# Equilibria in Complexes of *N*-Heterocyclic Molecules. Part 29.† An Electron Spin Resonance Study of some *N*-Heterocyclic Complex Ions of Silver(II)

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A critical assessment of the e.s.r. parameters for complex compounds of the silver(II) ion with the *N*-heterocyclic donors pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline is presented. In previous reports, nitric acid has often been used as an 'inert' solvent; this is wrong. Protons and silver(II) ions compete for the ligands, equilibria being fairly rapidly established. Species studied in nitric acid solutions made from solid compounds of silver(II) are usually not those present in the pure solid. Another important difference in the present investigation is in the assignment of the nitrogen superhyperfine coupling constants. It is now well established that $A_{\parallel}^{N}$ and $A_{\perp}^{N}$ cannot be immediately obtained from the e.s.r. spectra. This paper also introduces the use of a new line-sharpening device, suitable for obtaining extremely well resolved e.s.r. spectra of solids.

THE oxidation state +2 for silver is readily accessible and aqueous solutions containing $Ag^{2+}$ ions are fairly stable when strongly acidified with non-reducing acids. A large number of complex compounds of silver(II) has been prepared.[1,2] Silver(II) ions are usually four-co-ordinate with a square-planar configuration, but compounds containing the Ag(II) ion with a higher co-ordination number are also known.[1]

A general method for preparing the complexes with *N*-heterocyclic donors is to precipitate the peroxodisulphate from water as a sparingly soluble yellow to dark red crystalline powder through oxidation of an argentous salt solution with potassium persulphate in the presence of an excess of the appropriate ligand.[3,4] Complexes of other anions have been subsequently prepared by double decomposition. The species $PbO_2$, $BaO_2$, $CaO_2$, and $O_3$ have also sufficed as oxidants in the case of some *N*-heterocyclic ligands, due to the lowering of the Ag(I)–Ag(II) oxidation potential brought about by co-ordination. Alternatively, some complexes have been obtained by anodic oxidation techniques.[5]

The properties of the heterocyclic complexes of silver(II) have been reviewed recently;[1] however, there are still some conflicting assignments of the electron spin resonance spectra which require clarification. This paper therefore describes the e.s.r. spectra expected for *trans*-$[Ag(py)_2X_2]$ (X = $NO_3$, *etc*), *cis*-$[Ag(phen)(NO_3)_2]$, $[Ag(py)_4]^{2+}$, $[Ag(bipy)_2]^{2+}$, and $[Ag(phen)_2]^{2+}$ (py = pyridine, phen = 1,10-phenanthroline, bipy = 2,2′-bipyridyl) and compares reported data with our own findings.

## EXPERIMENTAL

*Preparations.—Tetrakis*(*pyridine*)*silver*(II) *peroxodisulphate*, $[Ag(py)_4][S_2O_8]$. A mixture of a 5% solution of $Ag[NO_3]$ (12 cm³, 1 mol) with pyridine (5 cm³, 12 mol) was poured into a well stirred cold solution of 7.5 g $K_2[S_2O_8]$ (8 mol) in $H_2O$ (500 cm³). A yellow-orange colouration was immediately apparent, and precipitation of an orange crystalline product soon began, and was complete within 0.5 h. It was collected and the crystals washed with cold water. Yield 2 g. When it had been vacuum dried over K[OH], the complex was stable for several months. As a precaution, the sample was stored in the dark.

For the doped samples, cadmium acetate (5.33 g) and $Ag[NO_3]$ (0.03 g, 1% or 0.01 g, *ca.* 0.3%) were dissolved in water (5 cm³). Pyridine (25 cm³) was then added followed by an excess of potassium persulphate in water. The pale yellow crystals were collected, washed with ice-water, and air-dried. *X*-Ray powder photographs of the series $[Pt(py)_4][S_2O_8]$, $[Cu(py)_4][S_2O_8]$, $[Ag(py)_4][S_2O_8]$, and $[Cd(py)_4][S_2O_8]$ were recorded and the *d* spacings are given in Table 1.

