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Synthesis, properties and Mössbauer spectra of bisaxially co-ordinated iron(II) phthalocyanine low-spin complexes: the first semi-quantitative explanation of the influence of the character of axial ligands on the spectral parameters †

Victor N. Nemykin,*[a,b] Ann E. Polshina,[a,c] Victor Y. Chernii,[b] Ernst V. Polshin[d] and Nagao Kobayashi *[a]

[a] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*
[b] *V.I. Vernadskii Institute of General and Inorganic Chemistry, Palladina Ave. 32/34, 252680 Kiev-142, Ukraine*
[c] *Institute of Sorption and Endoecology Problems, Kiev, Ukraine*
[d] *Institute of Geochemistry, Mineralogy and Ore formation, Palladina Ave. 34, 252680 Kiev-142, Ukraine*

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A series of bisaxially co-ordinated low-spin iron(II) phthalocyanine complexes (pc)FeL_2 with different types of nitrogen bases as axial ligands has been prepared and characterised by electronic, ^{1}H NMR and Mössbauer spectroscopies. The influence of electronic and steric effects of the axial ligands on Mössbauer quadrupole splitting (ΔE_Q) and isomer shift (δ), NMR parameters, and metal-to-ligand charge transfer (MLCT) band position are discussed. Mössbauer partial quadrupole splitting (p.q.s.) and partial isomer shift (p.i.s.) parameters for different ligands have been estimated and rationalised with the overall data for (pc)FeL_2 and $(nx)_2FeL_2$ (nx = nioxime) complexes. A semi-empirical AM1 method and the cone angle concept were used to factorise σ- and π-electronic and steric effects of the ligands. A good correlation between the predicted and experimental MLCT band position of (pc)FeL^1L^2 complexes, as well as predicted and experimental p.i.s. and p.q.s. values for different ligands, has been observed.

Introduction

Phthalocyanine (H_2pc) iron complexes have been the subject of wide interest, both for homogeneous and heterogeneous catalytic systems with high oxygenation activity,[1] and have been also studied intensively as hemeoprotein models.[2] The possibility of axial co-ordination and the stability of iron–axial ligand bonds are key steps in these systems which play an important role in catalytic and model biological processes.[1,2] The nature of the metal–ligand bonding in these systems has been discussed qualitatively over the past 30 years. A large number of bisaxially co-ordinated low-spin iron(II) pc's, (pc)FeL_2 or (pc)FeL^1L^2, with six-membered nitrogen bases, isocyanides, phosphines and phosphites has been studied.[3–6] However, despite their importance in modelling biological processes and co-ordination chemistry, (pc)FeL_2 complexes with aliphatic amines and five-membered heterocyclic nitrogen bases as axial ligands have not yet been systematically studied, since their spectroscopic characteristics are limited.[4] In this paper we report the synthesis, NMR, electronic absorption and Mössbauer spectra of a wide range of (pc)FeL_2 complexes with aliphatic and five-membered heterocyclic amines as axial ligands. The bonding properties of the ligands are discussed with respect to their σ-donor and/or π-acceptor ability and steric effects. The relationships between the electronic and geometric effects of axial ligands and Mössbauer isomer shift (δ), quadrupole splitting (ΔE_Q), as well as metal-to-ligand charge transfer (MLCT) band position in the electronic spectra of (pc)FeL_2 and (pc)FeL^1L^2 complexes, are discussed semiquantitatively.

† Electronic supplementary information (ESI) available: analytical data. See http://www.rsc.org/suppdata/dt/b0/b000096p/

Experimental

Synthesis

The following new (pc)FeL_2 complexes have been synthesized by a standard procedure:[4–6] [Fe(pc)(Pr^iNH_2)$_2$], [Fe(pc)(Bu^sNH_2)$_2$], [Fe(pc)(Bu^tNH_2)$_2$], [Fe(pc)(mf)$_2$], [Fe(pc)($CF_3CH_2NH_2$)$_2$], [Fe(pc)(app)$_2$], [Fe(pc)(pst)$_2$], [Fe(pc)(tmapip)$_2$], [Fe(pc)(pd)$_2$], [Fe(pc)(bd)$_2$], [Fe(pc)(ptd)$_2$], [Fe(pc)(hpd)$_2$], [Fe(pc)(Hpz)$_2$], and [Fe(pc)(Htzl)$_2$], where mf = morpholine, app = *N*-(3-aminopropyl)piperidine, pst = *N*-(2-aminoethyl)piperazine, tmapip = 4-amino-2,2,6,6-tetramethylpiperidine, pd = 1,3-diaminopropane, bd = 1,4-diaminobutane, ptd = 1,5-diaminopentane, hpd = 1,7-diaminoheptane, 1,2,4-Htzl = 1,2,4-triazole. All complexes have satisfactory elemental anaysis data and have been characterised by Mössbauer, ^{1}H NMR and electronic spectra.

Spectroscopy

An NGRS-4 spectrometer was used for the ^{57}Fe Mössbauer spectroscopy measurements, using a ^{57}Co-in-chromium source with an initial activity of 50 mCi. Isomer shift was referenced against sodium nitroprusside ($Na_2Fe(CN)_5(NO)$) at 298 K (the conversion factor from sodium nitroprusside to iron foil is -0.257 mm s^{-1}). The ^{1}H NMR spectra were recorded on a Bruker-CPX 200 MHz spectrometer, and electronic spectra on a Specord M-40 spectrometer.

