JOURNAL OF MAGNETIC RESONANCE **34**, 97–102 (1979)

Proton Resonance and Structure of Nickel Hexammine Chloride

I. SVARE AND S. M. SKJÆVELAND*

Physics Department, University of Trondheim NTH, Trondheim, Norway

Received May 2, 1978; revised July 31, 1978

Proton line splittings in single crystals of $Ni(NH_3)_6Cl_2$ measured down to liquid helium temperatures give the H–H distance 1.70 Å, the Ni–H distance 2.80 Å, the antiferromagnetic Neel temperature $T_N = 1.47$ K and the extrapolated Curie temperature $\theta_C = -9.6$ K.

1. INTRODUCTION

Nickel hexammine chloride $Ni(NH_3)_6Cl_2$ belongs to a large class of isostructural compounds where Ni^{2+} can be replaced by Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, etc., and Cl^- by Br^-, I^-, BF_4^-, ClO_4^-, etc. The hexammines are generally cubic at room temperature, and this is possible only because of very rapid rotation of the NH_3 ligands around their symmetry axes since the triangular NH_3 groups do not fit well into their square surroundings. At lower temperature the Coulomb interaction between the NH_3 multipoles will lock them together in an ordered and structurally distorted phase (*1, 2*). But the distortion of $Ni(NH_3)_6Cl_2$ at $T_c \approx 80$ K is not large enough to crack good single crystals. The phase transition can be seen as a large broadening of the Ni^{2+} EPR line (*3, 4, 5, 6*) and in thermal properties (*7, 8*).

Low temperature proton NMR in powdered $Ni(NH_3)_6Cl_2$ has been studied by Kim (*9*) but the broad line gave limited information. In a single crystal, however, the line splits into several sharp components due to H–H and H–Ni^{2+} dipolar interaction. From the line shapes and splittings we get information about $Ni(NH_3)_6^{2+}$ structure and motion which may be of value until more precise data from X-ray or neutron diffraction becomes available. The proton lines disappear at about 1.5 K because of antiferromagnetic ordering in $Ni(NH_3)_6Cl_2$.

2. MEASUREMENTS

The face-centered cubic structure of $Ni(NH_3)_6Cl_2$ has the lattice constant $a_0 = 10.064$ Å (*10*). The $Ni(NH_3)_6^{2+}$ octahedron is shown in Fig. 1 with the usual ionic radii 0.72 Å for Ni^{2+} and 1.71 Å for N^{3-}. From these radii we expect a Ni-N distance of about 2.43 Å, but it is said to be 2.136 Å in unpublished work by Langford and Thomas, quoted by Bates *et al.* (*11*). The NH_3 dimensions in the salt are probably

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* Now at Rogaland Distriktshøgskole, Stavanger, Norway.

