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Synthesis, Structure and EPR Studies of Mixed Hexafluoroacetylacetonatecopper(II) Complexes with some Diimine Ligands

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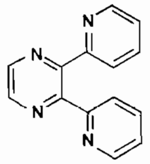
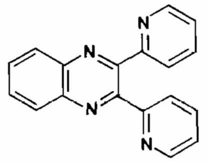
Abstract

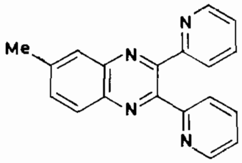
The synthesis, structure and magnetic properties of [CuL(hfacac)$_2$] and [Cu$_2$TPP(hfacac)$_4$], where L is 2,3-bis(2-pyridyl)pyrazine (DPP), 2,3-bis(2-pyridyl)quinoxaline (DPQ), 6-methyl-2,3-bis(2-pyridyl)quinoxaline (MeDPQ), 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (DMeDPQ), 6-chloro-2,3-bis(2-pyridyl)quinoxaline (ClDPQ), 2,3-bis(2-pyridyl)-benzoquinoxaline (BDPQ) and TPP is 2,3,5,6-tetrakis-(2-pyridyl)pyrazine and hfacac is hexafluoroacetylacetonate ion, are described. The [Cu(DMeDPQ)-(hfacac)$_2$] complex crystallizes in the monoclinic space group $P2_1/a$ with cell parameters $a = 23.643(5)$, $b = 15.245(3)$, $c = 9.044(2)$ Å, $\beta = 94.16(2)°$ and $Z = 4$. The two copper–nitrogen(pyridine) bond distances are equal, 1.998(7) Å. Polycrystalline powder EPR spectra of all the complexes and single crystal EPR spectrum of [Cu(DMeDPQ)(hfacac)$_2$] were recorded at room temperature. The spectra of [CuL(hfacac)$_2$] complexes show axial distortion with $g_\parallel = 2.31(1)$ and $g_\perp = 2.08(1)$; for [Cu$_2$(TPP)(hfacac)$_4$] $g_\parallel = 2.30(1)$ and $g_\perp = 2.09(1)$. In some cases weak evidence of hyperfine splitting in the parallel transition is shown.



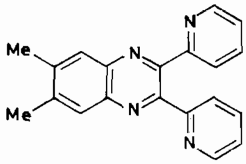
1 DPP



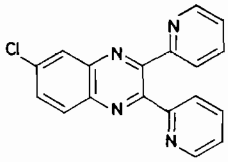
2 DPQ



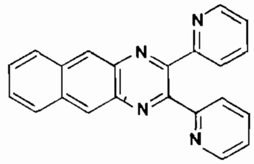
3 MeDPQ



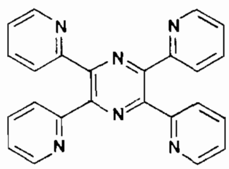
4 DMeDPQ



5 ClDPQ



6 BDPQ



7 TPP

Introduction

Some of the ligands of the diimine type which have been studied in this work, namely 2,3-bis(2-pyridyl)pyrazine (DPP) (1), 2,3-bis(2-pyridyl)-quinoxaline (DPQ) (2), 6-methyl-2,3-bis(2-pyridyl)-quinoxaline (MeDPQ) (3), 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (DMeDPQ) (4), 6-chloro-2,3-bis(2-pyridyl)quinoxaline (ClDPQ) (5), 2,3-bis(2-pyridyl)benzoquinoxaline (BDPQ) (6) and 2,3,5,6-tetrakis(2-pyridyl)pyrazine (TPP) (7), have been previously reported as analytical reagents [1–5].

