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Note

Bis[4-(2,6-dimethylphenyliminomethyl)-5-pyrazolethiolato]nickel(II) complexes with an unusual *trans*-planar structure

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Abstract

The nickel(II) complexes bis[1-phenyl-3-methyl-4-(2,6-dimethylphenyl)iminomethyl-5-pyrazolethiolato]nickel(II) (**1**) and bis[1,3-diphenyl-4-(2,6-dimethylphenyl)iminomethyl-5-pyrazolethiolato]nickel(II) (**2**), based on the 4-imino-methyl-5-thiopyrazole ligands containing a 2,6-xylyl substituent at the coordinating imino nitrogen atom, have been prepared and their structures investigated. Complex **1** is tetrahedral and high-spin in solution as indicated by its temperature-independent μ_{eff} value of 2.75 BM whereas **2** displays magnetic behaviour and ^{1}H NMR spectra consistent with a fast planar (LS)–tetrahedral (HS) equilibrium ($\Delta H° = 11.8$ kJ mol^{-1}, $\Delta S° = 34.6$ J mol^{-1} K^{-1}). **1** and **2** are low-spin in the solid state. An X-ray diffraction study of **1** revealed a *trans*-square-planar coordination geometry which is unusual for bis-chelate N_2S_2 metal complexes, in comparison to *cis*-planar geometry.

Keywords: Crystal structures; Nickel complexes; Thiolate complexes

1. Introduction

Elucidation of the stereochemistry and stereodynamics of tetracoordinate Ni(II) complexes with Schiff base ligands derived from vicinal hydroxy (mercapto, seleno, amino) aromatic, heteroaromatic and unsaturated aldehydes has been an area of intense research over the last few decades [1]. The remarkable feature of these compounds is a very labile molecular geometry so that by fine tuning of the ligand environment different coordination polyhedra may be produced, e.g. *cis*- or *trans*-planar (low-spin, LS) and tetrahedral Δ,Λ (high-spin, HS) which could also exist in a dynamic equilibrium in solution. Control of the spin state and stereochemistry of the Ni(II) centres is of general theoretical interest [2] and it is also important in relation to some particular properties of the complexes, such as aiding in the design of relevant synthetic models of metalloproteins [3] and of new materials able to display ionophore [4] and liquid crystalline [5] properties. Studies over the last 30 years revealed that the increased steric volume of the substituent R at the coordinated nitrogen atom (R = s-Alk, Bu^t) favours a tetrahedral HS isomer whereas for R = H, n-Alk or Ar a planar LS structure is preferred. Two other stereo effects have subsequently [6] been demonstrated: (i) occurrence of the *cis*-planar isomers for the complexes with an $N_2S_2(Se_2)$ coordination site in contrast to the *trans*-N_2O_2 complexes; (ii) substantial weakening of the ligand field in the case of annelation to the metallocycle of some five-membered heteroaromatic fragments such as pyrazole, pyrrole and furan resulting in formation of the HS tetrahedral isomers.

Complexes with Schiff bases of 4-formyl-5-mercapto(seleno)pyrazole were reported [7] to be purely tetrahedral both in solution and in the solid state irrespective of the R group. The barriers of interconversion between enantiomeric Δ and Λ forms were determined by dynamic ^{1}H NMR spectroscopy [7] to be in the range 45–70 kJ mol^{-1}. Assuming a diagonal

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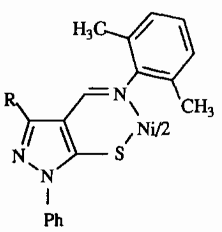
twist reaction mechanism, these values may be a rough estimate of the energy difference between the tetrahedral ground state and planar intermediate state. This contrasts dramatically with the usual occurrence of a planar ground state or a labile planar–tetrahedral equilibrium ($\Delta G^\circ = 0$–15 kJ mol^{-1}). We have been interested to see whether a planar structure can be stabilized for the above type of complex. There was some evidence in the literature [8], based on magnetic and dipole moments, that incorporation of bulky *ortho*-alkyl substituents into the phenyl group at the coordinated nitrogen atom can lead to formation of planar Co(II) and Cu(II) complexes. We report herein on two pyrazoleiminomethylthiolato Ni(II) complexes **1** and **2**, containing an N-2,6-xylyl group, that demonstrate a pronounced tendency for spin pairing both in solution and in the solid state and they also show an unexpected *trans*-N_2S_2 donor atom arrangement.



