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Metalcarbonylates of lanthanides. Unexpected formation of the trinuclear cluster $[Na(DME)_3]_2[W_3(CO)_{14}]$

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Abstract

The cluster $[Na(DME)_3]_2[W_3(CO)_{14}]$ (I) has been isolated after the treatment of $CpLuCl_2$ with an equimolar mixture of $Na_2W(CO)_5$ and $Na_2W_2(CO)_{10}$ in dimethoxyethane (DME). The structure of I has been established by X-ray crystal analysis (*Cmmm*, $a = 18.749(4)$, $b = 15.074(3)$, $c = 9.505(3)$ Å, $Z = 2$, 653 reflections, $R = 0.125$). The cluster skeleton turned out to be a chain of three tungsten atoms with octahedral coordination. The W–W distance is 2.79 Å.

1. Introduction

The synthesis of the carbonyl clusters $Na_2[M_3(CO)_{14}]$ (M = Cr, Mo) was investigated by Behrens and Haag [1]. These compounds were believed to be formed in the reaction of $M(CO)_6$ with $NaBH_4$ in THF. However, careful investigation of this reaction revealed the formation of the carbonylates $Na[M_2H(CO)_{10}]$ (M = Cr, Mo, W) [2].

The present investigation is prompted by our continuing interest in the metalcarbonylates of lanthanides. We investigated the reaction of the monocyclopentadienyl derivative of lutetium $CpLuCl_2(THF)_3$ with carbonylate $Na_2W(CO)_5$ in DME. This reaction is accompanied by the formation of the trinuclear tungsten cluster $[Na(DME)_3]_2[W_3(CO)_{14}]$, which has been isolated and unambiguously characterized.

2. Results and discussion

Dianion salts $Na_2[M(CO)_n]$ are of considerable current interest as reagents for the preparation of compounds with direct lanthanide–transition metal bonds [3]. We have investigated the reaction of $CpLuCl_2$ with $Na_2W(CO)_5$. The metalcarbonylate was prepared firstly by an established technique, *i.e.* the reduction of $W(CO)_6$ with Na-amalgam in DME (eqn. (1)) [4], and secondly by the reduction of $W(CO)_5NMe_3$ with Na-naphthalene in DME (eqn. (2)) [5].

$$W(CO)_6 + 2\ Na/Hg \xrightarrow[-CO]{DME} Na_2W(CO)_5 \qquad (1)$$

$$W(CO)_5NMe_3 + 2\ Na^+Naf^- \xrightarrow[-2Naf;\ -NMe_3]{DME} Na_2W(CO)_5 \qquad (2)$$

The reaction of $CpLuCl_2$ with $Na_2W(CO)_5$ in cold DME yields the heterobimetallic complex **II** as a main product (NMR). This compound was characterized by ^1H, ^{13}C NMR, IR spectroscopy [6]. It seems that the formation of **II** involves the formation of highly reac-

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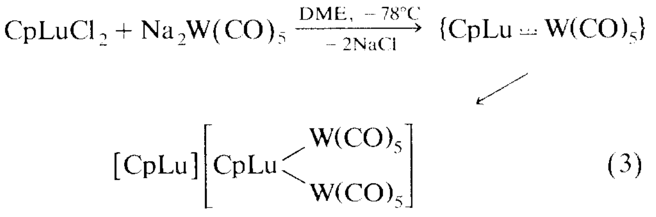
tive particles $CpLu=W(CO)_5$, which is followed by their dimerization.



$$CpLuCl_2 + Na_2W(CO)_5 \xrightarrow[-2NaCl]{DME,\ -78°C} \{CpLu=W(CO)_5\} \longrightarrow [CpLu]\left[CpLu\begin{matrix} W(CO)_5 \\ W(CO)_5 \end{matrix}\right] \qquad (3)$$

(II)

The formation of a new metalcarbonyl compound, in addition to **II**, was observed when $Na_2W(CO)_5$ was prepared by the first method. However, formation of this compound was not observed when $Na_2W(CO)_5$ was prepared by the more modern, second method.

