

CCA-1136

YU ISSN 0011-1643

546.733

Original Scientific Paper

Visible Spectra of Some Monoacidopentaammine and Diacidotetraammine Complexes of Cobalt(III)

Suk-Yee Chan and Wai-Kee Li*

Department of Chemistry, The Chinese University of Hong Kong
Shatin, N. T. Hong Kong

Received September 8, 1978

The spin-allowed transitions in the visible spectra of some monoacidopentaammine and diacidotetraammine complexes of Co(III), with the acido groups being CO_3^{2-} , H_2O , NO_2^- , $\text{O}_2\text{C}_3\text{H}_5^-$, F^- , NO_3^- , Cl^- , and Br^- , have been resolved and the relevant crystal field and Racah parameters determined with a modified version of the model originally proposed by Wentworth and Piper. The results appear to be consistent within the series and agree well with those reported in the literature for structurally related systems.

INTRODUCTION

In two previous notes^{1,2}, the visible spectra of the complexes $[\text{Co}(\text{RNH}_2)_5\text{X}]^{2+}$, where R = H, Me, Et, *n*-Pr, and *n*-Bu and X = Br and Cl, were analyzed in terms of a crystal field model. This model was a modified version of that originally devised by Wentworth and Piper³. In order to test this newly proposed model further, the following investigations have been carried out and are reported in this note:

(1) The visible spectra of some monoacidopentaamminecobalt(III) complexes, with the acido groups being CO_3^{2-} , H_2O , NO_2^- , $\text{O}_2\text{C}_3\text{H}_5^-$, F^- , and NO_3^- , are analyzed. This part is similar to what has been done before^{1,2} except that the range of the acido groups has been expanded considerably.

(2) The visible spectra of some *trans*-diacidotetraamminecobalt(III) complexes, with the acido groups being Cl^- and Br^- , are analyzed. This provides a good test since, according to the model, the values of the crystal field parameters D_s and D_t for these D_{4h} systems should be twice as large as those for the analogous C_{4v} complexes.

EXPERIMENTAL

The methods of synthesis for the complexes $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^{+4}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+5}$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+6}$, $[\text{Co}(\text{NH}_3)_5\text{O}_2\text{C}_3\text{H}_5]^{+27}$, $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+8}$, $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+9}$, *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^{+10}$, and *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]^{+11}$ can be readily found in the literature and are not described here. The spectra of the complexes were recorded by a Hitachi 323 UV-VIS-NIR recording spectrophotometer in the 210–700 nm range at room temperature. Reagent grade methanol was used as solvent for the diacido complexes since they are known to be unstable towards hydrolysis and isomerization in water. For

* To whom correspondence should be addressed.

other complexes water was used. All the spectra were recorded as soon as the complexes had been dissolved. Repeated recordings showed no change in the spectra.

THEORY

Within the framework of crystal field theory, the energies of low-lying singlet states above the ground state (Figure 1) for a d^6 ion in a strong octahedral field are¹⁻³

$$E({}^1T_{1g}) - E({}^1A_{1g}) = 10 Dq - C,$$

$$E({}^1T_{2g}) - E({}^1A_{1g}) = 10 Dq + 16 B - C,$$

where Dq , B , and C are the usual parameters encountered in crystal field theory. On decrease in symmetry to C_{4v} or D_{4h} , corresponding to tetragonal distortion, the degeneracy of the excited states is partially lifted as shown in Figure 1. Referring to the labelling given in the figure, the energies of the transitions are

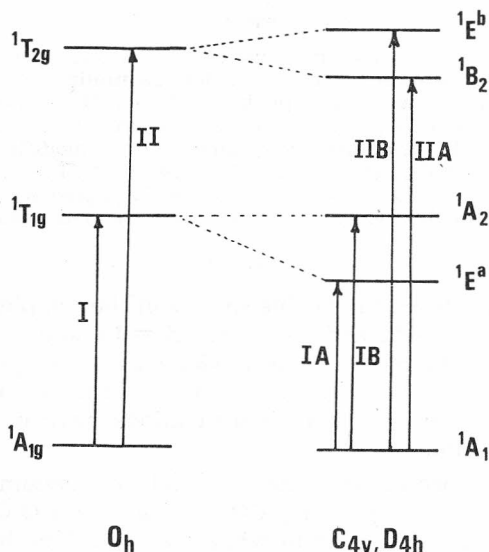


Figure 1. Tetragonal splitting of the excited states of Co(III).

$$E(IA) = 10 Dq - (35/4) Dt - C,$$

$$E(IB) = 10 Dq - C,$$

$$E(IIA) = 10 Dq - 4 Ds - 5 Dt + 16 B - C,$$

$$E(IIB) = 10 Dq + 2 Ds - (25/4) Dt + 16 B - C.$$

The additional parameters Ds and Dt have been defined elsewhere³. The only differences between the C_{4v} and D_{4h} complexes are

$$Ds(D_{4h}) = 2 Ds(C_{4v}),$$

$$Dt(D_{4h}) = 2 Dt(C_{4v}).$$

In the original model of Wentworth and Piper³, a key assumption is that the energy of the IB band of the distorted system is identical to the I band for the parent octahedral complex.