TABLE 1

*d* Values (Å) * for $[M(py)_4][S_2O_8]$

| Ag | Cu | Cd | Pt |
|---|---|---|---|
| 8.308s | | 8.386s | 8.631s |
| 7.345s | 7.792s | 7.501s | |
| | 7.110s | | 7.082m |
| 6.811s | | 6.863s | 6.837m |
| 6.304m | | 6.349m | 6.372s |
| 5.455w | 5.663m | | 5.489w |
| 5.097w | | 5.097m | |
| | 4.835m | | 4.956s |
| 4.647m | 4.635m | 4.784m | |
| 4.364vs | 4.429m | 4.291vs | 4.375s |
| | 4.014vs | | |
| | | 3.901s | |
| 3.810s | 3.802m | 3.762m | 3.770m |
| 3.641m | 3.626m | 3.701w | |
| 3.514m | 3.507m | 3.514m | 3.514m |
| 3.375m | 3.358m | 3.383m | 3.345m |
| 3.111w | 3.159w | 3.064m | 3.059m |
| 2.984m | 2.994m | 2.931m | 2.917m |
| 2.876w | 2.849w | | |
| 2.836vw | 2.789vw | | 2.780w |
| 2.739w | 2.731w | 2.727m | 2.711m |
| 2.575m | 2.622m | 2.637m | 2.671w |
| 2.519m | | 2.553w | 2.560m |
| 2.436w | | 2.478m | 2.522w |
| 2.313m | 2.284m | 2.386vw | 2.439w |
| 2.214m | 2.222m | 2.265m | 2.362w |
| 2.169w | 2.179m | | 2.293m |
| 2.127m | 2.118m | | |

* Cu-$K_\alpha$ nickel-filtered radiation, $\lambda_{av.} = 1.542$ Å.

*Tetrakis*(*pyridine*)*silver*(II) *perchlorate*, $[Ag(py)_4][ClO_4]_2$. Anodic oxidation of a solution of $Ag[NO_3]$ in aqueous pyridine in the presence of $K[NO_3]$ led to dark brown solutions containing $[Ag(py)_4]^{2+}$. Addition of $Na[ClO_4]$ gave a red-brown precipitate which was collected and washed with cold water.

In the absence of $Na[ClO_4]$, the red nitrate could be isolated as crystals if the solution was left to stand overnight. Attempts to prepare $[Ag(py)_2]^{2+}$, by dissolving either of these salts in nitric acid, were unsuccessful. In

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† Part 28, J. A. Arce Sagüés, R. D. Gillard, and P. A. Williams, *Inorg. Chim. Acta*, 1979, **36**, L411—412.

both cases the $Ag^{2+}$ aquo-ion was obtained (no nitrogen hyperfine in the frozen e.s.r. spectra).

*Tetrakis*(*4-methylpyridine*)*silver*(II) *peroxodisulphate dihydrate*, $[Ag(4Me\text{-}py)_4][S_2O_8]\cdot2H_2O$. $Ag[NO_3]$ (2g) was dissolved in water (5 $cm^3$). 4-Methylpyridine (4Me-py) (25 $cm^3$) was then added followed by an excess of potassium persulphate. The red-brown crystals produced were collected, washed with ice-water, and air-dried. The complexes $[Ag(bipy)_2][S_2O_8]$ and $[Ag(phen)_2][S_2O_8]$ were prepared by persulphate oxidations as described above. The complex *cis*-$[Ag(phen)(NO_3)_2]$ was not isolated but noted as an intermediate in the dissociation of $[Ag(phen)_2]^{2+}$ in concentrated nitric acid.

Electron spin resonance spectra were recorded on either a Varian E3 or E109 spectrometer. Details of the line-sharpening device were presented at the Chemical Society E.S.R. group meeting at Nottingham.[6] Diphenylpicrylhydrazyl was used as a field marker, $g = 2.003\,6$.

Computer simulation of e.s.r. lineshapes for the monomeric silver(II) systems was performed using the previously described methods,[7] on the South West University Regional Computer Network.

*Theory*.—The e.s.r. spectra obtained under magnetically-dilute conditions, either for frozen solution or for samples doped into the stoicheiometrically corresponding cadmium(II) complex, were in all cases consistent with an axially symmetric $g$ tensor. Consequently, they could be described by a spin Hamiltonian [equation (1)] where the

$$\mathscr{H} = \bar{S}.g.\bar{B}. + \bar{S}.\bar{A}.I. + \sum_{j} \bar{S}.\bar{A}_j.\bar{I}_j \qquad (1)$$

second term accounts for the hyperfine interaction with the silver nuclei, and the summation stands for the super-hyperfine interaction with the nitrogen nuclei of the *N*-heterocyclic ligand(s). Since natural silver has two isotopes $^{107}Ag$ and $^{109}Ag$, in approximately the same abundance, both of spin $I = \frac{1}{2}$, and their nuclear magnetic moments, differing by less than 15%, were not resolved in the spectra, the present interpretation considers that the interaction takes place with a single nucleus.

