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Chemistry of lanthanide–metal carbonyl systems: the ytterbium–chromium carbonyls interaction

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Abstract

The interaction of the chromium carbonyl hydrides $HCr_2(CO)_{10}^-$ or $HCr(CO)_5^-$ with $Yb(acac)_3{\cdot}3H_2O$ has been investigated, and the experimental conditions leading to the isolation of ytterbium–chromium carbonyl complex species are reported. Formulation of the coordination compounds produced by such interactions has been proposed on the basis of analytical data and IR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemical synthesis; Heteronuclear metal carbonyls; Lanthanide–transition metal carbonyls; Ytterbium–chromium carbonyl compounds

1. Introduction

Known coordination compounds containing metal carbonyl and lanthanide species involve ion pairs in which the metal carbonyl, as a Lewis base, appeared to favour a Ln–CO–M interaction (e.g. Ln=Sm, Eu, or Yb, M=$Co(CO)_4^-$) giving then compounds with bridging carbonyl groups [1–3]. Using organolanthanide species, compounds containing organo–lanthanide cations (Ln=Sm or Yb) and $[Co(CO)_4]^-$ as counter ion without bridging carbonyl groups, as well as some compound evidencing lanthanide–transition metal bond, have also been isolated and characterized [4,5].

With the goal to find routes to heteronuclear metal carbonyls containing lanthanides, of increasing interest for catalytic processes, we have extended our continuous work dealing with the synthesis and reactivity studies of homo- and heteronuclear group 6 metal carbonyls [6–13] to investigations on interactions, performed under either a nitrogen or a carbon monoxide atmosphere, involving reactive chromium carbonyl species isolated in our previous studies and lanthanide coordination compounds such as $Ln(acac)_3{\cdot}3H_2O$ (Ln=Yb or Sm).

We herein report on the synthesis of ytterbium–chromium carbonyl compounds by the interaction performed under N_2 of $Yb(acac)_3{\cdot}3H_2O$ with the chromium carbonyl hydrides $[HCr(CO)_5]^-$ or $[Cr_2(CO)_{10}(\mu\text{–}H)]^-$, both from long easily accessible in high yields as K^+ derivatives [6,11,12].

2. Experimental

All the operations were carried out under rigorous exclusion of air by using vacuum line and oxygen-free nitrogen. Carefully deaerated solvents and chemicals were reagent grade (C. Erba or Fluka or Strem Chemicals) and were used as received unless otherwise stated. The $K[HCr_2(CO)_{10}]$ and $K[HCr(CO)_5]$ compounds have been prepared according to our published procedures [6,11,12][1], as well as the $Yb(acac)_3{\cdot}3H_2O$ complex species [15]. Analytical determinations were performed in this laboratory. Ytterbium was determined by direct titration with EDTA using xylenol orange as indicator and chromium by atomic absorption (AA) spectroscopy. Gas-volumetric

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[1] A recent procedure for $K[HCr(CO)_5]$, reported as an improved one [14], examined in our laboratory did not give the cited yields, as expected. The concomitant use of short reaction times and low $KOH{:}Cr(CO)_6$ ratios such as 2:1, results in the separation of variable amounts of unreacted $Cr(CO)_6$ (recovered in the trap at −80°C upon evaporation under vacuum to dryness of reaction solutions), and in a greatly favoured conversion of $[HCr(CO)_5]^-$ into $[HCr_2(CO)_{10}]^-$, respectively. This conversion is also increasing to some extent owing to several THF treatments in which both the carbonyl hydrides are very soluble (IR ν(CO) evidence).

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analysis of CO was obtained by decomposition of the samples with EtOH iodine solutions. M.p.'s (uncorrected) were determined in capillaries sealed in vacuo. IR spectra were recorded as nujol mulls using a Perkin Elmer 1430 or a Spectrum 2000 FT–IR instrument between KBr discs. The formulation of the products isolated is in good agreement with the experimental data (analysis and IR) which it has so far been possible to obtain. Further work, X-ray studies included, for their complete characterization is in progress.