0022-2364/79/040097-06$02.00/0

Printed in Great Britain

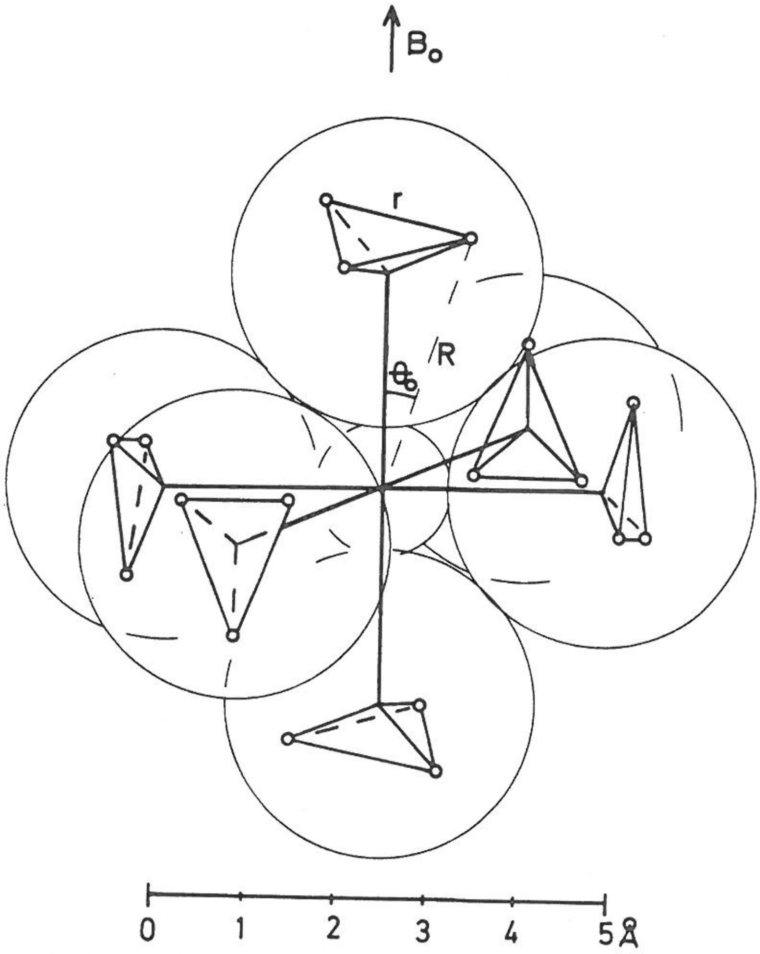

FIG. 1. The $Ni(NH_3)_6{}^{2+}$ octahedron in hexammines drawn with ionic radii 0.72 Å for Ni^{2+} and 1.71 for N^{3-} and approximate size of hydrogen triangles.

close to those of free ammonia where the H–H distance is 1.63 Å and the N–H-plane distance is 0.38 Å (*9*).

The NH_3 groups are rotating rapidly around their symmetry axes even at low temperature, as can be seen from the tunnelling hydrogen isotope effect in the heat capacity (*12*, *13*). The tunnel splitting is of the order 10^9 Hz.

Proton NMR line shapes in single crystals of $Ni(NH_3)_6Cl_2$ were measured with a Robinson type marginal oscillator and a Varian Fieldial controlled magnet. Temperatures in the liquid He or N_2 range were measured from the stabilized gas pressures with a Baratron gauge, above 4.2 K with carbon and Ge resistors during very slow warming, and above 73 K with a Comark thermocouple meter.

Low temperature measurements of resonance line derivatives at $f_0 = 17.75$ MHz with $\mathbf{B}_0$ along [100] as in Fig. 1 are shown in Fig. 2. The average moment $\bar{\mu} = \chi B_0/N$ on each Ni^{2+} ion splits the line in two main components of relative intensities 1:2.

