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

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Abstract

The synthesis and properties of the mononuclear [Co(L)(hfacac)$_2$], [Co(L)(tfacac)$_2$] and of the dinuclear complexes [Co$_2$(L)(acac)$_4$], 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 being hexafluoroacetylacetonate, trifluoroacetylacetonate and acetylacetonate, respectively, are described. The structures of [Co(L)(hfacac)$_2$] where L = BDPQ and DMeDPQ were solved. The [Co(BDPQ)(hfacac)$_2$] complex crystallizes in the $P\bar{1}$ space group with cell parameters $a = 14.382(4)$, $b = 12.853(3)$, $c = 9.094(3)$ Å, $\alpha = 92.55(3)$, $\beta = 100.80(3)$, $\gamma = 94.54(3)°$ and $Z = 2$. The [Co(DMeDPQ)(hfacac)$_2$] complex crystallizes in the $P2_1/a$ space group with cell parameters $a = 19.130(5)$, $b = 9.248(3)$, $c = 18.198(4)$ Å, $\beta = 95.18(3)°$ and $Z = 4$. Magnetic properties of the dinuclear complexes and a study of the coordination possibilities of this kind of ligands are presented.

Introduction

The diimine type ligands studied in this work, and summarized in Fig. 1, have acquired great interest principally for ruthenium-based systems [1–11] due to their similarity with the 2,2′-bipyridine ligand. The normal coordination for these ligands is assumed to be a five-membered ring involving the pyrazine ring (Fig. 2, **B**). However, only one structure was reported for this kind of complex: the mononuclear [Ru(DPQ)(bpy)$_2$]$^{2+}$ [7], which, effectively has the **B** coordination. On the other hand, little is reported on the behavior of these ligands towards other transition metal cations different from Ru(II) [12–21]. In previous work [18, 19] with Cu(II) and Ni(II) as central ions and the same diimine ligands, we have shown another possibility of chelating coordination: they can bind using the N atom of the two pyridine rings placed in a *cis* conformation. This kind of behavior gives a seven-membered ring (Fig. 2, **A**). In order to study if this new kind of coordination is repeated with other first row cations, we report here the synthesis of a series of Co(II) complexes with several of these diimines, together with structural information.

On the other hand, these ligands are closely related to the bipyrimidine (bpm) and pyrazine (pz) ligands, whose complexes have been extensively studied [17, 22–29]. In this work, we present new magnetic data about the pyridyl–pyrazine dinuclear complexes, with the aim of providing new examples of these kinds of systems.

Experimental

Preparation of reagents

[Co(hfacac)$_2$] and [Co(tfacac)$_2$] were prepared by the method described by Cotton and Holm [30]. The complex [Co(acac)$_2$] was purchased (Fluka) and used without purification.

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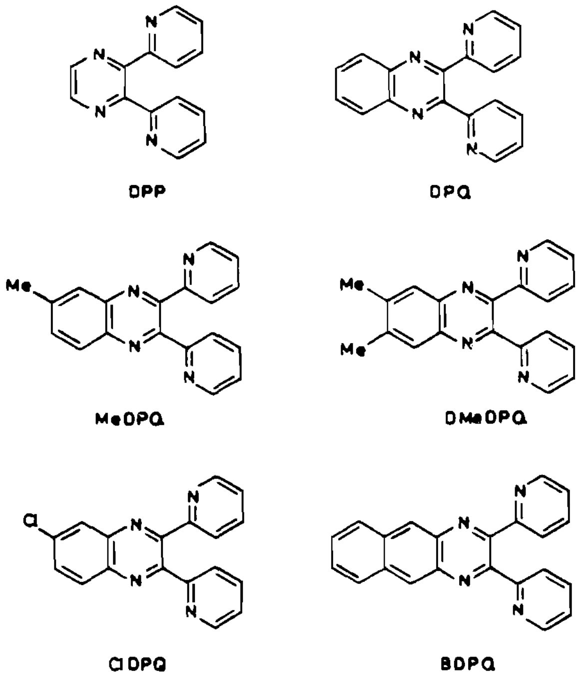

Fig.1. Schematic representation of the diimine type ligands used in this work.

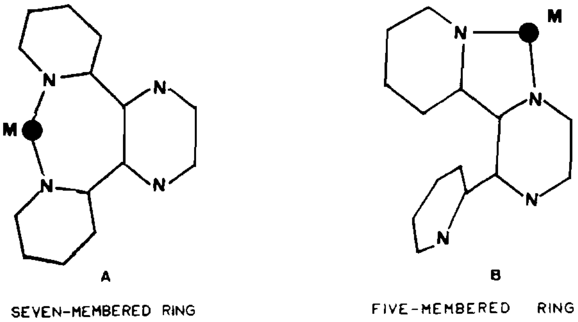

Fig. 2. Coordination possibilities for the diimine type ligands to act as a bidentate ligand.

Diimine ligands DPP, DPQ, MeDPQ, DMeDPQ, BDPQ and ClDPQ were prepared and purified as previously reported [18].

Preparation of the new complexes

The mononuclear hfacac and tfacac derivatives were obtained by direct reaction at room temperature, of a mixture of equimolar amounts of [Co(hfacac)$_2$] or [Co(tfacac)$_2$] and the ligand (DPP, DPQ, MeDPQ, DMeDPQ, BDPQ and ClDPQ), in acetonitrile. Slow evaporation gave the red crystalline compounds in 70–80% yield. All these compounds are very soluble in the common organic solvents.

