N,N′-bis(substituted-phenyl)oxamides and their dinuclear pentacoordinate nickel(II) complexes

M. Dolores Santana [a,*], Gabriel García [a], Consuelo Vicente-Hernández [a], Luís García [b], José Pérez [b], Teófilo Rojo [c], Luís Lezama [c]

[a] Departamento de Química Inorgánica, Universidad de Murcia, 30071 Murcia, Spain
[b] Departamento de Ingeniería Minera, Geológica y Cartográfica, Universidad Politécnica de Cartagena, 30203 Cartagena, Spain
[c] Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, E-48080 Bilbao, Spain

ABSTRACT

The preparation, spectroscopic characterization and magnetic study of N,N′-bis(substituted-phenyl)oxamidate-bridged nickel(II) dinuclear complexes of formula $\{[Ni(N_3\text{-mc})]_2(\mu\text{-CONC}_6H_4\text{-X})\}$ $(PF_6)_2$ (N_3-mc = 2,4,4-trimethyl-1,5,9-triazacyclo-dodec-1-ene (Me$_3$-N$_3$-mc) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene (Me$_4$-N$_3$-mc), X = 2-Cl, 4-Cl, 2-OCH$_3$, 4-OCH$_3$) are reported. These paramagnetic nickel(II) complexes have been characterized by both one- and two-dimensional (COSY) ^{1}H NMR techniques. The COSY spectrum of **5** has allowed to achieve the assignment of the phenyl protons of the N,N′-diphenyloxamidate. The crystal structures of [Ni(Me$_3$-N$_3$-mc)(μ-CONC$_6$H$_4$-4-Cl)]$_2$(PF$_6$)$_2$ (**6**), [Ni(Me$_3$-N$_3$-mc)(μ-CONC$_6$H$_4$-4-OMe)]$_2$(PF$_6$)$_2$ (**8**) and [Ni(Me$_4$-N$_3$-mc)(μ-CONC$_6$H$_4$-2-Cl)]$_2$(PF$_6$)$_2$ (**9**) have been determined and their magnetic properties have been studied. The value of magnetic coupling between the two nickel(II) ions across the oxamidate bridge [$J = -37.6$ (**6**), -39.9 (**8**) and -39.7 cm^{-1} (**9**)] is sensitive to the distortion of the coordination sphere of the metal ions and the topology of the molecular bridge.

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1. Introduction

Symmetrically N,N′-disubstituted oxamidate derivatives have been thoroughly investigated both in aqueous solution and in the solid state [1]. The great variety of N,N′-substituents make them very suitable ligands in the design of homo- and heterometallic species [2] and have played an important role in the development of molecular magnetism [3]. One of the most appealing aspects of this type of ligands is the remarkable efficiency that they exhibit to mediate strong antiferromagnetic interactions between paramagnetic centres when acting as bridges [2b,2e,2f,2g]. Moreover, paramagnetic mononuclear copper(II) complexes have been used as chelating bricks to synthesize polymetallic systems exhibiting predictable magnetic properties and irregular spin-state structures [4,5]. In the case of oxamidate-containing mononuclear nickel(II) complexes are obtained square planar diamagnetic species due to the coordination of strong-field amide N atoms. This fact explains the scarcity of magnetic studies con-

cerning these complexes [6] in contrast to the relevant magnetochemical role played by the corresponding copper(II) complexes [1,6,7]. In all reported cases, nickel(II) was in an octahedral geometry [8,9] or in heterodinuclear nickel(II)–copper(II) complexes [10] containing pentacoordinate nickel(II). In a recent paper [11], we reported the structure, spectroscopic and magnetic behaviour of dinuclear oxamidate-bridged nickel(II) complexes, in which the two nickel(II) atoms are in a pentacoordinate environment and we discussed the role of the distortion of the coordination sphere of the metal ion and the pendant organic groups on the bridging ligand in the magnetic interaction. In this paper, we have further explored these factors by studying a new family of N,N′-disubstituted-oxamidate-bridged nickel(II) complexes since the prediction of the magnetic behavior for new dinuclear compounds is not perfect, mainly due to the subtle interplay between different factors determining the magnetic properties [12]. In the context mentioned above new N,N′-bis-(substituted-phenyl)oxamides have been prepared and their dinuclear nickel(II) complexes $\{[Ni(N_3\text{-mc})]_2(\mu\text{-oxamidate})\}(PF_6)_2$ characterized by X-ray crystallography and spectroscopic and magnetic studies.

2. Experimental

2.1. General methods

The C, H, and N analyses were carried out with a microanalyzer LECO model CHNS-932. Conductance measurements were performed with a CRISON 525 conductimeter (in acetone solution, $c \approx 10^{-3}$ mol L^{-1}). The UV/Vis spectra (in acetone) were recorded on a UNICAM 520 spectrophotometer for 300–800 nm range. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The ^{1}H NMR spectra of $(CD_3)_2CO$ solutions were recorded on a Bruker AV-300 or a Bruker AV-400 spectrometer. Chemical shifts (in ppm) are reported with respected to the residual solvent signal. The ^{1}H COSY spectrum were recorded on the Bruker 200 MHz spectrometer at 0 °C in $(CD_3)_2CO$ solutions using 256 individual FID's with 4096 scans each and the mixing time was 30 ms. Experimental parameters were varied to obtain best resolution and the signal-to-noise. Electrospray ionization mass spectra were measured with an Agilent VL mass spectrometer. Magnetic susceptibilities of powdered samples were measured between 5 and 300 K with a Quantum Design MPMS-7 SQUID magnetometer in an external field of 0.1 T. The experimental susceptibilities were corrected for the diamagnetism of the sample-holders and the constituent atoms (Pascal tables) and for the temperature-independent paramagnetism estimated to be 100×10^{-6} cm^3 mol^{-1}.

2.2. Syntheses

All chemicals were of reagent grade and were used without further purification. Solvents were dried and distilled by general methods before use. The complexes $[Ni(N_3-mc)(\mu-OH)]_2(PF_6)_2$ (N_3-mc = Me_3-N_3-mc or Me_4-N_3-mc) were prepared by the previously described procedures [13,14].

2.2.1. Ligands preparations

The ligands N,N'-bis(substituted-phenyl)oxamides were synthesized by the following experimental procedure [15]: oxalyldichloride (10 mmol) in anhydrous tetrahydrofuran (25 mL) was added dropwise to an anhydrous tetrahydrofuran solution (50 mL) of the appropriate aniline X-C_6H_4-NH_2 (X = 2-Cl, 4-Cl, 2-OCH$_3$, 4-OCH$_3$) (20 mmol) and triethylamine (2 mmol) cooled in an ice bath. The resulting suspension was stirred at room temperature for 24 h. The white precipitate was filtered and the tetrahydrofuran solution was partially evaporated under reduced pressure and a white precipitate was obtained. It was filtered off, washed with diethylether and dried in vacuo.

