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COORDINATION COMPLEXES OF DI-π-CYCLOPENTADIENYLMOLYBDENUM(VI) AND -TUNGSTEN(VI) OXIDE COMPOUNDS WITH SOME BIDENTATE LIGANDS

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SUMMARY

Treatment of di-π-cyclopentadienylmolybdenum(VI) oxide dichloride or di-π-cyclopentadienyltungsten(VI) oxide dichloride with various bidentate ligands has given some chelated complexes of the type, $[(\pi\text{-}C_5H_5)_2MOL]^+ClO_4^-$ where M=Mo or W, and L represents a β-diketonic ligand, such as acetylacetonate or benzoylacetonate or dibenzoylmethane or a β-ketonic ester ligand, such as ethyl acetoacetate or benzoylacetoacetate. The IR spectra suggest that the ligand L may form a chelate in all cases, the metals having a coordination number of five.

INTRODUCTION

We have previously described the preparation of di-π-cyclopentadienylmolybdenum(VI) oxide dichloride (I)[1] and its tungsten analogue, (II)[2]. Green and coworkers[3-6] have reported the formation of di-π-cyclopentadienylmolybdenum(IV) and -tungsten(IV) compounds containing sulphur, nitrogen, oxygen and pseudohalide ligands. Coordination complexes of di-π-cyclopentadienyl compounds of titanium and vanadium have been reported by Doyle and Tobias[7,8] and π-cyclopentadienylchromium bromide acetylacetonate[9] and π-cyclopentadienylzirconium diacetoacetate[10] are also known.

We have previously described the reactions of di-π-cyclopentadienyltungsten oxide dichloride with primary and secondary alcohols[11,12] and with alkyl and aryl halides[13]. The present investigation deals with the preparation of coordination complexes prepared by treatment of (I) and (II) with a bidentate ligand (L) such as acetylacetonate benzoylacetonate, dibenzoylmethane, ethyl acetoacetate or benzoylacetoacetonate, in presence of sodium perchlorate. The products are of the type, $[(\pi\text{-}C_5H_5)_2MOL]^+ClO_4^-$, where M=Mo or W. Molecular weights determined by Semi-Micro Ebulliometer, indicate that the complexes are monomeric.

EXPERIMENTAL

All experiments were carried out under anhydrous conditions and reduced pressure. Solvents were purified and dried by conventional methods. Dried tetrahydrofuran was refluxed with $LiAlH_4$ and then distilled in nitrogen. All bidentate ligands were dried and distilled before use.

Molybdenum oxide tetrachloride and tungsten oxide tetrachloride were prepared by the methods described by Colton and coworkers[29]. Fresh sodium cyclopentadienide was prepared by a standard method[30]. Di-π-cyclopentadienylmolybdenum oxide dichloride (I) and di-π-cyclopentadienyltungsten oxide dichloride were prepared as previously described[1,2,13].

The IR spectra were recorded in KBr discs on Perkin–Elmer Infracord spectrophotometer, Model-237 and by Carl Zeiss UR-10. No evidence for bromide substitution resulting from the use of KBr was detailed in these spectra, by comparing them with the spectra recorded on solutions in $CHCl_3$, on films, in Nujol mull or in polyethylene sheets. Molecular weights were determined in benzene with a Gallenkamp Semi-Micro Ebulliometer.

Molybdenum and tungsten were determined gravimetrically as 8-hydroxyquinolate after decomposing the compounds in hot concentrated nitric acid or perchloric acid. Chloride was determined gravimetrically as silver chloride, while carbon and hydrogen were determined by micro analytical methods. Perchlorate derivatives are highly explosive and have to be handled carefully when being dried under reduced pressure.

