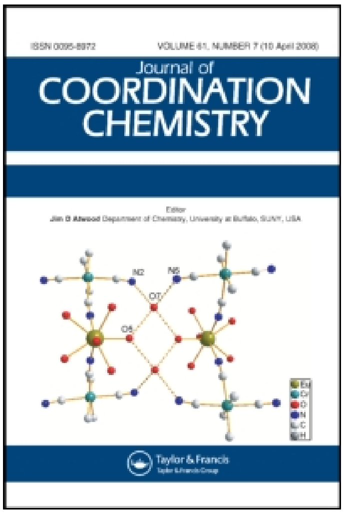

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ELECTRON PARAMAGNETIC RESONANCE STUDY OF COORDINATION IN FORMAZAN COPPER(II) COMPLEXES

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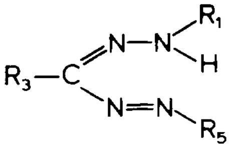
An EPR study of the 1:1 copper(II) complexes of 1,5-diphenylformazan, 1-(2-hydroxyphenyl)-3,5-diphenylformazan and 1-(2-carboxyphenyl)-3,5-diphenylformazan has shown that these complexes in ethanol-water solution can add ammonia to form a square-planar complex. Bonding coefficients (α) have been calculated from the copper hyperfine splitting parameters and indicate some covalent character (α lies between 0.79 and 0.84). It is shown that EPR spectra are a better criterium for details of bonding in these complexes than UVV spectra that have been used to this end hitherto. Also the present results on ammonia coordination to the copper(II) complexes have cleared up some dark points in the interpretation of the mechanism of metal-ion formazan complex formation.

INTRODUCTION

Formazans(I) are well known ligands. Numerous studies about structure[1,2] and properties of metal complexes have appeared. Also the kinetics of formazan metal complex formation and decomposition have recently received attention.[3,4]



(I)

For detailed studies of oxidation and complex formation of formazans higher pH values are necessary to shift the acid dissociation equilibrium of the formazan. If metal ions must be free from hydrolysis under these conditions the addition of complex forming agents is necessary. A practical combination of buffer and ligand properties proved to be present in the ammonia/ammonium perchlorate system.[3,4] For a detailed description of the mechanism it is then necessary to know the exact coordination of ammonia to the metal ion and to the formazan complexes. The problem stated first is easily solved by referring to tables of complex formation constants.[5] The second problem, coordination of ammonia to the metal complex has been said to be detectable from a change in the visible spectrum on the addition of ammonia.[6] A straightforward application of this principle seemed to be in contradiction to results of kinetic and equilibrium studies on the copper(II) complex of 1-(2-carboxyphenyl)-3, 5-diphenylformazan.[3] For this reason we have applied a more direct approach of copper(II)-ammonia coordination using nitrogen superhyperfine splitting effects in the copper(II) EPR spectra of the formazan complexes.

EXPERIMENTAL

Chemicals

Preparation of the formazans followed literature procedures: 1,5-diphenylformazan,[1,7] 1-(2-hydroxyphenyl)-3,5-diphenylformazan.[8] 1-(2-carboxyphenyl)-3,5-diphenylformazan.[8,9] The [1-(2-hydroxyphenyl)-3,5-diphenylformazanato] copper(II) complex was prepared by adding a solution of 8 g copper(II) perchlorate hexahydrate in 25 ml methanol slowly to a warm solution of 8 g 1-(2-hydroxyphenyl)-3, 5-diphenylformazan in 1 l methanol. Subsequent cooling to room temperature precipitated the copper complex that was washed with methanol and water and dried in vacuum over phosphorus pentoxide. Yield 35%. The ammine complex was prepared from the parent compound: 2 g of the [1-(2-hydroxyphenyl)-3,5-diphenylformazanato] copper(II)

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complex was dissolved at 50°C in 300 ml 96% ethanol to which 10 ml concentrated ammonia had been added. After 15 hours standing at 0°C the complex formed was filtered off, washed with 0.2 N ammonia solution and dried in vacuum over phosphorus pentoxide. Yield 50%. Analysis calculated for $CuC_{19}H_{17}N_5O$: Cu, 16.09; C, 57.78; H, 4.34; N, 17.74; O, 4.05. Found: Cu, 16.0; C, 57.5; H, 4.54; N, 17.7; O, 4.33. Other chemicals used were reagent grade. $^{15}NH_3$ was prepared in solution from $^{15}NH_4NO_3$ and sodium hydroxide. $^{15}NH_4NO_3$ was obtained from the British Oxygen Company Ltd. London.

