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ESR Spectra of Halo[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(I) Complexes

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The single crystal ESR spectra of halo[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(I), Nip_3X (X = Cl, Br, I) are reported. Due to short spin lattice relaxation the spectra were recorded at 4.2 K. Completely anisotropic g values were obtained for the chloride and the bromide doped into the corresponding copper(I) complex, and for the magnetically undiluted iodide. The hyperfine splitting due to two equivalent phosphorus atoms was resolved. Single crystal polarized electronic spectra of Nip_3I were recorded in order to gather information on the energies of the electronic levels. Attempts were made to calculate the g values through a ligand field model. An orbitally degenerate ground level is anticipated, which might be responsible for the unusual features of the spectra.

Introduction

We have recently reported the ESR spectra of iodo-[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(I), Nip_3I [1], a pseudotetrahedral d^9 species. We found that contrary to other reports of the ESR spectra of nickel(I) complexes [2, 3], a very low temperature, close to 4.2 K, was required in order to obtain a signal. Only the magnetically undiluted complex was studied, and the ESR spectra were found to be exchange narrowed, so that the observed g values could not be meaningfully used to obtain information on the electronic structure of this complex.

Since the interest in the characterization of the properties of nickel(I) is increasing [2–7], we recorded the single crystal ESR spectra of the nickel(I) doped into Cup_3X complexes (X = Cl, Br) and the single crystal polarized electronic spectra of Nip_3I.

Experimental

The Nip_3X and Cup_3X (X = Cl, Br, I) complexes were prepared as previously described [6]. Single crystals were grown by slow evaporation of appropriate solutions of methylene chloride and butyl ether in a nitrogen stream. It was not possible to dope Ni(I) into Cup_3I due to the large difference in the solubilities of the two compounds. Single crystal polarized electronic spectra of Nip_3Br and Nip_3I were recorded and were found to be identical.

All the crystals were oriented by Weissenberg techniques and found to be isostructural with Nip_3I [8].

Single crystal ESR and polarized electronic spectra down to 4.2 K were recorded with the apparatus described elsewhere [9, 10].

TABLE I. The Principal g Values of Diluted and Undiluted Nip_3X Complexes along the Crystal Axes.

	g_a	g_b	g_c
Nip_3Cl	2.14	2.12	2.24
Nip_3Br	2.12	2.16	2.23
Nip_3I	1.99	2.10	2.38
$(Ni, Cu)p_3Cl$	2.12	2.13	2.25
$(Ni, Cu)p_3Br$	2.08	2.21	2.23

Results

Single Crystal ESR Spectra of Undiluted Complexes

The single crystal ESR spectra of the undiluted complexes show at 4.2 K only one exchange narrowed signal for every orientation of the crystal in the static magnetic field. The principal directions of g were therefore parallel to the crystal axes. The principal g values are reported in Table I. As previously observed for the Nip_3I complex [1], only at temperatures close to 4.2 K was it possible to observe ESR spectra. A similar behavior was observed for the doped complexes, showing that its origin is molecular in nature. The most striking feature of the g values is the increase of the g_c value in the iodide derivative as compared to the corresponding g_c values in the bromide and chloride ones, and the corresponding decrease of the g_a value.

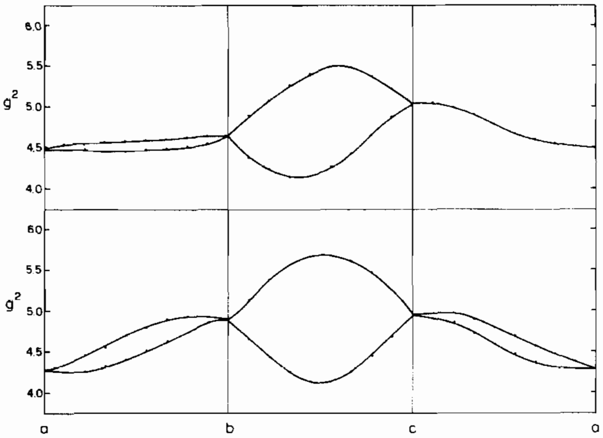

Fig. 1. The angular dependence of the $\mathbf{g}^2$ tensor of (Ni, Cu)-p$_3$Br (lower) and (Ni, Cu)p$_3$Cl (upper) in the rotations about, from left to right, *c*, *a* and *b* crystal axes.