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Table 1 Electronic, ^{1}H NMR and calculated MLCT band positions of the (pc)FeL_2 and (pc)FeL^1L^2 complexes

Complex	L[a]	λ/nm (relative intensity)			^{1}H NMR, δ[b]			MLCT (calc.)/ nm
		Q	MLCT	B	NH_n	α-CH_n	β-CH_n	
1	NH_3	664, 637, 604	425[c]	335[d]				425
2	$PrNH_2$	664(1.47), 637(0.81), 605(0.57)	427(0.28)	334(1)[e]	−7.27 (t, 4H)	−3.00 (m, 4H)	−1.44 (m, 4H)	
3	Pr^iNH_2	663(1.64), 636(0.7), 604(0.64)	425(0.28)	334(1)[e]	−7.46 (d, 4H)	−3.09 (m, 2H)	−1.94 (m, 12H)	
4	$BuNH_2$	664(1.58), 637(0.71), 605(0.6)	427(0.35)	334(1)[e]	−7.28 (t, 4H)	−2.98 (m, 4H)	−1.41 (m, 4H)	425
5	Bu^sNH_2	663(2.06), 636(0.8), 604(0.69)	425(0.32)	334(1)[e]	−7.36 (d, 4H)	−3.49 (m, 2H)	−2.06 (m, 5H)	425
6	Bu^tNH_2	661(2.23), 634(0.68), 600(0.57)	422(0.32)	331(1)[e]	−7.97 (s, 4H)		−1.76 (s, 18H)	424
7	$CF_3CH_2NH_2$	655(1.82), 628(0.6), 595(0.52)	416(0.29)	330(1)[e]				412
8	tmapip	664(1.50), 637(0.57), 604(0.49)	426(0.24)	330(1)[e]	−7.48 (d, 4H)	−3.23 (m, 2H)	−2.25 (m, 8H)	
9	app	664(1.91), 640(0.64), 606(0.55)	434(0.36)	334(1)[e]	−6.18 (t, 4H)	−2.90 (m, 4H)	−0.98 (m, 4H)	
10	pst	665(1.44), 640(0.66), 607(0.58)	430(0.29)	334(1)[e]	−6.65 (t, 4H)	−2.86 (m, 4H)	−0.70 (t, 4H)	
11	pd	665(1.72), 639(0.75), 607(0.69)	433(0.32)	334(1)[e]	−6.43 (t, 4H)	−2.86 (m, 4H)	−1.24 (m, 4H)	
12	bd	666(1.84), 640(0.81), 608(0.71)	433(0.35)	334(1)[e]	−6.46 (t, 4H)	−3.01 (m, 4H)	−1.31 (m, 4H)	430
13	ptd	665(2.51), 636(0.78), 604(0.66)	429(0.37)	337(1)[e]	−7.06 (t, 4H)	−3.00 (m, 4H)	−1.39 (m, 4H)	
14	hxd	664(2.89), 636(0.82), 604(0.72)	428(0.39)	335(1)[e]	−7.12 (t, 4H)	−3.07 (m, 4H)	−1.41 (m, 4H)	
15	hpd	664(3.41), 636(1.0), 603(0.87)	428(0.43)	334(1)[e]	−7.15 (t, 4H)	−3.09 (m, 4H)	−1.43 (m, 4H)	
16	pip	663, 636, 605	424[c]	334[d]	−7.88 (m, 2H)	−3.10 (m, 8H)	−1.45 (m, 8H)	423
17	mf	660(2.05), 633(0.82), 601(0.66)	423(0.28)	332(1)[e]	−7.93 (m, 2H)	−3.12 (m, 8H)	−0.81 (t, 8H)	422
18	Him	657, 596	422[c]	339[d]				420
19	meim	658, 597	422[c]	338[d]				420
20	Hpz	655(1.48) 594(0.38)	408(0.27)	335(1)[e]				414
21	Htzl	654(1.71), 595(0.45)	412(0.23)	327(1)[e]				414
22	py	655, 593	411[c]	332[d]				414
23	4-mepy	652, 592	411[c]	331[d]				415
24	4-HCOpy	654, 630, 595	410[f]					409
25	Bu^tNC	658, 598	387 (sh)	326[f]				378
26	NH_3/CO	659, 596	369[c]	317[d]				375
27	CN^-	664, 602	453[c]	394, 310[d]				453

[a] For the (pc)FeL_2 complexes only one axial ligand is shown. [b] In $CDCl_3$; δ in ppm relative to internal $SiMe_4$; d, doublet; t, triplet; m, multiplet. For complexes **2**–**6** and **8**–**17**, proton signals of the pc ring were observed at δ 9.2–9.3 (α, 8 H) and 7.85–7.95 (β, 8 H) (see Fig. 1 for the numbering of protons); protons of axial ligands are indicated by Fe–$NH_n\alpha CH_n\beta CH_n$. [c] Based on MCD data; for all other cases, the MLCT band position was estimated from the electronic spectra; sh, shoulder. [d] In CH_2Cl_2; ref. 16(*b*). [e] In benzene. [f] $CHCl_3$; ref. 4(*b*).

Computational details

All computations have been carried out using the HyperChem5.1Pro program (HyperCube Inc., Gainesville, FL, 1997) on a Pentium-series PC. All ligand structures were fully optimised by the Polak-Ribiere gradient method at the semi-empirical AM1 level.[7] Molecular electrostatic potentials (V_{MEP}) and "molecular back-bonding potentials" (V_b) were evaluated as described previously.[8] The ligands' resonance integrals were calculated with the zero differential overlap (ZDO) formalism using an expression $\beta = (\beta_A + \beta_B)/2 \cdot S_{\mu\nu}$, where β_A and β_B are parameters for the probe atom and ligand co-ordinating atom (LCA), respectively, while $S_{\mu\nu}$ is an overlap integral.[9] Steric parameters of ligands were evaluated by the cone angle concept.[10] Effective van der Waals radii of the π system were fixed at 1.7 Å.[11] Multiparameter regression analysis was carried out by the Powell quadratic convergence method.[12]