Recently, these ligands have been used to control the properties of metal to ligand charge-transfer excited states principally for ruthenium-based systems [6]. However little is known on the behavior of

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these ligands towards other transition metal cations different from Ru(II). One study has been reported on Fe(II) [7] complex and several works about haloderivatives of Co(II), Ni(II) and Cu(II) [8–12]. We report here the synthesis and characterization of a series of complexes [CuL(hfacac)$_2$] and [Cu$_2$(TPP)(hfacac)$_4$], where L and TPP are diimine-type ligands and hfacac is the hexafluoroacetylacetonate ion, and the X-ray structure determination of [Cu(DMeDPQ)(hfacac)$_2$]. Hfacac has been chosen to avoid the possible polymeric halide bridged compounds which can be obtained if the starting reagents are Cu(II) halides. These studies give new information about the structure and coordination mode of the ligands.

Experimental

Preparation of Reagents

[Cu(hfacac)$_2$] was prepared by the general method described by Berg and Truemper [13]. Copper nitrate was made up as a 5 wt.% solution and buffered immediately before use by adding 5 g of sodium acetate for every 100 ml of solution. The buffered solution was shaken for 2 h with an ethanolic solution of hexafluoroacetylacetone. After this time the reaction was complete. The [Cu(hfacac)$_2$] was collected by filtration and recrystallized in acetone.

2,3-Bis(2-pyridyl)pyrazine, DPP, was prepared according to the procedure of Goodwin and Lions [14]. Fifty mmol (30 g) of ethylenediamine and 50 mmol (10.6 g) of 2,2′-pyridyl (Aldrich) were refluxed in 50 ml of ethanol for 1 h. After immediate filtration, a brown precipitate was formed on cooling. Light yellow crystals of 2,3-bis(2-pyridyl)-5,6-dihydropyrazine were obtained by recrystallization from ethanol. This compound (9 g) was dissolved in 120 ml of mesitylene and refluxed for 24 h with 0.9 g of 10% Pd on charcoal (Fluka). The hot reaction mixture was then filtered, and the crude product was precipitated by cooling the filtrate. After filtration, the crude product was recrystallized from ethanol and 2,3-bis(2-pyridyl)pyrazine was obtained in 42% yield.

Substituted 2,3-bis(2-pyridyl)quinoxalines, (DPQ, MeDPQ, DMeDPQ, ClDPQ and BDPQ), were prepared according to the procedure indicated by Goodwin and Lions for DPQ [14]: 2,2′-pyridyl was dissolved in refluxing ethanol and a solution of equimolar amounts of *o*-phenylenediamine, substituted *o*-phenylenediamine or 2,3-diaminonaphthalene in ethanol, was added to the hot solution. The mixture was heated under reflux for 1 h. After immediate filtration to remove a black impurity formed, a brown compound was obtained on cooling. Recrystallization from boiling ethanol with a slurry of charcoal provided the 2,3-bis(2-pyridyl)quinoxalines in 50–60% yield. (DPQ, MeDPQ, DMeDPQ, white compounds; ClDPQ, light pink; BDPQ, light yellow).

2,3,5,6-tetrakis(2-pyridyl)pyrazine, TPP, was prepared [14] by heating for 2 h at 180 °C a mixture of 20 g of alpha-pyridoin (Aldrich) and 90 g of ammonium acetate. After cooling, a bright yellow precipitate was collected by filtration. After several recrystallizations, the pure 2,3,5,6-tetrakis(2-pyridyl)pyrazine as a white compound was obtained. Yield 6 g.

