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Steric Effects in Pyrrole-based Mixed Complex Systems

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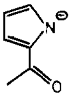
New systems of the type M(pyrenNR$_2$)Br, M(pyrtn NR$_2$)Br (M = Cu, Ni), M(pyr)(pyrenNR$_2$) (M = Cu, Ni), Cu(pyr)(pyrtnNR$_2$) (where Hpyr is pyrrole-2-aldehyde, pyrenNR$_2$ is Schiff base of pyr and NR$_2$CH$_2$CH$_2$NH$_2$ and pyrtnNR$_2$ is Schiff base of pyr and NR$_2$CH$_2$CH$_2$CH$_2$NH$_2$) are reported. The first two systems are shown to have planar geometry in which pyrenNR$_2$ and pyrtnNR$_2$ act as tridentate ligands. On the basis of magnetic, spectral and X-ray powder diffraction studies on pure crystals and on solid solutions of nickel(II) and copper(II) species, it is concluded that M(pyr)(pyren NR$_2$) has a 4-coordinate grossly planar geometry in which the NR$_2$ group of pyrenNR$_2$ fails to occupy a coordination position due to steric reasons. Models demonstrate that this steric difficulty should considerably decrease on replacement of pyrenNR$_2$ by pyrtnNR$_2$. Indeed the species Cu(pyr)(pyrtnNR$_2$) have electronic spectra strongly suggestive of pentacoordination.

Introduction

In previous works[1–9] from this laboratory the stereochemistry of metal(II) complexes of composition MLL′ (L = bidentate and L′ = tridentate) were reported. The structural situations met so far are: monomeric MLL′ with[3–5, 7–9] square pyramidal M, dimeric M$_2$L$_2$L′$_2$ with[1,2,6] octahedral or square pyramidal M. Interesting cases of solution equilibria have been thermodynamically characterized[7–9]. In the present work we report, among other things, the new situation where a monomeric MLL′ is unable to achieve pentacoordination due to steric crowding. It is also shown how this inability is readily removed by a minor change in the structure of L′. The pyrrole based ligand systems concerning us here are I and II. The general abbreviation for the systems of the type II will be T. The following specific abbreviations will also be used: I = pyr; II (n = 2) = pyrenNR$_2$; II (n = 3) = pyrtnNR$_2$.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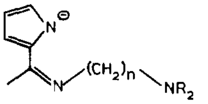


II

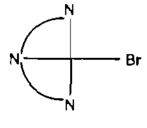
Results and Discussion

System MTBr

Both copper(II) and nickel(II) species of this type are readily obtained as dark coloured shining crystals by the reaction

$$MBr_4^{2-} + T \rightarrow MTBr + 3Br^-$$

carried out in dry tetrahydrofuran. Characterization data are set out in Table I. Results of physical measurements are displayed in Table II. NiTBr is diamagnetic while CuTBr has the normal magnetic moment of ~ 1.8 BM. Electrical conductivity data show that the complexes remain mostly undissociated in nitromethane solution. The observed results (Table II) suggest the planar structure III. Analogous systems derived from other tridentate systems are reported in literature[4, 10–14]. The important point to note here is that *both the ligand systems pyrenNR$_2$ and pyrtnNR$_2$ act in the tridentate fashion.*



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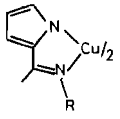

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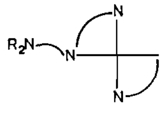


V

System Cu(pyr)(pyrenNR$_2$)

The system IV is readily obtained[15] by reacting I with RNH$_2$ in presence of copper(II) salts in aqueous medium. However when R$_2$NCH$_2$CH$_2$NH$_2$ is used as the primary amine, the complex coresponding to IV is *not* obtained. Instead green crystals of composition Cu(pyr)(pyrenNR$_2$) result. The same substance is also obtained by reacting Cu(pyr)$_2$[16] with one mol of R$_2$NCH$_2$CH$_2$NH$_2$ in boiling toulene. Characterization data for Cu(pyr)(pyrenNR$_2$) is set out in Table I. Cu (pyr)$_2$ shows the C=O stretch at 1650 cm^{-1} while CuTBr has the C=N stretch at ~ 1600 cm^{-1}. As expected the mixed ligand complexes show both C=O and C=N stretches (Table III). They have normal magnetic moments (Table III). Cu(pyr)(pyrenNEt$_2$) was found to be monomolecular in freezing benzene (Mol. Wt., Found 362, calcd., 350). The complexes could be either

TABLE I. Characterization Data.