Results and discussion

Synthesis

Unlike pyridines, imidazoles, phosphites, phosphines, isocyanides and carbon monoxide, aliphatic amines are pure σ donors.[8] As a consequence, in the latter case, the influence of the π-acceptor and/or π-donor properties of an axial ligand on the spectroscopic behaviour and stability of (pc)FeL_2 complexes can be ruled out. (pc)Fe readily reacts with monoalkylamines, including bulky *tert*-butylamine. Many (pc)FeL_2 complexes with various monoalkylamines, which differ in electronic and steric effects, have been synthesized (Table 1). Note that compound **7** can be studied only in solution, probably due to volatility and low basicity of the axial ligands. An additional doublet which can be assigned to a μ-oxo(phthalocyaninato)iron complex[13] has been observed in the Mössbauer spectrum of **7** in the solid state. On the other hand, only bands assigned to (pc)FeL_2 complexes[3–6] have been observed in electronic spectra in solution and frozen solution Mössbauer spectra for compound **7**.

Steric factors play a role in (pc)FeL_2 complex formation when dialkylamines are used as axial ligands. For example, branching of the carbon skeleton at the α-carbon atom ((*cyclo*-$C_6H_{11})_2NH$, Pr^i_2NH) makes the (pc)FeL_2 complex formation impossible. A similar phenomenon was observed when α-substituted pyridines were used.[4b,c]

Only two (pc)FeL_2 complexes with trialkylamines have been described in the literature,[3,4d] and Mössbauer spectra of [(pc)Fe(dabco)$_2$] suggest that the Fe–L bonds in this compound is the weakest compared with other (pc)FeL^1L^2 complexes.

When di- or poly-amines are used as axial ligands several possibilities arise, depending on which amino group co-ordinates to the iron atom. However, this can be elucidated from ^{1}H NMR and Mössbauer spectra. In NMR spectra the protons of axial ligands are strongly shielded by the loop current of the pc ring, and this effect is larger near the pc center.[1,3] In the cases of the Mössbauer spectra of (pc)FeL_2 (L = aliphatic amine), it is known that ΔE_Q values are grouped into three categories depending on the types of amines, *i.e.* for monoalkyl-, dialkyl-, and trialkyl-amines ΔE_Q is ≈2.0, ≈2.2, and ≈2.9 mm s^{-1}, respectively. Thus, on the basis of these, the data in Tables 1 and 2 suggested that only a primary amino group is co-ordinated to the central iron in compounds **8**–**10**, although a steric effect may also occasionally affect the co-ordination. It is well known that σ-donor strength and steric effects for aliphatic amines increase in the order $NH_3 < RNH_2 < R_2NH < R_3N$.[14] In the case of aliphatic polyamines in this study the experimentally observed data (Tables 1 and 2) indicate that the steric factor mainly controls the selectivity of axial co-ordination to (pc)Fe. A similar preferential co-ordination of primary aliphatic amines has been observed for several mixed-ligand phthalocyanine complexes of europium and praseodymium.[15]

It is also interesting to compare the stability of (pc)FeL_2

Table 2 Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters for the (pc)FeL_2 complexes, and the estimated and calculated partial isomer shift (p.i.s.) and partial quadrupole splitting (p.q.s.) values for the different types of ligands (all values in mm s^{-1})

Experimental[a]					Calculated				
Complex	L[b]	δ	ΔE_Q	$\Gamma_{1/2}$	L	p.i.s.[c]		p.q.s.[c]	
1	NH_3[d]	0.52	1.79		NH_3	0.14	(0.14)	−0.52	(−0.53)
2	$PrNH_2$[e]	0.50	1.97		$BuNH_2$	0.14	(0.14)	−0.48	(−0.45)
3	Pr^iNH_2	0.51	2.04	0.27	Bu^sNH_2	0.15	(0.14)	−0.45	(−0.43)
4	$BuNH_2$	0.52	1.97	0.26	Bu^tNH_2	0.18	(0.15)	−0.36	(−0.35)
5	Bu^sNH_2	0.52	2.05	0.26	$CF_3CH_2NH_2$	0.19	(0.16)	−0.34	(−0.39)
6	Bu^tNH_2	0.61	2.38	0.28	bd	0.12	(0.14)	−0.50	(−0.47)
7	$CF_3CH_2NH_2$	0.62	2.49	0.31	pip	0.14	(0.15)	−0.39	(−0.38)
8	tmapip	0.51	1.96	0.29	mf	0.14	(0.15)	−0.38	(−0.38)
9	app	0.46	1.76	0.34	dabco	0.18	(0.16)	−0.24	(−0.26)
10	pst	0.50	1.82	0.34	$PhNH_2$	0.15	(0.15)	−0.43	(−0.43)
12	bd	0.48	1.84	0.33	meim	0.14	(0.13)	−0.53	(−0.52)
16	pip	0.52	2.23	0.29	Hpz	0.14	(0.13)	−0.51	(−0.50)
17	mf	0.53	2.31	0.29	Htzl	0.14	(0.13)	−0.53	(−0.51)
28	dabco[f]	0.59	2.89		py	0.14	(0.13)	−0.48	(−0.50)
29	$PhNH_2$[e]	0.53	2.11		4-HOpy	0.12	(0.13)	−0.51	(−0.50)
19	meim	0.48	1.71		4-HCOpy	0.14	(0.13)	−0.50	(−0.50)
20	Hpz	0.51	1.79		prmd	0.14	(0.13)	−0.46	(−0.49)
21	Htzl	0.51	1.73		taz	0.13	(0.13)	−0.47	(−0.48)
22	py	0.52	2.02		prdz	0.12	(0.12)	−0.51	(−0.52)
30	4-HOpy[g]	0.53	1.80		tz	0.09	(0.11)	−0.51	(−0.51)
24	4-HCOpy[g]	0.58	1.84		CN^-	0.06	(0.06)	−0.84	(−0.86)
31	prmd[f]	0.52	1.99		Bu^tNC	0.09	(0.09)	−0.72	(−0.69)
32	taz[f]	0.52	1.95		PhNC	0.07	(0.08)	−0.70	(−0.69)
33	prdz[f]	0.47	1.82		CO	0.06	(0.04)	−0.74	(−0.74)
34	tz[f]	0.41	1.79		PEt_3	0.09	(0.14)	−0.59	(−0.58)
27	CN^-[f]	0.38	0.67		$P(OEt)_3$	0.09	(0.10)	−0.68	(−0.69)
25	Bu^tNC[f]	0.42	0.79		tht	0.15	(0.15)	−0.41	(−0.40)
35	PhNC[f]	0.37	0.67		pc/4	0.06	(0.06)	−0.96	(−0.93)
36	CO[h]	0.36	0.82		nx/2	0.05	(0.06)	−0.92	(−0.94)
37	PEt_3[i]	0.42	1.54						
38	$P(OEt)_3$[i]	0.39	1.07						
39	tht[j]	0.53	2.20						