Preparation of β-diketonic ester derivatives

Preparation of di-π-cyclopentadienylmolybdenum oxide acetylacetonate perchlorate complex. A mixture of 30 ml dry acetyl acetone, 3.12 g (0.01 mole) of $(\pi\text{-}C_5H_5)_2MoOCl_2$ and 1.5 g (0.01 mole) of sodium perchlorate, was stirred for 6–7 h and then gently refluxed at 140–145° for another 2–3 h. The excess of acetylacetone was removed under reduced pressure (5 mm) and the residual dark red oil was washed with light petroleum (b.p. 60–80°). The crystalline residue was dried under reduced pressure (2–3 mm) to yield a greenish crystalline compound of the composition $[(\pi\text{-}C_5H_5)_2MoO(C_5H_7O_2)]ClO_4$. This product, which is sensitive to moisture and light, was preserved in sealed tubes wrapped in black papers. The $[(\pi\text{-}C_5H_5)_2WO(C_5H_7O_2)]ClO_4$ complex was prepared analogously.

The preparations of benzoylacetonate and dibenzoylmethane derivatives of both molybdenum and tungsten metals containing perchlorate ligand were similarly carried out.

Preparation of β-ketonic ester derivatives

Preparation of di-π-cyclopentadienyl molybdenum oxide (ethyl acetoacetate)-perchlorate complex. A mixture of 3.1 g (0.01 mole) of $(\pi\text{-}C_5H_5)_2MoOCl_2$ and 1.5 g (0.01 mole) of sodium perchlorate in 30 ml acetone was stirred for 20–21 h at room temperature (27°) and then refluxed at 45–50° for 1–2 h. Acetone was removed under reduced pressure (5 mm) and 20 ml dry ethyl acetoacetate was introduced. The mixture was then stirred and refluxed at 120–130° for 4–5 h. The excess of the reagent was evaporated off under reduced pressure (5 mm) and the dark brown residue was washed with n-hexane, to leave a greenish residue. This was crystallized from diethyl ether and dried under reduced pressure (10 mm) to give dark crystals of the composition $[(\pi\text{-}C_5H_5)_2MoO(C_7H_{11}O_3)]ClO_4$. The product is quite stable.

The corresponding tungsten complex, $[\pi\text{-}(C_5H_5)_2WO(C_7H_{11}O_3]ClO_4$, was prepared analogously.

The preparations of the benzoylacetoacetate complexes of molybdenum and tungsten containing the perchlorate ligand were similarly prepared.

The properties of the complexes are given in Tables 1–3.

RESULTS AND DISCUSSION

The new complexes are green in colour, fairly soluble in halogenated solvents, alcohols, ethers and hydrocarbons and are decomposed by moisture and light on long exposure. They are readily hydrolysed in presence of hot water, dilute acids and alkalies. Unlike the other transition metal tetrabidentate complexes[14], they are non-volatile and decompose before melting.

TABLE 1

CHARACTERISTICS OF $[(\pi\text{-}C_5H_5)_2MOL)]ClO_4$ COMPLEXES

Compounds		Colour	Amt. of reagent added (ml)	Reaction time (h)	Yield (%)	M.p. (°C) with decomp.	Stability (in air)
M	L[a]						
W	Aa	Green	30	8–9	70	210–212	1–2 h
W	Ba	Green	25	8.5	85	190–193	6–7 h
W	Eaa	Brownish	30	6–7	80	225–226	1–2 h
W	Baa	Yellow green	25	9	70	239.5–240	3–4 h
W	Dbm	Yellow	30	7	75	215–216	4–5 h
Mo	Aa	Shining green	50	10	75	210	4–5 h
Mo	Ba	Yellow green	35	5.5	80	198–200	1–2 days
Mo	Eaa	Orange green	30	7	70	165–170	Stable
Mo	Baa	Reddish green	25	8	60	175–177	5–6 days
Mo	Dbm	Red brown	20	4	75	150–157	Stable

[a] Aa = acetylacetonate; Ba = benzoylacetonate; Eaa = ethyl acetoacetate; Baa = benzoylacetoacetate; Dbm = dibenzoylmethane.