For the present work, where possible, the absorption bands of the spectra are resolved into four Gaussian curves, assuming a sloping baseline^{1,2}. Since, at most, only four transitions may be resolved from the spectra and there are five parameters to be determined, an additional assumption has to be made. It is known that, among the five parameters, C is the one that remains remarkably constant over a wide range of crystal field strength. For example, the C values in $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{CN})_6]^{3-}$ have been reported as 3825, 3835, and 3650 cm^{-1} respectively³. Therefore, it should be reasonable to assign that, for the complexes under study,

$$C = 3800 \text{ cm}^{-1}.$$

In another model, Ban and Csaszar¹³ proposed that band II does not split so that

$$E(\text{II}) = E(\text{IIA}) = E(\text{IIB}).$$

Then,

$$D_s = (5/24) D_t,$$

$$B = (1/16) [E(\text{II}) - 10 D_q + C + 5 D_t + 4 D_s].$$

The results of the analyses are given in the next section, along with a comparison among the results based on the three models described here.

RESULTS AND DISCUSSION

The wavelengths, intensities, and half-widths of the resolved bands of the complexes are given in Table I, together with those reported by other workers for comparison. The crystal field parameters calculated from the experimental results along with those obtained by other workers are summarized in Table II, including those of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ obtained previously^{1,2}. The second bands of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$, $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+}$, and the two diacido complexes have not been resolved due to the onset of the charge transfer bands and therefore the values of D_s and B are missing.

Upon examining the results, the following remarks can be made:

(1) The order of the values of D_q obtained from the present treatment is $\text{NO}_2^- > \text{en} > \text{NH}_3 > \text{C}_4\text{H}_5\text{O}_2^- > \text{NO}_3^- > \text{H}_2\text{O} > \text{CO}_3^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^-$, an arrangement in good agreement with that normally listed.

(2) Comparing the values of $D_q(\text{Cl})$ and $D_q(\text{Br})$ of the trans-disubstituted complexes with those of the monosubstituted complexes reported by Book et al.^{1,2}, it is found that these values remain fairly constant in C_{4v} and D_{4h} complexes. Also, the values of $D_q(\text{en})$ and $D_q(\text{NH}_3)$ are almost unchanged irrespective of the particular substituted complex ion in which they are found. Thus the assumption that the crystal strength is characteristic of the ligand itself (for the same metal ion) is justified.

(3) The comparison of the parameters D_t and D_s of the C_{4v} and D_{4h} complexes indicates that the values of the latter are about twice as large as those of the former as predicted by the electrostatic model of the crystal field theory.

(4) In the case where the IA and IB bands were not resolved, Wentworth and Piper³ took for granted that the observed band maximum was the average of the energy of the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition of the parent compound and that of the ${}^1E^a$ state above the ground state. This approximation in effect assumes

TABLE I

The Wavenumbers ($\bar{\nu}_{\max}$), Intensities ($\log \epsilon$, $\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ being Molar Extinction Coefficient), and Half Width ($\Delta \bar{\nu}_{1/2}$) of the Resolved Bands

