

CHAPTER IV

REVIEW OF OPTICAL AND MAGNETIC PROPERTIES OF SOME CHLORIDE COMPOUNDS

There are extensive studies of optical and magnetic properties of transition metal chloride complexes and it is not feasible to include here all the results of the above studies. So we have confined our review mainly to octahedral, distorted octahedral and tetrahedral chloride complexes with special attention to doped crystals. The review is conveniently given in Table 7.

Table 7

| Config. | System | Symmetry (approx.) | Optical Absorption | | Ref. | Magnetic μ_{eff} in B.M. | Ref. |
|----------------|--|-----------------------|--|--|------|--|------|
| | | | Band max. cm ⁻¹ | Transition | | | |
| d ⁰ | TiCl ₄ (Vapour) | T _d | 35710 43100 | t ₁ → 2e → 2t ₂ | 85 | Diamagnetic | |
| d ¹ | α-TiCl ₃ | Dist. O _h | 14300 18900 27500 | 2T _g → 2E _g Charge transfer | 86 | $\mu_{eff} = 1.31$ | 87 |
| | VCl ₄ (Vapour) | T _d | 24800 33900 45400 50000 | T ₁ → 2E T ₁ → 3T ₂ 2T ₂ → 2E 2T ₂ → 3T ₂ | 88 | | |
| | VCl ₄ | T _d | 7900 | e → t ₂ | 89 | $\mu_{eff} = 1.607$ | 89 |
| d ² | (LiCl + KCl) : V ³⁺ (Molten) | O _h | 11000 18000 | 3T _{1g} → 3T _{2g} 3T _{1g} → 3T _{1g} (P) | 91 | | |
| | VCl ₃ | O _h | 12500 14600 18900 | 3T _{1g} → 3T _{2g} → 3T _{1g} (P) Charge transfer | 87 | $\mu_{eff} = 2.85$ | 90 |
| | CrAlCl ₄ : V ³⁺ | T _d | 8250 | | | | |
| | | O _h | 9400 10250 15000 | 3A ₂ → 3T ₁ (P) 3A ₂ → 3T ₁ (P) | 91 | | |
| d ³ | VCl ₂ | O _h | 9000 14000 21500 | 4A _{2g} → 4T _{2g} → 4T _{1g} → 4T _{1g} (P) | 87 | $\mu_{eff} = 4.15$ | 90 |
| | CrCl ₃ | O _h | 13500 18900 | 4A _{2g} → 4T _{2g} → 4T _{1g} | 87 | $\mu_{eff} = 3.69$ g = 1.997 at R.T. = 2.37 at 13.15°K | 92 |
| | (LiCl + KCl) : Cr(III) | O _h | 12500 18500 | 4A _{2g} → 4T _{2g} → 4T _{1g} | 87 | | |
| d ⁴ | CrCl ₂ | O _h | 8750 12000 16300 17500 19000 | 5E _g → 5T _{2g} Weak spin forbidden | 94 | $\mu_{eff} = 5.13$ | 90 |
| | [Rh(C ₃ H ₁₀ N ₂) ₃][MnCl ₆] | O _h | 17540 22400 | 5E _g → 5T _{2g} Charge transfer | 95 | | |

| Config. | System | Symmetry (approx.) | Optical Absorption | | Ref. | Magnetic P_{eff} in B.M. | Ref. | | | | | |
|----------------|--|-----------------------|--|---|--------------------------|--------------------------------|------|--------------------------|----------------------------------|----|--|--|
| | | | Band max. cm^{-1} | Transition | | | | | | | | |
| d^5 | $FeCl_3$ | O_h | 11400 | ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(S)$ | 87 | $P_{eff} = 5.73$ | 90 | | | | | |
| | | | 17300 24900 | Charge transfer | | | | | | | | |
| | $MnCl_2$ | Dist. O_h | 18500 | ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ | 96 | $P_{eff} = 5.73$ | 90 | | | | | |
| 22000 | | | $\rightarrow {}^4T_{2g}(G)$ | | | | | | | | | |
| 23590 | | | $\rightarrow {}^4A_{1g}(G)$ | | | | | | | | | |
| 23825 | | | $\rightarrow {}^4E_g(G)$ | | | | | | | | | |
| 26750 | | | $\rightarrow {}^4T_{2g}(D)$ | | | | | | | | | |
| 28065 | | | $\rightarrow {}^4E_g(D)$ | | | | | | | | | |
| 31300 | | | $\rightarrow {}^4T_{1g}(P)$ | | | | | | | | | |
| 34200 | | | $\rightarrow {}^4A_{2g}(F)$ | | | | | | | | | |
| 42000 | | | $\rightarrow {}^4T_{1g}(F)$ | | | | | | | | | |
| 42200 | | | $\rightarrow {}^4T_{2g}(F)$ | | | | | | | | | |
| | | | $[(C_2H_5)_4N]_2 MnCl_4$ | T_d | | | | 21300 | ${}^6A_1 \rightarrow {}^4T_1(G)$ | 97 | | |
| 22530 | | | | | | | | $\rightarrow {}^4T_2(G)$ | | | | |
| 23180 23400 | $\rightarrow {}^4A_1, {}^4E(G)$ | | | | | | | | | | | |
| 26600 | $\rightarrow {}^4T_1(P)$ | | | | | | | | | | | |
| 27300 27650 | $\rightarrow {}^4T_2(D)$ | | | | | | | | | | | |
| 28060 | $\rightarrow {}^4E(D)$ | | | | | | | | | | | |
| 35600 | $\rightarrow \begin{cases} {}^4A_2(F) \\ {}^4T_1(F) \end{cases}$ | | | | | | | | | | | |
| 37120 | $\rightarrow {}^4T_2(F)$ | | | | | | | | | | | |
| | $(PyH)_2 MnCl_4$ | T_d | | | 21050 | ${}^6A_1 \rightarrow {}^4T(G)$ | 98 | | | | | |
| 22000 | | | | | $\rightarrow {}^4T_2(G)$ | | | | | | | |
| 23040 | | | $\rightarrow \begin{cases} {}^4E(G) \\ {}^4A_1(G) \end{cases}$ | | | | | | | | | |
| 26200 | | | $\rightarrow {}^4T_2(D)$ | | | | | | | | | |
| 27600 | | | $\rightarrow {}^4E(D)$ | | | | | | | | | |