Single Crystal ESR Spectra of (Ni, Cu)p$_3$Br

The angular dependence of the $\mathbf{g}^2$ values in the three rotations along the *a, b,* and *c* crystal axes are shown in Fig. 1. If one compares the g values observed parallel to the crystal axes (Table I) in the doped crystals to those obtained in the undiluted ones, it is apparent that g_c has remained the same, but g_a and g_b are somewhat changed, so that it can be suspected that there are some small differences in the structures of the copper(I) and the nickel(I) complexes, although they are isomorphous. Since the crystal is orthorhombic, there is no possibility to assign unambiguously the signs to the off diagonal terms of g^2. This can be done arbitrarily in two planes, leaving the sign of the third g^2_{ij} undetermined. With this ambiguity the calculated g values fall into two sets, one with $g_1 = 2.39$, $g_2 = 2.10$, $g_3 = 2.01$; the other with $g_1 = 2.39$, $g_2 = 2.07$, $g_3 = 2.04$. A rotation about the bisector of the *bc* axes showed a g value close to 2.01 confirming the first set of g values. The direction cosines of the g axes relative to the crystal axes are shown in Table II. The spectra show a hyperfine structure so that each signal is split into three components, with intensity ratios 1:2:1, suggesting that the unpaired electron is coupled to two equivalent phosphorus atoms (I = ½). The broad lines and the overlap of the signals of different sites did not allow us to carry out a detailed analysis of the angular dependence of the hyperfine splitting, but it was found to vary in the range 72.5–80.0 $\times 10^{-4}$ cm^{-1}.

In the rotation along the *a* axis the signal corresponding to one site is split into up to ten components when g approaches the g_3 value and we interpret this as due to the effect of the coupling to the ^{79}Br and ^{81}Br nuclei, both of which have I = 3/2 and very similar nuclear moment. The splitting is of $\cong 19 \times 10^{-4}$ cm^{-1}. The fact that the signals are due to bromine is confirmed by the spectra of the chloride derivative where no such splitting is observed (Fig. 2). When the high field spectra show evidence of bromine hyperfine coupling the low field signals show a doubling of the peaks, which might be due to the interaction of the unpaired electron with the third phosphorus atom. A bromine hyperfine splitting is observed also in the rotation along *c* when the g value is close to its lowest limit, g_3.

TABLE II. Principal g values and Direction Cosines for (Ni, Cu)p$_3$X.[a]

Nip$_3$Cl		
2.344(4)[b]	2.124(3)	2.040(1)
+0.040(4)	+0.985(2)	+0.17(1)
+0.572(2)	+0.114(7)	−0.812(8)
+0.819(2)	−0.128(9)	+0.559(8)
Nip$_3$Br		
2.391(8)	2.102(4)	2.006(3)
+0.018(4)	−0.820(5)	+0.57(1)
+0.697(1)	−0.400(9)	−0.595(3)
+0.717(2)	+0.410(2)	+0.564(2)

[a] To each g value correspond four sets of direction cosines, according to the symmetry relationa l, m, n → l, m, $\bar{n}$ → l, $\bar{m}$, n → $\bar{l}$, m, n. [b] The errors on g values and on direction cosines are evaluated according to the method described by Schonland [20].

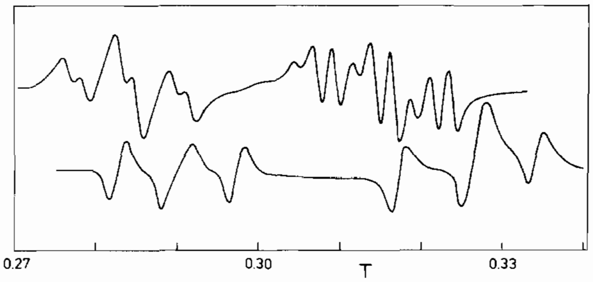

Fig. 2. Upper: single crystal ESR spectrum of (Ni, Cu)p$_3$Br in the (100) plane. The setting angle is 20° from *c*. Lower: single crystal ESR spectrum of (Ni, Cu)p$_3$Cl in the (100) plane. The setting angle is 30° from *c*.