Preparation of Complexes

All the compounds were obtained by direct reaction at room temperature of a mixture of equimolar amounts of [Cu(hfacac)$_2$] and the ligand in acetone or acetonitrile. Slow evaporation gave the crystalline compounds in 60–70% yield. Recrystallization was unnecessary. *Anal.* Calc. for [Cu(DPP)(hfacac)$_2$]: C, 40.49; N, 7.87; H, 1.84. Found: C, 40.6; N, 7.9; H, 1.8%. Calc. for [Cu(DPQ)(hfacac)$_2$]: C, 44.14; N, 7.35; H, 1.85. Found: C, 44.5; N, 7.5; H, 2.1%. Calc. for [Cu(MeDPQ)(hfacac)$_2$]: C, 44.89; N, 7.22; H, 2.08. Found: C, 45.0; N, 7.4; H, 2.2%. Calc. for [Cu(DMeDPQ)(hfacac)$_2$]: C, 45.61; N, 7.09; H, 2.30. Found: C, 45.8; N, 7.2; H, 2.4%. Calc. for [Cu(ClDPQ)(hfacac)$_2$]: C, 42.23; N, 7.03; H, 1.64; Cl, 4.45. Found: C, 42.8; N, 7.0; H, 1.8; Cl, 4.5%. Calc. for [Cu(BDPQ)(hfacac)$_2$]: C, 47.33; N, 6.90; H, 1.99. Found: C, 47.3; N, 7.0; H, 1.9%. Calc. for [Cu$_2$(TPP)(hfacac)$_4$]: C, 39.33; N, 6.25; H, 1.50. Found: C, 39.3; N, 6.5; H, 1.6%. These results suggest a dinuclear structure for this compound.

Techniques

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer. Samples were prepared by using the KBr technique. Vis–UV spectra were recorded with a Perkin-Elmer 550 S spectrophotometer.

Polycrystalline powder EPR spectra of [CuL(hfacac)$_2$], [Cu$_2$(TPP)(hfacac)$_4$] and single crystal EPR spectra of [Cu(DMeDPQ)(hfacac)$_2$] were recorded with a Bruker ER200 spectrometer at X-band frequency at room temperature. EPR suitable single crystal of the latter compound showing well developed (100) and ($\bar{1}$00) faces were oriented with an Enraf Nonius DELFT 586 Diffractometer.

Crystal Structure Determination

A prismatic crystal (0.1 × 0.1 × 0.15 mm) of [Cu(DMeDPQ)(hfacac)$_2$] was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω–2θ scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}. A total of 3437 reflections was measured in the range $2 \leqslant \theta \leqslant 25°$, 2761 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$,

R_{int}(on F) = 0.032. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz–polarization corrections were made, absorption ignored. The structure was solved by direct methods, using the MULTAN system of computer programs [15] and refined by full-matrix least-squares, using the SHELX76 program [16]. The function minimized was $\Sigma w[[F_o] - [F_c]]^2$ where $w = (\sigma^2(F_o) + 0.0016[F_o]^2)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography [17]. After three isotropic cycles fluoro atoms were located in disorder positions, an occupancy factor of 0.5 was assumed according to the peak height.

Positions of the H atoms were computed and refined isotropically with constrained bond length. The remaining atoms were refined anisotropically. The final R was 0.060(R_w = 0.064) for all observed reflections. Max. shift/e.s.d. = 0.4 in U_{11} of C(11). Max. peak in final difference synthesis was 0.5 e Å^{-3} at 0.5 Å of F(35).

Crystal Data for [Cu(DMeDPQ)(hfacac)$_2$]

$C_{30}H_{18}N_4O_4F_{12}Cu$, formula weight = 790.0, monoclinic, a = 23.643(5), b = 15.245(3), c = 9.044(2) Å, β = 94.16(2)°, V = 3251(1) Å^3, $P2_1/a$, D_x = 1.580 g cm^{-3}, Z = 4, F(000) = 1580, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 8.19 cm^{-1}, 288 K.

Results and Discussion

The ligand DPQ (2) can serve as a model to discuss the structural ways in which this series of diimine compounds may act as ligands. Geary performed this kind of analysis previously [8] and pointed out the impossibility for the pyridine rings to be coplanar simultaneously with the quinoxaline system because of steric interactions between protons attached to the 6-position of the pyridine rings. By analogy with the 2,2'-bipyridine (bipy) he considered the chelate formation only through one N-pyridine and one N-pyrazine as donor atoms. This assumption has been experimentally corroborated by the structural determination of [Ru(DPQ)(bipy)$_2$](PF$_6$)$_2$ [6]. Moreover, the angle between the plane of the pyrazine ring and the plane of the coordinated pyridine is 24°. The angle between the plane of the coordinated pyridine ring and the plane of the remote pyridine ring is 66°.

