CHAPTER 3
RESULTS AND DISCUSSION
Nature of the solid Ag(I) and Ag(II) complexes:

I.r. spectra of Ag(I) complexes:

In the absence of crystal structures, a clue to the coordination mode of the nitrate ligand may be sought from the i.r. spectral data which are collected in Table I. Of the three stretching vibrations expected for coordinated NO$_3^-$, the two higher frequency ones are known to have a separation of about 150 cm$^{-1}$ or more when the NO$_3^-$ binds in the bidentate chelating mode. For monodentate NO$_3^-$, the separation is usually much less. For the present complexes, the nitrate bands, in most cases, could be readily identified by comparing the spectra of the complex with that of the free aromatic ligand and their frequencies are underlined in Table I. The dmbp and dmp complexes have a separation of 160 cm$^{-1}$ and 150 cm$^{-1}$ respectively for the nitrate bands indicating chelation. Figure 1 shows the i.r. spectrum of the dmbp complexes.

Ag(Umbp)$_2$NO$_3$ on the other hand has only two bands at 1320 and 815 cm$^{-1}$ which are clearly distinct from the bands in the ligand and may be assigned to NO$_3^-$ vibrations. In this complex the NO$_3^-$ is not expected to coordinate. The molecular structure is expected to be analogous to that in the BF$_4^-$ salt. The complexes of mmbp, daf and daf-one also have only one band 1360-1370 cm$^{-1}$. While a firm conclusion about the coordination mode of the NO$_3^-$ is not warranted from these data, it is likely that these complexes do not have a bidentate nitrate. Since a trigonal geometry will be coordinatively unsaturated, a polymeric structure with NO$_3^-$ acting as bridging ligand is proposed for these compounds. Attempts to grow
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*a* Nitrate bonds are underlined; b: broad, s: sharp and intense, w: weak.
Figure 1: I.r spectra to show chelating nitrate (a) dmbp (b) Ag(dmbp)NO₃ and (c) (AgdmbpNO₃)PF₆·NH₄PF₆.
single crystals have not been successful.

3.1.2 I.r. spectra of Ag(II) complexes:

Three types of solid complexes were obtained upon persulfate oxidation of Ag(I) compounds. With dmp and dmbp a brown solid separated initially when the AgLNO₃ was added to (NH₄)₂S₂O₈ solution. These solids were extremely unstable and analysis was not attempted. They gave e.s.r. spectra (sub-section 3.5) typical of magnetically concentrated samples. They are believed to be either AgL(NO₃)₂ or [AgLNO₃]NO₃.

From the mother liquor, a pale yellow compound was precipitated by the addition of NH₄PF₆. The i.r spectra (Table II) shows bands corresponding to chelating NO₃⁻ and PF⁻. They also contain a broad absorption around 3300 cm⁻¹ suggesting the presence of NH₄⁺ ion (Figure 1). These compounds were therefore formulated as the double salts [AgLNO₃]PF₆·NH₄PF₆. In the case of dmbp this stoichiometry was confirmed by C₆H₃N₄Ag₂Ag²⁺ and ligand estimations (sub-section 2.3). The Photoacoustic spectrum of this sample showed a broad asymmetric band centered at 530 nm (Figure 2), very similar to that observed in solution (sub-section 3.2 and Figure 3) indicating that the Ag(II) centre in the double salt is similar to that obtained in solution. This type of double salts are unprecedented in Ag(II) chemistry and the e.s.r investigations on them have been particularly rewarding (sub-section 3.4 and Figures 8 and 9).

In the case of daf, daf-one and mmbp (unstable) solid complexes were obtained only upon the addition of NH₄PF₆ to the solution.
Table II. I.r. data (cm$^{-1}$) for Ag(II) Complexes$^a$.

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<th>[Ag(dmbp)NO$_3$]PF$_6$·NH$_4$PF$_6$</th>
<th>[Ag(dmp)NO$_3$]PF$_6$·NH$_4$PF$_6$</th>
<th>[Ag(mmbp)NO$_3$]PF$_6$</th>
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$^a$Nitrate bands are underlined. PF$_6$ bands are marked by an asterisk. $^b$Tentative formulation, see text.
Figure 2: P.a.s spectrum of \((\text{AgdmbpNO}_3)\text{PF}_6\cdot\text{NH}_4\text{PF}_6\).
containing the oxidised species. However, these precipitates were not double salts. The i.r. spectra (Table II) shows evidence for PF$_6^-$. Nitrate band can be assigned with confidence only for the mmbp complex. All the compounds gave e.s.r. corresponding to magnetically concentrated systems with no resolution of hyperfine splitting. It is not clear whether these complexes are [AgLNO$_3$]PF$_6$ or AgL$_2$(PF$_6$)$_2$.

**Electronic spectra of silver (II) complexes:**

The electronic spectra of the persulfate oxidised solutions of Ag(dmbp)NO$_3$ and Ag(dmp)NO$_3$ are shown in Figure 3. Ag(tmbp)$_2$NO$_3$ and Ag(daf)NO$_3$ in Figure 4 and Ag(mmbp)NO$_3$ in Figure 5. In all cases three bands are observed, a broad one in the visible and two sharp bands in the UV. The highest energy UV band corresponds to a transition mainly localised on the ligands.

The visible bands are assigned to d-d transitions and the first UV band to a ligand to metal charge transfer (LMCT) transition. It is possible that under each band there is more than one transition. The $\nu_{\max}$ values are collected in (Table III) which also includes values for the Ag (II) complexes of bpy and phen for comparison.

