BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (7), 2036—2040 (1978)

Synthesis and Oxygenation Reaction of Cobalt(II) Complexes with Jäger-Type Open-Chain Ligands[1]

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(Received December 22, 1977)

Cobalt(II) complexes with Jäger-type open-chain ligands, H_2(J-R) (R=en, pn, ph, and tn), were prepared. It was found that Co(J-en), Co(J-pn), and Co(J-ph) are in low-spin state, and Co(J-tn) in high-spin state with a pseudo-tetrahedral configuration. The formation constant of pyridine adduct of Co(J-en)was spectrophotometrically determined to be 2.70, 2.18, and 1.90 M^{-1} at 0, 20, and 30 °C, respectively. Co(J-en)py forms oxygen adducts, Co(J-en)pyO_2 and [Co(J-en)py$]_2O_2$, in a 1,2-dichloroethane solution at room temperature, exhibiting a characteristic band at 525 nm. The ease of oxygenation and the characteristic absorption in the visible region were interpreted in terms of the electron-withdrawing ability of acetyl group in the ligand.

The copper(II) and nickel(II) complexes of the quadridentate ligands (Fig. 1) were synthesized and characterized by Wolf and Jäger.[2] These ligands are abbreviated as H_2(J-R) in this paper, where R is en(ethylene), pn(propylene), ph(*o*-phenylene), or tn(trimethylene), representing the bridging chain in Fig. 1. One of the characteristics of Jäger's complexes is the ability of forming a macrocyclic ring when it is reacted with diamines.[2,3] The cyclization is facilitated by the electron-withdrawning ability of the acetyl group attached to the γ-position of the ligand. The acetyl group of the coordinated ligand is also expected to exert the electron-withdrawing effect on the coordination geometry, the reactivity, and the electronic configuration of the complex. In this study we have prepared cobalt(II) complexes of H_2(J-R) in order to examine their pyridine- and oxygen-adduct formation in relation to the electronic configuration of the cobalt ion, which may adopt either the $(d_{xy})^2(d_{z^2})^1$ or $(d_{xy})^2(d_{yz})^1$ configuration depending on its ligand.

Experimental

Syntheses. Syntheses of H_2(J-R) (R=en, pn, ph, and tn) were carried out following the method of Wolf and Jäger.[2]

Co(J-en): A mixture of H_2(J-en) (10 g), cobalt(II) acetate tetrahydrate (9 g) and sodium hydroxide (2.9 g) in ethanol (150 ml) was stirred at 60 °C for 1 h in nitrogen atomosphere in order to avoid the reaction with oxygen. After being left to stand overnight, the product was collected and recrystallized from chloroform to give orange needles.

Found: C, 49.89; H, 5.38; N, 8.38%. Calcd for $C_{14}H_{18}N_2O_4Co$: C, 49.86; H, 5.38; N, 8.31%.

Co(J-en)py: Co(J-en) was recrystallized from pyridine in an atmosphere of nitrogen, the complex being obtained as brown crystals.

Found: C, 55.19; H, 5.63; N, 10.16%. Calcd for $C_{19}H_{23}N_3O_4Co$: C, 54.81; H, 5.57; N, 0.10%.

Co(J-en)py$O_2\cdot 1/4C_6H_5CH_3$: Co(J-en) was dissolved in toluene containing pyridine (*ca.* 5%), and oxygen or air was bubbled through the solution until black-purple prisms separated.

Found: C, 52.53; H, 5.52; N, 8.86%. Calcd for $C_{19}H_{23}N_3O_6Co\cdot 1/4C_6H_5CH_3$: C, 52.88; H, 5.35; N, 8.92%.

Co(J-en): This complex was obtained as orange needles in the same way as that for Co(J-en) except for the use of H_2(J-pn) instead of H_2(J-en).

Found: C, 51.20; H, 5.71; N, 8.03%. Calcd for $C_{15}H_{20}N_2O_4Co$: C, 51.29; H, 5.74; N, 7.97%.

Co(J-pn)py: Co(J-pn) was recrystallized from pyridine to afford the complex as brown crystals.

Found: C, 55.41; H, 5.86; N, 9.67%. Calcd tor $C_{20}H_{25}N_3O_4Co$: C, 55.83; H, 5.86; N, 9.77%.

