further data set collected by using a different crystal, after the structure was solved, led to the same results.

Atomic scattering factors and anomalous dispersion corrections were from ref. 10. All calculations were performed on a GOULD-SEL 6040 computer by using the SHELX 76 suite of programs.[11] The other programs used have been cited elsewhere.[12] The final atomic parameters for the three compounds are given in Tables 2–4, selected bond distances and angles in Tables 5–7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

The most interesting features of this work pertain to the organic molecule. Especially noteworthy is its nature in the zinc complex. During the formation of this complex the original H_4L has undergone a modification through a hydrolysis process, resulting in partial cleavage of one arm to give H_3L'.

In the nickel complex, where two metal atoms and one ligand molecule are present, the ligand H_4L is doubly deprotonated and exhibits an interesting and rather unusual chelating behaviour which favours the formation of a tetranuclear cationic complex. In the cobalt complex H_4L is present in its neutral form and behaves as a pentadentate planar N_3O_2 ligand, as does H_3L' in the zinc complex, in analogy with the tendency shown by most 2,6-diacetylpyridine bis(acylhydrazones) (acyl = benzoyl, salicyloyl, pyridine-2-carbonyl, 2-aminobenzoyl or 2-thenoyl) previously studied.[2,3,13–15]

The crystal structure of all three compounds consists of discrete complex cations, as in Figs. 1–3, inorganic anions and solvating molecules.

Important features of the nickel structure are the tetranuclear nature of the complex cation, the presence of two non-equivalent nickel atoms and the enneadentate behaviour of the hydrazone molecule. The co-ordination geometry about each nickel atom may be described as distorted octahedral; in the case Ni(1), N_4O_2 co-ordination occurs through atoms belonging to the hydrazone (three are part of the ligand at *x,y,z*, and three of the centrosymmetrically related molecule), while in the case of Ni(2) the co-ordination sites are occupied by three other nitrogens of the hydrazone at *x,y,z*, two chlorine atoms and a water molecule. Through the bridging of two symmetry-related Ni(2) atoms by Cl ions, a four-membered Ni_2Cl_2 ring system is formed in which the angles are acute at nickel and obtuse at chlorine. The Ni ··· Ni distance of 3.414(7) Å rules out direct interaction between the metal atoms.