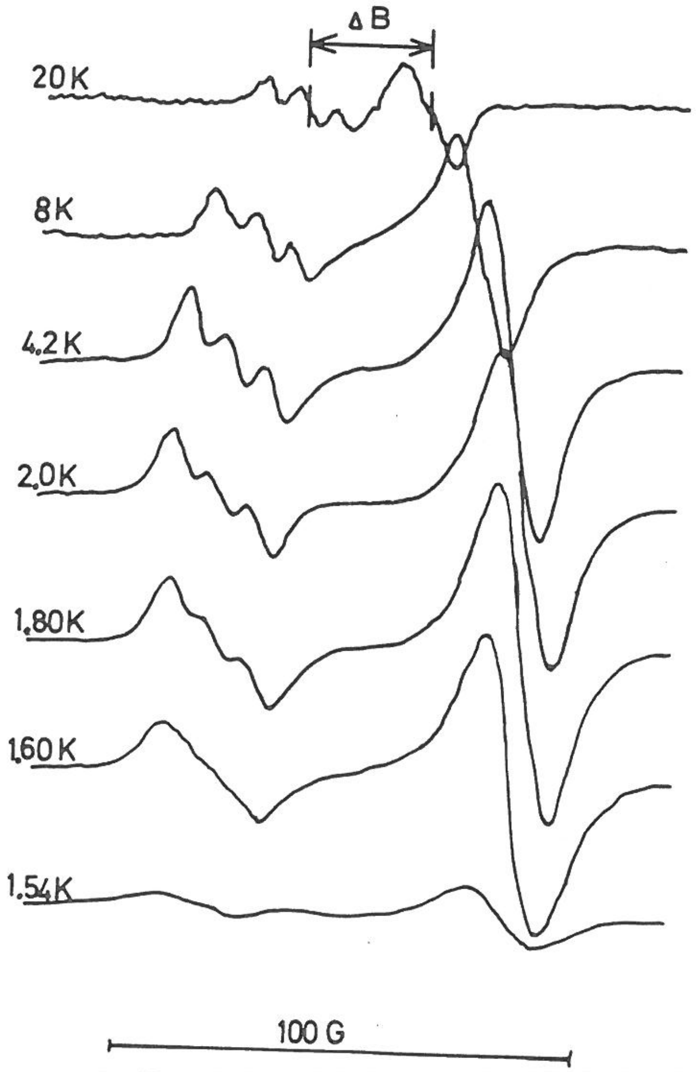

FIG. 2. Proton resonance at 17.75 MHz in $Ni(NH_3)_6Cl_2$ with $\mathbf{B}_0 \parallel [100]$ at some low temperatures.

The weaker, low-field line comes from the two ammonias with $\mathbf{B}_0$ along the Ni–NH_3 direction, and its dipolar shift due to the nearest Ni^{2+} is

$$\Delta B_{\mathrm{NiH}}(-) = -(\mu_0/4\pi)\bar{\mu}(3\cos^2\theta_0 - 1)R^{-3} \qquad [1]$$

Here R is the Ni–H vector making the angle θ_0 with $\mathbf{B}_0$, and $\mu_0 = 4\pi \cdot 10^{-7}$ in SI units. The stronger high-field line comes from the four ammonias with $\mathbf{B}_0$ perpendicular to the Ni–NH_3 direction, and its dipolar shift due to the nearest Ni^{2+} is approximately

$$\Delta B_{\mathrm{NiH}}(+) \approx (\mu_0/4\pi)\bar{\mu}[\tfrac{3}{2}\cos^2(90^\circ - \theta_0) - 1]R^{-3} \qquad [2]$$

when we assume rapid rotation of the NH_3 groups around their symmetry axes. We have computed the dipolar shifts from more distant Ni^{2+} ions out to 40 Å to give a correction factor to $\Delta B_{NiH}(-)$ and $\Delta B_{NiH}(+)$ of about $C = 0.90$ dependent upon R. Isotropic exchange Ni–H would shift the lines by equal amounts and not influence the splitting between the high- and the low-field line.

The low-field line has a further fine structure with $\Delta B_{HH} = 8.5 \pm 0.5$ G between components of relative intensities 1 : 2 : 1. This is caused by the dipolar interaction between the protons in a NH_3 group which form a triangle of sides r in a plane perpendicular to B_0. The splitting is

$$\Delta B_{HH} = (\mu_0/4\pi)(3\gamma\hbar/2r^3) \qquad [3]$$

independent of possible rotation of NH_3 around its symmetry axis. From Eq. [3] and the measured splitting we calculate $r = 1.70 \pm 0.03$ Å. The distortion below T_c of the hexammine structure away from cubic symmetry must be rather small for this fine splitting to be so sharp.

The stronger, high-field line is also in principle split by $(\Delta B_{HH}/2) = 4.2$ G into a 1 : 2 : 1 set of components if we assume a uniform distribution of NH_3 rotation angles. However, the width of the lines is somewhat larger than this and we observe no structure. Nonrotating NH_3 groups, however, would have given a much broader high-field line.

The proton line rapidly becomes weaker below 1.6 K, and it cannot be seen at all below the antiferromagnetic Neel temperature $T_N = 1.47$ K. This must be due to great width and short T_1 of the line in the antiferromagnetic state. Kim (*9*) reported the disappearance of the line at 1.6 K, and the Neel peak in the heat capacity has been found at 1.5 K to 1.45 K (*14, 12*).