Complex	Band IA			Band IB			Band IIA			Band IIB		
	$\bar{\nu}_{\max}$ 1000 cm^{-1}	$\log \epsilon$	$\Delta \bar{\nu}_{1/2}$ 1000 cm^{-1}	$\bar{\nu}_{\max}$ 1000 cm^{-1}	$\log \epsilon$	$\Delta \bar{\nu}_{1/2}$ 1000 cm^{-1}	$\bar{\nu}_{\max}$ 1000 cm^{-1}	$\log \epsilon$	$\Delta \bar{\nu}_{1/2}$ 1000 cm^{-1}	$\bar{\nu}_{\max}$ 1000 cm^{-1}	$\log \epsilon$	$\Delta \bar{\nu}_{1/2}$ 1000 cm^{-1}
[Co(NH ₃) ₅ CO ₃] ⁺	18.90 18.90 ^a	1.74	2.91	21.10 20.50 ^a	1.68	4.13				26.88 (shoulder; not resolved) 27.85 ^a (not resolved)		
[Co(NH ₃) ₅ H ₂ O] ³⁺	19.34	1.65	3.39	21.05 20.50 ^a 20.30 ^b	1.83	4.16 (not resolved) (not resolved)	27.86	1.59	3.74	29.50 30.40 ^a 30.30 ^b	1.79 (not resolved) (not resolved)	3.93
[Co(NH ₃) ₅ NO ₂] ²⁺	23.87	1.51	5.13	21.51 21.75 ^a 21.84 ^b	1.29	4.25 (not resolved) (not resolved)	31.65	2.55	4.94	28.57 30.80 ^a 30.80 ^b	2.66 (not resolved) (not resolved)	3.52
[Co(NH ₃) ₅ O ₂ C ₃ H ₅] ²⁺	19.38 19.87 ^a 19.88	1.67	2.87	20.70 21.35 ^a 21.00 ^b	1.58	3.54	28.09	1.73	3.41	29.94 28.41 ^a 28.39 ^b	1.47 (not resolved) (not resolved)	0.90
[Co(NH ₃) ₅ F] ²⁺	19.05 19.45 ^a 19.45 ^b	1.97	2.92	21.37 21.80 ^a 21.47 ^b	1.73	3.45	27.70	1.70	3.62	29.07 28.27 ^a 28.27 ^b	1.70 (not resolved) (not resolved)	3.76
[Co(NH ₃) ₅ NO ₃] ²⁺	19.34 16.20 ^a	1.61	3.16	21.37 21.20 ^a	1.45	4.15				28.90 (shoulder; not resolved) 28.40 ^a (not resolved)		
<i>trans</i> -[Co(en) ₂ Cl ₂] ⁺	16.34 19.20 ^a 16.12 ^b 16.48 ^c	1.59	2.58	21.84 22.50 ^c	1.40	4.43			24.25 ^c	25.91 (not resolved) 25.85 ^a (not resolved) 25.92 ^b (not resolved) 27.10 ^c (not resolved)		
<i>trans</i> -[Co(en) ₂ Br ₂] ⁺	15.24 15.25 ^a 15.21 ^b	1.72	2.20	21.69 21.72 ^a 21.68 ^b	1.39	2.95				Masked 26.12 ^a Masked ^b		

^a From reference 13. ^b From reference 3. ^c From reference 15.

TABLE II
Crystal Field Parameters Calculated from the Spectral Data

Complexes	Dq^{xy*}	$Dq^{z^{1*}}$	Dt	Ds	B
	1000 cm^{-1}	1000 cm^{-1}	1000 cm^{-1}	1000 cm^{-1}	1000 cm^{-1}
$[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$	2.490	1.612 1.638 ^a	0.251 0.246 ^a	0.0513 ^a	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$	2.485 2.490 ^b	1.803 2.058 ^a 1.888 ^b	0.195 0.126 ^a 0.172 ^b	0.314 0.0263 ^a	0.565 0.630 ^a
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$	2.531 2.490 ^b	3.476 3.058 ^a 3.120 ^b	-0.270 -0.160 ^a -0.180 ^b	-0.510 -0.0333 ^a	0.407 0.551 ^a
$[\text{Co}(\text{NH}_3)_5\text{O}_2\text{C}_3\text{H}_5]^{2+}$	2.450 2.490 ^b	1.922 2.020 ^a 2.021 ^b	0.151 0.135 ^a 0.134 ^b	0.340 0.028 ^a	0.594 0.509 ^a
$[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$	2.517 2.490 ^b	1.590 1.858 ^a 1.849 ^b	0.265 0.183 ^a 0.183 ^b	0.284 0.0381 ^a	0.549 0.518 ^a
$[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{2+}$	2.517	1.705 1.758 ^a	0.232 0.211 ^a	0.044 ^a	0.536 ^a
<i>trans</i> - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$	2.564 2.530 ^b 2.630 ^c	1.463 1.483 ^a 1.459 ^b 1.426 ^c	0.629 0.600 ^a 0.612 ^b 0.688 ^c	0.618 ^c	
<i>trans</i> - $[\text{Co}(\text{en})_2\text{Br}_2]^+$	2.549 2.530 ^b	1.259 1.293 ^a 1.277 ^b	0.737 0.709 ^a 0.716 ^b	0.147 ^a	0.550 ^a
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+ \text{ d}}$	2.51	1.46	0.299	0.222	0.501
$[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+ \text{ e}}$	2.48	1.31	0.334		

* Dq^{xy} denotes the Dq value of NH_3 or en ; $Dq^{z^{1}}$ denotes the Dq value of the remaining ligand(s).
^a From reference 13. ^b From reference 3. ^c From reference 15. ^d From reference 2. ^e From reference 1.

that the intensities of IA and IB bands were equal. This assumption is not valid since band IB is symmetry forbidden in both C_{4v} and D_{4h} complexes. As seen from the data given in Table I, the intensities of IA and IB bands are somewhat different.