However another coordination possibility in order for this kind of diimine ligand to act as a chelate, must be considered: in fact they can bind using the N atom of the two pyridine rings placed in a *cis*-conformation. This kind of behaviour, which gives a seven-membered ring, is observed in the new compound [Cu(DMeDPQ)(hfacac)$_2$].

Structure

The structure of [Cu(DMeDPQ)(hfacac)$_2$] consists of discrete molecules linked by van der Waals forces. The molecular structure of this compound is shown in Fig. 1, together with the atom-labelling scheme. Main bond distances and angles are given in Tables 1 and 2, respectively.

The coordination environment around the copper ion in [Cu(DMeDPQ)(hfacac)$_2$] can be described as a distorted elongated octahedron with the equatorial plane defined by the two nitrogen atoms (N1 and N24) belonging to the DMeDPQ ligand and by two

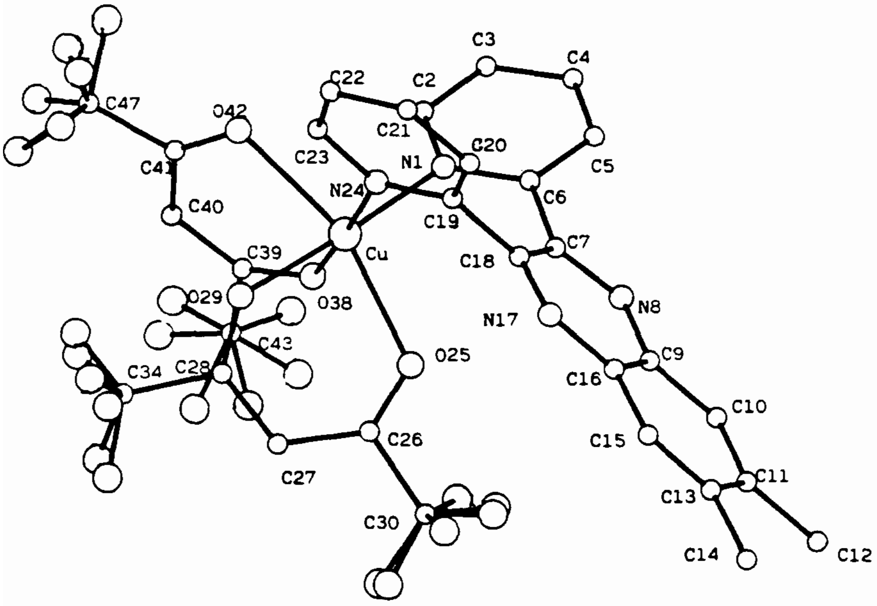

Fig. 1. Molecular structure of [Cu(DMeDPQ)(hfacac)$_2$].

TABLE 1. Selected bond distances (Å) for [Cu(DMeDPQ)(hfacac)$_2$]