1 R=CH$_3$

2 R=Ph

2. Experimental

2.1. General procedures

^{1}H NMR spectra were recorded in deuterochloroform on a Varian Unity-300 spectrometer equipped with a standard temperature controller. Chemical shifts are reported relative to HMDS as internal standard. Magnetic moments in solution were determined by the Evans method [9] (HMDS as reference, $c = 5 \times 10^{-2}$ mol cm^3) and those in the solid state by the Faraday method. Electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Mass spectra were obtained by electron impact at 70 eV on a Varian spectrometer.

2.2. Syntheses

Complexes **1** and **2** were prepared by the reaction of the corresponding ligands 1,3-diphenyl and 1-phenyl-3-methyl substituted 4-(2,6-dimethylphenyl)aminomethyl-5-pyrazolethiones and nickel(II) acetate tetrahydrate, in ethanol, as described previously [7b].

2.2.1. Bis[1-phenyl-3-methyl-4-(2,6-dimethylphenyl)iminomethyl-5-pyrazolethiolate]nickel(II) (1)

M.p. 222 °C. *Anal.* Calc. for $C_{38}H_{36}N_6S_2Ni$: C, 65.94; H, 5.19; N, 12.01. Found: C, 65.58; H, 5.24; N, 12.18%. m/z 698 (100%, M^+). ^{1}H NMR (303 and 331 K, primes denote protons of the 1-Ph group) δ: 135 (303 K) (br, s, 2H, C*H*=N), not detected at 331 K; 16.28, 15.43 (s, 12H, *o*-CH$_3$); 14.71, 14.30 (s, 4H, *m*-H); 14.35, 13.94 (s, 4H, *o*′-H); 8.63, 8.57 (t, ^3J 6.7 Hz, 2H, *p*′-H); 6.70, 6.76 (s, 4H, *m*′-H); −4.98, −4.62 (s, 6H, CH$_3$); −5.61, −4.87 (s, 2H, *p*-H). UV (CHCl$_3$, metal-centred transitions): λ (nm) (ϵ (l cm^{-1} mol^{-1})): 1750 (39.5), 1346 (32.9), 724 (345), 580 (690) sh, 499 (2580) sh.

2.2.2. Bis[1,3-diphenyl-4-(2,6-dimethylphenyl)iminomethyl-5-pyrazolethiolato]nickel(II) (2)

M.p. 284 °C. *Anal.* Calc. for $C_{48}H_{40}N_6S_2Ni$: C, 69.99; H, 4.89; N, 10.20. Found: C, 69.71; H, 4.99; N, 10.44%. m/z 822 (100%, M^+). ^{1}H NMR (292 K) δ: 55.6 (s, 2H, *CH*=N, 2H), 10.33 (d, ^3J 8.4 Hz, 4H), 9.96 (d, ^3J 6.0 Hz, 4H), 8.02 (s, 12H, *o*-CH$_3$), 7.80 (t, ^3J 8.2 Hz, 2H), 7.73 (d, ^3J 8.4 Hz, 4H), 7.51 (t, ^3J 8.4 Hz, 2H), 7.22–7.12 (m, 6H), 1.92 (br t, 2H). UV (CHCl$_3$, metal-centred transitions); λ (nm) (ϵ (l cm^{-1} mol^{-1})): 1795 (16.6), 1344 (12.0), 700 (235), 592 (340) sh, 511 (645) sh.

2.3. X-ray crystallography of 1

A single crystal of **1** was obtained by slow cooling of a saturated toluene–hexane (1:1) solution.