$(CONC_6H_4$-2-Cl$)_2$ (**1**). M.p. = 203–204 °C. ESIMS: m/z = 308 [M], 273 [M–Cl]. IR (nujol): ν_{max} = 3312 (NH), 1676, 1520 (CO), 1048 (Ph–Cl), 754 (C=C–H) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 9.900 (s; 2H, NH), 8.437 (dd; J = 7.9 Hz, J = 1.5 Hz; 2H, 6-H), 7.326 (td; J = 7.9 Hz, J = 1.5 Hz; 2H, 5-H), 7.423 (dd; J = 7.8 Hz, J = 1.5 Hz; 2H, 3-H), 7.127 (td; J = 7.8 Hz, J = 1.5 Hz; 2H, 4-H) ppm.

$(CONC_6H_4$-4-Cl$)_2$ (**2**). M.p. = 279–280 °C. ESIMS: m/z = 308 [M]. IR (nujol): ν_{max} = 3296 (NH), 1660, 1514 (CO), 1092 (Ph–Cl), 830 (C=C–H) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 9.286 (s; 2H, NH), 7.608 (AB, J = 8.85 Hz; 4H, 2,6-H), 7.354 (AB, J = 8.85 Hz; 4H, 3,5-H) ppm.

$(CONC_6H_4$-2-OMe$)_2$ (**3**). M.p. = 220–221 °C. ESIMS: m/z = 300 [M]. IR (nujol): ν_{max} = 3354 (NH), 1682, 1526 (CO), 756 (C=C–H) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 9.950 (s; 2H, NH), 8.375 (d, J = 7.5 Hz; 2H, 6-H), 6.998 (t, J = 7.5 Hz; 2H, 5-H), 6.925 (d, J = 7.5 Hz; 2H, 3-H), 7.131 (t, J = 7.5 Hz; 2H, 4-H), 3.920 (s; 6H, 2-OCH$_3$) ppm.

$(CONC_6H_4$-4-OMe$)_2$ (**4**). M.p. = 184–185 °C. ESIMS: m/z = 300 [M]. IR (nujol): ν_{max} = 3286 (NH), 1652, 1534 (CO), 822 (C=C–H) cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, 20 °C): δ = 9.236 (s; 2H, NH), 7.572 (d, J = 8.7 Hz; 4H, 2,6-H), 6.910 (d, J = 8.7 Hz; 4H, 3,5-H), 3.804 (s; 6H, 4-OCH$_3$) ppm.

2.2.2. Synthesis of the complexes $[Ni(N_3-mc)(\mu-CONC_6H_4-X)]_2(PF_6)_2$ (X = 2-Cl, 4-Cl, 2-OCH$_3$, 4-OCH$_3$)

To a suspension of $[Ni(N_3-mc)(\mu-OH)]_2(PF_6)_2$ (0.116 mmol) in acetone (25 mL) X-C_6H_4HNCOCONHC_6H_4-X (0.116 mmol) was added. The mixture was stirred at room temperature for 24 h. Acetone was evaporated under reduced pressure until $ca.$ 5 mL, and the addition of diethyl ether (15 mL) resulted in the formation of a light blue-violet solid which was filtered off, washed with diethyl ether and air-dried.

2.2.2.1. $[Ni(Me_3-N_3-mc)(\mu-CONC_6H_4-2-Cl)]_2(PF_6)_2$ (**5**). Yield: 0.124 g (94%). Anal. Calc. for $C_{38}H_{58}Cl_2F_{12}N_8Ni_2O_2P_2$: C, 40.1; H, 5.1; N, 9.9. Found: C, 40.1; H, 5.2; N, 9.7%. ES-MS: m/z (%) = 991 (100) [M]$^+$, 845 (45) [M]$^{2+}$. Λ_M = 257 S cm^{2}mol^{-1}. UV/Vis (acetone) λ_{max} (ε): 594 nm (130 M^{-1} cm^{-1}), 366 (491). IR (nujol): ν_{max} = 3278, 3255 (N–H$_{mc}$), 1656 (C=N$_{mc}$), 1602 (C–O$_{oxamidate}$), 1578 (C–C$_{oxamidate}$) cm^{-1}. ^{1}H NMR (300 MHz, (CD$_3)_2$CO, 20 °C): δ = 268.2 (H$_\alpha$), 178.5 (d, H$_\alpha$), 140.2 (d, H$_\alpha$), 118.0 (d, H$_\alpha$), 83.8 (H$_\alpha$), 50.7 (H$_\alpha$), 40.5 (4-Me, 3H), 26.5 (d, H$_\alpha$), 18.7 (H$_\alpha$),15.8 (m, 4-Me, 3H),15.4 (3-H),14.7 (5-H), −3.5 (6-H), −4.4 (m, 4-H) −9.6 (H$_\beta$), −10.4 (d, H$_\beta$), −12.6 (d, 2-Me, 3H), −18.4 (H$_\beta$), −20.7 (H$_\beta$), −24.6 (m, H$_\beta$), −26.7 (d, H$_\beta$) ppm.

2.2.2.2. $[Ni(Me_3-N_3-mc)(\mu-CONC_6H_4-4-Cl)]_2(PF_6)_2$ (**6**). Yield: 0.120 g (89%). Anal. Calc. for $C_{38}H_{58}Cl_2F_{12}N_8Ni_2O_2P_2$: C, 40.1; H, 5.1; N, 9.9. Found: C, 39.9; H, 5.2; N, 9.8%. ES-MS: m/z (%) = 991 (100) [M]$^+$. Λ_M: 220 S cm^2 mol^{-1}. UV/Vis (acetone) λ_{max} (ε): 591 nm (130 M^{-1} cm^{-1}), 369 (681). IR (nujol): ν_{max} = 3292, 3256 (N–H$_{mc}$), 1656 (C=N$_{mc}$), 1598 (C–O$_{oxamidate}$), 1578 (C–C$_{oxamidate}$) cm^{-1}. ^{1}H NMR (300 MHz, (CD$_3)_2$CO, 20 °C): δ = 261.7 (H$_\alpha$), 168.3 (H$_\alpha$), 137.1 (d, H$_\alpha$), 115.4 (m, H$_\alpha$), 78.9 (H$_\alpha$), 48.8 (d, H$_\alpha$), 39.0 (d, 4-Me, 3H), 25.9 (H$_\alpha$), 17.9 (H$_\alpha$), 15.5 (m, 4-Me, 3H), 15.3 (3,5-H, 2H), −3.6 (2,6-H, 2H), −9.4 (m, 2H$_\beta$), −12.8 (d, 2-Me, 3H), −18.5 (H$_\beta$), −20.9 (H$_\beta$), −24.6 (H$_\beta$), −27.9 (d, H$_\beta$) ppm.