EPR Studies

Solutions of the copper(II) complexes in ethanol-water mixtures up to a concentration of 10^{-3} M have been prepared by adding together copper(II) perchlorate and formazan solutions. Under the conditions used the complexes were formed instantaneously. Alternatively when ammonia adducts were studied an ammonia/ammonium perchlorate buffer was used. Apparatus and experimental conditions for recording the EPR spectra have been described.[1] Glasses of the complex solutions were prepared by rapid cooling in liquid nitrogen and measured at −160°C.

UVV Spectra

Absorption spectra were recorded on a Beckman Acta C III spectrophotometer using 1 cm glass cells.

RESULTS AND DISCUSSION

In this section the formazans will be denoted as the acids: $H_mF(n)$, in which HF(1) = 1,5-diphenylformazan, $H_2F(2)$ = 1-(2-hydroxyphenyl)-3,5-diphenylformazan, $H_2F(3)$ = 1-(2-carboxyphenyl)-3,5-diphenylformazan. Figure 1 shows some representative EPR spectra of liquid solutions at room temperature of a number of formazan complexes and the products obtained on the addition of ammonia to the complexes. All spectra show a primary structure of four lines due to hyperfine interaction of the unpaired electron with the copper (I = 3/2) nucleus. On the high field lines superhyperfine structure is clearly visible. When no ammonia is present five superhyperfine lines can be observed. The solubility of the CuF(3) complex under these conditions was to low to allow the recording of a reliable spectrum. The most straightforward interpretation is to ascribe the five superhyperfine lines to an interaction with the two supposedly equivalent nitrogen (I = 1) atoms of the formazan ring. The spectra are broadened by the presence of the two copper isotopes (^{63}Cu, ^{65}Cu). Beside this the EPR spectra of the complexes after addition of ammonia show more interactions. The only possible interpretation of this phenomenon is that ammonia is coordinated to the complexes giving extra super-hyperfine interactions. Indeed the spectrum of the [1-(2-hydroxyphenyl)-3,5-diphenylformazanato]-copper(II) complex (CuF(2)) prepared in solution after addition of ammonia (Figure 1-b) is exactly the same as the spectrum (not reproduced here) of the solid ammine[1-(2-hydroxyphenyl)-3,5-diphenylformazanato] copper(II) dissolved in the same solvent.

To test the interpretation we have simulated the observed spectra using a theoretical model and have also used $^{15}NH_3$ instead of $^{14}NH_3$(I = 1/2 respectively I = 1) as ligand (Figure 1-c). The theoretical model starts from the description of the (1,5-diphenyl-formazanato)-copper(II) cation; the EPR spectrum of which (see Ref. 1) is not reproduced here, but is nearly coincident with the one CuF(2) (Figure 1-a). A computer simulation of the spectrum assuming Lorentzian line shapes, could be effected by taking the formula for the peak-to-peak derivative line width as: $A + B.M + C.M^2$ (M is the z-component of the nuclear spin), where the same value was taken for the basic line width parameter A for all nuclei. It proved that the fit did not improve on introducing line broadening parameters (B and C) for the nitrogen nuclei. Therefore B and C were only given non-zero values for the copper nuclei (comprising the hyperfine structure of the spectrum). Using this model we could describe the spectrum of the CuF(2) and CuF(3) in ethanol with the parameters given in Table I. From Figure 1-a is seen that the agreement between observed and calculated spectra is very good.

The increased complexity of the spectrum of the CuF(n) complexes on the addition of ammonia can be brought into this model by introducing a super-hyperfine interaction with two equivalent (formazan) nitrogen atoms and one non-equivalent nitrogen atom (from ammonia). Again the agreement between the calculated and observed spectra is satisfactory (see Figure 1-b, d; fitting parameters are in Table I). The introduction of two nitrogen (ammonia) nuclei terminates the possibility of producing a good computer simulation of the spectra. The EPR spectrum of the CuF(2) complex in the presence of $^{15}NH_3$ (Figure 1-c) could be reproduced in the model calculation by taking the parameter values for the splitting constants from the

