Spectroscopic and Magnetic Properties of Cobalt(II) and Nickel(II) Clusters obtained from 1-(Hydroxymethyl)-3,5-dimethylpyrazole. *X*-Ray Structure of Tetrakis[chloro(μ_3-3,5-dimethyl-*N*-oxymethylpyrazolato-N^2,μ_3-*O*)-(ethanol)nickel(II)]†

Frans Paap, Elisabeth Bouwman, Willem L. Driessen,* Rudolf A. G. de Graaff, and Jan Reedijk
Department of Chemistry, Gorlaeus Laboratories, State University Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

The synthesis, and spectroscopic and magnetic characterisation of four isomorphous cluster compounds of general formula [{MX(L)(EtOH)}$_4$] [L = 3,5-dimethyl-1-oxymethylpyrazolate(1−); X = Cl or Br; M = Co^{II} or Ni^{II}] is described. The compounds are formed upon reaction of 1-(hydroxymethyl)-3,5-dimethylpyrazole (HL) with the metal(II) halides in ethanol in the presence of one equivalent of KOH. The deprotonated ligand co-ordinates as a bidentate ligand through its pyrazole N^2 nitrogen and the oxy-part. The oxygen atom bridges between three metal ions, thereby forming a M_4O_4 cubane-type cluster. In the case of M = Ni the metal ions are ferromagnetically coupled, whereas in the case of M = Co antiferromagnetic coupling occurs. The presence of the cubane-type structure was confirmed by the crystal structure determination of [{NiCl(L)(EtOH)}$_4$]. The complex crystallizes in space group $P2_1/n$ with a = 12.936(6), b = 18.152(5), c = 20.79(1) Å, β = 106.23°, and Z = 4. Standard least-squares refinement gave R = 0.039 (R' = 0.047). The Ni atom has a NiO$_4$NCl chromophore in a distorted octahedral geometry. Important averaged distances are: Ni–N = 2.06, Ni–Cl = 2.35, Ni–O(EtOH) = 2.08, Ni–O = 2.08 and, Ni • • • Ni = 3.18 Å. Intramolecular hydrogen bonds between Cl (bound to one Ni) and EtOH (bound to another Ni) with average O • • • Cl contacts of 3.01 Å stabilize the cluster.

The co-ordination chemistry of pyrazoles and other nitrogen-containing heterocyclic compounds has received much attention in the last decade.[1–4] Only recently, new chelating-type ligands based on pyrazole have been reported,[5–7] using a new synthetic method.[8] A route has now been opened to new interesting co-ordination compounds. A starting material in the synthesis of 3,5-dimethylpyrazole chelates is 1-(hydroxymethyl)-3,5-dimethylpyrazole (HL). In addition to its properties as a starting compound, HL has some features which make its co-ordination chemistry worth studying, since it contains both a nitrogen and an oxygen atom in the proper orientation to chelate. The similarity with aminoalcohols[9] suggests that after deprotonation of the oxygen, which results in the formation of the anion L$^-$ (= 3,5-dimethyl-*N*-oxymethylpyrazolate), metal clusters may be formed on co-ordination.

Cluster compounds with transition metals and pyrazoles[10,11] or imidazoles[12] are known, as well as cubane-type clusters with a M_4O_4 core (M = Co, Ni, or Cu).[13–15] Cluster compounds with chelating pyrazole ligands have not yet been studied. This paper describes the first results obtained with this ligand. Using nickel and cobalt halides as the initial choice, cubane-type clusters are formed, as evidenced by spectroscopic and magnetic measurements and a single-crystal *X*-ray structure determination of the compound [{NiCl(L)(EtOH)}$_4$] (**1**).

Experimental

Starting Materials.—Commercially available solvents and metal salts were used. The ligand HL was synthesized by the reaction of 3,5-dimethylpyrazole and paraformaldehyde as described by Driessen,[8] and used after crystallization from acetonitrile.