2.3.1. Crystal data

$C_{38}H_{36}N_6S_2Ni$, crystal dimensions $0.25 \times 0.21 \times 0.16$ mm, triclinic, space group $P1$, $a = 13.914(1)$, $b = 12.494(2)$, $c = 10.252(1)$ Å, $\alpha = 88.961(9)$, $\beta = 73.226(6)$, $\gamma = 88.940(6)^\circ$, $V = 1705.9(4)$ Å^3, $D_c = 1.36$ g cm^{-3}, $Z = 2$, $F(000) = 732$, $\mu = 22.1$ cm^{-1} for Cu Kα radiation ($\lambda = 1.5418$ Å), $T = 20(1)$ °C. Cell parameters were determined from 24 accurately centred reflections and were calculated by the standard Philips programs.

2.3.2. Structure determination

Intensity measurements were made on a Philips PW1100 diffractometer (Cu Kα graphite monochromated radiation, $6 < 2\theta \leqslant 120^\circ$, ω-scan, scan rate 0.05° s^{-1}). A total of 5061 unique data was collected ($\pm h, \pm k, +l$), 4061 of which were considered to be observed ($I \geqslant 3\sigma(I)$). Intensity data were processed as described previously [10]. A face-indexed numerical absorption correction was applied. The atomic scattering factors for neutral atoms corrected for anomalous dispersion were taken from Ref. [11].

The structure was solved by direct methods [12]. Full-matrix least-squares refinement employing anisotropic thermal parameters for all non-hydrogen atoms (a single isotropic thermal parameter for hydrogens (0.08 Å^2) placed in geometrically idealized positions: C–H 0.96 Å), reduced R to 0.045 and R' to 0.054, at convergence. The goodness of fit value ($[\Sigma w(|F_o|-|F_o|)^2/(N_{obs}-N_{par})]^{1/2}$) was 0.75. The asymmetric unit consists

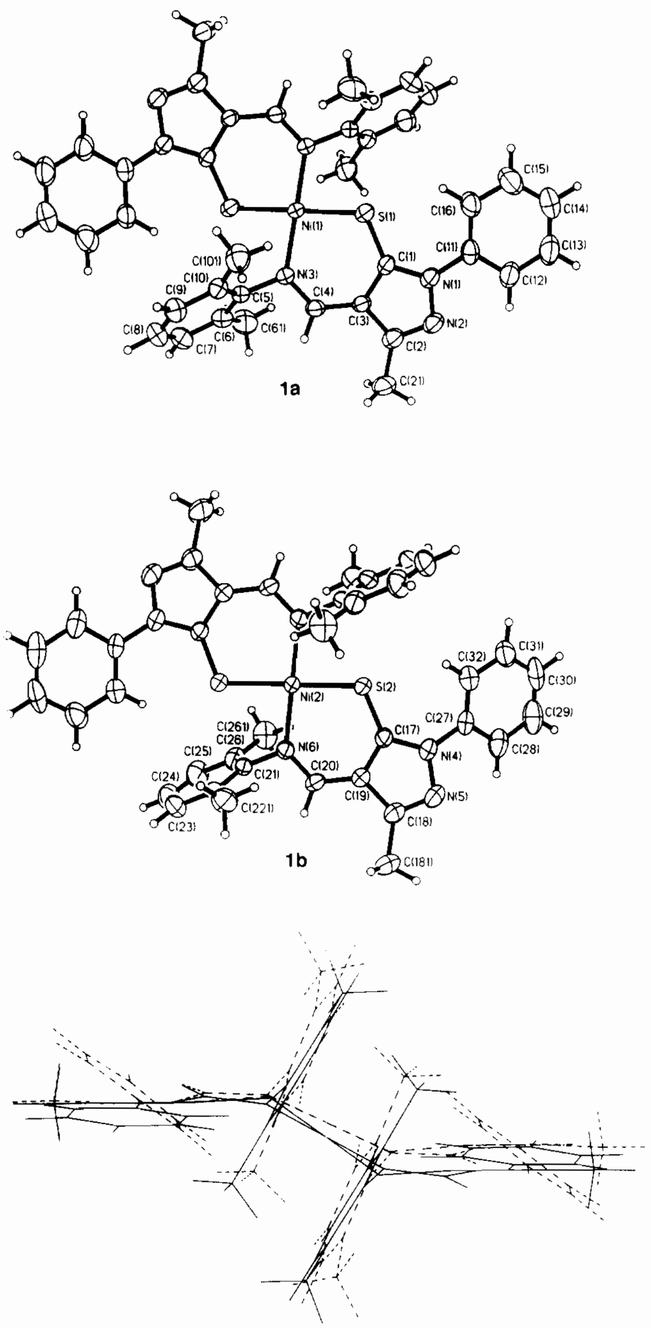


Fig. 1. ORTEP view of the two molecules of **1** in the asymmetric unit with atom labelling scheme and side view of both molecules showing a molecular conformation.

