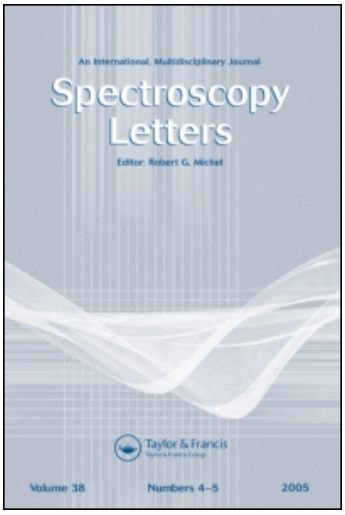

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The Vibrational Spectra of (1-Diacetylmonoximeimino-3-diacetylmonoximatoiminopropane)-methylaquocobalt (III), Perchlorate

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THE VIBRATIONAL SPECTRA OF (1-DIACETYLMONOXIMEIMINO-3-DIACETYLMONOXIMATOIMINOPROPANE)-METHYLAQUOCOBALT(III), PERCHLORATE

Key words: Infrared dichroism, Raman spectra, Diacetylmonoximato Cobalt complex.

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INTRODUCTION

Metal complexes of the tetradentate ligand bis(diacetylmonoximeimino)propane 1,3 = $[(DOH)_2pn]$ are interesting in several respects. They are representatives of molecular systems containing very short hydrogen bonds; moreover, the organo-cobalt derivatives were reported as first examples of stable water-soluble compounds besides Vitamin B_{12} coenzyme and alkylcobalamines [1]. From this point of view they were extensively investigated as models of Vitamin B_{12} [2]. However, vibrational data concerning these complexes are rather scarce: at our knowledge only a limited assignment was proposed by UHLIG and FRIEDRICH [3] for some Ni derivatives.

This paper reports the results of the investigation on the infrared crystal spectrum in polarized light of the perchlorate of the methylaquo complex, $[CH_3Co(III)(DO)(DOH)pnH_2O]^+ ClO_4^-$. The Raman spectrum of the polycrystalline complex is also reported.

EXPERIMENTAL

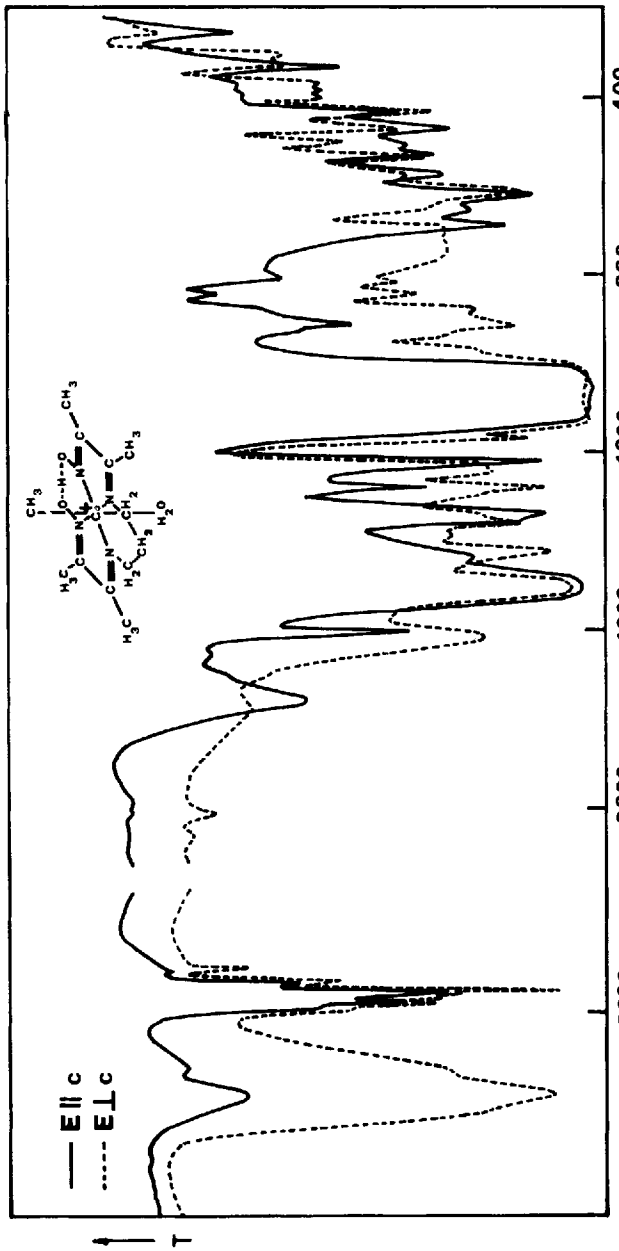
Samples of $[CH_3Co(III)(DO)(DOH)pnH_2O]^+ ClO_4^-$ were in the form of orthorombic crystals of small cross-section elongated along ⟨001⟩.Thin crystal slices were prepared by polishing:due to the small cross-section it was possible to obtain only planes of the type (hk0).The infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer.Polarized spectra were obtained using a wire-grid polarizer and a mirror beam-condenser.Spectra of polycrystalline samples were also obtained at ~100°K,between 4000 and 600 cm^{-1},using a Beckmann-RIIC VLT2 unit.