Preparation of Complexes (**1**)—(**4**).—The nickel complexes were synthesized by dissolving the appropriate nickel salt (11.0 mmol) in warm (≈ 75°C) ethanol (20 cm^3) and adding an equivalent amount of HL dissolved in warm ethanol (15 cm^3). Finally a solution of KOH in ethanol (1 cm^3 of 2.50 g in 25 cm^3) was added. The reaction mixture was filtered and allowed to cool, upon which green crystals of [{NiX(L)(EtOH)}$_4$] [X = Cl (**1**) or Br (**2**)] separated from the bright green solution within several hours; yields 47% and 31% respectively. The analogous cobalt complexes [{CoCl(L)(EtOH)}$_4$] (**3**) and [{CoBr(L)-(EtOH)}$_4$] (**4**) were synthesized by adding a solution of an equivalent amount of $CoCl_2 \cdot 6H_2O$ ($CoBr_2 \cdot 6H_2O$) dissolved in warm ethanol (20 cm^3) to a solution of HL (10.0 mmol) in warm ethanol (10 cm^3). After adding 1.00 cm^3 of a solution of KOH in ethanol (2.50 g in 25 cm^3) and filtration the reaction mixture was allowed to cool. Within 24 h purple crystals of [{CoCl(L)(EtOH)}$_4$] or [{CoBr(L)(EtOH)}$_4$] separated from the deep blue solution; yields 23% and 56% respectively.

Physical Methods.—Infrared spectra were recorded on a Perkin-Elmer PE580 spectrophotometer (4 000—180 cm^{-1}) in KBr pellets and in Nujol mulls. Far-i.r. spectra were recorded in Nujol mulls between polythene discs on a Nicolet 7000 FT-IR instrument (450—50 cm^{-1}). Electronic spectra (2 000—300 nm) were recorded on a Perkin-Elmer UV330 spectrophotometer, operating in the diffuse-reflectance mode. Magnetic susceptibilities were measured using a Foner balance (4—80 K) and a Faraday balance (80—300 K). Elemental analyses were performed at commercial institutes (Microanalytical Laboratory of the University College, Dublin, and Canadian Microanalytical Service Ltd., Vancouver) [Found for (**1**): C, 36.10; H, 5.60; N, 10.50. $C_{32}H_{64}Cl_4N_8Ni_4O_8$ requires C, 36.20;

---

† *Supplementary data available* (No. SUP 56158, 7 pp.): H-atom co-ordinates, thermal parameters, remaining bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office. *Non-S.I. unit employed:* B.M. = 0.927 × 10^{-23} A m^2.