The IR spectra of the molybdenum and tungsten compounds are very similar. The absorptions due to the $(\pi\text{-}C_5H_5)_2M$ moiety (M = Mo or W), were assigned on the basis of published work[15–19]. The absorption spectra of various bidentate ligands show the presence of carbonyl stretchings in the region of 1550–1730 cm^{-1}; according to Nakamoto[20–23] and other workers[24–26], for an oxygen bonded acetylacetone or ethyl acetoacetate group, two frequencies are expected in this range, and include the CO and C=C stretching modes which are normally found at ~1600 and ~1520 cm^{-1} respectively. In addition, the usual CH_3, C_2H_5 or C_6H_5 group frequencies are present in the spectra, while the bands at ~1095 cm^{-1} and at ~960 cm^{-1} may be due respectively to the ClO_4^- ion[7,8] and to the metal–oxygen bond[27–28] (*cf.* the spectra of $MoOCl_4$ or $WOCl_4$).

TABLE 2

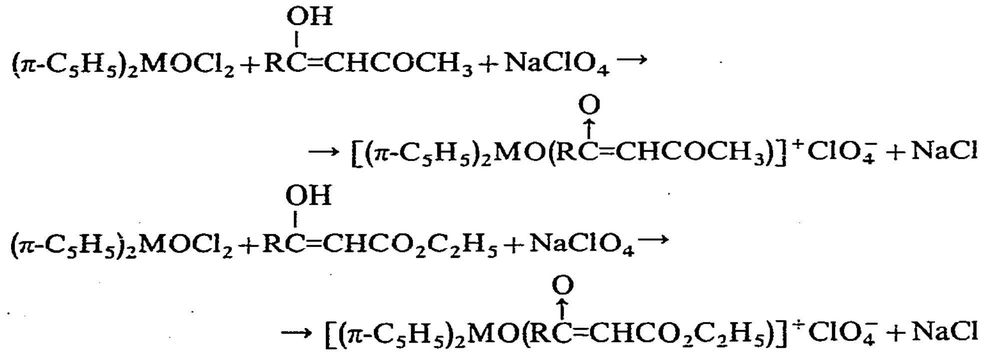
ANALYTICAL DATA OF $[(\pi\text{-}C_5H_5)_2MOL]ClO_4$ COMPLEXES

Compound		Mol. wt. found (calcd.)	Analysis found (calcd.) (%)			
M	L[a]		C	H	Cl	Metal
W	Aa	535 (528.5)	34.1 (34.27)	3.3 (3.26)	6.6 (6.70)	34.8 (34.97)
W	Ba	598 (590.6)	40.7 (40.66)	3.1 (3.06)	6.1 (6.00)	31.2 (31.23)
W	Eaa	566 (556.6)	36.5 (36.68)	3.5 (3.79)	6.4 (6.37)	33.1 (33.02)
W	Baa	610 (604.6)	41.5 (41.71)	3.4 (3.49)	5.9 (5.86)	30.4 (30.45)
W	DMB	648 (636.7)	47.2 (47.15)	3.5 (3.32)	5.6 (5.56)	28.9 (28.89)
Mo	Aa	435 (440.7)	40.7 (40.87)	3.7 (3.89)	8.1 (8.04)	21.6 (21.77)
Mo	Ba	495 (502.7)	47.6 (47.79)	3.7 (3.81	7.1 (7.05)	19.1 (19.08)
Mo	Eaa	478 (484.7)	42.0 (42.11)	4.4 (4.36)	7.2 (7.31)	19.8 (19.79)
Mo	Baa	510 (516.7)	48.6 (48.80)	4.1 (4.09)	6.8 (6.85)	18.4 (18.56)
Mo	DMB	558 (564.8)	53.2 (53.15)	3.6 (3.74)	6.3 (6.27)	18.7 (18.75)

[a] See footnote *a* Table 1.

The molybdenum complexes are more stable than the corresponding tungsten analogs. Molecular weight determinations in boiling benzene or chloroform indicate that all the complexes are monomeric.

It is clear that the reactions of $(\pi\text{-}C_5H_5)_2MoOCl_2$ and $(\pi\text{-}C_5H_5)_2WOCl_2$ with bidentate ligands in presence of sodium perchlorate, can be represented as follows:



$$(\pi\text{-}C_5H_5)_2MOCl_2 + R\overset{\overset{OH}{|}}{C}{=}CHCOCH_3 + NaClO_4 \rightarrow$$
$$\rightarrow [(\pi\text{-}C_5H_5)_2MO(R\overset{\overset{O}{\uparrow}}{C}{=}CHCOCH_3)]^+ClO_4^- + NaCl$$
$$(\pi\text{-}C_5H_5)_2MOCl_2 + R\overset{\overset{OH}{|}}{C}{=}CHCO_2C_2H_5 + NaClO_4 \rightarrow$$
$$\rightarrow [(\pi\text{-}C_5H_5)_2MO(R\overset{\overset{O}{\uparrow}}{C}{=}CHCO_2C_2H_5)]^+ClO_4^- + NaCl$$

where M=Mo or W and R=CH_3 or C_6H_5 groups.