Fig. 1 shows the geometry of two centrosymmetric dimeric

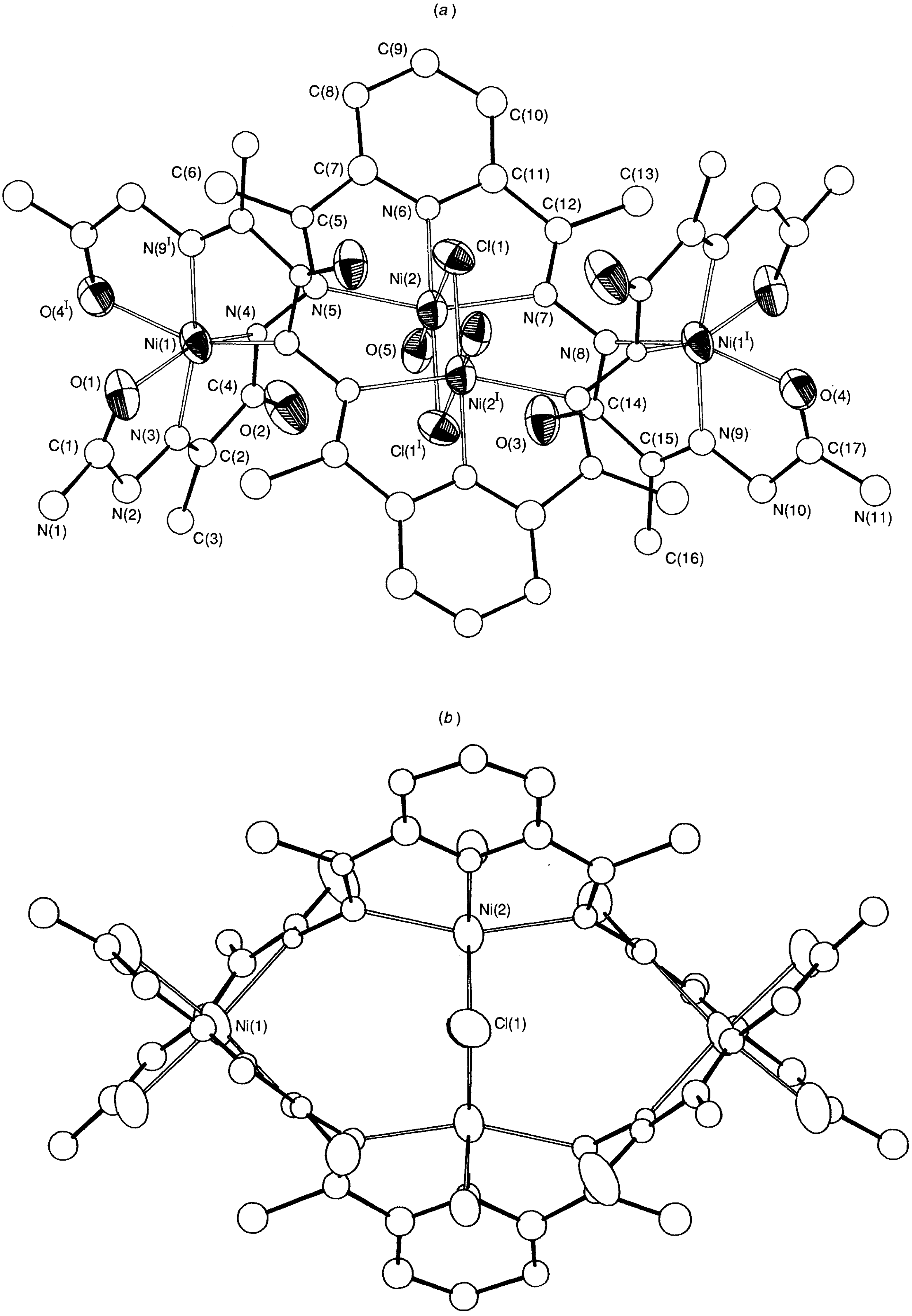


Fig. 1 (*a*) ORTEP diagram of the $[\{Ni_2(H_2L)(OH_2)Cl\}_2]^{2+}$ cation with the atomic numbering. The ellipsoidal boundaries are at the 50% probability level. Anisotropic parameters were used only for shaded atoms. Carbon atoms are shown artificially small. (*b*) Another view of the tetranuclear cation

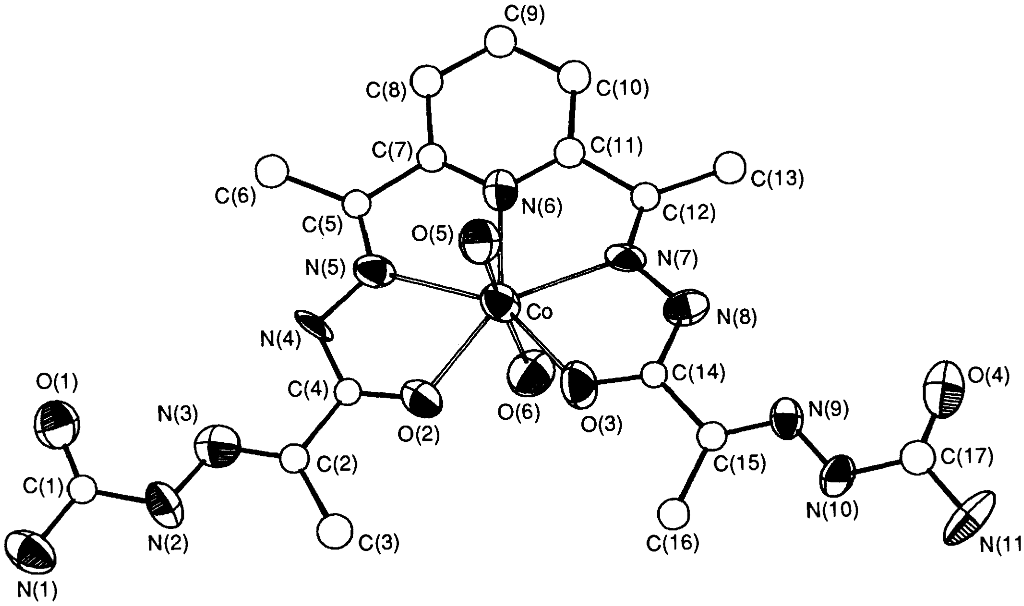


Fig. 2 ORTEP diagram of the $[Co(H_4L)(OH_2)_2]^{2+}$ cation with the atomic numbering. The ellipsoidal boundaries are at the 50% probability level. Anisotropic parameters were used only for shaded atoms

