

## A novel tridentate co-ordination mode for the carbonatonickel system

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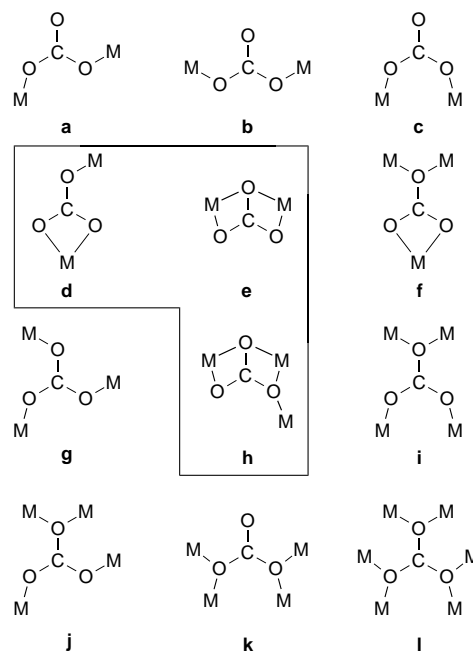
The trinuclear compound  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{dmpd})_4(\text{H}_2\text{O})][\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$  was obtained from the reaction of basic solutions of nickel(II) perchlorate and 2,2-dimethylpropane-1,3-diamine (dmpd) with atmospheric  $\text{CO}_2$ . It crystallises in the orthorhombic system, space group  $Pcab$ , with  $a = 18.634(10)$ ,  $b = 25.447(8)$ ,  $c = 25.598(4)$  Å,  $Z = 8$ ,  $R = 0.0437$ . The three nickel atoms show octahedral co-ordination with three different environments,  $\text{Ni}(\text{CO}_3\text{-}O, O')(\text{dmpd})_2$ ,  $\text{Ni}(\text{CO}_3\text{-}O')(\text{dmpd})_2(\text{H}_2\text{O})$  and  $\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2$ . The carbonate anion acts as a bridge between two nickel ions whereas the  $[\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2]^{2+}$  subunit is linked by hydrogen bonds to the dinuclear group. The dinuclear  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{dmpd})_4(\text{H}_2\text{O})]^{2+}$  subunit shows a moderately weak antiferromagnetic coupling with a  $J$  value of  $-7.8 \text{ cm}^{-1}$ . The tridentate co-ordination mode found in the carbonate ligand has not previously been reported for nickel. Its magnetic behaviour is discussed.

The co-ordination chemistry of the carbonate anion has received considerable attention in the past few years and a number of polynuclear carbonate-bridged metal systems in which the metal is a first-row transition-metal cation have been structurally characterised<sup>1</sup> in relation to bioinorganic models and catalytic studies (or also due to the accidental reaction of basic solutions with atmospheric  $\text{CO}_2$ ). Copper carbonate compounds offer examples of a wide range of nuclearity from two-dimensional to dinuclear systems,<sup>2,3</sup> but for the remaining cations the most common nuclearity is two;<sup>1</sup> as far as we know, twelve co-ordination modes have been structurally characterised for this extremely versatile ligand (Scheme 1).

The nickel-carbonate system remains poorly explored to date and the co-ordination modes previously described for the carbonate ion when it acts as a bridge in polynuclear nickel compounds are **e** (the most common)<sup>4-8</sup> and **h** (one compound).<sup>9</sup> Mode **h** has three superexchange pathways, which correspond to two 'e' and one 'd' simultaneous interactions. Magnetically the two **e** and **h** co-ordination modes are similar, showing very strong antiferromagnetic behaviour with typical  $J$  values close to  $-80 \text{ cm}^{-1}$  for this kind of nickel(II) compound.<sup>4,5,9</sup>