2.2.2.3. $[Ni(Me_3-N_3-mc)(\mu-CONC_6H_4-2-OMe)]_2(PF_6)_2$ (**7**). Yield: 0.123 g (94%). Anal. Calc. for $C_{40}H_{64}F_{12}N_8Ni_2O_4P_2$: C, 42.6; H, 5.7; N, 9.9. Found: C, 42.4; H, 5.6; N, 9.8%. ES-MS: m/z (%) = 981 (100) [M]$^+$, 835 (11) [M]$^{2+}$. Λ_M: 272 S cm^2 mol^{-1}. UV/Vis (acetone) λ_{max} (ε): 590 nm (100 M^{-1} cm^{-1}), 367 (480). IR (nujol): ν_{max} = 3290, 3260 (N–H$_{mc}$), 1660 (C=N$_{mc}$), 1608 (C–O$_{oxamidate}$), 1584 (C–C$_{oxamidate}$) cm^{-1}. ^{1}H NMR (400 MHz, (CD$_3)_2$CO, 25 °C): δ = 240.0 (H$_\alpha$), 172.2 (H$_\alpha$), 89.5 (H$_\alpha$), 83.7 (H$_\alpha$), 77.6 (H$_\alpha$), 47.3 (4-Me, 3H), 33.6 (H$_\alpha$), 25.0 (H$_\alpha$), 21.3 (H$_\alpha$), 19.1 (m, 4-Me, 3H), 15.4 (m, 3,5-H), 4.8 (2-OMe, 3H), −4.8 (m, 4-H), −5.3 (6-H), −7.2 (H$_\beta$), −10.9 (H$_\beta$), −11.5 (d, 2-Me, 3H), −12.6 (H$_\beta$), −19.5 (H$_\beta$), −24.5 (H$_\beta$), −25.6 (H$_\beta$).

2.2.2.4. $[Ni(Me_3-N_3-mc)(\mu-CONC_6H_4-4-OMe)]_2(PF_6)_2$ (**8**). Yield: 0.118 g (90%). Anal. Calc. for $C_{40}H_{64}F_{12}N_8Ni_2O_4P_2$: C, 42.6; H, 5.7; N, 9.9. Found: C, 42.4; H, 5.6; N, 9.8%. ES-MS: m/z (%) = 983 (100) [M]$^+$, 836 (10) [M]$^{2+}$. Λ_M: 276 S cm^{2}mol^{-1}. UV/Vis (acetone) λ_{max} (ε): 588 nm (130 M^{-1} cm^{-1}). IR(nujol): ν_{max} = 3288, 3250 (N–H$_{mc}$), 1658 (C=N$_{mc}$), 1608 (C–O$_{oxamidate}$), 1584 (C–C$_{oxamidate}$) cm^{-1}. ^{1}H NMR (400 MHz, (CD$_3)_2$CO, 25 °C): δ = 248.3 (H$_\alpha$), 160.3 (H$_\alpha$), 132.7 (d, H$_\alpha$), 108.3 (d, H$_\alpha$), 76.7 (H$_\alpha$), 49.6 (d, H$_\alpha$), 40.3 (4-Me, 3H), 25.5 (H$_\alpha$), 18.0 (H$_\alpha$), 14.8 (4-Me, 3H), 14.1 (3,5-H, 2H), 5.9 (4-OMe, 3H), −3.3 (2,6-H, 2H), −9.2 (d, H$_\beta$), −10.1 (d, H$_\beta$), −11.7 (m, 2-Me, 3H), −17.7 (H$_\beta$), −20.3 (H$_\beta$), −23.9 (H$_\beta$), −25.9 (H$_\beta$) ppm.

*2.2.2.5. [Ni(Me₄-N₃-mc)(μ-CONC₆H₄-2-Cl)]₂(PF₆)₂ (**9**)*. Yield: 0.119 g (91%). Anal. Calc. for $C_{40}H_{62}Cl_2F_{12}N_8Ni_2O_2P_2$: C, 41.2; H, 5.4; N, 9.6. Found: C, 41.0; H, 5.4; N, 9.5%. ES-MS: *m/z* (%) = 1019 (69) [M]⁺, 875 (54) [M]²⁺. Λ_M: 269 S cm²mol⁻¹. UV/Vis (acetone) λ_{max} (ε): 613 nm (140 M⁻¹ cm⁻¹), 377 (501). IR (nujol): ν_{max} = 3262 (N–H$_{mc}$), 1650 (C=N$_{mc}$), 1600 (C–O$_{oxamidate}$), 1578 (C–C$_{oxamidate}$) cm⁻¹. ¹H NMR (300 MHz, (CD₃)₂CO, 20 °C): δ = 251.5 (H$_\alpha$), 165.1 (m, H$_\alpha$), 120.0 (H$_\alpha$), 112.6 (H$_\alpha$), 103.7 (d, H$_\alpha$), 99.1 (d, 9-Me, 3H), 75.3 (m, H$_\alpha$), 40.5 (4-Me, 3H), 36.8 (m, H$_\alpha$), 25.8 (H$_\alpha$), 18.0 (m, 4-Me, 3H), 14.9 (m, 3,5-H, 2H), −2.1 (d, 6-H), −2.6 (m, 4-H), −10.2 (H$_\beta$), −10.9 (H$_\beta$), −12.9 (2-Me, 3H), −14.8 (H$_\beta$), −16.0 (H$_\beta$), −24.1 (H$_\beta$), −25.5 (H$_\beta$) ppm.

*2.2.2.6. [Ni(Me₄-N₃-mc)(μ-CONC₆H₄-4-Cl)]₂(PF₆)₂ (**10**)*. Yield: 0.118 g (90%). Anal. Calc. for $C_{40}H_{62}Cl_2F_{12}N_8Ni_2O_2P_2$: C, 41.2; H, 5.4; N, 9.6. Found: C, 41.0; H, 5.4; N, 9.5%. ES-MS: *m/z* (%) = 1019 (100) [M]⁺, 873 (32) [M]²⁺. Λ_M: 275 S cm²mol⁻¹. UV/Vis (acetone) λ_{max} (ε): 618 nm (140 M⁻¹ cm⁻¹), 375 (541). IR (nujol): ν_{max} = 3266 (N–H$_{mc}$), 1660 (C=N$_{mc}$), 1634 (C–O$_{oxamidate}$), 1598 (C–C$_{oxamidate}$) cm⁻¹. ¹H NMR (300 MHz, (CD₃)₂CO, 20 °C): δ = 258.0 (H$_\alpha$), 165.1 (d, H$_\alpha$), 146.3 (H$_\alpha$), 127.6 (H$_\alpha$), 107.8 (d, H$_\alpha$), 100.0 (d, H$_\alpha$), 88.0 (9-Me, 3H), 73.5 (d, H$_\alpha$), 66.2 (H$_\alpha$), 34.6 (4-Me, 3H), 15.4 (d, 4-Me, 3H), 14.4 (3,5-H, 2H), −4.6 (2,6-H, 2H), −8.0 (H$_\beta$), −9.8 (2-Me, 3H), −13.6 (2H$_\beta$), −14.8 (H$_\beta$), −16.1 (H$_\beta$), −20.6 (2H$_\beta$) ppm.

