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ESR Spectra of the Square Pyramidal Iodo[difluoro[3,3′-(trimethylenedinitrilo)-bis(2-butanone oximato)] borato] copper(II) Complex

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The single crystal ESR spectrum of the square pyramidal iodo[difluoro[3,3′-(trimethylenedinitrilo)-bis(2-butanoneoximato)] borato] copper(II), Cu(cyclops)I, complex diluted into the nickel(II) lattice has been recorded.

The spin Hamiltonian parameters ($g_1 = 2.05$, $g_2 = 2.07$, $g_3 = 2.18$, $A_3 = 190 \times 10^{-4}$ cm^{-1}*) have been interpreted using a symmetry independent angular overlap model. This analysis shows that the in-plane field is fairly strong thus explaining the observed diamagnetism of the Ni(cyclops)X adducts.*

Introduction

The metal complexes formed by the macrocyclic ligand difluoro[3,3′-(trimethylene-dinitrilo)bis(2-butanone oximato)] borate, cyclops, have been found to possess rather unusual properties and structures [1, 2]. For instance the crystal structure determination of five square pyramidal copper(II) complexes showed that the metal atom is radically displaced from the plane of the four basal atoms of the cyclops ligand [3–6]. The amount of the displacement is dependent on the axial ligand, being 0.32 Å in the aquo and 0.58 Å in the cyanato-N-complex.

Also with nickel(II), cyclops forms square pyramidal five coordinate complexes, which are low spin. Since in general nickel(II) chromophores NiN_4X are high spin [7], it might be suspected that for Ni(cyclops)X the fifth ligand is rather distant from the metal atom, so that a substantially square planar coordination is obtained. On this basis the diamagnetism of a nickel macrocyclic compound was rationalized by Fleischer [8]. However, in the crystal structure determination of Ni(cyclops)I, it was shown that although the nickel–iodide bond length is rather long (2.834 Å), the coordination around the metal is by no means square planar, since, the nickel atom is displaced by 0.23 Å toward the axial iodide [9].

In order to try to discriminate between electronic and steric factors influencing the bonding ability of cyclops, we decided to record the single crystal ESR spectrum of Cu(cyclops)I doped into the nickel analog, and wish to report here these results together with an Angular Overlap analysis of the spectrum.

Experimental

Cu(cyclops)ClO_4 has been prepared as previously described [1]. A similar procedure has been followed for obtaining the nickel complex.

Single crystals of copper(II) doped Ni(cyclops)I were obtained from a solution of Ni(cyclops)ClO_4 in methanol containing excess tetrabutylammonium iodide and Cu(cyclops)ClO_4 (<1%). Good crystals were obtained by keeping the solution in the freezer overnight before filtering.

Q-band (35 GHz) ESR spectra were recorded with a Varian E-266 cavity equipped with a variable temperature accessory.

The crystals were oriented with a Philips PW 1100 diffractometer which showed that the crystals are monoclinic, space group $P2_1/c$, with $a = 14.24$ Å, $b = 7.51$ Å, $c = 19.53$ Å, $\beta = 127.9°$. The single crystal spectra were recorded by rotating the static magnetic field around *a*, *b* and *c* (*x*, *y*, *z* laboratory axes).

The crystal structure of Ni(cyclops)I has been referred to a different monoclinic cell [9] (space group $P2_1/n$, $a' = 15.56$ Å, $b' = 7.51$ Å, $c' = 14.24$ Å, $\beta' = 98.2°$). These two cells are related by the matrix

	a′	*b′*	*c′*
a	0.915	0.	−1.
b	0.	1.0	0.
c	1.255	0.	0.

All the calculations were performed with a SEL 32/76 computer.