N(1)---Cu	1.998(7)
N(24)---Cu	1.998(7)
O(25)---Cu	2.270(7)
O(29)---Cu	2.018(6)
O(38)---Cu	2.004(6)
O(42)---Cu	2.323(7)
C(2)---N(1)	1.323(11)
C(6)---N(1)	1.363(10)
C(3)---C(2)	1.386(13)
C(4)---C(3)	1.352(14)
C(5)---C(4)	1.379(14)
C(6)---C(5)	1.394(12)
C(7)---C(6)	1.493(12)
N(8)---C(7)	1.331(11)
C(18)---C(7)	1.417(12)
C(9)---N(8)	1.368(11)
C(10)---C(9)	1.427(13)
C(16)---C(9)	1.411(14)
C(11)---C(10)	1.377(13)
C(12)---C(11)	1.513(15)
C(13)---C(11)	1.411(17)
C(14)---C(13)	1.532(15)
C(15)---C(13)	1.372(15)
C(16)---C(15)	1.430(13)
N(17)---C(16)	1.364(12)
C(18)---N(17)	1.307(11)
C(19)---C(18)	1.489(12)
C(20)---C(19)	1.411(12)
N(24)---C(19)	1.351(10)
C(21)---C(20)	1.393(14)
C(22)---C(21)	1.384(14)
C(23)---C(22)	1.381(13)
N(24)---C(23)	1.348(11)
C(26)---O(25)	1.209(12)
C(27)---C(26)	1.430(15)
C(28)---C(27)	1.401(16)
O(29)---C(28)	1.244(14)
C(39)---O(38)	1.237(12)
C(40)---C(39)	1.376(15)
C(41)---C(40)	1.423(17)
O(42)---C(41)	1.224(12)

TABLE 2. Selected bond angles (°) for [Cu(DMeDPQ)(hfacac)$_2$]

N(24)–Cu–N(1)	88.7(3)
O(25)–Cu–N(1)	100.3(3)
O(25)–Cu–N(24)	98.4(3)
O(29)–Cu–N(1)	175.8(3)
O(29)–Cu–N(24)	92.6(3)
O(29)–Cu–O(25)	83.5(3)
O(38)–Cu–N(1)	88.8(3)
O(38)–Cu–N(24)	175.4(3)
O(38)–Cu–O(25)	85.8(3)
O(38)–Cu–O(29)	89.6(3)
O(42)–Cu–N(1)	95.8(3)
O(42)–Cu–N(24)	93.1(3)
O(42)–Cu–O(25)	160.4(2)
O(42)–Cu–O(29)	80.1(2)
O(42)–Cu–O(38)	83.3(2)
C(2)–N(1)–Cu	117.3(5)
C(6)–N(1)–Cu	123.6(6)
C(19)–N(24)–Cu	123.8(6)
C(23)–N(24)–Cu	118.4(5)
C(26)–O(25)–Cu	121.9(6)
C(28)–O(29)–Cu	126.3(6)
C(39)–O(38)–Cu	127.7(7)
C(41)–O(42)–Cu	118.4(7)

oxygen atoms (O29 and O38) of two different hexafluoroacetylacetonate ligands, the remaining two oxygen atoms (O25 and O42) occupying the axial positions. The Cu–N distances are equal to each other (Cu–N1 = 1.998(7) and Cu–N2 = 1.998(7) Å) and slightly shorter than the Cu–O(eq) distances (Cu–O29 = 2.018(6) and Cu–O38 = 2.004(6) Å). The Cu–O axial bonds are definitely longer than the equatorial ones (Cu–O42 = 2.323(7) and Cu–O25 = 2.270(7) Å) revealing the asymmetric link of the hexafluoroacetylacetonate ligands and giving rise to a distorted coordination polyhedron, as usual for copper(II) hexacoordinated compounds [18].

Steric hindrance (O(25)...C(7) = 2.86(1); O(25)...C(18) = 2.81(1) and O(42)...H(2) = 2.43(2) Å) produces the increase of the O(25)–Cu–N(24) (98.4(3)°); O(25)–Cu–N(1) (100.3(3)°); O(42)–Cu–N(24) (93.1(3)°) and O(42)–Cu–N(1) (95.8(3)°) coordination bond angles.

The O,C,C,C,O,Cu six-membered rings have a skew-sopha form, with the Cu atom out of plane, defined by the remaining five atoms. The DMeDPQ ligand is linked to the Cu ion by the two N atoms of the pyridyl rings. This produces a dihedral angle between the two planes of 3.7(7)°, while it is 66° when a N atom of pyrazine and one of the pyridyl ring are linked in the metal [6]. The quinoxaline moiety is planar and the dihedral angles between the pyridyl rings and the quinoxaline are 45.7(7) and 49.4(7)°. This angle is 24° in the previously mentioned Ru complex. The orientation of the pyridyl rings produces the increase of the C(6)–C(7)–C(18) and C(7)–C(18)–C(19) bond angles (average value 126.2(3)°).

