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Complexes with diimine ligands
Part II. Synthesis, structure and magnetic studies of mixed acetylacetonatenickel(II) derivatives

Albert Escuer*, Ramon Vicente, Teresa Comas, Joan Ribas, Montserrat Gomez
Departament de Química Inorgânica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona (Spain)
and **Xavier Solans**
Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, c/Martí Franques s/n, 08028-Barcelona (Spain)

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Abstract

The synthesis, structure and magnetic properties of [Ni(L)(hfacac)$_2$], [Ni(L)(tfacac)$_2$], [Ni(BDPQ)(acac)$_2$] where L is 2,3-bis(2-pyridyl)pyrazine (DPP), 2,3-bis(2-pyridyl)quinoxaline (DPQ), 6-methyl-2,3-bis(2-pyridyl)quinoxaline (MeDPQ), 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (DMeDPQ), 6-chloro-2,3-bis(2-pyridyl)quinoxaline (ClDPQ), 2,3-bis(2-pyridyl)benzoquinoxaline (BDPQ), hfacac, tfacac and acac are hexafluoroacetylacetonate, trifluoroacetylacetonate and acetylacetonate ions, respectively, and [Ni$_2$(L')(acac)$_4$] where L' is DPQ, MeDPQ and DMeDPQ, are described. The crystal structures of the BDPQ ligand and the [Ni(BDPQ)(hfacac)$_2$] complex are also reported. The ligand BDPQ crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a=16.990(3)$, $b=7.982(2)$, $c=6.197(2)$ Å, $\alpha=96.74(2)$, $\beta=94.89(3)$, $\gamma=102.48(2)°$ and $Z=2$. The [Ni(BDPQ)(hfacac)$_2$] complex crystallizes in the monoclinic space group $P2_1/a$ with a cell parameters $a=24.272(4)$, $b=15.222(3)$, $c=8.964(2)$ Å, $\beta=97.61(3)°$ and $Z=4$. Two nickel–nitrogen (pyridine) bonds are present.

Introduction

In a previous paper [1] we presented the possibility for the diimine ligands of Fig. 1 to act as a chelate ligand like A (seven-membered ring, Fig. 2) in the series of coordination compounds [Cu(L)(hfacac)$_2$]. The crystal structure of one of them, [Cu(DMeDPQ)(hfacac)$_2$], was solved and is, at the moment, the only one reported with A coordination, whereas the B coordination (five-membered ring, Fig. 2) has no structural examples with first row transition elements and only one example exists with Ru^{2+}, [Ru(DPQ)(bpy)$_2$](PF$_6$)$_2$ [2].

We report here the synthesis and characterization of a series of mononuclear complexes [Ni(L)(hfacac)$_2$], [Ni(L)(tfacac)$_2$] and [Ni(BDPQ)(acac)$_2$], where L are diimine-type ligands and hfacac, tfacac and acac are hexafluoroacetylacetonate, trifluoroacetylacetonate and acetylacetonate ions, respectively, and the X-ray structure determination of the complex [Ni(BDPQ)(hfacac)$_2$], the second structural example of a coordination like A.

On the other hand, these ligands are closely related with the 2,2'-bipyrimidine and pyrazine ligands. Dinuclear complexes derived from them are well studied from structural and magnetical points of view [3–11] to try to explain the exchange pathway through the bridge from two different hypotheses: σ pathway [3–8] and π pathway [9, 10]. We also present in this work the synthesis and characterization of dinuclear [Ni$_2$(L')(acac)$_4$] complexes (L' = DPQ, MeDPQ and DMeDPQ) which can be only derived from the diimine type ligands acting like B. The magnetic studies of them are interesting with the aim of providing new examples of these kinds of coupled systems. We also present the crystal structure of the molecule 2,3-bis(2-pyridyl)benzoquinoxaline (BDPQ), the first structure of these kinds of ligands.