Co(J-pn)py$O_2\cdot 1/4C_6H_5CH_3$: This complex was obtained as dark purple prisms when oxygen or air was passed through a solution of Co(J-pn) in toluene–pyridine (95:5) mixture.

Found: C, 53.49; H, 5.76; N, 8.66%. Calcd for $C_{20}H_{25}N_3O_6Co\cdot 1/4C_6H_5CH_3$: C, 53.83; H, 5.60; N, 8.66%.

Co(J-ph): This complex was obtained as deep red needles by reacting H_2(J-ph) and cobalt(II) acetate tetrahydrate in ethanol. The product was recrystallized from ethanol.

Found: C, 55.79; H, 5.15; N, 6.85%. Calcd for $C_{18}H_{18}N_2O_4Co\cdot 1/2C_2H_5OH$: C, 55.89; H, 5.18; N, 6.86%.

Co(J-ph)py: This complex was obtained as deep red prisms by recrystallizing Co(J-ph) from pyridine.

Found: C, 59.29; H, 5.04; N, 8.96%. Calcd for $C_{23}H_{23}N_3O_4Co$: C, 59.49; H, 4.99; N, 9.05%.

Co(J-tn): H_2(J-tn), cobalt(II) acetate tetrahydrate, and sodium hydroxide were reacted in ethanol at 70—75 °C to afford the complex as reddish brown crystals. The product was throughly washed with warm ethanol in order to separate sodium acetate.

Found: C, 50.98; H, 5.72; N, 7.89%. Calcd for $C_{15}H_{20}N_2O_4Co$: C, 51.29; H, 5.74; N, 7.97%.

Determination of Pyridine Adduct Formation Constants. Absorption spectra of Co(J-en) in 1,2-dichloroethane containing pyridine were measured at 0, 20, and 30 °C by successively altering the pyridine content (0—1 M), where the concentration of the complex was kept constant (3×10^{-4} M). Equilibrium constants were determined from the absorbance at 375 nm by the method of Marzilli *et al.*[4]

Determination of Oxygen Adduct Formation Equilibrium. A thermostatted three necked flask (200 ml, filled with dry nitrogen) was fitted with a dropping funnel containing a solution of Co(J-en) (4×10^{-4} M) in deoxygenated 1,2-dichloroethane–pyridine (99.7:0.3), a tube connected to the cell for spectral measurement and a tube connected to the apparatus for controlling the partial pressure of oxygen (Fig. 2). The temperature of the flask was maintained at 0 °C by means of ice–water. The pressure in the flask was then partially reduced and oxygen introduced until it reached 760 mmHg. The partial pressure of oxygen was manometrically determined. A solution of the complex was then dropped into the flask and vigorously stirred for about 15 min. After equilibrium had been reached, the solution was introduced into the cell. Spectrophotometric measurements were carried out at 0 °C.

Other Physical Measurements. Electronic spectra on solid

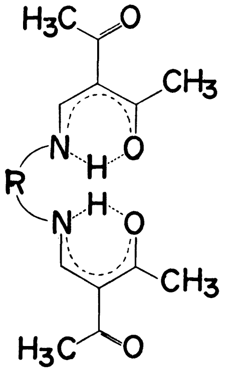

Fig. 1

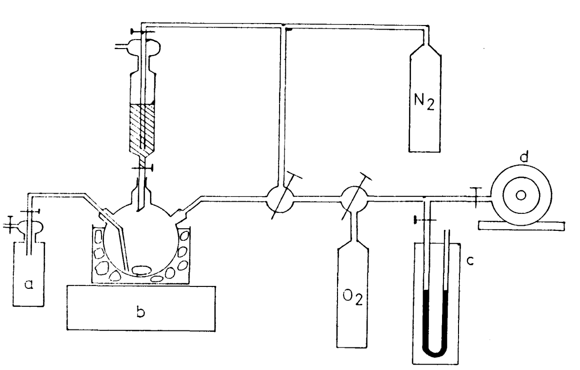

Fig. 2. Apparatus for the spectroscopic measurements under various oxygen pressures. a: Cell, b: magnetic stirrer, c: manometer, d: pump.

and in solution were measured with a Shimazu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibility was measured by the Faraday method, diamagnetic correction being carried out by means of Pascal's constants. ESR spectra (X-band) were measured on powder and in solutions with a JES-ME-3 spectrometer.