of two crystallographically distinct molecules **1a** and **1b** (Fig. 1). Each molecule is centrosymmetric, the Ni atoms being situated at 0,0,0.5 and 0.5,0.5,0.5. Atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. See also Section 4.

Table 1
Atomic coordinates and isotropic thermal parameters for **1a,b**

Atom	x	y	z	U_{eq}[a] (Å^2)
Ni(1)	0.0	0.0	0.5	0.0322(3)
Ni(2)	0.5	0.5	0.5	0.0283(2)
S(1)	−0.07625(7)	0.05228(7)	0.34762(9)	0.0471(3)
S(2)	0.39245(7)	0.43655(8)	0.39840(9)	0.0478(3)
N(1)	−0.0994(2)	−0.0643(2)	0.1315(3)	0.036(1)
N(2)	−0.0498(2)	−0.1427(2)	0.0408(3)	0.044(1)
N(3)	0.1158(2)	−0.0632(2)	0.3645(3)	0.034(1)
N(4)	0.3222(2)	0.5253(2)	0.1962(3)	0.041(1)
N(5)	0.3493(3)	0.5967(3)	0.0864(3)	0.056(1)
N(6)	0.5846(2)	0.5653(2)	0.3318(3)	0.031(1)
C(1)	−0.0490(2)	−0.0423(2)	0.2239(3)	0.031(1)
C(2)	0.0308(3)	−0.1685(3)	0.0765(3)	0.042(1)
C(21)	0.1031(3)	−0.2516(3)	0.0016(4)	0.057(2)
C(3)	0.0358(2)	−0.1096(3)	0.1911(3)	0.033(1)
C(4)	0.1151(2)	−0.1074(2)	0.2506(3)	0.034(1)
C(5)	0.2159(2)	−0.0667(3)	0.3832(3)	0.035(1)
C(6)	0.2572(3)	−0.1662(3)	0.4058(4)	0.045(1)
C(61)	0.1996(3)	−0.2684(3)	0.4226(5)	0.062(2)
C(7)	0.3554(3)	−0.1683(3)	0.4130(4)	0.057(2)
C(8)	0.4099(3)	−0.0746(4)	0.4009(4)	0.059(2)
C(9)	0.3667(3)	0.0211(3)	0.3802(4)	0.056(1)
C(10)	0.2684(2)	0.0274(3)	0.3727(3)	0.041(1)
C(101)	0.2219(3)	0.1342(3)	0.3552(5)	0.056(2)
C(11)	−0.1945(3)	−0.0286(3)	0.1204(3)	0.040(1)
C(12)	−0.2272(3)	−0.0679(4)	0.0156(4)	0.058(1)
C(13)	−0.3220(3)	−0.0392(4)	0.0059(5)	0.073(2)
C(14)	−0.3843(3)	0.0269(4)	0.1001(5)	0.065(2)
C(15)	−0.3509(3)	0.0666(3)	0.2028(5)	0.070(2)
C(16)	−0.2573(3)	0.0398(3)	0.2147(5)	0.055(2)
C(17)	0.3925(2)	0.5208(3)	0.2661(3)	0.033(1)
C(18)	0.4350(3)	0.6363(3)	0.0898(4)	0.053(2)
C(181)	0.4900(4)	0.7157(4)	−0.0169(5)	0.087(2)
C(19)	0.4656(2)	0.5936(3)	0.2020(3)	0.035(1)
C(20)	0.5584(2)	0.6039(2)	0.2271(3)	0.035(1)
C(21)	0.6918(2)	0.5732(3)	0.2132(3)	0.033(1)
C(22)	0.7341(3)	0.6722(3)	0.3212(3)	0.043(1)
C(221)	0.6706(3)	0.7722(3)	0.3553(4)	0.058(2)
C(23)	0.8376(3)	0.6746(4)	0.3018(4)	0.062(2)
C(24)	0.8943(3)	0.5823(5)	0.2736(4)	0.069(2)
C(25)	0.8514(3)	0.4862(4)	0.2649(4)	0.062(2)
C(26)	0.7491(3)	0.4796(3)	0.2831(3)	0.046(1)
C(261)	0.7013(3)	0.3739(3)	0.2717(5)	0.060(2)
C(27)	0.2354(2)	0.4618(3)	0.2121(4)	0.040(1)
C(28)	0.2141(3)	0.4286(3)	0.0947(4)	0.056(2)
C(29)	0.1329(3)	0.3614(4)	0.1089(6)	0.069(2)
C(30)	0.0754(3)	0.3307(3)	0.2342(6)	0.066(2)
C(31)	0.0946(3)	0.3679(3)	0.3485(5)	0.063(2)
C(32)	0.1751(3)	0.4342(3)	0.3395(4)	0.049(1)