The Raman spectra,excited by the 6471 Å line of a Spectra-Physics 165-01 Kr^+ laser,were recorded with the aid of a SPEX "Ramalog" instrument in conjunction with a rotating cell. Samples in the form of pellets were prepared by mixing the complex with powdered KBr.No colour change was observed after the measurements.Infrared spectra of disks prepared from the part of the pellet exposed to the laser radiation did not reveal signs of decomposition.

SELECTION RULES

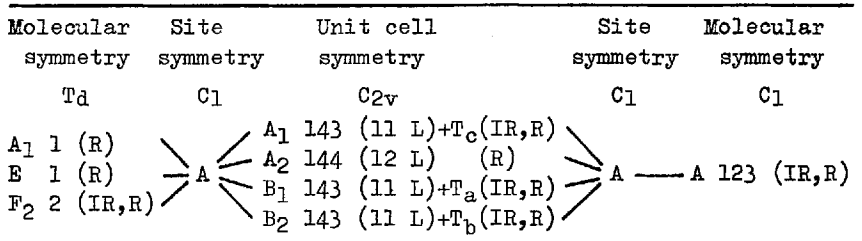
According to the crystal structure reported by BRÜCKNER et al.[4] the crystals of the title compound belong to the non-centrosymmetric space group Fdd2 (C_{2v}^{19}).The crystallographic cell contains 16 formula units on C_1 sites.The exact molecular symmetry is also C_1 for the organometallic cation,whereas a T_d symmetry is assumed for ClO_4^-.Choosing a primitive cell containing 4 formula units the selection rules should be as reported in Table 1.

A complicated crystal spectrum is expected on the basis of these selection rules.Two experimental observations can help



Polarized infrared spectrum of $[CH_3Co(DO)(DOH)pnH_2O]^+ ClO_4^-$, (hk0) crystal plane.

Table 1.
Symmetry classes and selection rules



L = lattice mode

to interpret the recorded spectra. Firstly, most infrared bands show a remarkable dichroism and maximum absorption wavenumbers which only slightly shift (2-3 cm^{-1}) when the electric vector direction is rotated. This suggests a small factor group splitting and justifies the use of the oriented gas approximation. Secondly, the spectra of complexes of the type LCo(DO)(DOH)L' (L=Br,J,C_2H_5,CH_3;L'=Br,J,H_2O) are very similar one another at least as far as the low wavenumber region is not concerned. Therefore it appears reasonable to discuss the chelate ring vibrations neglecting the axial ligands and to classify them on the basis of a C_s symmetry, with the mirror plane perpendicular to the chelate rings and bisecting the O..H..O bridge. Using the X-ray data [4] the direction cosines of the normal to the mirror plane with respect to the crystal axes may be obtained. The proportionality factors for the absorption intensities of the A" vibrations calculated from the values of the direction cosines are

