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THE SPECTRUM OF CoCl IN THE PHOTOGRAPHIC INFRARED AND THE VISIBLE

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Plate XII A & B

ABSTRACT. The spectrum of CoCl has been examined in the photographic infrared and the visible using both low and high dispersion. Several new brief systems have been observed in the visible region λ 4600—λ5100 Å, and in the photographic infrared region λ 6850—λ 7950 Å. Vibrational constants of the various systems have been derived from the analyses. The new systems, designated in this paper as F, G, H, I are observed to consist of single headed bands while the remaining systems J, K, L, N_1, N_2 and O are observed to be double headed. It is suggested that the two systems N_1 and N_2 in the photographic infrared might belong to two components of a $^3\Pi—^3\Sigma$ transition.

INTRODUCTION

The band spectrum of cobalt chloride has been investigated by several earlier workers, Mesnage (1935), More (1938), and Krishnamurty (1952). On the basis of high dispersion spectrograms, taken in the second order of a 21 ft. concace grating spectrograph, More (1938) gave vibrational analyses of three systems designated by him as 1, 2 and 3 in the region (λ4200—λ4750 Å). The bands in each of the three systems are single-headed and degraded to longer wavelengths. Recently, Krishnamurty has identified two more systems, designated as 4 and 5 in the same spectral region. These consist also of bands degraded to longer wavelengths. In addition, Krishnamurty proposed the vibrational analyses of six groups of line-like bands slightly degraded to red in the region (λ5350—λ6000 Å). on the basis of a $^5\Pi—^5\Sigma$ transition. His analysis was however based on measurements of plates taken under low dispersion, (25—30 Å/mm).

In a previous paper (Rao *et al.*, 1961) we have reported the results of a study of the spectrum of NiCl in the photographic infrared under high dispersion. In continuation of this work we have examined the spectrum of CoCl in the photographic infrared and the visible, both under low and high dispersion. This work has disclosed the existence of a number of new band systems of CoCl in the photographic infrared region (λ6850—λ7950 Å), and in the visible region (λ4600—λ5100 Å) The structure and analyses of these new band systems are discussed in this paper.

EXPERIMENTAL

The spectra were excited both in a heavy current discharge from a 2000 volt d.c. generator and in a high frequency discharge from a 100 watt oscillator

using an anhydrous B.D.H. sample of $CoCl_2$. The spectra were photographed under low dispersion on a Hilger three prism glass Littrow instrument (17 Å/mm), and also in the first and second orders of a 21 ft. concave grating spectrograph (dispersion 2.5 Å/mm and 1.25 Å/mm) using appropriate filters. Exposures of two to five hours duration were found necessary for obtaining the spectra on the grating, using Kodak I.N. plates and Agfa Isopan plates. Second order iron arc lines were used as standards for measurements of all grating plates.

RESULTS AND ANALYSIS

All the five band systems observed and analysed by More (1938) and Krishnamurty, (1952) in the spectral region (λ4200—λ4750 Å) were photographed in the present work both under low and high dispersion. In the order of increasing wavelength, systems 3, 2, 4, 5 and 1 are designated as A, B, C, D, E respectively. The bands in each of the systems appear single headed and arise from a transition in which $\Delta\Lambda = 0$ in Hund's case 'a' or $\Delta\Omega = 0$ in Hund's case 'c'.

The six groups of line like bands (designated as *M* in this paper) observed and analysed by Krishnamurty in the region (λ5350—λ6000 Å) were too weak to be photographed under high dispersion and therefore they are not considered in the present work. In the spectrum of CoCl excited in a high frequency discharge from a 100 Watt oscillator we have observed a number of new band systems in the region (λ4600—λ5100 Å). According to our analyses, based on a close scrutiny of both low and high dispersion spectrograms, the bands of CoCl in this region were classified as belonging to seven separate brief systems. Each of these systems is characterised by a strong $\Delta v = 0$ sequence with weaker $\Delta v = -1$ or $+1$ sequence. In the order of increasing wavelength these were designated as *F*, *G*, *H*, *I*, *J*, *K* and *L* systems respectively. The bands in each of the systems *F*, *G*, *H* and *I* are single headed, degraded to red and interpreted as the *R* heads. The bands in *J*, *K* and *L* systems are double headed and interpreted as the *R* and *Q* heads. The data and classifications of these bands are given in Table I. Low dispersion spectrograms of these seven systems are shown in strips (a and *b*) in Plate XII A, Fig. 1. Grating spectrograms of the prominent bands of the strong $\Delta v = 0$ sequence in different systems are shown in strips (*a*, *b* and *c*) in Plate XII B, Fig. 2. In the bands of the weaker $\Delta v = \pm 1$ sequences only the heads of the more abundant $Co^{35}Cl$ species could be identified.