Experimental

Preparation of reagents

[Ni(hfacac)$_2$] and [Ni(tfacac)$_2$] were prepared by the general method described by Berg and Truemper

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*Author to whom correspondence should be addressed.

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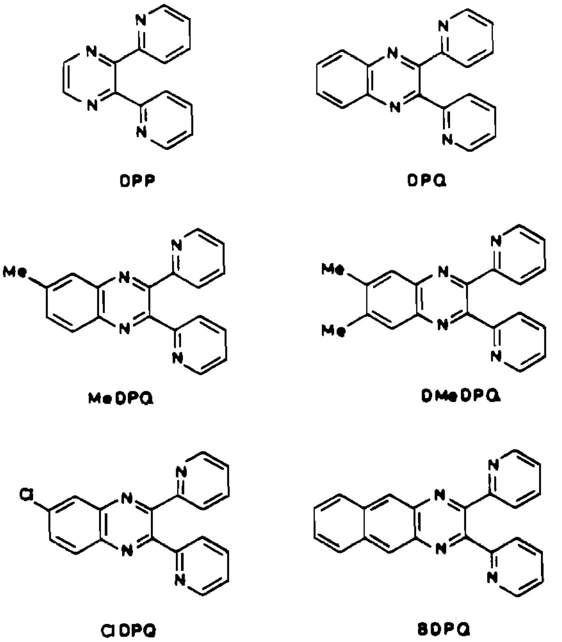

Fig. 1. Diimine type ligands studied in this work.

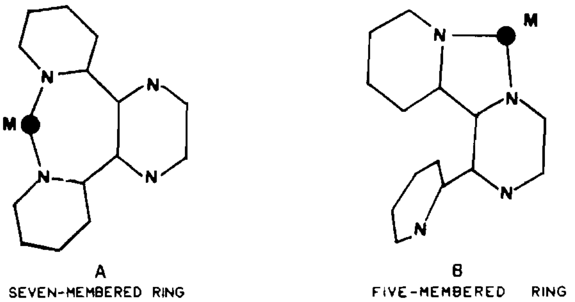

Fig. 2. Coordination possibilities for the diimine type ligands to act as a bidentate ligand.

[12]. The complex [Ni(acac)$_2$] (Fluka) was used without purification.

Diimine ligands DPP, DPQ, MeDPQ, DMeDPQ, ClDPQ, and BDPQ were prepared and purified as previously reported [1].

Preparation of complexes

[Ni(L)(hfacac)$_2$] and [Ni(L)(tfacac)$_2$]

All the compounds were obtained by direct reaction at room temperature of a mixture of equimolar amounts of [Ni(hfacac)$_2$] or [Ni(tfacac)$_2$] and the corresponding L ligand in acetone or acetonitrile. Slow evaporation gave the crystalline compounds in 60–70% yield. Recrystallization was unnecessary.

[Ni$_2$(L′)(acac)$_4$]

These compounds were obtained by mixing hot acetone solutions of [Ni(acac)$_2$] and the L′ ligand in the corresponding stoichiometric amounts. The attempts with the DPP and ClDPQ ligands were unsuccessful and with BDPQ the mononuclear [Ni(BDPQ)(acac)$_2$] was always obtained.

Analytical data are summarized in Table 1.

Techniques

Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. Samples were prepared by using the KBr technique. Electronic spectra were recorded in acetonitrile solutions with a Perkin-Elmer 550-S spectrophotometer. Voltammetric measurements were performed with a DACFAMOV 05-03 instrument, in deaerated acetonitrile solutions and (n-Bu$_4$N)PF$_6$ 0.1 M as supporting electrolyte. Potentials were referred versus an Ag/AgCl (0.1 M KCl) electrode. Variable temperature magnetic susceptibility data were measured by using a fully automatized Aztec DSM5 susceptometer equipped with a Oxford CF 1200 S continous-flow cryostat and a Bruker B-E15 electromagnet. Diamagnetic corrections were estimated from Pascal's constants and substracted from the experimental susceptibility data.