The uninegative perchloro complexes were isolated under strictly anhydrous conditions, in contrast to the conditions used for the preparation of complexes of Ti^{IV}, W^{IV} and Mo^{IV} (refs., 4, 7 and 8). Attempts to prepare the new compounds in aqueous media gave only hydrated metal oxides.

TABLE 3

IR SPECTRA[a] OF $[(\pi\text{-}C_5H_5)_2MOL]ClO_4$ COMPLEXES

Compound		H_5 frequencies	Bidentate ligand absorptions[c]	ClO_4 band[c]	M=O linkage[c]
M	L[b]				
W	Aa	3030 s, 1430 s, 1105 w, 1020 m, 810 w	1720 m, 1590 s, 1540 s, 1588 s, 1370 m, 1280 s, 915 m, 740m	1095 m	970 s
W	Ba	3105 s, 1435 w, 1120 w, 1015 m, 835 m	1755 w, 1580 m, 1515 m, 1375 w, 1250 w, 910 w, 780 m	1100 s	965 m
W	Eaa	3020 s, 1440 m, 1010 w, 1035 w, 825 w	1725 m, 1540 s, 1520 m, 1390 m, 1280 m, 1150 w, 900 m	1090 w	975 m
W	Baa	3070 s, 1430 s, 1110 w, 1020 m, 810 w	1750 m, 1720 s, 1620 s, 1530 s, 1515 s, 1380 m, 1170 m, 910 m, 800 m	1097 m	955 s
W	Dbm	3090 m, 1445 s, 1105 w, 1010 w, 830 s	1690 m, 1650 s, 1590 m, 1385 m, 1360 m, 1250 s, 940	1095 s	960 m
Mo	Aa	3015 s, 1415 m, 1040 w, 830 m	1710 m, 1575 s, 1260 m, 935 m, 845 m, 720 s	1100 s	945 m
Mo	Ba	3070 s, 1435 s, 1115 m, 1035 w, 815	1750 m, 1580 m, 1370 m, 1250 s, 910 m, 870 s, 710 m	1090 m	955 m
Mo	Eaa	3010 s, 2970 m, 1440 w, 1020 w, 825 m	1755 m, 1730 m, 1570 w, 1545 w, 1510 w, 1340 m, 1240 m, 930 m, 715 m	1098 m	970 m
Mo	Baa	3040 w, 1450 m, 1105 s, 1025 m, 830 w	1760 s, 1680 s, 1630 w, 1540 s, 1510 m, 1370 m, 1270 s, 1200 s, 920 m	1105 m	965 s
Mo	Dbm	3100 m, 1440 m, 1100 s, 1010 m, 835 w	1710 m, 1650 w, 1540 w, 1390, 1270, 1210, 910 m, 710 m	1100 s	960 s

[a] Recorded on Perkin–Elmer Infracord Model 137 and Carl Zeiss Infracord No. 10. [b] See footnote *a* Table 1. [c] Tentative assignements.

The formation of $(\pi\text{-}C_5H_5)_2MOCl_2$ (M=Mo or W) on treatment the new complexes with dry hydrogen chloride confirms that they contain the $(\pi\text{-}C_5H_5)_2M{=}O$ unit, as inferred from their IR spectra,

$$[(\pi\text{-}C_5H_5)_2MOL)]^+ClO_4 + 2\ HCl \rightarrow (\pi\text{-}C_5H_5)_2MOCl_2 + HL + HClO_4$$

The IR spectra and the chemical properties of the $[(\pi\text{-}C_5H_5)_2MOL)]^+ClO_4$ compounds suggest that the ClO_4^- ion is not involved in bridging of molybdenum or tungsten metal atoms, and that the bidentate ligands are chelated to the metal atoms. The metal atoms apparently possess a coordination number five, while the cyclopentadienyl rings retain their delocalized π-bonded character. These results are analogous to those observed for some related complexes[3–8].