Compound	Mp, °C[a]	%C		%H		%N		%M[b]	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cu(pyrenNEt$_2$)Br	127–128	39.34	39.50	5.41	5.56	12.56	12.30	18.91	18.77
Cu(pyrenNMe$_2$)Br	150–151	37.32	37.35	5.01	5.12	13.11	12.80	19.74	19.59
Ni(pyrenNMe$_2$)Br	216–217	35.67	35.22	4.66	4.31	13.92	13.80	19.37	19.50
Ni(pyrenNEt$_2$)Br	141–142	39.92	39.73	5.49	5.58	12.74	12.70	17.72	17.85
Ni(pyrenNHEt)Br	193–194	33.04	32.86	4.85	4.44	14.44	14.13	–	–
Cu(pyr)(pyrenNMe$_2$)	157–158	52.24	52.36	5.64	6.00	17.41	17.30	19.74	19.79
Cu(pyr)(pyrenNEt$_2$)	112–113	54.92	54.99	6.34	6.53	16.01	15.97	18.16	17.95
Ni(pyr)(pyrenNMe$_2$)	189–190	53.00	53.02	5.72	5.80	17.73	17.60	18.51	18.50
Cu(pyr)(pyrtnNMe$_2$)	180–181	53.64	53.75	6.00	5.84	16.68	16.88	18.92	18.97
Cu(pyr)(pyrtnNEt$_2$)	113–114	56.10	56.35	6.65	6.75	15.39	15.53	17.46	17.46

[a] All melting points are uncorrected. [b] Copper was estimated as CuSCN and nickel as dimethylglyoximate.

TABLE II. Conductivity, Magnetic Moment and Spectroscopic Data for MTBr.

Compound	Λ[a] (ohm^{-1} cm^2 mol^{-1})	μ_{eff} of Solid (BM)	Electronic Spectra[b]		C=N Stretch (cm^{-1})[c]
			Nujol mull	Toluene	
Cu(pyrenNEt$_2$)Br	15.2	1.80	620, 520sh, 410	650(168) 500sh(153)	1590
Cu(pyrtnNMe$_2$)Br	33.6	1.84	650, 530sh, 415	655(135)	1610
Ni(pyrenNMe$_2$)Br	14.9	Diamagnetic	620sh, 425	580sh(178)	1585
Ni(pyrenNEt$_2$)Br	18.9	Diamagnetic	620sh, 410	580sh(166)	1590
Ni(pyrenNHEt)Br[d]	–	Diamagnetic	–	–	1600

[a] Conductivity measurements were done in ~ 10^{-3} M nitromethane solution at 311° K. [b] Band maxima are in nm; figures in parentheses refer to extinction coefficients in l mol^{-1} cm^{-1}; sh is shoulder. [c] Measurements were made in KBr disc or in nujol mull. [d] A band at 3240 cm^{-1} is assigned as N–H stretch.

TABLE III. Magnetic Moment and Spectroscopic Data of M(pyr)T.

Compound	μ_{eff} of Solids (BM)	Electronic Spectra[a]		Infrared Frequencies[b]	
		Nujol mull	Benzene	C=O	C=N
Cu(pyr)(pyrenNMe$_2$)	1.88	580	620(186)	1615	1595
Cu(pyr)(pyrenNEt$_2$)	1.88	590	640(205)	1613	1598
Ni(pyr)(pyrenNMe$_2$)	Diamagnetic	415sh	410sh(176)	1640	1585
Cu(pyr)(pyrenNHEt)[c]	–	590	610(157)	Broad band at 1590	
Cu(pyr)(pyrtnNMe$_2$)	1.88	565	630(134) 790(105)	1610	1590
Cu(pyr)(pyrtnNEt$_2$)	1.98	625 800	640(123) 790(108)	1605	1595

[a] Band maxima are in nm; figures in parentheses refer to extinction coefficients in l mol^{-1} cm^{-1}. [b] Infrared stretching frequencies were measured in KBr disc or in nujol mull. [c] NH stretch at 3210 cm^{-1}.

pentacoordinated belonging to the class[7] M(bidentate) (tridentate) with all potential donor sites bound to the metal or tetracoordinated and planar with bidentate pyrenNR$_2$ as in V (NR$_2$ group is not coordinated to the metal).