Table 1. Fractional co-ordinates [Ni(3), Ni(4) × 10^5; C(52), C(51′), C(52′), C(61), C(62), C(61′), C(62′), C(71′), C(72′) × 10^3; others × 10^4] with estimated standard deviations in parentheses for [{NiCl(L)(EtOH)}$_4$] (**1**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni(1)	2 705(1)	−2 971(1)	1 527(1)	C(33)	1 955(7)	−1 480(5)	3 006(5)
Ni(2)	5 101(1)	−3 355(1)	1 556(1)	C(34)	2 299(8)	−1 808(6)	3 617(5)
Ni(3)	46 872(8)	−21 986(6)	25 905(5)	C(35)	3 289(8)	−2 111(5)	3 659(4)
Ni(4)	41 154(8)	−17 712(6)	10 508(5)	C(36)	963(7)	−1 062(5)	2 694(5)
Cl(5)	1 111(2)	−2 507(1)	803(1)	C(37)	4 038(7)	−2 527(5)	4 228(4)
Cl(6)	4 647(2)	−4 577(1)	1 209(1)	C(40)	3 395(7)	−3 034(4)	226(4)
Cl(7)	6 165(2)	−2 609(1)	3 454(1)	N(41)	4 096(5)	−2 633(4)	−97(3)
Cl(8)	4 722(2)	−559(1)	1 311(1)	N(42)	4 591(5)	−1 993(4)	198(3)
O(01)	4 148(4)	−3 247(3)	2 210(2)	C(43)	5 127(7)	−1 737(5)	−214(5)
O(02)	5 387(4)	−2 255(3)	1 797(2)	C(44)	4 996(8)	−2 205(6)	−766(5)
O(03)	3 372(4)	−1 916(3)	1 812(2)	C(45)	4 329(7)	−2 754(5)	−681(4)
O(04)	3 718(4)	−2 871(3)	907(2)	C(46)	5 772(8)	−1 050(5)	−68(5)
C(10)	4 045(7)	−3 800(4)	2 647(4)	C(47)	3 881(8)	−3 415(6)	−1 104(5)
N(11)	2 950(6)	−3 738(4)	2 756(3)	O(50)	2 446(5)	−4 034(3)	1 153(3)
N(12)	2 174(6)	−3 323(3)	2 328(3)	C(51)	1 444(10)	−4 398(9)	909(13)
C(13)	1 287(7)	−3 442(5)	2 534(5)	C(52)	144(2)	−512(1)	59(1)
C(14)	1 497(8)	−3 911(5)	3 066(5)	C(51′)	183(3)	−466(1)	120(2)
C(15)	2 551(8)	−4 100(5)	3 199(4)	C(52′)	135(3)	−459(2)	45(2)
C(16)	279(7)	−3 018(6)	2 211(5)	O(60)	6 300(5)	−3 705(3)	2 402(3)
C(17)	3 245(8)	−4 585(5)	3 730(4)	C(61)	713(2)	−420(2)	235(2)
C(20)	6 436(7)	−2 067(4)	1 839(4)	C(62)	786(3)	−429(2)	303(1)
N(21)	6 783(6)	−2 486(4)	1 325(3)	C(61′)	729(2)	−410(1)	260(1)
N(22)	6 262(5)	−3 125(4)	1 087(3)	C(62′)	712(3)	−488(2)	277(1)
C(23)	6 792(8)	−3 403(6)	669(5)	O(70)	5 247(5)	−1 115(3)	2 726(3)
C(24)	7 620(8)	−2 935(6)	653(5)	C(71)	5 202(12)	−626(9)	3 245(8)
C(25)	7 618(7)	−2 363(6)	1 069(5)	C(72)	6 164(15)	−163(15)	3 497(14)
C(26)	6 429(8)	−4 091(6)	295(5)	C(71′)	585(2)	−82(1)	336(1)
C(27)	8 344(7)	−1 725(5)	1 270(6)	C(72′)	557(3)	−4(2)	321(2)
C(30)	2 768(6)	−1 372(4)	2 021(4)	O(80)	2 636(4)	−1 372(3)	475(3)
N(31)	2 711(6)	−1 608(4)	2 696(3)	C(81)	2 421(8)	−1 036(5)	−173(5)
N(32)	3 558(5)	−1 994(4)	3 097(4)	C(82)	1 381(10)	−667(6)	−397(5)

Primed atoms are equivalent atoms in different positions within the disordered EtOH molecules.

H, 5.70; N, 10.55%. Found for (**2**): C, 30.05; H, 4.95; N, 9.05. $C_{32}H_{64}Br_4N_8Ni_4O_8$ requires C, 31.00; H, 4.90; N, 9.05%. Found for (**3**): C, 34.65; H, 5.25; N, 10.85. $C_{32}H_{64}Cl_4Co_4N_8O_8$ requires C, 36.20; H, 5.70; N, 10.55%. Found for (**4**): Co, 18.8. $C_{32}H_{64}Br_4Co_4N_8O_8$ requires Co, 19.0%].

Crystal Structure Determination.—Crystals of [{NiCl(L)(EtOH)}$_4$] (**1**), suitable for *X*-ray analysis, could be obtained from the reaction mixture.

