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Absorption Spectra of Tetrahedral Co(II) in Single Crystals of $[N(CH_3)_4]_2[CoX_4]$ (X=Cl,Br)

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The optical absorption spectra of single crystals of $[N(CH_3)_4]_2[CoCl_4]$ and $[N(CH_3)_4]_2[CoBr_4]$ have been measured over the range of 4000—33000 cm^{-1} at the temperature of liquid nitrogen and at room temperature. The spectra have been analyzed using the crystal-field theory which includes spin-orbit coupling. Some discussion of the Racah parameter *B* and of the $^4T_1(^4F)$ and $^4T_1(^4P)$ states is presented.

The electronic spectra of tetrahalocobaltate(II) have been extensively studied[1–17] in two types of compounds, R_2CoX_4 and R_3CoX_5, but most reports have covered either the spin-allowed or the spin-forbidden transition regions. For example, Cotton et al.[4] have studied the spin-allowed transitions of R_2CoX_4, while Harada et al.[10,12,13] and Bird et al.[11] have analyzed in detail the spin-forbidden transitions in single crystals of Cs_3CoCl_5 and Cs_3CoBr_5. Exceptionally, Ferguson[5] has investigated the spectra of both the spin-allowed and spin-forbidden transitions in the mixed crystals of $R_2[Co_xZn_{1-x}Cl_4]$ at low temperatures.

In the present paper, the absorption spectra of $[CoX_4]^{2-}$ in single crystals of tetramethylammonium salts $[N(CH_3)_4]_2[CoX_4]$, where X is Cl or Br, are reported over the range of 4000—33000 cm^{-1}; this study was undertaken in order to investigate both the spin-allowed and the spin-forbidden d-d transitions in $[CoX_4]^{2-}$ and to compare the electronic transitions in the chloro complex with those in the bromo complex. Tetramethylammonium salts are chosen for the present study because the $[CoCl_4]^{2-}$ complex ion in this salt is known to show only a little deviation from regular tetrahedral symmetry, T_d, at room temperature.[16,18,19]

The spectra of $[N(CH_3)_4]_2[CoCl_4]$ have been studied in the infrared region by Quinn and Smith[9] and from the visible to the near-ultraviolet region by Hosoya et al.[17] as well as Ferguson.[5] The spectra of $[N(CH_3)_4]_2[CoBr_4]$ have never been reported in any region.

Other interesting studies have also been presented concerned with magnetic properties,[2,4,6,20–22] theoretical calculations[23,24] of energy levels, and the electron-spin density[25–28] of $[CoX_4]^{2-}$ complexes.

Experimental

Single crystals of $[N(CH_3)_4]_2[CoX_4]$ were obtained by the slow evaporation, at room temperature, of aqueous solutions containing a stoichiometric composition of $N(CH_3)_4X$ and CoX_2. Crystals of $[N(CH_3)_4]_2[CoCl_4]$ and $[N(CH_3)_4]_2[CoBr_4]$ are blue and greenish-blue prisms respectively. Mixed crystals of $[N(CH_3)_4]_2[Co_xZn_{1-x}X_4]$ were prepared from aqueous solutions of $N(CH_3)_4X$, CoX_2, and ZnX_2.

The spectra were recorded on a Shimadzu MPS-50L spectrophotometer at 77 K and on a Hitachi 340 instrument at room temperature. For measurements at 77 K, cut and polished specimens about 2×2 mm^2 and 0.2—1.0 mm thick were either immersed (visible and near-infrared regions) or not immersed (ultraviolet region) in liquid nitrogen in a glass Dewar apparatus. Filters of POLAROID HN-42T (visible region) and HR-INFRARED (near-infrared region) were used to measure the polarized spectra of $[N(CH_3)_4]_2[CoCl_4]$. The crystarographic *c* axis was determined by the X-ray oscillation method. For measurements in the spin-allowed bands at room temperature, small specimens about 1×1 mm^2 and 0.1—0.2 mm thick were used.

