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Single Crystal Polarized Electronic Spectra of the Complex bis(N-t-butylpyrrole-2-carbaldimino)cobalt(II)

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Single crystal polarized electronic spectra of the complex bis(N-t-butylpyrrole-2-carbaldimino)cobalt (II) containing the elongated tetrahedral chromophore [CoN_4] have been measured and the bands assigned on the basis of D_{2d} symmetry. Ligand field calculations, in terms of crystal field and angular overlap parameters, have been reported. The donor strength of bidentate conjugated ligands in inner complexes has been discussed.

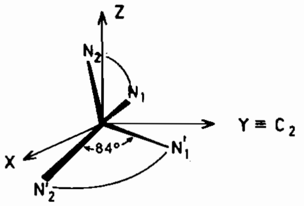

Figure 1. A sketch of the CoN_4 chromophore with some relevant structural parameters.

Introduction

Single crystal electronic studies of pseudotetrahedral cobalt(II) complexes are still needed in order to characterize the electronic situation of these complexes.[1] In particular to our knowledge no single crystal data are available for bis-chelate pseudotetrahedral complexes with conjugated ligands.

The X-ray structure report of the complex bis(N-t-butyl pyrrole-2-carbaldimino)cobalt(II), (CoN_4), with the metal ion possessing a C_2 site symmetry,[2] prompted us to investigate the electronic structure of this complex by means of single crystal spectroscopy.

Experimental

Single crystals of the pure [CoN_4] complex as well as of CoN_4 doped into the isomorphous zinc complex were obtained from n-heptane solutions, as described previously.[3] Weissenberg photographs confirmed that the crystals correspond to those of the X-ray report.[2] They are orthorhombic, space group *Pbcn*; $a = 17.20$ A, $b = 7.18$ A, $c = 15.23$ A, and $Z = 4$. The cobalt ions have C_2 site symmetry, with the twofold axis parallel to the *b* crystallo-graphic axis. The coordination polyhedron can be described in terms of an elongated tetrahedron since four of the six bond angles are larger, and two smaller, than the tetrahedral angle (see Figure 1). The distortion from an ideal elongated tetrahedron is quite small since the angles larger than 109° 28′ are quite close to each other (122°, 123°, 123°, and 126°) and the planes vertical to the elongation axis form angles of 90° between one another. The elongation axis is perpendicular to the C_2 axis, *b*, forming an angle of *ca.* 20° with the *a* axis.

Crystals of various forms were obtained so that the polarized spectra could be recorded on the (001), (100), and (110) faces. The spectra on the (110) face were recorded with the electric vector of the incident light parallel to *c* and normal to it (*r*). Obviously the spectra on the other faces were recorded parallel to *a*, *b*, and *c*. All the spectra were recorded with the apparatus described previously.[4]

Results

The spectra reported in Figures 2–3 show quite different absorptions in the regions below and above 15 kcm^{-1}, which will be discussed separately.

Bands below 15 kcm^{-1}

The spectra measured along the crystal *b* and *c* axes are essentially similar. They show two bands at 9.3 and 7.5 kcm^{-1}, the band at 9.3 kcm^{-1} being slightly more intense in the *c* polarization. The spectra measured on the (001) face gave an *a* spectrum with an intense absorption centered at 9.3 kcm^{-1} with a shoulder on the low frequency side presumably due to the residual intensity of the bands at 7.5 kcm^{-1} allowed in the other polarizations. The spectra recorded on the (100) face gave an *r* spectrum quite similar to the *a* spectrum although less intense.

Bands above 15 kcm^{-1}

The region above 15 kcm^{-1} is characterized by an intense absorption showing several distinct maxima. On the high frequency side of such absorption there is clear evidence of the tail of absorption of a charge transfer (or ligand) transition. The spectra measured along *b* and *c* appear to be essentially similar and are of higher intensity than those measured along *a* and *r*. These latter spectra show six maxima up to 23 kcm^{-1} located at 15.9, 17.1, 18.4, 19.5, 20.9, and 22.1 kcm^{-1}. The spectra measured along *b* and *c* show maxima at 17.0, 19.4, 20.8, and 22.0 kcm^{-1} with a shoulder at 16 kcm^{-1}.

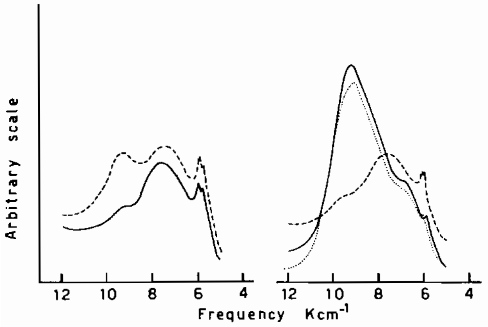

Figure 2. Single crystal polarized electronic spectra of the CoN_4 chromophore at 77K in the range 4–12 kcm^{-1}. Left: spectra recorded on the (100) face; – along *b;* ––– along *c*. Right: spectra recorded on the (110) and (001) faces; for the sake of simplicity the spectrum along *b* (–––) has been reported only once, scaling the *a* (––––) and *r* (· · ·) spectra.

