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A Study of the Co-ordination Behaviour of Various 2-Pyridyl-ketones. Part V.[1] The Interaction of Di-(2-pyridyl)ketone with Salts of Cobalt, Nickel and Iron

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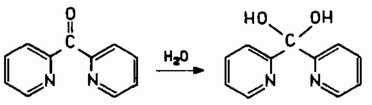
New compounds of cobalt(II), cobalt(III), iron(II) and iron(III) with di-(2-pyridyl)ketone (pyCOpy) are reported which in some cases constitute further examples of the metal promoted reaction of the ligand carbonyl group with water or alcohols. Under some circumstances it is difficult to prevent reaction of the carbonyl group whereas in other cases the group is very resistant to attack. A third group of systems exist in which the aquation or hemi-acetal formation is readily reversible.

The new compounds reported are characterised by elemental and spectroscopic analysis. In one case an authentic example of co-ordination via the carbonyl group is found and in another the ligand is present as the ketal pyC(OEt)₂py. The ligand field strength (Δ) of di-(2-pyridyl)ketone varies with the steric environment; in a complex such as $[Fe(pyCOpy)_2(NCS)_2]$*, which is shown to be cis, the value of Δ is comparable with that of 1,10-phenanthroline whereas it is considerably less in a compound such as* $[Co(pyCOpy)_2(pyC(OEt)(OH)py)](ClO_4)_2$.

Introduction

In recent years a number of authors have considered the co-ordination compounds formed by di-(2-pyridyl) ketone.[2] It has been argued that the ligand may co-ordinate *via* both pyridine nitrogen atoms (N,N co-ordination) or *via* one pyridine nitrogen and the carbonyl (N, O co-ordination).[3] An earlier claim to have demonstrated N,O co-ordination with copper(II)[3] has not been substantiated by later work[4] which provides good evidence that the disappearance of the ν(CO) vibration at 1688 cm^{-1} for the free base in some copper(II) complexes arises from aquation of the carbonyl group in the presence of the metal:



(1)

It was argued[4,5] that the driving force for a reaction such as (1) might arise from release of strain and steric interactions on changing the hybridisation of the central carbon atom from sp^2 to sp^3. Additional driving force may be supplied in some cases by the hydrated ligand functioning as a vicinal terdentate.[5] It is known that alcohols may be involved in such reactions[3,6] to afford co-ordinated hemi-acetals.[4] In this paper one better authenticated example of N,O co-ordination is presented.

The literature of di-(2-pyridyl)ketone complexes of first row transition metal ions is not yet complete. The generality of reactions such as (1) has not been completely investigated, the stereochemistry of bis di-(2-pyridyl)ketone complexes, $M(pyCOpy)_2X_2$ has been assumed by some authors to be *cis*, but this has not been confirmed. Also differing views have been expressed as to the possibility of co-ordinating three di-(2-pyridyl)ketone molecules to the same metal ion[5,6,7] and no information is available concerning ligand field parameters of the ligand. In this paper we present some new results concerning compounds of di-(2-pyridyl) ketone with cobalt(II), cobalt(III), iron(II and iron(III) in an attempt to deal with some of the problems listed above.

Experimental

Physical Measurements

Infra-red spectra were recorded for nujol mulls or KBr discs over the range 4000–250 cm^{-1} with a Perkin Elmer 457 instrument. The region 400–200 cm^{-1} was examined with a Perkin Elmer 225 instrument. Magnetic measurements were by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. Diffuse relectance spectra were recorded with a Unicam SP700 spectrophotometer incorporating the SP 735 diffuse reflectance unit. The Mössbauer spectra of the iron(II) and iron(III) complexes at room temperature were recorded using a ^{57}Co/Pd source and constant acceleration Mössbauer spectrometer which has been described elsewhere.[8] Conductivity measurements were made on $10^{-3}M$ solutions of the complexes with a Henelec bridge. Cobalt and iron were analysed by atomic absorption spectroscopy.

Preparations

Di-(2-pyridyl)ketone was obtained from Phase Separations Ltd. and used without further purification. Metal salts were commercial specimens of the highest available purity.