[a] All experimental parameters are within ±0.01 mm s^{-1}; room-temperature values are shown except for complexes **24** and **30** for which spectra were measured at 77 K; $\Gamma_{1/2}$ = half width at half height; the conversion factor from sodium nitroprusside to iron foil is −0.257 mm s^{-1}. [b] Abbreviations: pip = piperidine; prmd = pyrimidine; taz = 1,3,5-triazine; prdz = pyridazine; tz = 1,2,4,5-tetrazine; tht = tetrahydrothiophene. [c] Values of p.i.s. and p.q.s. are calculated using eqns. (2) and (4), respectively, on the basis of the (pc)FeL_2 and $(nx)_2FeL_2$ (ref. 4(*b*)) complexes; values in parentheses are calculated using eqns. (3) and (9) for p.i.s. and p.q.s., respectively. [d] Ref. 6(*a*). [e] Ref. 4(*a*). [f] Ref. 3. [g] Ref. 4(*b*). [h] Ref. 5(*b*). [i] Ref. 18(*c*). [j] Ref. 4(*j*).

complexes with pure σ-donor and σ-donor/π-acceptor nitrogenous bases. For an axial ligand containing two nitrogen centres, such as pyridine-type and pure σ-donor type, selective co-ordination was achieved by the pyridine-type nitrogen.[4e] Moreover, when the reaction of [Fe(pc)$(py)_2$] with different aliphatic amines (up to 1 : 5 mol/mol) was monitored by Mössbauer spectroscopy, [Fe(pc)$(py)_2$] did not react, while the reaction of (pc)FeL_2 (L = aliphatic amines) complexes with py easily proceeded to [Fe(pc)$(py)_2$]. Finally, concerning the compounds in this study, their Mössbauer spectra did not change over the course of a year when L = pyridine type, while when L = aliphatic amine the spectra showed an additional doublet after a few months. Thus, (pc)FeL_2 complexes co-ordinated by axial ligands having both σ-donor and π-acceptor properties appear to be more stable, compared with ones with axial ligands having pure σ-donor properties such as aliphatic amines.

Spectroscopic data

Spectroscopic data for all complexes in this study are presented in Tables 1–3, together with those published previously. Electronic spectra of the new complexes are typical for bisaxially co-ordinated low-spin iron(II) pc's, and consist of Q and B bands which correspond to two intramolecular π–π* transitions in the pc ligand and one MLCT band ($e_g(Fe_{d\pi})$–$b_{1u}(\pi^*$, pc)) in the ≈430 nm region, which is sensitive to electronic and steric effects of the axial ligands. The MLCT bands appeared at ≈450, ≈430, ≈410 and 400 nm when L = CN^-, aliphatic amines, six-membered nitrogenous bases, and isocyanides, respectively.[4–6,16] At first approximation, the relative energy of the MLCT band in (pc)FeL_2 and (pc)FeL^1L^2 complexes depends on the relative energies of the $e_g(Fe_{d\pi})$ and $b_{1u}(\pi^*$, pc) orbitals. Since the $b_{1u}(\pi^*)$ orbital of pc has nodes on the central metal, as well as on the atoms co-ordinating to the metal,[17] the influence of axial ligands on its energy can be neglected. The increase in the σ-donor and the decrease in the π-acceptor effects of axial ligands lead to a destabilisation of $e_g(Fe_{d\pi})$, and therefore a decrease in the MLCT energy. Thus, the MLCT band is observed at 427 nm for [Fe(pc)$(BuNH_2)_2$] (pK_a of $BuNH_2$ is 10.63) and 416 nm for [Fe(pc)$(CF_3CH_2NH_2)_2$] (pK_a of $CF_3CH_2NH_2$ is 5.70). The increase in the steric effects of the axial ligands, probably, leads to the elongation of the axial Fe–L bond and decreases the strength of the metal–ligand interactions. Ligands which are predominantly σ donors will result in a stabilisation of the $e_g(Fe_{d\pi})$ orbital and thus give a blue-shift of the MLCT band. In fact, the MLCT band is blue-shifted by 5 nm when the axial ligand is changed from $BuNH_2$ to Bu^tNH_2 (Table 1). On the other hand, for ligands which are predominantly π acceptors an increase in the steric effect of axial ligands destabilises the $e_g(Fe_{d\pi})$ orbital and accordingly leads to a red-shift of the MLCT band. Probably, the best candidates for supporting this assumption are the phosphites. However, unfortunately, the band positions in the electronic spectra of (pc)FeL_2 complexes with L = phosphite or phosphine are unreliable, since the previously reported data differ from group to group.[18a,b] If we compare the MLCT band positions of some (pc)FeL_2 complexes with L = polyamine,