Discussion

Assignment of the Electronic Spectra

The strict similarity of the spectra along *b* and *c* and their neat difference from the spectra along *a* (and *r*) suggests a unique choice of the position of the molecular axes. In fact one axis, say *y*, is determined by symmetry parallel to C_2 and *b*. The *z* and *x* molecular axes must lie therefore on the *ac* plane. In order to account for the strict similarity of the *b* spectrum to the *c* spectrum an axial symmetry must be assumed and the *z* axis must be located almost parallel to *a*, with *x* quite close to *c*. This choice of axes is consistent with the description of the chromophore presented in the experimental section (Figure 1), where the elongation axis of the tetrahedron is called *z*. Such axis is

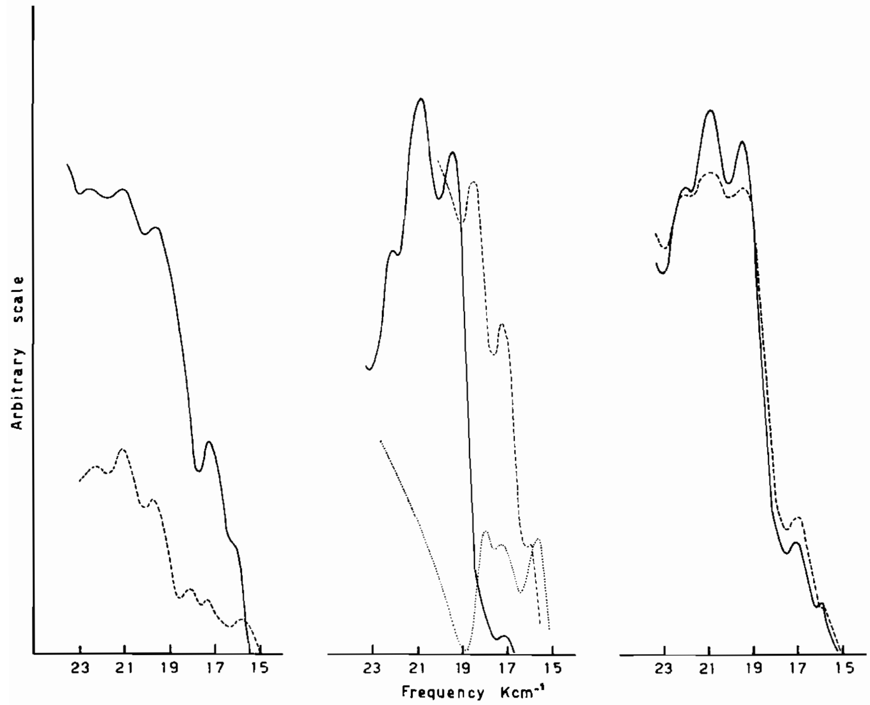

Figure 3. Single crystal polarized electronic spectra of the CoN_4 chromophore at 77K in the range 15–23 kcm^{-1}. Left: spectra recorded on the (110) face; – along *r;* ––– along *c*. Centre: spectra recorded on the (001) face; · · · · along *a;* ––– along *b* (Thick crystal); – along *b* (thin crystal). Right: spectra recorded on the (100) face; – along *b;* ––– along *c*.

close to both *a* and *r* directions: $\cos^2\widehat{az} = 0.88$; $\cos^2\widehat{rz} = 0.75$. The axial symmetry appropriate for the present chromophore is D_{2d} and therefore the band at 7.5 kcm^{-1} is assigned as ⊥ polarized, whereas the band at 9.3 kcm^{-1} is || polarized. The assignment of the bands above 15 kcm^{-1} is less straightforward due to the complex structure of the absorptions in that region. The intense charge transfer transition appears to be definitely ⊥ polarized, while the small maxima at 17.1, 18.4, 19.5, 20.9 and 22.1 kcm^{-1} do not show any definite relative change in the various polarizations. The band at 15.9 kcm^{-1} which appears as a shoulder in the *b* and *c* spectra might have larger intensity in the *a* and *r* spectra. It is therefore tentatively assigned as || polarized.

The ground level for a cobalt(II) ion in an elongated tetrahedral D_{2d} symmetry can be either $^4B_1(e^2b_2)$ or $^4A_2(e^2a_1)$ depending on the extent of distortion. The selection rules for the D_{2d} group are

$B_1 \rightarrow$	A_2	||	$A_2 \rightarrow$	A_2	no
	B_2	no		B_2	no
	E	⊥		B_1	||
				E	⊥

Since the 9.3 kcm^{-1} band is clearly || polarized it must be due to a transition involving the $^4A_2$ and $^4B_1$ levels. The $^4B_1$ level, which correlates to the $^4A_2$ ground level of T_d symmetry, must be either the ground level or a low lying excited one. So, if the $^4A_2$ were the lowest energy state, it would be quite improbable to observe a || polarized transition as high as 9.3 kcm^{-1}. Therefore the spectra are strongly suggestive of a $^4B_1$ ground level in a slightly distorted tetrahedral environment. A tentative assignment of the observed bands is proposed, together with the T_d symmetry parentage reported in brackets