Dinuclear complexes with acac were obtained, at room temperature, by mixing a concentrated solution of [Co(acac)$_2$] with the corresponding ligand in acetone (2:1). The solutions become deep red, and the compounds precipitate after 10–15 min. 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 Shimadzu UV 160 A spectrophotometer. Voltammetric measurements were performed using 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. Polycrystalline powder EPR spectra were recorded with a Bruker ER200 spectrometer at X-band frequence at 4.2 K. Variable temperature magnetic susceptibility data were measured by using a fully automatized Aztec DSM5 susceptometer equipped with an 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

Adequate crystals of the [Co(BDPQ)(hfacac)$_2$] and [Co(DMeDPQ)(hfacac)$_2$] complexes were obtained and mounted on a Philips PW-1100 four circle diffractometer. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed during the measurements of reflections. Lorentz–polarization but no absorption corrections were made.

Structures were solved by direct methods, using the MULTAN system of computer programs [31], and refined by full matrix least-squares method in two blocks, using the SHELX76 computer program [32]. Crystallographic data and other pertinent informations are summarized in Table 2.

For the [Co(BDPQ)(hfacac)$_2$] complex, 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. 33. Three F atoms were located in a disorder position, an occupancy factor of 0.5 was assigned to each, according to height of difference Fourier. The complete molecular structure of this compound is shown in Fig. 3(a). In Fig. 3(b) only the Co(II) ion and the atoms directly bound to it are shown. Atomic coordinates are gathered in Table 3, and main bond distances and angles are given in Table 4.

For the [Co(DMeDPQ)(hfacac)$_2$] complex, the function minimized was the same as that given above. F atoms show higher temperature coefficients, and attempts to determine disorder positions were un-

TABLE 1. Analytical data for the new complexes

	Calc. (found) (%)		
	C	N	H
[Co(DPP)(hfacac)$_2$]	40.76(41.0)	7.92(7.9)	1.71(1.6)
[Co(DPQ)(hfacac)$_2$]	44.40(44.6)	7.40(7.3)	1.86(1.9)
[Co(MeDPQ)(hfacac)$_2$]	45.16(45.3)	7.26(7.3)	2.09(1.9)
[Co(DMeDPQ)(hfacac)$_2$]	45.88(46.2)	7.13(7.2)	2.31(2.2)
[Co(ClDPQ)(hfacac)$_2$]	42.47(42.7)	7.08(7.1)	1.65(1.8)
[Co(BDPQ)(hfacac)$_2$]	47.60(47.6)	6.94(7.0)	2.00(2.0)
[Co(DPP)(tfacac)$_2$]	48.10(47.8)	9.35(9.2)	3.03(3.1)
[Co(DPQ)(tfacac)$_2$]	51.79(51.6)	8.62(8.5)	3.10(3.2)
[Co(MeDPQ)(tfacac)$_2$]	52.50(52.6)	8.45(8.5)	3.34(3.2)
[Co(DMeDPQ)(tfacac)$_2$]	53.19(52.9)	8.27(8.2)	3.57(3.5)
[Co(ClDPQ)(tfacac)$_2$]	49.18(49.3)	8.19(8.4)	2.80(2.7)
[Co(BDPQ)(tfacac)$_2$]	54.95(54.7)	8.01(8.0)	3.17(3.0)
[Co$_2$(DPP)(acac)$_4$]	54.55(54.6)	7.48(7.4)	5.12(5.2)
[Co$_2$(DPQ)(acac)$_4$]	57.15(57.0)	7.02(6.9)	5.05(5.1)
[Co$_2$(MeDPQ)(acac)$_4$]	57.64(57.3)	6.89(6.8)	5.21(5.1)
[Co$_2$(DMeDPQ)(acac)$_4$]	58.12(58.0)	6.78(6.5)	5.36(5.5)
[Co$_2$(ClDPQ)(acac)$_4$]	54.79(54.9)	6.73(6.8)	4.72(4.6)
[Co$_2$(BDPQ)(acac)$_4$]	59.44(59.4)	6.60(6.7)	4.99(5.1)

TABLE 2. Single crystal X-ray crystallographic analysis for [Co(L)(hfacac)$_2$]

	L=BDPQ	L=DMeDPQ
Formula	$C_{32}H_{16}N_4O_4F_{12}Co$	$C_{30}H_{18}N_4O_4F_{12}Co$
Unit weight	807.41	785.41
Crystal size (mm)	0.2×0.2×0.1	0.1×0.1×0.2
Space group	$P\bar{1}$	$P2_1/a$
Temperature (K)	298	298
Cell dimensions		
a (Å)	14.382(4)	19.130(5)
b (Å)	12.853(3)	9.248(3)
c (Å)	9.094(3)	18.198(4)
α (°)	92.55(3)	90
β (°)	100.80(3)	95.18(3)
γ (°)	94.54(3)	90
V (Å^3)	1643(1)	3206(3)
Z	2	4
D_{calc} (g/cm^3)	1.636	1.871
Radiation, λ (Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ(Mo Kα)	6.66	6.95
Scan width	0.8	0.8
Scan speed (s^{-1})	0.03	0.03
Orientation reflections: no.; range θ (°)	25; 4–12	15; 4–12
Data collection range, θ	2–25	2–25
No. reflections collected	3492	3994
No. reflections with $I \geqslant 2.5\ \sigma(I)$	2022	2283
No. parameters refined	504	550
R	0.033	0.076
R_w	0.035	0.079
Largest shift/e.s.d.	0.4	0.1
Largest peak (e/A^3)	0.6	1.0