those of **9**–**12** are red-shifted by up to 10 nm, compared with those of **1**–**5**. Moreover, the low-field shift for the co-ordinated NH_2 protons in the ^1H NMR (up to 1.1 ppm) and a lower ΔE_Q (up to 0.2 mm s^{-1}) and δ values in the Mössbauer spectra suggest that the σ-donor effect of axial ligands in **9**–**12** is higher than that in **1**–**5**. This kind of an unusual spectroscopic behaviour can be explained by the formation of an intramolecular hydrogen bond (IHB) in the axial ligands. Shifting the electron density from an axial nitrogen atom to the iron ion in (pc)FeL_2 complexes leads to an increase in the positive charge on an axial ligand group co-ordinated to iron, which is NH_2 in our case. In the case of polyamines, another unco-ordinated nitrogen atom can effectively compensate the increase in the positive charge on a co-ordinated NH_2 group by formation of an IHB. As a consequence, this leads to an increase in the electron density on the co-ordinated nitrogen atom and increases the σ-donor strength of the co-ordinated amino group. Our conclusion about the stronger σ-donor strength of axial ligands in compounds **9**–**12** compared to **1**–**5** may also be confirmed by the following data: (i) an IHB often occurs for nitrogen-containing compounds;[19] (ii) according to ref. 19, the n orbital which donates the electron density to an IHB is stabilised while the orbitals of an X–H fragment (where X = O, S, N, *etc*.) are destabilised; (iii) ^1H NMR spectra of complexes **11**–**15** suggest that the σ-donor property of axial ligands decreases in the order pd > bd > ptd > hpd ≈ $BuNH_2$ (Table 1). The stability of an IHB would decrease in the same order. In fact, our quantum-chemical calculations indicate that the σ-donor strength of an NH_2 group co-ordinated to a central atom increases with IHB formation compared with the aliphatic monoamines, and this kind of increase is in agreement with the above order.

Taking the above argument into account, one can conclude that the MLCT band position of the (pc)FeL_2 complexes depends on the axial ligands' σ-donor and π-acceptor properties and the steric effect. Recently, Fielder *et al*.[8] have developed a model for calculating the σ- and π-donor, and π-acceptor capabilities of ligands. In this model the σ- and π-donor properties were evaluated from the molecular electrostatic potential function, V_{MEP}, while the π-acceptor properties were derived using second-order perturbation theory. We adopted these two parameters (V_{MEP} and V_b) for factorisation of the electronic effects of ligands of interest. Steric factors of the axial ligands were evaluated using the cone angle concept.[10] It is easily inferred that only those atoms of axial ligands which lie within an interatomic distance of less than the sum of the van der Waals radii of the central metal and the co-ordinating atom can influence the metal–ligand bond length. Thus, considering that the average iron–axial ligand bond distance is about 2 Å[20] in (pc)FeL_2 and (pc)FeL^1L^2, contributions from the ligand atoms lying more than 3 Å away from the phthalocyanine plane can be ignored. The final expression for evaluation of the electronic and steric effects of axial ligands on the MLCT band position in the (pc)FeL_2 and (pc)FeL^1L^2 complexes becomes as in eqn. (1), where T is the cone angle of the axial ligand,[10] while

$$\text{MLCT(calc.)} = a_0 + a_1V_{MEP} + a_2V_b + a_3T \qquad (1)$$

V_{MEP} and V_b are derived as described previously.[8] The calculated values of the ligand electronic and steric effects are presented in Table 3, and the obtained results shown in Fig. 1. The final correlation coefficient is 0.980 for 18 compounds and the root-mean-square (rms) error is 3.54 nm. An analysis of parameters a_1–a_3, derived from expression (1), shows that the increase in σ-donor ability, decrease in π-acceptor ability and the steric effect of the axial ligands lead to a red-shift of the MLCT band, in good agreement with the qualitative assumptions discussed above and in the literature.[4–6]

Mössbauer spectra. Room temperature Mössbauer spectra of new complexes, as well as the selected data for the (pc)FeL_2 compounds, are presented in Table 2, and a typical spectrum is shown in Fig. 2. These data were analysed in terms of the point charge model,[21] and the partial isomer shift (p.i.s.) and partial quadrupole splitting (p.q.s.) were estimated for the ligands of interest (Table 2). In the confines of the point charge model, the observed δ is the sum of the p.i.s. of the individual ligands;[21] eqn. (2). In general, δ depends on the σ-donor and π-acceptor

$$\delta = \Sigma \text{ p.i.s.} \qquad (2)$$

effects of a ligand as $\delta = -\text{const.}\cdot(\sigma + \pi)$.[21d–f] Thus, an increase in the σ-donor effect of a ligand results in an increase of the 4s electron population and therefore a decrease of δ. For instance, δ for the [Fe(pc)(py)$_2$] complex (py is a moderate σ donor and π acceptor) is higher than that for $[Fe(pc)(CN)_2]^{2-}$ (CN^- is a