Mono(di-(2-pyridyl)ethoxymethanol)bis(di-(2-pyridyl)ketone)cobalt(II) perchlorate

Cobalt perchlorate hexahydrate (0.36 g, 1m*M*) was refluxed for 4 h in triethylorthoformate (50 ml) to remove water. The atmosphere of the reaction flask was changed to nitrogen and di-(2-pyridyl)ketone (0.55 g, 3m*M*) in triethylorthoformate (10 ml) was added to the solution. An orange solid formed and the reaction mixture was refluxed for a further 1 h. The product was filtered hot and washed with a little hot triethylorthoformate followed by ether. The sample was dried over P_4lO_{10} *in vacuo.* Found: C, 48.8; H, 3.60; N, 9.43. $C_{35}H_{30}Cl_2Co\,N_6O_{12}$ requires: C, 49.0; H, 3.50; N, 9.88%.

Dichloromono(di-(2-pyridyl)methoxymethanol) cobalt(II) methanol solvate

Anhydrous cobalt(II)chloride (0.26 g, 2m*M*) in 2,2′-dimethoxypropane (25 ml) was refluxed for 0.5 h after which di-(2-pyridyl)ketone (0.37 g, 2m*M*) in 2,2′-dimethoxypropane (10 ml) was added. The combined solution was refluxed for a further 1.5 h during which time a violet solid formed. The product was filtered hot and the compound was washed with 2,2′-dimethoxypropane and ether. Analysis of samples from different preparations showed that the complex crystallised with between 1 and 3 moles of methanol. Found (typically): C, 43.0; H, 3.42; Co, 15.2; N, 8.21. $C_{13.5}H_{18}Cl_2CoN_203.5$, *i.e.*, [Co(pyCopy · MeOH)Cl_2]1.5 MeOH requires: C, 42.5; H, 4.72; Co, 15.2; N, 7.34%; The C, H, N data were obtained after some delay whereas the cobalt analysis was carried out soon after the preparation.

Dibromomono(di-(2-pyridyl)ethoxymethanol) cobalt(II) and dibromomono(di-2-pyridyl)ketone) cobalt(II)

Di-(2-pyridyl)ketone (0.37 g, 2m*M*) in cold ethanol (25 ml) was added to an ethanolic (25 ml) solution of anhydrous cobalt(II) bromide (0.43 g, 2m*M*). The solution was refluxed for 1.5 h to afford a blue solid. Addition of petroleum ether to hot ethanolic solutions of the blue material afforded a green solid. Found (blue solid, [Co(pyCOpy · EtOH)Br_2]) C, 35.1; H, 3.00; N, 6.30. $C_{13}H_{14}Br_2CoN_2O_3$ requires C, 34.7; H, 3.10; N, 6.20%. Found (green solid, Co(pyCOpy)Br_2) C, 33.3; H, 2.10; Co, 13.7; N, 6.81. $C_{11}H_8Br_2CoN_2O$ requires C, 32.8; H, 1.99; Co, 13.7; N, 6.96%.

Complex of cobalt(III) with di-(2-pyridyl)ketone, [Co(OH)(pyCOpy · EtOH)$_2$](ClO$_4$)$_2$

Di-(2-pyridyl)ketone (0.55 g, 3m*M*) in ethanol (25 ml) was added to an ethanolic (25 ml) of cobalt(II) perchlorate hexahydrate (0.36 g, 1m*M*). The solution was heated under reflux for 2 min, then 20 vol. hydrogen peroxide (10 ml) was added and refluxing continued for 2 h. The pink product was filtered and washed with ethanol and ether. Found: C, 42.8; H, 3.85; Co, 8.22; $C_{26}H_{29}Cl_2CoN_4O_{13}$ requires: C, 42.4; H, 3.81; Co, 8.01%.

Dichlorobisdi-(2-pyridyl)ketone iron(II)

Di-(2-pyridyl)ketone (0.37 g, 2m*M*) in nitrogen saturated absolute ethanol (25 ml) was added to a solution of iron(II) chloride tetrahydrate (0.2 g, 1m*M*) and refluxed under nitrogen for 1.5 h. The blue product was filtered and washed well with ethanol and ether. Found: C, 52.9; H, 3.44; Cl, 13.5; Fe, 11.5; N, 11.0. Calculated for $C_{22}H_{16}Cl_2FeN_4O_2$: C, 53.3; H, 3.23; Cl, 14.3; Fe, 11.3; N, 11.3%.