Results and Discussion

The unpolarized spectra are shown in Figs. 1 and 2, while their numerical data are summarized in Table 1. The overall features of the spectra are similar to the previous data.[1,5,11,16,17] Considerable differences can be found between the spectra of $[N(CH_3)_4]_2[CoCl_4]$ and $[N(CH_3)_4]_2[CoBr_4]$ in the III and IV bands in Fig. 2; the spectra in both these bands are, however, remarkably sharpened by the cooling of the crystals to 77 K. The low-energy absorption in the $^4T_1(^4F)$ band (near-infrared region) in $[N(CH_3)_4]_2[CoCl_4]$ is resolved at 77 K. A shoulder observed in the spectra of $[N(CH_3)_4]_2[CoBr_4]$ at room temperature appears as a peak of 30960 cm^{-1} at 77 K. Bird et al.[11] have reported the corresponding peak in Cs_3CoBr_5 at 4.2 K.

Since the spectra of the $^4T_1(^4P)$ bands are too intense to be resolved even at 77 K, those of the mixed crystals at room temperature are shown in Fig. 3. There are four structures in these bands, and their patterns are almost unchanged at 77 K.

The polarized spectra of $[N(CH_3)_4]_2[CoCl_4]$ are shown in Figs. 4 and 5. No significant difference between the polarized spectra for ***E***//*c* and ***E***⊥*c* can be found, and these results are similar to Ferguson's observations.[5]

The spectra of tetraethylammonium salt $[N(C_2H_5)_4]_2[CoCl_4]$ are also observed (not shown) and are similar to those of the tetramethylammonium salt

Table 1. Observed and Calculated Energies (in 10^{-3} cm^{-1})

$[N(CH_3)_4]_2[CoCl_4]$		$[N(CH_3)_4]_2[CoBr_4]$		$[N(CH_3)_4]_2[CoCl_4]$		$[N(CH_3)_4]_2[CoBr_4]$	
Observed$^{a)}$	Calculated$^{b)}$	Observed$^{a)}$	Calculated$^{b)}$	Observed$^{a)}$	Calculated$^{b)}$	Observed$^{a)}$	Calculated$^{b)}$
	49.37			17.96		17.89	
	49.34**			17.59$^{c)}$			
	48.79			17.31	17.44**		
			47.76				
			47.73**	16.90	16.92	16.86$^{c)}$	16.77**
			47.22		16.60*	16.53	
32.57	32.61*	33.03		16.26$^{c)}$			16.23
32.05$^{c)}$	32.46						15.98*
	31.74**			15.74			
	31.50		31.44*	15.61$^{c)}$		15.60	
31.25	31.19**		31.29		15.56		
		30.96			15.47*		
			30.68**	d, e)	15.03		15.08
			30.44	14.93		14.97	
29.76		29.32	30.15**		14.89*		
		28.31			14.88		
26.64					14.88**	d, e)	14.81*
26.34					14.63		
	25.39			14.44			14.41*
25.06		25.02					14.40
24.41			24.24			14.27	14.24
24.03							14.20**
	23.70						14.14
	23.29**	23.28				13.82	
23.07				8.61$^{d,f)}$			
		22.89		6.05	6.03		
			22.72		5.92**		
	22.59*					5.51	5.57
	22.46	22.22$^{c)}$	22.30**	5.42	5.40		
22.12							5.27**
21.93	21.70*	21.74		4.94	4.97*	4.94	4.92
			21.63*	4.67		4.61	
	21.58	21.23$^{c)}$	21.49			4.43	4.47*
		21.10		4.41			
20.87	20.96		20.81*	4.28		4.20	
			20.73	4.17 f)			
		20.66		4.08		4.08 f)	
20.00$^{c)}$	19.86*	19.91	20.17			3.95	
	19.68				3.41**		
19.36$^{c)}$	19.24**				3.33		
	19.15		19.17*				3.13**
18.93			19.03		3.07*		3.05
		18.52$^{c)}$	18.59**		2.92		2.78*
18.22			18.45				2.62

a) Observed at 77 K. b) Γ_6(*), Γ_7(**), and the others are Γ_8. c) Shoulder. d) Observed for mixed crystals. e) Observed at room temperature. f) Vibrational bands.

$[N(CH_3)_4]_2[CoCl_4]$, except that the spectra in the region of 17000—25000 cm^{-1} in the tetraethylammonium salt are shifted to wavenumbers lower by 150-300 cm^{-1} compared with the tetramethylammonium salt.