Results

The polycrystalline powder spectrum of (Cu, Ni)(cyclops)I is shown in Fig. 1. It can be inter-

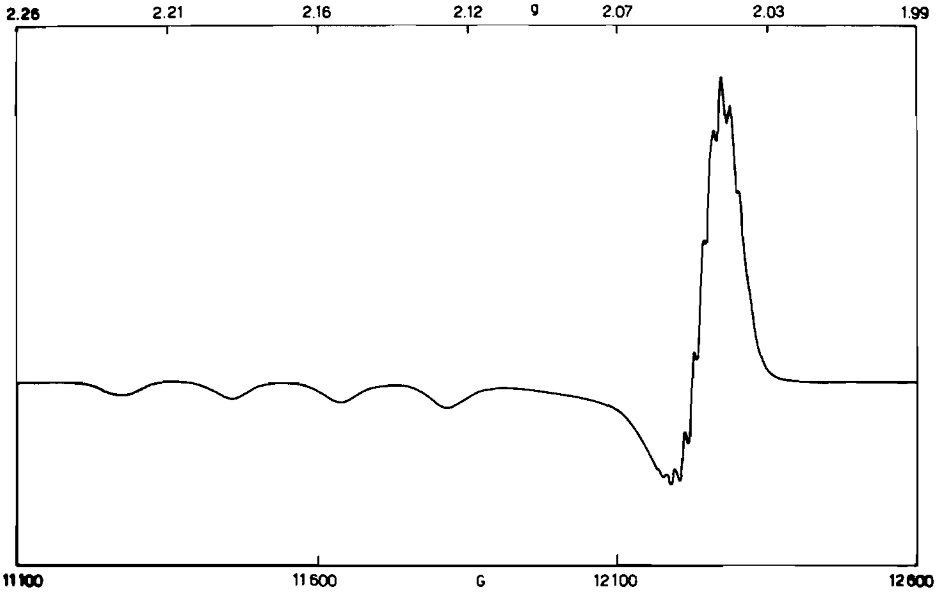

Fig. 1. The Q-band (35 GHz) polycrystalline powder spectrum of copper(II) doped Ni(cyclops)I.

preted using an axial spin Hamiltonian with $g_\parallel$ = 2.17, $g_\perp$ = 2.04 and $A_\parallel$ = 185 X 10^{-4} cm^{-1}. The $g_\perp$ feature shows evidence of hyperfine coupling with the ^{14}N nuclei.

Recording single crystal spectra was a rather difficult task due to the reduction of copper(II) to diamagnetic copper(I) in the presence of the excess iodide. First of all most of the well formed crystals did not give any ESR signal, showing that no copper(II) was included. Attempts to grow crystals starting from solutions containing higher percentages of copper complex yielded magnetically non dilute crystals. Finally we succeeded in selecting some crystals which gave reasonable signals, indicative of magnetically dilute copper chromophores. However the intensity of the signals was very low so that very high receiver gain had to be used in recording the spectra.

The lines are reasonably narrow in the $g_\perp$ area, where evidence of ^{14}N hyperfine splitting was obtained, however they became increasingly broader on moving towards the $g_\parallel$ region. In the rotation around x a g value of 2.17 is recorded, close to the $g_\parallel$ value of the powder spectrum. In this orientation the experimental linewidths are about 100 G. On cooling to liquid nitrogen temperature, no substantial sharpening of the lines was observed, suggesting that the linewidth is essentially due to non resolved ligand hyperfine splitting.

In the monoclinic cell of Ni(cyclops)I, two magnetically non equivalent molecules are expected in the xy and yz planes [10]. In some crystal orientations in these planes we observed some splitting of the signals which can be attributed to not equivalent molecules. However the broadness of the signals did not allow us to follow the two independent molecules. On the other hand, the fact that no large splitting of the signals is observed must be indicative that the two g tensors of the two molecules are not largely misaligned. As a matter of fact the crystal structure data [9] show that the Ni–I bond directions of the two magnetically non equivalent molecules in the crystal cell make an angle of ~45°, while the Ni–N directions on the average make an angle of ~27°.

TABLE 1. Principal g Values and Directions of (Cu, Ni) [(cyclops)]I.

		Principal Directions[a]		
g_1	2.05	0.227	−0.921	−0.317
g_2	2.07	0.973	0.223	0.051
g_3	2.18	0.023	−0.320	0.947

[a]These directions are given in a molecular frame XYZ with Z perpendicular to the basal plane and X parallel to the projection of the Ni–N$_1$ bond on this plane.

