An Electron Spin Resonance Study on the Interactions between Bis(pentane-2,4-dionato)copper(II) and Some Heterocycles. Part 2.[1] The 1 : 1 Adducts with Aza-aromatic Compounds and Azacyclohexanes

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E.s.r. spectra of a series of $Cu(acac)_2$ adducts of aza-aromatic compounds and azacyclohexanes (L) were measured. The 1 : 1 adduct $Cu(acac)_2L$ is formed almost exclusively in chloroform solution, L occupying an apical site. Their $g_\parallel$ and $|A_\parallel|$ values were determined in order to investigate the steric and electronic effects on co-ordination. When the frontal steric hindrance of the base is not large, the $|A_\parallel|$ values of $Cu(acac)_2L$ are linearly related to the pK_a values of L. Since the nitrogen atoms in 2,6-dimethylpyridine, 2- and 8-methylquinoline, acridine, and *N*-methylazacyclohexanes have considerable frontal steric hindrance, remarkable deviations from the straight line are observed for these compounds. The presence of two 1 : 1 adducts is shown for *N*-methylmorpholine, the *O*-adduct being more favourable than the *N*-adduct because of steric hindrance.

SEVERAL investigations have been reported on the co-ordination of bis(β-diketonato)copper(II) with nitrogen heterocycles.[2] However, only a few papers on the steric effects of substituents on co-ordination have been published.[3,4] We have reported steric effects on co-ordination of some five- and six-membered oxygen heterocycles toward bis(pentane-2,4-dionato)copper(II).[1] The co-ordination of Lewis bases to $Cu(acac)_2$ is shown to be affected by the environment around the donor atom. The investigation is now extended to co-ordination to $Cu(acac)_2$ of six-membered aza-aromatic and saturated heterocycles. Several papers on the quinoline adduct of bis(β-diketonato)copper(II) have been reported.[5-7] The chemistry of co-ordination of quinoline analogues to $Cu(acac)_2$ has not been studied systematically, however. On the other hand, the co-ordination of saturated six-membered nitrogen heterocycles to metal β-diketonato-chelates has been studied by ^1H n.m.r.,[8] ^{13}C n.m.r.,[9] e.s.r.,[10] and thermodynamic measurements.[11] The results showed that the dative bond formation is affected by the lone-pair orientation in saturated six-membered heterocycles containing nitrogen and/or oxygen.[8,9] In this paper, we report an e.s.r. study of the co-ordination of nitrogen heterocycles to $Cu(acac)_2$, with a discussion of the steric effects around the basic centre.

RESULTS AND DISCUSSION

Results are shown in Table 1. The co-ordination of a nitrogen base to $Cu(acac)_2$ occurs usually at an apical site of the chelate.[2] Thus, it has been shown by *X*-ray analysis that $Cu(acac)_2$(quinoline) has a structure in which the two pentane-2,4-dionato-ligands occupy four basal sites and the neutral quinoline ligand an apical site.[7] In the case of crystalline $Cu(acac)_2$(4-aminopyridine), a square pyramidal structure with the neutral ligand occupying the basal position has been demonstrated.[12] However, the diffuse reflectance spectrum of the 4-aminopyridine complex (637 nm) is different from those of the apical adducts. The light absorption spectra of the complexes in Table 1 are very similar to those of the apical complexes, having absorption maxima at *ca.* 660 nm. Since the spectra in solids are very similar to those in solutions, the $Cu(acac)_2L$ complexes in Table 1 probably have apical nitrogen ligands. Further evidence for the apical configuration comes from the fact that their e.s.r. spectra exhibit no resolvable ^{14}N hyperfine splittings.[13]

Axial ligation of the nitrogen base to $Cu(acac)_2$ causes an increase in the $g_\parallel$ value and a decrease in $|A_\parallel|$ value.[10,14] In our previous investigation using oxygen-containing ligands as solvents, a good linear relation has been found between the $|A_\parallel|$ values of $Cu(acac)_2$ in solution and the $\Delta\nu_D$[15] values of the solvents (correlation coefficient r 0.993),[1] where $\Delta\nu_D$ is the OD stretching frequency shift of [^{2}H]methanol in a given solvent relative to that in benzene and used as a measure of solvent donating ability. Solvent donating ability should be closely related to the basicity in nitrogen bases. Accordingly, the magnitudes of the shifts of these e.s.r. parameters are correlated with the basicities of the nitrogen heterocycles. The decrease in $|A_\parallel|$ might be caused by a decrease in spin density on the copper atom due to further delocalization of the unpaired electron onto the nitrogen atom.* Thus the stronger Cu–N co-ordinative bond results in a greater decrease in $|A_\parallel|$. For the series of aza-aromatic compounds under investigation, only a fair linear relation was shown to exist between $|A_\parallel|$ and pK_a values (r 0.837) when all the bases in Table 1 were included. In general, the co-ordinating ability of the ligand is affected by steric