Results and Discussion

Effective magnetic moments of Co(J-en), Co(J-pn), Co(J-ph), and Co(J-tn) at room temperature are 2.24, 2.43, 2.56, and 4.36 BM, respectively. It is evident that the complexes except for Co(J-tn) are in low-spin state. ESR spectra of Co(J-R) (R=en, pn, and ph) diluted in the cooresponding Ni(J-R) were measured by X-band at 78 K. The spectra are similar to each other, showing a rhombic pattern. A typical example is shown in Fig. 3a. A band at g=3.10 shows an eight-lined hyperfine structure due to ^{59}Co(I=7/2) hyperfine coupling, from which A is determined to be 150 G. On the other hand two bands around g=1.78—1.85 are not well resolved because of their similar g and A values. The spectra of this type have been interpreted by Nishida and Kida5) in terms of the $(d_{xy})^2(d_{yz})^1$ ground state for cobalt(II) ion. Electronic spectra of the present complexes exhibit one absorption around 1200 nm characteristic of low-spin cobalt(II) complexes.

The effective magnetic moment of Co(J-tn) is much larger as compared with other complexes, the electronic spectrum showing a complicated pattern with absorption bands at 1550, 695, 570, and 460 nm. Judging from the fact that the moment falls in the values of tetrahedral cobalt(II) ions and that the spectrum resembles that of *N*,*N'*-disalicylidenetrimethylenediaminatocobalt(II),6) whose configuration was found to be pseudo-tetrahedral, we may conclude that the coordination geometry of Co(J-tn) is pseudo-tetrahedral.

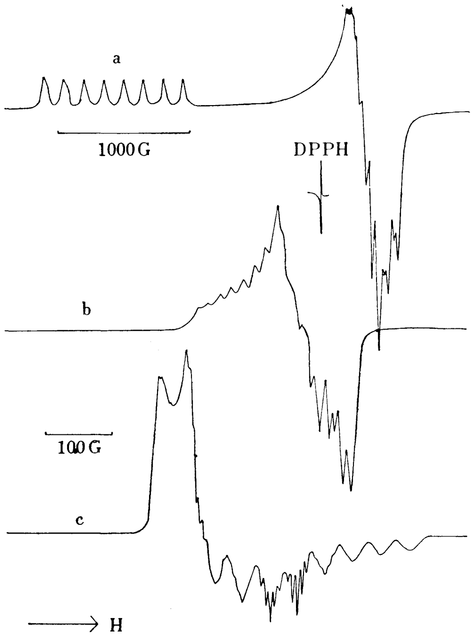

Fig. 3. Esr spectra at 78 K of a) Co(J-en) doped in Ni(J-en), b) oxygenated species of Co(J-en) in dichloroethane-pyridine, and c) pyridine adduct of Co(J-en) in dichloroethane-pyridine.

The pyridine adducts Co(J-R)py (R=en, pn, and ph) were obtained when Co(J-R) was recrystallized from pyridine. They are also low-spin complexes (Co(J-en)-py, 1.94; Co(J-pn)py, 2.09; Co(J-ph)py, 2.04 BM). It is supposed that the pyridine adducts have a square-pyramidal structure with a pyridine molecule at the apex.

The orange colored solution of Co(J-en) in 1,2-dichloroethane or toluene containing a small amount of pyridine turned purple when air or oxygen was bubbled through the solution at room temperature. Orange color was recovered when nitrogen was passed through the solution or the solution was warmed at *ca.* 60 °C. It seems that this process is reversible. The purple colored solution exhibited a well defined ESR spectrum indicating two signals of $g_{\parallel}$=2.081 and $g_{\perp}$=2.005 (Fig. 3b). Each signal consists of eight lines due to hyperfine splitting of ^{59}Co nucleus, $A_{\parallel}$ and $A_{\perp}$ being estimated at 18 and 12 G, respectively. The eight-lined hyperfine structure with the very small hyperfine splitting indicates that the 1:1 oxygen adduct is formed in the purple solution.