Since hexacoordinate Ag(II) has not been detected even with py as ligand, it is reasonable to assume that the electronic transition arises from four-coordinate species in solution. In view of the 1:1 complexes formed by dmbp, dmp, mmbp and daf ligands with AgNO$_3$ and also anticipating the discussion on the double salts containing Ag(II) (subsection 3.4) we suggest that in the case of these ligands the predominant species in solution is AgL(NO$_3$)$_+$ with chelating NO$_3^-$ ligand.
Figure 3: Electronic spectra of persulphate oxidised solutions of (a) Ag(dmbp)NO₃, (b) Ag(dmp)NO₃.
Figure 4: Electronic spectra of oxidised solutions of (a) Ag(tmbp)$_2$NO$_3$,
(b) Ag(daf)NO$_3$. 
Figure 5: Electronic spectrum of oxidised solution of Ag(mmbp)NO$_3$.
### TABLE III  \( \nu_{\text{max}} \) values (kK) for Ag(II) Complexes.

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<td>31.1</td>
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<td>Ag(mmbp)NO(_3)(^+)</td>
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\(^a\text{Ref. 12,} \quad ^b\text{Ref. 9b,} \quad ^c\text{In these the dominant species are Ag(bpy)NO}_3)_2 \quad \text{and} \quad \text{[Ag(phen)(NO}_3)_2]^+ (\text{Ref. 8}).
The four-coordinate species will have either planar, or more likely flattened tetrahedral structure. The distortion from planarity is expected to lower the energies of both the d-d band as well as the LMCT band. All the new complexes listed in (Table III) have considerably red-shifted LMCT band. For similar ligands the position of this band is a measure of the energy of the HOMO. Lowering of the HOMO energy is consistent with our observation that all these new species are much more unstable towards reduction. The redox potential of the stable Ag(bpy)$_2^{2+}$ is $E^0 = 1.453\, V$, whereas the present complexes are all rapidly reduced in solution implying a potential in the range 1.7 to 2.0 V.

Coming to the d-d bands, in square-planar or pseudotetrahedral geometry the highest orbital will be $d_{xy}$. The position of the remaining levels depends on the extent of the tetrahedral distortions as well as the amount of $\pi$-interactions involved. Since the degeneracy is completely removed (effective symmetry $C_{2v}$ or $D_{2h}$) four d-d transitions are expected. When the distortion is small and there is considerable $\pi$-interaction involving $d_{xz}$ and $d_{yz}$ orbitals, the lowest energy band will correspond to $d_{xz}$ or $d_{yz} + d_{xy}$ excitation. Since we observe only one broad maximum in the visible region we assign it to this transition. The $dz^2$ and $d_{x^2-y^2} + d_{xy}$ transition are most likely buried under the charge transfer band in the uv.

The d-d bands for dmbp, tmbp and mmbp complexes have considerably lower energies ($\sim 19kK$) compared to 22.0kK for the bpy complex. The red shift could be due to increased tetrahedral distortions as
well as due to the reduced ligand field provided by these ligands. The higher values of the d-d maximum for the dmp and daf complexes imply greater planarity of the coordination with these ligands. It may be noted that unlike the substituted bipyridyls the two rings in dmp and daf are constrained to remain coplanar or nearly coplanar thereby facilitating greater $d_{\pi} - p_{\pi}$ interaction. The difference in bonding involving dmbp and dmp are further discussed in sub-section 3.4 after presenting the e.s.r results.

3.3 E.s.r spectra of Ag(II) complex ions in frozen aqueous solution:

Spectra of Ag(dmbp)NO$_3$ complex oxidised to give brown coloured aqueous solutions were measured at 124 K. The first derivative spectrum (Figure 6a) shows an axial character with 6 lines in the perpendicular region and unresolved signals in the parallel region. The six line pattern suggests the presence of two equivalent nitrogen atoms coordinated to the metal. Thus there is no evidence for the formation of a bis bidentate complex with four nitrogens coordinating. The parallel region clearly shows the presence of at least three Ag(II) sites in the aqueous glass with $g_{||}$ values 2.34 (site I), 2.22 (site II) and 2.15 (site III). The site I with $g = 2.34$ corresponds to Ag$^{2+}$ aquo ion.

Figure 6b shows a spectrum of the above solution after aging the glass for a day at 77 K. The Ag$^{2+}$ aquo ion had gained in intensity. Further, two weak signals were observed at higher g values at 2.46 (site IV) and 2.58 (site V). The different sites probably involve mixed ligand complex ions like AgL(H$_2$O)$_2$$^{2+}$, Ag(H$_2$O)$_2$NO$_3^-$ and Ag(NO$_3$)$_2$H$_2$O.
Figure 6: Frozen solution e.s.r spectra of the oxidised Ag(dmbp)NO₃ complex (a) freshly prepared solution (b) on aging the glass at 77K for a day.
The high $g_{||}$ values of the weakly populated sites (IV and V) imply large orbital angular momentum induced by spin-orbit coupling which could result from greater distortion towards tetrahedron or from weak axial coordination by water or nitrate ion on an essentially planar complex.

Figure 7a shows a spectrum at 159 K for a pink aqueous solution obtained from $\text{Ag(tmbp)}_2\text{NO}_3^-$. The signals were weak because of the low concentration obtained in this case. The line pattern at $g_{||}$ is not fully resolved and $g_{\perp}$ is observed at 2.24 similar to the above complexes. An approximately six line pattern about $g_{\perp}$ can be observed suggesting the formation of $\text{Ag(tmbp)NO}_3^-$ or $\text{Ag(tmbp)(NO}_3^-)_2$ species in solution with only two equivalent nitrogens coordinating.

Figure 7b shows a spectrum of brown coloured aqueous solution of $\text{Ag(mmbp)NO}_3^+$ at 183 K. The solution shows a clear six line pattern about $g_{\perp}$ and a broad signal at $g_{||} = 2.24$ again suggesting two equivalent nitrogens coordinating to the metal ion.

Thus it can be concluded that in all cases the complex species contain only one aromatic ligand. The e.s.r. spectrum for oxidised solution of the daf complex could not be recorded as the signals were too weak.