Table 3 Electronic and steric effects of ligands

L	V_{MEP}/eV	V_b/eV	θ/°	C/e Å^{-3}
NH_3	−3.09	0.035	93	−0.02
$BuNH_2$	−3.24	0.036	110	−0.013
Bu^sNH_2	−3.28	0.035	113	−0.015
Bu^tNH_2	−3.35	0.036	129	−0.0154
$CF_3CH_2NH_2$	−1.67	0.038	110	−0.0134
bd	−3.84	0.031	110	−0.0164
pip	−3.13	0.036	123	−0.0054
mf	−3.02	0.038	123	−0.005
dabco	−2.99	0.041	145	0.001
$PhNH_2$	−2.45	0.036	110	0.028
Him	−3.31	0.079	98	−0.028
meim	−3.32	0.079	98	−0.032
Hpz	−2.67	0.087	98	−0.028
Htzl	−2.91	0.096	98	−0.041
py	−2.91	0.092	100	−0.0176
4-mepy	−2.86	0.093	100	−0.0174
4-HOpy	−2.99	0.091	100	−0.0292
4-HCOpy	−2.53	0.111	100	−0.0152
prmd	−2.57	0.125	100	−0.04
taz	−2.48	0.118	100	−0.052
prdz	−2.91	0.126	100	−0.0062
tz	−2.20	0.219	100	−0.0094
CN^-	−8.59	0.165	76	−0.05
Bu^tNC	−2.29	0.319	76	0.038
PhNC	−2.04	0.362	76	0.032
CO	−1.51	0.633	78	0.055
PEt_3	−1.90	0.121	118	0.5258
$P(OEt)_3$	−0.59	0.368	109	0.6592
tht	−1.28	0.101	122	0.17
pc/4	−11.97	0.060	85	−0.0157
nx/2	−12.07	0.048	85	−0.0032

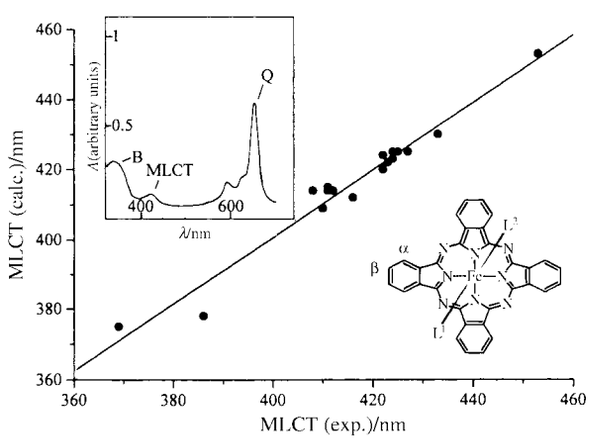

Fig. 1 Typical electronic spectrum of a (pc)FeL_2 complex (compound **2**) and correlation between the experimental and calculated MLCT band position in (pc)FeL^2 and (pc)FeL^1L^2 complexes [MLCT-(calc.) = (−8.18229 ± 0.73835) V_{MEP} + (−150.2302 ± 16.67371) V_b + (−0.10088 ± 0.10748)T + (414.89193 ± 13.52484); r^2 = 0.980; rms = 3.54 nm].

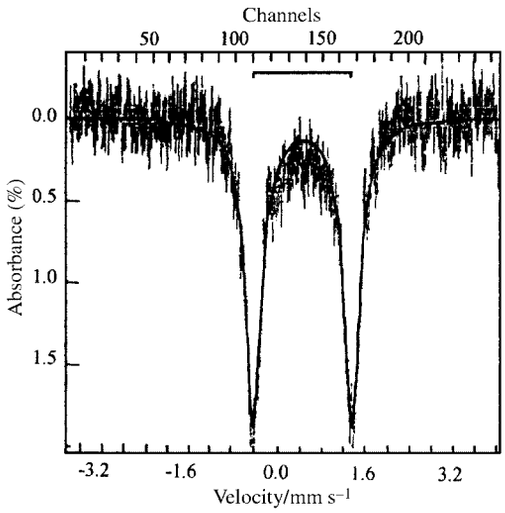

Fig. 2 Mössbauer spectrum of complex **9** at 293 K, referenced against sodium nitroprusside.

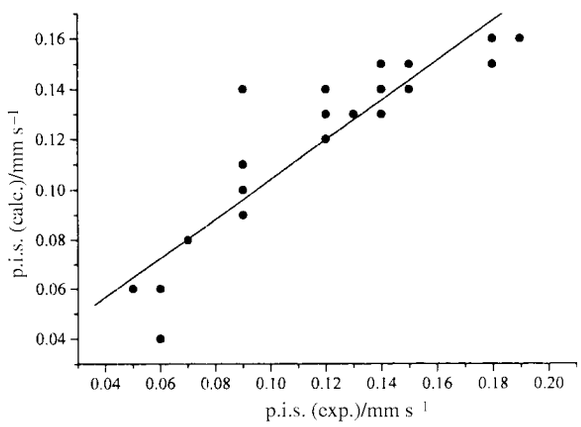

Fig. 3 Correlation between the experimental and calculated p.i.s. [p.i.s.(calc.) = (0.00839 ± 0.00162) V_{MEP} + (−0.18268 ± 0.03561) V_b + (0.000398973 ± 0.000297133)T + (0.13328 ± 0.03764); r^2 = 0.908; rms = 0.014 mm s^{-1}].

strong σ donor and a moderate π acceptor). On the other hand, the increase in the π-acceptor effect of a ligand leads to a decrease of $3d_\pi$ population on iron and thus a reduction of the shielding of the 4s electrons which reflects the increase of the electron density on iron nuclei and decrease in δ. In fact, δ for the $[Fe(pc)(RNC)_2]$ complexes (RNC is a weak σ donor and a strong π acceptor) is lower than that of $[Fe(pc)(BuNH_2)_2]$ ($BuNH_2$ is a strong σ donor and a weak π acceptor). The p.i.s. values obtained by fitting the experimental data for the $(pc)FeL_2$ and $(nx)_2FeL_2$ (nx = nioxime) complexes are in rough agreement with those reported in the literature. In general, as expected, strong σ donors and/or π acceptors have smaller p.i.s. values. Again, the steric effect of ligands must be brought into consideration since this changes the metal–ligand bond distance, and thus the σ-donor and π-acceptor interactions. Therefore it can be concluded that the p.i.s. values of ligands should decrease with increasing σ-donor and π-acceptor abilities and with decreasing steric effect of the ligands.