In the spectrum of CoCl excited in a heavy current discharge from a 2000 volt D.C. generator we have observed two new systems of bands in the photographic infrared region (λ6850—λ7960 Å). The observed spectrum in the region (λ6850—λ7200 Å) taken under low dispersion can be seen from strip (c) in Plate XII A, Fig. 1, to consist of four characteristic groups of bands. Of these, two stronger groups beginning at $\lambda = 7117.0$ Å and λ7171.2 Å are identified as the two $\Delta v = 0$ sequences of two components of $a\ ^3\Pi—^3\Sigma$ transition. The weaker groups beginning at $\lambda = 6892{\cdot}8$ Å and $\lambda = 6941.2$ are identified as two $\Delta v =$

± 1 sequences respectively. The double headed nature of the bands of this system designated as $N(N_1$ and $N_2)$ can be seen clearly from grating spectrograms shown in strip (d) in Plate XII B, Fig. 2. The data and classification of the bands are given in Table II.

TABLE I

Band heads of CoCl in the region (λ4600—λ5100 Å)

Wavenumber	Int.	Classification	Wavenumber	Int.	Classification
system—F			system—J		
21640.4	8	0,0	20358.4	7	1,0 R
21639.0	8	1,1	20356.4	5	1,0 Q
21230.5	5	0,1	20339.4	6	2,1 R
21228.2	5	1,2	20337.7	6	2,1 Q
21225.2	5	2,3	19950.9	9	0,0 R
system—G			19945.8	9	0,0 Q
21335.1	8	0,0	19927.5	8	1,1 R
21320.0	8	1,1	19925.1	8	1,1 Q
21306.0	8	2,2	system—K		
20933.1*	5	0,1	20279.6	5	1,0 R
20923.4*	5	1,2	20277.5	4	1,0 Q
20914.2*	5	2,3	20263.1	5	2,1 R
system—H			20260.3	5	2,1 Q
21263.9	10	0,0	19869.7	10	0,0 R
21257.1	7	1,1	19868.1	10	0,0 Q
21247.2	6	2,2	19851.9	8	1,1 R
20847.9*	3	3,1	19849.9	8	1,1 Q
20842.0*	4	1,2	system—L		
20832.7*	4	2,3	19829.5	9	0,0 R
20825.8*	4	3,4	19826.3	9	0,0 Q
system—I			19804.3	9	1,1 R
21372.5*	3	1,0	19801.2	9	1,1 Q
21365.2*	3	2,1	19781.2	7	2,2 R
21357.9*	3	3,2	19779.2	7	2,2 Q
20969.1*	7	0,0	*Measured on low dispersion plates only.		
20963.4*	5	1,1			

