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POLARIZED SINGLE-CRYSTAL ELECTRONIC SPECTRUM OF A HIGH-SPIN NiN_3O_2 CHROMOPHORE

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Polarized single crystal electronic spectra of the high-spin five-coordinated NiSALMeDPT complex have been reported. The assignment of the bands agrees with an effective C_2 symmetry. The energies of the transitions calculated through a crystal field treatment have been compared with experimental ones.

INTRODUCTION

Although many high-spin five coordinate nickel complexes have been prepared¹ and their electronic properties interpreted using simple Crystal Field calculations,²⁻⁵ little attempt has been made to assign the spectra on the basis of polarized single crystal measurements. Only recently Gerloch, Lewis *et al.* succeeded in assigning the polarized spectrum of a five-coordinate C_{4v} nickel chromophore.⁶

We report here the single crystal polarized spectra of the NiSALMeDPT complex⁷ (SALMeDPT is the Schiff base obtained from Salicylaldehyde and bis(3-aminopropyl)methyl amine) whose chromophore is known by X-ray analysis to have an approximate C_{2v} symmetry with a geometry intermediate between a trigonal bipyramid and a square pyramid.⁸

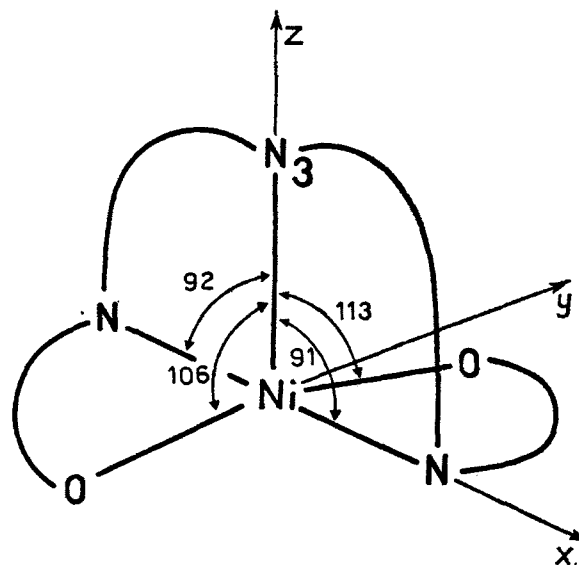


FIGURE 1 Molecular structure of NiSALMeDPT .

EXPERIMENTAL SECTION

Crystallographic Morphology

The green crystals of NiSALMeDPT are monoclinic,³ space group $P2_1/c$, $a=6.913$, $b=13.975$, $c=19.893$ Å, $\beta=91.49^\circ$ and $Z=4$. The molecular structure is shown in Figure 1 along with the molecular coordinate axes. The choice of the molecular axes is straightforward with the z axis fixed along the $\text{Ni}-\text{N}_3$ bond and x along the $\text{Ni}-\text{N}$ bonds. For bis(salicylaldiminate) metal(II) complexes, optical axes have been fixed in between the metal-donor atom bonds.⁹ In this case a similar choice is impossible because the $\text{O}-\text{Ni}-\text{N}$

planes are not orthogonal to the z axis. Furthermore no symmetry would be expected with the latter axes choice.

The crystals were obtained by slow evaporation of benzene-cyclohexane solutions. They are prisms elongated along the a axis with the (011) face the most highly developed, and the other axes oriented as shown in Figure 2. This orientation is confirmed by oscillating crystal technique. The four molecules in the unit cell occupy general positions. On the (100) face the extinction directions obviously are parallel to the b and c crystallographic axes. On the (011) face one extinction direction, r , is $+30^\circ$ to the $+a$ axis, the positive rotation being

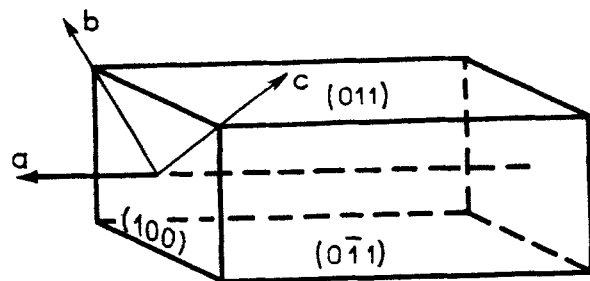


FIGURE 2 Crystal morphology of NiSALMeDPT.

toward the $+c$ axis, whereas s is orthogonal to it. The molecular projections for a unit electric vector along the extinction directions are reported in Table I.