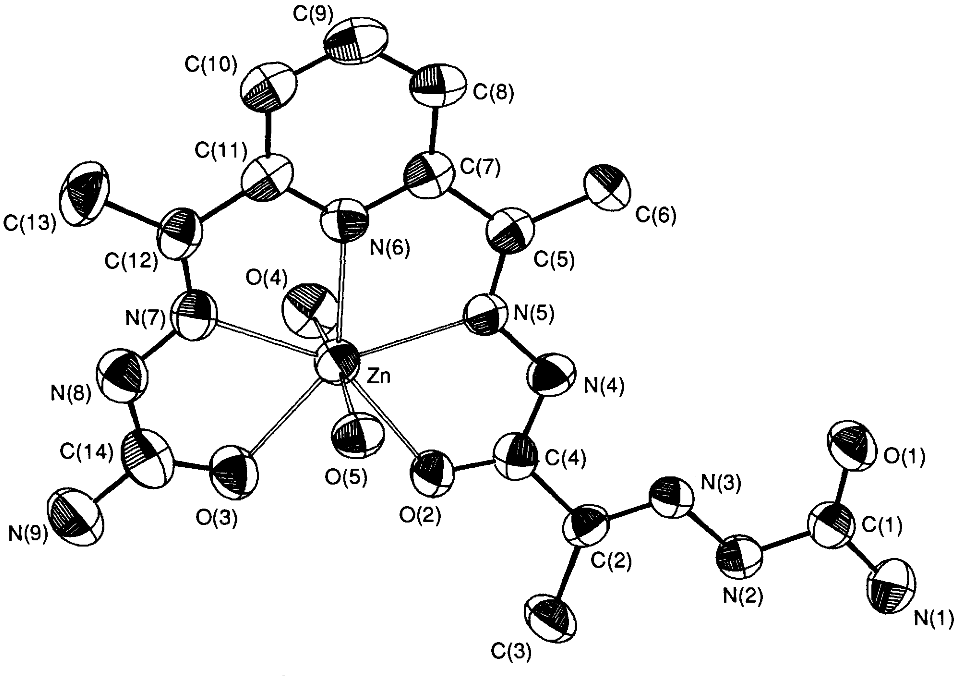


Fig. 3 ORTEP diagram of the $[Zn(H_3L')(OH_2)_2]^{2+}$ cation with the atomic numbering. The ellipsoidal boundaries are at the 50% probability level

units which comprise the tetranuclear units. The two Ni(2)–Cl bonds differ by a significant 0.11 Å. The extent of the asymmetry of the bridging is about the same as that in $[Ni_2(en)_4Cl_2]Cl_2$[16] (en = ethane-1,2-diamine) (Δ = 0.09 Å) and in $[Ni_2(en)_4Cl_2][BPh_4]_2$[17] (Δ = 0.10 Å), but much greater than in most related complexes (Δ = 0.01–0.03 Å) all of which contain a six-co-ordinate double chloro-bridged nickel system.[18–22] A search of the Cambridge Crystallographic Database yielded 38 examples of structures of tetranickel-containing systems, none of which, however, is particularly suitable for a comparison with the present compound.

The Ni–N and Ni–O bonds fall in the range of values reported for nickel hydrazone or semicarbazone complexes all of which are monomeric and seven-co-ordinated Ni–N 2.015–2.313,[23–28] Ni–O 2.216–2.664 Å.[23–26] As regards the Ni–N bonds, it is of interest to compare the values found here also with those reported for a nickel complex containing a hexadentate ligand derived from the condensation of one molecule of 2,6-diacetylpyridine with two molecules of diethylenetriamine and subsequent isomerisation.[29] In this compound the nickel atom is bound to six nitrogen atoms at distances ranging from 2.003(20) to 2.319(19) Å in an approximately octahedral array.

A closer examination of the data in Table 5 shows that the seven Ni–N bond distances may be divided into two groups: those involving the pyridine and semicarbazonic nitrogens and those involving the hydrazonic nitrogens, with the latter longer, on average, by 0.17 Å than the former. The hydrazone ligand, which is present in its doubly deprotonated form, uses nine of its fifteen potential donors in co-ordination, interestingly chelating three different metal atoms. It forms five five-membered chelate rings, three to Ni(1) and two to Ni(2), all of which are planar within experimental error. The ligand, as a whole, is fully non-planar, the side arms being twisted by 121.2(6) and 52.2(7)° out of the central pyridine ring.

In the cobalt and zinc compounds the co-ordination

Table 1 Crystal data and summary of intensity data collection and structure refinement