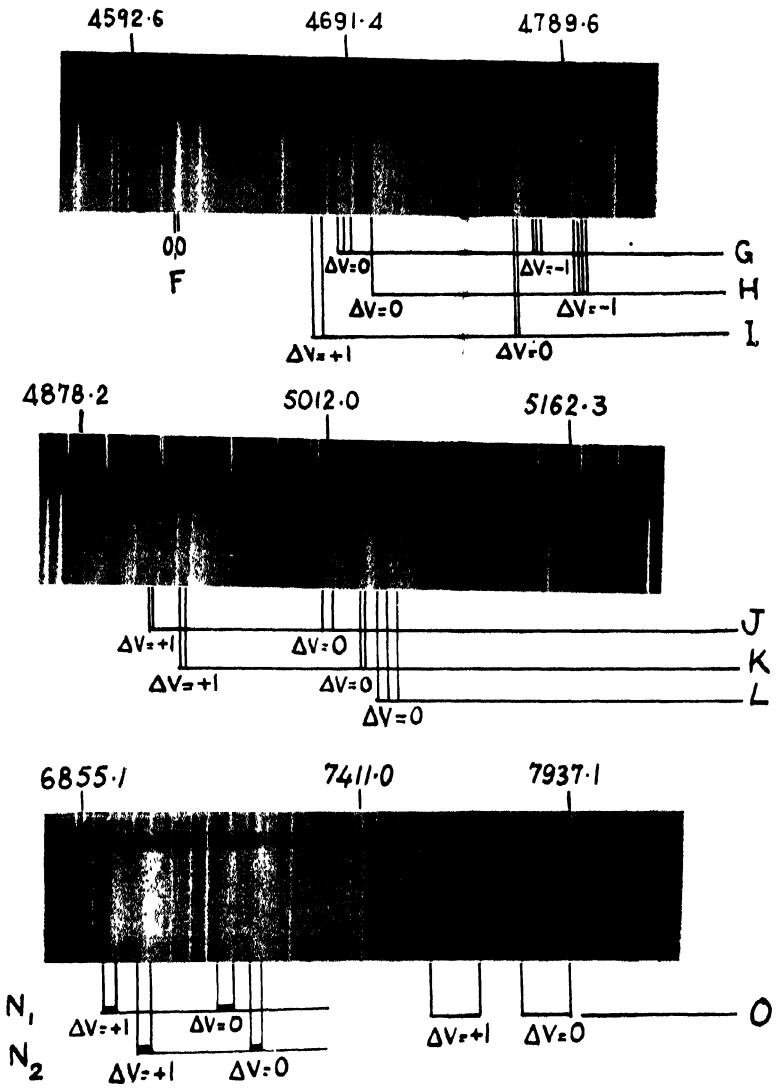

Fig. 1. New band systems of CoCl in the photographic infrared and the visible (low dispersion spectrograms).

a — systems F, G, H and I.

b — systems J, K and L.

c — systems N_1 , N_2 and O.

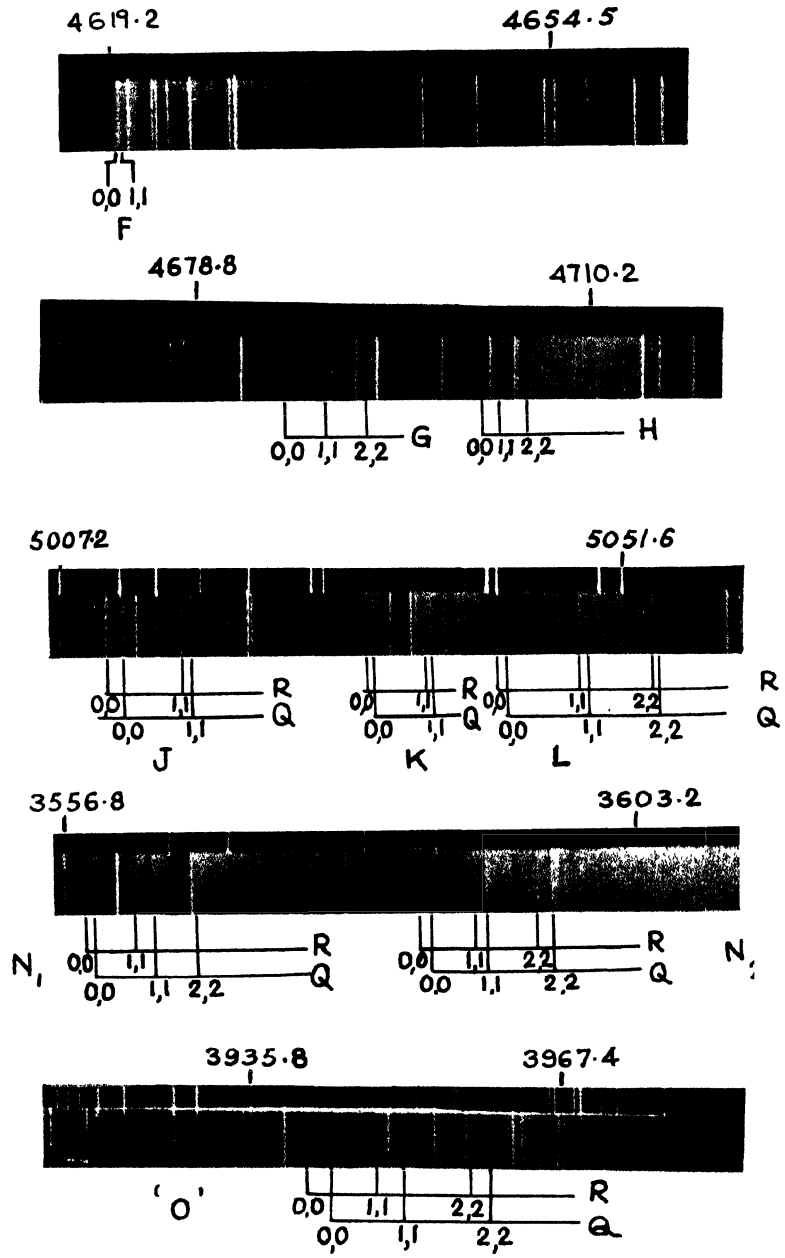

Fig. 2. New band systems of CoCl in the photographic infrared and the visible (21 ft. grating spectrograms).

a — $\Delta V=0$ sequence of system F.

b — $\Delta V=0$ sequence of systems G, H.

c — $\Delta V=0$ sequence of systems J, K and L.

d — $\Delta V=0$ sequence of systems N_1 and N_2.

e — $\Delta V=0$ sequence of system O.