| Config. | System | Symmetry (approx) | Optical Absorption | | Ref. | Magnetic μ_{eff} in B.M. | Ref. |
|--|--|----------------------|---|--------------------------------------|------------------------|--|------|
| | | | Band max. cm ⁻¹ | Transition | | | |
| d ⁶ | FeCl ₂ (Vapour) | | 4600 | 5 Δ \rightarrow 5 Π | 99 | P _{eff} = 5.38 at 100°K | 90 |
| | | | 7140 | 5 Δ \rightarrow 5 Σ | | | |
| | [(CH ₃) ₄ N] ₂ FeCl ₄ in C ₆ Cl ₆ mull | T _d | 3880 | 5 _E \rightarrow 5 Π | 100 | | |
| | [Me ₄ N] ₂ [FeCl ₄] | T _d | | | | P _{eff} = 5.41 at 340°K = 5.3 at 78°K | 101 |
| d ⁷ | CoCl ₂ | O _h | 6600 | 4 T_1 \rightarrow 4 T_2 | 102 | P _{eff} = 5.29 | 93 |
| | | | 10000 | \rightarrow 2 _{Eg} | | | |
| | | | 15150 | \rightarrow 2 T_1 | | | |
| | | | 15870 | \rightarrow 2 T_2 | | | |
| | | | 16150 | | | | |
| | | | 17156 | \rightarrow 4 T_1 (P) | | | |
| | | | 17356 | | | | |
| | | | 19030 | \rightarrow 2 T_1 | | | |
| | | | 19360 | | | | |
| | | | 19780 | \rightarrow 2 A_1 | | | |
| | | | 19820 | | | | |
| | | | 19850 | | | | |
| | | | 2153 | \rightarrow 2 T_2 (G) | | | |
| | | | 22380 | \rightarrow 2 T_1 (H) | | | |
| OsMgCl ₃ : Co ²⁺ | Dist. O _h | 5900 | 4 T_{1g} \rightarrow 4 T_{2g} | 103 | g = 7.37 | 103 | |
| | | 12100 | \rightarrow 4 A_{2g} | | g _⊥ = 2.51 | | |
| | | 16800 | \rightarrow 4 T_{1g} (P) | | | | |
| AgCl : Co ²⁺ | O _h | 6150 | $\Gamma_5(4F) \rightarrow \Gamma_4(4F)$ | 104 | | | |
| | | 16880 | $\rightarrow \Gamma_4(4P)$ | | | | |
| | | 19000 | $\rightarrow \Gamma_1(2G)$ | | | | |