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* Spin delocalization in the aza-aromatic molecule arises from $d\pi$–$p\pi$ overlap between the occupied Cu *d* orbital and the π^* orbital on the nitrogen atom (back donation), since the unpaired electron of copper occupies the $d_{x^2-y^2}$ or d_{xy} orbital.[14] However, the $p\pi$–$d\pi$ overlap can be assumed to be nearly proportional to the overlap integral of the dative bond.

TABLE 1

E.s.r. parameters of the Cu(acac)$_2$L complexes

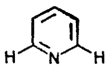
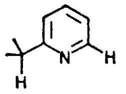
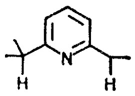
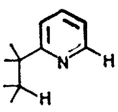
No.	L	$g_{\parallel}$	$10^4 \lvert A_{\parallel}\rvert/\mathrm{cm}^{-1}$	pK_a
	Toluene[a]	2.246	197	
1	Pyridine	2.290	165	5.2
2	4-Methylpyridine	2.291	163	6.0
3	3-Methylpyridine	2.290	164	5.7
4	2-Methylpyridine	2.289	165	6.0
5	4-Ethylpyridine	2.292	163	6.0
6	3-Ethylpyridine	2.290	165	5.7
7	2-Ethylpyridine	2.288	166	6.0
8	2,4,6-Trimethylpyridine	2.283	170	7.6
9	2,4,6-Triethylpyridine	2.281	171	
10	2-Chloropyridine	2.284	169	
11	2-Bromopyridine	2.274	177	0.9
12	Quinoline	2.289	165	4.9
13	2-Methylquinoline	2.280	172	5.8
14	8-Methylquinoline	2.282	171	5.0
15	Benzo[*h*]quinoline	2.282	172	
16	Isoquinoline	2.290	166	5.4
17	Acridine	2.280	174	5.6
18	Pyrazine	2.280	172	0.7
19	Piperidine	2.301	156	11.2
20	*N*-Methylpiperidine	2.290	165	10.1
21	Morpholine	2.295	161	8.4
22	*N*-Methylmorpholine	2.289	163	7.4
		2.270	178	

[a] Cu(acac)$_2$ in 1 : 1 toluene–chloroform is given as a reference, in which axial ligation can be neglected.

factors in addition to the electronic effect.[2] In order to discuss the steric effect systematically, the steric environment around the nitrogen atom is classified as shown in Table 2. Lanthanoid induced shift measurements in the ^{1}H n.m.r. spectra rationalized the classification.[16] When the least squares calculations to draw the line were carried out with the ligands carrying nitrogen atoms of types (I) and (II) in Table 2, the $|A_{\parallel}|$ *versus* pK_a plot becomes linear (*r* 0.994) (Figure 1). This is due to the fact that the effect of steric hindrance is not large for aza-aromatic ligands carrying type (I) and (II) nitrogen atoms. The ligands of types (III) and (IV) have some substituents (or *peri*-hydrogen atoms attached to the fused rings) in the neighbourhood of the nitrogen atoms, considerably hindering the approach of the chelated copper ion. The deviation upwards from the line may be caused by Cu–N bond weakening by steric hindrance. As a large excess of the nitrogen base is present, the equilibrium lies so far towards the adduct that the effect of free Cu(acac)$_2$ is negligible under the experimental conditions. Thus the degree of the deviation is a measure of the magnitude of the steric effect between Cu(acac)$_2$ and the ligand. The largest deviations were observed with aza-aromatic compounds of type (III). In these compounds, the two C–H bonds on both sides of the nitrogen atom are parallel to the orbital of the lone pair electrons so as to push away the approaching copper chelate molecule. In this way, both the 2-methyl group and the *peri*-hydrogen atom hinder the approach of the chelated copper ion to the nitrogen atom of 2,6-dimethylpyridine, 2-methylquinoline, or acridine. The nitrogen atom in 8-methylquinoline seems considerably less hindered and 2-bromo- and 2-ethyl-pyridine