(5) In the determination of the Dt value, Wentworth and Piper³ assumed that the energy of the IB band was approximately equal to that of the I band in the parent complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$. However, this assumption is not always correct as seen from the results of $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reported by them. If the energy of the IB band is used in the calculation instead of the first band of the parent complex, a value close to ours will be obtained, which is about 25% greater than theirs.

(6) The values of Ds obtained by Ban and Csaszar¹³ are very much smaller than ours as a result of their neglecting the splitting of the second band. Unfortunately, the crystal field model does not make a prediction on the magnitude of the splitting of the ${}^1T_{2g}$ level. Based on a molecular orbital model, Yamatera¹⁴

suggested that the splitting of band II should be less than that of band I, which is about 2000 cm^{-1} . Since our results do not contradict this prediction, our values of D_s calculated from the splitting of band II do seem to be reasonable. Furthermore, the values of D_s for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ obtained by Book et al.^{1,2} and that for $t\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ calculated from the polarized crystal spectrum by Dingle¹⁵ are also substantially greater than those obtained by Ban and Csaszar¹³.

(7) Unlike other complexes the energy of the 1A_2 state above the ground state of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ is less than that of the $^1E^g$ state (Figure 1) since the field strength of NO_2^- is greater than that of NH_3 .

In conclusion, it is believed that a rather simple crystal field model is successful in the interpretation of the spectra of complexes. In addition, the resolution of the bands can lead to consistent, and therefore hopefully meaningful, values for the crystal field parameters.

Acknowledgement. — The authors wish to thank Dr. K. Y. Hui for his sample of $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ and helpful discussions.

REFERENCES

1. L. F. Book, K. Y. Hui, O. W. Lau, and W.-K. Li, *Z. Anorg. Allg. Chem.* **426** (1976) 215.
2. L. F. Book, K. Y. Hui, O. W. Lau, and W.-K. Li, *Z. Anorg. Allg. Chem.* **426** (1976) 227.
3. R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.* **4** (1965) 709.
4. F. Basolo and R. K. Murman, *Inorg. Synth.*: Vol. 4, p. 171, J. C. Bailar, Jr. (Ed.), (McGraw-Hill, 1953).
5. S. M. Jørgensen, *Z. Anorg. Allg. Chem.* **19** (1899) 78.
6. G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd ed., Vol. 2, p. 1534, (Academic Press, 1965).
7. F. Basolo and R. K. Murman, ref. 4, p. 175.
8. F. Basolo and R. K. Murman, ref. 4, p. 172.
9. F. Basolo and R. K. Murman, ref. 4, p. 174.
10. J. C. Bailar, Jr., *Inorg. Synth.*: Vol. 2, p. 222, W. C. Fernelius (Ed.), (McGraw-Hill, 1946).
11. S. M. Jørgensen, *J. Prakt. Chem.* **41** (1890) 440.
12. R. D. B. Fraser and E. Suzuki, *Spectral Analysis*, p. 174, J. A. Blackburn (Ed.), (Marcel Dekker, 1970).
13. M. Ban and J. Csaszar, *Magy. Kem. Foly.* **73** (1967) 509; **74** (1968) 333, 587; *Acta Chim. (Budapest)* **57** (1968) 153.
14. H. Yamatera, *Bull. Chem. Soc. Jap.* **31** (1958) 95.
15. R. Dingle, *J. Chem. Phys.* **46** (1967) 1.

SAŽETAK

Vidljivi spektri nekih monoacidopentaamin i diacidotetraamin kompleksa kobalta(III)

Suk-Yee Chan i Wai-Kee Li

Snipljeni su spinski dopušteni prijelazi u vidljivom području monoacidopentaamin i diacidotetraamin kompleksa kobalta(III) gdje su acido grupe bile: CO_3^{2-} , H_2O , NO_2^- , $\text{O}_2\text{C}_3\text{H}_5^-$, F^- , NO_3^- , Cl^- i Br^- . Parametri kristalnog polja i Racah-ovi parametri određeni su modificiranom metodom Wentworth-a i Piper-a. Rezultati su konzistentni unutar niza i u skladu s literaturnim podacima na srodnim sistemima.

DEPARTMENT OF CHEMISTRY
THE CHINESE UNIVERSITY OF HONG KONG
SHATIN, N. T.,
HONG KONG

Prispjelo 8. rujna 1978.