Ligand field spectra throw some light on this problem. Usually pentacoordinated copper(II) species give rise to two bands in the visible region[17, 18]. Cu(pyr)(pyrenNR$_2$) shows only one broad band at ~600 nm (Table III, Fig. 1). The complex Cu(pyr)$_2$ having the

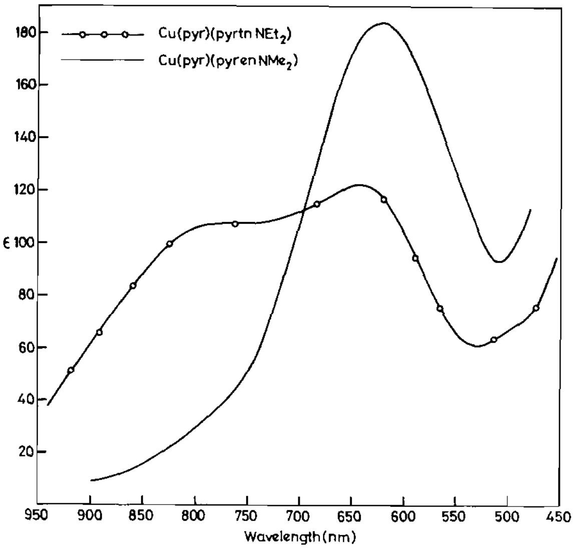


Figure 1. Ligand field spectra of the complexes. Cu(pyr)(pyrtn NEt$_2$) -O-O-O-, Cu(pyr)(pyrenNMe$_2$) ——, in benzene.

CuN_2O_2 chromophore shows a single broad ligand field transition centred at 650 nm. On the other hand IV with CuN_4 coordination sphere shows[15] the corresponding transition around 550 nm. The structural type V has CuN_3O coordination sphere and may be expected to give rise to a ligand field band in the intermediate region *viz.*, 650–550 nm. This is in line with experimental observation.

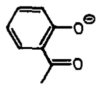
Mixed Crystals

More definitive evidence in favour of structure V is obtained from studies on mixed crystals of Cu(pyr)(pyrenNMe$_2$) and Ni(pyr)(pyrenNMe$_2$). The pure nickel(II) complex is brown and diamagnetic with an electronic band at 410 nm. Obviously it belongs to the structural type V.

X-Ray powder patterns were taken on the pure copper(II) and nickel(II) complexes. These are *not* isomorphous with each other (Table IV). However mixed crystals of the two complexes containing more than 50% Cu(pyr)(pyrenNMe$_2$) could be readily grown from benzene. These mixed crystals (Table IV) (i) are isomorphous with pure Cu(pyr)(pyrenNMe$_2$), (ii) have all the nickel(II) in diamagnetic state, while copper(II) has normal magnetic moment, (iii) have ligand field spectra which can be qualitatively analysed as the superpositions of the spectra Cu(pyr)(pyren NMe$_2$) and Ni(pyr)(pyrenNMe$_2$). In view of observation (ii), it is concluded that nickel(II) in the mixed crystals is in a planar environment of type V. Consequently copper(II) also has the same environment in the mixed crystal. In light of the observation (i), this means that the pure Cu(pyr)(pyrenNMe$_2$) also has copper(II) in the planar environment V.

Steric Effects

It is firmly established[4,5] that Cu(sal)(salenNR$_2$) (VI, sal; VII, salenNR$_2$) has the square pyramidal structure VIII.



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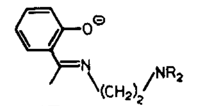

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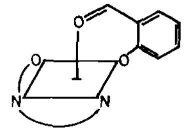
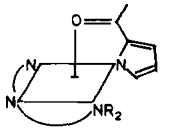


VIII

In view of this and in view of the observation that in MTBr pyrenNR$_2$ *is* tridentate, it is pertinent to examine why pyrenNR$_2$ fails to use NR$_2$ coordination in M(pyr)(pyrenNR$_2$). We strongly suspect that the phenomenon is of steric origin. Like salenNR$_2$ in VIII and other structures[19], pyrenNR$_2$ in its tridentate mode will be able to span only in the meridional fashion due to the short length of the –(CH$_2$)$_2$– chain. Models show that this brings the bidentate pyr moiety unfavourably close to the methyl groups of NMe$_2$ in pyrenNMe$_2$ in the *hypothetical* square pyramidal structure IX.



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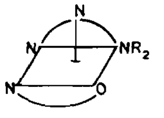

X

We strongly suspect that this steric hindrance leads to the delinking of NMe$_2$ from the metal atom. In VIII, the benzene ring of sal is situated one bond (O–C) away from the corner of the basal plane and also the chelate ring is six-membered. Models clearly demonstrate that steric interaction between sal and NR$_2$ is virtually absent.

If the above thesis regarding the steric effect in M(pyr)(pyrenNR$_2$) is correct, the complexes Cu(pyr)

TABLE IV. Selected d Spacings (Å).[a]

Ni(pyr)(pyrenNMe$_2$):	8.43, 6.92, 5.72, 5.47, 5.25, 4.63, 4.27, 4.21
Cu(pyr)(pyrenNMe$_2$):	8.84, 8.35, 7.03, 6.03, 5.16, 4.98, 4.42, 4.26
Mixed Crystal[b,c]:	8.82, 8.19, 7.03, 6.03, 5.22, 5.04, 4.42, 4.29

[a] The first eight reflections with 2Θ in the range 10–21° are reported. [b] Contains 56% copper complex and 44% nickel complex. [c] The magnetic moment of copper is found to be 1.95 ± 0.1 BM; nickel is diamagnetic.