REFERENCES

1 S. P. ANAND, R. K. MULTANI AND B. D. JAIN, *J. Organometal. Chem.*, 24 (1970) 427.
2 S. P. ANAND, R. K. MULTANI AND B. D. JAIN, *Curr. Sci.*, 37 (1968) 487.
3 M. G. HARRISS, M. L. H. GREEN AND W. E. LINDSELL, *J. Chem. Soc. A*, 10 (1969) 1453.
4 M. L. H. GREEN, M. HARRISS, W. E. LINDSELL AND H. SHAW, *J. Chem. Soc. A*, 13 (1969) 1981.
5 M. L. H. GREEN AND W. E. LINDSELL, *J. Chem. Soc. A*, 9 (1967) 1455; 14 (1969) 2150, 2215.
6 M. L. H. GREEN AND J. R. SANDERS, *Chem. Commun.*, 18 (1967) 956.

7 G. Doyle and R. S. Tobias, *Inorg. Chem.*, 6 (1967) 1111.
8 G. Doyle and R. S. Tobias, *Inorg. Chem.*, 7 (1968) 2479, 2484.
9 J. C. Thomas, *U. S. Pat.*, (1962) 3,030,399.
10 E. M. Brainina and M. Kh. Minacheva, *Izv. Akad. Nauk SSSR, Ser. Khim*, 8 (1968) 1421.
11 S. P. Anand, R. K. Multani and B. D. Jain, *J. Organometal. Chem.*, 17 (1969) 423.
12 S. P. Anand, R. K. Multani and B. D. Jain, *Bull. Chem. Soc. Jap.*, 42 (1969) 3459.
13 S. P. Anand, R. K. Multani and B. D. Jain, *J. Organometal. Chem.*, 19 (1969) 387.
14 S. C. Chattoraj, C. T. Lyach and K. S. Mazdiyasni, *Inorg. Chem.*, 7 (1969) 2501.
15 E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 10 (1958) 307.
16 F. A. Cotton in J. Lewis and R. G. Wilkins (Eds.), *Modern coordination Chemistry*, Interscience, New York, 1960.
17 H. P. Fritz, *Advan. Organometal. Chem.*, 1 (1964) 239.
18 I. J. Hyams, R. T. Bailey and E. R. Lippincotts, *Spectrochim. Acta, Part A*, 23 (1967) 273.
19 D. J. Parkar and M. H. B. Stiddard, *J. Chem. Soc. A*, 3 (1970) 480.
20 K. Nakamoto, *Infrared spectra of Inorganic Coordination Compounds*, Wiley, New York, N.Y. 1963.
21 H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, 45 (1966) 3113.
22 K. Nakamoto and A. R. Market, *J. Chem. Phys.*, 32 (1960) 588.
23 G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6 (1967) 433, 441; 7 (1968) 330.
24 M. F. Richardson, W. F. Wanger and D. E. Sands, *Inorg. Chem.*, 7 (1968) 2495.
25 D. Gibson, B. F. Gibson and J. Lewis, *J. Chem. Soc. A*, 3 (1970) 367; (1966) 1453; (1968) 1993; *Chem. Ind. (London)*, (1966) 342.
26 H. F. Holtzclaw and J. P. Kollman, *J. Amer. Chem. Soc.*, 79 (1957) 3318.
27 M. Cousins and M. L. H. Green, *J. Chem. Soc.*, (1963) 889; (1964) 1567.
28 Yu. Ya. Kharitonov, Yu. A. Buslaev and A. A. Kuzaetsove, *Zh. Neorg. Khim.*, 11 (1966) 821; *Chem. Abstr.*, 65 (1966) 1595.
29 R. Colton, I. B. Tomkins and P. W. Wilson, *Aust. J. Chem.*, 17 (1964) 496.
30 G. Wilkinson, *Org. Syn.*, 36 (1956) 32.