The inverse of the measured splitting $\Delta B = [\Delta B_{NiH}(+) - \Delta B_{NiH}(-)]C$ is shown in Fig. 3 as function of temperature. We find the extrapolated Curie–Weiss temperature $\theta_C = -9.6 \pm 1$ K. This is in good agreement with θ_C from −8 to −9 K determined from static susceptibility measurements (*3, 15, 16*).

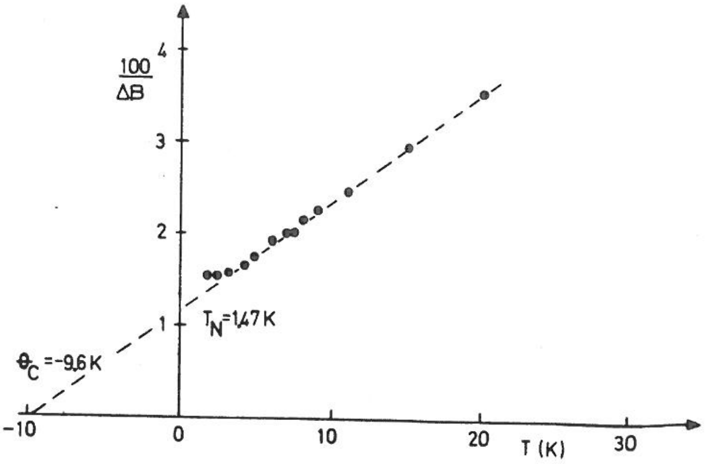

FIG. 3. Inverse of proton line splitting in $Ni(NH_3)_6Cl_2$ at 17.75 MHz as function of temperature.

At 4.2 K the main splitting is $\Delta B = 60 \pm 3$ G in $B_0 \approx 4120$ G where $\bar{\mu} = 5.88 \cdot 10^{-25}\ J/T$ from

$$\bar{\mu} = g^2 \mu_B^2 S(S+1) B_0 / 3k(T - \theta_C) \qquad [4]$$

with $g = 2.17$, which is also in agreement with the static susceptibility (*16*). Hence from the sum $\Delta B_{\mathrm{NiH}}(+) - \Delta B_{\mathrm{NiH}}(-)$ corrected by C for dipolar interaction with other Ni^{2+} ions we calculate the Ni–H distance $R = 2.80 \pm 0.05$ Å with $\theta_0 = 20°$.

At liquid N_2 temperatures and above, the line components overlap due to the small paramagnetic shift, and they are difficult to separate. Still, the three low-field components seem to have the same splitting up to room temperature, and this indicates that no tumbling motion of the NH_3 ligands around Ni^{2+} with frequency faster than 40 kHz occurs. Tumbling motion of $Cd(NH_3)_6{}^{2+}$ with this frequency starts in $Cd(NH_3)_6(BF_4)_2$ around 300 K (*17*) where it can be seen in the relaxation time $T_{1\rho}$.

We could see no clear change in the spectrum at the structural phase transition $T_c \approx 80$ K, again confirming that the change in structure is small.

3. DISCUSSION

We have found the H–H distance $r = 1.70 \pm 0.03$ Å in $Ni(NH_3)_6Cl_2$. This may be an indication that the ligand NH_3 geometry is slightly different from the geometry of a free NH_3 molecule, but the apparent difference can also be a result of zero-point rocking of NH_3. To get $r = 1.63$ Å from the measured splitting we would only have to take the average angle θ_{HH} in Eq. [3] to be 84° instead of 90°, and we believe that a r.m.s. deviation of 6° for the NH_3 symmetry axis away from the [100] direction is possible for zeropoint rocking.