3. 4

E.s.r. spectra of $[\text{Ag(dmbp)NO}_3^-]\text{PF}_6^-\cdot \text{NH}_4\text{PF}_6^-$ and $[\text{Ag(dmp)NO}_3^-]\text{PF}_6^-\cdot \text{NH}_4\text{PF}_6^-$. Solid $[\text{Ag(dmbp)NO}_3^-]\text{PF}_6^-\cdot \text{NH}_4\text{PF}_6^-$ and $[\text{Ag(dmp)NO}_3^-]\text{PF}_6^-\cdot \text{NH}_4\text{PF}_6^-$ complexes show highly resolved e.s.r. spectra at room temperature.

The light brown coloured complexes exhibit 8 lines
Figure 7: E.s.r spectra of the oxidised aqueous solution of (a) Ag(tmbp)$_2$NO$_3$ at 159K, (b) [Ag(mmbp)NO$_3$]$^+$ at 183K.
about \( g_\parallel \) and 7 lines about \( g_\perp \) for the dmbp complex and 8 lines about \( g_\parallel \) and 6 lines about \( g_\perp \) in the case of dmp complex. The resolution is slightly improved when the temperature is lowered (Figures 8 and 9). The former spectrum implies

\[
A_\parallel (Ag) \approx 3A_\parallel (N)
\]

and

\[
A_\perp (Ag) \approx 2A_\perp (N)
\]

while for the latter we have

\[
A_\parallel (Ag) \approx 3A_\parallel (N)
\]

and

\[
A_\perp (Ag) \approx A_\perp (N)
\]

As discussed in sub-section 2.5, the \( A_\parallel (N) \) and \( A_\perp (N) \) are related to the A and B components of nitrogen hyperfine tensor, where A is along the Ag-N bond directions, by the following relation

\[
A_\parallel (N) = B \quad \text{and} \quad A_\perp (N) = \frac{1}{\sqrt{2}}(A^2 + B^2)^{1/2}
\]

The spin Hamiltonian parameters obtained by computer simulation are given in Table IV.

3.4.1 Theoretical analysis of e.s.r. spectra:

While the symmetry of the AgN\(_2\)O\(_2\) moiety cannot be higher than \( C_{2v}(x) \), as is often the case, the electronic structure may be described in terms of \( D_{2h}\) (planar) or \( C_{2v}(z) \) (pseudotetrahedral) point groups. The higher values of the transition energies and greater delocalisation of the odd electron are responsible for the reduced
Figure 8: E.s.r spectra of the double salt (a) \((\text{AgdmbpNO}_3)\text{PF}_6\cdot\text{NH}_4\text{PF}_6\) at 112K.

The weak signals, shown by the asterisk, on the low field side of the amplified portion are probably due to a weakly populated chemically inequivalent Ag(II) site (b) Computer simulated spectrum.
Figure 9: E.s.r spectra of the double salt (a) \((\text{AgdmpNO}_3)\text{PF}_6.\text{NH}_4\text{PF}_6\)

at 149K, asterisk shows an unidentified organic radical which was present in the free ligand, dmp, superimposed on the highest-field line of the experimental spectrum.

(b) Computer simulated spectrum.
Table IV. E.s.r. parameters from computer fit spectra.

| Complex | $g_{||}$ | $g_{\perp}$ | $10^4 A_{||}^{(107,109\text{Ag})}$ (cm$^{-1}$) | $10^4 A_{\perp}^{(107,109\text{Ag})}$ (cm$^{-1}$) | $10^4 A^{(14\text{N})}$ (cm$^{-1}$) | $10^4 B^{(14\text{N})}$ (cm$^{-1}$) |
|---------|---------|-------------|---------------------------------|---------------------------------|----------------|----------------|
| $[\text{Ag(dmbp)}\text{NO}_3]\text{PF}_6 \cdot \text{NH}_4 \text{PF}_6$ | 2.165 | 2.032 | 45.0 | 30.0 | 16.0 | 14.6 |
| $[\text{Ag(dmp)}\text{NO}_3]\text{PF}_6 \cdot \text{NH}_4 \text{PF}_6$ | 2.194 | 2.037 | 47.5 | 24.0 | 25.0 | 15.8 |
anisotropy in the case of silver(II) complexes compared to similar complexes of copper(II). Among the silver(II) complexes of nitrogen heterocyclic ligands the dmp and dmbp complexes have the smallest g-anisotropy. On the other hand, they have rather small $^{14}$N hyperfine splittings. Therefore, the extensive $\sigma$- and $\pi$- delocalisation implied by the small g-anisotropy is mainly taking place into the chelating NO$_3^-$ ligand. The molecular orbital containing the odd electron (the HOMO) can be written as,

$$\Psi_1 = \beta_1 d_{xy} - \beta_1' \phi_{L1}$$

where

$$\beta_1' \phi_{L1} = C_1 \phi_{NN} + C_2 \phi_{NO_3^-} \quad \text{with} \quad C_2 > C_1^2.$$

The other molecular orbitals which are coupled to the HOMO via spin-orbit interaction are

$$\Psi_2 = \beta_2 d_{x^2} - \beta_2' \phi_{L2}$$

$$\Psi_{3,4} = \epsilon d_{xz}, yz - \epsilon' \phi_{L3, 4}$$

The experimental spin-Hamiltonian parameters can be related to the characteristics of the electronic state of the system using the Abragam-Pryce Hamiltonian.$^2$ The following equations, based on the second-order perturbation treatment, then connect the experimental numbers to the molecular parameters.

$$g_{||} - g_e = \Delta g_{||}$$

$$g_{\perp} - g_e = \Delta g_{\perp}$$

$$A_{||} = A_F + 2A_D + A_{||}^{(1)}$$

$$A_{\perp} = A_F - A_D + A_{\perp}^{(1)}$$
where $g_\text{c} = 2.0023$ is the free electron g-value. The significance of the various terms in the above equations are briefly discussed below.

