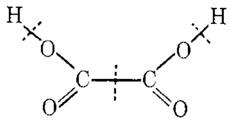

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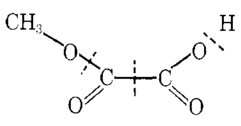

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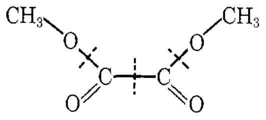

present work

In none of the cases is HCO_3^- or H_2CO_3 formed as an intermediate stage in the oxidation. Much of course remains to be said on the detailed sequence of events in these reactions.

Acknowledgments.—Financial support by the Atomic Energy Commission under Contracts AT(11-1)-378 (University of Chicago) and AT(04-3)-326 (Stanford University) is gratefully acknowledged. C. A. expresses gratitude for fellowship support to the International Cooperation Administration, the Organization of American States, and the University of Chile.

CONTRIBUTION NO. 1344 FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

Polarized Crystal Spectra of the *trans*-Dihalobis(ethylenediamine)cobalt(III) Ion

BY R. A. D. WENTWORTH

Received October 13, 1965

Recently the implications of both crystal field and molecular orbital calculations for tetragonal amine complexes of cobalt(III) have received renewed interest.[1,2] Of fundamental importance was the discovery that the splitting of the $^1T_1$ band in the tetragonal field could be readily interpreted in terms of $\delta\Delta$, the difference in the crystal field stabilization energies of the axial and in-plane ligands. However, a complete knowledge of the one-electron energy levels of a tetragonal complex has been hindered by a lack of experimental information concerning the splitting of the $^1T_2$ band. Using data from solution spectra, it was previously shown[2] that the position of the band maximum of the apparently unsplit $^1T_2$ band varied almost linearly with $\delta\Delta$. With an empirical molecular orbital model as a basis, it was shown that accompanying a monotonic decrease in the field strength of the axial ligand there was an apparent monotonic increase in π bonding. Furthermore, it appeared that for π-bonding ligands of relatively weak field strength such as chloride and bromide ions, the crystal spectra of the *trans* disubstituted complexes should reveal splitting of this band if, indeed, splitting is to be found. However, Yamada, Nakahara, Shimura, and Tsuchida[3] (hereafter YNST), who measured the polarized crystal spectra of *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$, found no more information in this regard than that afforded from solution spectra. Consequently, a low-temperature investigation of the polarized crystal spectra of these compounds was undertaken.

Experimental Section

The insolubility of *trans*-$[Co(en)_2X_2]X \cdot HX \cdot 2H_2O$ (X = Cl or Br) precluded the growth of spectroscopically suitable crystals by direct methods. However, this situation was avoided by effecting the hydrolysis of these compounds in hot aqueous solution to form $Co(en)_2(H_2O)_2^{3+}$, which is extremely soluble in the presence of halide ion, followed by the addition of the appropriate hydrohalic acid to the cooled solution. Crystals of the desired compound began to appear in several days and could be grown as large as 1 cm on edge and 3 to 4 mm thick. If a large crystallizing dish was used, very thin plates of large surface area could be invariably obtained from the sides of the dish. These were suitable for spectroscopy using ordinary techniques since the optical density of the d–d spectrum never exceeded 1.5 absorbancy units. Moreover, the large surface area ensured that slit widths remained below 0.08 mm.

Both of these compounds are unstable to loss of HX and H_2O, which leads to opacity within several hours. The application of a rubber cement (transparent between 5000 and 30,000 cm^{-1}), which was diluted with acetone, effectively prevented this occurrence. Spectra taken on coated and uncoated crystals were identical.

The crystallographic axes were located with a polarizing microscope using the excellent descriptions of the crystal habit and dichroism of these compounds which are contained in the reports of their crystal structures.[4,5] Spectra were then recorded with the incident light polarized perpendicular and parallel to the c axis. To ensure the best alignment of the electric vector with this axis, the spectrum of the region between 14,000 and 17,000 cm^{-1} was recorded at 2° intervals until the absorbancy reached a maximum, where the electric vector was truly parallel to the c axis. The perpendicular spectra were then obtained by rotating the polarizer through 90°. Extinction coefficients in $M^{-1}\ cm^{-1}$ were computed from the known density,[4,5] formula weight, and thickness of a crystal which was measured with a micrometer.

The experimental apparatus has been previously described[6] with one exception. In the present work, the Cary spectrophotometer was equipped with its accessory high-intensity source.

