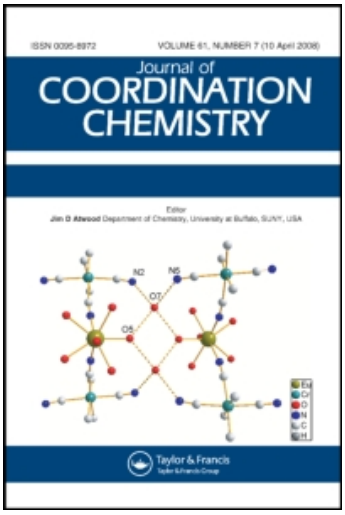

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POLARIZED SPECTRA OF THE TRIGONAL BIPYRAMIDAL $CoNP_3Br$ CHROMOPHORE

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SHORT COMMUNICATIONS

Polarized Spectra of the Trigonal Bipyramidal $CoNP_3Br$ Chromophore

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The electronic spectra of high-spin pentacoordinate cobalt(II) complexes have been tentatively assigned on the basis of a ligand field approach.[1–3] A controversy has arisen about the assignment of the spectrum of a typical chromophore, CoN_4Br, having strictly C_{3v} symmetry in the compound $[CoBr(Me_6tren)]Br$, where Me_6tren is $N[CH_2CH_2N(CH_3)_2]_3$. This spectrum shows four distinct bands well separated from charge transfer bands at 5.7, 12.3, 16.1 and 19.2–19.8 kK.[4] Ciampolini and Bertini[2] assigned these bands to transitions from the $^4A_2$(F) ground state to the ^4E(F), ^4E(F), $^4A_2$(P), and ^4E(P) excited states whereas Wood[3] assigned the second band to a spin forbidden transition, the third band to a transition to the ^4E(F) level and the last band to the two transitions to the highest two levels. Because of the cubic symmetry of the crystal lattice of this compound,[5] polarized spectra were of no aid in deciding the correct assignment.

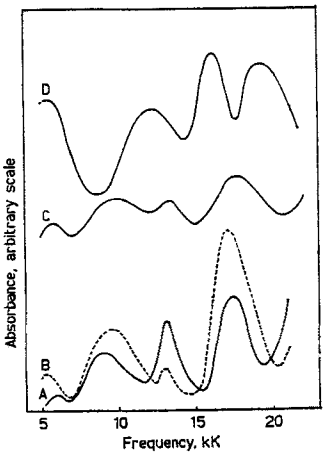

FIGURE 1 Spectra of $[CoBr(NP_3)]PF_6$: A, polarized along "a" direction; B, polarized along "b" direction; C, unpolarizated reflectance spectrum. The D curve is the reflectance spectrum of $[CoBr(Me_6tren)]Br$.

In this communication additional clarifying data are reported concerning the polarized spectra of the chromophore $CoNP_3Br$ in the compound $[CoBr(NP_3)]PF_6$,[6] where NP_3 is $N[CH_2CH_2P(C_6H_5)_2]_3$, which has essentially C_{3v} symmetry.[7,8] The trigonal bipyramidal structure of this chromophore is distorted toward a tetrahedron in that the cobalt ion lies below the P_3 plane, the N–Co–P angle is less than 90° and the Co–N distance is larger than usual.[7,8] The polarized spectra on single crystals of this compound have been obtained with a Unicam SP 700 spectrophotometer[9] and are reported in Figure 1 together with the reflectance spectrum.[10] The reflectance spectrum of the $[CoBr(Me_6tren)]Br$ complex is also reported for comparative purposes.[4]

The spectrum of the former complex consists of four well resolved bands at 5.7, 10.0, 13.3, and 17.5 kK.[6] Their polarization is quite clear. The bands at 5.3, 9.6, and 17.2 kK are polarized in the same direction while the band at 13.0 kK is polarized perpendicularly.[10] By comparison with the calculated polarization, the only possible assignment is that shown in Table I. Given the close similarity of this spectrum with that of the CoN_4Br chromophore, the assignment of the bands for this complex must also be the same. This

TABLE I

Polarized spectral data for the $[CoBr(NP_3)]PF_6$ compound

Absoption maxima (kK)	Transition	Expected Polarization	Relative direction of polarization
5.7	$^4A_2$(F) → ^4E(F)	xy	b
10.0	→ ^4E(F)	xy	b
13.3	→ $^4A_2$(P)	z	a
17.5	→ ^4E(P)	xy	b

supports the assignment proposed by Ciampolini and Bertini.[2]

The most significant difference between the spectra of the chromophores CoN_4Br and $CoNP_3Br$ is a red shift of the bands of the latter complex in respect of those of the former one. This is well accounted for by the tetrahedral distortion of the $CoNP_3Br$ chromophore. In fact tetrahedral complexes with C_{3v} symmetry are known to have a compressed *d–d* spectrum (until 16 kK) and the bands have been found to have the same polarization properties.[11]

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