It is believed [4] that the formation of $Na_2W(CO)_5$ by the reduction of $W(CO)_6$ with Na/Hg is complicated by the formation of ditungsten salt $Na_2W_2(CO)_{10}$ (about 15–20% of all tungsten nuclei). We have shown that the latter salt when in the pure state does not react with $CpLuCl_2$, but it does react readily in the presence of $Na_2W(CO)_5$. This new compound has been found to be the trinuclear cluster of tungsten $[Na(DME)_3]_2[W_3(CO)_{14}]$ (**I**). Maximum yield of **I** was observed when the ratio of $Na_2W(CO)_5$ and $Na_2W_2(CO)_{10}$ was equimolar. Unfortunately, lutetium compounds formed in this reaction could not been identified.

$$Na_2W(CO)_5 + Na_2W_2(CO)_{10} \xrightarrow[DME,\ -78°C]{CpLuCl_2} Na_2W_3(CO)_{14} \qquad (4)$$

The structure of **I** has been established by X-ray crystal analysis. It consists of anions $[W_3(CO)_{14}]^{2-}$ (fig. 1) with *mm* position symmetry and cations $[Na(DME)_3]^+$ with *mm* position symmetry. Owing to poor regulation of crystals, the vicinity of the cation has not been refined. The tungsten atoms possess octahedral coordination. The central tungsten atom of the W–W–W chain occupies the inversion centre of the anion. The W–W distance is 2.79 Å. CO-ligands have eclipsed conformation. Because of the high temperature factor and the poorly regulated crystal, a rigorous analysis of anion geometry is impossible. However it should be mentioned that there is an effective decrease of W–C bond length (1.75 Å) for the *trans*-CO ligand. In accord with the traditional notion of *trans*-effect in coordination chemistry the W–W distance should increase. However, the W–W bond turned out to be very short indeed. The average distance of the other four independent W–CO bonds is 2.16 Å (2.06 Å for $W(CO)_6$ [7]). The shortest Na ··· O(CO) distance is 5.367 Å.

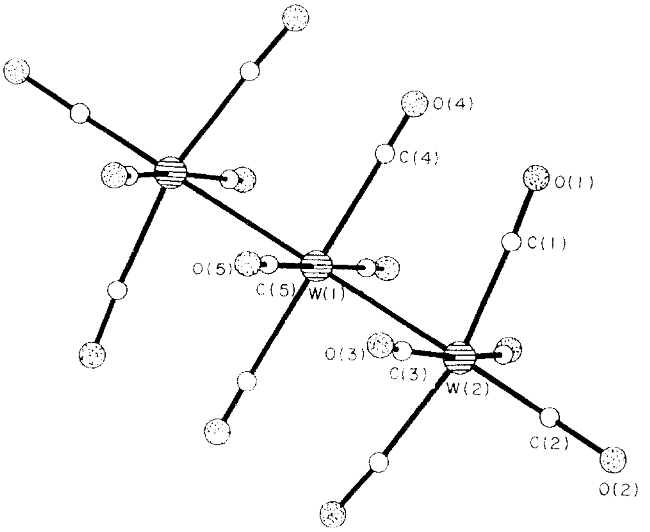


Fig. 1. The structure of the anion $[W_3(CO)_{14}]^{2-}$.

The characteristic ^{13}C NMR spectrum of **I** in DME:THF-d_8 = 4:1 consists of three groups of signals: 199.80 ppm with $J(^{13}C-^{183}W) = 121.1$ Hz of *cis*-CO ligands of terminal tungsten atoms; 201.55 ppm with $J(^{13}C-^{183}W) = 122.2$ Hz of CO-ligands of central tungsten atom; 201.73 ppm of *trans*-CO ligands. IR spectrum of **I** has four absorption bands in the CO vibration area at 2048m, 2005w, 1946vs and 1887s cm^{-1} (DME). The characteristic narrow band at 2048 cm^{-1} is near to the respective band of the spectrum of $Na[W_2H(CO)_{10}]$ at 2043 cm^{-1} (THF) [8]. The presence of such a band in the spectrum is believed always to reveal the presence of $Na[W_2H(CO)_{10}]$ in solution, but our result demonstrates that such conclusions should be drawn only with great care.