Taking all the above-mentioned into account, the final expression in evaluating the influence of the ligand's electronic and steric effects on the p.i.s. values becomes as in eqn. (3) where T,

$$\text{p.i.s.(calc.)} = a_0 + a_1 V_{MEP} + a_2 V_b + a_3 T \qquad (3)$$

V_{MEP} and V_b were derived as in eqn. (1) (Table 3). The obtained results are shown in Fig. 3. The final correlation coefficient is 0.908 for 29 ligands and the root-mean-square error is 0.014 mm s^{-1}. The relatively small correlation coefficient suggests that the point-charge model is valid only as a first approximation.[21d,f] Within the confines of the partial quadrupole splitting model, the quadrupole splitting for *trans*-$[FeA_2B_4]$ and *trans*-$[FeACB_4]$ complexes can be derived using eqns. (4) and (5), respectively;[21] where p.q.s. = $1/2e^2Q$[L] and [L] is p.f.g.

$$\Delta E_Q = 4\text{p.q.s.[A]} - 4\text{p.q.s.[B]} \qquad (4)$$

$$\Delta E_Q = 2\text{p.q.s.[A]} + 2\text{p.q.s.[C]} - 4\text{p.q.s.[B]} \qquad (5)$$

(partial field gradient). Application of eqns. (4) and (5) to the $(pc)FeL_2$, $(pc)FeL^1L^2$, and $(nx)_2FeL_2$ complexes, where B is pc/4 or nx/2, A is L or L^1, and C is L^2, leads to an estimation of the p.q.s values of the ligands of interest. When comparisons are possible, our p.q.s. values, fitted for $(pc)FeL_2$, $(pc)FeL^1L^2$ and $(nx)_2FeL_2$ complexes, are in a close agreement with the literature data.[21]

In general, the influence of electronic and steric effects of ligands on the p.q.s. values can arise from three contributions: (i) "valence" contribution, which arises from the σ and π interaction in the orbitals between the iron and the ligand coordinating atom (LCA), and leads to a change in the effective population on the orbitals of iron. For example, the σ donation of electron density from an axial ligand in the $(pc)FeL_2$ complexes changes the effective population of the $3d_{z^2}$ and $4p_z$ orbitals on the iron atom. The relationship between the σ-donor/π-acceptor properties of ligands and the p.q.s. values has been discussed in the literature, and the general expression is as in eqn. (6).[21a–g] (ii) "Lattice" contribution, q_{lat} which was

$$\text{p.q.s.} \approx \text{const.}\cdot(\sigma - \pi) \qquad (6)$$

originally included in expression (6), as follows:[21e] p.q.s. ≈ const.·(σ − π) − q_{lat}. This depends on the charge on the LCA and on the distance between the LCA and the iron atom, as in eqn. (7),[22] where Z_i is a point charge of the LCA, θ the

$$q_{lat} = \text{const.}\cdot Z_i(3\cos^2\theta - 1)r^3 \qquad (7)$$

angle from the z axis of the electric field gradient (EFG) and r the iron–LCA distance. This interaction leads to a change in q_{lat}. Usually, for low-spin iron(II) complexes, this kind of lattice contribution is small and can be ignored.[3–6,22] However, recent Density Functional Theory (DFT) calculations in a local density approximation (LDA) for $[Fe(oep)(PMe_3)_2]$ have shown that, at least in some cases, the lattice contribution can play a dominant role.[23] Taking into account the fact that, for ligands in the $(pc)FeL_2$ complexes, $\theta \approx 0$, 90 or 180° (from eqn. (7)), the "lattice" contribution from ligands to p.q.s. can be roughly proportional to $2Z_{LCA}/r^3$ for axial ligands or $-Z_{LCA}/r^3$ for the macrocycle, where Z_{LCA} is the charge on the LCA and r is the probe atom–LCA bond distance. (iii) "Steric" contribution of the axial ligand, on which the metal–ligand distance and, accordingly, the metal–ligand interaction depends. The relationship between the ligand's cone angle and p.q.s. parameters for phosphorus-containing ligands has been discussed recently.[21g] The "steric" contribution can play an important role in the case of axially co-ordinated square-planar conformationally inflexible macrocyclic complexes, such as $(pc)FeL_2$. Thus, in the case of pure σ-donor axial ligands such as alkylamines, an increase in the σ-donor property of the axial ligands should lead to a decrease in ΔE_Q, as can be seen from an analysis of eqn. (8) (from which the valence contribution to

$$q_{val} = (4/7)(1 - R)\langle r^{-3}\rangle_{3d}[n(d_{xy}) + n(d_{x^2-y^2}) - n_{z^2} - \tfrac{1}{2}(n(d_{xz}) + n(d_{yz})) + (4/5)(1 - R)\langle r^{-3}\rangle_{4p}[\tfrac{1}{2}(n(p_x) + n(p_y)) - n(p_z)] \qquad (8)$$

ΔE_Q can be derived);[22] where $\langle r^{-3}\rangle_{3d}$ and $\langle r^{-3}\rangle_{4p}$ are the radial parts of the 3d and 4p orbitals, respectively, of the iron atom, and n is an effective population on the atomic orbital designated in parentheses. However, despite the increase in the