Single Crystal EPR Spectra of (Ni, Cu)p$_3$Cl

The angular dependence of the g^2 values in the three rotation along the *a, b,* and *c* crystal axes are shown in Fig. 1. The behavior is rather similar to that found for the bromide derivative, although there are some differences. For instance the plane in which the largest anisotropy is found is also in this case (100), but the maxima and minima are now found at

TABLE III. Angles between g Directions and Bonds of Nip_3X Chromophore.[a,b]

	l, m, n			$l, m, \bar{n}$			$l, \bar{m}, n$			$\bar{l}, m, n$		
	g_1	g_2	g_3	g_1	g_2	g_3	g_1	g_2	g_3	g_1	g_2	g_3
Ni–Cl	41	58	68	79	53	40	82	68	25	44	63	59
$Ni–P_1$	76	21	75	81	9	90	77	21	74	81	9	89
$Ni–P_2$	82	78	15	28	84	63	29	88	62	83	87	10
$Ni–P_3$	24	69	80	59	80	34	59	65	42	20	77	75
Ni–Br	31	64	75	72	24	66	73	85	18	37	73	57
$Ni–P_1$	73	25	74	87	6	87	74	25	73	87	6	88
$Ni–P_2$	73	81	20	19	90	71	22	82	70	74	89	16
$Ni–P_3$	33	63	72	65	82	27	69	63	35	25	82	67

[a] The structural data are relative to the X-ray structure of the Nip_3I complex. [b] The calculated error on each angle is ±2° [20].

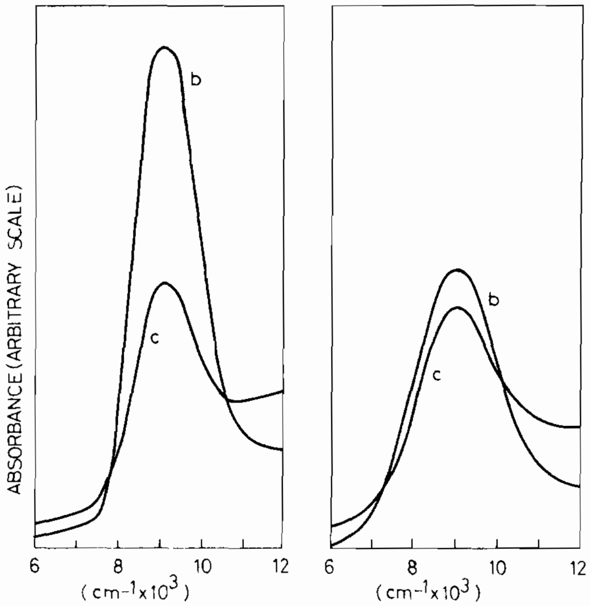

Fig. 3. Single crystal polarized electronic spectra of Nip_3I recorded with the electric vector of the incident radiation parallel to *b* and *a* crystal axes. Left: spectra recorded at 4.2 K; right: room temperature spectra.

±35° from the crystal axes, while they were at ±45° in the bromide derivative. Also in the rotation in the plane (010) the extreme g values are found along the crystal axes rather than rotated by 15° from them. This simplifies the evaluation of the g^2 matrix and only one set of g values is calculated, as shown in Table II.

Single Crystal Polarized Electronic Spectra of Nip_3I

They were recorded with polarized light inciding perpendicularly to the (100) face. Only one maximum is clearly resolved at ~9 X 10^3 cm^{-1} (Fig. 3), which is not appreciably shifted neither in the two polarization directions nor on cooling. The comparison of the spectra at 300 and 4.2 K shows that the polarization ratio increases on cooling, and that the bands are considerably sharpened, with the band seen with the electric vector parallel to *b* which is more affected by temperature. The oscillator strengths of both bands are practically constant in the range 4.2–300 K.