The equilibrium between Co(J-en) and pyridine was studied in order to elucidate the oxygenation reaction of Co(J-en). A solution of Co(J-en) in 1,2-dichloroethane exhibits an absorption band at 377 nm. By addition of pyridine to this solution the band gradually disappeared and two isosbestic points were observed at 365 and 400 nm (Fig. 4). The spectrum converged when pyridine concentration exceeded 1M.

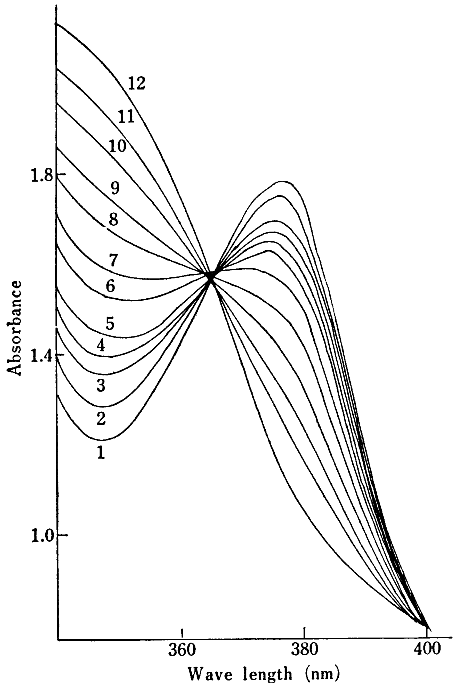

Fig. 4. Electronic spectra of Co(J-en) in dichloroethane with various contents of pyridine: 1), 0; 2), 5×10^{-4}; 3), 1.0×10^{-3}; 4), 1.5×10^{-3}; 5), 2.0×10^{-3}; 6), 3.0×10^{-3}; 7), $4.\times10^{-3}$; 8), 6.0×10^{-3}; 9), 9.0×10^{-3}; 10), 1.5×10^{-2}; 11), 2.4×10^{-1}; 12), 1.0 M. The concentration of Co(J-en) is maintained constant (3×10^{-4} M).

The equilibrium constant of the equation, Co(J-en) + $n$py$\rightleftarrows$Co(J-en)(py)$_n$, is given by the relation,

$$K_{\text{py}} = [\text{Co(J-en)(py)}_n]/[\text{Co(J-en)}][\text{py}]^n. \qquad (1)$$

If we denote the absorbances of Co(J-en) at 377 nm in the absence of pyridine, in the presence of large excess of pyridine, and in the presence of proper amount of pyridine by A_0, A_∞, and A, respectively, the equilibrium constant is given by

$$\log K_{\text{py}} = \log[(A_0-A)/(A-A_\infty)] - n\log[\text{py}]. \qquad (2)$$

Absorption spectra of Co(J-en) were determined at 0, 20, and 30 °C at various concentrations of pyridine and $\log[A_0-A/(A-A_\infty)]$ was plotted against log [py] (Fig. 5). The plot gives a straight line with a slope nearly equal to 1. This indicates that the main species formed in the solution is Co(J-en)py and the formation of Co(J-en)(py)$_2$ is negligibly small even at the concentration of pyridine higher than 1M. This seems to contradict the fact that the ESR spectrum of the solution of Co(J-en) in 1,2-dichloroethane–pyridine (99 : 1) at 77.4 K displays the five-lined superhyperfine structure in addition to the eight-lined hyperfine structure, indicating that the unpaired electron interacts with two ^{14}N(I=1) nuclei in apical positions (Fig. 3c). This can be explained by assuming that Co(J-en)(py)$_2$ is preferred to Co(J-en)py at liquid nitrogen temperature, while Co(J-en)py is preferred at room temperature. The equilibrium constants ($\log K_{\text{py}}$) were evaluated to be 2.70, 2.18, and 1.90 M^{-1} at 0, 20, and 30 °C, respectively, by extraporating log[py] to zero. The equilibrium constant of Co(J-en)py is a little lower than that of N,N'-disalicylidene-o-phenylenediaminatocobalt(II).[4]

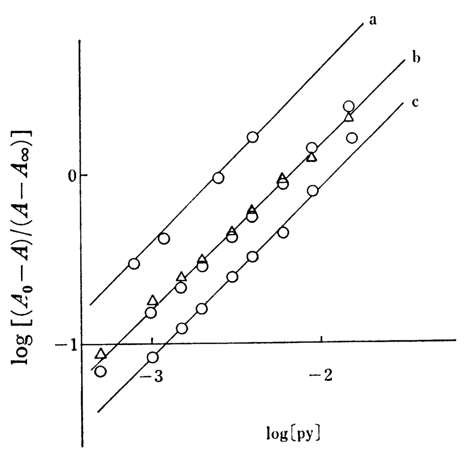

Fig. 5. Plots of $\log[(A_0-A)/(A-A_\infty)]$ *versus* log [py] at a) 0, b) 20, and c) 30 °C, based on the absorbance at 375 nm (○) and at 350 nm (△).

