Vibronic Structure in the Circular Dichroism of α-$Ni(H_2O)_6SO_4$

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Summary The circular dichroism of single crystals of α-$Ni(H_2O)_6SO_4$ at cryogenic temperatures reveals extensive vibronic structure in the "red band" of the $Ni(H_2O)_6^{2+}$ chromophore which leads to new conclusions as to the assignment of and origin of intensity in this band system.

VIBRONIC structure in circular dichroism (c.d.), though previously observed in several organic chromophores,[1-4] has been reported in only one transition-metal complex, the (+)-$Co(en)_3^{3+}$ ion.[5] We report here our work on α-$Ni(H_2O)_6SO_4$, not only because of the novelty of the results, but because of (1) the growing recognition of the importance of vibronic interactions in the c.d. of forbidden transitions,[1-3] (2) the fundamental relation of this work to the optical activity of helices,[6] and (3) the conclusions regarding the assignment of the spectrum, which vary considerably from those previously reached on the basis of absorption measurements and theoretical calculations.[7-11]

α-$Ni(H_2O)_6SO_4$ belongs to a relatively small group of verified examples of enantiomorphic crystals that contain no inherently dissymmetric molecules. In these substances optical activity is associated only with the crystalline state. Such crystals provide ideal models for the study of intrinsically symmetric chromophores in the classic dissymmetric environment of an infinite helix.[6] This is particularly true when the lattice is cubic or, as in the case of α-$Ni(H_2O)_6SO_4$, uniaxial, thus offering at least one view free of linear birefringence effects.[12] The crystals of α-$Ni(H_2O)_6SO_4$ belong to enantiomorphic space groups $P4_12_12$ and $P4_32_12$, with four molecules per unit cell arranged spirally along either right or left-handed four-fold screw axes.[13] Recent neutron-diffraction studies[14] have established that the configuration of the Ni–O_6 cluster is octahedral within the limits of experimental error. However, the site symmetry of the nickel ion is only C_2 and no axis of the octahedron is aligned with the tetragonal crystal axis. Earlier low-resolution studies[15,16] of the optical activity have established the rough shape and $\Delta\epsilon$'s of the c.d. bands associated with the three spin-allowed ligand-field transitions.

Our c.d. spectra have been measured on single-crystal plates cleaved along the (001) plane. The path of the light was parallel to the tetragonal (helix) axis. The visible and near-u.v. spectra were measured on a Durrum–Jasco ORD/CD/-5 c.d. recorder and the near-i.r. spectra on a Cary Instruments Model 1402 c.d. accessory to the Cary Model 14R spectrophotometer. A quartz cryostat was used for measurements at 80° K and an Andonian Associates model 0-24/7M variable-temperature cryostat at temperatures between 3·4 and 20° K. The sample temperature below 20° K was measured by a calibrated germanium resistor and a conductance bridge. The temperatures are believed accurate to $\pm 0{\cdot}1°$ K in this region. The energies and $\Delta\epsilon$'s of the maxima in the spectrum are given in the Table.

Circular dichroism of α-Ni(H$_2$O)$_6$SO$_4$ *at* 5°K

Band maxima (K)	$\lvert\Delta\epsilon\rvert \times 10^3$	Excited state
25,732	18	$^3T_{1g}(P)$
23,450	4·0	$^1T_{2g}(D)$, $^1A_{1g}(G)$
21,350	0·65	
19,300 (s)	1·9	$^3T_{1g}(F)$
18,600 (s)	2·8	
16,949 (s)	15	
16,447	28	
15,974	45	
15,601	59	
15,360	65	
14,970	62	
14,577	49	
14,184	37	
13,908	27	
13,794 (s)	26	
13,404	14	
13,072	8	
13,014	8	
8800 (a)	370	$^3T_{2g}(F)$
8600 (a)	378	

(a) Observed at 80°K
(s) Shoulder.

The most intriguing results of this study involve the temperature-dependence and fine structure of the so-called "red band" of the Ni(H$_2$O)$_6^{2+}$ chromophore. Although at 300°K the c.d. spectrum of the "red band" (Figure) is similar in contour to the axial absorption spectrum, the contrast at lower temperatures is striking. Whereas even at liquid-helium temperatures the absorption spectrum of the "red band" is rather poorly resolved, the c.d. spectrum already shows clean resolution into eleven distinct maxima and shoulders at 80°K. At 20° K and below, still more resolution is obvious.