Crystal data. $C_{32}H_{64}Cl_4N_8Ni_4O_8$, M = 1 065.52, monoclinic, a = 12.936(6), b = 18.152(5), c = 20.79(1) Å, β = 106.23°, U = 4 152.9 Å^3 (as determined by measuring 24 independent $h\,k\,l$ reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), D_m = 1.65 g cm^{-3}, Z = 4, D_c = 1.70 g cm^{-3}. Green box-shaped crystal. Crystal dimensions 0.45 × 0.21 × 0.15 mm, μ(Mo-K_α) = 20.28 cm^{-1}.

Data collection. CAD-4 diffractometer, ω/θ scan mode with ω scan width = 0.60 + tan θ, using Mo-K_α radiation. Transmission factors between 0.69 and 0.80, correction for absorption was applied following the method given by de Graaff.[16] Using a θ range of 2—22°, the independent section of the reciprocal lattice segment, h, k, l, −13 to 13, 0 to 19, and 0 to 21 respectively, was covered. 6 158 Reflections were measured, of which 5 963 were independent; 3 227 reflections with $I \geqslant 2\sigma(I)$ as obtained from counting statistics were used for analysis. For these data, $R_{int.}$ = 0.024.

Structure analysis and refinement. Direct methods were followed by Fourier and least-squares routines. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and the hydrogens with one overall $B_{iso.}$ (2.0 Å^2). In difference-Fourier maps 19 hydrogens could be found, among which were the hydrogens bonded to the ethanol oxygens. All other hydrogens were placed in idealized, calculated positions. A weighting scheme of the form $w = 1/\sigma^2[I(H)]$ $\{\sigma^2[I(H)] = \sigma^2$ from counting statistics + $0.033\ F^2(H)\}$ was used. Three of the four ethanol molecules appeared to be disordered into several non-equivalent positions of which two were refined. Because of this effect, some electron density remained in the final difference-Fourier map. Final values for R $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}\}$ were 0.039 and 0.047 respectively. A set of standard programs, written and modified by E. Rutten-Keulemans and R. A. G. de Graaff for use on the local Amdahl computer, was used for the calculations. Table 1 lists the final atomic co-ordinates for the non-hydrogen atoms.

Results and Discussion

Description of the Structure of [{NiCl(L)(EtOH)}$_4$] (**1**).—The compound [{NiCl(L)(EtOH)}$_4$] (**1**) has a cubane-like Ni_4O_4 core consisting of two interpenetrating tetrahedra of different dimensions with nickel–nickel distances of 3.18 Å and oxygen–oxygen distances of 2.68 Å. As a result the Ni–O bond angles around the oxygens and around the nickel atoms are 99 and 80°, respectively. The nickel(II) ions are in a distorted octahedral environment with a NiO$_3$NO′Cl chromophore, and do not show unusual features. A projection of the tetranuclear unit is depicted in the Figure. Table 2 lists selected bond lengths and relevant hydrogen-bond contacts, whereas relevant bond angles are given in Table 3. Other geometric information is given as SUP 56158.