*2.2.2.7. [Ni(Me₄-N₃-mc)(μ-CONC₆H₄-2-OMe)]₂(PF₆)₂ (**11**)*. Yield: 0.117 g (90%). Anal. Calc. for $C_{42}H_{68}F_{12}N_8Ni_2O_4P_2$: C, 43.6; H, 5.9; N, 9.7. Found: C, 43.4; H, 5.9; N, 9.6%. ES-MS: *m/z* (%) = 1011 (100) [M]⁺, 863 (51) [M]²⁺. Λ_M: 287 S cm²mol⁻¹. UV/Vis (acetone) λ_{max} (ε): 621 nm (120 M⁻¹ cm⁻¹), 374(440). IR (nujol): ν_{max} = 3264 (N–H$_{mc}$), 1656 (C=N$_{mc}$), 1606 (C–O$_{oxamidate}$), 1582 (C–C$_{oxamidate}$) cm⁻¹. ¹H NMR (300 MHz, (CD₃)₂CO, 20 °C): δ = 309.5 (H$_\alpha$), 278.5 (H$_\alpha$), 247.9 (H$_\alpha$), 157.6 (H$_\alpha$), 105.0 (H$_\alpha$), 94.1 (9-Me, 3H), 55.9 (H$_\alpha$), 45.4 (H$_\alpha$), 36.6 (4-Me, 3H), 24.9 (H$_\alpha$), 19.0 (m, 4-Me, 3H), 14.5 (m, 3,5-H, 2H), 5.5 (2-OMe, 3H), −2.9 (4-H), −4.4 (6-H), −8.8 (H$_\beta$), −11.4 (H$_\beta$), −11.7 (H$_\beta$), −13.2 (2-Me, 3H), −14.4 (H$_\beta$), −20.0 (H$_\beta$), −23.2 (H$_\beta$) ppm.

*2.2.2.8. [Ni(Me₄-N₃-mc)(μ-CONC₆H₄-4-OMe)]₂(PF₆)₂ (**12**)*. Yield: 0.120 g (92%). Anal. Calc. for $C_{42}H_{68}F_{12}N_8Ni_2O_4P_2$: C, 43.6; H, 5.9; N, 9.7. Found: C, 43.4; H, 5.8; N, 9.5%. ES-MS: *m/z* (%) = 1011 (97) [M]⁺. Λ_M: 257 S cm² mol⁻¹. UV/Vis (acetone) λ_{max} (ε): 602 nm (170 M⁻¹ cm⁻¹). IR (nujol): ν_{max} = 3262 (N–H$_{mc}$), 1654 (C=N$_{mc}$), 1606 (C–O$_{oxamidate}$), 1582 (C–C$_{oxamidate}$) cm⁻¹. ¹H NMR (300 MHz, (CD₃)₂CO, 20 °C): δ = 244.8 (H$_\alpha$), 155.9 (H$_\alpha$), 127.9 (H$_\alpha$), 120.5 (H$_\alpha$), 103.1 (d, H$_\alpha$), 95.5 (9-Me, 3H), 74.5 (d, H$_\alpha$), 59.2 (H$_\alpha$), 38.0 (4-Me, 3H), 26.2 (H$_\alpha$), 14.6 (m, 4-Me, 3H), 14.2 (m, 3,5-H, 2H), 6.2 (4-OMe, 3H), −4.2 (2,6-H, 2H), −8.9 (H$_\beta$), −10.2 (2H$_\beta$), −12.9 (2-Me, 3H), −17.6 (H$_\beta$), −20.6 (H$_\beta$), −23.4 (H$_\beta$) ppm.

2.3. Crystallographic data collection and structure determination

Crystals of **6**, **8** and **9** suitable for a diffraction study were prepared by slow diffusion of diethyl ether into their acetonitrile solution. Diffraction data were measured on a Bruker SMART APEX using Mo Kα radiation (λ = 0.71073 Å). Crystallographic data are summarised in Table 1. The diffraction frames were integrated using the SAINT package [16] and corrected for absorption with SAD-ABS [17]. The raw intensity data were converted (including corrections for Lorentz and polarization effects) to structure amplitudes and their esd using the SAINT program. The structures were solved by direct methods [18] and refined [18] by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were set at calculated positions.

Table 1
Crystallographic data for complexes **6**, **8** and **9**

Complex	**6**	**8**	**9**
Formula	$C_{38}H_{58}Cl_2F_{12}N_8Ni_2O_2P_2$	$C_{40}H_{64}F_{12}N_8Ni_2O_4P_2$	$C_{40}H_{62}Cl_2F_{12}N_8Ni_2O_2P_2$
M	1137.18	1128.35	1165.24
T (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pcab*	*Pbca*	*P2₁/c*
a (Å)	12.7060(8)	13.3116(10)	10.1932(7)
b (Å)	13.3751(8)	13.7772(11)	18.8848(14)
c (Å)	27.5048(16)	26.045(2)	13.6223(10)
α (°)	90	90	90
β (°)	90	90	108.490 (1)
γ (°)	90	90	90
V (Å³)	4674.3(5)	4776.5(6)	2486.9(3)
Z	4	4	2
D_{calc} (Mg/m³)	1.616	1.569	1.556
μ (mm⁻¹)	1.081	0.952	1.018
Reflections collected	51 410	52 814	28 495
Independent reflections [R_{int}]	5554 [0.1416]	5664 [0.0556]	5754 [0.0457]
Goodness-of-fit on F^2	1.247	1.080	1.047
Final R indices [$I > 2\sigma(I)$]ᵃ,ᵇ	$R_1 = 0.0951$	$R_1 = 0.0758$	$R_1 = 0.0951$
	$wR_2 = 0.1970$	$wR_2 = 0.1870$	$wR_2 = 0.2429$
R indices (all data)	$R_1 = 0.1166$	$R_1 = 0.0964$	$R_1 = 0.1104$
	$wR_2 = 0.2108$	$wR_2 = 0.2036$	$wR_2 = 0.2546$
Maximum/minimum $\Delta\rho$ (e Å⁻³)	1.035 and −0.964	2.722 and −0.448	2.052 and −1.535

ᵃ $R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$ for reflections with $I > 2\sigma I$.
ᵇ $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, in which $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The *N,N′*-bis(substituted-phenyl)oxamides were synthesized by treating oxalyldichloride with the corresponding aniline(X-C₆H₄-NH₂) in THF and Et₃N at 0 °C for 24 h (Scheme 1). These oxamides behave as weak acids towards the dinuclear hydroxo-complexes [Ni(N₃-mc)(μ-OH)]₂(PF₆)₂ (N₃-mc = 2,4,4-trimethyl-1,5,9-triazacy-clo-dodec-1-ene (Me₃-N₃-mc) or 2,4,4,9-tetramethyl-1,5,9-triaza-cyclododec-1-ene (Me₄-N₃-mc)), these hydroxo complexes have been used as precursors in the synthesis of mono- [19] and dinuclear [20] pentacoordinate nickel(II) complexes in different coordination environments. The oxamidate complexes of pentaco-ordinate nickel(II) were obtained from reaction mixtures of [Ni(N₃-mc)(μ-OH)]₂(PF₆)₂ and *N,N′*-bis(substituted-phenyl)oxamides (1:1 molar ratio) in acetone. The isolated complexes are sketched in Scheme 2.