Compound	**1**	**2**	**3**
Formula	$C_{40}H_{70}Cl_4N_{24}Ni_4O_{17}$	$C_{17}H_{31}CoN_{13}O_{14}$	$C_{14}H_{26}Cl_2N_9O_{14.5}Zn$
M	1535.80	700.44	688.70
Crystal shape	Red-brown lance-like	Yellow-orange platelets	Pale yellow irregularly shaped
Crystal size (mm)	*	0.08 × 0.49 × 0.43	0.17 × 0.18 × 0.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$	$C2/c$
a/Å	12.141(8)	23.405(10)	24.481(10)
b/Å	21.284(12)	10.627(6)	10.607(6)
c/Å	12.504(7)	11.749(6)	20.182(9)
β/°	96.09(2)	92.80(2)	90.12(3)
U/Å^3	3212(3)	2919(3)	5241(4)
Z	2	4	8
D_c/g cm^{-3}	1.588	1.594	1.746
μ/cm^{-1}	35.56	6.69	40.08
F(000)	1588	1452	2824
θ range/°	3–65	3–21	3–70
Scan mode	θ–2θ	θ–2θ	θ–2θ
Standard reflection	$\bar{3}$ 6 2	6 2 5	$\bar{7}$ 3 11
Number of reflections measured	5911	3515	5423
Number of unique reflections	5474	3118	4998
Criterion for observed reflections	$I > 2.5\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
Number of observed reflections	1135	1321	3053
Parameters refined	229	283	341
R	0.0886	0.0780	0.0857
R'	0.1130	0.0924	0.1134
Max. height in final ΔF map/e Å^{-3}	0.37	0.55	1.22
k,g in $w = k/[\sigma^2(F_o) + gF_o^2]$	0.9444, 0.006 582	0.8198, 0.002 629	3.8248, 0.000 708

* The crystal was inadvertently lost after data collection and prior to its measurement.

Table 2 Atomic coordinates (× 10^4) of compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni(1)	465(4)	1165(2)	3081(4)
Ni(2)	−14(4)	680(2)	−726(4)
Cl(1)	1374(5)	−1(4)	−7(6)
Cl(2)	107(8)	3742(6)	178(9)
O(1)	1014(15)	965(9)	4733(14)
O(2)	2082(15)	1662(10)	416(15)
O(3)	1712(15)	342(9)	−2554(14)
O(4)	−274(14)	−2108(9)	−3645(14)
O(5)	1100(14)	1227(8)	−1452(13)
O(6)	1417(21)	2780(13)	−956(23)
O(7)	−4444(19)	1256(12)	215(21)
O(8)	5131(33)	3206(20)	1483(34)
O(9)	1326(50)	2839(30)	6634(53)
O(10)	364(59)	4977(43)	915(57)
N(1)	2688(18)	965(10)	5867(19)
N(2)	2752(18)	1214(11)	4083(19)
N(3)	2055(17)	1259(10)	3119(17)
N(4)	641(15)	1431(9)	1482(15)
N(5)	−60(17)	1377(10)	513(17)
N(6)	−1264(16)	1207(10)	−1285(18)
N(7)	−371(17)	284(10)	−2292(17)
N(8)	104(18)	−234(10)	−2757(17)
N(9)	1135(18)	−1196(11)	−3299(18)
N(10)	1554(18)	−1757(11)	−3683(18)
N(11)	1016(19)	−2730(11)	−4375(19)
N(12)	−4630(32)	541(18)	−1158(31)
C(1)	2014(28)	1072(15)	4910(26)
C(2)	2513(23)	1478(13)	2263(24)
C(3)	3742(21)	1680(12)	2242(22)
C(4)	1705(23)	1505(12)	1325(24)
C(5)	−912(20)	1746(12)	316(21)
C(6)	−1112(24)	2298(15)	1095(25)
C(7)	−1605(24)	1704(15)	−721(25)
C(8)	−2547(22)	2072(14)	−1026(23)
C(9)	−3062(22)	1921(14)	−2083(24)
C(10)	−2674(24)	1455(15)	−2728(25)
C(11)	−1721(23)	1088(15)	−2317(25)
C(12)	−1181(23)	543(13)	−2835(23)
C(13)	−1624(23)	404(14)	−4107(25)
C(14)	1208(22)	−184(13)	−2698(20)
C(15)	1765(21)	−741(14)	−3079(21)
C(16)	3021(21)	−718(13)	−3172(21)
C(17)	667(25)	−2200(14)	−3850(23)
C(18)	−4123(33)	790(22)	−220(38)
C(19)	−4135(33)	−4(22)	−1601(34)
C(20)	−5794(45)	769(23)	−1480(40)

geometry at the metal is essentially seven-co-ordinate pentagonal bipyramidal, with three N and two O of the hydrazone molecule making up the equatorial girdle and two water molecules at the axial sites. The N_3O_2 equatorial donor sets are very nearly coplanar, the maximum least-squares deviation being 0.08 Å for the cobalt and 0.05 Å for the zinc compound, with the metal atom sitting in the plane. The five interior angles in the pentagon range from 70.4(5) to 76.4(4)° for the former and from 69.7(3) to 78.2(3)° for the latter, with an average, in both cases, of 72.0°, which is the ideal value for a plane pentagon.

