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TRANSITION-METAL COMPLEXES OF PYRROLE PIGMENTS. VIII. SYNTHESIS AND CHARACTERIZATION OF ACETATOBIS(3,3',5,5'-TETRAMETHYLDIPYRROMETHENATO)CHROMIUM(III)[1]

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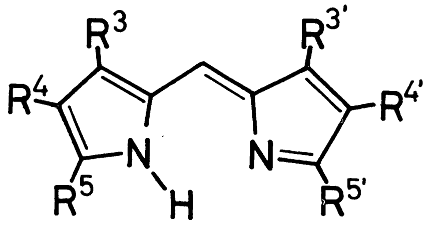
The reaction of chromium(II) acetate with 3,3',5,5'-tetramethyldipyrromethene in methanol under nitrogen atmosphere resulted in the formation of a unique mononuclear chromium(III) chelate consisting of metal, dipyrromethene, and acetate at a 1 : 2 : 1 molar ratio. Both ligand-field bands and ESR spectra are consistent with the distorted octahedral coordination geometry (C_2 symmetry) of M-*cis*-O_2N_4 type.

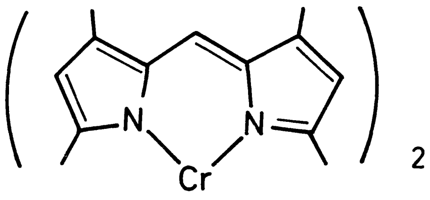
As a continuation of our structural studies on the transition-metal complexes of substituted dipyrromethenes I, we have prepared some manganese and iron complexes in their divalent and trivalent states and investigated them by means of various spectroscopic methods.[2] The degree of bulkiness extended by substituents at 5,5'-positions in dipyrromethenes was observed to determine the preferable oxidation state of these metal ions for the complex formation. Substitution at 5,5'-positions with methyl groups resulted in the formation of divalent metal complexes at a 1 : 2 molar ratio of metal to ligand, while the lack of any particular substituents at these positions in the stable formation of trivalent metal complexes at a 1 : 3 molar ratio. These facts seem to suggest that methyl groups placed at 5,5'-positions generate steric hindrance among ligand molecules in the same complex molecule to inhibit the formation of 1 : 3 metal complexes. In the present work, the chromium–3,3',5,5'-tetramethyldipyrromethene chelate system was studied to clarify the effect of methyl substituents on the metal complex formation in connection with the manganese



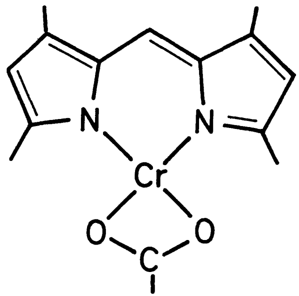
I

and iron complexes.

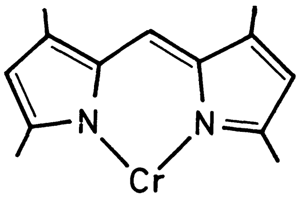
A 5.5-g sample of chromium(II) acetate dihydrate was added in a homogeneous mixture of 10 g of 3,3',5,5'-tetramethyldipyrromethene (free base) and 250 m*l* of deoxygenated methanol under nitrogen atmosphere. The resulting mixture, through which nitrogen gas was continuously bubbled, was stirred for 13 hr at room temperature. Then, the mixture was allowed to stand overnight in a freezer. The precipitates were separated, washed with water and methanol successively, and then extracted with chloroform. After removal of the solvent from the extract, the product was recrystallized from benzene as glittering green plates: yield 1.93 g (17 %); mp>300°C. Found: C, 66.37; H, 6.60; N, 10.62; mol wt (osmometric method), 506; M^+, 508. Calcd for $C_{28}H_{33}O_2N_4Cr$: C, 66.00; H, 6.53; N, 10.99; mol wt, 509.5. The mass spectral signals observed at m/e 450, 310, and 251 among others may correspond to the fragments having structures II, III, and IV, respectively. The presence of oxygen atom was also detected by the mass spectral measurement.



II

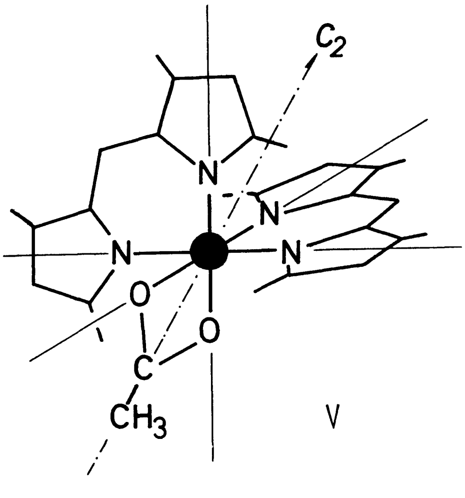


III



IV

In addition, the present chromium complex is soluble in benzene and chloroform while water and alcohols do not act as solvents for the complex. Thus, the acetate group is believed to be coordinated to the metal ion. The mass spectral data as well as the solubility property of the chromium complex are consistent with structure V where the chromium(III) ion is hexacoordinated in Cr-*cis*-O_2N_4 type. The coordination behavior of chromium with dipyrromethene ligands is certainly different from those of manganese and iron. In spite of the fact that the present ligand possesses methyl substituents at 5,5'-positions, the chromium ion is bound to the dipyrromethene ligand at a 2 : 1 molar ratio of ligand to metal upon its oxidation



V

from divalent to trivalent state. The extra positive charge is neutralized by coordination of the acetate anion.