TABLE I

The molecular projections for a unit electric vector along the extinction directions of NiSALMeDPT

	b	c	r^h	s^h
$\cos^2(x, E_d)$.061	.726	.034	.460
$\cos^2(y, E_d)$.018	.195	.804	.059
$\cos^2(z, E_d)$.921	.079	.161	.482

^h These values have been obtained as $(\cos^2(i, E_d)_1 + \cos^2(i, E_d)_2)/2$ where 1 and 2 are referred to the two pairs of molecules which make different projections on the (011) plane.

Electronic Spectra

The spectra have been recorded using a spectrophotometer Unicam SP 700 equipped with the

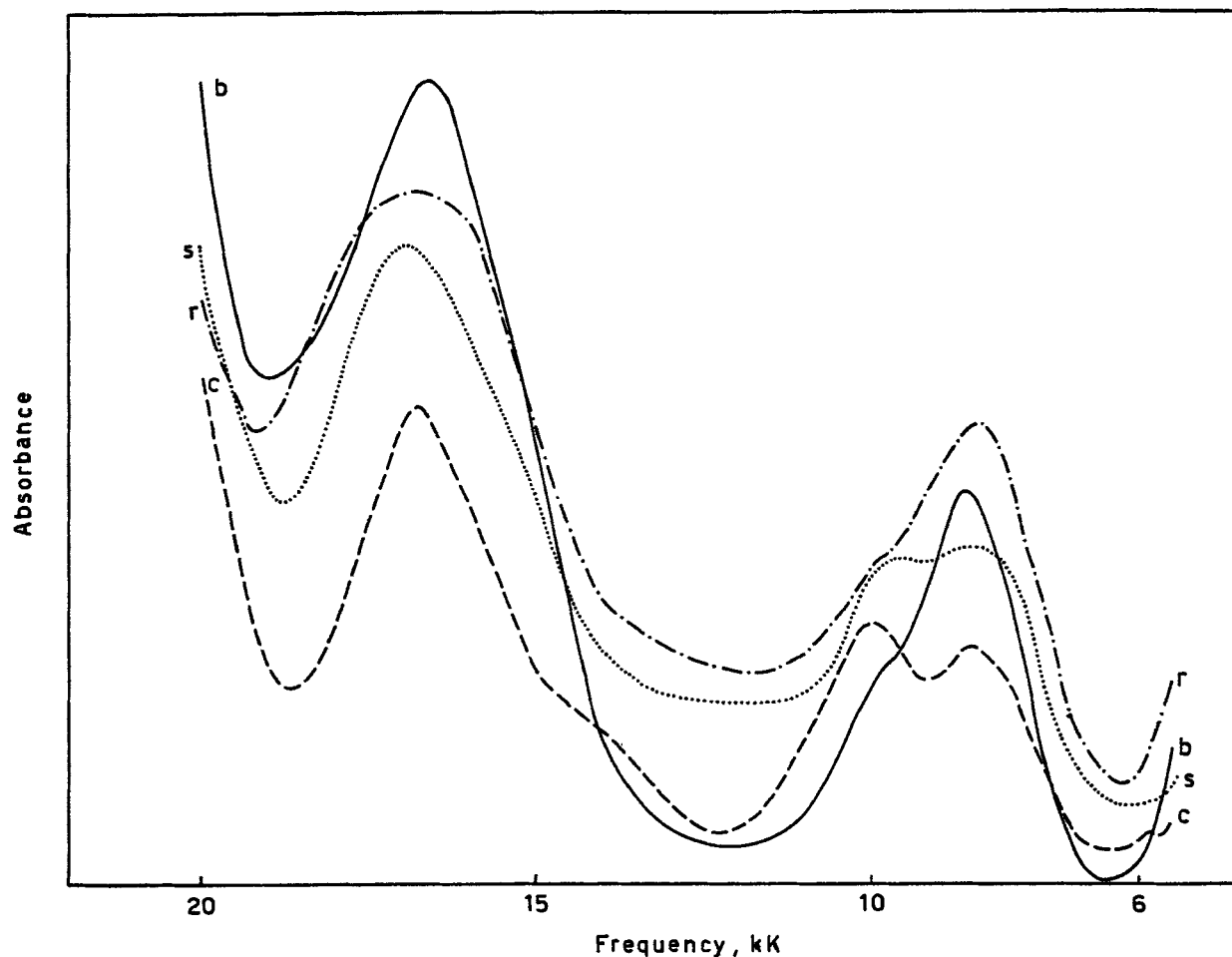


FIGURE 3 Polarized single-crystal electronic spectra of NiSALMeDPT; along r (— · — · —), along s (·····) along b (——), along c (----).

accessories described by Hathaway *et al.*¹⁰ Polarized single crystal electronic spectra were recorded on the side face (100) and on the main face (011). No attempt was made to determine absolute absorbancies. The relative absorbancies between *c* and *b* spectra are quite correct because they were measured by simply rotating the nicols.¹⁰ To record the spectra along *r* and *s*, a different crystal was used. Since the spectrum recorded along *s* was close (a part a scaling factor) to half of *c* + *b* spectra, the spectrum along *r* is compared to those along *c* and *b* as shown in Figure 3.

RESULTS

Electronic Spectra. The spectrum measured along *b* yielded the almost pure *z* component. The spectra along *c* and *r* are predominantly *x* and *y* polarized (see Table I). The spectra are qualitatively very similar in the *z* and *y* directions. By inspecting the spectra and keeping in mind the figures of Table I,

it results that the bands at 10.0 and 12.8 kK are *x*-polarized whereas the band at 8.4 kK is polarized both along *y* and *z*. No clear polarization is shown by the absorption at *ca.* 16.8 kK even if this band is more intense in *y* and *z* polarizations.

The site symmetry of the nickel atom and the symmetry of a single molecule is C_1 . For the chromophore however, whose geometry is intermediate between a trigonal bipyramid and a tetragonal pyramid, we may assume a C_s (*zy* plane) symmetry. Moreover if the two N_3-Ni-O angles could be averaged at the same value, the symmetry of the chromophore would be C_{2v} (C_2 along the *z* axis).

Since there is no apparent difference in the selection rules along *z* and *y*, the effective symmetry, which may explain the observed spectra, must be C_s (*zy* symmetry plane).

Fitting of the Electronic Transitions. Since the geometry of the chromophore is intermediate between a trigonal bipyramid and a tetragonal