Di-isothiocyanatobisdi-(2-pyridyl)ketoneiron(II)

Anhydrous iron(III) chloride (0.16 g, 1m*M*) in ethanol (25 ml) was mixed with potassium thiocyanate (1 g) in ethanol (25 ml) and the whole solution was filtered into di-(2-pyridyl)ketone (0.55 g, 3m*M*) in ethanol (25 ml). The resulting solution was refluxed for 2 h after which the dark red–brown complex was filtered and washed with ethanol and ether. Found: C, 52.8; H, 3.30; Fe, 9.42; N, 15.6. $C_{24}H_{16}FeN_6O_2S_2$ requires: C, 53.1; H, 2.96; Fe, 10.2; N, 15.5%.

Bis(di-(2-pyridyl)ethoxymethanol)mono(di-(2-pyridyl)ketone)iron(III) perchlorate hydrate

Di-(2-pyridyl)ketone (0.55 g, 3m*M*) in absolute ethanol (25 ml) was added to iron(III) perchlorate hexahydrate (0.46 g, 1m*M*) in absolute ethanol (25 ml) The resulting solution was refluxed for 1.5 h. The solution was cooled in the refrigerator to afford a yellowish white solid product which was filtered and washed with ethanol and ether. Found C, 43.9; H, 4.13; Fe, 5.96; N, 7.62: $C_{37}H_{38}Cl_3FeN_6O_{18}$ requires: C, 43.7; H, 3.74; Fe, 5.49; N, 8.26%.

Trichloromono(di-(2-pyridyl)ketone di-ethylacetal) iron(III)

Di-(2-pyridyl)ketone (0.55 g, 3m*M*) in absolute ethanol (25 ml) was added to anhydrous iron(III) chloride (0.16 g), 1m*M*) in absolute ethanol (25 ml). The resulting solution was refluxed for 1.5 h and then set aside in a refrigerator to afford a yellow solid which was filtered and washed with ethanol and ether. Found:

C, 42.2; H, 3.85; Fe, 13.6. $C_{15}H_{18}Cl_3FeN_2O_2$ requires: C, 42.8; H, 4.28; Fe, 13.3%.

Results

Relevant spectroscopic data for all complexes considered here is presented in Table I. Mössbauer data for the iron compounds are collected in Table II.

Discussion

Cobalt Compounds

The reaction of cobalt(II) perchlorate with di-(2-pyridyl)ketone under nitrogen affords an orange compound which we formulate as $[Co^{II}(pyCOpy)_2 \cdot (pyC(OEt)(OH)py)](ClO_4)_2$. The evidence may be briefly summarised. An effective magnetic moment of 5.30 B.M. confirms the dipositive oxidation state. of cobalt and further implies an octahedral geometry about the

TABLE I. Physical Data for Compounds Derived from Metal Salts and Di-(2-pyridyl)ketone.

Compound	μ_{eff} (BM)	Infra-red Absorption Bands (cm^{-1})				Diffuse Reflectance Spectrum (kK)	Λ_M ($10^{-3}M$)
		ν(CO)	ν(OH)	ν(py)	ν(MX)		
$[Co^{II}(pyCOpy)_2(pyCOpy \cdot EtOH)](ClO_4)_2$	5.30	1698s 1705sh	3500br	1590s 1605s	–	9.35 19.8 21.9	140
$[Co^{II}(pyCOpy \cdot MeOH)Cl_2]nMeOH$	4.95	–	3120br	1609s	249s 233s	7.9 14.9 17.8 19.3	32
$[Co^{II}(pyCOpy \cdot EtOH)Br_2]$	4.30	–			243s 229s	6.90 7.30 10.5 15.7sh 16.2 22.0	35
$[Co^{II}(pyCOpy)Br_2]$	4.23	1675s	–	1590s	268s 245s	7.30 10.0 15.6 16.9sh 18.0sh	35
$[Fe^{II}(pyCOpy)_2Cl_2]$	5.30	1680s	–	1590s	260s	16.0 24.5	30
$[Fe^{II}(pyCOpy)_2(NCS)_2]$	0	1680s	–	1590s	ν(NCS) 2090s 805s 480s	16.3 24.3 30.0	insol
$[Co^{III}(pyCOpy \cdot EtOH)_2(OH)](ClO_4)_2$	0	–	3585s 3500s 3200s 2800br	1610s	–	18.1 21.1 25.9 31.0	72[a]
$[Fe(pyCOpy \cdot EtOH)_2(pyCOpy)](ClO_4)_3 \cdot H_2O$	5.70	1530s	3500s 3400s 3000s (v.br.)	1618s 1602s		9.0 18.4 21.2	220
$[Fe(pyC(OEt)_2py)Cl_3]$	6.20	–	–	1605s	347s 326s 293s 283s	10.0 11.5 17.2 19.5	4.2

[a] Measured in DMF. All other values are for solutions in nitromethane.