The four pyrazole rings are planar (largest deviation from the

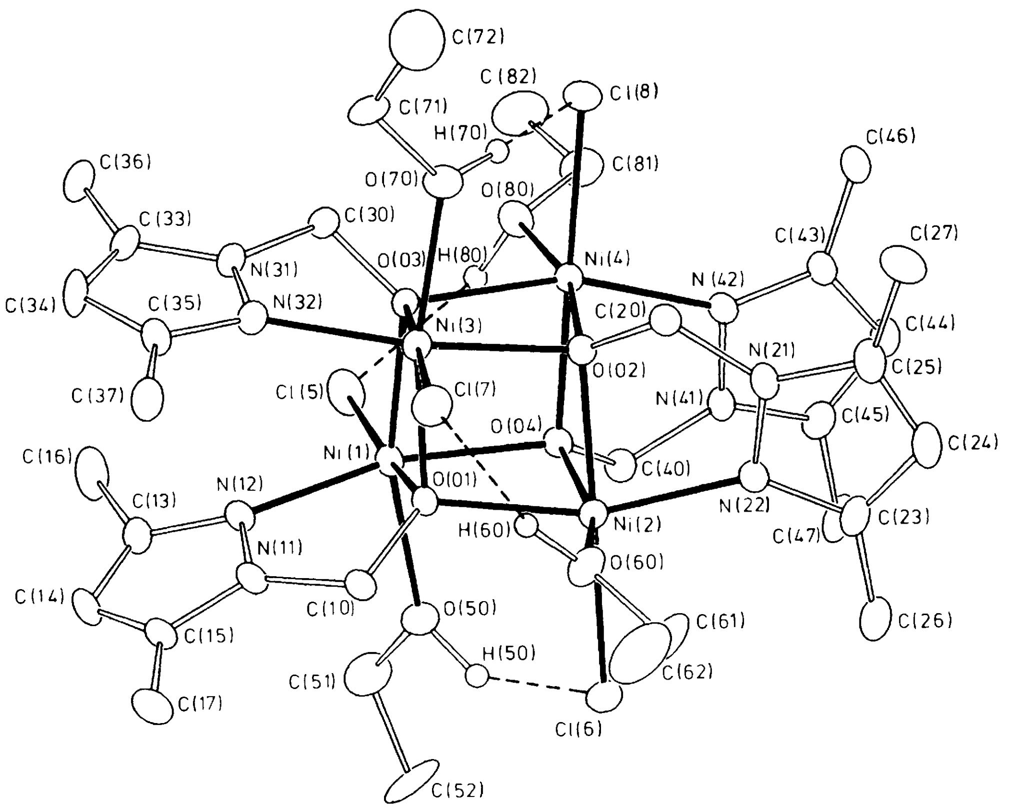

Figure. Projection of the tetranuclear unit of (**1**). Hydrogen atoms of the pyrazole ligands and ethanol have been omitted for clarity. Intramolecular hydrogen-bond interactions between ethanol oxygens and Cl^- anions are indicated by dashed lines

Table 2. Selected bond lengths and hydrogen bridge contacts (Å) with estimated standard deviations for $[\{NiCl(L)(EtOH)\}_4]$ (**1**)

Ni(1)–Cl(5)	2.343(2)	Ni(3)–Cl(7)	2.347(2)
Ni(1)–O(01)	2.065(5)	Ni(3)–O(03)	2.058(5)
Ni(1)–O(03)	2.114(5)	Ni(3)–O(01)	2.101(5)
Ni(1)–O(04)	2.089(5)	Ni(3)–O(02)	2.096(5)
Ni(1)–N(12)	2.073(7)	Ni(3)–N(32)	2.061(7)
Ni(1)–O(50)	2.069(6)	Ni(3)–O(70)	2.085(5)
Ni(2)–Cl(6)	2.352(2)	Ni(4)–Cl(8)	2.345(2)
Ni(2)–O(02)	2.065(5)	Ni(4)–O(04)	2.059(5)
Ni(2)–O(01)	2.086(5)	Ni(4)–O(02)	2.110(5)
Ni(2)–O(04)	2.107(5)	Ni(4)–O(03)	2.087(5)
Ni(2)–N(22)	2.050(7)	Ni(4)–N(42)	2.074(7)
Ni(2)–O(60)	2.092(6)	Ni(4)–O(80)	2.082(5)
Cl(5)–O(80)	3.056(6)	Cl(7)–O(60)	2.996(6)
Cl(6)–O(50)	2.986(6)	Cl(8)–O(70)	3.004(6)

least-squares planes through the respective ring atoms is 0.0095 Å) and are situated on two opposite sides of the cluster framework. The angle between each pair of pyrazole rings is 22°. Between the pyrazole rings, through the centre of the cluster framework, runs a pseudo-two-fold axis.