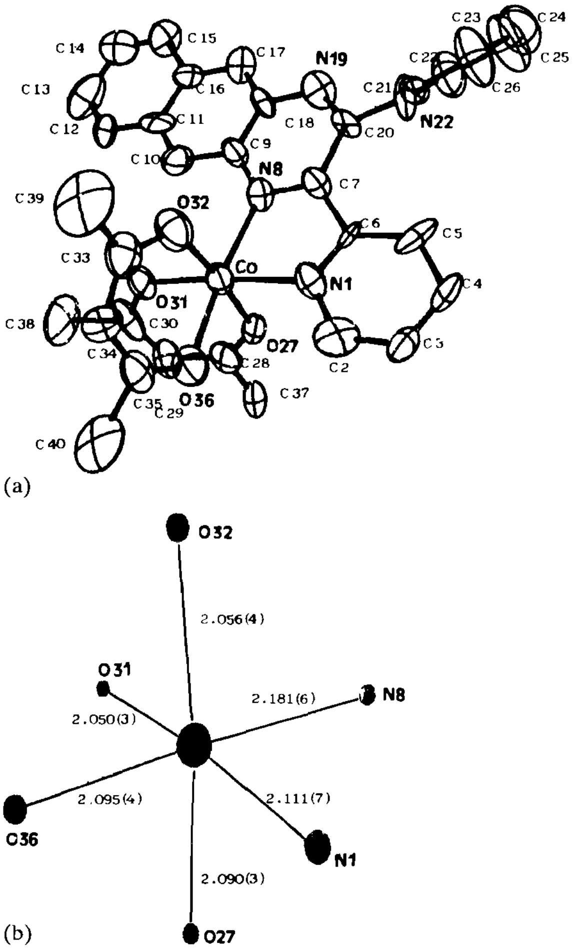

Fig. 3. Molecular structure of [Co(BDPQ)(hfacac)$_2$] (a) and coordination environment of Co atom (b).

successful. The structure of this compound is shown in Fig. 4. Atomic coordinates are gathered in Table 5, and main angles and bond distances in Table 6.

Results and discussion

Synthesis of the complexes

After the structural confirmation of the five-membered ring coordination mode of the cobalt atoms in the mononuclear species, we tried the synthesis of the corresponding dinuclear derivatives, using a ratio Co:L of 2:1. All the attempts made with the hfacac and tfacac cobalt complexes (at room temperature, under reflux conditions and varying the solvent) were unsuccessful. In all cases only the mononuclear compound crystallized. With acac, we were able to synthesize Co(II) dinuclear complexes, but all attempts to obtain suitable crystals for X-ray determination were unsuccessful.

TABLE 3. Final atomic coordinates ($\times 10^4$) of $C_{32}H_{18}N_4O_4F_{12}Co$

	x/a	y/b	z/c	B_{eq}[a]
Co	6963(1)	2673(1)	6510(1)	3.50(6)
N(1)	5883(5)	3397(5)	5129(8)	3.91(35)
C(2)	6085(7)	4254(8)	4361(12)	5.01(52)
C(3)	5441(7)	4663(7)	3350(9)	4.09(46)
C(4)	4539(8)	4098(9)	2915(9)	5.44(52)
C(5)	4341(7)	3133(7)	3649(9)	4.78(48)
C(6)	5050(6)	2860(6)	4768(8)	2.98(37)
C(7)	4915(6)	1941(7)	5683(10)	4.23(44)
N(8)	5700(4)	1605(5)	6457(7)	3.37(32)
C(9)	5594(5)	768(7)	7272(9)	3.87(42)
C(10)	6417(6)	395(7)	8239(10)	4.36(45)
C(11)	6306(6)	−465(7)	8988(9)	4.60(48)
C(12)	7131(6)	−890(8)	9910(10)	4.82(50)
C(13)	7060(11)	−1732(8)	10685(12)	7.57(76)
C(14)	6065(9)	−2300(8)	10569(13)	6.40(65)
C(15)	5313(8)	−1985(7)	9710(12)	5.16(54)
C(16)	5423(6)	−1111(7)	8816(9)	4.03(44)
C(17)	4613(6)	−733(7)	7922(10)	4.31(44)
C(18)	4737(5)	137(7)	7186(9)	3.27(38)
N(19)	3932(5)	506(6)	6373(9)	4.64(39)
C(20)	3973(5)	1404(7)	5741(8)	3.35(38)
C(21)	3074(5)	1820(7)	5202(9)	3.81(43)
N(22)	2960(5)	2797(6)	5710(8)	2.86(37)
C(23)	2118(7)	3173(9)	5353(12)	6.77(61)
C(24)	1376(7)	2576(9)	4549(14)	6.73(63)
C(25)	1444(7)	1551(9)	3876(15)	7.77(72)
C(26)	2334(8)	1158(10)	4304(12)	6.67(60)
O(27)	7346(2)	2017(2)	4590(3)	4.05(16)
C(28)	8135(4)	1759(3)	4550(5)	4.46(26)
C(29)	8906(4)	1585(4)	5718(7)	5.40(29)
C(30)	8787(3)	1682(4)	7258(8)	5.30(28)
O(31)	8059(2)	1945(3)	7692(4)	4.84(17)
O(32)	6734(2)	3396(3)	8458(4)	5.35(18)
C(33)	7335(4)	4111(4)	9309(6)	5.06(28)
C(34)	8162(4)	4588(4)	8989(6)	5.40(28)
C(35)	8445(3)	4412(4)	7609(7)	4.60(26)
O(36)	8014(2)	3882(3)	6422(4)	5.18(19)
C(281)	8398(6)	1605(8)	2981(7)	7.79(49)
C(301)	9655(6)	1473(9)	8627(9)	9.11(53)
C(331)	7023(8)	4597(9)	10784(10)	11.48(70)
C(351)	9525(7)	4865(7)	7517(7)	8.47(49)
F(281)	7643(3)	1529(3)	1956(4)	7.32(21)
F(282)	9149(9)	2068(11)	2832(12)	8.68(74)
F(283)	8650(7)	466(9)	2891(11)	8.74(58)
F(301)	9778(4)	2152(4)	9621(6)	4.12(26)
F(302)	9635(4)	−1264(4)	11973(6)	5.30(31)
F(303)	9315(4)	565(5)	9144(7)	5.33(31)
F(331)	6820(3)	3568(3)	11479(5)	9.06(24)
F(332)	6161(4)	4789(4)	10461(6)	3.87(24)
F(333)	7583(6)	5123(6)	11582(8)	7.34(41)
F(351)	9446(3)	5195(3)	6088(4)	7.60(20)
F(352)	9976(10)	5474(11)	8560(18)	9.55(78)
F(353)	10107(4)	4212(4)	7796(6)	3.58(25)
F(282)	8829(7)	2642(8)	2702(10)	6.03(47)
F(283)	9076(7)	1073(10)	2851(9)	7.10(54)
F(352)	9656(7)	5864(7)	8292(11)	4.64(41)

[a] $B_{eq} = 8\pi^2/3(U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j)$.