X-ray structure determination

Well formed crystals of the BDPQ ligand and the [Ni(BDPQ)(hfacac)$_2$] complex were obtained and mounted on a Phillips PW-1100 four circle diffractometer. Unit cell parameters were determined from automatic centring of 15 reflections ($4° \leqslant \theta \leqslant 12°$), and refined by the least-squares method. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed during the measurements of reflections.

TABLE 1. Analytical data for the new complexes

	Calc. (found) (%)		
	C	N	H
[Ni(DPP)(hfacac)$_2$]	40.77(41.0)	7.92(8.0)	1.71(1.8)
[Ni(DPQ)(hfacac)$_2$]	44.42(44.5)	7.40(7.2)	1.86(1.8)
[Ni(MeDPQ)(hfacac)$_2$]	45.17(45.2)	7.27(7.3)	2.09(2.0)
[Ni(DMeDPQ)(hfacac)$_2$]	45.89(45.8)	7.14(7.3)	2.31(2.5)
[Ni(ClDPQ)(hfacac)$_2$]	42.49(43.1)	7.08(7.0)	1.66(1.8)
[Ni(BDPQ)(hfacac)$_2$]	47.61(47.5)	6.94(7.1)	2.00(1.9)
[Ni(DPP)(tfacac)$_2$]	48.11(48.1)	9.35(9.3)	3.03(3.2)
[Ni(DPQ)(tfacac)$_2$]	51.80(51.7)	8.63(8.5)	3.11(3.0)
[Ni(MeDPQ)(tfacac)$_2$]	52.52(52.6)	8.45(8.5)	3.34(3.2)
[Ni(DMeDPQ)(tfacac)$_2$]	53.20(53.1)	8.27(8.4)	3.57(3.7)
[Ni(ClDPQ)(tfacac)$_2$]	49.19(49.4)	8.20(8.1)	2.80(2.9)
[Ni(BDPQ)(tfacac)$_2$	54.96(54.7)	8.01(8.2)	3.17(3.0)
[Ni(BDPQ)(acac)$_2$]	65.00(64.4)	9.48(9.4)	4.77(4.5)
[Ni$_2$(DPQ)(acac)$_4$]	57.18(57.3)	7.02(7.0)	5.05(5.0)
[Ni$_2$(MeDPQ)(acac)$_4$]	57.67(57.8)	6.90(6.8)	5.21(5.4)
[Ni$_2$(DMeDPQ)(acac)$_4$]	58.15(58.0)	6.78(6.7)	5.37(5.5)

Lorentz–polarization but no absorption corrections were made.

The structures were solved by direct methods, using the MULTAN system of computer programs [13], and refined by the full matrix least-squares method, using the SHELX76 computer program [14].

BDPQ ligand

Scan width 0.6°, scan speed 0.03° s^{-1}. A total of 2176 reflections was measured in the range $2° \leqslant \theta \leqslant 25°$, 1382 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = [\sigma^2(F_o) + 0.010(F_o)^2]^{-1}$; f, f' and f'' were taken from the International Tables of X-ray Crystallography [15]. The positions of the hydrogen atoms were obtained from a difference synthesis and refined with an overall isotropic temperature factor. The final R factor was 0.050 ($R_w = 0.052$) for all observed reflections. Max. shift/e.s.d. = 0.05 in U_{11} of C(18); max. and min. peaks in final difference synthesis were 0.2 and −0.2 e $Å^{-3}$, respectively.

Crystal data for BDPQ ligand

$C_{22}H_{14}N_4$, formula weight = 334.4, triclinic $P\bar{1}$, $a = 16.990(3)$, $b = 7.982(2)$, $c = 6.197(2)$ Å, $\alpha = 96.74(2)$, $\beta = 94.89(3)$, $\gamma = 102.48(2)$, $V = 809.6(6)$ $Å^3$, $D_x = 1.371$ g cm^{-3}, $Z = 2$, $F(000) = 348.0$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 0.91 cm^{-1}, 298 K.