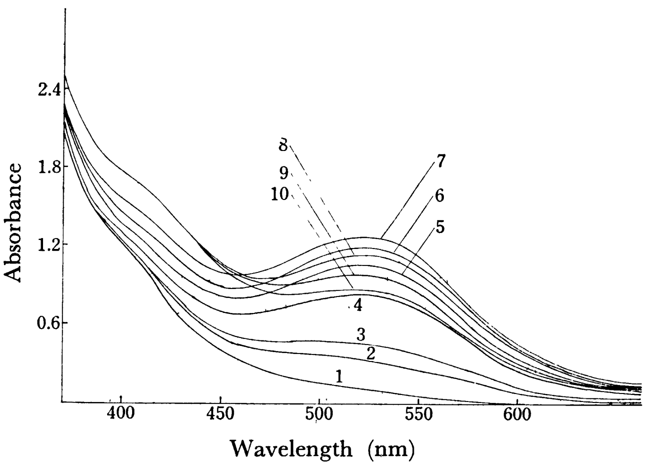

Fig. 6. Electronic spectra of Co(J-en) (4×10^{-4} M) in dichloroethane containing pyridine (0.3%) at 0 °C under various oxygen pressures: 1), 0; 2), 5; 3), 7; 4), 15; 5), 36; 6), 75; 7), 190; 8), 400; 9), 620; 10), 760 mmHg.

The electronic spectra of Co(J-en) in 1,2-dichloroethane containing 0.3% pyridine were measured under various oxygen partial pressures. As is shown in Fig. 6 a new absorption was observed when the complex was oxygenated. The intensity of this band reached maximum when the partial pressure of oxygen was *ca.* 200 mmHg and then gradually decreased with the increase in oxygen pressure. This implies that there are at least two oxygenated species in the solution. The species formed under high oxygen partial pressure may be the 1 : 1-type complex, Co(J-en)pyO$_2$, since this solution exhibits the absorption spectrum similar to the reflectance spectrum of Co(J-en)pyO$_2$·1/4C$_6$H$_5$CH$_3$ and ESR spectrum characteristic of the 1:1 oxygenated cobalt(II) complexes. Thus, it can be concluded that the species formed under low oxygen pressure is the 2 : 1-type "peroxo-bridged" complex. The oxygenation reaction of Co(J-en) is represented as follows:

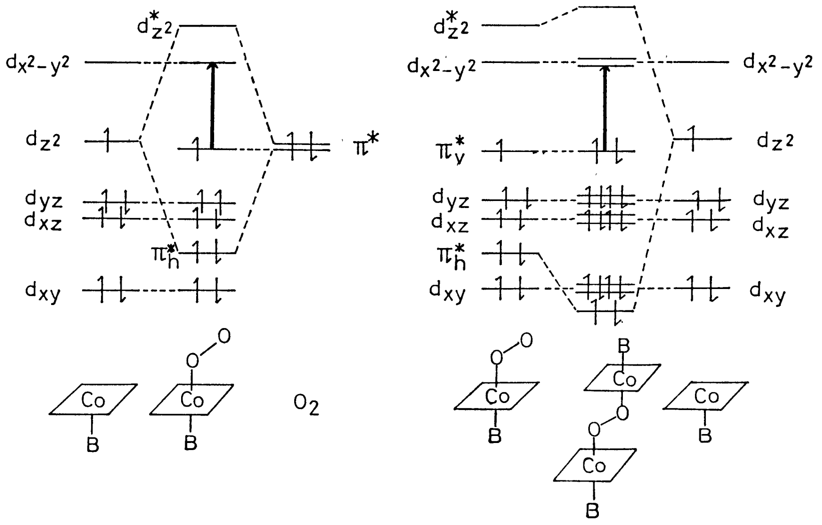

Fig. 7. Qualitative molecular orbital diagrams for Co(J-en)pyO$_2$ (left) and [Co(J-en)py]$_2$O$_2$ (right).