X = 2-Cl (**1**), 4-Cl (**2**), 2-OCH₃ (**3**), 4-OCH₃ (**4**)
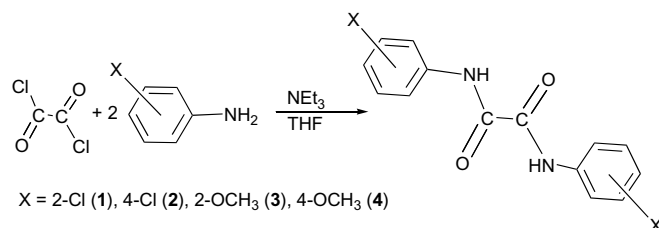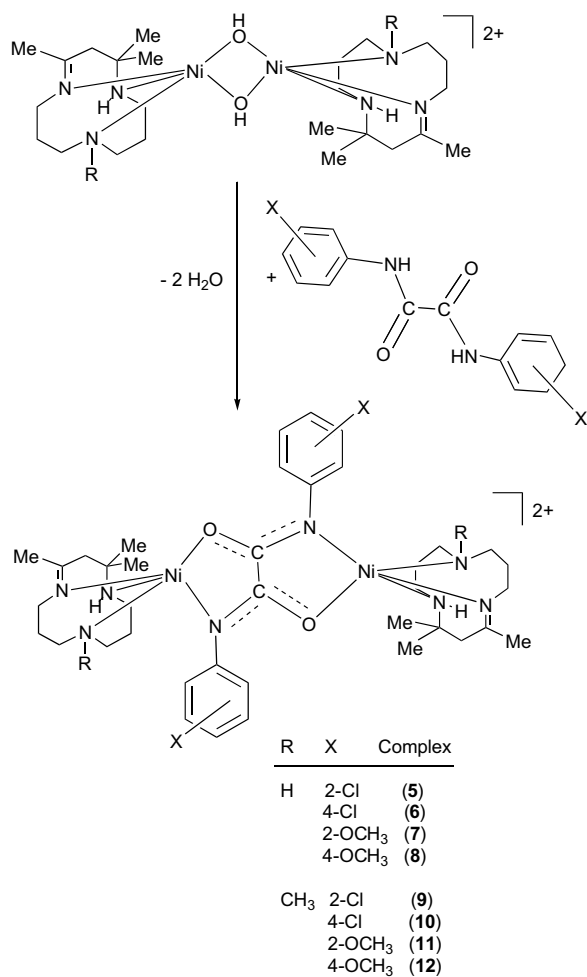
Scheme 1.

Scheme 2.

When the oxamides are deprotonated both oxygen and nitrogen are coordinated to nickel ions with an effective π-delocalization in the NCO fragments. The anion oxamidate acts as a nickel–nickel bound ligand. The IR spectra of all the dinuclear complexes are similar: the signals attributable to N_3-mc ligands and two strong characteristic bands due to the PF_6^- anion appear at normal frequencies [19]. The v(C–O) stretching frequencies of the oxamidate groups at ∼1600 cm^{-1} are consistent with the presence of a bridging oxamidate ligand in **5–12** [11].

The ^{1}H NMR spectra for complexes **5–12** show the resonance line pattern observed for the N_3-macrocycle ligands that has been assigned on the basis of previous studies of nickel macrocyclic complexes [20]. The spectra of derivatives **5–12** are similar to that of the previously reported oxamidate complexes [11] in both signals and magnitudes of contact shifts, but some striking differences are evident upon their inspection (see Fig. 1); thus some signals related to a given proton occur as doubled signal. The magnitude of contact shift differences for some α-CH protons and for 4-Me and 2-Me groups implies that these differences arise from distinct configurations. The intrinsically dissimilar forms are possibly further differentiated by a lack of free rotation of the phenyl groups about the C–N bond [21]; even so the presence of conformers in solution has been observed also by Curtis et al. [13] and Dei et al. [22] in other complexes containing this Ni(II) [12]aneN$_3$-macrocycle moiety and has been attributed to the two possible reciprocal chiralities of nitrogen atoms. The isotropically shifted ^{1}H NMR signals observed for the phenyl group of *N,N'*-bis(substituted-phenyl)oxamidates can be initially assigned by inspection of their peak areas. Definitive assignment of these signals comes from two-dimensional NMR techniques. A magnitude COSY spectrum of **5** was recorded at 0 °C and shows cross-signals between resonances at 15.8, 15.2, −3.8 and −4.9 ppm (Fig. 2). These signals can be assigned to the phenyl 3-H, 5-H, 6-H and 4-H protons, respectively. The shift direction alternation of the *N*-phenyl protons is characteristic when the π-contact shift is dominant, therefore the unpaired electrons could polarize the net spin density in the d$_\pi$ orbitals [23].
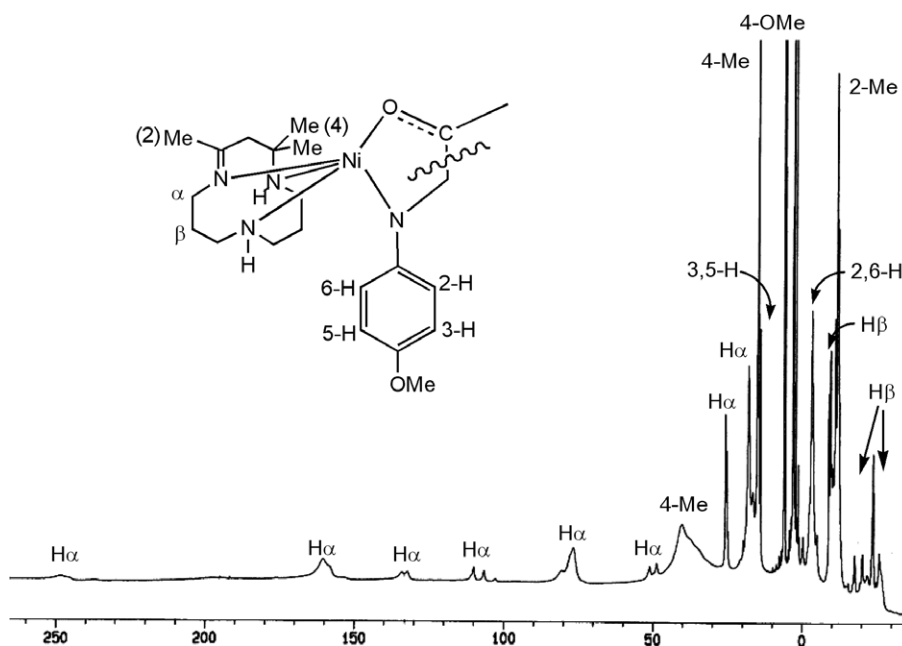
Fig. 1. ^{1}H NMR spectra of **8** in (CD$_3$)$_2$CO solution at room temperature.
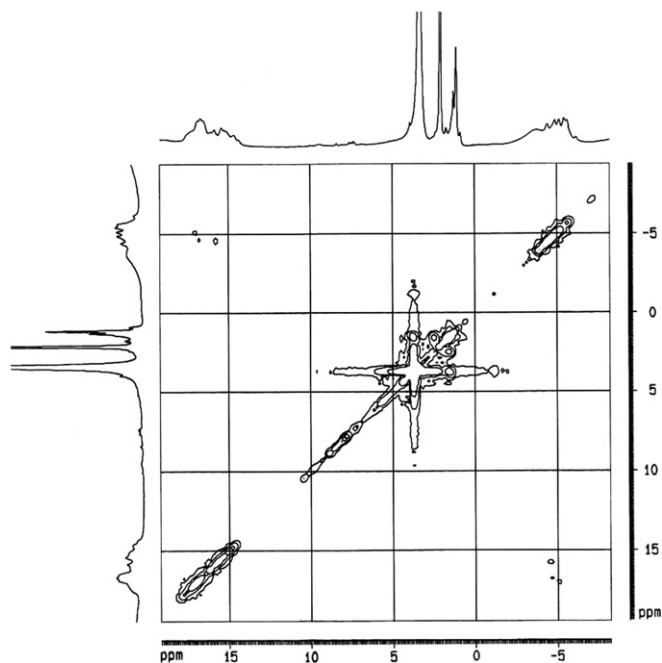
Fig. 2. ^{1}H COSY spectrum of **5** obtained at 200 MHz at 0 °C in (CD$_3$)$_2$CO solution. This map was collected with a 30 ms mixing time, 256 t1 values (4096 scans each) using 1 K data points in F2 dimension, only the region relevant to assign resonances is shown in the top trace.