The most important difference between the two structures concerns the nature of the hydrazone ligand. As mentioned above, the results of the X-ray analysis reveal that the original ligand found in the nickel and cobalt structures has undergone a modification to give the asymmetric ligand in the zinc structure as a result of hydrolytic processes. In spite of this, the manner of chelation of the hydrazone to metal is the same as found in the cobalt compound, leading to four essentially planar five-membered chelate rings. The M–N and M–O bond distances in the pentagon average 2.183 and 2.134 Å for the cobalt compound and 2.205 and 2.250 Å for the zinc compound, and compare fairly well with the values found for corresponding bonds in related seven-co-ordinated cobalt and zinc complexes

Table 3 Atomic coordinates (× 10^4) of compound **2** with e.s.d.s in parentheses *

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Co	5026(1)	2228(3)	1951(2)	C(7)	6262(7)	2796(19)	2636(15)
O(1)	4549(6)	3967(12)	8102(11)	C(8)	6865(8)	2900(19)	2586(15)
O(2)	4380(4)	2553(12)	3133(10)	C(9)	7099(8)	2648(19)	1533(15)
O(3)	4260(5)	1614(12)	1056(10)	C(10)	6748(8)	2329(19)	583(15)
O(4)	3821(6)	24(13)	−3838(11)	C(11)	6154(8)	2222(19)	766(15)
O(5)	5128(5)	274(11)	2611(9)	C(12)	5726(8)	1850(17)	−185(15)
O(6)	4819(5)	4010(11)	1196(10)	C(13)	5901(8)	1724(19)	−1408(16)
N(1)	3614(7)	4144(15)	8602(13)	C(14)	4265(8)	1332(17)	27(16)
N(2)	3829(6)	3566(15)	6744(13)	C(15)	3726(8)	1063(18)	−669(17)
N(3)	4229(6)	3378(15)	5950(14)	C(16)	3171(8)	1216(18)	−55(15)
N(4)	5065(6)	3082(14)	4474(11)	C(17)	3340(10)	188(22)	−3414(20)
N(5)	5424(6)	2878(14)	3583(11)	O(7)	2388(8)	3799(19)	8032(18)
N(6)	5930(5)	2451(13)	1762(11)	O(8)	2622(8)	4107(17)	6361(16)
N(7)	5233(6)	1697(12)	212(11)	O(9)	1870(12)	4712(28)	6842(21)
N(8)	4766(6)	1347(13)	−526(12)	O(10)	3734(9)	5058(18)	1122(17)
N(9)	3785(6)	761(12)	−1704(12)	O(11)	3318(15)	5452(26)	2693(24)
N(10)	3284(6)	520(15)	−2310(13)	O(12)	2845(12)	4749(27)	1348(26)
N(11)	2827(7)	−5(19)	−4044(14)	O(10′)	3032(29)	4469(66)	774(62)
C(1)	4032(9)	3882(18)	7835(17)	O(11′)	2840(49)	5601(99)	2373(93)
C(2)	4050(7)	3045(18)	4933(16)	O(12′)	3756(65)	5200(139)	2224(143)
C(3)	3436(8)	2810(21)	4492(16)	N(12)	2255(14)	4063(31)	7043(28)
C(4)	4516(7)	2898(19)	4111(16)	N(13)	3318(13)	5078(24)	1694(25)
C(5)	5969(8)	3008(18)	3729(14)	O(13)	418(6)	933(15)	6579(12)
C(6)	6301(8)	3310(19)	4842(16)	O(14)	4326(8)	−370(20)	4062(17)

* Atoms O(10), O(11) and O(12) have occupancy 0.8; O(10′), O(11′) and O(12′) occupancy 0.2.

Table 4 Atomic coordinates (× 10^4) of compound **3** with e.s.d.s in parentheses *