[a] The equivalent isotropic temperature factor is defined as one-third of the orthogonalized U tensor (Å^2).

3. Results and discussion

In our previous paper [7b] on bis[1-isopropyl-3-methyl-4-(2,4,6-trimethylphenyliminomethyl)-5-pyrazolethiolato]nickel(II) we found a constant value of μ_{eff} of 3.21 BM and a Curie type behaviour of the isotropic chemical shifts in $CDCl_3$ solution, in the temperature range from −55 to +55 °C, consistent with a tetrahedral HS form of the complex. Similarly, isotropic chemical shifts for **1** are virtually linear versus $1/T$ and the magnetic moment is constant at 2.75 BM in the same solvent and temperature range. This value of the moment is somewhat lower than typical values of HS Ni(II)

Table 2
Selected bond lengths (Å) and angles (°) for **1a**,**b**

1a		**1b**	
Bond lengths			
Ni(1)–S(1)	2.211(1)	Ni(2)–S(2)	2.220(1)
Ni(1)–N(3)	1.962(2)	Ni(2)–N(6)	1.959(2)
S(1)–C(1)	1.706(3)	S(2)–C(17)	1.702(3)
C(1)–N(1)	1.366(5)	C(17)–N(4)	1.369(5)
C(1)–C(3)	1.398(4)	C(17)–C(19)	1.386(4)
N(1)–N(2)	1.393(4)	N(4)–N(5)	1.391(4)
N(1)–C(11)	1.424(5)	N(4)–C(27)	1.426(5)
N(2)–C(2)	1.308(5)	N(5)–C(18)	1.309(6)
C(2)–C(3)	1.417(5)	C(18)–C(19)	1.429(6)
C(2)–C(21)	1.491(5)	C(18)–C(181)	1.507(6)
C(3)–C(4)	1.408(5)	C(19)–C(20)	1.396(5)
C(4)–N(3)	1.304(4)	C(20)–N(6)	1.311(4)
N(3)–C(5)	1.459(4)	N(6)–C(21)	1.453(4)
Bond angles			
S(1)–Ni(1)–N(3)	94.18(9)	S(2)–Ni(2)–N(6)	93.33(9)
S(1)–Ni(1)–N′(3)	85.82(9)	S(2)–Ni(2)–N′(6)	86.67(9)
Ni(1)–S(1)–C(1)	106.5(1)	Ni(2)–S(2)–C(17)	107.5(1)
S(1)–C(1)–N(1)	128.6(2)	S(2)–C(17)–N(4)	126.3(2)
S(1)–C(1)–C(3)	125.7(3)	S(2)–C(17)–C(19)	127.5(3)
N(1)–C(1)–C(3)	105.5(3)	N(4)–C(17)–C(19)	106.1(3)
N(1)–N(2)–C(2)	105.8(3)	N(4)–N(5)–C(18)	105.4(3)
N(2)–C(2)–C(3)	111.2(3)	N(5)–C(18)–C(19)	111.5(3)
N(2)–C(2)–C(21)	121.2(3)	N(5)–C(18)–C(181)	121.1(4)
C(3)–C(2)–C(21)	127.6(3)	C(19)–C(18)–C(181)	127.4(4)
C(1)–C(3)–C(2)	106.0(3)	C(17)–C(19)–C(18)	105.5(3)
C(1)–C(3)–C(4)	125.7(3)	C(17)–C(19)–C(20)	125.3(3)
C(2)–C(3)–C(4)	127.9(3)	C(18)–C(19)–C(20)	127.9(3)
C(3)–C(4)–N(3)	128.0(3)	C(19)–C(20)–N(6)	127.0(3)
Ni(1)–N(3)–C(4)	126.4(2)	Ni(2)–N(6)–C(20)	128.7(2)