IR and Electronic Spectra

The IR spectra of the complexes show the bands characteristic of the hfacac and the nitrogenated ligands. All the spectra are very complex, and it is very difficult to obtain correlations with the structure of the complex. In the 600–800 and 1100–1350 cm^{-1} regions, the intense absorptions of hfacac overlap with those of the ligands. The best defined absorptions occur in the 1450–1700 cm^{-1} region, showing important shifts. Hfacac shows five bands centered at 1680, 1630, 1555, 1530 and 1480 cm^{-1} and all the ligands show two well defined bands at 1580–90 and 1560–70 cm^{-1}. The IR spectra of the

TABLE 3. Electronic spectra of the new complexes, in acetone (λ in nm)

[Cu_2(TPP)(hfacac)$_4$]	704	364	352(min)	320	316(sh)
[Cu(DPQ)(hfacac)$_2$]	716			328	316(sh)
[Cu(ClDPQ)(hfacac)$_2$]	620	508	350(sh)	330	316(sh)
[Cu(BDPQ)(hfacac)$_2$]	712	380	366(sh)	327	316(sh)
[Cu(DMeDPQ)(hfacac)$_2$]	732		350(sh)	329	316(sh)
[Cu(DPP)(hfacac)$_2$]	716			329	316(sh)
[Cu(MeDPQ)(hfacac)$_2$]	720		348(sh)	320	316(sh)

TABLE 4. Room temperature polycrystalline powder EPR spectra for the copper compounds

Compound	$g_\parallel$	$g_\perp$	$A_\parallel$ (G)
[Cu(hfacac)$_2$DPP]	2.30	2.09	
[Cu(hfacac)$_2$DPQ]	2.31	2.07	140
[Cu(hfacac)$_2$DMeDPQ]	2.31	2.08	140
[Cu(hfacac)$_2$BDPQ]	2.30	2.08	
[Cu(hfacac)$_2$ClDPQ]	2.31	2.09	
[(hfacac)$_2$Cu–TPP–Cu(hfacac)$_2$]	2.30	2.09	

new complexes show in this region a characteristic, well defined, absorption with six bands centered at 1650–1655(vs), 1600–1610(m), 1580–1590(m), 1550–1555(m), 1530(s) and 1480–1500(s) cm^{-1}. According to the literature [11] the shift of the two bands of the diimine ligands is characteristic of its coordination mode.

The UV–Vis spectra of the series of complexes are all similar. Spectral results for the new complexes, all in acetone, are summarized in Table 3.

EPR Spectra

The room temperature polycrystalline EPR spectra of the monomeric compounds, [CuL(hfacac)$_2$], with L = DPP, DPQ, BDPQ, DMeDPQ and ClDPQ, are axial with the $g_\parallel$ and $g_\perp$ values shown in Table 4. The [Cu(DPQ)(hfacac)$_2$] spectrum shows a hyperfine structure in the $g_\parallel$ region, with an $A_\parallel \approx 140$ G (see Fig. 2), while only weak evidence of hyperfine splitting ($A_\parallel \approx 130$–140 G) is observed for [Cu(DMeDPQ)(hfacac)$_2$].

The polycrystalline powder spectrum of the dinuclear compound [Cu_2(TPP)(hfacac)$_4$] is similar to those of the mononuclear complexes with only slightly different g values, $g_\parallel \approx 2.32$ and $g_\perp \approx 2.09$, indicating that, at room temperature, no exchange interaction is operative between the two metal ions.