The fixation of atmospheric  $\text{CO}_2$  with basic solutions of nickel derivatives was systematically studied by Tanase *et al.*<sup>10</sup> for *N*-alkyl-substituted ethane-1,2-diamine ligands with the aim of analysing the substituent effect on the  $\text{CO}_2$  uptake. Effective fixation was only obtained by using *N,N*-dimethylethylenediamine (*N,N*-dmen) and perchlorate as counter anion. A triangular arrangement of three nickel atoms was reported for the compound  $[\text{Ni}_3(\text{N,N-dmen})_6(\text{CO}_3)(\text{H}_2\text{O})_4][\text{ClO}_4]_4$ , in which one of the nickel atoms has a  $[\text{Ni}(\text{N,N-dmen})_2(\text{CO}_3)]$  environment whereas the other two have *cis*- $[\text{Ni}(\text{N,N-dmen})_2(\text{H}_2\text{O})_2]^{2+}$  co-ordination, but in this compound the carbonate does not act as a bridge but only supports the four hydrogen bonds which permit the triangular arrangement. For a large number of diamines explored in the above work tris(diamine)nickel(II) complexes were obtained without reaction with  $\text{CO}_2$ .<sup>10</sup>

Recently, using reaction of solutions of propane-1,3-diamine derivatives with copper or nickel(II), we structurally and magnetically characterised some triangular compounds in which



Scheme 1

the carbonato bridge acts as a tridentate<sup>11</sup> (M = copper, co-ordination mode **g**, ferromagnetic) or pentadentate<sup>9</sup> ligand linked to three nickel atoms (co-ordination mode **h**, strongly antiferromagnetic). Continuing with our systematic research in this field, several alkyl-substituted propanediamines were used as starting reagents with different nickel salts in order to study the ability of this system to fix atmospheric  $\text{CO}_2$ . The reaction fails for propane-1,2- and -1,3-diamine and 2-methylpropane-1,2-diamine due to the formation of the tris(amine)nickel compounds, whereas with *N*-methyl-, *N,N*-dimethyl-, *N,N*-diethyl-, *N,N,N,N*-tetramethyl-, *N,N,N*-trimethyl- and *N,N,N*,2-tetramethyl-propane-1,3-diamine, partial precipitation of nickel(II) hydroxide occurs and effective reaction with atmospheric  $\text{CO}_2$  was not observed. The only reaction which allows a carbonate complex started from 2,2-dimethylpropane-1,3-diamine and perchlorate as counter anion.

† WWW: ub.es/inorgani/molmag.htm

In this work we present the synthesis, structure and magnetic properties of the first nickel(II) compound for which co-ordination mode **d** of the carbonate bridge has been structurally characterised. The lower antiferromagnetic behaviour of the new pathway **d** in comparison with the previously reported **e** and **h** is discussed.

## Experimental

### Synthesis

2,2-Dimethylpropane-1,3-diamine (6 mmol) (dmpd) was added in drops to a stirred aqueous ethanol solution (1:1, 60 cm<sup>3</sup>) of nickel perchlorate hexahydrate (2 mmol, 0.73 g). The resulting blue mixture was stirred at room temperature for 24 h under atmospheric conditions. Slow evaporation gave blue crystals suitable for X-ray determination after several days. The same compound was obtained by mixing the nickel perchlorate solution with 2,2-dimethylpropane-1,3-diamine (4 mmol) and a small excess of diethylamine (Found: C, 28.2; H, 7.1; N, 12.9. Calc. for C<sub>31</sub>H<sub>92</sub>Cl<sub>4</sub>N<sub>12</sub>Ni<sub>3</sub>O<sub>23</sub>: C, 28.2; H, 6.95; N, 12.75%). When the reaction was tried with other nickel salts (chloride, bromide, nitrate or sulfate), only very little fixation of CO<sub>2</sub> was observed and a characterisable compound could only be obtained from the perchlorate salt.

### Spectral and magnetic measurements

Infrared spectra were recorded on a Nicolet 520 FTIR spectrophotometer. Magnetic measurements were carried out on polycrystalline samples with a pendulum-type magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat working in the 300–4 K range under a magnetic field of approximately 1.5 T. Diamagnetic corrections were estimated from Pascal tables.