TABLE 4. Selected bond lengths and angles for [Co(BDPQ)(hfacac)$_2$]

Co–N(1)	2.111(7)	N(1)–C(6)	1.312(10)
Co–N(8)	2.181(6)	C(6)–C(7)	1.496(12)
Co–O(27)	2.090(3)	C(7)–N(8)	1.328(10)
Co–O(31)	2.050(3)		
Co–O(32)	2.056(4)		
Co–O(36)	2.095(4)		
N(1)–Co–N(8)	76.7(2)	O(27)–Co–O(31)	86.0(1)
N(1)–Co–O(27)	89.3(2)	O(27)–Co–O(32)	173.8(1)
N(1)–Co–O(31)	175.1(2)	O(27)–Co–O(36)	85.8(1)
N(1)–Co–O(32)	93.9(2)	O(31)–Co–O(32)	90.7(1)
N(1)–Co–O(36)	93.9(2)	O(31)–Co–O(36)	84.6(1)
N(8)–Co–O(27)	96.5(2)	O(32)–Co–O(36)	88.6(1)
N(8)–Co–O(31)	104.9(2)	N(1)–C(6)–C(7)	115.2(6)
N(8)–Co–O(32)	89.4(2)	C(6)–C(7)–N(8)	116.2(7)
N(8)–Co–O(36)	170.3(2)		

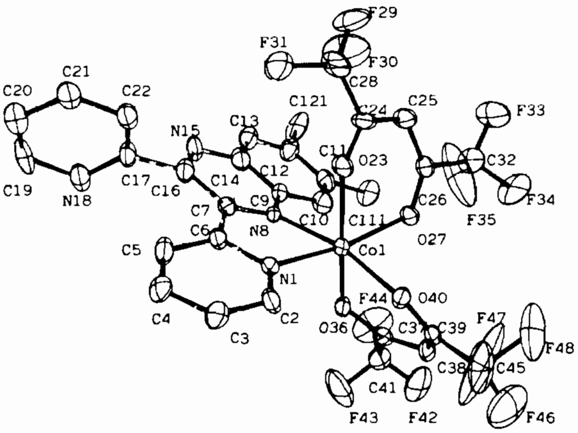

Fig. 4. Molecular structure of [Co(DMeDPQ)(hfacac)$_2$].

IR spectra

The IR spectra of the complexes show the characteristic bands of the corresponding diketone and diimine ligands. As indicated in a previous work with similar complexes in which M = Cu(II) and diketone = hfacac [18], it is difficult to obtain structural information from IR spectra due to the overlap between the bands of the different ligands. In this case, however, it is interesting to notice a possible indication of coordination mode of the diimine ligands, related with the intense band which appears at *c.* 1600 cm^{-1}. The free ligands show this intense absorption centered at 1580–1590 cm^{-1}, and according to the literature [12–16], the shift of this band to 1600–1610 cm^{-1} is indicative of the coordination. This band is present in the spectra of all Cu(II) and Ni(II) complexes which have a type **A** (seven-membered) coordination [18, 19] but this absorption does not appear in the analogous compounds of cobalt(II), with a coordination type **B** (five-membered, involving the pyrazine ring).