[Ni(BDPQ)(hfacac)$_2$] complex

Scan width 0.8°, scan speed 0.03° s^{-1}. A total of 3173 reflections was measured in the range $2° \leqslant \theta \leqslant 25°$, 2526 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = \sigma^{-2}(F_o)$; f, f' and f'' were taken from ref. 15. Fluorine atoms occupy disorder localizations. An occupancy factor of 0.5 was assumed for each atom according to difference synthesis peaks. Twenty H atoms were computed, their positions being refined with an overall isotropic temperature factor, using a riding model. The fluorine atoms were only refined isotropically, while the remaining atoms were refined anisotropically. The final R factor was 0.033 ($R_w = 0.038$) for all observed reflections. Number of refined parameters 475. Max. shift/e.s.d. = 0.2 in U_{11} of F(38); max. and min. peaks in final difference synthesis were 0.2 and −0.2 e $Å^{-3}$, respectively.

Crystal data for [Ni(BDPQ)(hfacac)$_2$]

$C_{32}H_{18}N_4O_4F_{12}Ni$, formula weight = 809.21, monoclinic, $P2_1/a$, $a = 24.272(4)$, $b = 15.222(3)$, $c = 8.964(2)$ Å, $\beta = 97.61(3)°$, $V = 3283(2)$ $Å^3$, $D_x = 1.637$ g cm^{-1}, $Z = 4$, $F(000) = 1624.0$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 7.14 cm^{-1}, 298 K.

Results and discussion

Structures

BDPQ

The structure of the BDPQ ligand consists of discrete molecules linked by van der Waals forces. The molecular structure of this compound is shown in Fig. 3, and main distances and angles are given in Tables 2 and 3, respectively.

The pyridyl groups are not placed in the relative positions that are indicated in the typical coplanar representation of diimine ligands, like in Fig. 1, in which the minimum N atoms distance is represented between the N-pyrazine/N-pyridine atoms. However, in the structure of BDPQ the nearest nitrogen atoms are the two N-pyridine ones. This position minimizes the repulsion between the hydrogen atoms of pyridyl rings. Torsion angles N26–C21–C20–C7 and

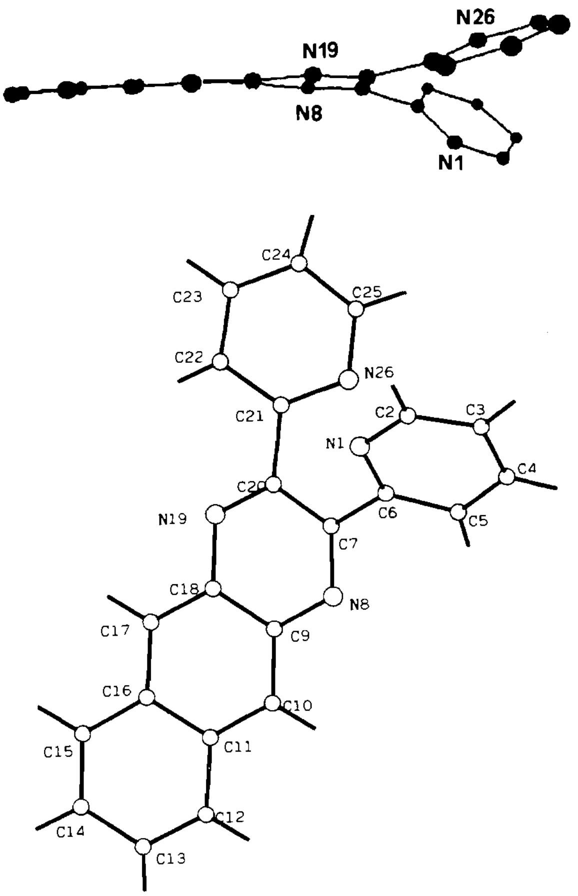

Fig. 3. Molecular structure of BDPQ. The upper view shows the distortion of the pyrazine ring and the relative position of the two pyridyl ones.

