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Single-Crystal Polarized Electronic Spectra of Tetra-*n*-Butylammonium Tribromo(quinoline)cobaltate(II)

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*Single-crystal polarized electronic spectra of the pseudo-tetrahedral tetra-*n*-butylammonium tribromo(quinoline)cobaltate(II) have been recorded along three independent directions. To a first approximation the spectra have been assigned on a C_{3v} symmetry, whereas a more detailed interpretation requires the introduction of C_1 low symmetry components. Such a behaviour has been compared with that of several other chromophores, both of nickel and cobalt, whose actual symmetry is C_1, whereas the gross features of the spectra have been accounted for on the basis of higher symmetries.*

Introduction

The polarization properties of the *d-d* transitions of metal complexes can be often interpreted on the basis of an idealized symmetry which is higher than the actual one.[1] For example the polarization properties of 5-coordinated nickel(II) and cobalt(II) complexes with Me_6tren (tris(2-dimethylaminoethyl)amine) have been accounted for on the basis of an axial C_3 symmetry,[2,3] although they have a C_1 site symmetry and a rather distorted arrangement of the five donors around the metal. On the contrary the triiodo(triphenylphosphine)nickelate(II) complex showed a polarization pattern of the bands which could not be accounted for on the basis of axial symmetry.[4] This was related to the existence of a degenerate ^3E ground level split under spin orbit coupling, which is large in tetrahedral complexes, and low symmetry components. It appears therefore interesting to see if the polarization properties of pseudotetrahedral complexes for which an orbitally non-degenerate ground level is expected can be accounted for on the basis of an idealized geometry. For these purposes the tetra-*n*-butyl-ammonium tribromo(quinoline)cobaltate(II), Co(quin)Br_3 $(C_4H_9)_4N$, having a pseudoaxial symmetry within the $CoNBr_3$ chromophore, has been chosen. Also the spectra of the triiodo(triphenylphosphine)cobaltate(II) complex, $CoPI_3$, have been recorded for comparison purposes.

Experimental Section

Single crystals of Co(quin)Br_3 and Co(quin)Br_3 doped into Zn(quin)Br_3 (Co/Zn = 1/5) were obtained from the respective solutions of the complexes in *n*-butyl alcohol. After standing under nitrogen atmosphere for several days thin plates of the pure complex and thick prismatic crystals of the doped complex were obtained. The Weissenberg photographs showed that the crystals were isomorphous to those of Ni(quin)Br_3 described by Horrocks, Templeton, and Zalkin.[5] The crystals belong to the P1 space group with $Z = 2$. The most developed face was found to be (010). For the prismatic crystals the (100) face too was suitable for recording electronic spectra. The extinction directions on the (010) face are at 14° from *c*, towards *-a* (R) and perpendicular to it (*S*); on the (100) face at 40° from *c* towards *b* (*U*), and perpendicular to it (*V*).

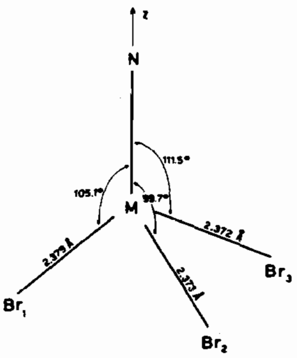

Figure 1. A scheme of the $NiNBr_3$ chromophore with the relevant bond distances and angles. The cobalt analogue is isostructural[5].

A scheme of the chromophore is shown in Figure 1 together with relevant distances and angles as found for the Ni complex.[5] If the M-N axis is assumed as the *z* axis of the $MNBr_3$ chromophore, the squares of the projections of the electric unit vector along the four extinction directions are *R* (0.12), *S* (0.10), *U* (0.00), *V* (0.88).

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[1] B.J. Hathaway, and D.E. Billing, *Coord. Chem. Rev.*, *5*, 143 (1970). N.S. Hush and R.J.M. Hobbs, *Prog. Inorg. Chem.*, *10*, 259 (1968).

[2] I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem.*, *11*, 2254 (1972)

[3] I. Bertini, M. Ciampolini, and D. Gatteschi, *Inorg. Chem.* *12*, 693 (1973).

[4] I. Bertini, D. Gatteschi, and F. Mani, *Inorg. Chem.*, *11*, 2464 (1972).

[5] W. De W. Horrocks, Jr. D.H. Templeton, and A. Zalkin, *Inorg. Chem.*, *7*, 2303 (1968).