	a	b	c
normal	0.7697	0.2188	0.0101

It follows that,on a (hk0) plane,the A" bands should appear when the electric vector is perpendicular to the c crystal axis, showing only a small intensity in the parallel polarization.The A' transition moments lie in the mirror plane,but their direction is not further fixed so that the polarization of the corresponding bands cannot be safely predicted.However,keeping in mind the orientation of the cations in the crystal,bands showing a prevailing parallel character,or both parallel and perpendicular components of comparable intensity,may be assigned to A' modes.

RESULTS AND DISCUSSION

The proposed assignments are collected in Table 2 and only the most relevant features are discussed in the following.

The OH stretching modes of the coordinated water appear resolved only at low temperature.The H_2O scissoring mode is observed at 1635 cm^{-1} at low temperature:at room temperature only a shoulder appears on the high frequency side of the skeletal stretching band at 1605 cm^{-1}.

The strong absorption near 1500 cm^{-1},with prevailing parallel character,may be attributed to a vibration corresponding to the B_{1u} skeletal stretching assigned between 1600 and 1500 cm^{-1} in the spectra of dimethylglyoximates [5].A shoulder,with counterpart in the Raman spectrum,appears at 1545 cm^{-1} at low temperature suggesting the presence of another fundamental in this region.Other components are not apparent in the absorption spectra.The Raman spectrum,however,shows an additional component on the high frequency side of the fundamental at 1500 cm^{-1}. Although correlation field effects cannot be ruled out,an explanation in terms of LO-TO splitting may be proposed keeping in mind the polar nature of the phonons in the investigated crystals and the high intensity of the infrared band [6].

Table 2.
Experimental spectral data for $[CH_3Co(III)(DO)(DOH)pnH_2O]^+ ClO_4^-$

i.r.frequencies and polarization		Raman shifts		Assignment	
3440 ±	⊥,∥				
3380 ±	⊥			H_2O ν_1, ν_3	
3280 sh	⊥				
2990 sh	∥,⊥				
2965	∥,⊥	2961	vw	A'	CH_3 stretching
2943	⊥			A"	CH_3 stretching
2921	∥,⊥	2916	sh	A'	CH_3,CH_2 stretching
2906	∥,⊥	2901	w	A'	CH_3,CH_2 stretching
		2983	sh		
2854	∥,⊥	2847	vw	A'	CH_2 stretching
....		....			
1780 }	⊥<			A'	O..H..O in-plane deformation
1760 }	<∥				
1620	⊥				H_2O ν_2
1605	∥,⊥	1600	w	A"	skeletal stretching
		1559	vw		
1545 ±		1545	vw	A'	skeletal stretching
1500 ±±	∥,⊥	1509		A'	LO
		1492			TO skeletal stretching
1473 sh	∥,⊥	1477	mw	A'	CH_3 asym.deformation,CH_2 scissoring
1432	⊥	1437	w	A"	CH_3 asym.deformation,CH_2 scissoring
1385	⊥			A"	CH_3 sym.deformation,CH_2 wagging
1360	∥,⊥	1355	m	A'	CH_3 sym.deformation
1345	∥			A'	CH_3 wagging
1278	⊥>∥	1280	w	A"	CH_2 twisting
1252	⊥			A"	CH_2 wagging
1232	∥,⊥	1240	vw	A'	skeletal stretching
1174	⊥	1163	w	A"	CH_2 twisting
		1134	w		skeletal stretching
‡		1090	w		
		1053	vw		
		1039	vw		CH_3 rocking + skeletal stretching
1020	∥,⊥	1026	vw	A'	
		998	w		
		954	vw		
		941	m		ClO_4^- ν_1

(continued...)