### X-Ray crystallography

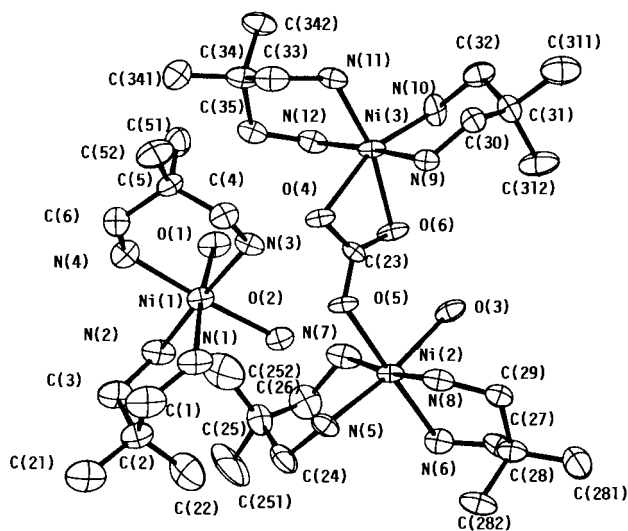
A prismatic blue crystal (0.1 × 0.1 × 0.2 mm) of [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][ClO<sub>4</sub>]<sub>4</sub>·H<sub>2</sub>O was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections (12 < θ < 21°) and refined by the least-squares method. Intensities were collected at 293(2) K with graphite-monochromatised Mo-Kα radiation (λ 0.710 69 Å), using the ω-2θ scan technique. 17 570 Reflections were measured in the range 1.57 < θ < 29.94°, 6178 of which were assumed observed applying the condition *I* > 2σ(*I*). Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarisation but not absorption corrections were made. The crystallographic data, collection conditions, and relevant features of the structure refinement are listed in Table 1. The structure was solved by Patterson synthesis, using the SHELXS computer program<sup>12</sup> and refined by full-matrix least squares, with SHELXL 93.<sup>13</sup> The function minimised was  $\sum w||F_o|^2 - |F_c|^2|^2$ , where  $w = [\sigma^2(I) + (0.0894P)^2]^{-1}$  and  $P = (|F_o|^2 + 2|F_c|^2)/3$ . Values of *f*, *f'* and *f''* were taken from ref. 14. Hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter, using a riding model for atoms linked to C or N; the seven remaining H atoms linked to oxygen (water molecules) were not located. The number of parameters refined was 630. The final *R* (on *F*) factor was 0.0437 for 17 477 reflections. Maximum shift/e.s.d. = 1.4, mean = 0.15. Maximum and minimum peaks in the final difference synthesis were 0.699 and -0.763 e Å<sup>-3</sup>, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/304.

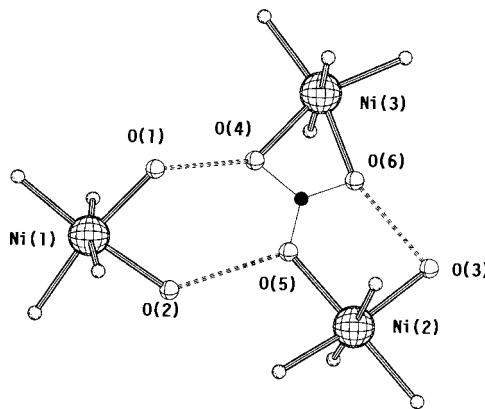
**Table 1** Crystal data for [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][ClO<sub>4</sub>]<sub>4</sub>·H<sub>2</sub>O

Formula	C <sub>31</sub> H <sub>92</sub> Cl <sub>4</sub> N <sub>12</sub> Ni <sub>3</sub> O <sub>23</sub>
<i>M</i>	1347.06
Crystal symmetry	Orthorhombic
Space group	<i>Pcab</i>
<i>a</i> /Å	18.634(11)
<i>b</i> /Å	25.447(8)
<i>c</i> /Å	25.598(4)
<i>U</i> /Å <sup>3</sup>	12 138(8)
<i>Z</i>	8
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.439
μ(Mo-Kα)/cm <sup>-1</sup>	11.74
<i>R</i> <sup>a</sup>	0.0437
<i>R</i> <sup>b</sup>	0.112

$$^a R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R'(F_o)^2 = \{ \sum w(F_o)^2 - (F_o)^2 \}^2 / \sum w(F_o)^4 \}^{1/2}.$$



**Fig. 1** An ORTEP<sup>15</sup> drawing of [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][ClO<sub>4</sub>]<sub>4</sub>·H<sub>2</sub>O with the atom labelling scheme. Thermal ellipsoids are at the 50% probability level



**Fig. 2** Hydrogen-bonding scheme for [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][ClO<sub>4</sub>]<sub>4</sub>·H<sub>2</sub>O