Results and Discussion

The results at both room and liquid nitrogen temperatures are listed in Table I. Average extinction coefficients were obtained from the spectra of ten crystals of each compound with a precision of 10%, and these are compared in the table to the earlier room temperature results of YNST. Good agreement can be seen in both cases below 24,000 cm^{-1}. The polarizations are referred to the crystallographic c axis, which is nearly coincident with the halide–cobalt–halide bonds.[4,5] Resolution of the perpendicular and parallel components into the true σ and π spectra was not necessary since the differences between the observed and resolved spectra were much too small to be meaningful.

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[1] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[2] R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 1524 (1965).

[3] S. Yamada, A. Nakahara, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **28**, 222 (1955); see also the earlier spectra of S. Yamada and R. Tsuchida, *ibid.*, **25**, 127 (1952).

[4] A. Nakahara, Y. Saito, and H. Kuroya, *ibid.*, **25**, 331 (1952).

[5] S. Ooi, Y. Kamiyama, Y. Saito, and H. Kuroya, *ibid.*, **32**, 263 (1959).

[6] R. A. D. Wentworth and T. S. Piper, *J. Chem. Phys.*, **41**, 3884 (1964).

TABLE I

POLARIZED CRYSTAL SPECTRA OF *trans*-$[Co(en)_2X_2]X \cdot HX \cdot 2H_2O$ (X = Cl AND Br)

	Polarization	300°K		80°K		Results of YNST at 300°K		Assignment
		ν_{max}, kK	ϵ_{av}	ν_{max}, kK	ϵ_{av}	ν_{max}, kK	ϵ	$^1A_{1g} \rightarrow$
$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$	$\parallel$	15.9	20	16.0	14	16.1	20	^1E_g[a]
	$\perp$	16.1	8	16.4	6	16.1	7	^1E_g[a]
	$\perp$	23.1	17	23.3	15	23.3	15	$^1A_{2g}$
	$\parallel$	~24.0[a]		23.9	5	*c*		$^1A_{2g}$
$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$	$\parallel$	14.9	31	15.1	23	14.9	30	^1E_g[a]
	$\perp$	15.2	8	15.4	6	15.0	6	^1E_g[a]
	$\parallel$	*d*		~22.0[a]	~12 (~2)[b]	*c*		$^1A_{2g}$
	$\perp$	21.9	16	22.3	15 (10)[b]	21.7	14	$^1A_{2g}$
	$\parallel$	*d*		25.4	40	*d, e*		^1E_g[b]
	$\perp$	*d*		26.8	42	*d, e*		$^1B_{2g}$
	$\parallel$	*d, e*		*d, e*		25.6	152	*e*
	$\perp$	*d, e*		*d, e*		29.0	135	*e*

[a] Not clearly defined. [b] Result of curve analysis. [c] Not reported. [d] Not observed. [e] See text.

Moffitt and Ballhausen[7] have performed a vibrational analysis using the results of YNST and an effective symmetry of D_{4h}. The success of their treatment was based on the assumption that only the lowest vibrational level ($\nu = 0$) of the ground state was appreciably populated and that there was no vibration in this symmetry which could give intensity in parallel polarization to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, which was not observed by YNST. In Table I, however, it can be seen that the temperature dependence of the spectra indicates that higher vibrational levels are occupied and that, while the $^1A_{2g}$ absorption is poorly defined at room temperature, it is clearly resolved at 80°K, especially in the case of the chloro complex. Since the true site symmetry is only C_i,[4,5] it is probably not profitable to attempt to rationalize the observed polarizations, but rather to utilize them as a means of sorting out the total number of transitions.

Only in the case of $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ (Figure 1) are any new bands resolved at 80°K. These appear at 25,400 and 26,800 cm^{-1} in opposite polarizations and have sufficiently small values of ϵ to warrant their assignment as d–d transitions. However, this assignment merits more consideration. For the chloro complex the onset of charge transfer occurs at about 27,000 cm^{-1}, while in the bromide, if these two bands are assigned to transitions within the d orbitals, it apparently does not appear until about 29,000 cm^{-1}. This is certainly not the expected order of appearance. However, it must be remembered that these two bands appear only as shoulders on the low-energy side of an intense band and that the "tail" of this band probably extends well below 25,000 cm^{-1}. Finally YNST have observed two bands at 25,600 and 29,000 cm^{-1} with ϵ ~130–150 (Table I). It may be assumed that these correspond (especially the absorption at lower wavenumbers) to the bands found in this work, but with larger values of ϵ due to the increased temperature. However, their ultraviolet spectra must be viewed with caution since the bands are peculiarly flat-topped and resemble solution spectra only slightly. Using the present experimental method, rather than the microscopic technique of YNST, it has been impossible to confirm or refute their results at 300°K since it would require a crystal of adequate surface to ensure minimum slit widths but with a thickness of approximately only 0.003 mm. This was not experimentally possible, and crystals were typically about 0.01 mm thick.