(i) $\Delta g_{||}$ and $\Delta g_{\perp}$: These quantities measure the deviation of the proposed g-values from the free electron value. In an electronically non-degenerate state ($L=0$) the g-anisotropy arises due to mixing of the excited state into the ground state by spin-orbit interaction. Using perturbation theory, and retaining only terms in the first power of the interaction, these quantities are given as

$$\Delta g_{||} = -8 \left(\frac{E_{||}}{E_{||}}\right) k_{||}$$

$$\Delta g_{\perp} = -2 \left(\frac{E_{\perp}}{E_{\perp}}\right) k_{\perp}$$

where

$$E_{||} = \lambda / (E_1 - E_2)$$

$$E_{\perp} = \lambda / (E_1 - E_{3,4})$$

$E_1$, $E_2$, $E_3$ and $E_4$ are the energies of the appropriate molecular orbitals and $\lambda$ is the spin-orbit coupling constant. $k_{||}$ and $k_{\perp}$ are the covalency reduction factors which are functions of the overlap integral, $S$ and a quantity, $T$ which is related to the orbital angular momentum matrix elements of the ligand part of the molecular orbitals.

$$k_{||} = B_1^2 B_2^2 \{1 - (B_1'/B_1)S_1 - (B_1'B_2'/2B_1B_2)T\}$$

$$k_{\perp} = B_1^2 \epsilon^2 \{1 - (B_1'B_1)S_1 - (B_1' \epsilon'/2 B_1 \epsilon)T\}$$
Since \( \lambda \) is negative for a \( d^9 \) system, equations (11) and (12) imply that \( g_\| \) and \( g_\perp \) will be greater than \( g_e \). \( g_\| \) deviates from \( g_e \) due to mixing of the \( |d_{x^2-y^2}\rangle \) state, and \( g_\perp \) deviates from \( g_e \) due to mixing of \( |d_{xz}\rangle \) and \( |d_{yz}\rangle \) states into the ground state derived from \( |d_{xy}\rangle \). The deviation is proportional to the spin-orbit coupling constant and is inversely proportional to the energy separation between the ground state and the respective excited states connected by the spin-orbit interaction. Equation (13) implies that the anisotropy is reduced by covalent delocalisation. It may be noted that spin-orbit coupling due to ligand atoms is negligible due to the much smaller values of \( \lambda \) (N or O).

(ii) \( A_F \) is the Fermi contact interaction constant and it is an isotropic term contributing equally to \( A_\| \) and \( A_\perp \). This interaction arises due to the presence of unpaired electron (spin) density, \( \phi_{\text{spin}}(O)^2 \), at the nuclei. \( \phi_{\text{spin}}(O) \) can be either due to s contribution (5s in the case of Ag) to the HOMO via configuration interaction or, more importantly, due to core polarisation. In simple terms polarisation of the inner s-shells takes place because the unpaired electron in 4d orbital (\( \uparrow \) spin) repels one of the two electrons (the \( \uparrow \) spin electron) in the s-shell less than the other. In other words the exchange interaction between the electrons having identical spins (\( \uparrow \) or \( \alpha \)) leaves a net \( \uparrow \) spin density at the nucleus. The contact contribution is given as,

\[
A_F = \frac{8\pi}{3} g_e E_e q_n^2 \sum (|\phi_\uparrow(0)|^2 - |\phi_\downarrow(0)|^2)
\]

...14,
Where \( g_e \) and \( g_n \) are electronic and nuclear Lande factors, and \( \beta_e \) and \( \beta_n \) are electronic and nuclear Bohr magnetons respectively.

For convenience, we define,
\[
\beta_1^2 \kappa = -\frac{\hbar^2}{3m^2} \left\{ |\phi_1(0)|^2 - |\phi_4(0)|^2 \right\} <r^{-3}>_{dxy}
\]
and
\[
P = g_e \beta_e g_n \beta_n <r^{-3}>_{dxy}
\]
so that,
\[
A_F = -\beta_1^2 P \kappa
\]
It is clear that in the free atom or ion (i.e., in the absence of covalency) \( A_F = -P \kappa \). Both \( P \) and \( \kappa \) can be obtained for atoms and ions by unrestricted Hartree-Fock calculations. Accurate calculations for molecules are more involved, and approximation methods like X-α have been used for this purpose with some success.

(iii) \( A_D \) is the dipolar contribution to hyperfine splitting and is primarily responsible for the anisotropy in the observed splittings. Its value depends on the \( d \)-orbital containing the unpaired electron. For the present case (dxy ground state), we have
\[
A_D = (-2/7) \beta_1^2 P
\]
Here again, covalency reduces the anisotropy due to the factor \( \beta_1^2 <1> \) in equation (18), and also due to the reduction in the value of \( P \). \( P \) is reduced by covalency because the \( d \) orbital becomes more diffuse due to reduction in effective nuclear charge of the metal.

(iv) \( A_{||}^{(1)} \) and \( A_{\perp}^{(1)} \) are the first order corrections to hyperfine splitting due to spin-orbit interaction. These corrections are related to the \( g \)-anisotropy by the following equation,
\( A^{(1)}_{||} = (\Delta g_{||} + 3/7 \Delta g_{\perp})^P = -8E_{||} P B_1^2 B_2^2 - (6/7) E_{\perp} P B_1^2 \epsilon^2 \) \ldots 19.

\( A^{(1)}_{\perp} = \frac{11}{14} \Delta g_{\perp} P = (-22/14) E_{\perp} P B_1^2 \epsilon^2 \) \ldots 20.

3.4.2

Interpretation of e.s.r. parameters of Ag(II) complexes of heteroaromatic ligands:

Using equation (10) all the bonding parameters for the Ag(II) complexes listed in Table V, have been calculated and are tabulated in Table VI. It is seen that the odd electron is delocalised to the extent of 35-50\%.