For $[N(CH_3)_4]_2[CoCl_4]$, the very weak peak of 8610 cm^{-1} observed distinctly at room temperature (Fig. 1) and the four peaks of 4410, 4280, 4170, and 4080 cm^{-1} may all be due to the vibrational transitions in $[CoCl_4]^{2-}$, accompanied by the $^4A_2 \rightarrow {}^4T_1(^4F)$ electronic transition. The spectra of these vibrations can not be assigned, although some

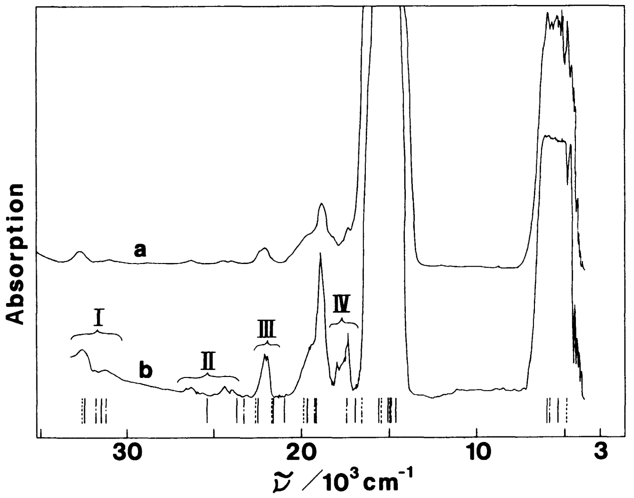

Fig. 1. Absorption spectra of $[N(CH_3)_4]_2[CoCl_4]$ at room temperature (a) and 77 K (b). Calculated energy levels are shown by vertical lines; Γ_8(——), Γ_7(— — —), and Γ_6(----).

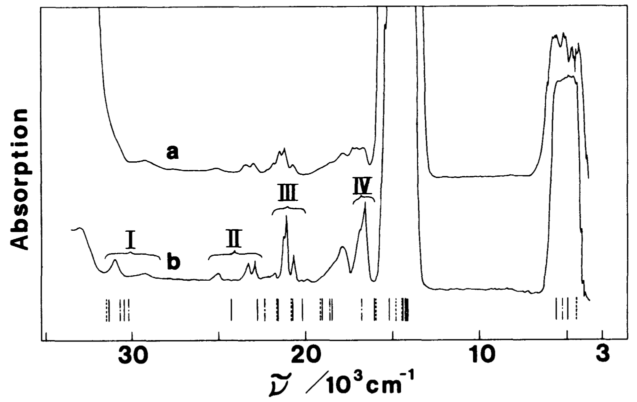

Fig. 2. Absorption spectra of $[N(CH_3)_4]_2[CoBr_4]$ at room temperature (a) and 77 K (b). Calculated energy levels are shown by vertical lines; Γ_8(——), Γ_7(— — —), and Γ_6(----).

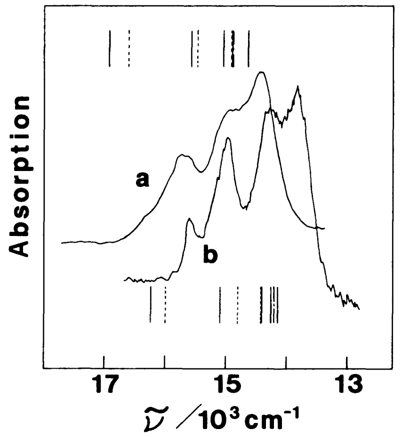

Fig. 3. The $^4A_2 \rightarrow {}^4T_1(^4P)$ absorption bands of mixed crystals $[N(CH_3)_4]_2[Co_xZn_{1-x}Cl_4]$ (a) and $[N(CH_3)_4]_2$-$[Co_xZn_{1-x}Br_4]$ (b) at room temperature. Note that the scale of the ordinate for b is enlarged than that of a. Calculated energy levels are shown by vertical lines; Γ_8(——), Γ_7(— — —), Γ_6(----).

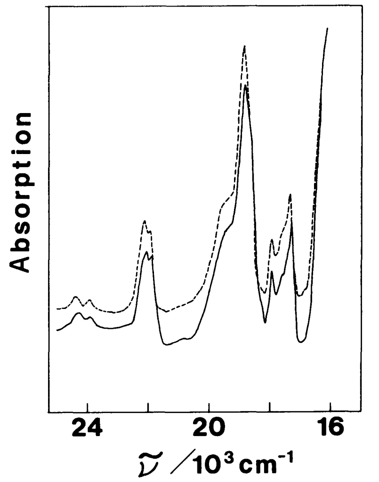

Fig. 4. The polarized spectra of the spin-forbidden bands in $[N(CH_3)_4]_2[CoCl_4]$ at 77 K; $E_{\perp c}$ (——) and $E_{/\!/c}$ (----).

vibrational bands in the $[CoCl_4]^{2-}$ complex have been reported.[13,16,29,30] For $[N(CH_3)_4]_2[CoBr_4]$, the corresponding bands are at 4200, 4080, and 3950 cm^{-1}, but those intensities are low relative to the bands of $[N(CH_3)_4]_2[CoCl_4]$.

