Inorganica Chimica Acta, 44 (1980) L309–L311
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Preparation and Characterization of an Oxochromium (V) Complex with a Macrocyclic N_4-Ligand: Oxo-(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)-chromium(V)

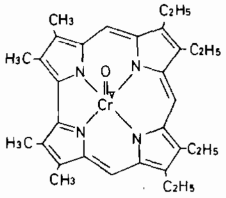
YOSHIHISA MATSUDA, SUNAO YAMADA and YUKITO MURAKAMI*

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

Received January 28, 1980

In recent years, planar complexes of transition metal ions which belong to the first half of each transition series, have attracted much attention in connection with the preparation of polymeric complexes of high electric conductivity. These metal ions have a strong tendency to form metal to metal bonds in their low oxidation states [1]. Thus, mononuclear complexes of planar coordination structure would form linear polymers by stacking them through formation of such metal–metal bonds. We have previously prepared niobium, molybdenum and rhenium complexes of corroles and porphyrins and investigated their redox behaviors in order to find out the means of providing such monomer components [2–4]. These mononuclear complexes are most stable when the metal ions are pentavalent in both solid and solution states.

For metal ions of the first transition series, the oxidation states less than +4 are stable when they are incorporated into porphyrins. On the other hand, the electronic structures of corrole complexes of the first transition metals have been poorly established. Corrole is one of the highly conjugated macrocyclic tetrapyrrole ligands, and its structure has a close resemblance to porphyrin. A significant structural difference between corrole and porphyrin is that the former has a direct linkage between A and D pyrrole rings while those rings are linked with a methylene group for the latter. The direct A–D linkage may cause deformation of the macrocyclic skeleton so that the four pyrrole rings cannot stay on the same plane as the molecular model indicates; the complete square planar alignment of four nitrogen donors is not attained for coordination of a metal ion. Corrole coordinates to metal ions as a trinegative ligand while porphyrin as a dinegative one. Since the structural feature of corrole is somewhat different from that of porphyrin, it became necessary to clarify the coordination behavior characteristic to the former ligand. The most stable oxidation state of chromium for the formation of porphyrin [5] and phthalocyanine [6] complexes has been found to be tervalent. Although an oxochromium(V) complex was reported to be formed with phthalocyanine [6], it has been poorly characterized. Very recently, Groves and Kruper indicated the existence of an oxoporphinatochromium(V) complex as a stable reaction intermediate in solution by means of IR spectroscopy and magnetic measurements [7]. We report in this communication the formation of the oxochromium(V) complex of 2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrole (abbreviated as MEC for its anionic form). This is the first example of a well characterized oxochromium complex formed with a macrocyclic N_4-ligand.



Cr(O)(MEC)

For the preparation of oxo(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)chromium(V), [Cr(O)-(MEC)], oxygen was eliminated by bubbling nitrogen gas through a mixture of H_3MEC (100 mg), anhydrous sodium acetate (25 mg), and dry N,N-dimethylformamide (15 ml). After the mixture had been refluxed for 30 min, anhydrous chromium(II) chloride (50 mg) was added to it in one portion. The mixture was then refluxed with stirring for 5 min under a nitrogen stream. Completion of the reaction was confirmed by visible spectroscopy. After being cooled down to room temperature, the reaction mixture was poured into 20 ml of cold water. A crystalline solid was recovered by filtration and washed with water. The solid was dried in air at room temperature and redissolved in dichloromethane for further purification. Chromatographic purification on a column of silica gel (Wako gel C-100, 250 X 30 mm; eluant, dichloromethane) was performed: the first main effluent of reddish brown color was collected and evaporated to dryness *in vacuo*. The solid residue was recrystallized from n-hexane–dichloromethane (3:1 v/v) to give dark prisms; yield 40 mg (36%). *Anal.* Found: C, 69,82; H, 6,65; N, 10.30%. Calcd. for $C_{31}H_{35}CrN_4O$: C, 70.03; H, 6.64; N, 10.54%.

IR spectra of Cr(O)(MEC) and the related compounds are shown in Fig. 1 for the region of 800–1100 cm^{-1}. All the compounds exhibit strong absorption bands in the confined regions of 950, 1000, and 1050 cm^{-1}. Intensities of these characteristic bands for Co(MEC)Py and H_3MEC are com-

---

*To whom correspondence should be addressed.