There is also extensive \( \pi \) -interaction involving \( d_{xz} \) and \( d_{yz} \) orbitals.

The lower values of the d-d transition energies for the dmbp complex imply a greater tetrahedral distortion compared to the dmp complex.

This distortion as well as a possible twisting of the bipyridyl ligand about the C-C single bond will considerably relieve the steric strain in Ag(dmbp)NO\(_3\)\(^+\). A greater degree of metal-ligand interaction is therefore expected and it is reflected in the lesser value of \( B_1^2 \) for this compound. The Fermi contact contribution to hyperfine splitting varies from 0.0033 to 0.0041 cm\(^{-1}\) for the systems listed in Table VI.

The contact interaction is very sensitive to 5s contribution which in turn is usually a strong function of metal-ligand bond length\(^3\). In the absence of structural data and theoretical estimates no attempt will be made here to explain the observed variation in \( A_F \).

Coming to the nitrogen hyperfine splitting, the two components, \( A \) and \( B \) can be written as,

\[
A = f_{\sigma s} a_s + 2f_{\sigma p} a_p + 2A_D'
\]

\[
B = f_{\sigma s} a_s - f_{\sigma p} a_p - A_D'
\]

\ldots 21.
Table V. E.s.r. parameters for Ag(II) Complexes.

| Complex | $g_{||}$ | $g_{\perp}$ | $A_{||}$(Ag) | $A_{\perp}$(Ag) | A(N) | B(N) | $E_{xy}$ (kK) | $E_{xz,yz}$ (kK) | Ref. |
|---------|---------|-------------|---------------|-----------------|------|------|--------------|----------------|------|
| [Ag(dmbp)NO$_3$]PF$_6$·NH$_4$PF$_6$ | 2.165   | 2.032       | 45.0          | 30.0            | 16.0 | 14.6 | 30.4         | 18.9           | this work |
| [Ag(dmp)NO$_3$]PF$_6$·NH$_4$PF$_6$ | 2.192   | 2.031       | 47.5          | 24.0            | 25.0 | 15.8 | 31.1         | 23.5           | this work |
| Ag(bpy)$_2$S$_2$O$_8$ | 2.210   | 2.047       | 42.2          | 26.0            | 21.1 | 30.1 | 28.0         | 22.0           | 14b, 12 |
| Ag(phen)(NO$_3$)$_2$ | 2.214   | 2.048       | 34.0          | 23.5            | 23.5 | 20.5 | 31.1         | 25.6           | 8, 9b  |
| Ag(py)$_4$S$_2$O$_8$/Cd(py)$_4$S$_2$O$_8$ (A) | 2.204   | 2.042       | 18.0          | 34.5            | 21.0 | 19.6 | 22.0         | 20.4           | 8, 4n  |
| Ag(py)$_4$S$_2$O$_8$/Cd(py)$_4$S$_2$O$_8$ (B) | 2.18    | 2.04        | 34.0          | 22.0            | 17.0 | 22.0 | 22.0         | 22.0           | 37, 4n |
Table VI: Calculated bonding parameters\(^a\):

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\Delta q\parallel)</th>
<th>(\Delta q\perp)</th>
<th>(10^{-3} E_{xy})</th>
<th>(10^{-3} E_{xz,yz})</th>
<th>(10^{4} A_{F})</th>
<th>(10^{4} A_{D})</th>
<th>(10^{4} A^{(1)})</th>
<th>(10^{4} A^{(1)})</th>
<th>(\beta_1^2)</th>
<th>(\beta_2^2)</th>
<th>(\epsilon^2)</th>
<th>(\kappa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(dmbp)NO(<em>3)](</em>{6})PF(_6) · NH(_4)PF(_6)</td>
<td>0.163</td>
<td>0.030</td>
<td>30.4</td>
<td>18.9</td>
<td>41.1</td>
<td>8.9</td>
<td>-13.9</td>
<td>-2.2</td>
<td>0.49</td>
<td>0.84</td>
<td>0.46</td>
<td>1.32</td>
</tr>
<tr>
<td>[Ag(dmp)NO(<em>3)](</em>{6})PF(_6) · NH(_4)PF(_6)</td>
<td>0.192</td>
<td>0.035</td>
<td>31.1</td>
<td>23.5</td>
<td>38.6</td>
<td>12.3</td>
<td>-15.6</td>
<td>-2.2</td>
<td>0.68</td>
<td>0.71</td>
<td>0.42</td>
<td>0.896</td>
</tr>
<tr>
<td>[Ag(bpy)(_2)]S(_2)O(_8)</td>
<td>0.208</td>
<td>0.045</td>
<td>28.0</td>
<td>22.0</td>
<td>39.0</td>
<td>10.1</td>
<td>-17.3</td>
<td>-2.9</td>
<td>0.56</td>
<td>0.84</td>
<td>0.62</td>
<td>1.10</td>
</tr>
<tr>
<td>(in frozen HNO(_3))</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Ag(phen)(NO(_3))(_2)</td>
<td>0.212</td>
<td>0.046</td>
<td>31.1</td>
<td>25.6</td>
<td>34.4</td>
<td>8.1</td>
<td>-14.9</td>
<td>-2.8</td>
<td>0.65</td>
<td>1.00</td>
<td>0.89</td>
<td>1.22</td>
</tr>
<tr>
<td>(in frozen HNO(_3))</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ag(py)(_4)]S(_2)O(_8)/Cd(py)(_4)]S(_2)O(_8)</td>
<td>(A)</td>
<td>0.202</td>
<td>0.040</td>
<td>22.0</td>
<td>20.4</td>
<td>-16.4</td>
<td>18.0</td>
<td>-16.8</td>
<td>-2.1</td>
<td>1.00</td>
<td>0.24</td>
<td>-0.228</td>
</tr>
<tr>
<td>(B)</td>
<td>0.178</td>
<td>0.038</td>
<td>22.0</td>
<td>20.4</td>
<td>33.0</td>
<td>8.5</td>
<td>-16.0</td>
<td>-2.6</td>
<td>0.47</td>
<td>0.74</td>
<td>0.62</td>
<td>1.12</td>
</tr>
<tr>
<td>Ag(TPP)/H(_2)O/Zn(TPP)(^C)</td>
<td>0.106</td>
<td>0.035</td>
<td>36.7</td>
<td>43.7</td>
<td>48.1</td>
<td>12.0</td>
<td>-9.6</td>
<td>-2.1</td>
<td>0.66</td>
<td>0.51</td>
<td>0.74</td>
<td>1.15</td>
</tr>
</tbody>
</table>