[6] F.A. Cotton and D.M.L. Goodgame, *J. Am. Chem. Soc.*, *82*, 2967 (1960).

Thin plates of the CoPI$_3$ complex[6] were obtained from *n*-butanol solutions. They are not isomorphous to the nickel analogue,[7] therefore no structural data are available for this complex.

Polarized electronic spectra were recorded with a Unicam SP700C spectrophotometer, as described elsewhere.[4]

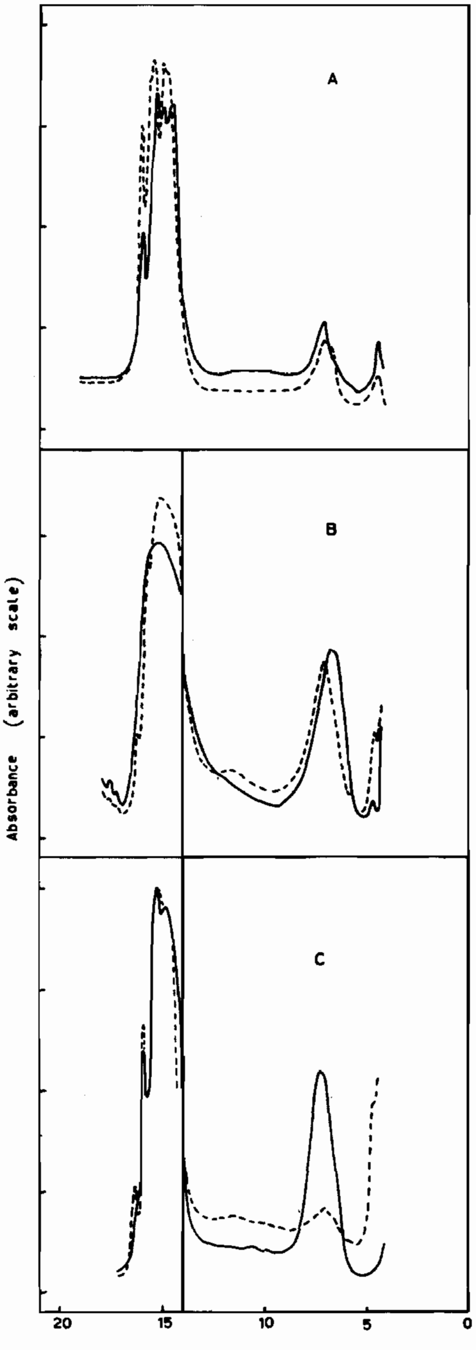

Figure 2. Single crystal polarized electronic spectra recorded at 77 K of: A, Co(quin)Br$_3$, face (010), full line, along *R*, broken line, along *S*; B, Co(quin)Br$_3$ doped in Zn, face (010), full line, along *S*, broken line, along *R*; C, Co(quin)Br$_3$ doped in Zn, face (100), full line, along *U*, broken line, along *V*.

Results and Discussion

The two pair of single crystal spectra obtained at 77 K on the (010) and (100) faces of the doped crystals of Co(quin)Br$_3$ are shown in Figure 2 together with the spectra on the (010) face of the pure complex. No substantial differences are observed between the room temperature spectra and the liquid nitrogen temperature spectra except for the better resolution of the sharp bands around 15 kK in the latter spectra. The spectra on the (100) face show a net polarization of the bands in the near infrared region, *i.e.* at *ca.* 7 kK and possibly below 5 kK, whereas the system of bands centered at 15 kK is almost unaffected by the change of the light polarization. The spectra on the (010) face on the contrary are quite similar, although minor changes in the peak maxima and intensity variations in some components of the complex system centered at 15 kK (especially for the pure complex) are observed. From the square of the components of the *z* axis along the four extinction directions, no changes in the polarization properties are expected on the spectra recorded on the (010) face, whereas the spectrum along *V* (100 face) is expected to be mostly parallel polarized and the spectrum along *U* 100% normal polarized. Therefore if the axial model is operative, the band at 7 kK is normal whereas the band below 5 kK is parallel.