The distance between the pyrazole rings on the same side of the framework is 3.4 Å, which in combination with the above-mentioned angle of only 22° suggests that some interaction between the pyrazoles occurs, giving additional stabilization to the tetrameric molecule. Relatively strong hydrogen bridges are formed between the chloride of one nickel(II) ion and the ethanolic oxygen of a second nickel(II) ion in the same cluster. These intramolecular hydrogen bonds apparently contribute to the stability of the cluster. This suggests that ligands other than ethanol with a similar hydrogen-bond donor function may form similar or related cluster-type compounds.

The Ni_4O_4 core of the tetramer described by Andrew and Blake,[13] $[\{Ni(OMe)(o\text{-}OC_6H_4CHO)(EtOH)\}_4]$, also consists of interpenetrating nickel and oxygen tetrahedra. The resulting cubane-like core also has T_d symmetry with Ni–O distances of 2.04 Å and Ni–O–Ni and O–Ni–O angles of 98 and 82° respectively. Differences arise in the co-ordination modes of the salicylate ligand, which chelates to one nickel ion only, and the methoxide ligand, which binds to three nickel ions.

The packing of the tetrameric units in the crystal lattice is determined mainly by van der Waals forces and no unusual contacts have been observed.

Spectroscopic and Magnetic Measurements.—As mentioned above, related compounds with almost the same properties have been found starting from cobalt chloride, cobalt bromide, or nickel bromide. The spectroscopic and magnetic properties of the four compounds $[\{NiCl(L)(EtOH)\}_4]$ (**1**), $[\{NiBr(L)(EtOH)\}_4]$ (**2**), $[\{CoCl(L)(EtOH)\}_4]$ (**3**), and $[\{CoBr(L)(EtOH)\}_4]$ (**4**) have been studied and the relevant data are presented in Table 4.

The four complexes have very similar i.r. spectra, only differing significantly in the far-i.r. region. In combination with the almost identical *X*-ray powder diffraction patterns (intensities, lineshapes, and *d* spacings), it can be concluded that the four compounds are isomorphous and thus have the same tetranuclear structures. The assignments for the M–X vibrations in the far-i.r. (Table 4) agree with those known for other octahedral metal–halogen vibrations.[17] All four compounds show typical octahedral ligand-field spectra (see Table 4). The *Dq* value of (**1**) (870 cm^{-1}) is somewhat larger than that

Table 3. Selected bond angles (°) with estimated standard deviations for [{NiCl(L)(EtOH)}$_4$] (**1**)