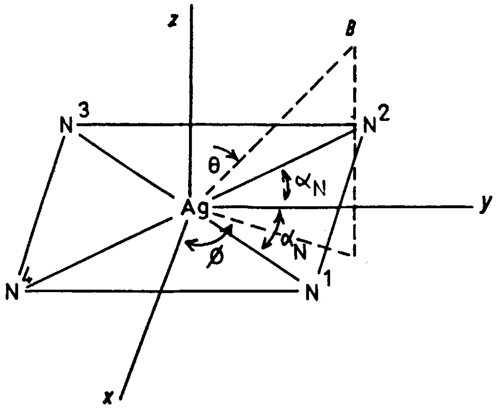

FIGURE 1 Disposition of the hyperfine and magnetic axes relative to the metal–ligand directions

The form of the hyperfine splitting patterns for the ligand nitrogens has previously been calculated for $N_4$[8] and *cis*-$N_2X_2$[9] symmetries, and will not be presented here in detail. They were required in the computer simulation program used in this work.

The disposition of the hyperfine and magnetic axes relative to the metal–ligand directions are shown in Figure 1. If the angle between the field direction, $B$, and the Ag–N axis is $\gamma$, then the well known relation exists between $A^N$ and its components perpendicular and parallel (to Ag–N) [equation (2)]. The parallel and perpendicular

$$(A^N)^2 = (A_{\parallel}{}^N)^2\cos^2\gamma + (A_{\perp}{}^N)^2\sin^2\gamma \qquad (2)$$

components were used in the calculations since it was not possible experimentally to resolve the $x$, $y$, and $z$ components. It follows that for N(1) equation (3) holds while

$$(A_1{}^N)^2 = (A_{\parallel}{}^N)^2\sin^2\theta\sin^2(\phi + \alpha_N) + (A_{\perp}{}^N)^2[1 - \sin^2\theta\sin^2(\phi + \alpha_N)] \qquad (3)$$

for N(2) we have equation (4). Similar expressions are

$$(A_2{}^N)^2 = (A_{\parallel}{}^N)^2\sin^2\theta\sin^2(\phi - \alpha_N) + (A_{\perp}{}^N)^2[1 - \sin^2\theta\sin^2(\phi - \alpha_N)] \qquad (4)$$

obtained for N(3) and N(4). The value of $\alpha_N$ was set at 45° since the four nitrogen atoms were assumed to be crystallographically equivalent.

It is clear that when the magnetic field is applied in the direction of $Z$, it should be possible to observe $A_{\parallel}{}^{Ag}$ and $A_{\perp}{}^N$. Similarly, when the magnetic field is applied perpendicular to $Z$, then $A_{\perp}{}^{Ag}$ should be observed, although the nitrogen hyperfine splitting observed in this orientation is not $A_{\parallel}{}^N$ but rather approximates the average $(\frac{1}{2})^{\frac{1}{2}}[(A_{\parallel}{}^N)^2 + (A_{\perp}{}^N)^2]^{\frac{1}{2}}$ due to random orientation in the frozen solution.

In some cases for the undiluted solids, the $g$ tensor apparently has rhombic symmetry. In these cases, no silver or nitrogen hyperfine could be resolved, and the spin Hamiltonian used to describe the spectra was as shown in equation (5).

$$\mathscr{H} = g_xS_xB_x + g_yS_yB_y + g_zS_zB_z \qquad (5)$$

## RESULTS

In contrast to a recent report,[10] no difficulty was encountered in the preparation of $[Ag(4Me\text{-}py)_4][S_2O_8]\cdot2H_2O$, by either $S_2O_8{}^{2-}$ oxidation or electrolytic methods. In keeping with earlier findings,[5] no tris-chelated species could be isolated for bipy or phen. Consequently, data reported [1] for these complexes are almost certainly incorrect. In this context it is worth remarking that a bis(2,2′,2″-terpyridyl)silver(II) cation has been isolated and claimed [11] to be a six-co-ordinate species.