TABLE 5. Final atomic coordinates ($\times 10^4$) of $C_{30}H_{20}N_4O_4F_6Co$

	x/a	*y/b*	*z/c*	B_{eq}^{a}
Co(1)	578(1)	283(1)	2694(1)	3.32(5)
N(1)	617(4)	871(8)	3788(4)	3.3(3)
C(2)	138(5)	1707(12)	4057(5)	4.6(5)
C(3)	148(6)	2073(12)	4810(5)	5.5(6)
C(4)	705(6)	1532(12)	5277(5)	5.1(5)
C(5)	1197(5)	620(13)	5006(5)	5.2(5)
C(6)	1146(4)	245(10)	4265(4)	3.6(4)
C(7)	1636(4)	−655(10)	3880(5)	3.5(4)
N(8)	1571(4)	−559(8)	3162(4)	2.3(3)
C(9)	2039(5)	−1243(10)	2771(5)	4.1(5)
C(10)	2036(5)	−1082(12)	2005(5)	5.0(5)
C(11)	2524(6)	−1830(13)	1613(5)	5.1(5)
C(111)	2490(7)	−1609(16)	793(6)	6.8(7)
C(12)	3008(6)	−2772(14)	1995(6)	5.9(6)
C(121)	3495(7)	−3646(20)	1539(7)	8.9(9)
C(13)	3024(5)	−2943(13)	2747(6)	5.6(6)
C(14)	2556(5)	−2164(12)	3151(5)	5.1(6)
N(15)	2399(4)	2689(10)	6104(4)	5.0(4)
C(16)	2840(5)	3422(12)	5737(5)	4.6(5)
C(17)	2758(5)	3165(13)	4919(5)	4.5(5)
N(18)	3231(5)	2355(10)	4672(5)	5.2(5)
C(19)	3144(7)	2018(14)	3904(6)	6.3(7)
C(20)	2584(7)	2594(15)	3449(7)	6.3(7)
C(21)	2112(7)	3376(17)	3738(6)	7.1(8)
C(22)	2175(6)	3766(13)	4505(6)	5.8(6)
O(23)	154(4)	−1660(7)	3056(3)	4.4(3)
C(24)	153(6)	−2857(11)	2740(5)	4.8(5)
C(25)	231(7)	−3125(11)	1981(5)	5.4(6)
C(26)	325(6)	−1977(12)	1504(5)	4.4(5)
O(27)	435(3)	−662(7)	1655(3)	4.1(3)
C(28)	131(10)	−4135(15)	3250(7)	7.6(8)
F(29)	230(6)	4626(8)	2953(4)	11.0(6)
F(30)	571(6)	−4038(9)	3834(4)	11.1(6)
F(31)	−474(6)	−4181(10)	3539(6)	11.3(7)
C(32)	266(10)	−2307(16)	689(6)	7.2(8)
F(33)	52(7)	−3576(10)	498(4)	12.2(6)
F(34)	815(7)	−2044(25)	403(6)	22.2(13)
F(35)	−217(7)	−1542(12)	297(4)	13.0(7)
O(36)	1140(3)	1845(7)	2212(3)	4.0(3)
C(37)	887(5)	2600(10)	1658(6)	4.4(5)
C(38)	185(5)	2878(11)	1440(5)	4.1(5)
C(39)	−335(4)	2415(10)	1819(5)	3.3(4)
O(40)	−302(3)	1515(7)	2364(3)	3.9(3)
C(41)	1446(6)	3296(15)	1249(7)	5.7(6)
F(42)	1224(4)	4014(12)	674(5)	10.9(6)
F(43)	1894(6)	2392(13)	1053(7)	13.2(8)
F(44)	1841(6)	4213(14)	1683(6)	13.4(7)
C(45)	−1068(7)	3098(29)	1642(10)	11.4(13)
F(46)	−1460(6)	2951(25)	2028(6)	23.7(13)
F(47)	−1095(5)	4068(16)	1175(9)	15.2(9)
F(48)	−1388(5)	2206(20)	1069(7)	16.0(10)

^{a}$B_{eq} = 8\pi^2/3(U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j)$.

Electronic spectra and voltammetric measurements

Electronic spectra of these compounds provide poor information about the studied complexes. In all cases only the intense UV charge transfer bands

TABLE 6. Selected bond lengths and angles for [Co(DMeDPQ)(hfacac)$_2$]

Co–N(1)	2.057(7)	N(1)–C(6)	1.398(10)
Co–N(8)	2.156(7)	C(6)–C(7)	1.475(12)
Co–O(23)	2.100(7)	C(7)–N(8)	1.305(11)
Co–O(27)	2.079(6)		
Co–O(36)	2.046(6)		
Co–O(40)	2.076(6)		
N(1)–Co–N(8)	76.1(3)	O(23)–Co–O(27)	84.4(2)
N(1)–Co–O(23)	84.5(3)	O(23)–Co–O(36)	166.1(3)
N(1)–Co–O(27)	168.9(3)	O(23)–Co–O(40)	103.6(3)
N(1)–Co–O(36)	104.7(3)	O(27)–Co–O(36)	86.4(2)
N(1)–Co–O(40)	95.3(3)	O(27)–Co–O(40)	86.0(2)
N(8)–Co–O(23)	85.3(3)	O(36)–Co–O(40)	86.1(2)
N(8)–Co–O(27)	104.2(2)	N(1)–C(6)–C(7)	113.2(7)
N(8)–Co–O(36)	86.9(3)	C(6)–C(7)–N(8)	115.5(7)
N(8)–Co–O(40)	170.3(2)		

characteristic of the ligand are observed, and in the visible range, the d–d bands of the octahedral cobalt atom are shown only as a shoulder in the 500–550 nm region.

Voltammetric measurements were recorded to study the possible oxidation of the Co(II) ions and the possible redox behaviour of the ligands. For this kind of ligand, the possibility of formation of radical species has been suggested [34, 35]. In our measurements, negative results were obtained: in all cases only irreversible processes were observed, with an oxidation wave at *c.* +0.6–0.8 V and the return peak at +0.05–0.15 V.

Structures

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

The structure of [Co(BDPQ)(hfacac)$_2$] consists of discrete molecules linked by van der Waals forces.

The coordination environment around the cobalt ion can be described as a distorted octahedron (Fig. 3). The Co–O distances are 2.050 (O31), 2.090 (O27), 2.056 (O32) and 2.095 (O36) Å for each acetylacetonate ion, respectively. The Co–N distances are 2.111 (N1 of pyridine ring) and 2.181 (N8 of pyrazine moiety) Å. These M–N distances are in agreement with those reported by Rillema *et al.* [7] for the similar coordinated complex [Ru(DPQ)(bpy)$_2$]$^{2+}$, in which the longest distance is the M–N (N-pyrazinic). These distances agree also with the stronger σ donor strength of the pyridine unit ($pK_a = 5.23$) compared to that of the pyrazine ($pK_a = 0.8$). The main distortion involves the pyrazine bond Co–N8: the angle N1–Co–N8 is 76.7°, N8–Co–O31 is 104.9° and N8–Co–O36 is 170.3°. The pyrazine ring is distorted from the planarity (dihedral angle between N8–C18–C20 and N19–C7–C9 is 6.4°) (Fig. 3) that occurs in the free BDPQ ligand [19]. The Co atom is in plane with the benzoquinoxaline. Another interesting feature is the orientation of the main planes of the molecule: the dihedral angle between the two pyridyl groups is 56.6°; between the non-coordinated pyridyl and benzoquinoxaline it is 54.8° and between the coordinated pyridyl and benzoquinoxaline 14.6°.