$$\mathrm{Co(J\text{-}en) + py \rightleftharpoons Co(J\text{-}en)py}$$

$$\mathrm{2Co(J\text{-}en)py + O_2 \rightleftharpoons [Co(J\text{-}en)py]_2O_2}$$

$$\mathrm{[Co(J\text{-}en)py]_2O_2 + O_2 \rightleftharpoons 2Co(J\text{-}en)pyO_2}.$$

It is to be noted that Co(J-en)py forms "μ-peroxo-bridged" species even in dilute solution (4×10^{-4}M). In contrast, the formation of the 2:1 oxygen adduct for *N,N'*-disalicylidenealkanediaminatocobalt(II) complexes is negligibly small in dilute solution (less than 10^{-3} M).

Only a few cobalt(II) complexes showing absorption in the visible region upon oxygenation are known.[7,8] Oxygenation reactions of the cobalt(II) complexes with the quadridentate Schiff bases, in general, occur at low temperature.[9] Thus, Co(J-en) is characterized by 1) oxygenation at room temperature, 2) resistance against oxidation to cobalt(III), and 3) a new absorption in the visible region. These characteristics are closely connected with the electron-withdrawing effect of acetyl groups.

The metal-oxygen bond is interpreted in terms of the σ-type overlapping between the d_{z^2} orbital of cobalt(II) and the antibonding orbital (π_h^*) of molecular oxygen.[10] The d_{z^2} orbital in five-coordinated cobalt(II) complexes is generally higher in energy than the antibonding π^* orbital of oxygen. This often causes the irreversible oxidation of cobalt(II) to cobalt(III) during the course of oxygenation. The fact that the oxygen adducts of synthetic iron(II) complexes are obtainable only under a selected conditions, at low temperature and in aprotic solvents, and that the oxygen adduct of *meso*-tetraphenylporphyrinmanganese(II) is barely obtained at low temperature without sixth donor[11] can also be explained in terms of the correlation of the energies of the metal d_{z^2} orbital and the molecular oxygen π^* orbital (electronegativity increases in the order Mn(II)<Fe(II)<Co(II)).

Recently, Pillsbury and Busch[12] studied electrochemical properties of a series of nickel(II) complexes of the fifteen-membered N$_4$-macrocycles and found that the oxidation potential of Ni(II)→Ni(III) becomes higher when the γ-substituent is replaced by the more electron-attracting group. This suggests that in the present complexes the electron-attracting effect of the acetyl group lowers the energy of the cobalt d-orbitals. In this case the d_{z^2} orbital of Co(J-en)py might be low-lying as compared to the molecular oxygen π_h^* orbital, thereby forming a stable cobalt-oxygen bond even at room temperature without oxidation to cobalt(III) (Fig. 7).

Miskowski *et al.*[13] and McLendon *et al.*[14] studied the characteristic band around 500 nm for the μ-superoxo complex, $[\mathrm{Co(CN)_5{-}O_2{-}Co(CN)_5}]^{5-}$, and the 1:1 oxygen adduct, $[\mathrm{Co(CN)_5O_2}]^{3-}$, and assigned this band to the charge-transfer transition from the metal d_π orbital to the π_v^* orbital of oxygen. However, the assignment is invalid for the present complexes, since the π_v^* orbital of [Co(J-en)py]$_2$O$_2$ is occupied. For the origin of the band at 525 nm of Co(J-en)pyO$_2$ and [Co(J-en)py]$_2$O$_2$ it seems reasonable to assign it to the charge-transfer transition from the π_v^* orbital to the vacant $d_{x^2-y^2}$ orbital (Fig. 7). The $\pi_v^*(\mathrm{O_2})\rightarrow d_{x^2-y^2}(\mathrm{Co})$ charge-transfer transition is expected at a wavelength less than 400 nm for most cobalt oxygen carriers.[10] It can be concluded that in the present complexes the electron-attracting effect of the acetyl group lowers the energy of metal d orbital, so that the $\pi_v^*\rightarrow d_{x^2-y^2}$ charge-transfer band appears in the visible region.

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