3.2. Structural investigations

The complexes **6** and **8** crystallize in an orthorhombic space group, *Pcab* and *Pbca*, respectively, and the compound **9** crystallizes in the monoclinic space group *P*21/*c*. The structure of the three compounds consist of non-coordinated PF$_6^-$ ions and a {[Ni(N$_3$-mc)]$_2$(μ-oxamidate)}$^{2+}$ dinuclear cations, Figs. 3–5. The oxamide ions join two adjacent coordination polyhedra with its nitrogen and oxygen atoms occupying in both polyhedra two *cis* positions and the N$_3$-mc ligands act as a facially coordinated tridentate ligand. The complexes lie on a crystallographic inversion center. The coordination geometry around each nickel ion can be regarded as a distorted square pyramid; the equatorial plane is built by the O1 and N4 atoms from the oxamidate group and N1 and N2 nitrogen atoms from the N$_3$-macrocycle, whereas the apical position is
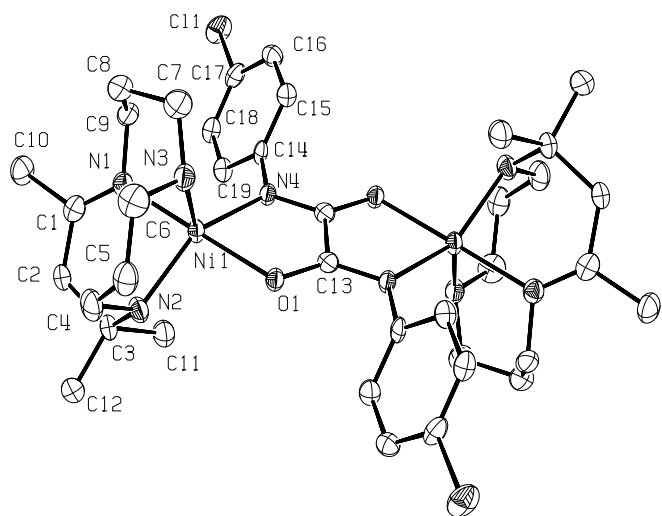
Fig. 3. ORTEP plot of the cation of [Ni(Me$_3$-N$_3$-mc)(μ-CONC$_6$H$_4$-4-Cl)]$_2$(PF$_6$)$_2$ (**6**).
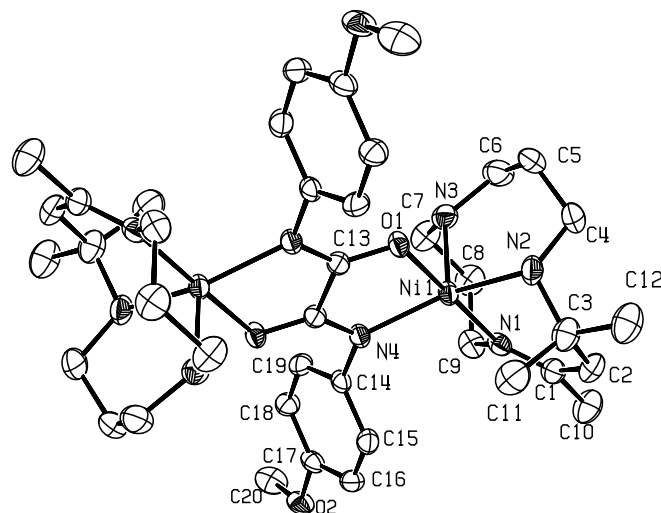
Fig. 4. ORTEP plot of the cation of [Ni(Me$_3$-N$_3$-mc)(μ-CONC$_6$H$_4$-4-OMe)]$_2$(PF$_6$)$_2$ (**8**).
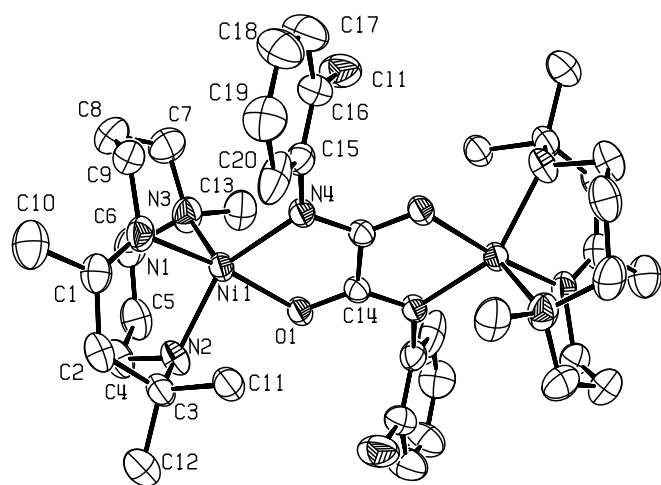
Fig. 5. ORTEP plot of the cation of [Ni(Me$_4$-N$_3$-mc)(μ-CONC$_6$H$_4$-2-Cl)]$_2$(PF$_6$)$_2$ (**9**).