Discussion

The ESR spectra of the Nip_3X complexes are rather surprising. First of all the fact that it is necessary to cool the crystals to liquid helium temperature to record the spectra [11] is uncommon for $S = ½$ systems. Similar behavior was observed for copper(II) doped ZnO [12], and must be attributed to the presence of low energy excited levels in the tetrahedral ligand field. Second, the observation of the coupling of the unpaired electron to two equivalent phosphorus atoms is unexpected, since in the room temperature X-ray structure of Nip_3I the three metal–phosphorous distances are identical within error [8], the only differences being in the I–Ni–P angles (125° for P_1 and P_2, 116° for P_3). The single crystal ESR spectra unfortunately are not sufficient to give an exhaustive answer to the questions raised by these experimental data. As a matter of fact, although the overall symmetry of the Nip_3I chromophore seen in the crystal structure is not far from C_3, the main deviation being the above mentioned difference in the I–Ni–P angles, the g values of the doped chloride and bromide are highly anisotropic. Further the principal directions of g are not found close to any relevant symmetry element of the chromophore. In Table III are reported the angles made by the principal g values and the bond directions of Nip_3I. Since the crystals are orthorhombic [8] there are four magnetically not equivalent molecules in the unit cell, the symmetry relations between corresponding direction cosines of the four molecules being (l, m, n); (–l, m, n); (l, –m, n); (l, m, –n). In particular the Ni–I direction, which in the idealized symmetry would individuate the trigonal axis, is in every case pretty far from every g direction. The smallest angle made by the Ni–X direction with a g value is 25° and 18° with g_3 in the chloride and the bromide respectively. For the iodide the g values of the undiluted complex are similar to those of the doped chloride and bromide derivatives. This might be indicative of the fact that the crystal g values of the iodide are sufficiently close to the molecular g values, *i.e.* the principal g directions in the iodide are closer to the crystal axes than are the principal directions of the chloride and of the bromide.

The value of the ^{31}P hyperfine coupling constant correlates well to those reported for a trigonal planar nickel(I) complex [2]. Not much can be said for the coupling constant to the third phosphorus but if the splitting seen in Fig. 2 is attributed to it, A_p can be guessed to be 20–25 × 10^{-4} cm^{-1}. Also in $(Ph_3P)_2$-NiBr [2] the two phosphorus atoms were found to be extremely different in the ESR spectra although not large differences were found in the structure, and it was suggested that this was somehow correlated to different π back-bonding interaction.

In order to obtain information on the electronic energy levels we recorded the single crystal polarized electronic spectra. The main value of these data shows that there is essentially one band which can be attributed to d–d transitions, with a maximum at ~9 × 10^3 cm^{-1}. The band is more intense with the electric vector parallel to *b*. If one uses the Ni–I direction to identify the *z* molecular axis the transition would be essentially ⊥ polarized, but due to the non-coincidence of the principal axes of g with the axes of idealized symmetry [13], it is better not to speculate further on the electronic spectra, and to use them only as a source of information on the number of transitions which are present.

In order to rationalize the above g values, a ligand field approach can be used. The electronic energy levels were calculated through an Angular Overlap formalism [14], without imposing any symmetry to the complex, but using the coordinates of the X-ray crystal structure determination. It was found that the ground level in the absence of the spin orbit coupling interaction is almost orbitally doubly degenerate, correlating to ^2E of C_{3v} symmetry, which in turn correlates to $^2T_2$ of T_d symmetry. In order to have a transition at 9 × 10^3 cm^{-1} the values of the parameters must be: $e_\sigma^I = 4300$–5300, $e_\pi^I = 1500$–2000, $e_\sigma^P = 4000$–5000, $e_\pi^P = -750$– -1000 cm^{-1}. Negative values of e_π^P in the angular overlap formalism correspond to predominant back donation of the metal to ligand [15]. Similar negative values were calculated for the interpretation of the electronic spectra of some low symmetry high spin phosphine cobalt(II) complexes [16]. It must be noted that the fit of the electronic spectra cannot be considered completely satisfactory since the calculations suggest the presence of a band at 6 × 10^3 cm^{-1} which is not found in the spectra.