Another aspect of the preparation of the persulphate salts was highlighted by the *X*-ray powder photographs. Based on the evidence [12] of ease of doping at all levels of the silver and copper complexes into the cadmium species, isomorphism was assumed. Our present results clearly indicate that our samples of $[M(py)_4][S_2O_8]$ are not isomorphous [$Ag \not\simeq Cu \not\simeq Cd \not\simeq Pt$].

The e.s.r. spectrum of a frozen aqueous solution of $[Ag(py)_4][NO_3]_2$ is shown in Figure 2(*a*). This spectrum is identical to that obtained for $[Ag(py)_4][S_2O_8]$ in frozen pyridine solution. In addition, apart from the resolution, it is very similar to that found for $[Ag(py)_4][S_2O_8]$ doped into the corresponding cadmium complex at *ca.* 0.5%, Figure 2(*b*). Originally, 1% Ag in Cd was tried to compare our results with the published data [13] and the line-sharpening device (see Experimental section) used to enhance the resolution. Comparable resolution to this was achieved in another experiment by reducing the amount of Ag present to *ca.* 0.5%. No extraneous lines were introduced by the sharpening process, confirming its validity. The effect of sharpening, by a composite of 1st, 3rd, and 5th derivative spectra of the latter sample is given in Figure 3. Poorly resolved features in the first derivative spectrum become readily discernible. The computer simulated line shape is also shown in Figure 3.

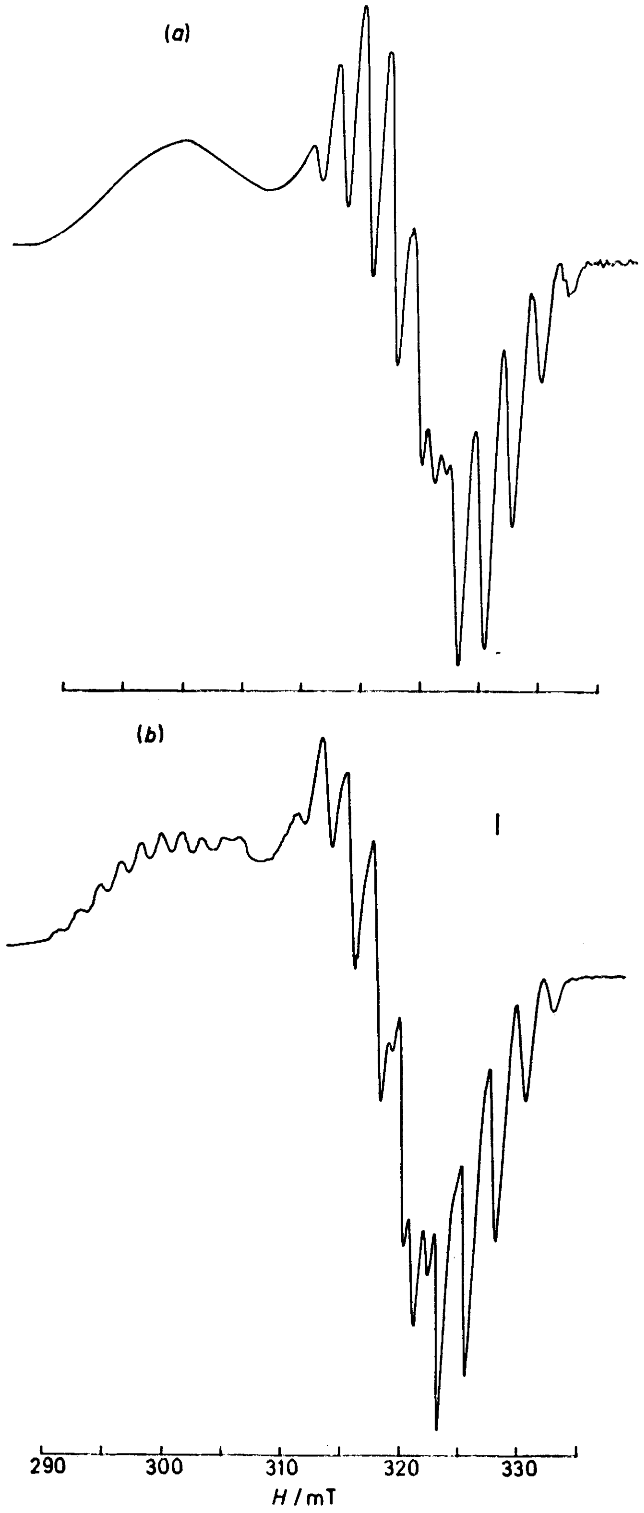

FIGURE 2 E.s.r. spectra obtained for (*a*) frozen aqueous solution of $[Ag(py)_4][NO_3]_2$ at 77 K and (*b*) for *ca.* 0.5% $[Ag(py)_4][S_2O_8]$ doped into the corresponding cadmium salt at 77 K