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Zn	552.9(5)	2 090.2(12)	9 573.9(6)	C(9)	2 369(4)	4 161(11)	9 677(5)
O(1)	−968(3)	5 980(7)	12 097(3)	C(10)	2 281(4)	3 166(9)	9 234(5)
O(2)	−289(2)	2 201(6)	10 054(3)	C(11)	1 762(4)	2 615(9)	9 223(5)
O(3)	117(3)	511(6)	9 082(3)	C(12)	1 611(4)	1 556(9)	8 779(4)
O(4)	767(3)	727(6)	10 274(3)	C(13)	2 033(4)	955(12)	8 330(6)
O(5)	221(2)	3 278(6)	8 835(3)	C(14)	374(5)	−72(11)	8 626(5)
N(1)	−1 858(3)	5 497(8)	12 273(4)	Cl(1)	−2 926(1)	2 954(3)	1 306(2)
N(2)	−1 382(3)	4 409(7)	11 508(4)	Cl(2)	1 353(1)	1 919(3)	1 998(2)
N(3)	−903(3)	4 165(7)	11 189(4)	O(6)	−3 319(7)	3 533(18)	877(9)
N(4)	49(3)	3 833(8)	10 626(4)	O(7)	−3 292(5)	2 734(11)	1 815(6)
N(5)	530(3)	3 636(7)	10 305(3)	O(8)	−2 524(4)	3 791(10)	1 503(5)
N(6)	1 354(3)	2 982(7)	9 622(3)	O(9)	−2 719(7)	1 789(17)	1 177(9)
N(7)	1 116(3)	1 205(7)	8 844(4)	O(10)	1 103(8)	694(21)	2 091(10)
N(8)	911(3)	256(8)	8 475(4)	O(11)	912(10)	2 648(21)	2 202(12)
N(9)	174(4)	−1 093(10)	8 305(5)	O(12)	1 435(9)	1 843(20)	1 321(11)
C(1)	−1 385(4)	5 360(9)	11 974(4)	O(13)	1 874(13)	2 128(31)	2 293(16)
C(2)	−899(3)	3 232(9)	10 790(4)	O(10′)	1 657(11)	3 014(26)	1 822(14)
C(3)	−1 362(4)	2 358(10)	10 618(5)	O(11′)	1 264(14)	1 865(32)	2 621(18)
C(4)	−356(4)	3 024(9)	10 456(4)	O(12′)	1 794(27)	1 340(66)	2 279(32)
C(5)	958(4)	4 275(8)	10 466(4)	O(13′)	800(33)	1 658(73)	1 616(38)
C(6)	1 001(4)	5 274(11)	10 995(5)	O(14)	526(3)	−2 179(8)	1 979(4)
C(7)	1 444(4)	3 937(9)	10 061(4)	O(15)	55(11)	4 258(22)	2 235(11)
C(8)	1 945(4)	4 547(9)	10 108(5)				

* Atoms O(10), O(11), O(12) and O(13) have occupancy 0.7; O(10′), O(11′), O(12′) and O(13′) occupancy 0.3

having an equatorial donor set formed by N and/or O atoms of a quinquedentate ligand (Co–N 2.084–2.366,[24,30–38] Co–O 2.131–2.347,[24,31,32,37–39] Zn–N 2.057–2.344 [30,31,40] and Zn–O 2.184–2.207 Å [31]).

In both these compounds the hydrazone can be considered, even if very roughly, planar, the largest deviations from the plane of best fit being 0.32 and 0.19 Å for Co and Zn respectively. In the cobalt structure, characterised by a C_{2v} pseudo-symmetry, the two symmetrical halves make a dihedral angle of only 3.5° and the mean planes of the two side arms are inclined at an angle of *ca.* 2° to the pyridine plane. In the zinc structure the seven-atom short side arm is planar to 0.09 Å, while a maximum deviation from coplanarity of 0.12 Å occurs in the 13-atom long side arm. The two arms are twisted slightly, 2.1(3) and 3.3(2)°, respectively, relative to the central pyridine ring.

A feature common to both compounds is the disordered distribution involving only one of the two anions (NO_3^- or ClO_4^-), with the O atoms each distributed over two sites with different populations.

As regards the crystal packing, the three structures are stabilised by an extensive network of hydrogen bonds which involves the complex cations, the anions and the solvent molecules.

Selected vibrational bands of the three complexes are compared with those of unco-ordinated H_4L in Table 8. With the exception of the vibrations of the nitrate and perchlorate groups, whose frequencies agree well with their ionic nature,[41–44] a similar spectroscopic pattern for the cobalt and zinc complexes is observed, in spite of the different nature of the organic ligand. For both complexes two different absorptions

Table 5 Selected bond distances (Å) and angles (°) in compound **1**

Ni(1)–O(1)	2.15(2)	C(2)–C(4)	1.45(4)
Ni(1)–N(3)	1.94(2)	C(4)–O(2)	1.31(4)
Ni(1)–N(4)	2.11(2)	C(4)–N(4)	1.34(3)
Ni(1)–O(4$^{\mathrm{I}}$)	2.15(2)	N(4)–N(5)	1.41(3)
Ni(1)–N(8$^{\mathrm{I}}$)	2.12(2)	N(5)–C(5)	1.30(3)
Ni(1)–N(9$^{\mathrm{I}}$)	1.99(2)	C(5)–C(6)	1.56(4)
Ni(2)–Cl(1)	2.330(8)	N(11)–C(17)	1.39(4)
Ni(2)–O(5)	2.13(2)	C(17)–O(4)	1.21(3)
Ni(2)–N(5)	2.15(2)	C(17)–N(10)	1.43(4)
Ni(2)–N(6)	1.96(2)	N(10)–N(9)	1.40(3)
Ni(2)–N(7)	2.13(2)	N(9)–C(15)	1.25(4)
Ni(2)–Cl(1$^{\mathrm{I}}$)	2.444(8)	C(15)–C(14)	1.47(4)
N(1)–C(1)	1.39(4)	C(14)–O(3)	1.28(3)
C(1)–O(1)	1.23(4)	C(14)–N(8)	1.34(3)
C(1)–N(2)	1.47(4)	N(8)–N(7)	1.40(3)
N(2)–N(3)	1.40(3)	N(7)–C(12)	1.26(3)
N(3)–C(2)	1.34(4)	C(12)–C(11)	1.51(4)