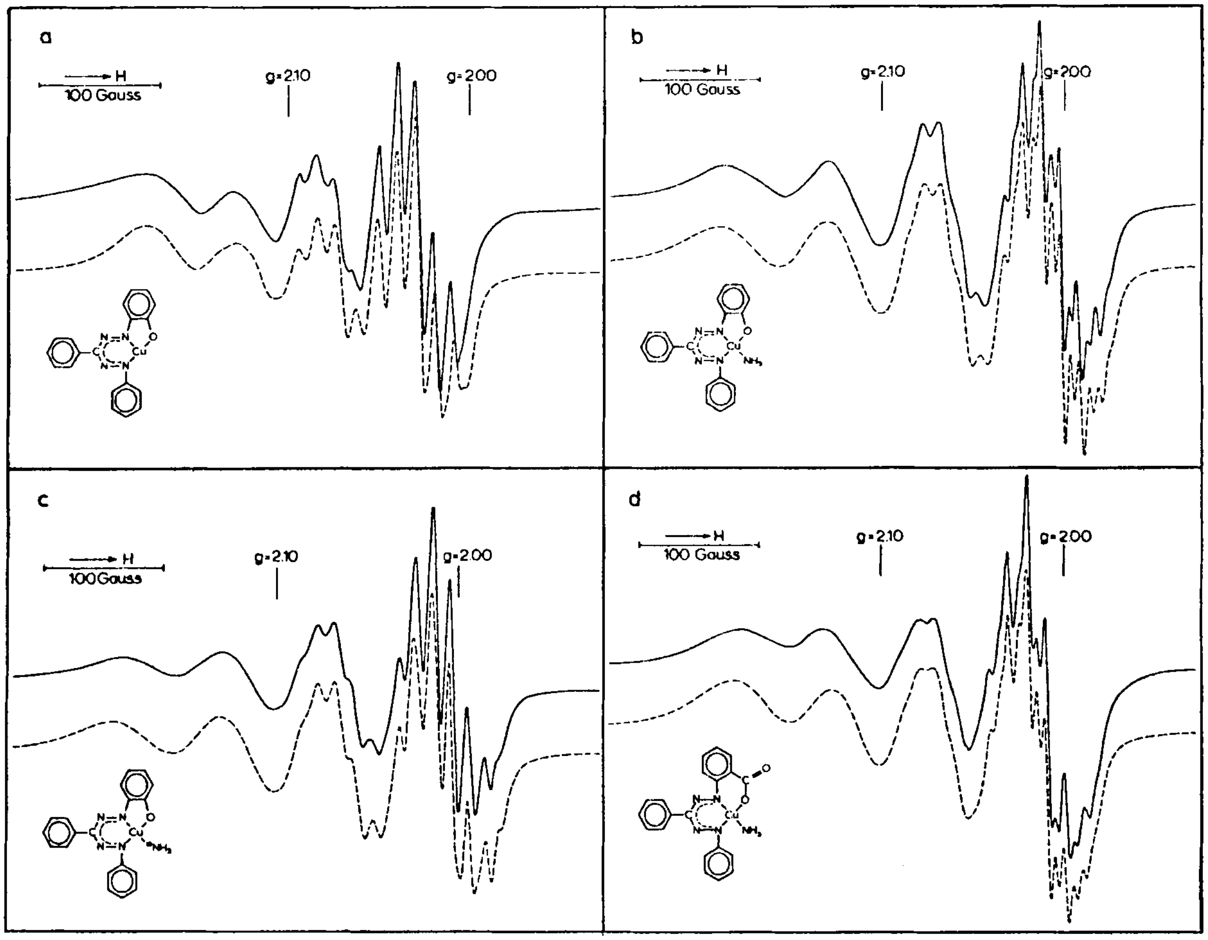

FIGURE 1 EPR spectra of some formazan copper(II) complexes: liquid solutions at room temperature in ethanol (containing ca. 10% water); experimental data: solid line and calculated data: dotted line.

[a] CuF[2]
[b] CuF[2]; $[NH_3] = 0.018$ M, $[Na^+] = [NH_4^+] = 0.05$ M
[c] CuF[2]; $[^{15}NH_3] = 0.06$ M, $[^{15}NH_4^+] = 0.04$ M
[d] CuF[3]; $[NH_3] = 0.04$ M, $[Na^+] = 0.10$ M

TABLE I

EPR parameters[a] for the formazan copper(II) complexes calculated from spectra of liquid solutions in ethanol (containing ca. 10% water) at room temperature.