\(^a\)Calculated with \(\lambda = -1840\) cm\(^{-1}\), \(P = -63.0 \times 10^{-4}\) cm\(^{-1}\), \(S_1 = 0.1\), \(S_2 = 0.0\), \(S_{\lambda,4} = 0.05\), \(T = 0.33\), \(A_\parallel\), \(A_\perp\) were taken to be positive, except for Ag(py)\(_4\)]S\(_2\)O\(_8\)/Cd(py)\(_4\)]S\(_2\)O\(_8\) (A) for which the results quoted are for \(A_\parallel > 0\), \(A_\perp < 0\).

\(^b\)Not physically meaningful. Other combinations for \(A_\parallel\) and \(A_\perp\) also fail to give meaningful results.

\(^C\)Ref. 35(e.s.r, ENDOR), ref. 56 (theoretical estimates of transition energies).
where \( a_s = (8\pi/3)gB_0B_n|\Psi_0|^2 \) and \( a_p = (2/5)gB_0B_n\langle r^{-3}\rangle_{2p} \),

the atomic values being 0.05179 cm\(^{-1}\) and 0.00155 cm\(^{-1}\) respectively\(^{33}\).

The correction due to direct dipolar interaction \( A_D \) is of the order of 1 \( \times 10^{-5} \) cm\(^{-1}\) and can be neglected. The quantities \( f_{os} \) and \( f_{op} \) are the 2s and 2p\(_o\) electron densities for the HOMO. This data has often been used in the past to estimate the \( s:p \) hybridisation ratio for the nitrogen \( \sigma \) orbital and even to calculate bond angles\(^{14b}\). However, the ratio depends on the difference, \( A - B \), which, due to the proximity of \( A \) and \( B \) will often be subject to large errors. Further, the appreciable difference in the energies of 2s and 2p and also any significant core polarisation in the bonded nitrogen atom can further complicate the analysis. For \( \text{Ag(dmbp)NO}_3^+ \) and \( \text{Ag(dmp)NO}_3^- \) we get 1.0 and 0.2 respectively for the ratio \( f_{os}/f_{op} \). The small \( s:p \) ratio for the dmp complex is evident in the unusually high anisotropy in the nitrogen hyperfine splitting. We postulate that the large \( p \) contribution relative to \( s \) is due to a much longer Ag-N bond which favours greater interaction of the silver \( \sigma \) orbitals with the nitrogen 2p\(_o\) orbital compared to the less diffuse 2s component.

A good system to compare with the simple N-heterocyclic ligands is porphyrins, which readily induce disproportionation of silver (I) forming silver (II) complexes with square-planar N\(_4\) coordination. Single crystal ENDOR studies on \( \text{Ag(TPP)} \) doped into \( (\text{H}_2\text{O})\text{Zn(TPP)} \) yielded very accurate metal and ligand hyperfine tensors for this system\(^{35}\). Subsequently, \( \chi_\alpha - \) calculations have also been reported\(^{36}\). The data from our analysis of the g and \(^{109}\)Ag hyperfine splitting are included in (Table VI). It has been pointed out that first order
perturbation treatment of g and metal hyperfine tensors gives less reliable bonding parameters than a zeroth order analysis of the $^{14}$N hyperfine data, and the latter procedure is to be preferred whenever precise $^{14}$N coupling parameters are available$^{35}$. We do find that the bonding coefficients are sensitive to transition energies. The low value of $B_2^2$ (0.51) implying greater in-plane $\pi$-bonding than $\sigma$-and out-of-plane $\pi$-bonding is unrealistic. $B_2^2$ is raised to 0.75 when $E_{xy}$ is raised by about 50%, while the other coefficients are not significantly modified. What is clear from the comparison of data in (Table VI) is that the higher values of d-d transition energies in Ag(TPP) compared to other compounds are responsible for its lower g-anisotropy as well as the reduced magnitude of spin-orbit contribution to hyperfine splitting ($A_||^{(1)}$ and $A_{\perp}^{(1)}$). Since the latter contributions are negative, the experimental hyperfine splitting values are considerably higher for Ag(TPP).

Finally, it may be mentioned that the recent analysis$^8$ of the Ag/Cd(py)$_2$S$_2$O$_8$ is likely to be in error with regard to the silver hyperfine splittings because their assignment leads to unreasonable bonding parameters and a negative $A_F$ (Table VI). We tend to favour the earlier analysis$^{37}$. The difference between the two lies in counting the number of lines in the parallel region of the spectrum where 10 lines are expected if $A_||^{(Ag)} = A_||^{(N)}$, and 11 lines if $A_||^{(Ag)} = 2A_||^{(N)}$. However, we agree with Evans et al.$^8$ that the nitrogen hyperfine splittings$^{37}$ have to be revised. The revised values are also included in (Table VI).