O(1)–Ni(1)–N(4)	156.0(7)	N(5)–Ni(2)–N(7)	156.3(8)
N(3)–Ni(1)–N(9$^{\mathrm{I}}$)	167.9(9)	N(6)–Ni(2)–Cl(1)	175.5(7)
O(4$^{\mathrm{I}}$)–Ni(1)–N(8$^{\mathrm{I}}$)	152.9(8)	O(5)–Ni(2)–Cl(1$^{\mathrm{I}}$)	176.4(5)
N(3)–Ni(1)–N(8$^{\mathrm{I}}$)	113.9(9)	O(5)–Ni(2)–N(6)	90.5(8)
N(8$^{\mathrm{I}}$)–Ni(1)–N(9$^{\mathrm{I}}$)	75.8(9)	N(6)–Ni(2)–Cl(1$^{\mathrm{I}}$)	86.8(6)
N(9$^{\mathrm{I}}$)–Ni(1)–O(4$^{\mathrm{I}}$)	77.5(8)	Cl(1$^{\mathrm{I}}$)–Ni(2)–Cl(1)	88.7(3)
O(4$^{\mathrm{I}}$)–Ni(1)–N(3)	92.1(8)	Cl(1)–Ni(2)–O(5)	94.0(5)
C(1)–N(2)–N(3)	105(2)	N(9)–N(10)–C(17)	108(2)
Ni(1)–N(3)–N(2)	122(2)	Ni(1$^{\mathrm{I}}$)–N(9)–N(10)	118(2)
Ni(1)–N(3)–C(2)	121(2)	Ni(1$^{\mathrm{I}}$)–N(9)–C(15)	122(2)
Ni(1)–N(4)–C(4)	112(2)	Ni(1$^{\mathrm{I}}$)–N(8)–C(14)	113(2)
Ni(1)–N(4)–N(5)	133(1)	Ni(1$^{\mathrm{I}}$)–N(8)–N(7)	132(2)
Ni(2)–N(5)–N(4)	128(1)	Ni(2)–N(7)–N(8)	130(2)
Ni(2)–N(5)–C(5)	111(2)	Ni(2)–N(7)–C(12)	113(2)
Ni(2)–N(6)–C(7)	122(2)	Ni(2)–N(6)–C(11)	117(2)

Symmetry operation: I $-x, -y, -z$.

Table 6 Selected bond distances (Å) and angles (°) in compound **2**

Co–O(2)	2.132(12)	C(4)–N(4)	1.35(2)
Co–N(5)	2.202(14)	N(4)–N(5)	1.39(2)
Co–N(6)	2.151(13)	N(5)–C(5)	1.29(2)
Co–N(7)	2.196(14)	C(17)–N(11)	1.39(3)
Co–O(3)	2.136(12)	C(17)–O(4)	1.27(3)
Co–O(5)	2.225(12)	C(17)–N(10)	1.36(3)
Co–O(6)	2.137(12)	N(10)–N(9)	1.37(2)
C(1)–N(1)	1.39(3)	N(9)–C(15)	1.27(2)
C(1)–O(1)	1.24(3)	C(15)–C(16)	1.52(3)
C(1)–N(2)	1.39(2)	C(15)–C(14)	1.50(3)
N(2)–N(3)	1.37(2)	C(14)–O(3)	1.25(2)
N(3)–C(2)	1.30(2)	C(14)–N(8)	1.37(2)
C(2)–C(3)	1.53(3)	N(8)–N(7)	1.41(2)
C(2)–C(4)	1.50(3)	N(7)–C(12)	1.28(2)
C(4)–O(2)	1.23(2)		

O(2)–Co–N(5)	70.4(5)	Co–N(5)–C(5)	122(1)
N(5)–Co–N(6)	71.3(5)	N(4)–N(5)–C(5)	121(1)
N(6)–Co–N(7)	70.7(5)	N(5)–C(5)–C(7)	111(1)
N(7)–Co–O(3)	71.4(5)	C(5)–C(7)–N(6)	116(1)
O(3)–Co–O(2)	76.4(4)	C(17)–N(10)–N(9)	115(1)
O(5)–Co–O(6)	171.8(5)	N(10)–N(9)–C(15)	115(1)
Co–N(6)–C(7)	120(1)	Co–O(3)–C(14)	120(1)
Co–N(6)–C(11)	120(1)	O(3)–C(14)–N(8)	121(2)
C(7)–N(6)–C(11)	120(1)	C(14)–N(8)–N(7)	112(1)
C(1)–N(2)–N(3)	117(1)	Co–N(7)–N(8)	116(1)
N(2)–N(3)–C(2)	118(1)	Co–N(7)–C(12)	123(1)
Co–O(2)–C(4)	120(1)	N(8)–N(7)–C(12)	120(1)
O(2)–C(4)–N(4)	123(2)	N(7)–C(12)–C(11)	110(1)
C(4)–N(4)–N(5)	110(1)	C(12)–C(11)–N(6)	115(1)
Co–N(5)–N(4)	117(1)		

due to the stretching modes of the C=O group are present (cobalt, 1675 and 1610; zinc, 1675 and 1625 cm^{-1}) in agreement with the participation of only two C=O groups in the co-ordination.[45–50]