Table 2.(Contd.)

920	⊥ > ∥	924 w	A"	CH_2 rocking
880	⊥		A"	skeletal stretching
850	⊥	853 vw	A"	skeletal stretching
		841 vw		
820	⊥	821 w	A"	
810	∥	811 w	A'	CH_2 rocking
		802 sh		
770	⊥		A"	O..H..O asym.stretching
723 ✱		713 w	(A')	CH_2 rocking
695	∥,⊥	695 w	A'	skeletal deformation
672 ✱	∥,⊥			H_2O wagging
625	∥,⊥	628 vw		ClO_4^- ν_4
586	∥>⊥	588 m	A'	skeletal deformation
535 }	⊥		A'	skeletal deformation
532 }	∥			
505	∥,⊥	508 vs	A'	skeletal stretching (Co-N)
474	∥,⊥		A'	skeletal deformation
		462 w		ClO_4^- ν_2
436	∥,⊥	440 w	A'	skeletal deformation
403	⊥	403 w	A"	
392	⊥		A"	skeletal stretching (Co-N)
378	⊥	377 w	A"	skeletal deformation
340 }	∥ >		A'	skeletal stretching (Co-N)
330 }	>⊥			
310	⊥	315 s	A"	skeletal stretching (Co-N)
		293 m		
260	∥	266 m	A'	skeletal deformation
		186 s		skeletal deformation
		123 s		skeletal deformation
		87 sh }		lattice vibrations
		78 s }		

✱): value quoted from low-temperature spectrum; ✱✱): value quoted from powder spectrum; ‡): region obscured by ClO_4^- absorption.

The parallel polarization of the band at 1232 cm^{-1} is consistent with the assignment to a skeletal stretching mode corresponding to the B_{1u} vibration of dimethylglyoximates found in the same region [5]. A Raman band at 1134 cm^{-1} may be assigned to a similar vibration corresponding to the B_{2u} mode of the dimethylglyoximates observed near 1100 cm^{-1}. The infrared band is probably hidden by the strong absorption due to the ν_3 vibration of ClO_4^-.

The dichroism supports the assignment of most of the CH_2 wagging, twisting and rocking vibrations: the assignment of the A' rocking mode at 723 cm^{-1} is tentative since the band is clearly resolved only at low temperature and polarization data are not available.

Metal-ligand stretching vibrations are assigned in the range 500-300 cm^{-1} by analogy with dimethylglyoximates [5].

A diffuse absorption on which skeletal bands are superimposed stretches from 2000 to 300 cm^{-1}. The part ranging from 1000 to 700 cm^{-1} appears strongly polarized in the direction perpendicular to the c axis with almost complete disappearance in the parallel spectrum. The frequency of maximum absorption cannot be measured because the breadth and superimposed bands, but it may be estimated near 770 cm^{-1} from the polarized and low temperature spectra. It may be associated to a motion of the hydrogen atom along the normal to the mirror plane of the chelate and represents a likely candidate for the assignment to the asymmetric O..H..O stretching which belongs to the A" species in our classification.

Reliable assignments can hardly be proposed for other vibrational modes of the O..H..O bridge on the basis of the presently available data. In particular neither low temperature

spectra nor polarization measurements (due to the strong ClO_4^- absorption) give a clear evidence for the assignment of the out-of-plane O..H..O deformation in the region predicted for this mode [7]. The proposal of the band at 1760 cm^{-1} as the in-plane O..H..O deformation is tentative and suggested by the prevailing parallel character.

Wagging, twisting and rocking vibrations of the coordinated water are likely hidden by the broad O..H..O stretching absorption occurring in the wavenumber range predicted for these vibrations [8]. However, a comparison between the low temperature spectrum of the title compound and the low temperature spectra of the complexes having Br and J as axial ligands, suggests that a band appearing at 672 cm^{-1} for the aquo-complex might be associated to one of the external modes of the coordinated water, likely the wagging.

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