[Co(DMeDPQ)(hfacac)$_2$]

The structure of [Co(DMeDPQ)(hfacac)$_2$] (Fig. 4) is similar to the former with BDPQ. The largest bond distance around the Co(II) ion is Co–N8 (2.156(7) Å) and the most significant distortion in the environment of the cobalt ion is also associated with the Co–N8 bond, as reflected in the angles N1–Co–N8 = 76.1(3)°, N8–Co–O27 = 104.2(3)° and N8–Co–O40 = 167.2(3)°. Important distortion involves also the position of the O40 atom. The most interesting trend for this structure, different to when L = BDPQ (see above), is the planarity of the pyrazine ring, and the fact that the Co atom is placed 0.58 Å over the plane defined by the atoms N8–C14–C16 of the pyrazine (Fig. 5). The axis O23–Co–O36 determines an angle of 10° with respect to the principal plane of the pyrazine. The dihedral angle between the two pyridyl groups is 72.3°; between the non-coordinated pyridyl and quinoxaline it is 73.5° and between the coordinated pyridyl and quinoxaline 13.4°.

The values of the N–Co–N angles are similar to those of the related compounds [Ru(DPQ)(bpy)$_2$]$^{2+}$ (angle N–Ru–N = 77.6°) [7] and [Co$_2$(bpm)(hfacac)$_4$] (angle N–Co–N = 76.8°) [17].

It is interesting to point out that the coordination of the ligands using the two N-pyridyl rings, as in the complexes with M = Cu [18] and Ni [19], is

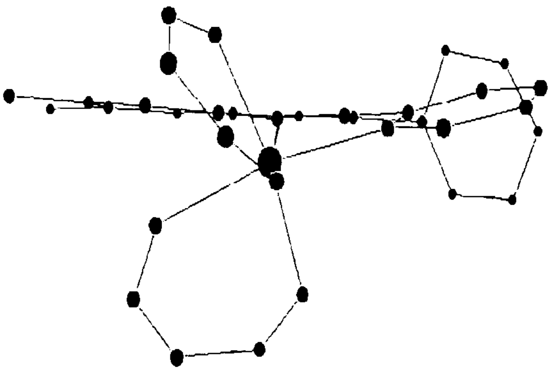

Fig. 5. Molecular structure of [Co(DMeDPQ)(hfacac)$_2$]. This view show the position of the Co atom over the plane defined by the atoms N8–C14–C16 of the pyrazine ring.

apparently more favorable than the coordination with one N-pyridyl and one N-pyrazine atom, as in these Co(II) complexes. Effectively, only in the former case, are the distances M–N equal, the angles N–M–N close to 90°, and the corresponding octahedron regular.

Coordination of the ligands with bis-bidentate character

For the diimine ligands presented in Fig. 1, several authors [7, 12–17] have pointed out the problem which arises from both H atoms in position 6,6′ of the pyridyl groups allowing the stability of the dinuclear compounds: it is not possible to place the three main planes of the ligand in the same plane due to steric hindrance between the 6,6′ H atoms, as shown in Fig. 6(a). A computational model for this hypothetical conformation gives a H6–H6′ distance of 0.15 Å. However, several dinuclear complexes with these ligands and interaction through the pyrazine have been reported [3, 4, 9–11, 17]. The logical conclusion is that a necessary structural requirement should be imposed: from the in-plane conformation, the pyridyl groups must rotate in opposite directions with respect to the pyrazine plane in a reasonable angle, so that the steric hindrance becomes negligible but the overlap with the N-pyrazine will still be effective. This condition has been theoretically explored: if the two pyridyls turn symmetrically the distance H...H increases proportionally to the angle, while the distance between the N-pyridinic and the N-pyrazinic atoms is practically constant. In these conditions, it is possible to obtain dinuclear compounds with a minimum 6H–6H′ distance of 1.8 Å with a torsion angle of *c.* 20° (Fig. 6(b)). This requirement forces the two metal centers out of the plane, one of them above and the other below, with the axis of coordination rotated with respect to the pyrazine plane (Fig. 6(c)).

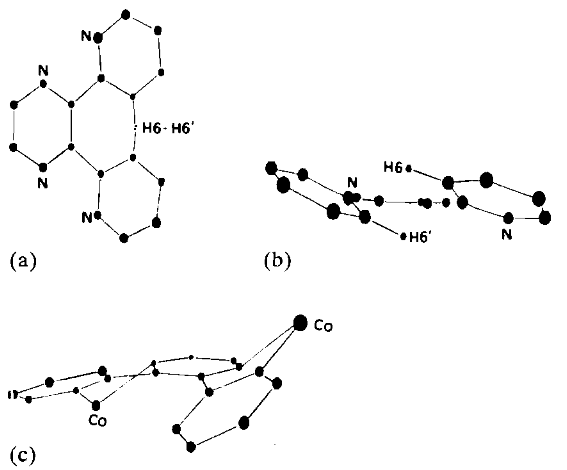

Fig. 6. Conformational possibilities for the diimine type ligands to act as a bisbidentate ligand. (a) Three in-plane rings. Perpendicular view to the pyrazine ring. (b) 20° symmetrical rotation of the pyridyl rings with respect to the pyrazine plane. (c) Possibility of coordination of two Co atoms for the last conformation.

This torsion angle is not a requirement for the existence of mononuclear complexes type **B**, because it is possible to have in the same plane the pyrazine and the pyridine rings which possess the N-coordinating atom, but from the structural information, the torsion angle exists: 24° in $[Ru(DPQ)(bipy)_2]^{2+}$ [7] and 14.6 and 13.40° in $[Co(BDPQ)(hfacac)_2]$ and $[Co(DMeDPQ)(hfacac)_2]$, respectively.