All our attempts to produce the spectrum previously reported [14] for *trans*-$[Ag(py)_2(NO_3)_2]$ by addition of $HNO_3$ to the compound obtained electrochemically, resulted in the spectrum shown in Figure 4(*a*). This spectrum shows no nitrogen superhyperfine and is identical to that previously reported [15,16] for the $Ag^{2+}$ aquo-ion.

In contrast, addition of nitric acid to either $[Ag(bipy)_2]^{2+}$ or $[Ag(phen)_2]^{2+}$ leads to spectra of the type shown in Figure 4(*b*). These spectra must be assigned to *cis*-$[AgLX_2]$ type species (L = bipy or phen) (compare ref. 17). Thus under our conditions only partial dissociation occurs in the presence of the bidentate chelating ligands [see equation (6),

$$[AgL_2]^{2+} + 2HNO_3 \longrightarrow cis\text{-}[AgL(NO_3)_2] + HL^+ + H^+ \quad (6)$$

where $HL^+$ and $H^+$ on the product side describes the equilibrium composition of L, $HL^+$, and $H_2L^{2+}$].

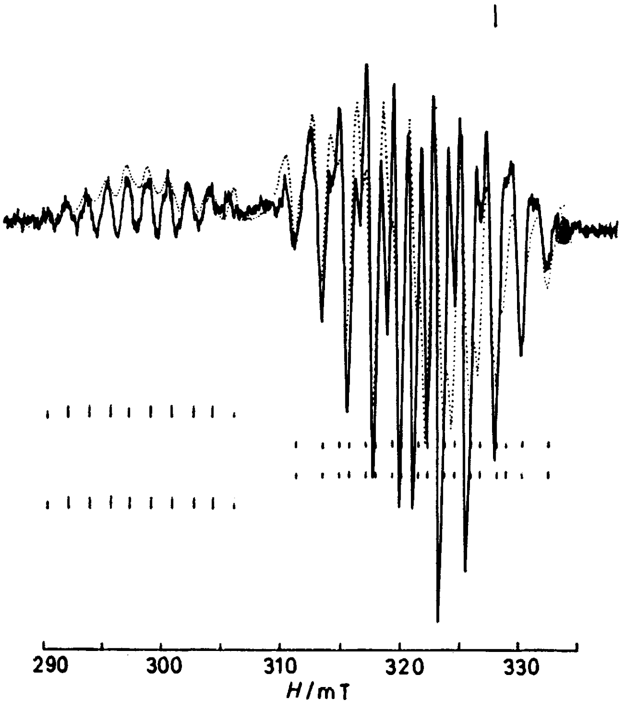

FIGURE 3 1st, 3rd, and 5th composite derivative e.s.r. spectrum of 0.5% Ag in $[Cd(py)_4][S_2O_8]$ at 77 K (——) and computer line shape (· · · ·) found by simulation

A spectrum reported recently [18] for the species formed by $\gamma$ irradiation of Ag–X zeolite and then exposed to pyridine vapour, appears to have a number of nitrogen hyperfine lines intermediate between those shown in Figures 3 and 4(*b*). It was interpreted in terms of two pyridine groups co-ordinated to the silver ion. However, this does not appear to be the same as that reported earlier [14] for *trans*-$[Ag(py)_2(NO_3)_2]$ (note that the 2nd derivative only was reported), and may in fact be more readily accounted for by there being three pyridine groups around the $Ag^{II}$ ion.

The e.s.r. spectra of polycrystalline samples of $[Ag(py)_4]^{2+}$, $[Ag(4Me\text{-}py)_4]^{2+}$, $[Ag(bipy)_2]^{2+}$, and $[Ag(phen)_2]^{2+}$ show axial or rhombic $g$ tensor symmetry. As in previous studies [19,20] no silver or nitrogen hyperfine could be resolved. Figure

5 shows the spectra obtained for $[Ag(py)_4][S_2O_8]$ and $[Ag(4Me\text{-}py)_4][S_2O_8]\cdot 2H_2O$.