occupied by a N3 atom from N$_3$-mc. The values of the Ni–N bond lengths are in the range 2.034–2.089 Å and are comparable with those reported for complexes of pentacoordinate nickel(II) containing N$_3$-macrocycle [19]. The Ni–O$_{oxamide}$ and Ni–N$_{oxamide}$ bond distances are a little longer than those observed in dinuclear Ni(II) complexes containing oxamides with square pyramidal environment for Ni(II) [11]. The Ni atom is 0.291(2) (**6**), 0.267(2) (**8**) and 0.348(3) (**9**) Å out of the basal plane defined by N1, N2, N4 and O1 toward the axial nitrogen, respectively. The dihedral angles between the basal and the bridging ligand mean planes are 13.83(15)° (**6**), 12.39(16)° (**8**) and 16.04(29)° (**9**), respectively. The nickel–nickel separations through the oxamidate bridges are 5.474(1), 5.463(1) and 5.467(1) Å for complexes **6**, **8** and **9**, respectively, these distances are longer than the reported for dinuclear Ni–Ni complexes with the bridging-oxamidate ligands [1,6,8,9]; whereas the shortest intermolecular Ni···Ni separations are 9.056(1) (**6**), 9.452(1) (**8**) and 9.432(2) (**9**) Å, respectively. The geometry of pentacoordinate complexes can be described by a structural index parameter τ [24] such that $\tau = (\beta - \alpha)/60°$, where β and α are the two largest angles ($\beta > \alpha$). Thus, the geometric parameter τ is applicable to pentacoordinate structures as an index of the degree of trigonality, between $\tau = 1$ for trigonal bipyramid (TBP) ($\beta - \alpha = 60°$) and $\tau = 0$ for square pyramid (SP) ($\beta - \alpha = 0°$). Complexes **8** and **9** have τ values of 0.37 and 0.38, respectively

indicating a moderated distortion from perfect SP. However, complex **6** has a τ value of 0.52 and the environment around nickel atom is intermediate between square pyramidal and trigonal bipyramidal. Moreover, the angles between the plane of the substituent at the bridging nitrogen atom and the plane of the bridging ligand are 57.47(18)° for **6**, 67.51(14)° for **8** and 68.72(23)° for **9**, respectively. All of these structural factors influence the magnitude of the exchange coupling constant, these facts are studied in the next section.

3.3. Magnetic properties

The thermal evolution of the magnetic molar susceptibility (χ_m) and the $\chi_m T$ product for compounds **6**, **8** and **9** are shown in Fig. 6. For the three compounds, the susceptibility values increase with decreasing temperature until a broad maximum about 50 K. The curves drop to relative minima at 12 K (**6**), 9.5 K (**8**) and 6.5 K (**9**), at which χ_m values exponentially increases upon further cooling. At room temperature $\chi_m T$ is about 2.1 cm^3 K mol^{-1} for **6**, **8** and **9**, which agrees well with the value expected for two uncoupled $S = 1$ ions with g values slightly greater than 2. Upon cooling, the $\chi_m T$ magnitude continuously decreases and it tends to zero at very low temperatures indicating the occurrence of one $S = 0$ ground state. On the other hand, Curie–Weiss behaviour is not well defined even at room temperature. Both the continuous decrease in the magnetic effective moment and the maximum observed in the thermal variation of the molar susceptibility clearly indicate the existence of relatively strong antiferromagnetic interactions between two Ni(II) ions. The low temperature increase of χ_m can be explained by considering the presence of a small amount of monomeric Ni(II) ions in the polycrystalline powder sample. From these considerations the experimental susceptibility data can be
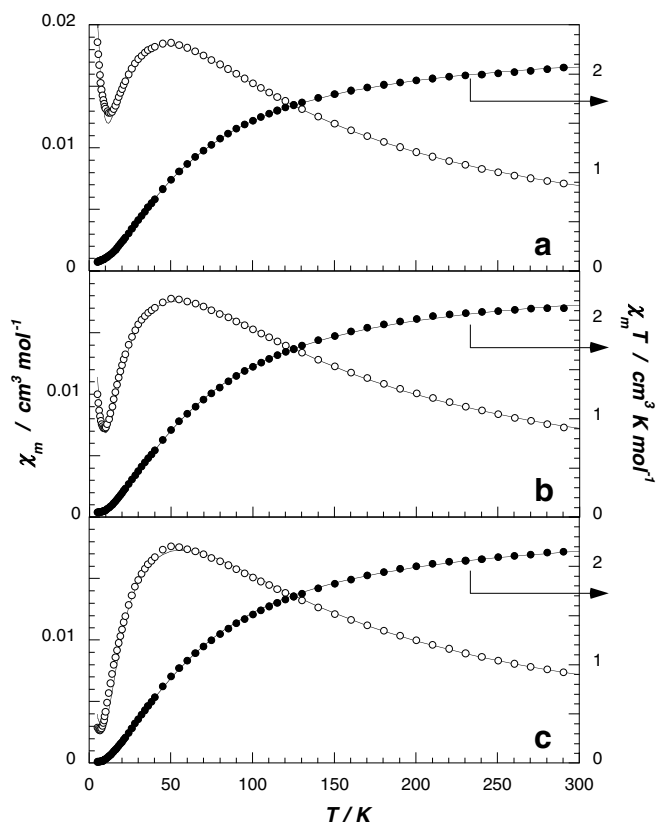
Fig. 6. Thermal variation of χ_m and $\chi_m T$ for compounds **6** (a), **8** (b) and **9** (c). The solid lines correspond to the best fits obtained with Eq. (1).

Table 2
Selected magnetostructural parameters for oxamidate-bridged pentacoordinate nikel(II) complexes[a]

Complex	−J	τ	d_{Ni-Ni}	h_{Ni}[b]	d_{Ni-Nox}	d_{Ni-Oox}	d_{Ni-Neq}	d_{Ni-Nax}	$d_{Ni\cdots Ni}$[c]	α (°)[d]	β (°)[e]	d_{O-Cox}	d_{N-Cox}	∠NiNC	∠NiOC	∠NNiO	∠OCN	δ[f]	Reference
[Ni(Me₃-N₃-mc)(μ-CON)]₂²⁺	57.0	0.12	5.427	0.266	2.014	2.052	2.058	2.056			11.9	1.289	1.291	115.7	112.6	80.70	129.0		[11]
[Ni(Me₃-N₃-mc)(μ-CONC₆H₄-4-OMe)]₂²⁺ (**8**)	39.9	0.37	5.463	0.267	2.041	2.070	2.045	2.048	9.452	67.51	12.39	1.269	1.304	114.9	113.3	80.16	128.3	14.1	This work
[Ni(Me₄-N₃-mc)(μ-CONC₆H₄-2-Cl)]₂²⁺ (**9**)	39.7	0.38	5.467	0.348	2.064	2.052	2.041	2.089	9.432	68.72	16.04	1.270	1.319	113.5	113.6	80.30	127.4	14.9	This work
[Ni(Me₃-N₃-mc)(μ-CONC₆H₄-4-Cl)]₂²⁺ (**6**)	37.6	0.52	5.474	0.291	2.060	2.058	2.041	2.049	9.056	57.47	13.83	1.269	1.309	114.4	114.0	80.04	128.6	15.3	[11]
[Ni(Me₃-N₃-mc)(μ-CONC₆H₅)]₂²⁺	30.5	0.48	5.384	0.322	2.019	2.043	2.051	2.026			13.6	1.262	1.313	113.6	112.2	81.58	127.6	25.6	[11]