TABLE 2. Selected bond distances (Å) for the BDPQ ligand

N(1)-C(2)	1.327(5)
N(1)-C(6)	1.337(4)
C(2)-C(3)	1.372(5)
C(3)-C(4)	1.378(5)
C(4)-C(5)	1.373(5)
C(5)-C(6)	1.384(5)
C(6)-C(67)	1.486(5)
N(26)-C(25)	1.342(5)
N(26)-C(21)	1.341(4)
C(20)-C(21)	1.487(4)
C(7)-C(20)	1.450(4)
N(8)-C(7)	1.308(4)
N(8)-C(9)	1.370(4)
C(9)-C(18)	1.418(4)
N(19)-C(18)	1.376(4)
N(19)-C(20)	1.304(4)

TABLE 3. Selected bond angles (°) for the BDPQ ligand

C(2)-N(1)-C(6)	116.7(3)
N(1)-C(6)-C(5)	123.2(3)
N(1)-C(2)-C(3)	124.3(4)
C(21)-N(26)-C(25)	117.0(3)
N(26)-C(21)-C(22)	122.7(3)
N(26)-C(25)-C(24)	123.5(4)
N(1)-C(6)-C(7)	115.1(3)
N(26)-C(21)-C(20)	116.2(3)
N(8)-C(7)-C(20)	121.2(3)
C(7)-C(20)-N(19)	121.5(3)
C(20)-N(19)-C(18)	117.4(3)
N(19)-C(18)-C(9)	120.3(3)
C(18)-C(9)-N(8)	120.7(3)

Ni–C6–C7–C20 are 24.4(3) and 43.0(3)°, respectively. The quinoxaline ring is not planar (6.4° is the dihedral angle between the planes determined by the C_7, C_9 and N_{19} and C_{20}, C_{18} and N_8 atoms, respectively).

[Ni(BDPQ)(hfacac)$_2$]

The molecular structure of [Ni(BDPQ)(hfacac)$_2$] is shown in Fig. 4, and the main distances and angles are given in Tables 4 and 5, respectively. The coordination environment around the nickel atom can be described as a pseudo-regular octahedron, defined with four oxygen atoms (O27, O31, O40, O44) of two different hexafluoroacetylacetonates, and two N-pyridine atoms in the remaining positions. The Ni–ligand distances are similar, between 2.042(1) Å for O27–Ni and 2.104(2) Å for N–Ni. Coordination type A (Fig. 2) for BDPQ produces a dihedral angle between the pyridine rings of 74.1(3)°. The benzoquinoxaline moiety is planar, and the dihedral angles between the pyridyl rings and the benzoquinoxaline are 53.5(3) and 48.8(3)°. The position of two pyridyl groups is similar to the free ligand.

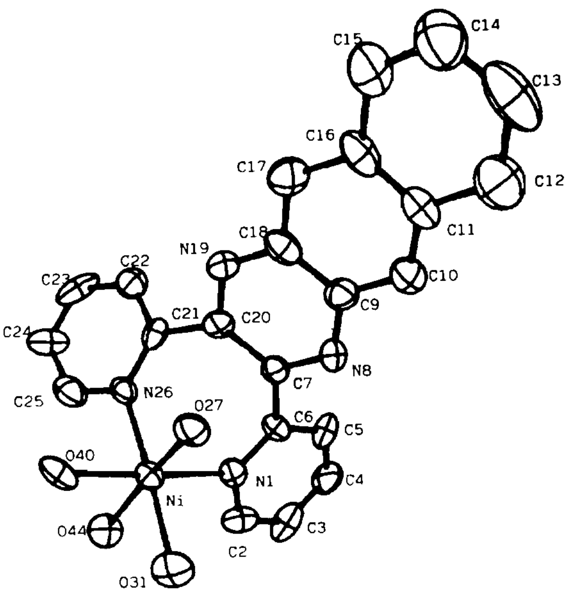

Fig. 4. Molecular structure of [Ni(BDPQ)(hfacac)$_2$]. Only coordinating atoms of the hfacac are showed.