## DISCUSSION

The equilibria in acids between free and complexed ligand and silver(II) may be described by either (7) and (8), or by (8) and (9) of the following overall equations where L = py, ½ phen, ½ bipy, *etc.*

$$Ag^{2+}(aq) + 4\ HL^+ \rightleftharpoons [AgL_4]^{2+} + 4H^+ \quad (7)$$

$$L + H^+ \rightleftharpoons HL^+ \quad (8)$$

$$Ag^{2+}(aq) + 4\ L \rightleftharpoons [AgL_4]^{2+} \quad (9)$$

No stability constants for equations (7) and (9) are available. However, by comparison with the data [21,22] for Ni, Pd, and Cu, an estimate can be made for the equilibrium constants relating to equation (9). For L = pyridine, $\beta_4Pd = 22.9$, $\beta_4Ni = 5.56$, $\beta_4Cu = 6.52$, and a value $\beta_4Ag$ can be estimated as *ca.* 27, by assuming that $\beta_4Pd : \beta_4Ag = \beta_4Ni : \beta_4Cu$.

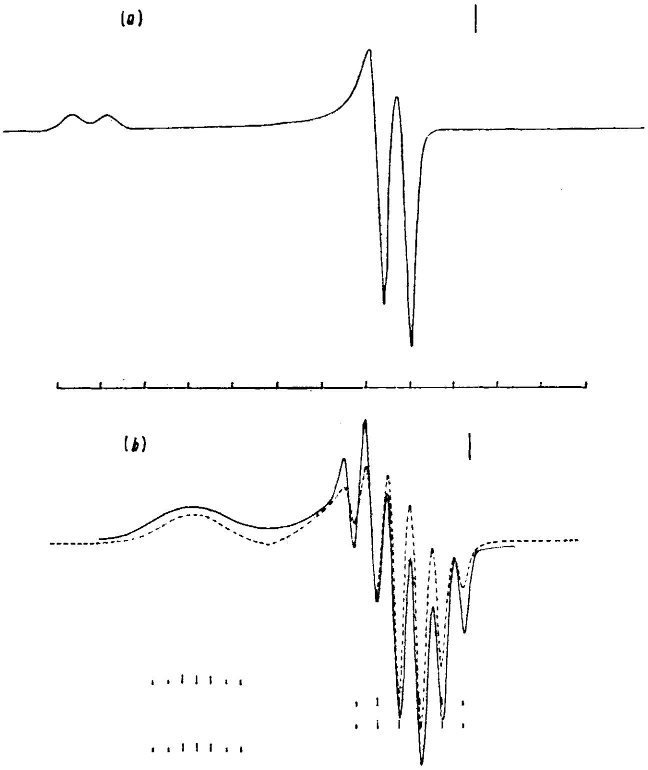

FIGURE 4 E.s.r. spectra of (*a*) $Ag^{2+}$ aquo-ion at 77 K and (*b*) of $[Ag(phen)(NO_3)_2]$ at 77 K (——) and computer simulated line shape (– – – –)

From our results, the equilibria between silver(II) ions (with the $4d^9$ configuration) and protons competing for *N*-donors are fairly quickly set up, just as they are for copper(II) with the $3d^9$ configuration, and the tacit assumption in all the earlier work in nitric acid media that silver(II) [like palladium(II)] is kinetically inert is not correct.

E.s.r. spectra obtained for $Ag^{2+}$ in neat pyridine are identical to that for $[Ag(py)_4]^{2+}$ indicating that complexes with more than four pyridine groups are not formed to any extent under these conditions, a result like that given by Bjerrum [23] for the analogous copper system: the nature of the few solids with py : Cu greater than 4 : 1 remains to be established.