$^4B_1(A_2) \rightarrow$	$E(T_1)$	7.5	⊥
	$A_2(T_1)$	9.3	||
	$A_2(T_1P)$	15.9	||
	$E(T_1, P)$	>17	⊥

A further analysis of the spectra would require a detailed assignment of all the band maxima above 16 kcm^{-1}. They presumably arise from the mixing *via* spin–orbit coupling of the levels arising from the ^4P and the doublet terms of the free ion[5]. When spin–orbit mechanisms have to be considered for the intensities the selection rules are governed by a double point group, which in general corresponds to the actual molecular site symmetry, since the low symmetry components of the ligand field cannot any longer be neglected. However, in the present case, the bands above 15.9 kcm^{-1} appear to be allowed in every polarization, despite the actual C_2 site symmetry and the lack of symmetry of the bidentate ligand.

Ligand Field Calculations

In order to fit the spectra ligand field calculations were performed. The results are reported in Figure 4. The $^4B_1$ is the ground level in a large range of the parameter space, while the energy of the $^4A_2$ is dramatically affected by the value of the radial integral ratio, B_2/B_4, and, less impressively, by the nephelauxetic β. In particular low β values and high B_2/B_4 ratios tend to stabilize $^4A_2$ as the ground level. A systematic variation of the parameters was performed with the aim of reproducing the suggested assignment. In particular it was requested to find a high energy B_1—–$A_2(F)$ transition, with a B_1—E(F) slightly below, and F—P transitions with A_2 lying lower. In the range of Dq 1.0–1.5 kcm^{-1} such order could be reproduced for high β values (> 0.8) and B_2/B_4 ratios in the range 0.1–0.5. The high β values are not unexpected since the F—P transitions are quite high in energy for a pseudotetrahedral cobalt(II) complex[6]. The low B_2/B_4 ratio can be discussed in terms of the corresponding angular overlap parameters[7,8]. As is reported in Figure 4, B_2/B_4 ratios in the range 0.1–0.5 correspond to negative values of the e'_π/e'_σ ratio suggesting the involvement of low energy empty π orbitals of the ligand in the bonding to the metal ion[7].

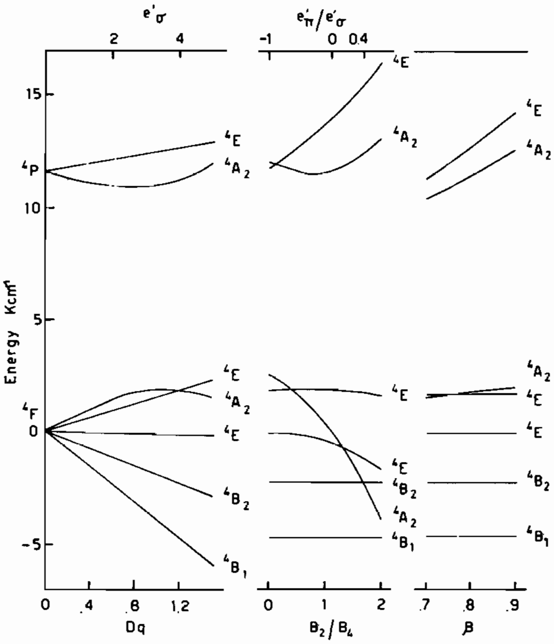

Figure 4. Energy level diagrams for pseudotetrahedral Co^{II} in D_{2d} symmetry as a function of Ligand Field and Angular Overlap parameters. From the left: the effect of varying Dq for $B_2/B_4 = 0.55$, $\beta = 0.80$; the effect of relaxing the B_2/B_4 ratio and the nephelauxetic β parameter. All the diagrams were calculated with Θ, the angle formed by the pseudosymmetry axis and the Co–N direction, of 42°.

Conclusions

The quantitative agreement between the observed and calculated transitions, although not fully satisfactory, can be considered as encouraging, as is shown by Table I, which reports a typical fitting of the transitions. It must be kept in mind that, although polarization properties are indicative of D_{2d} symmetry, it is quite surprising that the two different nitrogen donor atoms of the bidentate ligand are felt as similar by the metal ion. Furthermore the ligand has relatively low energy π orbitals[3] which might interact strongly with the metal orbitals, introducing some inaccuracy in the results of ligand field calculations[7].

TABLE I. A Typical Fitting of the Observed Transitions.

Transition	Observed	Calculated[a]
$B_1 \rightarrow A_1$		2.5
E		5.0
E	7.5	7.0
A_2	9.3	7.6
A_2	15.9	16.7
E	>17	17.2

[a] The parameters used were: Dq = 1300 cm^{-1}; B_2/B_4 = 0.20; β = 0.80. The corresponding angular overlap parameters are e'_σ = 2754 cm^{-1}; e'_π/e'_σ = –0.43.

The high Dq value of Table I, however, strongly suggests that inner complexes with bidentate conjugate ligands are characterized by a high donor strength, as previously proposed[6].

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