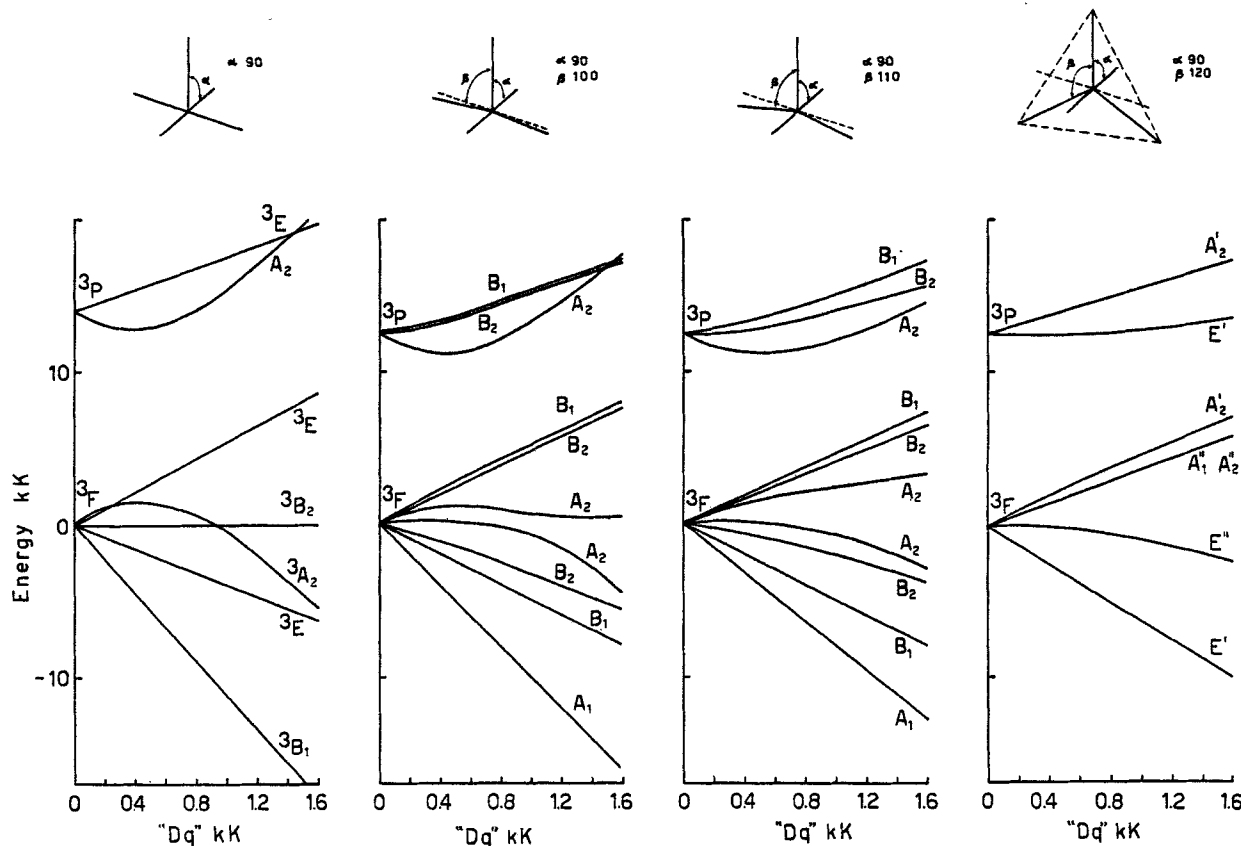


FIGURE 4 Electronic energy levels against "Dq" for the nickel (II) ion in C_{4v} (left), D_{3h} (right) and intermediate C_{2v} symmetries.

pyramid it is interesting to evaluate the pattern of the electronic levels passing from the latter (with an apical angle of 90°) to the former geometry. This interconversion is obtained by lowering the two *trans* donors of the square pyramid 30° . The diagrams of the electronic energy levels against *pseudo-Dq* ("*Dq*")³ corresponding to the D_{3h} , C_{4v} , and intermediate C_{2v} symmetries are reported in Figure 4. The diagram corresponding to a C_{2v} symmetry with a β angle of 110° should be representative of the actual electronic situation of the NiSALMeDPT chromophore. In fact, although the selection rules agree with C_s symmetry, the energy levels will not sensibly differ from those of a C_{2v} chromophore where the N_3 -Ni-O angles are equal. In Table II the order of levels of such

TABLE II

Symmetry Field		Polarization	Transitions (kK)			
C_{2v}	C_s		Expected	Found		
A_1	B_1	A'	A''	x	4.0	<5.0
	B_2	A'	A''	y, z	7.6	8.4
	A_2	A''	A''	x	8.8	10.0
	A_2	A''	A''	x	13.4	12.8
	B_2	A'	A''	y, z	15.8	16.8
	B_1	A''	A''	x	16.6	
	A_2	A''	A''	x	23.8	
	B_2	A'	A''	y, z	25.2	<i>a</i>
	B_1	A''	A''	x	26.6	

^a Masked by charge transfer.

a geometry together with the C_s labelling and expected polarizations are reported. On the right-

hand side the expected values of the transitions evaluated for a "*Dq*" of 1.3 kK are satisfactorily compared with the found values. Any attempt to get better agreement would require consideration of a set of three different *pseudo-Dq* values and a parameterization of the radial integral ratios G_2/G_4 . We feel that this large number of variables would make unsound a possible better fit. However, in spite of the simplicity of the model used the order of levels is correctly predicted. This confirms the validity of crystal field calculations as a powerful theoretical tool for the interpretation of transition metal ion spectra.

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