Cl(5)–Ni(1)–O(01)	172.8(2)	Cl(7)–Ni(3)–O(03)	175.9(2)	Cl(6)–Ni(2)–N(22)	101.5(2)	Cl(8)–Ni(4)–N(42)	102.6(2)
Cl(5)–Ni(1)–O(03)	94.1(2)	Cl(7)–Ni(3)–O(01)	96.6(2)	Cl(6)–Ni(2)–O(60)	92.1(2)	Cl(8)–Ni(4)–O(80)	90.1(2)
Cl(5)–Ni(1)–O(04)	99.4(2)	Cl(7)–Ni(3)–O(02)	98.5(2)	O(02)–Ni(2)–O(01)	81.3(2)	O(04)–Ni(4)–O(02)	79.4(2)
Cl(5)–Ni(1)–N(12)	101.3(2)	Cl(7)–Ni(3)–N(32)	102.0(2)	O(02)–Ni(2)–O(04)	79.3(2)	O(04)–Ni(4)–O(03)	80.8(2)
Cl(5)–Ni(1)–O(50)	94.1(2)	Cl(7)–Ni(3)–O(70)	91.0(2)	O(02)–Ni(2)–N(22)	79.3(3)	O(04)–Ni(4)–N(42)	79.0(2)
O(01)–Ni(1)–O(03)	78.9(2)	O(03)–Ni(3)–O(01)	79.3(2)	O(02)–Ni(2)–O(60)	92.8(2)	O(04)–Ni(4)–O(80)	95.0(2)
O(01)–Ni(1)–O(04)	80.9(2)	O(03)–Ni(3)–O(02)	80.6(2)	O(01)–Ni(2)–O(04)	80.0(2)	O(03)–Ni(4)–O(02)	79.7(2)
O(01)–Ni(1)–N(12)	79.2(2)	O(03)–Ni(3)–N(32)	79.0(2)	O(01)–Ni(2)–N(22)	159.6(3)	O(03)–Ni(4)–N(42)	159.3(2)
O(01)–Ni(1)–O(50)	93.1(2)	O(03)–Ni(3)–O(70)	92.9(0)	O(01)–Ni(2)–O(60)	85.1(2)	O(03)–Ni(4)–O(80)	86.2(2)
O(03)–Ni(1)–O(04)	79.4(2)	O(01)–Ni(3)–O(02)	80.2(2)	O(04)–Ni(2)–N(22)	102.4(2)	O(02)–Ni(4)–N(42)	101.0(2)
O(03)–Ni(1)–N(12)	104.8(2)	O(01)–Ni(3)–N(32)	98.5(2)	O(04)–Ni(2)–O(60)	164.0(2)	O(02)–Ni(4)–O(80)	165.6(2)
O(03)–Ni(1)–O(50)	163.4(2)	O(01)–Ni(3)–O(70)	165.7(2)	N(22)–Ni(2)–O(60)	89.6(3)	N(42)–Ni(4)–O(80)	91.2(2)
O(04)–Ni(1)–N(12)	158.5(2)	O(02)–Ni(3)–N(32)	159.5(3)				
O(04)–Ni(1)–O(50)	85.0(2)	O(02)–Ni(3)–O(70)	86.7(2)	Ni(1)–O(01)–Ni(2)	99.3(2)	Ni(3)–O(03)–Ni(1)	100.2(2)
N(12)–Ni(1)–O(50)	87.7(3)	N(32)–Ni(3)–O(70)	91.8(3)	Ni(1)–O(01)–Ni(3)	100.4(2)	Ni(3)–O(03)–Ni(4)	99.9(2)
Cl(6)–Ni(2)–O(02)	175.1(2)	Cl(8)–Ni(4)–O(04)	173.9(2)	Ni(2)–O(01)–Ni(3)	97.9(2)	Ni(1)–O(03)–Ni(4)	98.0(2)
Cl(6)–Ni(2)–O(01)	98.4(2)	Cl(8)–Ni(4)–O(02)	94.5(2)	Ni(2)–O(02)–Ni(3)	98.7(2)	Ni(4)–O(04)–Ni(1)	99.7(2)
Cl(6)–Ni(2)–O(04)	95.8(2)	Cl(8)–Ni(4)–O(03)	98.0(1)	Ni(2)–O(02)–Ni(4)	100.0(2)	Ni(4)–O(04)–Ni(2)	100.3(2)
				Ni(3)–O(03)–Ni(4)	98.0(2)	Ni(1)–O(04)–Ni(2)	97.8(2)

Table 4. Spectroscopic and magnetic data of compounds [{MX(L)(EtOH)}$_4$]

		(**1**)	(**2**)	(**3**)	(**4**)	HL
Ligand-field absorption bands (maxima) (in 10^3 cm^{-1})	σ_1	8.7	8.4	7.8	7.7	
	σ_2	14.7	14.4	15.2	15.1	
	σ_3	23.9	23.6	18.3	18.5	
Far-i.r. (cm^{-1}) absorption bands		485	484		471	473
		471	470	465	460	447
		394^a	394^a	370^a	369^a	
						326
		344	342	323	324	
		306	302	299	296	302
						271
		256^b	214^b	249^b	200^b	
						214
		192	173	173	171	193
		142	133	133	147	138
					103	113
Magnetic data	$\mu_{eff.}$(10 K)/B.M.	3.62	4.24	^{c}	^{c}	
	$\mu_{eff.}$(300 K)/B.M.	3.3	3.2	5.1	^{c}	
	θ(80—300 K)/K	9.6(9)	8.3(2)	−6.1(2)	−5.5(1)^d	