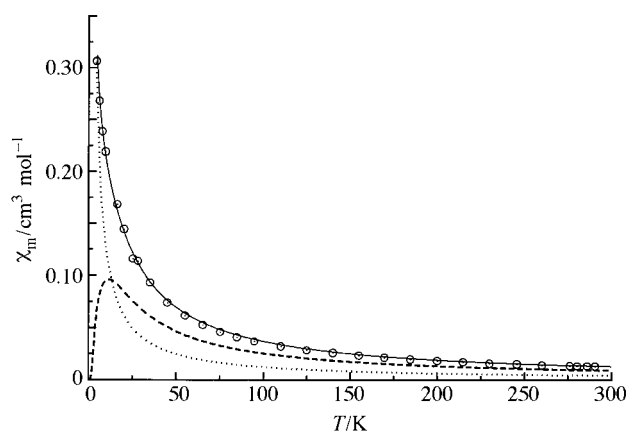
## Results and Discussion

### Structure of [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][ClO<sub>4</sub>]<sub>4</sub>·H<sub>2</sub>O

The structure consists of trimeric units of the cationic compound {[Ni<sub>2</sub>(μ-CO<sub>3</sub>)(dmpd)<sub>4</sub>(H<sub>2</sub>O)][Ni(dmpd)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]}<sup>4+</sup>, four perchlorate counter anions and one water molecule of crystallisation. The main bond lengths and angles are in Table 2. A labelled diagram is shown in Fig. 1. Each trimeric unit consists of monomeric and dinuclear cationic subunits related by hydrogen bonds, as is schematised in Fig. 2. The monomeric

**Table 2** Main bond lengths (Å) and angles (°) for  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{dmpd})_4(\text{H}_2\text{O})][\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$

Nickel environments			
Monomeric subunit			
Ni(1)–N(3)	2.056(4)	Ni(1)–N(1)	2.111(4)
Ni(1)–N(2)	2.082(4)	Ni(1)–O(1)	2.136(3)
Ni(1)–N(4)	2.098(5)	Ni(1)–O(2)	2.173(4)
Dimeric subunit			
Ni(2)–N(5)	2.059(4)	Ni(3)–N(10)	2.030(4)
Ni(2)–N(7)	2.099(4)	Ni(3)–N(11)	2.079(4)
Ni(2)–N(8)	2.108(4)	Ni(3)–N(9)	2.093(4)
Ni(2)–N(6)	2.121(4)	Ni(3)–O(6)	2.138(3)
Ni(2)–O(5)	2.174(3)	Ni(3)–N(12)	2.137(4)
Ni(2)–O(3)	2.184(5)	Ni(3)–O(4)	2.174(3)
Carbonato bridge			
C(23)–O(6)	1.240(6)	C(23)–O(4)	1.314(5)
C(23)–O(5)	1.289(5)		
Monomeric unit			
N(3)–Ni(1)–N(2)	172.0(2)	N(4)–Ni(1)–O(1)	88.8(2)
N(3)–Ni(1)–N(4)	91.9(2)	N(1)–Ni(1)–O(1)	171.1(2)
N(2)–Ni(1)–N(4)	92.8(2)	N(3)–Ni(1)–O(2)	87.3(2)
N(3)–Ni(1)–N(1)	95.9(2)	N(2)–Ni(1)–O(2)	87.3(2)
N(2)–Ni(1)–N(1)	89.6(2)	N(4)–Ni(1)–O(2)	173.9(2)
N(4)–Ni(1)–N(1)	99.4(2)	N(1)–Ni(1)–O(2)	86.7(2)
N(3)–Ni(1)–O(1)	87.3(2)	O(1)–Ni(1)–O(2)	85.2(1)
N(2)–Ni(1)–O(1)	86.3(2)		
Dimeric subunit			
N(5)–Ni(2)–N(7)	90.9(2)	N(10)–Ni(3)–N(11)	100.8(2)
N(5)–Ni(2)–N(8)	93.6(2)	N(10)–Ni(3)–N(9)	91.0(2)
N(7)–Ni(2)–N(8)	173.2(2)	N(11)–Ni(3)–N(9)	92.3(2)
N(5)–Ni(2)–N(6)	95.6(2)	N(10)–Ni(3)–O(6)	95.4(2)
N(7)–Ni(2)–N(6)	95.2(2)	N(11)–Ni(3)–O(6)	163.8(2)
N(8)–Ni(2)–N(6)	89.4(2)	N(9)–Ni(3)–O(6)	87.8(2)
N(5)–Ni(2)–O(5)	84.9(2)	N(10)–Ni(3)–N(12)	92.3(2)
N(7)–Ni(2)–O(5)	87.9(2)	N(11)–Ni(3)–N(12)	88.8(2)
N(8)–Ni(2)–O(5)	87.4(2)	N(9)–Ni(3)–N(12)	176.3(2)
N(6)–Ni(2)–O(5)	176.8(2)	O(6)–Ni(3)–N(12)	90.2(2)
N(5)–Ni(2)–O(3)	172.4(2)	N(10)–Ni(3)–O(4)	156.4(2)
N(7)–Ni(2)–O(3)	83.4(2)	N(11)–Ni(3)–O(4)	102.8(2)
N(8)–Ni(2)–O(3)	91.6(2)	N(9)–Ni(3)–O(4)	88.6(1)
N(6)–Ni(2)–O(3)	90.0(2)	O(6)–Ni(3)–O(4)	61.0(1)
O(5)–Ni(2)–O(3)	89.8(1)	N(12)–Ni(3)–O(4)	87.8(2)
Carbonato bridge			
O(6)–C(23)–O(5)	124.5(4)	C(23)–O(4)–Ni(3)	88.7(3)
O(6)–C(23)–O(4)	118.0(4)	C(23)–O(5)–Ni(2)	126.8(3)
O(5)–C(23)–O(4)	117.5(5)	C(23)–O(6)–Ni(3)	92.3(3)