Compound[b]	A	B	C	$a_{Cu}(^{63}Cu)$	$a_N(NH_3)$	$a_N(F)$[c]	g_{iso}	α
$CuF(1)^+$	16.0	7.0	1.0	66.0	–	15.5	2.090	0.79
$H_3N–CuF(1)^+$	13.5	8.0	2.5	80.6	7.5	15.5	2.082	0.83
CuF(2)	16.0	7.0	1.0	66.0	–	15.5	2.089	0.79
$H_3N–CuF(2)$	16.5	11.0	3.0	81.3	7.5	15.5	2.083	0.84
$H_3^{15}N–CuF(2)$	16.5	11.0	3.0	81.3	10.5	15.5	2.083	0.84
$H_3N–CuF(3)$	19.0	10.0	1.5	74.0	7.5	15.5	2.082	0.81

[a] The (hyper)fine splitting constants are given in Gauss
[b] For the symbols used see text
[c] $a_N(F)$ is the hyperfine splitting constant of the formazan nitrogen donor-atoms

corresponding $^{14}NH_3$ spectrum and introducing the correct gyromagnetic ratio and the different ^{15}N nuclear spin. This excludes the possibility of the presence of a mixture of complexes in the solutions studied. All this proves that in the three complexes mentioned (H_3N-CuF(n)) ammonia is clearly coordinated to the copper(II) central atom in solution.

In addition to the analysis described above the EPR solution spectra of the formazan complexes yield values for the isotropic g-value. These have also been entered in Table I as g_{iso}.

Contrasting with the EPR spectra the absorption spectra of the complexes studied only showed minor changes on coordinating ammonia. In contradiction to earlier papers,[3,6] a change in the visible spectrum of the CuF(3) complex is observed when ammonia is added to a solution of this complex in ethanol–water mixtures. The changes in the principal band of the CuF(n) complexes situated at about 18,000 cm^{-1} amounted to a lowering of the maximum by about 5% together with a shift to higher wavenumbers of 150–200 cm^{-1}.

BONDING COEFFICIENTS

From the EPR results information can be obtained about covalency and bonding in the complexes in terms of bonding coefficients that may be calculated from the g-tensor and the superhyperfine tensors. Analysis of the solution EPR spectra has given the isotropic g value (g_{iso}) and the isotropic a_{Cu} and a_N parameters. To obtain further information we have also tried to analyse glass spectra of the compounds studied. Generally the glass spectra can be explained by assuming effective D_{4h} symmetry: only two g values, $g_{\parallel}(2.18)$ and $g_{\perp}(2.05)$ are detected. Although some copper hyperfine and some nitrogen superhyperfine structure is observed in the glass spectra, no accurate values of both $a_{\parallel}(Cu)$ (185 gauss) and $a_{\perp}(Cu)$ ($\cong$ a (N) $\cong$ 15 gauss) could be obtained. So we use in the following the isotropic constants obtained from the analysis of the solution spectra. In view of the many assumptions needed when we start from the a_N parameters it seems to be the most reliable procedure to obtain the covalency parameters from the copper hyperfine splitting.[10] We assume the odd copper 3d electron to be in an MO derived from a symmetry-adopted d orbital.[10,11,12] This MO can be written as:

$$|\ \Gamma > = \alpha \,.\, d(\Gamma) \quad \alpha' \,.\, \psi(\Gamma)$$

$\alpha' \,.\, \psi(\Gamma)$ will be a complicated expression containing contributions from the different ligand donor atoms, as copper is not only bonded to the formazan, but also to solvent and/or ammonia ligands. The isotropic a_{Cu} is related to the bonding coefficient α as given by Eq. (127) of Ref. 13:

$$\alpha^2 = \frac{|\,a_{Cu}\,|}{P\,.\,K} + \frac{g_{iso} - 2.0023}{K}$$

Using[13] the value P = 0.036 cm^{-1} and K = 0.43, we find for the complexes studied α to be between 0.79 and 0.84 (Table I). This indicates some covalent character. Unfortunately the complexity of the coordination and the unknown role of coordinated water ligands makes it impossible to deduce bonding coefficients from the ^{14}N superhyperfine tensor.[10] The values obtained agree well with the ones found for similar complexes: for instance Falk a.o.[14] have found for copper(II)-dimethylglyoxime complexes in aqueous solution α values close to 0.85 while Vierke has brought together[15] some related copper complexes having N or N, O coordination with α values between 0.86 and 0.91.