[a] J in cm⁻¹; d and h in Å.
[b] Nickel height from the basal plane.
[c] $d_{Ni\cdots Ni}$ is the shortest intermolecular Ni··· Ni separation.
[d] α is the angle between the plane of the substituent at the bridging nitrogen atom and the plane of the bridging oxamidate.
[e] β is the dihedral angle between the basal and the bridging ligand mean plane.
[f] δ is the isotropically shifted ¹H NMR signals observed for 3-H and 5-H protons of the phenyl group in ppm.

fitted by using the expression for a dinuclear $S = 1$ unit ($\boldsymbol{H} = -J\boldsymbol{S}_1\boldsymbol{S}_2$) modified to take into account the contribution of isolated Ni(II) ions:

$$\chi_{\mathrm{m}} = (1 - \rho)\frac{2Ng^2\beta^2}{kT}\frac{1 + 5\exp(2x)}{3 + 5\exp(2x) + \exp(-x)} + \rho\frac{4Ng^2\beta^2}{3kT} \quad (1)$$

where $x = J/kT$, J is the intradimeric exchange parameter, ρ the proportion of paramagnetic contribution, of which the susceptibility is assumed to follow Curie's law, and N, β and k have their usual meanings. The same isotropic g value has been used for the dimeric and monomeric entities in order minimize the number of adjustable parameters. Least-squares fit of the susceptibility data through Eq. (1) leads to $J = -37.6\ \mathrm{cm}^{-1}$, $g = 2.17$, $\rho = 0.046$ and $R = 1.6 \times 10^{-3}$ for **6**, $J = -39.9\ \mathrm{cm}^{-1}$, $g = 2.23$, $\rho = 0.022$ and $R = 1.0 \times 10^{-3}$ for **8**, and $J = -39.4\ \mathrm{cm}^{-1}$, $g = 2.22$, $\rho = 0.008$ and $R = 2.3 \times 10^{-3}$ for **9**, respectively. R is the minimized agreement factor defined as $R = \sum\left[\chi_{\mathrm{m}}^{\exp} - \chi_{\mathrm{m}}^{\mathrm{calc}}\right]^2 / \sum\left[\chi_{\mathrm{m}}^{\exp}\right]^2$. As can be seen in Fig. 6, the theoretical curves reproduce very well the main features of the experimental data.

On the other hand, all the compounds are completely EPR silent from 4.2 K to 300 K. This behaviour is in concordance with the presence of a Ni(II) single-ion zero-field splitting parameter, D, of 5–10 cm^{-1} and negative in sign, i.e. the $M_s = 0$ state lying below the $M_s = \pm 1$ doublet [25]. However, in the precedent calculations we have not considered the zero-field splitting of the $^3A_2$ ground state, because this contribution on the magnetic behaviour of dimers with strong antiferromagnetic interactions ($-J > 20\ \mathrm{cm}^{-1}$) is usually negligible [26]. In fact, the experimental data have been also fitted by the classical Ginsberg equation [27] modified to take into account the magnetic contribution of Ni(II) ions with ZFS. The agreement R factors are slightly lowers than those obtained with Eq. (1), but the J values remain practically unchanged. The calculated D values are at $-7.6\ \mathrm{cm}^{-1}$ **6**, $-11.1\ \mathrm{cm}^{-1}$ **8** and $-8.3\ \mathrm{cm}^{-1}$ **9**, but a strong correlation is observed between D and ρ and therefore we have little confidence on the accuracy of those values.

Usually, mononuclear oxamidate-containing nickel(II) complexes are diamagnetic square planar species due to the coordination of the strong field-amide nitrogen atoms [2g,8,28]. However, paramagnetic pentacoordinate Ni(II)-oxamidate complexes can be prepared blocking partially the coordination sphere of the nickel(II) ion by a polydentate ligand prior to its complexation with the oxamidate ligand. The macrocyclic ligands Me₃-N₃-mc and Me₄-N₃-mc allow us to illustrate this strategy and the N,N'-substituted oxamides which can introduce some angular strain when bound to the nickel atom. The nickel atom in complexes **5–12** is paramagnetic and five-coordinate with a stereochemistry intermediate between square pyramidal and trigonal bipyramidal: the three nitrogen atoms from the macrocycle and two oxamidate atoms (N,O) form a distorted five-coordinate environment around the nickel atom. It seems that these macrocyclic ligands are specially suited to induce a unusual five-coordinate surrounding around the nickel(II) ion. The structures of the complexes **6**, **8** and **9** of the present work reinforce this observation. The environment of each nickel(II) ion in the case of complexes **8** and **9** are square pyramid fairly distorted while the substitution 4-chloro in the N-phenyl group in **6** causes a significant modification of the stereochemistry of the nickel(II) ions from square pyramidal towards trigonal bipyramidal (τ values of 0.37, 0.38 for **8** and **9** and 0.52 for **6**).

The previously reported oxamidate-bridged nickel(II) complexes together with their most relevant magnetostructural data are listed in Table 2. There are three important factors that can affect the magnetic properties in this family of compounds: (i) the geometric distortion in the coordination sphere of metal ions, (ii) the topology of the oxamidate bridge and (iii) the different ligand

substitution in the bridging ligand. The first conclusion that can be derived from Table 2 is that the replacement of the oxamidate hydrogen by a bulkier group causes a decrease in the antiferromagnetic interactions. It is probably due to the important increase of the distortion of the coordination sphere of the metal ion (τ is only 0.12 for the unsusbtituted compound). This result agrees well with a DFT study previously reported showing that stronger antiferromagnetic interactions must be expected for nickel(II) ions in square pyramidal than in trigonal bipyramidal environments [11]. However, it appears that this is not the only factor with influence on the exchange parameter. In this way, the calculated J value is slightly larger for compound **6** than for the phenyl derivative despite its greater τ distortion factor. Considering the structural data recorded in Table 2 this anomalous behaviour can be ascribed to the topology of the bridging ligand. Thus the phenyl compound has the larger asymmetry between the N–C and C–O distances in the oxamidate bridge indicating a poor π-delocalization and therefore a less effective exchange pathway. In summary, both the stereochemistry of the metal ion and the topology of the bridging ligand play a relevant role on the magnetic properties, whereas the substitution on the N-phenyl group has less influence. However, the magnitudes of contact shifts, due to both π-spin delocalization and spin polarization effects, increase as result of the delocalization of the lone pair throughout the aromatic group and it is reflected in a smaller spin density at the donor atom and so in weaker antiferromagnetic coupling.

Acknowledgement

Appendix A. Supplementary material

CCDC 663968 , 663969 and 663970 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.03.001.

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