(pyrtnNR$_2$) with a more flexible –(CH$_2$)$_3$– chain may be pentacoordinated. In this the potentially tridentate ligand can span facially. Models show that the configuration X is free from steric strain.

System Cu(pyr)(pyrtnNR$_2$)

With the above ideas in mind these complexes were synthesised by using methods analogous to those used for Cu(pyr)(pyrenNR$_2$). The complex Cu(pyr)(pyrtn NEt$_2$) was found to be monomolecular in freezing benzene (Mol. Wt., Found, 369; calcd, 364). They have normal magnetic moments (Table III). The electronic spectra of these complexes in benzene solution are quite different from those of Cu(pyr)(pyrenNR$_2$) with two distinct bands in the visible region (Fig. 1). The spectra strongly suggest pentacoordination. Interestingly, the spectrum of Cu(pyr)(pyrtnNMe$_2$) in the *solid state* (one band at 565 nm) is very different from that in solution but is closely akin to the spectrum of Cu(pyr)(pyrenNR$_2$) (Table III). The former complex thus provides an important link being planar in the solid state and pentacoordinated in solution.

Experimental

Preparation of the Compounds

Pyrrole-2-aldehyde was synthesised[20] from pyrrole. The appropriate amine (0.01 mol) and pyrrole-2-aldehyde (0.01 mol) were taken in 20 ml ethanol and refluxed for 0.5 hr. Alcohol was then stripped using a rotary evaporator. The resulting Schiff base (brown liquid) was used without further purification.

MTBr

The Schiff base (0.01 mol) was taken in 40 ml dry tetrahydrofuran. To this was added potassium t-butoxide (0.01 mol) followed by (Et$_4$N)$_2$MBr$_4$ (0.01 mol). The mixture was magnetically stirred for about 6 hr. During this period the solution became dark brown (M = Ni) or dark green (M = Cu). This was filtered and the residue was extracted several times with toluene. The toluene extract on concentrating gave dark coloured crystals. These were recrystallised form toluene. The yield was 50%.

Cu(pyr)(pyrenNR$_2$)

(i) Excess of the appropriate amine was added to 0.02 mol of pyrrole-2-aldehyde and 0.01 mol of CuSO$_4$·5H$_2$O dissolved in 50 ml water. The solution was heated on a steam bath and was then cooled. About 2 ml of 5% NaOH solution was added. In the case of *Cu(pyr)(pyrenNMe$_2$)* the precipitated material was filtered and then extracted with ethanol–dichloromethane mixture. The extract was concentrated and cooled. Dark green crystals thus obtained were recrystallised from dichloromethane. In the case of *Cu (pyr)(pyrenNEt$_2$)*, a green gummy substance deposited. The aqueous portion was removed by decantation. The residue was dissolved in benzene and dried over anhydrous sodium sulphate. The solution was then concentrated and hexane was added. A gum separated which on standing for several days in air slowly transformed into microcrystals of the required complex. They were collected by filtration and washed with hexane. The yield was 35%.

(ii) 0.02 mol of Cu(pyr)$_2$[16] and 0.02 mol of the appropriate amine were taken in 40 ml toluene and the mixture was heated to reflux for 1 hr. This was filtered and the volume of the filtrate was reduced to 10 ml. 10 ml of hexane was added. Green crystals separated on cooling. These were collected and recrystallised from toluene–hexane mixture.

Cu(pyr)(pyrtnNR$_2$)

These were prepared by procedures similar to those used for Cu(pyr)(pyrenNR$_2$).

Ni(pyr)(pyrenNMe$_2$)

A nonaqueous chelation reaction [pyrrole-2-aldehyde (0.01 mol), pyrenNMe$_2$ (0.01 mol), potassium t-butoxide (0.02 mol) and (Et$_4$N)$_2$NiBr$_4$ (0.01 mol] in tetrahydrofuran using a procedure entirely analogous to that used for MTBr gave dark brown crystals of composition Ni(pyr)(pyrenNMe$_2$). The yield was 50%.

Physical Measurements

Magnetic moments were measured using a sensitive Gouy balance described elsewhere[21]. Infrared spectra were recorded on a Perkin–Elmer 521 recording spectrophotometer. Molecular weight was determined cryoscopically in purified dry benzene[22]. Electronic spectra were studied on a Cary Model 14 recording spectrophotometer. Electrical conductivity measurements were done in nitromethane solution using Systronics (India) conductivity bridge. Powder pattern data were collected on a GE XRD-6 diffractometer with CuKα radiation.

Acknowledgments

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