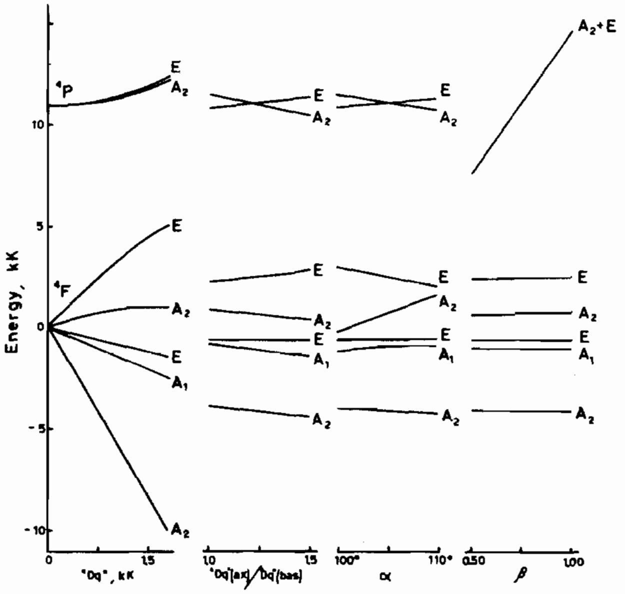

Figure 3. Energy level diagram for a pseudotetrahedral Co(II) ion in C$_{3v}$ symmetry: Dq(ax)/Dq(bas) = 1.2; β = 0.75; B$_2$/B$_4$ = 1.0; average N-Co-Br angle 105°. From the left the effect of relaxing the Dq(ax)/Dq(bas) ratio, the N-Co-Br angle α, and the nephelauxetic parameter β is shown for Dq(eq) = 0.75 kK. Relaxing the B$_2$/B$_4$ ratio in the range 0-4 *accidentally* does not affect the energy levels.

Ligand field calculations of pseudotetrahedral Co^{II} complexes with C$_{3v}$ symmetry (Figure 3 show that the ground level is $^4A_2$ under a large variation of the parameters describing the ligand field).

If the energy level order is taken as resulting from Figure 3 the following transitions and polarizations are expcted

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(7) R.P. Taylor, D.H. Templeton, Z. Zalkin, and W. De W. Horrocks, Jr *Inorg. Chem.*, *7*, 2629 (1968).

${}^4A_2\rightarrow{}^4A_1$ not allowed
${}^4E$ ($\perp$)
${}^4A_2$ ($\|$)
${}^4E$ ($\perp$)
${}^4A_2(P)$ ($\|$)
${}^4E(P)$ ($\perp$)

By comparing these expectations with the polarized spectra, the band below 5 kK is assigned to the ${}^4A_2\rightarrow{}^4A_2(F)$ transition and that at 7 kK is assigned to ${}^4A_2\rightarrow{}^4E(F)$. The band at *ca.* 15 kK must be assigned to the F→P transitions. It is quite surprising that the gross intensity of the band remains practically unchanged as the polarization plane is rotated while it is supposed to be composed of two main transitions parallel and normally polarized respectively. This assignment is consistent with other assignments proposed for pseudotetrahedral Co^{II} complexes as the transitions to the levels arising from the ${}^4T_2$ (T_d symmetry) are expected below the range of investigation.[8-14]

The observed energy order can be reproduced quite closely by ligand field calculations for Dq(bas)[15] .75-.80 kK, Dq(ax) .90-1.00 kK, nephelauxetic β .75-.65. These ranges of variability of the parameters are those usually found for chromophores with symmetry lower than cubic[16] containing nitrogen and halogen donor atoms.[2,3] Relaxing the B_2/B_4 radial integral ratio in the range 0-4 has little effect on the energy levels. The splitting of the $A_2(P)$ and E(P) levels, due to the reduction of the α angle from the tetrahedral value, is partly balanced by Dq(ax) being larger than Dq(basal) in such a way that these two levels are always quite close in energy.

These results, in particular the F→F transitions, show the validity, at least to a first approximation, of the axial model for matching the polarization properties. Such model was found inadequate[4] for the analogously trigonally distorted $NiPI_3$ chromophore; presumably the different behaviours of the two chromophores can be ascribed also to the different orbital degeneracy of the ground level. A relatively small low symmetry distortion of a chromophore having a degenerate ground level in the idealized symmetry can be magnified (both in the energy separations of the various states and in the wave functions mixing) by spin-orbit coupling effects in such a way that the idealized symmetry is not capable anymore to account for the polarization properties. When the ground level is not degenerate, spin-orbit coupling effects are expected to be small (second order perturbation). Therefore, provided the energy separations of the states arising from the excited levels are within the band envelope, the band polarizations can possibly be explained on the basis of the idealized symmetry. This seems to be the case of the $CoNBr_3$ chromophore. This interpretation can be applied quite well to the spectra of the nickel and cobalt complexes reported by Quagliano *et al.*[9] Although they did not know the structures of the complexes[17] they were able to propose an assignment for both complexes in C_{3v} symmetry; however the spectra of the nickel complexes are reported to show large intensity variations with temperature. It is possible that, as in the case of the $NiPI_3$ chromophore, the temperature dependent intensities of the bands result from a temperature dependent population of the levels arising from the zero field splitting.