**Fig. 3** Plot of  $\chi_m$  vs.  $T$  for  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{dmpd})_4(\text{H}_2\text{O})][\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$ . The solid line shows the best fit obtained whereas the dashed and dotted lines show the contributions of the dinuclear subunit  $[\text{Ni}(2), \text{Ni}(3)]$  and the mononuclear subunit  $\text{Ni}(1)$  respectively

subunit  $[\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2]^{2+}$  shows a *cis*-octahedral arrangement of the ligands around the nickel atom. Bond lengths to the oxygen atoms, Ni(1)–O(1) 2.136(3) and Ni(1)–O(2) 2.173(4) Å, are slightly larger than the Ni–N distances 2.056–2.111 Å. Hydrogen bonds are present between O(2) and O(5) (2.707 Å) and O(1) and O(4) (2.605 Å). The dinuclear subunit consists of two *cis*-octahedrally co-ordinated nickel atoms but in a different environment: Ni(2) is surrounded by two dmpd ligands, one water molecule Ni(2)–O(3) at 2.184(5) Å and one oxygen atom of the carbonato bridge, Ni(2)–O(5) at 2.174(3) Å, whereas Ni(3) in addition to the two diamines is bonded to two oxygen atoms of the carbonato bridge, Ni(3)–O(4) 2.174(3) Å and Ni(3)–O(6) 2.138(3) Å. The bond angles around Ni(3) are strongly distorted due to the bidentate co-ordination of the carbonato bridge, being O(4)–Ni(3)–O(6) 61.0(1), O(4)–Ni(3)–N(10) 156.4(2) and O(6)–Ni(3)–N(11) 163.8(2)°. The O(3) water molecule bonded to Ni(2) also shows a hydrogen bond to O(6) of the carbonato bridge, O(3)···O(6) 2.544 Å.

The co-ordination mode found in the dinuclear subunit has previously been reported in some copper(II) compounds,<sup>2b,f</sup> bridging equatorial–axial sites of square-pyramidal environments, but this is the first case in which it has been found for a cation other than copper(II).

### Infrared spectrum

The infrared spectrum of  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{dmpd})_4(\text{H}_2\text{O})][\text{Ni}(\text{dmpd})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_4 \cdot \text{H}_2\text{O}$  shows bands corresponding to the bidentate amines, the co-ordinated water and the perchlorate counter anions at normal frequencies. The most significant bands correspond to those of the carbonato bridge for which a local symmetry  $C_s$  should be assumed. By comparison with copper and cobalt carbonato compounds,<sup>16,17</sup> together with the previously reported  $[\text{Ni}_3(\mu_3\text{-CO}_3)(\text{bapma})_3(\text{NCS})_4]$  [bapma = bis(3-aminopropyl)methylamine],<sup>9</sup> the weak bands at 755 and 850  $\text{cm}^{-1}$  may be assigned to the in-plane deformation  $\nu_4$  and to the out-of-plane deformation  $\nu_2$ , which is very close to the ionic carbonate, and the strong and well defined bands at 1590 and 1387  $\text{cm}^{-1}$  to the asymmetric stretching  $\nu_3$  split in the low-symmetry environment. The strong splitting of  $\nu_3$  is commonly attributed to the presence of at least bidentate co-ordination.