TABLE 4. Selected bond distances (Å) for [Ni(BDPQ)(hfacac)$_2$]

Ni-N(1)	2.104(2)
Ni-N(26)	2.064(2)
Ni-O(27)	2.042(1)
Ni-O(31)	2.057(2)
Ni-O(40)	2.048(2)
Ni-O(44)	2.058(2)
N(1)-C(2)	1.352(3)
N(1)-C(6)	1.314(2)
N(26)-C(21)	1.339(2)
N(26)-C(25)	1.345(3)
C(6)-C(7)	1.477(3)
C(21)-C(20)	1.519(3)
C(7)-C(20)	1.456(3)
N(8)-C(7)	1.311(3)
N(19)-C(20)	1.305(3)

IR and electronic spectra

The IR spectra of the complexes show the characteristic bands of the acetylacetonate and the nitrogenated ligands. The IR spectra of the new complexes agree with the previously reported conclusions [1]. All the spectra are very complex due to the overlap of the intense absorptions of the acetylacetonate ligands with those of the diimines. The only significant feature is related to the absorption of the diimines centered ~1600 cm^{-1}: the free ligands show two well defined absorptions at 1580–90 and 1560–70 cm^{-1}, and the new complexes show these bands centered at 1600–10 and 1580–90 cm^{-1}. According to the literature [16] the shift of these two bands is characteristic of the coordinate ligands. The

TABLE 5. Selected bond angles (°) for [Ni(BDPQ)(hfacac)$_2$]

O(27)-Ni-O(44)	166.8(1)
O(31)-Ni-N(26)	176.4(1)
O(40)-Ni-N(1)	176.5(1)
O(27)-Ni-O(40)	83.9(1)
O(27)-Ni-O(31)	86.6(1)
O(27)-Ni-N(26)	96.4(1)
O(27)-Ni-N(1)	96.5(1)
O(44)-Ni-O(40)	88.0(1)
O(44)-Ni-O(31)	82.8(1)
O(44)-Ni-N(26)	93.9(1)
O(44)-Ni-N(1)	92.2(1)
O(40)-Ni-O(31)	89.0(1)
O(31)-Ni-N(1)	94.5(1)
O(40)-Ni-N(26)	89.4(1)
N(1)-Ni-N(26)	87.1(1)
Ni-N(1)-C(6)	125.1(1)
Ni-N(26)-C(21)	126.1(1)
N(1)-C(6)-C(7)	121.3(2)
C(6)-C(7)-C(20)	124.6(2)
C(7)-C(20)-C(21)	127.0(2)
C(2)-N(1)-C(6)	117.7(2)
C(21)-N(26)-C(25)	116.6(2)

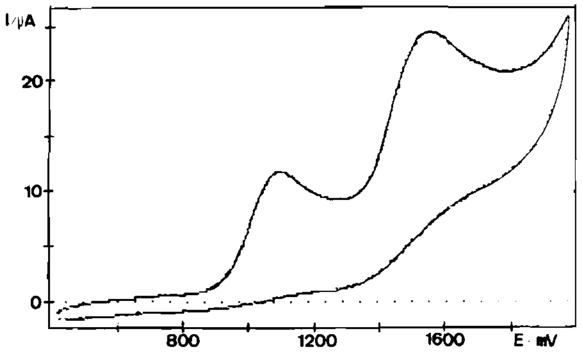

Fig. 5. Cyclic voltammogram for [Ni$_2$(DPQ)(acac)$_4$].

structurally analogous complexes with Cu show a very similar spectra [1].

Voltammetric measurements

For this kind of ligand the possibility of the formation of radical species [17, 18] or mixed valence compounds with first row ions [8] is described. But in our case, only irreversible oxidation processes were observed for the dinuclear complexes [Ni$_2$(L')(acac)$_4$]. For L' = DPQ, (Fig. 5), two irreversible peaks are present, centered at 1.1 and 1.5 V. For the remaining compounds the result is similar.