The mechanism of formation of cluster **I** is not yet clear. It seems that the reaction of $CpLuCl_2$ and $Na_2W(CO)_5$ takes place first. The second stage of this transformation is the interaction of the intermediate $CpLu=W(CO)_5$ with either the same molecule to form the dimer **II** or $Na_2W_2(CO)_{10}$ salt to form trinuclear cluster **I** and unidentified compounds of lutetium. The investigation of this mechanism is in progress now.

3. Experimental section

All manipulations were done either on the high-vacuum line in all-glass apparatus equipped with PTFE stopcocks or in an atmosphere of thoroughly purified argon using standard Schlenk techniques, or in the drybox (Vacuum Atmospheres). Tetrahydrofuran and dimethoxyethane were purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents were distilled and stored over

CaH_2. $CpLuCl_2(THF)_3$ [8], $W(CO)_5NMe_3$ [9], $Na_2W(CO)_5$ [4,5], $Na_2W_2(CO)_{10}$ [10] were prepared by published methods. ^{13}C NMR spectra were recorded with a Bruker AM 360 instrument. IR spectra were taken with a Perkin-Elmer 457 spectrometer using a vacuum-tight cell. Electron probe X-ray analyses were done with a scanning electron microscope SEM-505 (Phillips) equipped with a unit for X-ray energy dispersive analysis (Edax).

3.1. $[Na(DME)_3]_2[W_3(CO)_{14}]$ (I)

$Na_2W(CO)_5$ was prepared using 0.29 g (0.76 mmol) $W(CO)_5NMe_3$ in 20 ml DME and 8.5 ml 0.18 M solution of NaNaf in DME. After the purification of this salt (from naphthalene) 0.51 g (0.74 mmol) $Na_2W_2(CO)_{10}$ and 0.39 g (0.74 mmol) $CpLuCl_2(THF)_3$ in 20 ml DME were added to the solution of $Na_2W(CO)_5$ in DME cooled to −78°C. The reaction mixture was stirred for 2 h and after slow warming to room temperature was stirred for 5 h. The solution was decanted from the NaCl precipitate and evaporated to about 5 ml. The crystals precipitated after 3 days at −30°C were separated, washed with a small amount of diethyl ether, and dried *in vacuo*. Yield 0.86 g (76%) of bright-orange needles **I** with m.p. 142–144°C (decomp.). The data from the ^{13}C NMR and IR spectra are given in the text. Anal. Calcd. for $C_{38}H_{60}Na_2O_{26}W_3$: C, 29.80; H, 3.92. Found: C, 30.19; H, 3.80%. Electron probe microanalysis: Na : W : Lu : Cl = 2 : 3 : 0.04 : 0.01.

3.2. X-ray crystal analysis of complex I

Crystal of **I** were grown by slow cooling of a saturated solution of the compound in DME. X-ray data acquisition was accomplished with single crystals packed in thin-walled glass capillaries under argon. X-ray data were collected at ambient temperature using an Enraf-Nonius CAD-4 diffractometer (Mo Kα radiation, ω-2θ scan method, $4° \leq 2\theta \leq 42°$). Crystals are orthorhombic, $a = 18.749(4)$, $b = 15.074(3)$, $c = 9.505(3)$ Å, $Z = 2$, space group C_{mmm}. The structure was partially solved using the SHELP program on an IBM PC AT (653 data with $I \geq 1\sigma(I)$). The data were corrected for absorption using three azimuthal scan curves. The structure was refined isotropically up to $R = 0.125$. The coordinates of located atoms are listed in Table 1.

TABLE 1. The coordinates of located atoms in the structure $[Na(DME)_3]_2[W_3(CO)_{14}]$ (**I**)

Atom	*x*	*y*	*z*
W(1)	0	0	0
W(2)	0	0.185(2)	0
C(1)	0	0.178(4)	0.214(4)
C(2)	0	0.301(4)	0
C(3)	0.121(4)	0.175(4)	0
C(4)	0	0	0.224(4)
C(5)	0.118(4)	0	0
O(1)	0	0.165(4)	0.328(4)
O(2)	0	0.382(4)	0
O(3)	0.154(4)	0.175(4)	0
O(4)	0	0	0.320(4)
O(5)	0.167(4)	0	0
Na	0.296(4)	0	0.5

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