TABLE 2

Classification of the steric circumstances of the pyridine-like nitrogen atoms

Type	(I)	(II)	(III)	(IV)
Structure				
Examples	Pyridine, isoquinoline	2-Methylpyridine, quinoline	2,6-Dimethylpyridine, 2-methylquinoline, acridine	8-Methylquinoline, benzo[*h*]quinoline

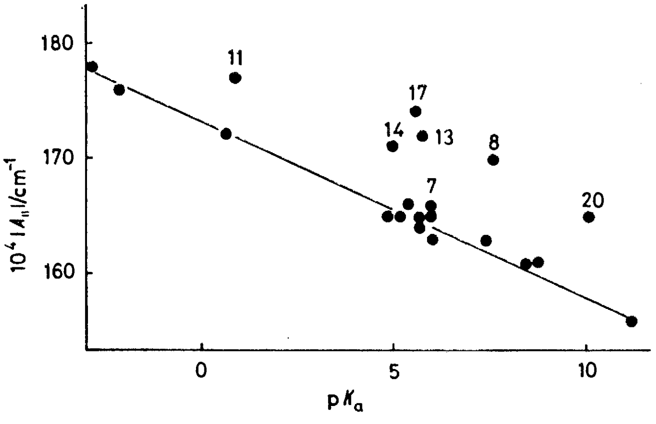
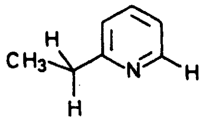
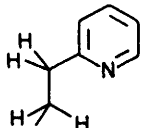


FIGURE 1 Plot of pK_a *versus* $|A_{\parallel}|$. Numbers are those of compounds in Table 1

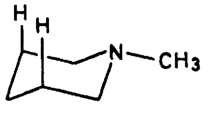
have far less hindered nitrogen atoms. This may be due to the fact that these compounds are unhindered on one side of the nitrogen atom as are quinoline and 2-methylpyridine, though the other side is much more crowded in 8-methylquinoline [classified as a type (IV) compound in Table 2]. Similar tendencies have been observed for the Eu(dpm)$_3$ adducts of these nitrogen bases.[16]



(V)



(VI)



(VII)

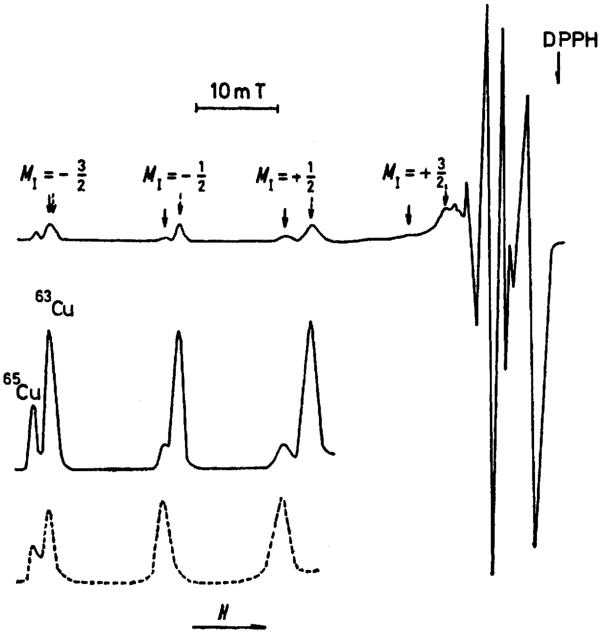


FIGURE 2 The e.s.r. spectrum of Cu(acac)$_2$ (*N*-methylmorpholine). The spectrum shows two sets of transitions with different $|A_{\|}|$ values. The transitions with larger $|A_{\|}|$ (——►) are assigned to the *O*-adduct and those with smaller $|A_{\|}|$ (——►) to the *N*-adduct. The spectrum of Cu(acac)$_2$ (*N*-methylpiperidine) (broken line) is quite similar to that of the *N*-adduct. The $M_I = \pm\frac{1}{2}$ transitions show no resolvable splittings due to ^{63}Cu and ^{65}Cu isotopes in the spectra of Cu(acac)$_2$ (*N*-methylpiperidine), Cu(acac)$_2$ (H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1078), and Cu(acac)$_2$ (pyridine)[13]