Magnetic measurements

The variable temperature powder-magnetic susceptibility data were recorded for the two dinuclear [Ni$_2$(L')(acac)$_4$] complexes with DPQ and DMeDPQ as L' bridging ligands. The plots of XT versus T between 4–280 K, show a practically constant value up to 50 K and below this temperature XT decreases slightly in both cases (Fig. 6). These data were analyzed with the isotropic spin Hamiltonian $\mathscr{H} = -JS_1S_2$ where J is the exchange parameter and $S_1 = S_2 = 1$ (local spins). X_M may be expressed as

$$X_M = \frac{2N\beta^2g^2}{KT}\,\frac{\exp(J/kT) + 5\exp(3J/kT)}{1 + \exp(J/kT) + 5\exp(3J/kT)} \times (1-\rho) + \frac{2N\beta^2g^2}{3kT}\,\rho$$

In this expression N, β, k and ρ have their usual meanings. A least-square fitting of all the experimental points leads to J and ρ values of approximately -1.5 cm^{-1} and 0.05, respectively. On the other hand no maximum in the plot of X_M versus T is observed. The plots of $1/X_M$ versus T (Fig. 6) obey the Curie–Weiss law with $X_M = 2.24909/(T + 2.9988)$ and $X_M = 2.72384/(T + 3.1959)$ for [Ni$_2$(DMeDPQ)(acac)$_4$] and [Ni$_2$(DPQ)(acac)$_4$], respectively. These low values of the J parameter and the non-existence of a maximum in the plot of X_M versus T are consistent with a very low or non-existent superexchange pathway between the two nickel atoms, which can be rationalized in terms of the previsible position of the two metal centers with respect to the pyrazine ring: for a dinuclear diimine complex, the interaction between the two 6,6' H atoms of the pyridine rings [2, 8, 16, 19–21] must turn the pyridyl rings and make it impossible to place the three rings in the same plane. In this case the Ni atoms must necessarily be placed in opposite sites out of the main plane, with a Ni–Ni distance evaluated as *c.* 7 Å. The position of the Ni atoms out of the pyrazine π pathway exchange is consistent with the experimental magnetic results.

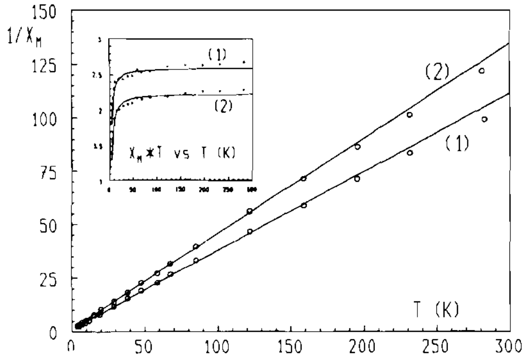

Fig. 6. Temperature dependence of $1/X_M$ vs. T for [Ni$_2$(DPQ)(acac)$_4$] (1) and [Ni$_2$(DMeDPQ)(acac)$_4$] (2). Inset: the temperature dependence of X_MT vs. T; the solid line shows the best fitting with theoretical values.

Conclusions

We have presented the synthesis, characterization, magnetic and structural studies of several mono- and dinuclear mixed acetylacetonatenickel(II) complexes with some diimine ligands. From the structural data of [Ni(BDPQ)(hfacac)$_2$] and taking into account the similarities in IR and UV–Vis spectra of the new complexes, we suggest the same type of coordination A, seven-membered ring) for all of them.

For the dinuclear complexes, the only possibility is the coordination B. The powder-magnetic susceptibility data indicates a very low or non-existent magnetic coupling.

Supplementary material

A listing of all the bond distances and angles, final atomic coordinates, anisotropic thermal parameters, hydrogen atom coordinates and observed and calculated structure factors are available from the authors on request.

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