TABLE II. Room Temperature Mössbauer Data for Iron Complexes of Di-(2-pyridyl)ketone.

Compound	δ mm sec^{-1} [a]	Δ mm sec^{-1}
$[Fe(pyCOpy)_2Cl_2]$	1.03	3.32
$[Fe(pyCOpy)_2(NCS)_2]$	0.41	0.22
$[Fe(pyCOpy)(pyC(OEt)(OH)py)_2](ClO_4)_3 \cdot H_2O$	~0.34	–
$[Fe(pyC(OEt)_2py)Cl_3]_n$	0.47	0.15

[a] Chemical isomer shift data are quoted relative to natural iron. Both δ and Δ are considered accurate to ±0.05 mm sec^{-1}.

cation. Both the infra-red spectrum (ν_3 at 1100 cm^{-1}) and the molar conductivity of the complex in nitromethane confirm the ionic nature of the perchlorate groups. The infra-red spectrum also supports the presence of an OH group and shows that at least one carbonyl function has not been converted to a hemiacetal. However the presence of pyridine ring vibrations at 1590 and 1605 cm^{-1} suggests, following the reasoning of Feller and Robson[4] with which we concur, the presence of both di-(2-pyridyl)ketone and di-(2-pyridyl) ethoxymethanol as ligands. The elemental analysis allows the incorporation of only one molecule of ethanol and the given formulation follows. We have thus been successful in co-ordinating three molecules derived from di-(2-pyridyl)ketone to the same metal atom, however attempts to remove ethanol to give a tris di-(2-pyridyl)ketone complex failed.

The electronic spectrum of the compound (Table I) is in agreement with octahedral stereochemistry. A self consistent assignment of the bands as $\nu_1(^4T_{2g} \leftarrow {}^4T_{1g})$ at 9350 cm^{-1}, $\nu_2(^4A_{2g} \leftarrow {}^4T_{1g}$; weak two electron transition) at 19,800 cm^{-1} and $\nu_3(^4T_{1g} \leftarrow {}^4T_{1g})$ at 21,900 cm^{-1} is obtained using values of the ligand field splitting parameter (Δ) of 10,630 cm^{-1} and of the reduced Racah parameter (B′) of 925 cm^{-1}. These numbers refer to a mixed ligand environment and do not afford direct information concerning Δ for di-(2-pyridyl) ketone.

A cobalt(III) complex was deliberately prepared by the use of hydrogen peroxide as oxidant. Analytical data and infra-red spectroscopy confirm that the ligands present are di-(2-pyridyl)ethoxymethanol. The OH stretching region of the spectrum is of interest. A band at 3585 cm^{-1} could imply a hydroxo-group, probably bridging,[9] whereas the very broad bands at 3200–2800 cm^{-1} indicate the presence of hydrogen bonded hydroxo-groups. No real evidence of co-ordinated oxyanions is available consequently possible structures are (a) monomeric with one terdentate di-(2-pyridyl) ethoxymethanol molecule or (b) a di-μ-hydroxo-complex with bidentate organic ligands. The pink colour is consistent with an "octahedral" N_4O_2 environment and the complexity of the electronic spectrum is in line with the low symmetry environment envisaged in both (a) and (b). However a note of doubt is struck by the surprisingly low value of the molar conductivity in DMF.

We have also prepared three complexes of cobalt(II) chloride and bromide in which the metal:ketone ratio is 1:1. We briefly comment upon these materials. $[Co(pyC(OMe)(OH)py)Cl_2]nMeOH$ (n = 1,2 or 3) and $[Co(pyC(OEt)(OH)py)Br_2]$ clearly (i.r. and analysis) contain co-ordinated hemiacetals, however the available data suggest a polymeric "octahedral" structures for the chloro-complex whereas the bromo compound is more clearly tetrahedral. Specifically the high (4.95 B.M.) effective magnetic moment and the location of cobalt–chlorine stretching frequencies lower than 250 cm^{-1} are inconsistent with a tetrahedral environment for the chloro-complex and there are now many precedents where cobalt(II) ions in a very distorted six co-ordinate environment can give complex and intense electronic spectral bands – as in this case. The bromo-complex has a much lower magnetic moment and also shows cobalt–bromine stretching frequencies above 200 cm^{-1}. The tetrahedral environment is most clearly indicated by the electronic spectrum where the band at 16.2 kK has the characteristic fine structure.[10] Removal of ethanol to afford $[Co(pyCOpy)Br_2]$ leaves the tetrahedral stereochemistry intact but, as judged from increased cobalt–bromine stretching frequencies, increases the effective positive charge on the metal ion.