### Magnetic data and coupling constants

The  $\chi_m$  value increases continuously upon cooling, Fig. 3. At room temperature the  $\chi_m T$  value is 3.70  $\text{cm}^3 \text{K mol}^{-1}$ , decreasing slightly to 50 K. Below this temperature it decreases quickly to reach 1.40  $\text{cm}^3 \text{K mol}^{-1}$  near 4 K. From the structural data and taking into account the antiferromagnetic coupling found for the same co-ordination mode of the carbonate in  $[\{\text{Cu}(\mu\text{-CO}_3)(\text{NH}_3)_2\}_n]$  it seems reasonable to assume that the superexchange coupling present is mainly related with the superexchange pathway between Ni(2) and Ni(3) provided by the carbonato bridge, and the contribution of the triangular hydrogen-bond pathways Ni(1)–O(1)···O(4)–Ni(3), Ni(1)–O(2)···O(5)–Ni(2) and Ni(2)–O(3)···O(6)–Ni(3) may be taken as negligible.<sup>18</sup> From these considerations the experimental susceptibility data can be fitted as the sum of the contributions of a dinuclear  $S = 1$  unit ( $H = -JS_1S_2$ )<sup>19</sup> and a monomeric nickel unit [equation (1)], where  $x = J/kT$  and  $N$ ,  $\beta$  and  $k$

$$\chi_m = (2Ng_D^2\beta^2/kT)[2 \exp(x) + 10 \exp(3x)] / [1 + 3 \exp(x) + 5 \exp(3x)] + (0.25g_m^2/T) \quad (1)$$

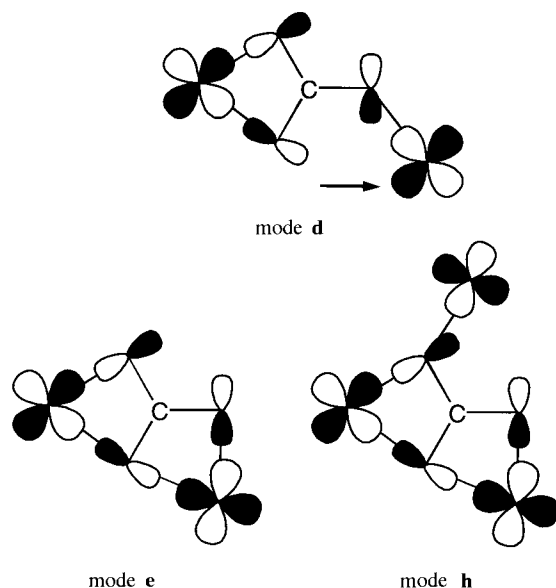
have their usual meanings. Two different  $g$  parameters were used for the dimeric and the monomeric nickel(II) units.

The best-fit parameters obtained by minimising the  $R$  factor =  $\sum[(\chi_m)^{\text{calc}} - (\chi_m)^{\text{obs}}]^2 / \sum[(\chi_m)^{\text{obs}}]^2$ , and assuming an isotropic  $g$  factor for the three nickel atoms were  $J = -7.8(2) \text{ cm}^{-1}$ ,  $g_D = 2.34(2)$ ,  $g_m = 2.15(4)$ ,  $R = 6.2 \times 10^{-4}$ . Fig. 3 shows the best fit obtained and the contributions of each subunit of the

**Table 3** Structural and magnetic data for polynuclear nickel(II) compounds with carbonate bridges. taec = *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane; L = 1-(3-dimethylaminopropyl)-1,5,9-triazacyclododecane; acac = acetylacetonate; tmen = *N,N,N',N'*-tetramethylethane-1,2-diamine; dipz = 3,5-diisopropylpyrazol-1-yl