Including the spin orbit coupling determines a splitting of the ground level into a couple of Kramers doublets separated by100–300 cm^{-1}. The g values were calculated with the method first suggested by Gerloch [17], which we previously used for high spin cobalt(II) [18]. Since no symmetry restriction is imposed on the calculation, the principal g values and directions are evaluated by diagonalization of the g^2 matrix. The g values which correspond to the lowest doublet are in the range: g_1 = 2.8–2.4, g_2 = 1.79–2.00, g_3 = 1.3–1.9. The best results are obtained for $e_\sigma^I = 4200$, $e_\pi^I = 2000$, $e_\sigma^P = 5000$, $e_\pi^P = -1000$ cm^{-1}, yielding $g_1 = 2.44$, $g_2 = 2.01$, $g_3 = 1.94$. It is perhaps worth mentioning here that the g_1 value is not calculated to be close to the Ni–I direction but to make an angle of 64° with it, showing that the principal g directions can be determined by the ligand field to be far from the positions competing to idealized symmetry. However the calculated values are not satisfactory, and it was not possible to improve them keeping the geometrical parameters fixed to the values of the X-ray crystal structure.

We think that the experimental data and the results of the calculation indicate that the structure at room temperature of Nip_3I is rather different from the low temperature structure which is amenable to study by ESR. An obvious explanation of this is the orbitally degenerate ground level which competes to the room temperature structure. It is possible that the system undergoes some Jahn–Teller distortion [19], for instance removing the degeneracy by coupling to an E vibration of C_{3v} symmetry, which lengthens one nickel–phosphorus bond and strengthens the other two. With this model it should be possible to justify the observed coupling of the unpaired electron to two phosphorus atoms, instead than to three. Unfortunately the impossibility to record ESR spectra at higher temperature prevents us from substantiating this statement.

References

1 A. Bencini, C. Benelli, D. Gatteschi and L. Sacconi, *Inorg. Chim. Acta, 29,* L243 (1978).

2 M. J. Nilges, E. K. Barefield, R. L. Belford and P. H. Davis, *J. Am. Chem. Soc., 99,* 755 (1977).

3 R. Barbucci, A. Bencini and D. Gatteschi, *Inorg. Chem., 16,* 2117 (1977).

4 P. Heimbach, *Angew. Chem. Int. Ed. Eng., 3,* 648 (1964).

5 L. Sacconi, C. A. Ghilardi, C. Mealli and F. Zanobini, *Inorg. Chem., 14,* 1380 (1975).

6 L. Sacconi and S. Midollini, *J. Chem. Soc. Dalton,* 1213 (1972).
7 F. C. Senftleber and W. E. Geiger, Jr., *Inorg. Chem., 17,* 3615 (1978).
8 P. Dapporto, G. Fallani and L. Sacconi, *Inorg. Chem., 13,* 2847 (1974).
9 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 16,* 1973 (1977).
10 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 15,* 203 (1976).
11 B. R. McGarvey, *Transition Met. Chem., 3,* 90 (1966).
12 R. E. Dietz, H. Kamimura, M. D. Sturge and A. Yariv, *Phys. Rev., 132,* 1559 (1963).
13 A. Bencini and D. Gatteschi, *Inorg. Chem., 16,* 1994 (1977).
14 C. E. Schäffer, *Struct. Bonding* (Berlin), *14,* 69 (1973).
15 C. E. Schäffer, *Struct. Bonding* (Berlin), *5,* 68 (1968).
16 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem. 14,* 812 (1975).
17 M. Gerloch, R. F. McMeeking, *J. Chem. Soc. Dalton,* 2443 (1975).
18 A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Inorg. Chem., 18,* 2137 (1979).
19 R. Englman, 'The Jahn–Teller Effect in Molecules and Crystals', Wiley–Interscience, London, 1972.
20 D. S. Schonland, *Proc. Phys. Soc. London, 73,* 788 (1959).