Magnetic data and EPR spectra

The polycrystalline powder EPR spectra of $[Co(L)(hfacac)_2]$, $[Co(L)(tfacac)_2]$ and $[Co_2(L)(acac)_4]$ with L = DPP and BDPQ, were recorded at X-band frequency at 4.2 K. The spectra of the monomeric compounds can be interpreted with an anisotropic spin Hamiltonian with an $S = 1/2$ effective spin, yielding the results reported in Table 7. The spectra of the two monomeric complexes $[Co(BDPQ)(hfacac)_2]$ and $[Co(BDPQ)(tfacac)_2]$ appear to be more axial with respect to $[Co(DPP)(hfacac)_2]$ and $[Co(DPP)(tfacac)_2]$, however the shape of the low field features seems to be due to the superposition of two bands, so indicating an unresolved small anisotropy in the $g_\perp$ region. A similar behavior was also observed in the powder EPR spectra of the base adducts of cobalt(II) acetylacetonate with 6-methylquinoline, $[Co(6Mequin)_2(acac)_2]$, and pyridine, $[Co(py)_2(acac)_2]$, show-

TABLE 7. Polycrystalline powder EPR spectra parameters for selected cobalt(II) complexes

Compound	g_1		g_2	g_3
$[Co(DPP)(hfacac)_2]$	5.4(1)		3.4(1)	2.0(1)
$[Co(DPP)(tfacac)_2]$	5.4(1)		3.4(1)	1.9(1)
$[Co(BDPQ)(hfacac)_2]$		4.6(2)[a]		2.3(1)[a]
	5.2(1)[b]		4.5(1)[b]	2.3(1)[b]
$[Co(BDPQ)(tfacac)_2]$		4.4(1)		2.2(1)
$[Co_2(DPP)(acac)_4]$[c]	8.0(5)		3.5(1)	2.2(1)
	2.0(3)		1.4(1)	
$[Co_2(BDPQ)(acac)_4]$[c]	8.5(5)		6.6(3)	3.9(1)
	2.8(1)		2.0(1)	1.6(1)

[a] Experimental values. [b] Values calculated with the following parameters in the AOM calculations: $B = 800$ cm^{-1}; $\zeta = 533$ cm^{-1}; $K = 0.80$; $e_\sigma{}^{O} = 4500$ cm^{-1}; $e_\pi{}^{O} = 1500$ cm^{-1}; $(e_{\pi_\parallel}{}^{O}/e_{\pi_\perp}{}^{O} = 1.0)$; $e_\sigma{}^{N} = 3900$ cm^{-1}; $e_\pi{}^{N} = 1300$ cm^{-1}; $(e_{\pi_\parallel}{}^{N}/e_{\pi_\perp}{}^{N} = 0.5)$. [c] The indicated values correspond to the observed distinct features in the EPR spectra.

ing $g_{\parallel} < g_{\perp}$, for which single crystal measurements provided evidence for the $g_{\perp}$ anisotropy [36]. The previously reported hexafluoroacetylacetonate copper(II) complexes [18], [Cu(L)(hfacac)$_2$], for which structural and IR spectra results indicate a seven-membered coordination of the diimine type ligand, did not show any low symmetry effects and exhibited axial EPR spectra with $g_{\parallel} = 2.30$, $g_{\perp} = 2.09$ and $g_{\parallel} = 2.30$, $g_{\perp} = 2.08$ for [Cu(DPP)(hfacac)$_2$] and [Cu(BDPQ)(hfacac)$_2$], respectively. For the cobalt(II) complexes a five-membered coordination involving the pyrazine ligand is evidenced in the structure of [Co(DMeDPQ)(hfacac)$_2$] and [Co(BDPQ)(hfacac)$_2$], and the IR spectra suggest that it remains unchanged in the series. These considerations and the well stated extreme sensitivity of the EPR parameters of the cobalt(II) ion to the low symmetry effects [37] indicate that the variability in the powder EPR spectra of the cobalt compounds with the DPP and BDPQ ligands cannot be attributed to differences in the coordination mode of the diimine ligands, but reasonably to different distortions of the octahedral coordination environment of the metal ion, mainly determined by the diimine type ligand rather than by the acetylacetonate type ligand.

The temperature dependence of the magnetic susceptibility for [Co(BDPQ)(hfacac)$_2$] is reported in Fig. 7. The value of the magnetic moment at 280 K is 4.83 μ_B, in the range expected for a cobalt(II) ion [38], and decreases down to 3.73 μ_B at 7 K. The solid lines in Fig. 7 represent the best fits obtained with the Van Vleck equation [39], where the energy eigenvalues and eigenvectors are obtained through angular overlap model (AOM) calculations [37], in which the energies and the electronic levels and the g and χ tensors are calculated using the e_λ parameters ($\lambda = \sigma, \pi$) which are expected to be related to the metal–ligand interactions. The geometrical parameters are obtained by the experimental structural data, so that no idealization of the coordination geometry is assumed. Unfortunately, it was not possible to obtain single crystals of [Co(BDPQ)(hfacac)$_2$] suitable for EPR measurements, so that we cannot have indication on the principal directions of the g tensor to compare with the calculated ones. However a good fit of the g values (see Table 7) and of the temperature dependence of the magnetic susceptibility was obtained with the values of the e_λ parameters in the range $e_\sigma{}^{O} = 4400$–4600 cm^{-1}; $e_\pi{}^{O} = 1300$–1500 cm^{-1} ($e_{\pi_\parallel}{}^{O}/e_{\pi_\perp}{}^{O} = 0.9$–$1.1$ where $\parallel$ and $\perp$ refer to the π interaction parallel and orthogonal to the equatorial plane of the coordination environment [36]); $e_\sigma{}^{N} = 3800$–3900 cm^{-1}; $e_\pi{}^{N} = 1200$–1300 cm^{-1} ($e_{\pi_\parallel}{}^{N}/e_{\pi_\perp}{}^{N} = 0.5$–$0.6$ where $\parallel$ and $\perp$ refer to the π interaction parallel and orthogonal to the plane of the aromatic ligand [36–40]). These values compare well with those previously obtained for [Co(6Mequin)$_2$(acac)$_2$] and [Co(py)$_2$(acac)$_2$], with an anisotropic interaction perpendicular to the aromatic plane of the BDPQ ligand. These values indicate that the ground $^4T_{2g}$ state is splitted by low symmetry ligand field components into the lowest $^4A_2$ and ^4E states [37].