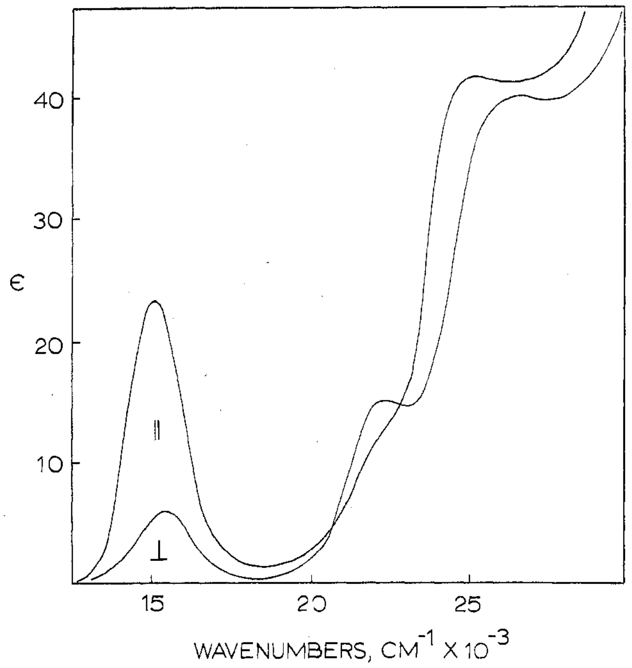

Figure 1.—The polarized crystal spectra of *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ at 80°K with the incident light polarized parallel and perpendicular to the crystallographic *c* axis.

The absorptions at 25,400 and 26,800 cm^{-1} at 80°K can represent either the splitting of the $^1T_2$ band in the low-symmetry field or charge-transfer transitions of low probability. Compelling empirical evidence for the first assignment can be had by comparing these results to those from solution spectroscopy. Although this band is not observed in the solution spectra of $Co(en)_2Br_2^+$ due to the onset of charge transfer, the nearly linear wavenumber dependence of the $^1T_2$ band with $\delta\Delta$ for other similar complexes[2] allows a prediction to be made with considerable confidence. Since $\delta\Delta$ was previously found[1] to be −12,530 cm^{-1} for the di-

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(7) W. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

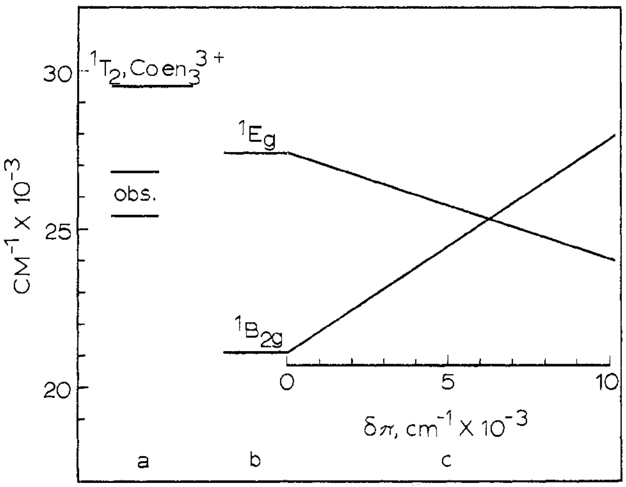

Figure 2.—(a) The observed wavenumber of the $^1T_2$ absorption in $Co(en)_3^{3+}$ and the wavenumbers of the high-energy bands from the polarized crystal spectra of *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$. (b) The predicted wavenumbers of the $^1E_g^b$ and $^1B_{2g}$ absorptions with $\delta\Delta = -12{,}600$ cm^{-1} and $\delta\pi = 0$. (c) The predicted wavenumbers of these absorptions as a function of $\delta\pi$.

bromide, the unobserved and unresolved $^1T_2$ band should occur in solution at 4000 to 5000 cm^{-1} lower than the corresponding 29,500 cm^{-1} absorption in $Co(en)_3^{3+}$. From the crystal spectra the bands in question occur at 4100 and 2700 cm^{-1} lower than the absorption in $Co(en)_3^{3+}$, with $\delta\Delta$ evaluated as $-12{,}600$ cm^{-1}. It is difficult to believe that this agreement is fortuitous and altogether reasonable to assume that these two bands arise from the splitting of the $^1T_2$ state.

