E.P.R. determination of the hybridisation and the H-N-H bond angle of ammonia in 
[Cu(NH3)4][PtCl4]

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Fritz and Keller¹ have made a very detailed investigation of the e.p.r. parameters of [Cu(NH3)4] 
[PtCl4] substituted in the host lattice of M a g n u s's salt [Pt(NH3)4][PtCl4]. From the g-tensor and the metal hyperfine coupling tensor, the bonding parameters have been obtained. In this note, I wish to point out an error in the analysis of the nitrogen superhyperfine tensor deduced from the powder, and with the modified values, show that the interaction of the unpaired electron with the nitrogen atom of the ammonia ligands may give information about the hybridisation of the nitrogen lone pair electrons and hence the H — N — H bond angle.

The [Cu(NH3)4]²⁺ ion has strictly square planar symmetry in this lattice (ignoring the hydrogen atoms). In D4h symmetry, when the applied field lies parallel to the z-axis, the nitrogen superhyperfine splittings observed are B(14N) since the principal directions of the ¹⁴N tensor lie parallel to the Cu — N bonds. Likewise, the features attributable to ¹¹N when the applied field is perpendicular to the z-axis are not B(15N). When the applied field is parallel to the x-axis, two nitrogen atoms along the x-axis contribute to A(h4N) but the other two, along the y-axis, contribute to B(h4N). A similar argument applies when the field is along y. Hence the turning points of the powder spectrum occur at ² (A + B). The superhyperfine splittings measured by Fritz and Keller from their powder spectrum were A = 10.5 ± 10⁻⁴ cm⁻¹ and B = 13 ± 10⁻⁴ cm⁻¹. These measured values were reassigned as follows: B = 10.5 ± 10⁻⁴ cm⁻¹ (≡ 10.2 gauss) and ² (A + B) = 13 ± 10⁻⁴ cm⁻¹ (≡ 15.6 gauss), from which A — 17.0, B = 10.2 and A_D = 12.5 gauss. The dipolar interaction of the tensor must be subtracted (using the point-dipole approximation, A_d = 2RSR² = 0.47 gauss, where r is the Cu — N distance). The principal value of the ¹⁴N superhyperfine tensor is thus 4.0 gauss.

The 2 p-character of the unpaired electron c_p² = 34.1
= 11.7% and the 2 s-character c_s² = 12.5
550 = 2.3 per cent.²

The unpaired electron has been shown to lie in the ¹⁴N molecular orbital whose wavefunction is
Ψ = b¹⁴N + ² (d_x² — y²) — ² (a₁ + a₂ + a₃ + a₄).

(1)

The corresponding bonding molecular orbital is given by
Ψ = b¹⁴N + ² (d_x² — y²) — ² (a₁ + a₂ + a₃ + a₄).

(2)

Since all four nitrogen atoms are equivalent, the wavefunctions of the lone-pair electrons on the nitrogen atoms of the NH₃ group are equal, thus
a₁ = a₂ = a₃ = a₄ = 0 .

(3)

The wavefunction of σ is itself a linear combination

σ = c₆Ψ₂₂ + c₉Ψ₂₂,

(4)

where Ψ₂₂ and Ψ₂₂ are the nitrogen 2 s and 2 p orbitals from which the hybridisation σ_p² may be deduced, viz.

n = ² = c₆² / c_s² .

(5)

Coulson⁴ has shown that if one assumes that the bonds formed from hybridisation of s- and p-orbitals on an atom are orthogonal to each other, then it is possible to estimate the bond angle from the hybridisation ratio. For ligands like NH₃ with C₃v symmetry, the bond angle H — N — H (σ) is given by

\cos \theta = \frac{1.5}{2} ± 3 - \frac{1}{2} .

(6)

In the case of [Cu(NH3)4][PtCl4], t² = 5.1 and it follows that H — N — H = 112° 45'.

This value is greater than that for NH₃ (107°). An increase of this magnitude is to be expected since the lone pair electrons will be further away from the nitrogen atom because Cu²⁺ is more electronegative. This decreases the Cu — N bond-pair — N — H bond-pair repulsion and allows the H — N — H bond angle to relax.

It should be emphasised that this method of calculating bond angles from the spin distribution of unpaired electrons is only applicable if the wave function of the unpaired electron is related to the wavefunction of the bonding electrons. This is so in this case because corresponding bonding and antibonding orbitals are involved. The importance of this simple method of determining bond angles is highlighted by the experimental difficulties of measuring such bond angles in this type of complex by neutron diffraction techniques.