Quite analogous to the present $CoNBr_3$ spectra are the spectra of $CoPI_3$ (see Figure 4). Although the structure is not known it seems reasonable to assign the band at ~7 kK to the $A_2\rightarrow E$ transition ($\perp$), possibly the band below 5 kK to the $A_2\rightarrow A_2$ transition ($\|$), and the band at 13.5 kK to the two F→P transitions. The bathochromic shift of the latter transitions is presumably due to nephelauxetic effects.

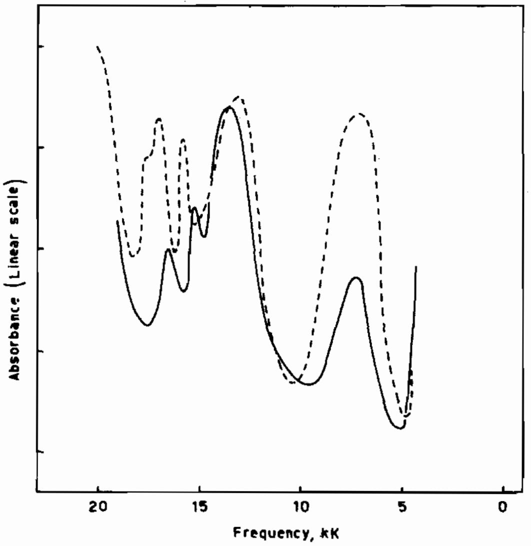

Figure 4. Single-crystal polarized electronic spectra of the $CoPI_3$ chromophore recorded at 77°K.

The non-dependence of the intensity of the band attributed to F→P transitions from the polarization direcions is presumably to be ascribed both to the proximity of the two A_2 and E levels[18] and to the presence in that region of numerous doublet levels. The mixing *via* spin-orbit coupling of all of these levels may account for the lack of polarization and for the high number of peaks observed, the shape of most of them being typical of spin forbidden transitions. The proximity of the A_2 and E levels by itself cannot account for the polarization properties of the main band since the F→F bands, although close to each other, in general show a dependence of the intensity on the polarization directions.[1,19] On the other hand

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(8) F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.* 83, 4690 (1961).

(9) B.B. Garret, V.L. Goedken, and J.V. Quagliano, *J. Am. Chem. Soc.*, *92*, 489 (1970).

(10) J. Ferguson, *J. Chem. Phys.* 35, 528 (1960). *Ibid.* 39, 116 (1963).

(11) A.B.P. Lever and S.M. Nelson, *J. Chem. Soc.*, (*A*) 859(1966).

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(13) E.M. Holt, S.L. Holt, and K.J. Watson, *J. Am. Chem. Soc.*, *92*, 2721 (1970).

(14) A.A.G. Tomlinson, C. Bellitto, D. Piovesana, and C. Furlani, *JCS Dalton*, 350 (1972).

(15) *Dq* is $B_4/6$.

(16) M. Ge loch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc.*, (*A*), 3269 (1970).

(17) An X-Ray structure determination in progress at Pennsylvania State University has shown that the complexes have a C_1 site symmetry. W. De W. Horrocks, Jr. private communication.

(18) A. Flamini, L Sestili, and C. Furlani, *Inorg. Chim. Acta*, *5*, 241 (1971).

(19) I. Bertini and D. Gatteschi, *J. Coord. Chem.*, *1*, 285 (1971).

the presence of numerous doublet levels does not appear to invalidate the orbital selection rules in every case. In fact the two F→P transitions, which are well separated in high spin trigonal bipyramidal cobalt complexes, are neatly polarized.[3,20]

Now the residual polarizations of the spikes located above the F→P transitions and the small frequency shifts in the band maxima of the spectra recorded along the *R* and *S* directions remain to be explained. Evidently the C_{3v} symmetry is not quite satisfying as the two spectra should be identical: low symmetry components, together with spin-orbit coupling effects, should be taken into account. Since in the present case the effective symmery is presumably C_1 any further analysis is precluded. However the above pattern could in principle be explained by a C_1 low symmetry component.

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(20) I. Bertini, M. Ciampolini, and L. Sacconi, *J. Coord. Chem.*, *1*, 73 (1971).