Compound	Mode <sup>a</sup>	<i>J</i> /cm <sup>-1</sup>	Ni–O–Ni <sup>o</sup>	Ref.
[Ni <sub>2</sub> (μ-CO <sub>3</sub> )(taec)][ClO <sub>4</sub> ] <sub>2</sub>	e	-75.8	174.6	4
[Ni <sub>2</sub> (μ-CO <sub>3</sub> )(HL) <sub>2</sub> (NCS) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	e	-94.6	174.1	5
[Ni <sub>2</sub> (μ-CO <sub>3</sub> )(acac) <sub>2</sub> (tmen) <sub>2</sub> ]	e	—	174.7	7
[Ni <sub>2</sub> (μ-CO <sub>3</sub> ){HB(dipz) <sub>3</sub> }] <sub>2</sub>	e	—	178.0	8
[Ni <sub>3</sub> (μ <sub>3</sub> -CO <sub>3</sub> )(bapma) <sub>3</sub> (NCS) <sub>4</sub> ]	h	<i>e</i> - <i>J</i> <sub>1</sub> -88.4 <i>e</i> - <i>J</i> <sub>2</sub> -57.7 <i>d</i> - <i>J</i> <sub>3</sub> -9.6	172.5 141.4 —	9
[Ni <sub>2</sub> (μ-CO <sub>3</sub> )(dmpd) <sub>4</sub> (H <sub>2</sub> O)][Ni(dmpd) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>4</sub>	d	-7.8	—	b

<sup>a</sup> See Scheme 1. <sup>b</sup> This work.



**Scheme 2** Representation of the singly occupied  $d_{x^2-y^2}$  orbitals for the three co-ordination modes described to date for the nickel-carbonate system, together with the main interaction pathway of the carbonate bridge. Pathway **d** loses overlap with respect to **e** according to the schematised movement of one of the nickel atoms

complex. This result compares well with  $J_3$  for the previously reported [Ni<sub>3</sub>(μ<sub>3</sub>-CO<sub>3</sub>)(bapma)<sub>3</sub>(NCS)<sub>4</sub>] compound<sup>9</sup> and the two data may be accepted as characteristic of this co-ordination mode of the carbonate bridge. For [Cu(μ-CO<sub>3</sub>)(NH<sub>3</sub>)<sub>2</sub>]<sub>n</sub>, in which the same co-ordination mode was found, the bridge links axial-equatorial co-ordination sites of square-pyramidal neighbouring copper(II) centres and delocalisation of unpaired electron density along the axial co-ordination site was found to be very poor; consequently, the antiferromagnetic interaction should be weak ( $J = -4.5$  cm<sup>-1</sup>), and comparison with the values reported for nickel(II) is not possible.

Co-ordination modes **e** and **h** are very effective for transmitting the coupling due to the interaction between the magnetic orbital of the nickel atoms through the  $a_2'$  molecular orbital (MO) of carbonate ( $D_{3h}$  point group), which gives a very efficient superexchange pathway, Table 3, which has been compared with the interaction through a single oxo bridge.<sup>3b</sup> As occurs with the monoatomic bridges, the main factor which controls the magnitude of  $J$  is the M–O–M bond angle, as is seen by comparing  $J_1$  and  $J_2$  in [Ni<sub>3</sub>(μ<sub>3</sub>-CO<sub>3</sub>)(bapma)<sub>3</sub>(NCS)<sub>4</sub>], Table 3. In contrast mode **d** allows a low coupling, due to the inadequate superexchange pathway provided by the carbonate group. Several MOs of the carbonate ligand of adequate energy, such as  $1a_2'$ ,  $2e'$  or  $3e'$  ( $D_{3h}$  symmetry) show a reasonable overlap with the  $x^2 - y^2$  atomic orbitals of the nickel atom, which supports co-ordination of the carbonate, but in any case the magnitude of the interaction is comparable to

those which occur in the previously characterised co-ordination modes **e** and **h**. This becomes evident in a comparison of the main superexchange pathway through the  $1a_2'$  MO of the carbonate bridge, as in Scheme 2: co-ordination modes **e** and **h**, for which the Ni–O–Ni bond angle has a high value, close to 180° in some cases, provide a very efficient overlap through one of the oxygen atoms which allows a strong antiferromagnetic coupling, whereas for **d** one of the nickel atoms has lost the interaction with the oxygen atom which offers the best superexchange pathway and the interaction with the second oxygen atom of the bridge is simultaneously reduced due to the Ni(2)–O(5)–C(23) bond angle which is close to 127°, allowing weak antiferromagnetism which is in agreement with the experimental data.

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