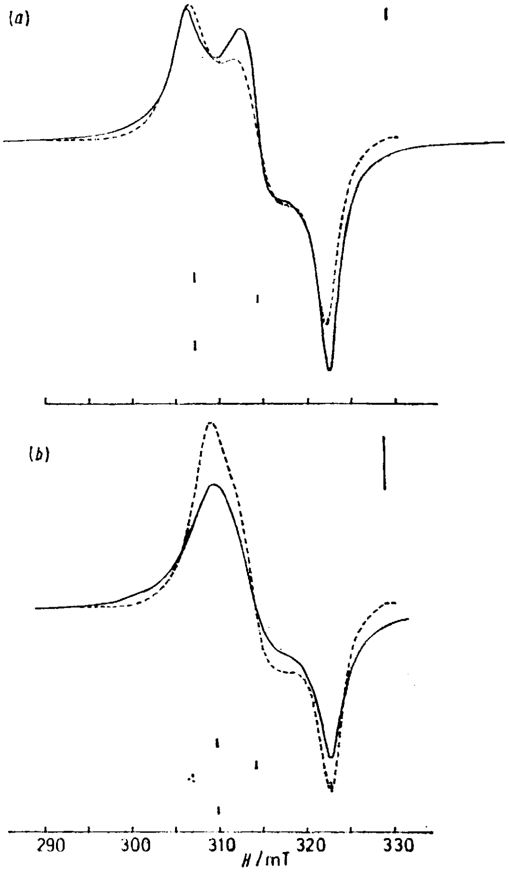

FIGURE 5 E.s.r. spectrum of (*a*) $[Ag(py)_4][S_2O_8]$ solid at 77 K and (*b*) of solid $[Ag(4Me\text{-}py)_4][S_2O_8]\cdot 2H_2O$ at 77 K. Dashed lines represent computer simulated line shapes

The spin Hamiltonian parameters determined in this study are given in Table 2. The previously reported results are included for comparison.

Several differences are immediately obvious. One reason for this has been the use of concentrated nitric acid as a solvent. The persulphate salts are generally only sparingly water soluble but may dissolve in nitric acid without reduction. However, in all cases dissociation or partial dissociation of the ligands occurs on dissolution. Consequently, all results collected in this medium should be treated with suspicion. These include many reported electronic spectra for silver(II) complexes.

Another difference between parameters determined here, and some reported previously lies in the interpretation of the nitrogen superhyperfine terms. In

TABLE 2

Spin Hamiltonian parameters obtained from e.s.r. studies of silver(II) complexes *

| Complex | Medium | $g_x$ | $g_y$ | $g_z = g_{\parallel}$ | $A_{\parallel}^{Ag}$ | $A_{\perp}^{Ag}$ | $A_{\parallel}^{N}$ | $A_{\perp}^{N}$ | Reference |
|---|---|---|---|---|---|---|---|---|---|
| $[Ag(py)_4][S_2O_8]$ | Solid | 2.044 | 2.089 | 2.158 | | | | | 19 |
| | | 2.049 | 2.098 | 2.148 | | | | | 20 |
| | | 2.048 | 2.100 | 2.150 | | | | | This work |
| | Diluted with $[Cd(py)_4][S_2O_8]$ | | 2.04 | 2.18 | 34 | 22 | 17 | 22 | 13 |
| | | | 2.042 | 2.204 | 18.0 | 34.5 | 21.0 | 19.6 | This work |
| $[Ag(4Me\text{-}py)_4][S_2O_8]\cdot 2H_2O$ | Solid | 2.044 | 2.100 | 2.130 | | | | | This work |
| *cis*-$[Ag(phen)(NO_3)_2]$ | Frozen $HNO_3$ solution | | 2.048 | 2.214 | 34.0 | 23.5 | 23.5 | 20.5 | This work |
| $[Ag(bipy)_2][S_2O_8]$ | Frozen $HNO_3$ solution | | 2.047 | 2.210 | 42.2 | 26.0 | 30.1 | 21.1 | 17 |
| *trans*-$[Ag(py)_2(NO_3)_2]$ | | | 2.050 | 2.178 | | | | | 14 |

* All spectra were recorded at 77 K. $g$ Values $\pm 0.005$. $A$ Values $\pm 1 \times 10^{-4}$ cm$^{-1}$.

many cases it has not been appreciated that $A_{\parallel}^{N}$ and $A_{\perp}^{N}$ are not immediately obtainable from the spectra. This problem is always present when the major hyperfine tensor directions are not coincident.

Finally, the controversy over the difference between the magnetically undiluted and diluted samples can be explained as follows. The undiluted samples will show rhombic symmetry if the molecular axes associated with magnetically non-equivalent sites are misaligned.

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