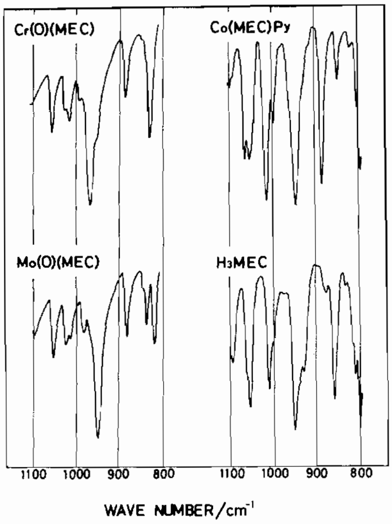


Fig. 1. IR spectra of Cr(O)(MEC) and the related compounds (Nujol mull).

parable to each other; assigned to the ligand vibrations. As reported previously [8], the M=O stretching mode gives rise to a strong absorption at 948 cm^{-1} for Mo(O)(MEC). Even though it overlaps with a band due to ligand vibration, a marked increase in intensity for the band appearing in the 950 cm^{-1} range is observed for Mo(O)(MEC) as seen in Fig. 1. The absorption band at 964 cm^{-1} observed for Cr(O)(MEC) shows a similar intensity increment and, consequently, is attributed to the Cr=O stretching mode. A shoulder observed at 950 cm^{-1} is obviously assigned to a ligand vibration.

Core electron binding energies obtained by XPS spectroscopy are summarized in Table I. The O $1s_{1/2}$ peak for all the corrole complexes falls in a narrow energy range (529.5–530.5 eV), while Cr(TPP)(OMe) exhibits the peak distinctively in a higher energy range. Cr(O)(MEC) provides higher binding energies for inner core electrons of the metal relative to those of Cr(TPP)(OMe), indicating that chromium exists in a higher valency state in the former than in the latter. The binding energy difference between Cr(O)(MEC) and Cr(TPP)(OMe) for the corresponding peaks increases in the following sequence: Cr $2p_{1/2}$ < Cr $2p_{3/2}$ < Cr $3s_{1/2}$. This implies that energy levels for the outer core electrons is affected by the valence state more than those for the inner ones.

A magnetic susceptibility of 1.71 μ_B was obtained on a Faraday balance for the crystalline solid of Cr(O)(MEC) at room temperature, while that for Cr(TPP)(OMe) was 3.93 μ_B. The magnetic susceptibility values indicate that the former has the nuclear chromium in a formal oxidation state of +5, while the latter is referred to involve the tervalent chromium state. Groves *et al.* reported an experimental magnetic susceptibility of 2.05 μ_B for Cr(O)(TPP) in solution [7]. This value is slightly larger than that expected for the pentavalent chromium species. The apparent discrepancy for the TPP complex may be due to the incomplete formation of Cr(O)(TPP) in solution.

The ESR spectrum of Cr(O)(MEC) measured in dichloromethane at room temperature consists of nine intense lines at the center and many weaker lines in a wider range as shown in Fig. 2. The central intense lines are assigned to the superhyperfine structure due to the interaction with four nitrogen nuclei around diamagnetic chromium nucleus (^{50}Cr, ^{52}Cr, or ^{54}Cr), while the weaker lines to the superhyperfine structure caused by the interactions with

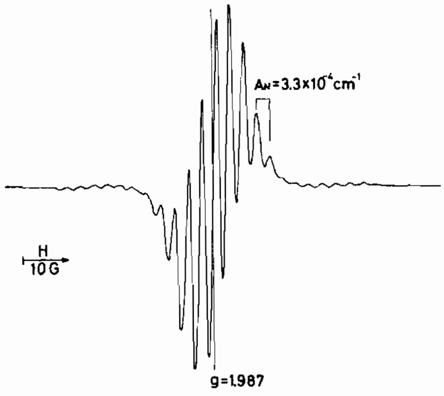


Fig. 2. ESR spectrum of Cr(O)(MEC) in dichloromethane at room temperature.

TABLE I. Core Electron Binding Energies (eV)^a.