*2.1. Synthesis of (**1**): by $K[HCr_2(CO)_{10}]/Yb(acac)_3 \cdot 3H_2O$ at 2:1 molar ratio*

An EtOH (95%) solution of $Yb(acac)_3 \cdot 3H_2O$ (0.524 g, 1 mmol in 30 ml) was slowly added to a stirred yellow EtOH solution of $K[HCr_2(CO)_{10}]$ (0.848 g, 2 mmol in 20 ml). From the resulting solution a yellow solid gradually separated. The mixture was rapidly warmed with stirring to 45°C and left to stir at 45–47°C for ca. 5 h during which turned yellow–orange, then to room temperature for ca. 24 h. The crystalline reaction product (**1**) was filtered, washed with EtOH, (in which any unreacted $K[HCr_2(CO)_{10}]$ or $Yb(acac)_3 \cdot 3H_2O$ is very soluble) until the solvent was colourless (three times, 3 ml), and then well dried under high vacuum; 0.32 g, 76.24% (referred to Yb). The filtrate was evaporated at 25°C in vacuo to dryness, and the residue was treated with anhydrous CH_2Cl_2 (15 ml) by which only the unreacted slightly soluble $K[HCr_2(CO)_{10}]$ separated; this was collected by filtration, washed with CH_2Cl_2 and then dried under high vacuum (0.61 g, 1.44 mmol). The yellow filtrate was evaporated in vacuo to dryness, and the residue treated with water (10 ml). After ca. 10 min of stirring, the separated pale yellow compound (**2**) was collected by filtration, washed with water (three times, 3 ml), and then well-dried under high vacuum (0.10 g, 18.33%).

(**1**) was recrystallized by $CHCl_3$-toluene in 60–70% yields. It is very soluble in CH_2Cl_2 or $CHCl_3$, soluble in THF and Me_2CO, slightly soluble in EtOH or MeOH, insoluble in toluene, Et_2O and in H_2O. In the solid state, it appeared moderately air-stable but sensitive to moisture; well dried samples could be stored under N_2 for some days without appreciable decomposition. Its solution, particularly the CH_2Cl_2 or $CHCl_3$ ones, are instead air sensitive. It melts at 208–210°C.

Found: C, 31.6; H, 3.7; Yb, 41.1; Cr, 2.7; CO, 7.7%. Calcd. for $Yb_9(acac)_{18}Cr_2(CO)_{10} \cdot 3H_2O$: C, 31.78; H, 3.52; Yb, 41.21; Cr, 2.75; CO, 7.41%.

*2.2. Synthesis of (**2**): by $K[HCr(CO)_5]/Yb(acac)_3 \cdot 3H_2O$ at 2:1 molar ratio*

The addition of a THF solution of $Yb(acac)_3 \cdot 3H_2O$ (1.75 mmol in 30 ml) to a stirred pale-yellow solution of $K[HCr(CO)_5]$ in anhydrous THF (3.5 mmol in 50 ml) gave an orange solution from which some white solid gradually separated. The mixture was left to stir for 1 h at room temperature, then evaporated under vacuum to dryness. The orange residue was treated with EtOH (99.8% absolute, 60 ml), and the resulting mixture was warmed with stirring to 48°C, and left to stir at 48–50°C for ca. 5 h, then to room temperature for 18 h. Upon evaporation under vacuum to dryness and treatment of the yellow residue with anhydrous CH_2Cl_2 (40 ml), a solid separated which, collected by filtration, washed with CH_2Cl_2 until the solvent was colourless, and dried under high vacuum, proved to be a mixture of $K[HCr_2(CO)_{10}]$ and of a white by-product which analysis and IR indicated it was an ytterbium acetylacetonate not yet well characterized. The former was isolated by treatment of the solid mixture with anhydrous Me_2CO, in which it was the only soluble species, and, after filtration, by subsequent evaporation in vacuo to dryness of the solution (0.63 g, 1.5 mmol). The CH_2Cl_2 filtrate evaporated under vacuum to dryness gave a residue which rapidly treated with water (15 ml) induced separation of (**2**) as described before. Yield, 0.45 g, 47.14%.

This pale yellow compound appeared less air-stable and sensitive to moisture than (**1**) in the solid state as well as in its solutions under N_2. Moreover, it tended to a variable extent to undergo conversion into species containing ligand redistribution (IR evidence). Well-dried samples can be stored for some days under N_2 and in a freezer. It is soluble in the common polar solvents, somewhat soluble in Et_2O and insoluble in water. It decomposes without melting at 180°C.

Found: C, 32.9; H, 3.33; Yb, 31.5; Cr, 4.66; K, 3.75; CO, 12.78%. Calcd. for $K[Yb_2(acac)_5\ Cr(CO)_5] \cdot H_2O$, C, 33.03; H, 3.42; Yb, 31.7; Cr, 4.77; K, 3.6; CO, 12.85%.