We have found the Ni–H distance $R = 2.80 \pm 0.05$ Å. With the free NH_3 dimensions this corresponds to a Ni–N separation 2.25 ± 0.05 Å. This is a reasonable Ni–N distance falling between the 2.43 Å we expect from the ionic radii and the 2.16 Å we get from atomic radii. It is considerably longer than the surprisingly short X-ray result 2.136 Å (*11*). Our result may be slightly uncertain because the Ni^{2+} unpaired electron cloud is not a point charge when seen from one of the nearest protons. Then Eqs. [1] and [2] are not strictly valid. The zeropoint motion of the protons would also contribute to the difference between $\overline{(R^{-3})}^{-1/3}$ found by us and $\bar{R}$ found in diffraction experiments. However, these averaging effects would probably cause the R derived from NMR line splitting to be too small. A possible error of a few degrees in the alignment of the single crystals is not enough to reduce our derived Ni–H distance significantly.

The Ni^{2+} electron cloud may perhaps extend out to the proton positions or interact with the ligand wavefunctions to give some contact shift of the proton resonance. This would be expected in view of the relatively large antiferromagnetic Ni^{2+}–Ni^{2+} coupling in $Ni(NH_3)_6Cl_2$. But the isotropic part of the contact coupling would not influence the line splitting from which we have calculated R. The anisotropic part from ligand *p*-electrons (*18*) has unknown magnitude and varies with angle as the dipolar coupling already discussed. To get agreement with the X-ray result (*11*) the anisotropic contact coupling would have to reduce the dipolar splitting by some 40%.

But for σ-bonding around Ni^{2+} (d^8) we would rather expect that the anisotropic contact splitting should be added to the dipolar splitting, (*18*), although this conclusion is uncertain in view of the structure of the NH_3 ligands.

In conclusion, we have not been able to resolve the difference between our derived Ni-H distance and the X-ray result (*11*).

ACKNOWLEDGMENT

We are grateful to NTH's Fond for the supply of liquid helium.

REFERENCES

1. A. R. Bates and K. W. H. Stevens, *J. Phys. C. Solid State Phys.* **2,** 1573 (1969).
2. A. R. Bates, *J. Phys. C. Solid State Phys.* **3,** 1825 (1970).
3. M. B. Palma-Vittorelli, M. U. Palma, G. W. J. Drewes, and W. Koerts, *Physica* **26,** 922 (1960).
4. G. Aiello, M. U. Palma, and F. Persico, *Phys. Lett.* **11,** 117 (1964).
5. C. Trapp and C. I. Shyr, *J. Chem. Phys.* **54,** 196 (1971).
6. G. Aiello and M. B. Palma-Vittorelli, *Collective Phenomena* **1,** 87 (1973).
7. A. Elgsæter and I. Svare, *J. Phys. Chem. Solids* **31,** 1405 (1970).
8. S. J. Smith, J. G. Bunting, and H. Steeple, *J. Phys. Chem. Solids* **35,** 893 (1974).
9. P. H. Kim, *J. Phys. Soc. Japan* **15,** 445 (1960).
10. R. W. G. Wyckoff, "Crystal Structures," Vol. 3, p. 783, Interscience, New York, 1965.
11. A. R. Bates, I. L. A. Crick, and R. O. Davies, *J. Phys. C. Solid State Phys.* **9,** 3013 (1976).
12. H. van Kempen, W. T. Duffy, Jr., A. R. Miedema, and W. J. Huiskamp, *Physica* **30,** 1131 (1964).
13. H. van Kempen, T. Garofano, A. R. Miedema, and W. J. Huiskamp, *Physica* **31,** 1096 (1965).
14. K. Ukei and E. Kanda, *J. Phys. Soc. Japan* **16,** 2061 (1961).
15. T. Watanabe, *J. Phys. Soc. Japan* **16,** 1131 (1961).
16. N. F. de Oliveira, Jr. and C. Quadros, *Solid State Commun.* **7,** 1531 (1969).
17. N. Piślewski, J. Stankowski, and L. Lary, *Phys. Status Solidi* **a31** 415 (1975).
18. A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance," p. 396, Oxford, 1970.