| Config. | System | Symmetry (approx.) | Optical Absorption | | Ref. | Magnetic P_{eff} in B.M. | Ref. | |
|---------------------------------------|-----------------------------------|-----------------------------|--|--|---|--------------------------------------|----------------------------------|-------------------------------|
| | | | Band max. cm^{-1} | Transition | | | | |
| d ⁷ | Cs ₂ CoCl ₄ | T _d | 3100 | 4 _{A₂} → 4 _{T₂} | 105,106 | P _{eff} = 4.56 | 107 | |
| | | | 5400 | → 4 _{T₁} | | | | |
| | | | 15300 | → 4 _{T₁} (P) | | | | |
| | | | 17700 | → terms from (2 _G) | | | | |
| | | | 26342 - 26962 | → terms from (2 _G , 2 _D) (2 _H , 2 _P) | | | | |
| | 30437 - 32710 | → terms from 2 _F | | | | | | |
| | Cs ₃ CoCl ₅ | T _d | 5500 | 4 _{A₂} → 4 _{T₁} (F) | 108 | P _{eff} = 4.49 | 111 | |
| | | | 16000 | → 4 _{T₁} (P) | | | | |
| | | | The polarised crystal spectra was observed by Pelletier-Allard ^{109, 106, 110} More than 140 lines were revealed at 4°K in the region 15390 - 32870 cm ⁻¹ | | | | | |
| | d ⁸ | CsNiCl ₃ | O _h | 6100 | 3 _{A_{2g}} → 3 _{T_{2g}} | 113 | P _{eff} = 3.37 | 114 |
| 10300 | | | | → 3 _{T_{1g}} | | | | |
| 12000 | | | | → 1 _{E_g} | | | | |
| 20450 | | | | → 3 _{T_{1g}} (P) | | | | |
| KMgCl ₃ : Ni ²⁺ | | Dist. O _h | 5500 | 3 _{A_{2g}} → 3 _{T_{2g}} | 115 | | | |
| | | | 6640 | | | | | |
| | | | 9450 | | | | | → 3 _{T_{1g}} |
| | | | 10300 | | | | | |
| | | | 12810 | | | | | → 1 _{E_g} |
| | | | 18050 | | | | | → 1 _{T_{2g}} |
| 20300 | → 3 _{T_{1g}} (P) | | | | | | | |
| AgCl : Ni ²⁺ | O _h | 6680 | 3 _{A_{2g}} → 3 _{T_{2g}} | 104 | | | | |
| | | 18480 | → 1 _{T_{2g}} | | | | | |
| | | 20920 | → 3 _{T_{1g}} (P) | | | | | |
| NiCl ₂ | O _h | 11600 | 3 _{Γ₂} → 3 _{Γ₄} (F) | 116 | P _{eff} = 3.32 | 90 | | |
| | | 12900 | | | | | | |
| | | 22100 | | | | | → 3 _{Γ₄} (P) | |

$g = 2.25$ at 293°K
 $= 2.30$ at 20°K

| Config. | System | Symmetry (approx) | Optical Absorption | | Ref. | Magnetic μ_{eff} in B.M. | Ref. |
|---------|------------------------------|----------------------|------------------------|-------------------------|------|---------------------------------|------|
| | | | Band max. cm^{-1} | Transition | | | |
| d^8 | Cs_2NiCl_4 in Cs_2ZnCl_4 | T_d | 7750 | $3T_1 \rightarrow 3A_2$ | 117 | | |
| | | | 11400 | $\rightarrow 1D$ | | | |
| | | | 14200 | | | | |
| | | | 15150 | $\rightarrow 3T_1 (P)$ | | | |
| | | | 16400 | | | | |
| | | | 20620 | $\rightarrow 1G$ | | | |
| | | | 4080 | $3T_1 \rightarrow 3T_2$ | | 118 | |
| | | | 7460 | $\rightarrow 3A_2$ | | | |
| | | | 11200 | | | | |
| | | | 11600 | $\rightarrow 1D$ | | | |
| | | | 12600 | | | | |
| | | | 14160 | | | | |
| | | | 15510 | $\rightarrow 3T_1 (P)$ | | | |
| 16300 | | | | | | | |
| 20200 | | | | | | | |
| 23500 | $\rightarrow 1G$ | | | | | | |
| 35840 | | | | | | | |
| 42100 | | Charge transfer | | | | | |

| Config. | System | Symmetry (approx) | Band max. cm ⁻¹ | Optical Absorption Transition | Ref. | Magnetic | Ref. |
|----------------------|--|----------------------|-------------------------------|---|------------------|------------------------|------------------------|
| d ¹⁰ CuCl | Cs ₂ CuCl ₄ in Cs ₂ ZnCl ₄ | T _d | 8685 | ² B ₂ → ² A ₁ | 125 | g ₁ = 2.083 | 124 |
| | | | 7500 | → ² B ₁ | | g ₂ = 2.010 | |
| | | | 5210 ± 20 | | → ¹ E | | g ₃ = 2.446 |
| | | | 4450 ± 50 | | | | |
| Fine series | | | | | | | |
| | | | 27151 | Settled band | | | 126 |
| | | 27300 | | | | | |
| | | 27382 | | | | | |
| | | 27533 | | | | | |
| Diffuse series | | | | | | | |
| | | | 27624 | Vibronic character | | | |
| | | 27839 | | | | | |
| | | 28050 | | | | | |
| | | 28272 | | | | | |
| | | 28566 | | | | | |