*2.3. Synthesis of (**3**): by $K[HCr(CO)_5]/Yb(acac)_3 \cdot 3H_2O$ at 1:2 molar ratio*

By slow addition of a solution of $Yb(acac)_3 \cdot 3H_2O$ (7 mmol, 50 ml) in anhydrous THF to an analogous stirred solution of $K[HCr(CO)_5]$ (3.5 mmol, 50 ml), some gas evolution was detectable and the lemon–yellow solution soon turned orange, then deep red. It was left to stir at room temperature for ca. 30 min. during which the already observed solid gradually separated. The mixture was then evaporated under vacuum to dryness and the orange residue was treated with EtOH (99.8%, 100 ml). The resulting mixture was warmed with stirring at 48–50°C for ca. 5 h, then left to stir at room temperature for 12 h, and then evaporated in vacuo to dryness. The residue was treated with anhydrous CH_2Cl_2 (50 ml) which induced separation of a orange–red solid; this was collected by filtration, washed with CH_2Cl_2 (three times, 3 ml), and then well dried under high vacuum. It was treated with anhydrous Me_2CO (25 ml) and the residual white solid (some amounts of the uncharacterized ytterbium acetylacetonate) filtered off. The orange–red filtrate, evaporated to dryness under high vacuum, gave a crystalline residue which proved to be a pure sample of the heteronuclear compound (**3**). Yield, 0.3 g, 5.2%.

This complex species is soluble in Me_2CO, slightly soluble in EtOH, insoluble in CH_2Cl_2 and Et_2O. It decompose at 135°C. Found: C, 33.9; H, 3.75; Yb, 20.87; Cr, 6.4; CO, 9.95%. Calcd. for $K_2[Yb(acac)_4\ Cr(CO)_3]\cdot 2H_2O$, C, 33.7; H, 3.93; Yb, 21.1; Cr, 6.34; K, 9.54; CO, 10.25%.

The CH_2Cl_2 filtrate (in which the compounds (**1**) and (**2**) might be dissolved) was evaporated in vacuo to dryness, and the residue treated as previously described gave 25% of (**1**), ca. 18% of (**2**).

3. Results and discussion

3.1. A. The interaction $K[HCr_2(CO)_{10}]/Yb(acac)_3\cdot 3H_2O$

Under various sets of conditions involving $K[HCr_2(CO)_{10}]:Yb(acac)_3\cdot 3H_2O$ molar ratios from 0.5:1 to 3:1, reaction solvents such as EtOH or MeOH, THF or Me_2CO in which both the reactants are soluble, temperatures from 25 to 58°C with reaction times from 4 to 24 h, such an interaction proved to produce two heteronuclear compounds, (**1**) and (**2**); the former as main complex product, in variable yields, from 60 to 75%, depending on the experimental conditions (molar ratios of the reactants, and/or reaction solvent, and/or temperature or times). Temperatures above 50°C induced decomposition of reactants and products to a variable extent. The use of THF and 2:1 $K[HCr_2(CO)_{10}]:Yb(acac)_3\cdot 3H_2O$ ratios appeared to favour a relatively higher yield of (**2**) which however was rather low, whereas the reactions carried out in EtOH inducing only separation of the slightly soluble (**1**) easily permitted its isolation as a yellow solid. In EtOH, the reactions took place rather readily and occurred with direct formation of (**1**) upon interactions at any of the before mentioned $K[HCr_2(CO)_{10}]:Yb(acac)_3\cdot 3H_2O$ molar ratio. 0.5:1 ratios gave this heteronuclear complex species in yields up to 64%, while higher molar ratios, such as 1:1 or 2:1, up to 77% yields. Using the latter ratios however, unreacted $K[HCr_2(CO)_{10}]$ was recovered (Exp.) in yields corresponding to the used excess with respect to the 0.5:1 ratio. Such a reactants ratio can indeed be considered the most convenient for the synthesis of (**1**) since no CH_2Cl_2 treatment has to be performed to remove any unreacted $K[HCr_2(CO)_{10}]$. The $K[HCr_2(CO)_{10}]/Yb(acac)_3\cdot 3H_2O$ interaction performed in EtOH at 0.5:3 molar ratios instead yielded (**1**) as the almost alone reaction product up to ca. 68% yields; the isolated samples required, as expected, EtOH treatments removing any impurity.