^{a} ν(M–O) (tentatively assigned). ^{b} ν(M–X). ^{c} Not measured. ^{d} θ(80—200 K).

of (**2**) (850 cm^{-1}), in agreement with a stronger ligand field for Cl compared to Br. The *Dq* values of the cobalt compounds follow the same trend and in fact confirm the isomorphism.

The metal ions are held together in a cubane-type unit at rather short distances [3.18 Å for (**1**)], with bridging oxygen atoms and additional hydrogen bridges. Therefore it seemed interesting to study the possible presence of magnetic exchange interactions. The analysis of the magnetic susceptibilities at low temperatures has resulted in the parameters given in Table 4. Despite the relatively short metal–metal contacts only small interactions were detected, as can be concluded from the small θ values. In contrast to the slight antiferromagnetic behaviour of the cobalt compounds (**3**) and (**4**), the nickel compounds (**1**) and (**2**) show a ferromagnetic behaviour, a phenomenon which has been observed earlier.[18]

Conclusions

The results presented above have shown that the ligand (L$^-$) has interesting properties as a chelating ligand. It appears that the oxygen atom is able to form linkages to three different metal ions. Such behaviour is also known to occur for deprotonated aminoalcohols.[9,15] The cubane-type clusters seem to gain additional stabilization from intramolecular hydrogen-bond formations of the type –OH ··· Cl and –OH ··· Br (see Figure). This suggests that variation of the ligands and the anions is possible, and opens the route to a variety of other new compounds. A study of these and other compounds with a M_4O_4 chromophore may provide a better knowledge of, and insight into, the nature of the magnetic exchange which occurs in such M_4X_4 clusters. Investigations of this type are in process in our laboratories.

Acknowledgements

The authors are indebted to Mr. S. Gorter for assistance with the *X*-ray data collection, to Mr. G. H. Renes and Mr. R. de Groot for the magnetic susceptibility measurements, and to Mr. G. C. Schoemaker (University of Amsterdam) for the far-i.r. spectra.

References

1 S. Trofimenko, *Adv. Chem. Ser.*, 1976, **150**, 289.
2 R. J. Sundberg, D. C. Mente, and I. Yilmaz, *J. Heterocycl. Chem.*, 1977, **14**, 1279.

3 M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
4 'Copper Coordination Chemistry; Biochemical and Inorganic Perspectives,' eds. K. Karlin and J. Zubieta, Adenine Press, New York, 1983.
5 J. W. F. M. Schoonhoven, W. L. Driessen, J. Reedijk, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1053.
6 T. N. Sorrell and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 1014.
7 F. Mani and C. Mealli, *Inorg. Chim. Acta*, 1982, **63**, 97.
8 W. L. Driessen, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 441.
9 G. Nieuwpoort and J. Reedijk, *Transition Met. Chem.*, 1982, **7**, 321.
10 R. W. M. ten Hoedt and J. Reedijk, *Inorg. Chim. Acta*, 1981, **51**, 23.
11 F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1983, 539.
12 J. C. Jansen, H. van Koningsveld, and J. Reedijk, *Nature (London)*, 1977, **269**, 318.
13 J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1969, 1457.
14 J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240.
15 K. Smolander, *Acta Chem. Scand., Ser. A*, 1982, **36**, 189.
16 R. A. G. de Graaff, *Acta Crystallogr., Sect. A*, 1973, **29**, 298.
17 D. M. Adams, 'Metal-Ligand and Related Vibrations,' Edward-Arnold, London, 1967.
18 G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot, and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 1404.

Received 29*th June* 1984; *Paper* 4/1116