In view of the considerable amount of previous work with nickel(II) complexes of this ligands[5,7,11] we reported no further derivatives.

Iron complexes

The complex $[Fe(pyCOpy)_2Cl_2]$ has been reported by Feller and Robson[4] and the anaytical, electronic spectroscopic and magnetic data are in good agreement with the Australian work. It is interesting to note that we took no precautions to exclude ethanol or water from our preparative procedure, yet no aquation or hemi-acetal formation occurred as shown by ν(CO) at 1680 cm^{-1} and ν(CN)(pyridyl) at 1590 cm^{-1} together with the absence of bands attributable to OH groups. It is possible to assign a strong band at 260 cm^{-1} with a shoulder at 258 cm^{-1} as ν(FeCl), but this small splitting hardly constitutes strong evidence for *cis*-stereochemistry. The electronic spectrum is dominated by an intense band at 16.0 kK which certainly cannot be a d$\leftrightarrow$d transition for high spin iron(II). The band is most likely of charge transfer origin – a possible cause may be slight contamination with iron(III), but if this is so the amounts involved are insufficient to affect the analysis or to be detectable by Mössbauer spectroscopy. The Mössbauer parameters are given in Table II and are typical of high spin iron(II). The room temperature values of the chemical isomer shift (δ) and quadrupole splitting (Δ) for [Fe(phen)$_2$Cl$_2$] (phen = 1,10-phenanthroline), a complex of established *cis*-stereochemistry, are remarkably similar to those reported[12] in Table II for [Fe(pyCOpy)$_2$Cl$_2$], *viz.*: $\delta = 1.06$ mm sec^{-1}, $\Delta = 3.28$ mm sec^{-1}, also $\mu_{eff} = 5.27$ B.M. There is a strong implication that iron(II) is in a very similar electronic environment in the two complexes.

We attempted to prepare an iron(III) complex containing thiocyanato-ligands but instead our method afforded a diamagnetic iron(II) compound, [Fe(pyCOpy)$_2$(NCS)$_2$], which was insufficiently soluble for conductivity measurements. The data of Table I establish that the di-(2-pyridyl)ketone ligands are intact and also that isothiocyanato-groups are present.[13] Two plausible formulations are available: (a) molecular [Fe(pyCOpy)$_2$(NCS)$_2$] and (b) ionic [Fe(pyCOpy)$_3$][Fe(pyCOpy)(NCS)$_4$]. The Mössbauer parameters (Table II) confirm the presence of low spin iron(II) but also imply the presence of only one iron site, thus our preference is for (a). A single ν(CN) (thiocyanate) vibration is seen which might imply *trans*-stereochemistry. However an early claim[14] to have prepared *cis*- and *trans*-[Fe(phen)$_2$(CN)$_2$] (i.r. evidence) was not substantiated by Mössbauer data[15] which showed both specimens to be *cis*. The complex *cis*-[Fe(phen)$_2$(NCS)$_2$] has been of exceptional interest[16] because it shows anomalous magnetic behaviour being paramagnetic ($^5T_{2g}$ ground state) at room temperature but diamagnetic ($^1A_{1g}$ ground state) at liquid nitrogen temperature. Our complex is diamagnetic at room temperature, but we may compare the values of δ and Δ with those for low spin [Fe(phen)$_2$(NCS)$_2$][17], *viz.*: $\delta = 0.37$ mm sec^{-1}, $\Delta = 0.34$ mm sec^{-1}. Normally, for low spin iron(II), Δ for *trans* FeA$_4$B$_2$[15] is roughly twice the value for *cis* FeA$_4$B$_2$, thus with Δ as small as 0.22 mm sec^{-1} there is a strong implication that [Fe(pyCOpy)$_2$(NCS)$_2$] has *cis*-stereochemistry.