It appears that the structure of this band in the c.d. spectrum is entirely vibronic in origin and that two progressions account for virtually all the features observed at 5° K. The drastic decrease of intensity in the region of the low-energy side of the double-peaked room-temperature band suggests strongly that the intensity in this part of the band is due entirely to "hot bands."[2] At 5° K, an almost symmetrical band envelope remains, with its maximum extinction at 6510 Å (15,360 cm.$^{-1}$). A distinct seven-membered progression in quanta of 390 ± 10 cm.$^{-1}$ appears on the low-energy side with a second progression in quanta of 470 ± 10 cm.$^{-1}$ becoming dominant on the high-energy side. This second progression is more prominent near 80° K. Where these two progressions are of comparable intensity, near the maximum of the band, an unusual exchange of intensity occurs between the maxima at 6510 and 6410 Å (15,360 and 15,601 cm.$^{-1}$) over the temperature range from 3·4 to 80° K, with the 6410 Å peak dominating at 17° K and higher and the 6510 Å peak becoming dominant below 9° K. In thicker crystals the dichroism due to the progression in the symmetric stretching vibration of the H$_2$O ligands previously reported in the absorption spectrum[10] is also observed and has been verified by its 800 cm.$^{-1}$ isotopic shift in the c.d. of the α-Ni(D$_2$O)$_6$SO$_4$ crystal.

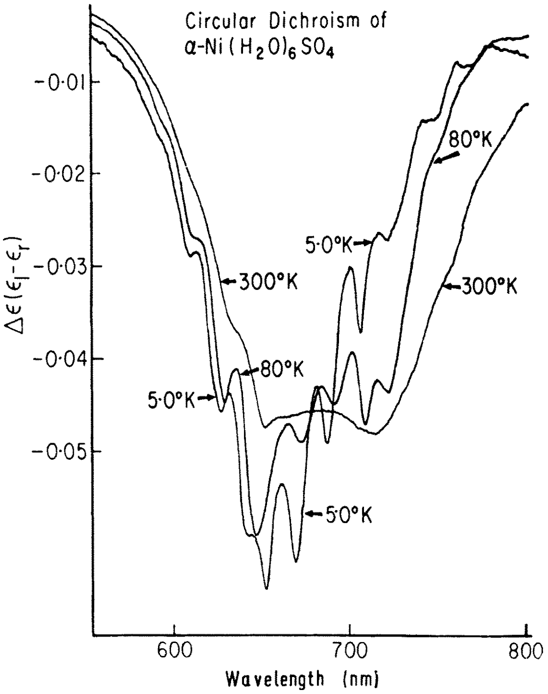

FIGURE. *Photographed traces of circular dichroism spectra of* ($-$)α-Ni(H$_2$O)$_6$SO$_4$ *at* 300° K, 80° K, and 5·0° K *in the region of the* $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ *band.*

We suggest the following conclusions:

(1) The "red band" in the c.d. spectrum of the Ni(H$_2$O)$_6^{2+}$ chromophore can be assigned to vibronic progressions associated with the transition $T^3{}_{1g}(F) \leftarrow {}^3A_{2g}$ only. It is likely that this is true for the absorption spectrum as well.[17] The lack of comparable low-temperature resolution in the absorption spectrum may be due to low-energy *ungerade* bending modes which are not effective in loaning c.d. intensity.

(2) The origin of the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ band, that is, the energy of the pure electronic transition, is at *ca.* 13,000 cm.$^{-1}$. This assumes that the first observed member of the 390 cm.$^{-1}$ progression is the (1–0) component.

(3) Evidence for spin-orbit splitting[9,11] in the "red-band" is lacking in the c.d. spectrum. The possibility that the 390 cm.$^{-1}$ and 470 cm.$^{-1}$ progressions arise from different origins seems less likely than that the two progressions are based on the same origin and reach their maximum intensity at different energies owing to dissimilar vibrational energies

and potential well shapes. It seems reasonable that this conclusion also can be extended to include the absorption spectrum.

(4) There is no clear evidence in the c.d. spectrum of the ${}^1E_g(D) \leftarrow {}^3A_{2g}$ transition, which has figured prominently in the controversy over the assignment of the red band.[7,9,10] Because of the correlation of the ${}^1E_g$ level with the $t_{2g}{}^6e_g{}^2$ configuration, this transition should be most intense in the first member of a rapidly weakening progression with an origin at approximately 13,000 cm.$^{-1}$. Though such a transition should be more intense in c.d.[18] than absorption, it is not observed.

(5) Indication of trigonal splitting as suggested by Gillard[19] is lacking in the c.d. spectrum. However, that such a splitting might be observed in the ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition is conceivable owing to the effective precession of the pseudo-C_3 axes of the $Ni(H_2O)_6{}^{2+}$ clusters about the tetragonal crystal axis, giving an average trigonal aspect to their orientation. In such a space-averaged D_3 symmetry only the ${}^3E({}^3T_{1g}) \leftarrow {}^3A_2$ transition would be observed in the axial spectrum.

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