The room temperature single crystal spectra of [Cu(DMeDPQ)(hfacac)$_2$] were recorded at X-band frequency with the static magnetic field in the a^*b, bc and a^*c orthogonal planes. The angular dependence of the transition fields is shown in Fig. 3. Even if the compound crystallizes in the monoclinic system, with two magnetically non-equivalent sites in the unit cell, only one transition is observed for each crystal orientation in the a^*b and bc planes. In the a^*c plane, where only a signal is expected, the spectra recorded with the static magnetic field at 110°–140° from c show evidence of hyperfine splitting of about 140 G. Standard least-squares fit yielded the g tensor principal values and directions reported in Table 5. The calculated

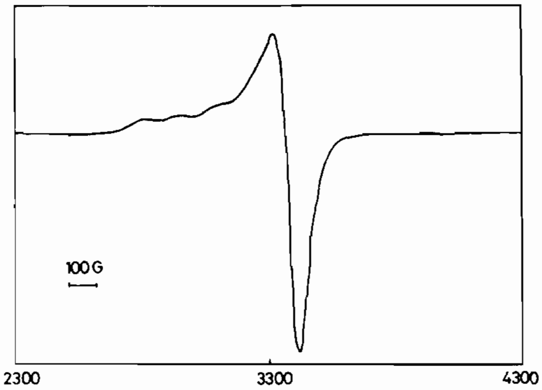

Fig. 2. Room temperature polycrystalline powder EPR spectrum of [Cu(DPQ)(hfacac)$_2$].

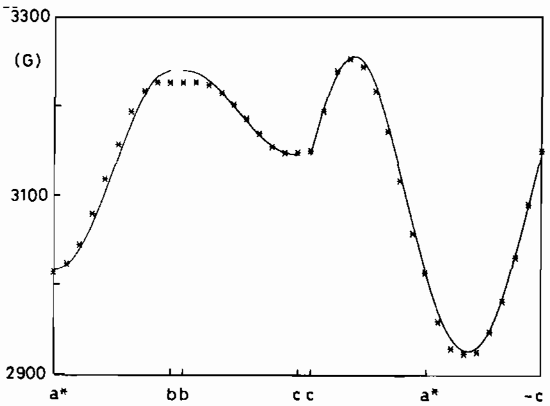

Fig. 3. Angular dependence of the transition fields for [Cu(DMeDPQ)(hfacac)$_2$] in the three orthogonal a^*b, bc and ca^* planes. The solid lines represent the calculated values (see text).

TABLE 5. Principal values and directions of the g tensor for [Cu(hfacac)$_2$(DMeDPQ)] [a]

g_1	g_2	g_3
2.066(5)	2.076(5)	2.300(3)
0.55[b]	0[b]	0.836(3)
0[b]	1[b]	0
0.836[b]	0[b]	−0.55(5)

[a] The direction cosines are given in the reference frame a^*bc. [b] The direction of g_1 and g_2 are largely undetermined due to the practically isotropic g value in the plane perpendicular to g_3.

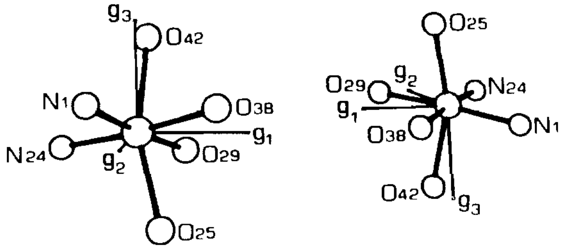

Fig. 4. Principal directions of the g tensor within the molecular frames of the two magnetically non-equivalent sites of [Cu(DMeDPQ)(hfacac)$_2$].

transition fields are indicated by the full lines in Fig. 3.

In Fig. 4 the principal directions of the g tensor are shown within the molecular frame of both the two magnetically non-equivalent sites in which the equatorial coordination planes make a dihedral angle of 17.4(4)°. As expected the largest g value, $g_3 = 2.300(5)$, is observed along a direction making an angle of 8.7(2)° with the perpendicular to the equatorial least-squares coordination plane of the copper(II) ion. g_1 and g_2 are observed approximately bisecting the angles between the equatorial bonds, but, due to their practically isotropic value, their direction cosines are affected by large error.