CONCLUSION

The analysis of the EPR spectra of the formazans in ammonia containing ethanol–water solutions can lead to three clear conclusions:

1) The copper(II) complexes of the 1-(2-hydroxyphenyl)-3,5-diphenylformazan and 1-(2-carboxyphenyl)-3,5-diphenylformazan in alcoholic solutions on the addition of ammonia coordinate to ammonia forming a four-coordinated complex (excluding coordinated solvent molecules). In view of the expected planarity of the formazan ligand due to resonance stabilization it is reasonable to assume that copper(II) uses square planar coordination. This conclusion is reinforced by preliminary X ray results on the ammine-[1-(2-hydroxyphenyl)-3,5-diphenylformazanato]copper(II) complex.[16] Consequently the extensively discussed[6,17-20] possibility of three-coordination of the formazan complex in solution is disproved by our EPR results. At the same time this study has shown that UVV spectra give a much less reliable indicative criterium for ammonia coordination in the formazan copper(II) compounds.

2) A straightforward interpretation of the reaction kinetics of the system copper(II)- 1-(2-carboxyphenyl)-3,5-diphenylformazan is now possible. From the analysis of the rate constant as a function of the medium the conclusion had to be drawn[3] that the

formation and the decomposition reaction of the complex (denoted as CuF(3)) did not have the same stoichiometry:

formation $Cu(NH_3)_3(H_2O)_3^{2+} + HF(3)^- \rightarrow$

decomposition $CuF(3) + NH_3 + NH_4^+ \rightarrow$

Clearly the decomposition reaction contains one ammonia molecule less than the formation reaction. The present results however have proved that the copper(II) complex in the ammonia buffers used should be formulated as H_3N-Cu-F(3), which eliminates the problem. This means that the reaction between copper(II) and 1-(2-carboxyphenyl)-3,5-diphenylformazan can be described as being completely analogous to the reaction between nickel(II) and 1-(2-carboxyphenyl)-3,5-diphenylformazan.

3) The bonding coefficients obtained from the hyperfine splitting constants have not given a detailed picture of coordination in the formazan complexes studied. However it is clear that the complexes have some covalent character and that the value of the bonding coefficient is in the range of the ones published for similar N, O-coordinated complexes.

REFERENCES

1. S. Balt, C. van Capelleveen, W. E. Renkema and C. H. Stam, *J. Inorg. Nucl. Chem.*, **38**, 459 (1976, and references therein).
2. N. P. Bednyagina, I. Ya. Postovskii, A. D. Garnovskii and O. A. Osipov, *Russ. Chem. Rev.*, **44**, 493 (1975).
3. A. M. A. Verweij and S. Balt, *Inorg. Chim. Acta*, **4**, 351 (1970).
4. A. M. A. Verweij and S. Balt, *Inorg. Chim. Acta*, **4**, 357 (1970).
5. L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, Special Publication no. 17 (1964) and no. 25 (1971) of The Chemical Society, London.
6. R. Wizinger, *Chimia*, **22**, Suppl. 82 (1968).
7. H. von Pechman, *Chem. Ber.*, **25**, 3175 (1892).
8. R. Wizinger and W. Biro, *Helv. Chim. Acta*, **32**, 901 (1949).
9. A. M. A. Verweij and S. Balt, *Inorg. Chim. Acta*, **3**, 178 (1969).
10. C. M. Guzy, J. B. Raynov and M. C. R. Symons, *J. Chem. Soc. A*, 2299 (1969).
11. F. A. Walker, H. Sigel and D. B. McCornick, *Inorg. Chem.*, **11**, 2756 (1972).
12. D. W. Smith, *J. Chem. Soc. A*, 3108 (1970).
13. H. A. Kuska and M. T. Rogers, in *Coordination Chemistry*, Vol. 1, A. E. Martell, ed., Van Nostrand, New York, 1971.
14. K. E. Falk, E. Ivanova, B. Roos and T. Vänngard, *Inorg. Chem.*, **9**, 556 (1970).
15. G. Vierke, Z. Naturforsch., **26a**, 554 (1971), Table I.
16. W. E. Renkama, Dissertation, Amsterdam (1975).
17. M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **23**, 372 (1957).
18. M. Kishita, Y. Muto and M. Kubo, *Naturwissenschaften*, **23**, 612 (1957).
19. W. Freiesleben and F. Grün, *Chimia*, **11**, 276 (1957).
20. R. von Tobel, Thesis, Basel (1952).