E.s.r spectra of undiluted solid bivalent silver complexes:

The dark brown coloured solids which precipitated on oxidation of
the AgL(NO$_3$)$_3$ complexes showed ESR spectra corresponding to magnetically concentrated systems with rhombic g-tensor. The line widths are about 40 G implying that magnetic exchange interaction frequency is greater than 10$^7$ - 10$^9$ Ag hyperfine frequency ~ 150 MHz. They are shown in Figures (10) and (11). Figure 10(a) and (b) show the spectrum of Ag(dmbp)(NO$_3$)$_2$ and Ag(dmp)(NO$_3$)$_2$ respectively. The asterisk shows the presence of an unidentified organic radical which was seen also in the ligand. g values are $g_1$=2.142, $g_2$=2.083 and $g_3$=2.047 for the dmbp complex and $g_{||}$=2.193 and $g_{\perp}$=2.048 for dmp complex.

Figures 11a, b and c show the spectra of [AgL(NO)$_3$]PF$_6$, where L=mmbp, bpx and daf-one respectively. Figure 11c shows the spectrum of [Ag(daf-one)NO$_3$]PF$_6$. In this spectrum an organic radical is present at $g$ = 2.0. The anisotropic spectrum of Ag(II) was found to reduce in intensity on keeping the complex for a few days whereas the intensity of the organic radical increased. The radical is probably the anion radical

![Diagram](image-url)

which is analogous to 38

![Diagram](image-url)

Na$^+$
Figure 10: E.s.r spectra of solid complexes at room temperature (a) Ag(dmbp)(NO$_3$)$_2$ (b) Ag(dmp)(NO$_3$)$_2$, asterisk shows the signal from an unidentified radical.
Figure 11: E.s.r spectra of solid complexes \([\text{AgLNO}_3]PF_6\) at room temperature
(a) \(L=\text{mmbp}\), (b) bpy (c) daf-one,
the asterisk shows an unidentified organic radical.
The experimental g-values for Ag(mmbp)NO$_3$PF$_6$ are $g_{||}$ = 2.18 and $g_{\perp}$ = 2.049, and for the daf-one complex $g_{||}$ = 2.16 and $g_{\perp}$ = 2.045.

3.6 Observations on the solid state electron-transfer in [Ag(dmbp)NO$_3$]PF$_6$·NH$_4$PF$_6$ Formation of the hitherto unknown PF$_6^-$ radical (?):–

The highly resolved spectra from Ag(II) sites in the double salts shown in Figures 8 and 9 are observed only in freshly prepared samples. If the sample is exposed to the atmosphere it quickly takes up moisture and no e.s.r signal is seen after a few minutes. Even when sealed under dry nitrogen the signal intensity goes down drastically over a period of several days. In the case of [Ag(dmbp)NO$_3$]PF$_6$·NH$_4$PF$_6$, while the Ag(II) signal intensity decreases, a large number of new e.s.r lines are seen to appear on the wings of the Ag(II) spectrum, which continue to grow in intensity. Finally when the Ag(II) signals have completely disappeared the spectrum consists of large number of narrow (width = 8 G) lines spread over the field region 1000 G to 5800 G, as shown in Figure 12. The spectral width (~ 5000G) allows us to exclude the possibility of a nitrogen containing radical or silver atom cluster as possible centres responsible for this spectrum. While the pattern in Figure 12 is uninterpretable, we propose that the signals arise from one or more radicals containing P and F atoms. The most reasonable candidate is the PF$_6^-$ radical formed by the electron transfer reaction,

$$\text{PF}_6^- + \text{Ag(dmbp)NO}_3^- \rightarrow \text{PF}_6 + \text{Ag(dmbp)NO}_3$$ ...

This radical is unknown in the literature. The mechanism of formation viz., electron capture by a transition metal ion in an unstable oxidation...
Figure 12: ESR spectra of radicals observed over the field region 1000G to 5800G. Insert shows enlarged field from 2000G to 2500G.
state is also unusual, if not unknown. The most popular method to prepare inorganic radicals is radiation damage of solids using uv, x-ray or γ-ray radiation. In the next sub-section the literature pertaining to radicals observed in \( \text{PF}_6^- \) salts by γ-irradiation is reviewed.

3.6.1 Review of the literature on radicals derived from \( \text{PF}_6^- \) salts:

A survey of the literature suggested the formation of different radicals with the salts of \( \text{PF}_6^- \) ion. These salts are sometimes referred to as 'rotator solids' at room temperature due to the free rotation of the octahedral \( \text{PF}_6^- \) ion in the lattice. Upon γ-irradiation they give isotropic e.s.r. spectra. \( \text{NH}_4\text{PF}_6 \) and \( \text{KPF}_6 \) on γ-irradiation were reported to generate \( \text{FPPO}_2^-\text{PO}_3^2^- \) and \( \text{PF}_4^- \) radicals. The signals assigned to \( \text{PF}_4^- \) were later shown to be due to \( \text{PF}_5^- \). However the spread of the whole spectrum was only 1500 G with the lines split into interpretable spacings as shown in Figure 13. But it was stated that on γ-irradiation of single crystals of \( \text{NH}_4\text{PF}_6 \) uninterpretable spectrum was observed at low temperatures which was speculated to be due to different fragments taking up random orientations. Later the same authors have verified the formation of \( \text{PF}_5^- \) in place of \( \text{PF}_4^- \). However, there was no mention of the uninterpretable low temperature spectrum in the recent publication on γ-irradiated \( \text{KPF}_6 \) and \( \text{KAsF}_6 \). They have reported the formation of \( \text{PF}_5^- \), \( \text{FPPO}_2^- \), a geometrical isomer of \( \text{PF}_4^-\text{PF}_3\text{O}_6 \) or a possible alternative \( \text{PF}_5\text{O}(\text{OH})\text{eq}^- \) in which hyperfine splitting due to the hydroxyllic proton is unresolved. Weak spectra detected were assigned to geometrical isomers \( \text{PF}_4\text{O}^{2-}_\text{ap} \) and \( \text{PF}_4\text{O}^{2-}_\text{bs} \) of \( \text{PF}_5^- \) species. Another \( \text{PF}_4\text{O}(\text{OH})\text{eq}^- \) was also thought to be isostructural to \( \text{PF}_5^- \), where ap = apical,
Figure 13. The e.s.r. spectrum of a γ -irradiated single crystal of NH₄PF₆. The three radicals produced have been attributed to PF₄⁻, FPO₂⁻, and PO₃⁻. The splittings of the PF₄ lines are due to second-order interactions. [Ref.41(a).] Here J(F) refers to the total fluorine nuclear spin quantum number in the coupled representation.
eq = equatorial and bs = basal position.