The principal g values and directions obtained by a least squares fit of the experimental data using the method by Schonland [11] are shown in Table I. The principal directions of g are chosen to make the minimum angle with the in-plane bonds.

The linewidth of the spectrum made also the analysis of the A tensor impossible. The value of A = 190 X 10^{-4} cm^{-1} associated with g_3 is in agree-

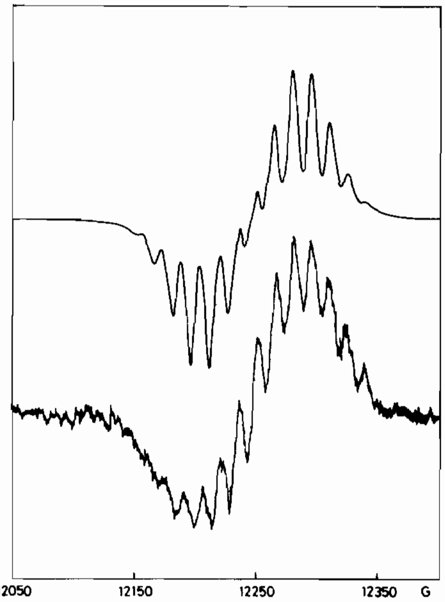

Fig. 2. Lower: single crystal spectrum of (Cu, Ni)(cyclops)I observed with the static magnetic field in the *xz* plane at 20° from *x*. Upper: the computer simulated spectrum using lorentzian lineshapes (see text) and $A^{Cu} = 20 \times 10^{-4}$ cm^{-1}, $A^N = 14.3 \times 10^{-4}$ cm^{-1}, linewidth W = 9 G.

ment with the value obtained from the powder spectrum. The other A values can be estimated from the linewidth of the signals corresponding to g_1 and g_2 and are less than 40×10^{-4} cm^{-1}.

In some crystal spectra recorded with the static magnetic field in the plane (010) up to 13 lines are observed. These are due to the coupling of the unpaired electron with the ^{14}N nuclei of the macrocycle. The spectra can be simulated as sum of Lorentzian components [10] given by four ^{14}N nuclei in a plane. A representative observed–simulated spectrum is shown in Fig. 2. The simulation shows that the nitrogen hyperfine coupling is about 14×10^{-4} cm^{-1}, which agrees with the literature reports [12, 13] and requires a copper hyperfine of the same magnitude. In this simulation the four nitrogen atoms were considered to be identical in all the orientations for which we obtained data. No substantial improvement of the fit of the spectrum was obtained by allowing for differences in the hyperfine tensors of the four nitrogen atoms. As a consequence no information about the anisotropy of the interaction could be obtained from the spectrum.

Discussion

The copper and the nickel derivatives are not isomorphous [5, 9] and some significant differences are seen in the two chromophores. In particular the metal iodide bond is longer in the nickel (2.83 Å) as compared to the copper complex (2.74 Å), the average metal–nitrogen bond is shorter in the nickel and the average iodide–metal–nitrogen angle is larger in the copper as compared to the nickel complex. When copper(II) enters as a substitutional impurity into the nickel lattice it presumably is forced to assume the nickel structure, and in the following analysis of the experimental data we will use the nickel coordinates.

The site symmetry of the metal ion in the crystal lattice is C_1, but the overall symmetry of the chromophore is not far from C_{4v}, and we will use this symmetry for a first estimation of the values of the Angular Overlap parameters [14] which are required to interpret the spectral and electronic properties of Cu(cyclops)I. The energies of the electronic transitions for a CuN$_4$I chromophore with an I–Cu–N angle of 100°, are given by [13]

$$E(xy \rightarrow z^2) = 1.994\, e_\sigma^N - 0.234\, e_{\pi\parallel}^N - e_\sigma^I$$

$$E(xy \rightarrow xz, yz) = 2.646\, e_\sigma^N - 1.649\, e_{\pi\parallel}^N - 0.6\, e_{\pi\perp}^N - e_\pi^I \qquad (1)$$

$$E(xy \rightarrow x^2 - y^2) = 2.822\, e_\sigma^N + 0.117\, e_{\pi\parallel}^N - 3.879\, e_{\pi\perp}^N$$

$e_{\pi\parallel}^N$ and $e_{\pi\perp}^N$ are the bonding parameters parallel and perpendicular to the tetragonal axis respectively. In the present case it may reasonably be assumed that $e_{\pi\perp}^N = 0$, since the nitrogen donors are essentially sp^2 hybridized in the equatorial plane. Also, at least in the first stage, e_π^I can be set equal to zero since, according to eqn. 1, it is expected not to have a very large influence on the calculated electronic spectrum.