Complex	Metal						O	C	N	Reference
	$2p_{3/2}$	$2p_{1/2}$	$3s_{1/2}$	$3d_{5/2}$	$3d_{3/2}$	$4d_{5/2}$	$1s_{1/2}$	$1s_{1/2}$	$1s_{1/2}$	
Cr(O)(MEC)^b	577.6	586.9	77.2				529.9	283.5	397.6	This work
Mo(O)(MEC)^c				230.1	233.1		529.5	283.2	396.1	3
Re(O)(OEC)^{c,d}						261.8	530.5	283.2	397.5	2
Cr(TPP)(OMe)^{b,e}	576.5	586.4	75.6				531.6	284.4	398.2	This work

^{a}Signals due to Au $4f_{5/2}$ and $4f_{7/2}$ were used for calibration.
^{b}Measured on a Vacuum Generator ESCA-3 spectrometer.
^{c}Measured on a Shimadzu–DuPont 650B spectrometer.
^{d}OEC; 2,3,7,8,12,13,17,18-octaethylcorrolate anion.
^{e}TPP; 5,10,15,20-tetraphenylporphinate anion.

TABLE II. Spin Hamiltonian Parameters for the Corrole Complexes[a,b].

Complex	g	$A_M \times 10^4$/ cm^{-1}	$A_N \times 10^4$/ cm^{-1}	Reference
Cr(O)(MEC)	1.987	19.3	3.3	This work
Mo(O)(MEC)	1.967	41.8	2.3	3

[a] Measured in dichloromethane at room temperature.
[b] Recorded on a JEOL JES-ME-3 X-band spectrometer with 100 kH field modulation; magnetic field was calibrated with a MgO:Mn^{2+} standard sample.

four nitrogen nuclei and paramagnetic chromium (^{53}Cr) nucleus. The spin Hamiltonian parameters for Cr(O)(MEC) are listed along with those for Mo(O)(MEC) in Table II. The strong π-bonded interaction between chromium and axial oxygen atom destabilizes the d_{xz} and d_{yz} orbitals of the metal, so that the unpaired electron must occupy the d_{xy} orbital with high population. This explanation is consistent with the fact that the very intense ESR signal was observed for the complex even at room temperature. A_N for the chromium complex is slightly larger than that for the molybdenum. This indicates that the d_{xy} orbital of chromium overlaps with the ligand σ-orbitals to a greater extent compared to that of molybdenum, suggesting the symmetry of the local coordination site is lowered toward C_s. Cr(O)(MEC) has no tendency to bind a ligand at the 6th coordination site *trans* to the oxo group in a manner as observed for the corresponding oxomolybdenum(V) complex [3].

In conclusion, the chromium ion forms a corrole complex which has the N$_4$O-penta-coordination structure of oxo-type in the pentavalent state of the nuclear metal and the local symmetry is a distorted square pyramid. The present result provides the first example, to the best of our knowledge, of the oxo-chromium complex formed with a macrocyclic N$_4$-ligand as isolated in a pure solid state. The extent of distortion of such highly conjugated macrocycles from planarity needs to be correlated with the charge distributions in the whole molecules and with the energy levels of d-orbitals of nuclear metals. Investigations are in progress in our laboratory along this line.

References

1 For example: F. A. Cotton, *Chem. Soc. Rev., 4,* 27 (1975).
2 Y. Murakami, Y. Matsuda, S. Yamada, T. Goto and M. Kuramoto, *Reports of the Asahi Glass Foundation for Industrial Technology, 34,* 295 (1979).
3 Y. Murakami, Y. Matsuda and S. Yamada, *Chemistry Letters,* 689 (1977).
4 Y. Murakami, F. Kubota and Y. Murakami, *Chemistry Letters,* 1281 (1977).
5 J. W. Buchler, 'The Porphyrins', Vol. I, Part A, D. Dolphin, Ed., Academic Press, New York (1978) Chapter 10.
6 J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.,* 1257 (1961).
7 J. T. Groves and W. J. Kruper, Jr., *J. Am. Chem. Soc., 101,* 7613 (1979).
8 M. Ohta, W. Scheuermann, K. Nakamoto, Y. Matsuda, S. Yamada and Y. Murakami, *Inorg. Chem., 18,* 457 (1979).