We could not assign any of the lines in the observed spectrum to the above mentioned radicals. In the next sub-section some of the experiments performed in an attempt to simplify the spectrum are discussed.

3.6.2 Attempts to simplify the spectrum:

In Fig. 14, repetitive scan at lower modulation with different scan times are shown to check the reproducibility of the pattern. Figure 15 shows the 2900-3100 G region of the spectrum scanned at different scan times which show reproducibility of all the sharp lines. Figure 16 shows a spectrum at 2975-3025 G region with 32 mts. scan time along with an immediately repeated spectrum with almost all features reproduced.

Figure 17 shows spectra at 2000-2500 G at lower modulation with different scan times. From these studies we observed that the pattern is essentially reproducible if low modulations and long scan times (or small time constant) are employed. However, the pattern was found to change slowly as a function of time over several hours. The reason for this is not clear. One plausible explanation is modulation of the spectrum by very slow dynamics of the radical species.

The following experiments were carried out with a view to simplify the spectrum:

(a) The sample in the sealed tube was heated at about 60°C hoping to get a simpler isotropic spectrum. Eventhough there was no marked change in the clarity of the spectrum the exact details of the pattern had changed,
Figure 14: E.s.r spectrum of radical at lower modulation and different scan times.
Figure 15: E.S.R. spectrum of radical at 2900 - 3100 GHz region.
Figure 16: E.s.r. spectrum of radical at 2975-3025G region.
Figure 17: E.s.r spectrum of radical at 2000-2500G region.
(b) The sample was removed from the sealed tube and powdered and was sealed back. However, there was no change in the complexity of the pattern,

(c) high temperature e.s.r. spectra were observed at every 10°C raise in the temperature. The complex uninterpretable spectrum was observed up to about 110°C and above that no signals were observed. At 150°C the sample had already melted and no signals were recovered on cooling,

(d) there was essentially no change upon cooling the sample to LNT,

(e) annealing of the sample for about 6-8 hours at 100°C produced no change in the spectrum.

(f) the sealed quartz tubes preserved in the dark at room temperature containing the sample were observed for several weeks. Eventually the radical faded and the tube was found to be etched suggesting the formation of some elemental fluorine. We have also observed etching of quartz tube on heating NH₄PF₆ on flame for a few minutes,

(g) Analysis of the final product for PF₅ was not considered practical due to the small concentrations expected.

(h) We attempted to prepare the PF₆ salt of the more stable Ag(bpy)₂⁺ ion. However, the solid obtained by adding NH₄PF₆ to Ag(bpy)₂NO₃ in nitric acid in presence of (NH₄)₂S₂O₈ gave a magnetically concentrated e.s.r. spectrum with g₁ = g₂ = 2.174 and g₃ = 2.044 (Figure 11b) we could not observe any formation of radicals
even on heating the sample or annealing it. Nor was there any change in the bright orange colour of the sample.

The double salt of dmp, did not give the radical signals. The Aq(II) spectra in it decayed with time but no new paramagnetic species was observed other than the single line of the organic radical which it initially contained (Figure 9). It is likely that the organic radical impurity destroyed any new radical formed by electron transfer. Attempts to purify the dmp ligand by recrystallisation from methanol were not successful.

3. 6. 3 The PF₆ radical:

The PF₆ radical is interesting because it is expected to have an electronically degenerate ground state. One reason it has been eluding detection is the potential instability of the electronic state. Y-irradiation is expected to provide sufficient energy to dissociate one F atom from PF₆⁻ leading to PF₅⁻. Any PF₆⁻ formed by irradiation will also have sufficient kinetic energy to loose a fluorine atom to give the stable PF₅ molecule.

An energy level diagram for the PF₆⁻ obtained using the Extended Hückel molecular orbital (EHMO) method is shown in Figure 18. It is seen that the ground state is \( 2T_{1g} \), and there are three more degenerate states within about 2800 cm⁻¹ of the ground state. The total energy vs distortion along an \( e_g \) mode was found to have a very shallow minimum. The vibronic interactions are expected to be complicated by multimode coupling effects. No attempt will be made here to treat this problem here. However, the above obser-
Figure 18. Energy level diagram for the PF$_6$ radical.
vations show a possible method to search for PF₆⁻ radical in other systems, preferably in single crystals, where Ag²⁺ sites with a high redox potential is in proximity of a PF₆⁻ ion for a facile electron transfer to occur.

3.7 Comparison between Copper and Silver complexes of hindered ligands:

The bidentate N-heterocyclic ligands increased the Cu⁺ / Cu²⁺ potential from 0.167 V to 0.251 V in the case of bpy and to ≫ 0.75 V for dmbp. The same ligands reduce the Ag⁺ / Ag²⁺ potential from 1.9 V to 1.45 V (bpy) and to ≫ 1.7 V (dmbp,dmp). The major reason for the increase of the Cu⁺ / Cu²⁺ potential is the tetrahedral distortion of the CuL₂⁺ ions, especially for the hindered ligands. The unhindered ligands tend to form cis-octahedral CuL₂(H₂O)₂²⁺ species in aqueous solution which lowers the potential. On the other hand, the reduction in the Ag⁺ / Ag²⁺ potential appears to be due to the extensive delocalisation of charge via π-bonding interaction. Here again the tetrahedral distortion in the case of dmbp and dmp complexes tend to raise the potential.