The electronic spectrum of Cu(cyclops)I is rather featureless, with a broad maximum at 15,400 cm^{-1}. The band extends in the low frequency region down to ~10,000 cm^{-1}, while in the high frequency range an intense charge transfer band sets in at ~20,000 cm^{-1}. In order to have one transition at ~15,400 cm^{-1}, the other two being not lower than 11,400 cm^{-1} and not higher than 20,500 cm^{-1}, the e_λ parameters of eqn. 1 ($\lambda = \sigma, \pi$) must be in the ranges: $e_\sigma^N = 6900 \pm 300$ cm^{-1}, $e_{\pi\parallel}^N = 2000 \pm 400$ cm^{-1}, $e_\sigma^I = 1300 \pm 500$ cm^{-1}. Both the e_σ^N and $e_{\pi\parallel}^N$ values are large, and also the $e_{\pi\parallel}^N/e_\sigma^N$ ratio is large. This is in line with the well established ligand field strength of conjugated macrocyclic ligands [15, 16], and gives an idea of why the nickel complex is low spin. If the Dq value of the nitrogen donors is defined as $10\,\mathrm{Dq} = 3e_\sigma^N - 2e_{\pi\parallel}^N - 2e_{\pi\perp}^N$, it is calculated to be ~1670 cm^{-1} in the present case. On the other hand the corresponding parameter for the axial iodide

TABLE II. A Representative Fit of the Electronic Transitions and of the Principal *g* and *A* Values and Directions of (Cu, Ni([(cyclops)])I).

Electronic transitions[a] (cm^{-1})

Obs.	Calcd.[a,b]
>10000	11460
15400	15150
	16350
<20500	19630

g values

Obs.	Calcd.[a,b]	Calcd. principal directions[a,b]		
2.05	2.05	−0.298	0.954	−0.021
2.07	2.06	0.954	0.298	−0.007
2.18	2.18	0.	0.	1.

A values ($cm^{-1} \times 10^4$)

Obs	Calcd.[a,b]	Calcd. principal directions[a,b]		
<40	16	−0.369	−0.929	0.019
<40	20	0.929	−0.369	0.001
190	190	0.	0.	1.

[a] The reference system is defined in Table I. [b] The parameters [18, 19] used in the calculation are: $e_\sigma^N = 6840$ cm^{-1}, $e_{\pi\parallel}^N = 1710$ cm^{-1}, $e_{\pi\perp}^N$, = 0. cm^{-1}, $e_\sigma^I = 1250$ cm^{-1}, $e_\pi^I = 62.5$ cm^{-1}, $\zeta = 829$ cm^{-1}, $k = 0.73$, $P = 0.025$ cm^{-1}, $x = 0.4$.

donor is rather small [17], the Dq value corresponding to only ~400 cm^{-1}.

By including the *g* values and directions in the fitting procedure [18] using the actual C_1 symmetry seen in the crystal structure of Ni(cyclops)I, we have calculated more precise e_λ parameters. However, in this case we assumed identical parameters for the four nitrogen donors. A representative fit of the electronic transitions and of the *g* and *A* values and directions [19] is given in Table II. The fit seems to be reasonably good, and also the Stevens' reduction factor κ compares well with the values observed for other CuN_4X chromophores [20].

It is apparent from the above analysis that the equatorial field in (Cu,Ni)(cyclops)I is very strong and largely determines the magnitudes of the d-orbital energies for copper(II) doped in a $Ni(cyclops)^+$ lattice. Naturally the same statement applies for the d-orbital energies of nickel(II) wherein the equatorial ligand field is very strong and the axial field due to X^- is quite weak; hence the diamagnetism of all known Ni(cyclops)X adducts.

Acknowledgement

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