Detailed single crystal EPR studies are available for other adducts of Cu(hfacac)$_2$, namely [Cu(py)$_2$(hfacac)$_2$] [19] and [Cu(bipy)(hfacac)$_2$] [20] doped in the corresponding [ZnL(hfacac)$_2$] compounds (with L:py = pyridine, and bipy = bipyridine). The environment of the copper(II) ion in the two pure compounds [21, 22] is very similar to that of [Cu(DMeDPQ)(hfacac)$_2$], showing a *cis*-coordination of the nitrogen atoms belonging to the two pyridine moieties in the former complex and to a bipyridine ligand in the latter, with the oxygen atoms of each hfacac ligand binding the metal ion with a long axial bond and a shorter equatorial one. The similarity of the structure reflects in similar g tensors. In particular the g_3 values of 2.300(3) for [Cu(DMeDPQ)(hfacac)$_2$] correspond nicely to the $g_z = 2.278$ for [Cu(py)$_2$(hfacac)$_2$], observed along a direction perpendicular to the equatorial coordination plane, and to the $g_{\parallel} = 2.292$ reported for [Cu(bipy)(hfacac)$_2$].

The angular dependence of the EPR linewidth, δB_{pp}, follows the behavior of the g values, showing its maxima and minima in the a^*c plane, with values of $\delta B_{\mathrm{pp}} = 40$ G at 30° from c and $\delta B_{\mathrm{pp}} = 300$ G at 120° from c. The values of the linewidth along the three orthogonal axes are: $\delta B_{\mathrm{pp}}(a^*) = 240$ G; $\delta B_{\mathrm{pp}}(b) = 90$ G and $\delta B_{\mathrm{pp}}(c) = 180$ G. Two broadening mechanisms are expected to determine the linewidth: one is the unresolved hyperfine splitting, the other is due to the presence of two magnetically non-equivalent sites; these signals are unresolved in the planes containing the b axis.

For hexacoordinated copper(II) complexes $A_{\parallel}$ is expected to be much larger than $A_{\perp}$ [18] and the polycrystalline powder spectra of [Cu(DMeDPQ)(hfacac)$_2$] confirm this behavior. Following the hypothesis that the dominant broadening mechanism of the EPR lines is the first, the g and A tensors being parallel to one another, we have to expect an increase in the linewidth on increasing the g value, i.e. on going from $g_{\perp}$ to $g_{\parallel}$. This is the actual behavior observed for the linewidth of the present compound.

Another relevant mechanism might be given by the magnetic anisotropy of the two inequivalent molecules present in the monoclinic cell. This situation can be attributed to the small misalignments, 17.4(4)°, between the 'axial' directions of the two sites. Simple calculations, made considering an angle of 20° between the $g_{3(\mathrm{M})}$ directions of the molecular g_{M} tensors, indicate a maximum of 80 and 60 G in the difference between the resonanting fields of the two molecules in the a^*b and bc planes respectively, at about 40°–50° from the axes. This suggests that the linewidth is mainly determined by the unresolved hyperfine splitting.

Conclusions

We have presented the synthesis, characterization and EPR studies of several mixed hexafluoroacetylacetonatecopper(II) complexes with some diimine ligands. From room temperature single crystal EPR spectra of [Cu(DMeDPQ)(hfacac)$_2$] we deduce the principal values and directions of the g tensor. From its structure we can conclude that this is possibly a new non-reported chelate mode of coordination of this kind of diimine ligand through the N atoms of the two pyridine rings placed in a *cis*-conformation giving a seven-membered ring. Taking into account the similarities in EPR, IR, and UV–Vis spectra of all the new complexes, we suggest the same type of coordination for all of them.

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 (12 pages) are available from the authors on request.

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