In order to calculate the energy levels on the basis of the strong crystal-field theory, the symmetry of the $[CoX_4]^{2-}$ ion is assumed to be T_d, for little anisotropy is observed in the polarized spectra at 77 K (Figs. 4 and 5). Tanabe-Sugano energy matrices,[31] including spin-orbit ones,[32] are diagonalized, using a HITAC M-160H computer, for various values of the D_q, B, C, and ζ parameters, where D_q is the crystal-field strength, B and C are Racah parameters, and ζ is the spin-orbit coupling constant. The calculated energy levels are shown as vertical lines in Figs. 1—3 and in Table 1. Those levels are calculated with D_q=310 cm^{-1}, B=740 cm^{-1}, C=4.6B, and ζ=490 cm^{-1} for $[N(CH_3)_4]_2[CoCl_4]$ and D_q=280 cm^{-1}, B=720 cm^{-1}, C=4.6B, and ζ=500 cm^{-1} for $[N(CH_3)_4]_2[CoBr_4]$. From these calculations, it is shown that the bands of the regions of I and II are mainly due to the transitions of $^4A_2 \rightarrow {}^2T_1(^2F)$, $^2T_2(^2F)$, $^2A_2(^2F)$, and $^4A_2 \rightarrow {}^2E(^2D)$, $^2T_2(^2D)$ respectively. The other absorption bands in the regions of III and IV can be ascribed to the transitions to some components of the ^2P, ^2H, and ^2G terms.

The values calculated for the two complexes do not agree precisely with the observed data in the regions of II and III. If the higher energy states arising from the ^2D, ^2P, and ^2H terms were estimated with B over

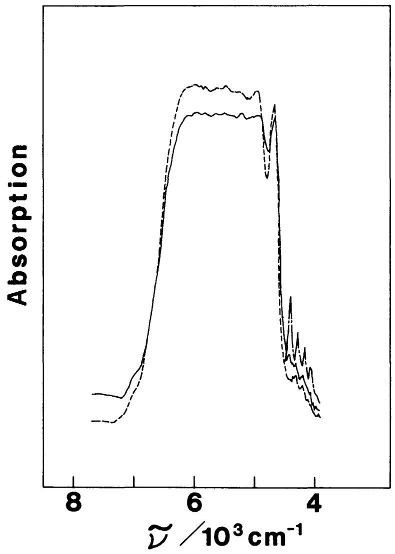

Fig. 5. The polarized spectra of the $^4T_1(^4F)$ band in $[N(CH_3)_4]_2[CoCl_4]$ at 77 K; $\boldsymbol{E}_{\perp c}$ (——), $\boldsymbol{E}_{//c}$ (----), and unpolarized (– – –).

Table 2. Main Contributions (%) of Electronic Configurations to the $^4T_1$ States of $[CoCl_4]^{2-}$ in $[N(CH_3)_4]_2[CoCl_4]$

State	Calculated energy	Configuration	
	10^{-3} cm⁻¹	$\lvert ^4T_1t_2^4(^3T_1)e^3\rangle$	$\lvert ^4T_1t_2^5e^2(^3A_2)\rangle$
$^4T_1(^4F)$			
Γ_6	4.97	29.5	67.8
Γ_8	5.40	29.5	65.6
Γ_7	5.92	32.0	66.7
Γ_8	6.03	30.6	64.1
$^4T_1(^4P)$			
Γ_7	14.88	67.2	32.5
Γ_8	14.88	65.0	30.5
Γ_8	15.03	53.2	25.4
Γ_6	15.47	67.9	28.0