Attempts to synthesise a complex of iron(II) perchlorate gave products containing both iron(II) and iron(III) as demonstrated by Mössbauer spectroscopy. Reaction of iron(III) perchlorate with di-(2-pyridyl)ketone did however afford a compound of some interest. The analysis, the presence of ν(OH) and the position of ν(CN)(pyridyl) at 1618 cm^{-1} require the presence of co-ordinated hemi-acetal ligands and a formulation of [Fe(pyCOpy)(pyC(OEt)(OH)py)$_2$](ClO$_4$)$_3 \cdot$H$_2$O meets the analytical requirements and is consistent with the conductivity (1:3 electrolyte). However there is no free carbonyl absorption at 1690 cm^{-1}, instead a band not previously observed in the spectrum of a di-(2-pyridyl)ketone complex is seen at 1530 cm^{-1}. The only reasonable assignment for this vibrational mode is ν(CO) for a molecule of di-(2-pyridyl)ketone which is N,O co-ordinated. We note that the downward shift of ν(CO) (158 cm^{-1}) is very comparable to that observed for 2-benzoylpyridine when co-ordinated to tripositive metal ions ($\sim$145 cm^{-1}).[6] The quality of the room temperature Mössbauer spectrum was poor, however from the value of δ (0.34 mm sec^{-1}) and the effective magnetic moment of 5.70 B.M. confirmation of high spin iron(III) is obtained. The electronic spectrum consists of a series of weak bands which probably arise from spin forbidden transitions from the $^6A_1$ state in a distorted octahedral environment.

Ferric chloride reacts with di-(2-pyridyl)ketone in ethanol to give a yellow complex in which the nature of the co-ordinated ligand is of interest. The i.r. spectrum shows no evidence for OH, also ν(CO) has vanished. The magnetic moment clearly indicates high spin iron(III) and the compound is a non-electrolyte in nitromethane. Analysis indicates the stoichiometry FeCl$_3 \cdot$(pyCOpy)$\cdot$Et$_2$O. It is hardly probable that diethylether is present, hence the most probable explanation is that a co-ordinated acetal is present, [Fe(pyC(OEt)$_2$py)Cl$_3$]$_n$. The far infra-red spectrum shows at least four bands assignable as ν(FeCl), hence a five co-ordinate monomeric structure or a six co-ordinate structure with a terdentate ketal lignad seem improbable whereas a dimeric structure with chloro-bridges is plausible with the higher frequency bands at 347 and 326 cm^{-1} arising from terminal Fe–Cl bonds and those at 293 and 283 cm^{-1} from the bridge bonds. The Mössbauer parameters are reasonably typical for a high spin iron(III) complex.

General comment

The results of this investigation have provided further examples of the metal promoted reaction of the carbonyl group of di-(2-pyridyl)ketone. The mechanism of the reaction remains unknown and the driving force and influence of experimental conditions remain matters for some speculation. The pH of the preparative medium may be a factor since hemiacetal and acetal formation is often acid catalysed and indeed the use of Lewis acid catalysts, *e.g.* FeCl$_3$, to promote ketal formation is known.[18] Experimentally we may now define three situations: (a) reactions with metal nitrates and perchlorates where, with the exception of copper(II), it seems impossible to prevent the reaction of at least one co-ordinated ligand, (b) compounds of the type *cis*-M(pyCOpy)$_2$X$_2$ where the co-ordinated ligand is very resistant to reaction, and (c) examples, mainly from copper(II) chemistry but including for example Co(pyCOpy)Br$_2$, where hemi-acetal formation is readily reversible.

Molecular models suggest that inter-ligand contacts are likely to become a problem in a tris-di(2--pyridyl)ketone complex if all ligands are to be planar. The situation could be relieved by some degree of non planarity for some di-(2-pyridyl)ketone molecules and by conversion of the ketonic (sp^2) carbon atom to an sp^3 situation in other molecules. The degree of planarity of the ligand will influence conjugation within the base and also the π acceptor capacity of the ligand, thus planarity and π acceptor capacity are likely to be a maximum in complexes such as [Co(pyCOpy)Br_2], [Fe$(pyCOpy)_2Cl_2$] and [Fe$(pyCOpy)_2(NCS)_2$] where no obvious steric problems arise, indeed we may regard di-(2-pyridyl)ketone and 1,10-phenanthroline as ligands procuding fairly similar electronic environments for iron(II) in similar *cis*-bis-complexes.

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