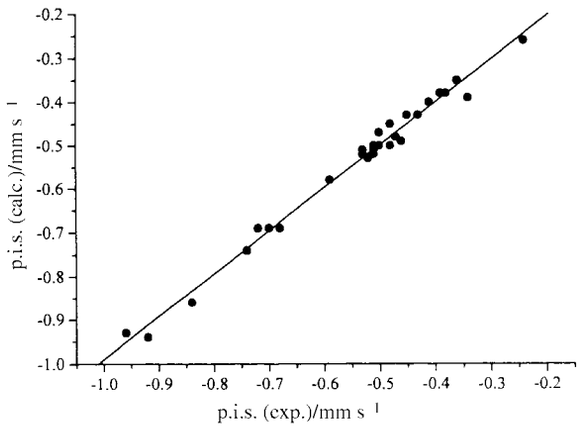

Fig. 4 Correlation between experimental and calculated p.q.s. [p.q.s.(calc.) = (0.03937 ± 0.0019) V_{MEP} + (−0.26685 ± 0.04726) V_b + (0.0054 ± 0.0003796) T + (−0.37811 ± 0.02956)C + (−0.91241 ± 0.04754); r^2 = 0.993; rms = 0.019 mm s^{-1}].

σ-donor ability on going from NH_3 to $PrNH_2$, pip and further to dabco, ΔE_Q increased from 1.79 to 2.89 mm s^{-1}. For σ-donor ligands with similar donor strength, such as $BuNH_2$, Bu^sNH_2, and Bu^tNH_2, ΔE_Q increased from 1.97 to 2.38 mm s^{-1} (Table 2). In these cases, the increase in the cone angle of the axial ligand probably induces an elongation of the axial Fe–N bond. This elongated bond would result in a decrease in the overlap between the lone pair orbital of the axial ligand and the $3d_{z^2}$ and $4p_z$ orbitals of iron, leading to an increase in ΔE_Q. Thus, one can conclude that the ligand p.q.s. values depend on the σ-donor and π-acceptor properties of the ligands, as well as their cone angle and LCA charge. The final expression for evaluating the influence of the electronic and steric factors of the ligands on the p.q.s. values becomes as in eqn. (9), where T,

$$\text{p.q.s.(calc)} = a_0 + a_1V_{MEP} + a_2V_b + a_3C + a_4T \quad (9)$$

V_{MEP} and V_b were derived as described for eqn. (1) and C is the "lattice" contribution of LCA (Table 3). The obtained results are shown in Fig. 4. The final correlation coefficient is 0.993 for 29 compounds with a root-mean-square error of 0.019 mm s^{-1}. Our correlation line combines different classes of ligands: alkyl- and aryl-amines, six- and five-membered heterocycles, isocyanides, carbon monoxide, sulfides, phosphines, and phosphites. Taking into account the fact that we used Mössbauer data from different sources, which sometimes differ by up to 0.05 mm s^{-1} for the same compound, our analysis of the ligand's p.q.s. values with a root-mean-square error of 0.019 mm s^{-1} looks satisfactory for the prediction of p.q.s., and thus ΔE_Q values, not only for the $(pc)FeL_2$ or $(pc)FeL^1L^2$ complexes (Table 2), but also for different inorganic and organometallic compounds. Any increase in the σ-donor effect of the ligand leads to a decrease in the p.q.s. values, which is in agreement with qualitative assumptions reported previously.[3,4a,5a,21] As can be concluded from the results of the above regression analysis, an increase in the steric effect of ligands leads to an increase in p.q.s. and thus axial ligands in the $(pc)FeL_2$ complexes shown in Table 2 result in increases in ΔE_Q, in accord with experimental observations. The predicted "lattice" ligands contribution to p.q.s. is also in good agreement with the recent calculations. That is, according to the LDA[23] and B3LYP[24] DFT calculations for a large number of $(mac)FeL_2$ and $(mac)FeL^1L^2$ complexes, where mac is a macrocycle ligand such as pc, tpp, oep, *etc.*, only phosphorus-containing axial ligands may have a relatively large contribution to q_{lat}, in good agreement with our regression analysis of p.q.s. According to the latter regression analysis, an increase in the ligand π-acceptor effect leads to a decrease in the p.q.s. value. This result is contrary to our argument, which can be concluded from an analysis of eqn. (8), that an increase in the π-acceptor ability of an axial ligand should increase the p.q.s. value. However, experimental data, particularly for the $(mac)FeL_2$ and $(mac)FeL^1L^2$ complexes, strongly suggest that ΔE_Q decreases with increasing ligand π-acceptor ability, and many authors have discussed this phenomenon qualitatively.[3,4b,5b,25]

Conclusion

In this work a series of bisaxially co-ordinated low-spin iron(II) phthalocyanine complexes ($(pc)FeL_2$) with different types of nitrogenous bases as axial ligands have been prepared and characterised by electronic, ^1H NMR and Mössbauer spectroscopies. The influences of electronic and steric effects of axial ligands on the Mössbauer quadrupole splitting (ΔE_Q), isomer shift (δ), NMR parameters, and the MLCT band position were discussed. Mössbauer partial quadrupole splitting (p.q.s.) and partial isomer shift (p.i.s.) parameters for different ligands have been estimated and rationalised with the overall data for the $(pc)FeL^1L^2$ and $(nx)_2FeL^1L^2$ complexes. A semi-empirical AM1 method and the cone angle concept were used to factorise the σ- and π-electronic and steric effects of the ligands. The obtained correlation coefficients, r^2 = 0.980 and 0.993 with small root-mean-square errors of 3.54 nm and 0.019 mm s^{-1} for the MLCT band position for the $(pc)FeL_2$ and $(pc)FeL^1L^2$ complexes and ligand p.q.s. parameters, respectively, make the proposed technique a simple and accurate tool for estimating the CT band position and p.q.s. values for a number of inorganic and organometallic compounds.

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