740 cm⁻¹, the results of calculation should be in good agreement with the spectral regions of II and III. Hosoya et al.[17] have successfully estimated the energies only for the spin-forbidden transitions in $[N(CH_3)_4]_2[CoCl_4]$ with the large B value of 780 cm⁻¹. On the other hand, Ferguson[5] has obtained the small B value of 720 cm⁻¹. This may result from the disregard for the ≈26500 cm⁻¹ band due to the ^2D term. Harada and Tsujikawa[12] have estimated the various values of B viz 740—840 cm⁻¹ for Cs_3CoCl_5 and 710—798 cm⁻¹ for Cs_3CoBr_5 in the regions of II and III. This can be explained by the fact that a different B value is necessary for each energy level, as in Ferguson's suggestion[5] that e orbitals differ from t_2 orbitals in the extent of expansion. There is a marked tendency for small B values and large B values to be obtained from the spectra for the spin-allowed and for the spin-forbidden transitions respectively.

Horrocks and Burlone[24] have obtained e_σ=2300 cm⁻¹ and B=740 cm⁻¹ for $[CoCl_4]^{2-}$ in both Cs_3CoCl_5 and Cs_2CoCl_4 by using the angular-overlap model for the spin-allowed transitions. This e_σ value corresponds to the D_q value of 307 cm⁻¹, which agrees with the D_q value in this study. The angular-overlap model is useful for the study of low-symmetry complexes and is a realistic model for metal-ligand covalent bonding, but the formalism is in the ligand-field theory. An analysis of the spectra due to the spin-forbidden transitions by the angular-overlap model is to be hoped for.

Hiller et al.[23] have obtained much valuable information on the cobalt-ligand bonding in $[CoCl_4]^{2-}$ by using the ab initio MO calculations only for the $^4A_2$, $^4T_2$, and $^4T_1$, states. The calculated energies of 3450 cm⁻¹ ($^4A_2 \rightarrow {}^4T_2(^4F)$), 6100 cm⁻¹ ($^4A_2 \rightarrow {}^4T_1(^4F)$), and 21600 cm⁻¹ ($^4A_2 \rightarrow {}^4T_1(^4P)$) do not seem to account successfully for the experimental data of 3000, 5500, and 15000 cm⁻¹ respectively. Results for the spin-forbidden transitions are also desirable. Hiller et al. have described that the $^4T_1(^4P)$ and $^4T_1(^4F)$ states are composed mainly (≈60%) of the $e^3t_2^4$ and $e^2t_2^5$ configurations respectively and that these results disagree with the results of the simple crystal-field theory. This configuration has already been reported for CoO_4 complexes by Pappalardo et al.[33] Our results for the $^4T_1$ states for $[N(CH_3)_4]_2[CoCl_4]$ are shown in Table 2. A similar relation can be found in this study between the states of electronic configuration. The low-energy state of $^4T_1(^4F)$ is composed of the 64—68% $e^2t_2^5$ configuration, while the high-energy $^4T_1(^4P)$ state is composed of the 53—68% $e^3t_2^4$ configuration, where the e orbital has lower energies than the t_2 orbital in the T_d symmetry. On the contrary, Ferguson[5] has reported that $^4T_1(^4F)$ has the configurations of 66% $e^3t_2^4$ and 33% $e^2t_2^5$ and that $^4T_1(^4P)$ has 31% $e^3t_2^4$ and 69% $e^2t_2^5$. The reason for these inverse results can not be found in his report.

For $[N(CH_3)_4]_2[CoBr_4]$, the results are similar to those in Table 2 (not shown).

In the bands of I and $^4T_1(^4P)$, the computed energies agree less with the observed spectra in $[N(CH_3)_4]_2[CoBr_4]$ than with those of $[N(CH_3)_4]_2[CoCl_4]$; this may be due to the difference in the covalency of the Co–X bond between the two complexes.

The $^4A_2 \rightarrow {}^4T_2(^4F)$ transition may be expected to be in the infrared region, outside the spectral region in the present study. The computed energies of this transition for both the complexes are listed in Table 1. For $[N(CH_3)_4]_2[CoCl_4]$, those energies are predicted to be at 3410, 3330, 3070, and 2920 cm⁻¹; hence, the split width is 490 cm⁻¹. For the corresponding transition, Quinn and Smith[9] have observed relatively sharp absorptions in the region of 3340—3540 cm^{-1} which lie at higher energies than our calculated ones. On the other hand, Stapele et al.[6] have reported this corresponding absorption band in the range of 2800—3500 cm^{-1} for $Cs_3Zn_{0.9}Co_{0.1}Cl_5$.

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