The electronic spectrum for the present chromium chelate in chloroform at room temperature is shown in Fig. 1. The absorption bands appearing above 19,000 cm^{-1} are attributed to charge transfer transitions from metal to ligand and $\pi \longrightarrow \pi^*$ transitions within a ligand molecule. The ligand-field bands are located at 14,300 cm^{-1} (ε 357) and 13,300 cm^{-1} (ε 387). Under O_h coordination symmetry, two ligand-field bands due to spin-allowed transitions are expected to appear in the visible region; ${}^4T_{2g} \longleftarrow {}^4A_{2g}$ and ${}^4T_{1g} \longleftarrow {}^4A_{2g}$ in an increasing order of energy. The unsymmetric nature of ligand coordination and the structural property of the acetate anion tend to distort the complex molecule along the C_2-axis. The decent in coordination symmetry from O_h to C_2 (or C_{2v}) is accompanied with this distortion. Consequently, T_{2g} (O_h) is split into A and 2B levels (C_2). The above two ligand-field bands are then attributed to $A \longleftarrow A$ and $B \longleftarrow A$ transitions in an increasing order of energy; where the 2B levels of higher energy seem not to be well-resolved. The Dq value on the basis of these assignments is estimated to be 1400 cm^{-1}.

The ESR spectra measured at -40° and -120°C are shown in Fig. 2. An isotropic spectral pattern was provided at -40°C and gave g=1.987 and A_N=2.54x10^{-4} cm^{-1}. An anisotropic character was observed for the spectrum measured at -120°C, giving $g_\perp$= 1.988 and $g_\parallel$=1.949. These values are comparable with those reported for $Cr(en)_3Cl$ by McGarvey.[3)] Since a relation of $g_\perp > g_\parallel$ holds, the ligand field in the direction of C_2-axis is undoubtedly weaker than that produced in the perpendicular direction. In crystal-field theory the g-value is given by the following equation under the O_h coordination symmetry.

$$g = 2.0023 - (8\lambda/10Dq)$$

For λ_0=91 cm^{-1} and Dq=1400 cm^{-1}, the calculated g value is 1.950 which is much smaller than the observed one. An appreciable covalent nature of the coordinate bonds seems to be responsible for this apparent reduction of λ-value as well as for the high intensity of ligand-field bands in part.

Acknowledgment. The authors are indebted to the Research Institute of Yoshitomi Pharmaceutical Co., Ltd. for the mass spectral measurement, which was carried out on a JEOL JMS-01SG mass spectrometer.

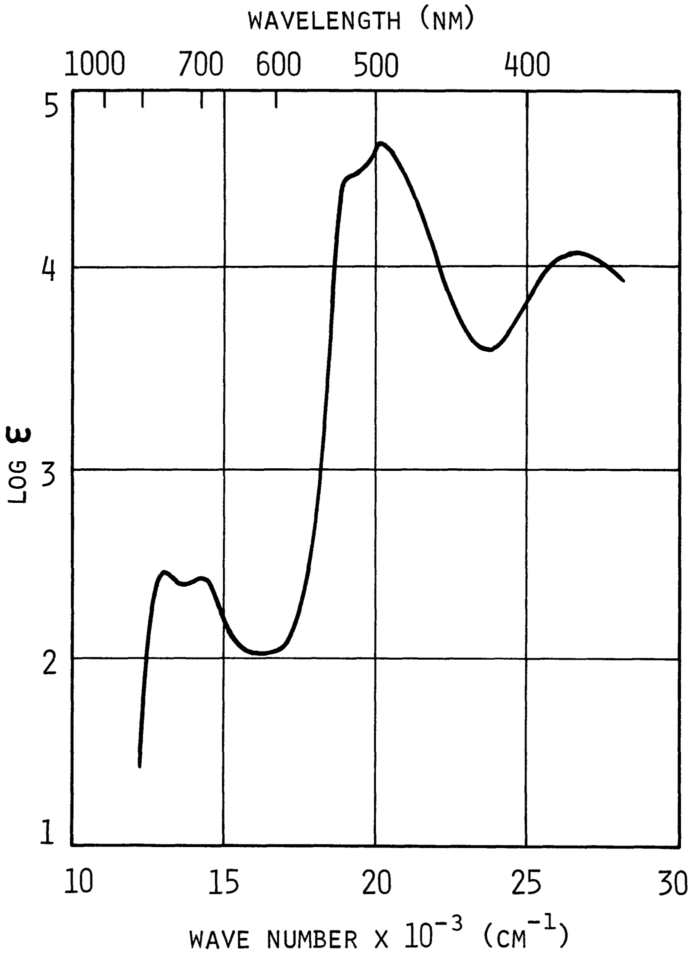


Fig. 1. Electronic absorption spectrum of acetato-bis(3,3',5,5'-tetramethyldipyrromethenato)chromium(III) in chloroform at room temperature.

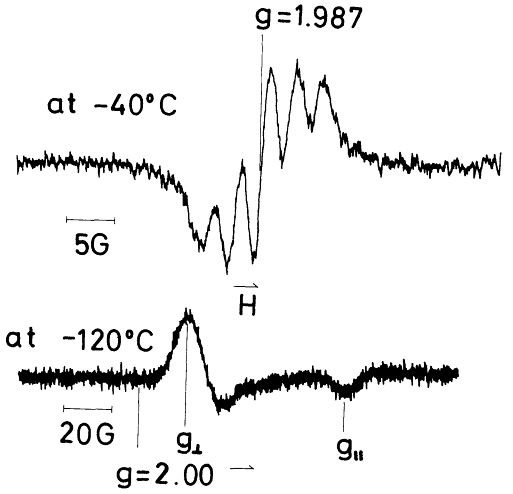


Fig. 2. ESR spectra of acetato-bis(3,3',5,5'-tetramethyldipyrromethenato)chromium(III) in xylene — benzene (6 : 4).

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