complexes and may be due to some residual amount of the LS isomer or reduced orbital contribution in the HS form. However, in the solid state, complex **1** was found to be essentially low-spin (μ_{eff} varied from 0.57 to 0.22 BM in the temperature range 292–4.7 K). In order to establish its structure, an X-ray single-crystal study was performed. This showed a planar coordination geometry and a *trans*-N_2S_2 configuration (Fig. 1). Thus,, the presence of four *o*-methyl groups in two N_{coord}-xylyl fragments has a considerable influence on the electronic and structural features of pyrazolethiolato complexes. This is also a rare case where a planar LS form crystallizes from a solution in which the tetrahedral HS form predominates.

It may be suggested that stabilization of the planar structure is caused either by unfavourable steric interactions in the tetrahedral isomer or by the electronic donation of the methyl groups increasing the ligand field strength. The latter seems unlikely since our previous study [7b] has shown a stable tetrahedral structure invariably exists for pyrazolethiolato complexes with various NC_6H_4Y-4 substituents ($Y = N(CH_3)_2$, OCH_3, CH_3, H, COOEt, NO_2). A previous report on triazene-1-oxide Co(II) complexes [8c], which possess tetrahedral geometry in unsubstituted species, has shown that a planar geometry results when *o*-Me groups are incorporated, because of steric interactions of the type seen here. However, the probable formation of a tetrahedral isomer was also shown [13] for bis(*β*-aminopropenethiolato) Cd(II) and Zn(II) complexes with N-mesityl groups. Noteworthy is the fact that the xylyl groups in **1** are essentially twisted with respect to the parent metal-containing rings (torsion angles (Ni(1)–N(3)–C(5)–C(6) (**1a**) and Ni(2)–N(6)–C(21)–C(22) (**1b**) are 68.7 and 72.3°, respectively) whereas a twist angle for the NPh group [7c] is 54°. Preferential conformation of the NR substituent was proposed [8c] to have some influence on the ligand charge distribution and thus on the ligand field strength.

Whatever the reasons are which lead to the square-planar nickel geometry, the occurrence of the *trans*-isomer instead of the *cis*-isomer may be explained by the requirements to minimize the steric interactions between *o*-Me groups of the different halves of the molecule. To illustrate this point, Pd(II) pyrazolealdiminethiolate complexes [14] may be considered, since a planar geometry is strongly preferred for Pd(II). In agreement with this, complexes with NPh and NPy-*α* substituents display a square-planar structure with a *cis*-N_2S_2 ligand environment typical for sulfur coordination. However, in the case of bulky NC_6H_{11} groups, a *trans*-square-planar isomer is formed as was shown by an X-ray diffraction study. Some sterical constraints also seem to be retained in a fully planar molecular conformation for the *trans*-isomer resulting in a 'stepped' shape of molecule **1** due to the folding of two metal chelate rings along the N···S axis by 32.4° (**1a**) and 28.7° (**1b**). The larger 'stepped' distortion in **1a** compared to **1b** is accompanied by a smaller twisting of that xylyl group and therefore the relation between the overall molecular conformation and a particular orientation of the N-xylyl substituents may be assumed. Packing forces seem to be responsible for the quite different orientation of the 1-Ph substituents, relative to the pyrazole ring, in **1a** and **1b**: the torsion angles C(1)–N(1)–C(11)–C(12) and C(17)–N(4)–C(27)–C(28) are 1.8 and 51.3°, respectively.