Table 7 Selected bond distances (Å) and angles (°) in compound **3**

Zn–O(2)	2.281(6)	C(4)–N(4)	1.36(1)
Zn–N(5)	2.207(7)	N(4)–N(5)	1.36(1)
Zn–N(6)	2.181(7)	N(5)–C(5)	1.29(1)
Zn–N(7)	2.227(8)	N(3)–C(2)	1.28(1)
Zn–O(3)	2.219(7)	C(2)–C(3)	1.50(1)
Zn–O(4)	2.087(7)	C(2)–C(4)	1.51(1)
Zn–O(5)	2.113(6)	C(14)–N(9)	1.35(1)
C(1)–N(1)	1.32(1)	C(14)–O(3)	1.28(1)
C(1)–O(1)	1.24(1)	C(14)–N(8)	1.39(1)
C(1)–N(2)	1.38(1)	N(8)–N(7)	1.35(1)
N(2)–N(3)	1.36(1)	N(7)–C(12)	1.28(1)
C(4)–O(2)	1.20(1)		

O(2)–Zn–N(5)	69.7(3)	C(4)–N(4)–N(5)	114.5(8)
N(5)–Zn–N(6)	70.9(3)	N(4)–N(5)–C(5)	120.2(8)
N(6)–Zn–N(7)	69.8(3)	O(1)–C(1)–N(2)	121.3(9)
N(7)–Zn–O(3)	71.5(3)	N(2)–N(3)–C(2)	116.9(8)
O(3)–Zn–O(2)	78.2(3)	Zn–N(6)–C(11)	121.1(6)
O(4)–Zn–O(5)	170.4(3)	Zn–O(3)–C(14)	116.9(7)
C(7)–N(6)–C(11)	119.2(8)	Zn–N(7)–N(8)	116.8(6)
O(1)–C(1)–N(1)	125.1(9)	Zn–N(7)–C(12)	122.3(7)
C(1)–N(2)–N(3)	117.8(8)	O(3)–C(14)–N(8)	120.1(9)
Zn–N(6)–C(7)	119.7(6)	C(14)–N(8)–N(7)	114.6(9)
Zn–O(2)–C(4)	116.6(6)	N(8)–N(7)–C(12)	120.9(8)
Zn–N(5)–N(4)	117.1(6)	N(1)–C(1)–N(2)	113.6(9)
Zn–N(5)–C(5)	122.5(6)	N(3)–C(2)–C(4)	113.7(8)
O(2)–C(4)–N(4)	122.0(9)		

Table 8 Selected vibrational bands (cm^{-1})

H$_4$L	**1**	**2**	**3**[a]	Assignment
3540 (sh)	3500 (sh)		3500 (sh)	ν(OH)
3500 (br) ms		3500 (vbr) ms	3490s	
3460ms	3420 (vbr) vs			ν(NH$_2$)
3350s	3300 (sh)	3360 (vbr) ms		
3200m (sh)		3200 (sh)	3260 (vbr) ms	
3150m (sh)			3140 (sh)	
1740s	1685 (sh)			ν(CO)
1690s	1663 (br) vs	1675s	1675s	Amide I
1665vs	1650 (sh)	1610s	1625s	
1585s	1578s		1590 (sh)	Ring
1515s	1525m (br)	1530ms	1525s	Amide II
1505 (sh)		1495ms	1490s	
1450s	1433mw	1450mw	1445ms	Ring
1430s		1420mw	1425ms	
1365m	1356ms	1375vs[b]	1365ms	
		1345m		
1290m	1268mw	1260m	1290m	Amide III

[a] ν(ClO$_4$) 1180 (sh), 1140vs, 1100 (sh) and 1075vs cm^{-1}. [b] ν(NO$_3$) 1375 cm^{-1}.

It is of note that in the spectrum of the nickel complex only one band, even if broad, is observed in the 1700–1600 cm^{-1} region (1663 cm^{-1}) which can be attributed to ν(CO), in spite of the participation of only two CO groups in the co-ordination. In this case the impossibility of distinguishing the co-ordinated and unco-ordinated CO groups is probably due to the doubly deprotonated nature of H$_4$L.

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