The ordering of the components of this state presents a more serious problem. With small π bonding by bromide ion the $^1E_g^b$ state should lie higher than the $^1B_{2g}$ state, but with increasing π bonding the energy separation decreases until at $\delta\pi = -{}^1/_2\delta\Delta$ (6300 cm^{-1}) these states cross. In Figure 2 it can be seen that the best fit of the observed spectrum is obtained with $\delta\pi > 6300$ cm^{-1}. A better fit can be had by assuming both bands are allowed in either polarization,[8] thereby increasing the splitting somewhat. Without resorting to Gaussian analysis, it is not unreasonable to choose $\delta\pi \approx 9000$ cm^{-1}.[9] The splittings of the one-electron energy levels are then as follows[10]

$$E(b_{1g}^*) - E(b_{2g}) = \Delta^{en} \qquad = 25{,}300 \text{ cm}^{-1}$$

$$E(a_{1g}^*) - E(b_{2g}) = \Delta^{en} + {}^2/_3\,\delta\Delta + {}^2/_3\,\delta\pi \approx 22{,}900 \text{ cm}^{-1}$$

$$E(e_g^*) - E(b_{2g}) = {}^1/_2\,\delta\pi \qquad \approx 4500 \text{ cm}^{-1}$$

The energy separation between the e_g^* and b_{2g} orbitals is perhaps unexpectedly large and there are no means in hand to ensure the reliability of this result. A smaller choice of $\delta\pi$, although resulting in a poorer fit of the spectra, would have reduced this separation. It is hoped, however, that investigations of the circular dichroism of the complete series of *trans*-dihalobis(*cis*-cyclohexanediamine)cobalt(III) ions, which is currently in progress at the University of Illinois, will eventually lead to an unambiguous assignment.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Stereochemistry and P=O Bond Order in Trialkyl Phosphate Extractants

BY S. C. GOODMAN AND J. G. VERKADE

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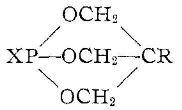
Our recent investigations of the ligand properties of polycyclic phosphites such as I with first-row transition metal ions,[1] transition metal carbonyls,[2] and boron-containing Lewis acids[3] revealed that constraint of the alkoxy moieties on the phosphorus allowed formation of strong-field complexes, strongly π-bonded complexes, and stable adducts, respectively. These results prompted us to investigate the rare earth extractant properties of the bicyclic phosphate 1-oxo-4-pentyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane(IV), which is similar in structure to tri-*n*-butyl phosphate (TBP) except for the drastically reduced steric requirement. Compound IV was more desirable than II for this investigation, since it is far less soluble in aqueous acid than II. The reversed phase partition chromatographic technique described by Banks and O'Laughlin[4] was employed to show that IV does not function as an extractant for trivalent lanthanum, neodymium, samarium, gadolinium, and ytterbium ions under the variety of conditions herein described.



$$XP(OCH_2)_3CR$$

I, X = nothing; R = CH_3
II, X = oxygen; R = CH_3
III, X = nothing; R = $(CH_2)_4CH_3$
IV, X = oxygen; R = $(CH_2)_4CH_3$

Experimental Section

Preparation of IV.—The synthesis of $CH_3(CH_2)_4C(CH_2OH)_3$ was carried out in a manner similar to that described by Dermer

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[8] Such an assumption is not unwarranted. If, as in ref 7, the effective symmetry was taken as D_{4h}, vibronic selection rules indicate that transitions to the $^1E_g^b$ and $^1B_{2g}$ states are allowed in either polarization. Therefore in any lower symmetry retaining the center of inversion, transitions to the states which correlate to those in D_{4h} symmetry will always find allowance in either polarization providing the axis of quantization remains coincident with the cobalt–halide radius vector.

[9] Configurational interaction between the ^1E_g states has been neglected in arriving at this result. For *trans*-CoA_4X_2, the requisite off-diagonal matrix element is $\sqrt{3}/6(\delta\Delta + \delta\pi)$. Using the values of $\delta\Delta$ and $\delta\pi$ derived in the text, this matrix element is only equal to 1040 cm^{-1}, a negligible amount. It should be noted that an analogous treatment of CoA_5X indicates that the contributions of $\delta\Delta$ and $\delta\pi$ should be multiplied by one-half.

[10] See H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958), and reformulation in ref 2.

[1] T. J. Huttemann, Jr., B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, **4**, 950 (1965).

[2] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965).

[3] J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

[4] C. V. Banks and J. W. O'Laughlin, *Anal. Chem.*, **36**, 1222 (1964).