In the region (λ7600--λ7950Å) a weaker system (designated as 0) shown in strips (c) in Plate XII A, Fig. 1 and (e) in Plate XII B, Fig. 2, has been observed. The strong group beginning at $\lambda = 7882{\cdot}4$Å is identified as the $\Delta v = 0$ sequence and the weaker group beginning at $\lambda = 7612.2$Å as $\Delta v = +1$ sequence. In the $\Delta v = 0$ sequence the R and Q heads are identified while in the weaker $\Delta v = +1$ sequence only R heads have been identified. The data and classifications of the bands are given in Table II. Table III summarizes the vibrational constants of the different band systems of CoCl.

TABLE II

Band heads of CoCl in the region (λ6850—λ7950Å)

Wavenumber	Int.	Classification	Wavenumber	Int.	Classification
system—N_1			system—0		
14503.9	4	1,0 R	13159.1	4	1,0 R
14501.4	4	1,0 Q	13130.8	5	2,1 R
14483.3	4	2,1 R	13098.8	5	3,2 R
14480.4	5	2,1 Q	12683.0	7	0,0 R
14461.5	6	3,2 R	12674 6	6	0,0 Q
14459.0	6	3,2 Q	12658.6	8	1,1 R
14047.0	3	0,0 R	12650.6	7	1,1 Q
14044.2	3	0,0 Q	12628.2	8	2,2 R
14031.2	5	1,1 R	12621.8	8	2,2 Q
14026.1	5	1,1 Q			
14012.4*	L	2,2 Q			
system—N_2					
14402.8	4	1,0 Q			
14380.4	5	2,1 Q			
14389.7	5	3,2 Q			
13940.8	4	0,0 R			
13937.7	4	0,0 Q			
13924.1	5	1,1 R			
13920.3	7	1,1 Q			
13904.0	6	2,2 R			
13899.7	10	2,2 Q			

*Superposed by atomic line.

TABLE III

Summary of the vibrational constants of CoCl

System	Wave number of the (0,0) band	ω_e'	$x_e'\omega_e'$	ω_e''	$x_e''\omega_e''$
A	22966.2	420.0	1 66	421.8	1.34
B	22402.7	416.6	0.82	419.4	0.28
C	22182.5	401.0	—	416.2	—
D	22072.3	410.2	—	416.4	—
E	22014.8	420.0	1.14	421.2	0.74
F	21640.4	408.0	—	409.0	—0.45
G	21335.1	391.2	2.15	407.1	2.55
H	21263.9	413.2	2.00	416.8	0.38
I	20969.1	405.0	0.80	409.0	—
J	19945.8	408.6	—1.00	431.0	—
K	19868.1	408.4	—0.50	428.0	—
L	19826.3	—	—	—	—
M	17484.1	412.3	—	416.0	—
N_1	14044.2	462.5	2.65	482.6	3.65
N_2	13937.7	467 6	1.25	484.3	0.90
O	12683.0	478.8	1.38	498.4	—1.05

DISCUSSION

From the magnitude of the vibrational constants of the upper and lower states, More (1938) has suggested that systems A, B and E might belong to a triplet-triplet transition, with intervals of 390 and 562 cm^{-1}. After the ientification of two more systems C and D, Krishnamurty considers that systems E, D and C with separations of 55 and 110 cm^{-1} may better be represented as belonging to an electronic triplet, while A and B may be identified as two component systems of a triplet→ triplet transition. According to us, each of the brief systems A to I consisting of single headed bands arises from a transition with $\Delta\Lambda = 0$ in Hund's case (a). However in view of the large multiplet splittings known in the ground and low excited states of Co_1, it is possible that they are all separate systems with $\Delta\Omega = 0$ corresponding to Hund's case (c). This view is supported by the fact that Heimer, (1937) from a detailed rotational analysis of CoH bands, has previously identified the $A \rightarrow X$ transition in CoH as $\Omega = 4 \rightarrow \Omega = 4$ with $\Delta\Omega = 0$, corresponding to Hund's case (c).

The characteristic appearance of the N_1 and N_2 systems observed in the photographic infrared region (λ6850—λ7200Å) shown in strip (d) in Plate XII B, Fig. 2, would suggest that they may arise from two components of a $^3\Pi$—$^3\Sigma$ transition. The magnitude of the vibrational constants of the upper and lower states, the observed double headed nature of the bands, and the close proximity of these two systems lend support to this view. However, both the upper and lower states of this $^3\Pi$—$^3\Sigma$ transition do not correspond to those observed already in the visible region. They appear to belong to two different excited states of the CoCl molecule. A similar situation is also observed in the band systems of MnF, MnCl and MnBr in the photographic infrared.

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