Similar structural features may be anticipated for the solid complex **2** which is apparently low-spin. The μ_{eff} values (0.91–0.58 BM in the temperature range 292–77 K) are attributed to temperature independent paramagnetism (TIP). In $CDCl_3$ solution a planar $\rightleftharpoons$ tetrahedral equilibrium was found, indicating that by varying a distant 3-pyrazole substituent, the electronic and structural properties may be altered for a given type of pyrazoleiminethiolato nickel(II) complex. The magnetic moment in solution, of **2**, varies from 1.97 at 292 K to 2.15 BM at 331 K which corresponds to the ratio of the HS form n_{HS} from 0.64 to 0.72 ($n_{HS} = K/1 + K$, where $K = (\mu_{obs}^2 - \mu_{LS}^2)/(\mu_{HS}^2 - \mu_{obs}^2)$, where μ_{HS} is assumed to be 2.96 BM. A TIP value of 250×10^{-6} cgs units was estimated [15], corresponding to μ_{LS} values varying from 0.87 to 0.91 BM in the temperature range 292 to 331 K. Thermodynamic parameters of the equilibrium were estimated from a van't Hoff plot to be $\Delta H^\circ=11.8\pm0.1$ kJ mol^{-1}, $\Delta S^\circ=34.6\pm1$ J mol^{-1} K^{-1} which are comparable to values found for other similar systems [6].

The electronic spectra of complexes **1** and **2** both show a complicated spectral pattern, with at least five bands in the range 500–1800 nm where the ligand field transitions are expected to appear. According to the magnetic measurements in chloroform, solution **1** is purely high-spin, whereas **2** is a mixture of the HS and LS molecules. Surprisingly however, none of the observed transitions in **2** can be assigned to the LS component. From our study [3] on similar complexes, **3**, derived from tetradentate Schiff base ligands containing 2,2′-diaminobiphenyl backbones, a band around 700 nm is assigned to the transition of the LS form, but this can be broad and hidden under the HS bands. The lowest energy transition observed for **1** and **2**, at 1750 and 1795 nm, respectively, is assigned to the $^3A_2$ transitions in the pseudo-tetrahedral D_{2d} HS form. The actual symmetry is only C_2, but no further splitting is expected in going from D_{2d} to C_2. The intensity ratio of this band is $\epsilon(\mathbf{2})/\epsilon(\mathbf{1})=0.42$ which is in fair agreement with the value of $K_{eq}(\mathbf{2})$ from the planar $\rightleftharpoons$ tetrahedral equilibrium determined from magnetic data (0.64). The values of Δ_T estimated from the position of the $^3A_2$ transition are 3175 (**1**) and 3095 (**2**) cm^{-1}. The relative magnitudes suggest that **1** has the strongest ligand field, which contrasts with the magnetic behaviour, however both values are only 70% of those observed [3] for complexes of type **3** that show a spin equilibrium behaviour.

It should be emphasized that the so-called critical Δ_T(HS) will vary with the alteration of the donor atoms as well as with the geometry of the HS form. Typical values of the tetrahedral twist angle in the bis-chelate complexes **1** and **2** are [7c] about 85°, whereas for **3** these are [3] about 74°. Ideally, any Δ_T value quoted in the literature ought to be extrapolated to the twist angle of 90°. However, this is usually complicated due to the lack of information on the structural features in solution. The positions of the $^3T_1$ transitions (580 and 592 nm for **1** and **2**, respectively), which mainly reflect the Racah interelectronic repulsion parameter B, are also red-shifted compared to other similar complexes. This suggests a significant nephelauxetic effect occurs for **1** and **2**, which partly compensates for the relatively low Δ_T values and therefore brings Δ_T/B up to the critical values. Complex **2** has the lowest B value, corresponding to a stabilization of the LS state. Apparently, a higher degree of electronic delocalization involving the phenyl group in position 3 of the pyrazole ring is a crucial factor leading to the higher stability of the LS state for **2**, compared to **1**, the latter containing the 3-Me substituent.

4. Supplementary material

Full tables of bond lengths and angles, thermal parameters and H atom coordinates are available on request, from the authors A.N. and K.S.M.

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