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ESR Spectra of a Trigonally Distorted Pseudotetrahedral Nickel(I) Complex

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The number of relatively stable nickel(I) complexes is steadily increasing [1]. The characterization of their electronic energy levels, however, is still largely to be done. Since nickel(I) is a d^9 species it should be easily amenable to study by electron spin resonance spectroscopy. The other representative d^9 species is copper(II), which has been studied by ESR spectroscopy in almost all the geometries which can be conceived [2]. There are some geometries, however, which have never been investigated because they cannot be obtained by copper(II).

Recently Belford and Barefield [3] reported the ESR spectra of a unique trigonal planar tricoordinated nickel(I) complex. We wish to report now the ESR spectra of a pseudotetrahedral trigonally distorted nickel(I) complex. It is the first time that a d^9 complex with such a geometry can be investigated since all the known pseudotetrahedral copper(II) complexes are tetragonally distorted. Other reasons of interest for this complex are to see how the $^2T_2$ term of tetrahedral symmetry splits and to check the relevance of Jahn–Teller distortions in low symmetry complexes.

Iodo[1,1,1-tris(diphenylphosphinomethyl)ethane] nickel(I) (Nip_3I) was prepared as previously described [4]. No ESR spectra could be detected in the temperature range 300–77 K. Only the use of liquid helium allowed us to detect the ESR spectra of this compound. The polycrystalline powder spectra recorded at 4.2 K are shown in the Figure. An increase of the temperature to 20 K determines a dramatic broadening of the lines and at 40 K practically no signal is detected. This unusual behaviour can be explained if one considers that the $^2T_2$ manifold of tetrahedral symmetry is not largely split and low lying excited states are available to yield fast relaxation of the electron spin. The spectra are typical of a completely anisotropic S = 1/2 spin system, with g_1 = 1.99, g_2 = 2.10, and g_3 = 2.38.

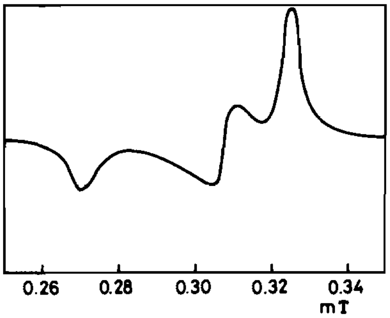

Figure. Polycrystalline powder ESR spectrum of Nip_3I at X-band frequency.

Also single crystal spectra were recorded. The undiluted crystals are reported to be orthorhombic [5], space group *Pn*2$_1$*a*, with four molecules per unit cell. ESR spectra with the static magnetic field in the three principal planes showed only one signal for every orientation of the crystal, suggesting that spin exchange is operative between the magnetically non-equivalent sites. The principal crystal *g* values were found to be: $g_a = 1.993, g_b = 2.099, g_c = 2.378 \pm 0.001$, in good accord with the powder data. The presence of spin exchange does not allow us to obtain the molecular *g* values. However, from the reported coordinates [5], the Ni–I direction, which would be the trigonal axis of a C_{3v} distorted tetrahedron, is calculated to make an angle of 35° with the *c* crystal axis, suggesting that the g_c crystal value is close to the g_{zz} molecular value. At this stage it is not possible to decide whether the rhombic crystal *g* values reflect rhombic molecular values. If however axial symmetry is assumed for the sake of simplicity, the pattern of the *g* values, with $g_\parallel > g_\perp$, is similar to that observed for copper(II) complexes where the unpaired electron is in either $x^2 - y^2$ or xy orbitals. The g_a value lower than 2.00 is presumably due to the effect of the large spin orbit coupling constant of iodine [6].

Ligand field calculations [7, 8], performed using the geometrical parameters of the X-ray structure determination, with the I–Ni–P angles averaged to 122° in order to obtain C_{3v} symmetry, predict that ^2E is lowest in energy. Since spin orbit coupling effects are anticipated to be small [7] in this term, it is probable that Jahn–Teller distortions are operative to some extent.

Single crystal ESR spectra of the copper(I) doped Nip_3I complex, as well as of the chloride and bromide derivatives are in progress in order to obtain the molecular *g* values, and single crystal polarized electronic spectra in the range 4–300 K will be recorded in order to obtain a detailed knowledge of the electronic energy levels of these nickel(I) complexes.

References

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