Since ring reversal and inversion at the nitrogen atom occur in piperidine and morpholine derivatives, the evaluation of the steric effect should be carried out for the most stable conformation expected to be found in Cu(acac)$_2$L. In the case of *N*-methylpiperidine (VII), the nitrogen lone-pair orbital is considered to occupy predominantly the axial position.[8,*] The co-ordination of the lone-pair axial conformer to planar Cu(acac)$_2$ is prevented by axial hydrogen atoms at the 3- and 5-positions. As these hydrogen atoms are nearly equivalent to the *peri*-hydrogen of quinoline or the methyl hydrogen of 2-methylpyridine, their presence should cause some steric effect. Similar steric hindrance is also observed in the Cu(acac)$_2$–*N*-methylmorpholine complex. The e.s.r. spectrum of the ternary Cu(acac)$_2$–*N*-methylmorpholine–chloroform system showed the presence of two distinct species (Figure 2). The $g_{\|}$ and $|A_{\|}|$ values of the two species both correspond to those of a 1 : 1 adduct and the splittings in the spectrum are not due to the formation of a 1 : 2 adduct.[17] The e.s.r. signals at higher fields are similar to those of tetrahydropyran. The result suggests that the signals arise from the 1 : 1 adduct with the oxygen atom of *N*-methylmorpholine. The other signal is attributed to the *N*-adduct. The ratio of the *N*- and *O*-adduct is 1 : 5.7, Cu(acac)$_2$ preferring *O*-addition because of the steric crowding around the nitrogen atom.

EXPERIMENTAL

Cu(acac)$_2$ was prepared by the usual procedure and recrystallized from chloroform. Other materials and solvents used in this investigation were purified by standard procedures. The e.s.r. spectra of Cu(acac)$_2$ were measured in frozen chloroform solution containing 20% of the heterocycle as ligand. The concentration of Cu(acac)$_2$ was kept at 1.0×10^{-2} mol dm^{-3} for all measurements. E.s.r. spectra were recorded on a JEOL JES ME-1X instrument. E.s.r. parameters were determined by comparison with the values of diphenylpicrylhydrazyl (DPPH) and Mn^{2+}–MgO.

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REFERENCES

[1] Part 1, T. Kogane, H. Yukawa, and R. Hirota, *Nippon Kagaku Kaishi*, 1975, 1115.
[2] D. P. Graddon, *Coord. Chem. Rev.*, 1969, **4**, 1.
[3] D. P. Graddon and K. B. Heng, *Aust. J. Chem.*, 1971, **24**, 1059, 1781.
[4] B. Maiti and R. M. Sathe, *Indian J. Chem., Sect. A*, 1977, **15**, 1101.
[5] A. Morgan and B. Smith, *J. Chem. Soc.*, 1926, 912.
[6] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 5399.
[7] S. Ooi and Q. Fernand, *Chem. Commun.*, 1967, 532.
[8] I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, *Chem. Commun.*, 1971, 33; T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.*, 1970, **92**, 1267.
[9] I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, 1971, **93**, 3922.
[10] H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2054.
[11] K. Ueda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 805.
[12] G. W. Bushnell, *Can. J. Chem.*, 1971, **49**, 555.

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[*] The co-ordination of *N*-methylpiperidine and related bases has been shown to occur at an apical position by u.v. spectroscopic and other evidence.[17,18] The additon complex of Cu(acac)$_2$ with the nitrogen base at a basal position seems to be unstable in chloroform and other solutions.

[13] B. B. Wayland and M. D. Wisniewski. *Chem. Commun.* 1971, 1025.

[14] H. Kuska and M. T. Rogers, *J. Chem. Phys.*, 1965, **43**, 1744.

[15] T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 767.

[16] Y. Nagawa, M. Ono, M. Hirota, Y. Hamada, and I. Takeuchi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1322.

[17] T. Kogane, H. Yukawa, and R. Hirota, *Chem. Lett.*, 1974, 477.

[18] T. Kogane and R. Hirota, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 91.