The temperature dependences of the magnetic susceptibility for the dinuclear [Co$_2$(DPP)(acac)$_4$] and [Co$_2$(BDPQ)(acac)$_4$] are reported in Fig. 8. The actual value of the magnetic moment of [Co$_2$(DPP)(acac)$_4$] at 276 K is 6.61 μ_B (4.67 μ_B per cobalt), decreasing to 5.31 μ_B (3.76 μ_B per cobalt) on cooling down to 7 K. For [Co$_2$(BDPQ)(acac)$_4$] a magnetic moment of 6.47 μ_B (4.57 μ_B per cobalt) is observed at 276 K, with a value of 5.52 μ_B (3.90 μ_B for cobalt) at 4.6 K.

In the previously reported oxobridged dimeric complex [41] [Co$_2$(tren)$_2$OH](ClO$_4$)$_3$·H$_2$O (tren=

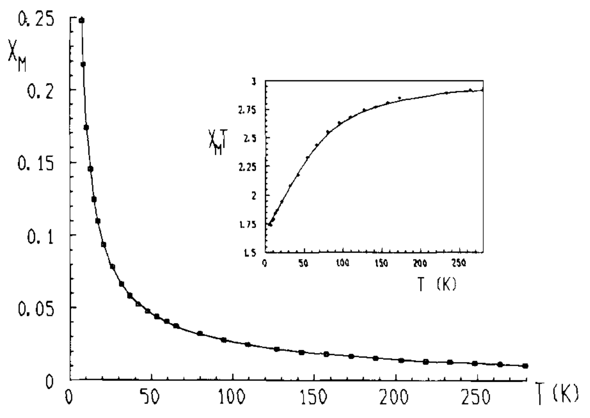

Fig. 7. Temperature dependence of X_M vs. T and $X_M T$ vs. T for [Co(BDPQ)(hfacac)$_2$]. Solid lines show the best fitting with theoretical values.

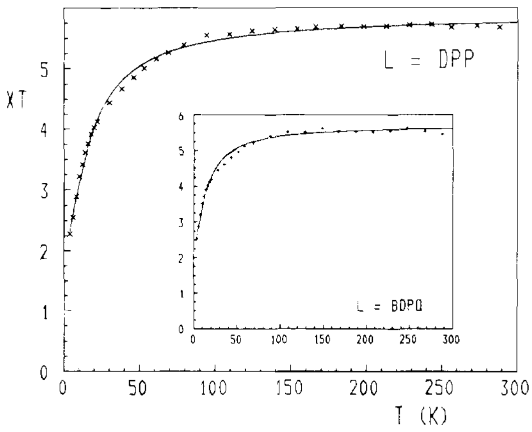

Fig. 8. Temperature dependence of $X_M T$ vs. T for [Co$_2$L(acac)$_4$], L = DPP and BDPQ. Solid lines show the best fitting with theoretical values.

tris(2-aminoethyl)amine) the temperature dependence of the magnetic susceptibility showed a completely different behavior, with a maxima suggesting the presence of an antiferromagnetic exchange interaction, evaluated, using the Bleaney–Bowers equation, as large as 38 cm^{-1}. However evidence has been given for the strong correlation between the J parameter and D, the single ion zero-field splitting, which may be of the same order of magnitude as J [41].

In the present cases the behavior of the magnetic susceptibility indicates that the single ion zero-field splitting is the main factor in determining the magnetic properties of the dimeric complexes, which can be interpreted as the sum of two practically non-interacting cobalt(II) ions.

The polycrystalline powder EPR spectra of the dinuclear $[Co_2(DPP)(acac)_4]$ and $[Co_2(BDPQ)(acac)_4]$ appear to be consistent with the magnetic data, indicating the presence of at least two cobalt(II) ions in different coordination environments. The results are summarized in Table 7.

It is interesting to note that the cobalt chromophores observed in the EPR spectra of the dinuclear compounds are all different from those observed in the corresponding monomeric complex, with g tensors exhibiting a larger anisotropy. This is surely due to the above mentioned largest and different distortion of the cobalt(II) ions coordination environment in the dinuclear compounds, even if an attribution of the observed g values to the paramagnetic ions bounded at the two coordinate positions of the DPP and BDPQ ligands is impossible without the aid of structural data.

Conclusions

We have presented the synthesis, characterization, structure and magnetic data of several mixed acetylacetonatecobalt(II) complexes with some diimine ligands. From structural results we can observe the possibility of three types of compound for this kind of 2,3-(bis-pyridyl) ligand: mononuclear compounds formed by coordination with the two N-pyridyl atoms, (as in previous Cu(II) and Ni(II) complexes [18, 19]), and mono or dinuclear compounds in which the coordination is made by using the N-pyridyl and N-pyrazine atoms as in the Co(II) complexes here reported, in function of the dihedral angle between the pyridyl and pyrazine groups. Taking into account the structural, IR and magnetic results, we suggest the same type **B** (Fig. 1) coordination for all of the complexes presented in this work. From magnetic results, a little or non-existent antiferromagnetic coupling is observed for the dinuclear compounds.

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.

Acknowledgements

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