Compound (**2**) could be isolated up to ca. 25% yields. It has shown to undergo easy conversion by water–ethanol treatment into a ytterbium–chromium carbonyl still under investigation. As almost alone complex species it was obtained by the $K[HCr(CO)_5]/Yb(acac)_3\cdot 3H_2O$ interaction performed at given ratios (see Exp.). Work is in progress to clearify better its easy decomposition when produced by the reactions carried out under N_2; preliminary investigations of interactions performed under CO evidences its formation as a much more stable reaction product.

3.2. B. The interaction $K[HCr(CO)_5]/Yb(acac)_3\cdot 3H_2O$

Such an interaction provided the evidence for its ability to produce another heteronuclear complex species besides the compounds (**1**) and (**2**), depending on the experimental conditions among which the molar ratios of the reactants and temperature appeared to be important factors.

The initial course of the reaction was carried out for 1 h in dried THF for in this solvent the soluble $K[HCr(CO)_5]$ undergoes a slower conversion into the dinuclear hydride. The reactions allowed to proceed in this solvent induced separation of remarkable amounts of a insoluble white solid which by IR and analysis was shown to be a currently not well characterized ytterbium acetylacetonate. When the initial THF reaction mixture was evaporated under vacuum to dryness after ca. 1 h at room temperature, and the resulting residue was treated with EtOH (see Exp.), the interaction allowed to proceed in this solvent led to the isolation of much less amounts of this white slightly soluble species which separated together with compound (**1**).

Among the various set of conditions investigated, those using temperatures from 25 to 48°C proved to favour the higher yields in product in all cases, while the molar ratios of the reactants appeared much to influence the type of heteronuclear complex species isolable as final reaction product. Thus, the 1:1 $K[HCr(CO)_5]:Yb(acac)_3\cdot 3H_2O$ molar ratio induced formation of (**1**) as prevalent species and low yields of (**2**), whereas the 2:1 one afforded only (**2**). In both cases variable amounts of $K[HCr_2(CO)_{10}]$ were also obtained, this suggesting a course of the reaction involving a redox process during which part of the mononuclear $[HCr(CO)_5]^-$ hydride would undergo conversion into the dinuclear one as follows: $2\ HCr(CO)_5^- \rightarrow HCr_2(CO)_{10}^- + H^-$.

The interaction at 1:2 $K[HCr(CO)_5]:Yb(acac)_3\cdot 3H_2O$ ratios produced a unexpected red heteronuclear carbonyl species (**3**) with different Yb:Cr and Cr:CO ratios in ca. 5% yields besides (**1**) and (**2**) (see Exp.); whereas the 1:3 ratios favoured almost only formation of (**1**), did not afford any dinuclear chromium carbonyl hydride, and gave very little amounts (2.5%) of the red ytterbium–chromium carbonyl species (**3**).

3.3. IR spectra

Comparison of the IR ν(CO) spectra (Fig. 1) of the heteronuclear compounds in the solid state (nujol mulls)

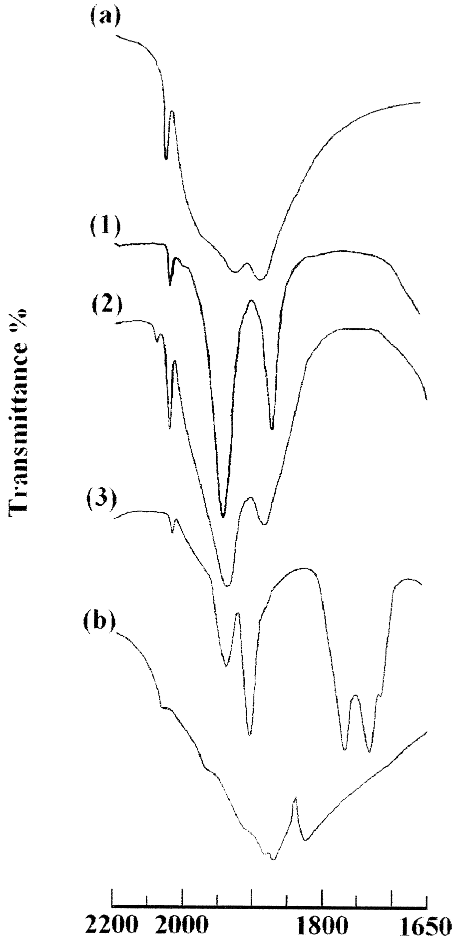

Fig. 1. IR ν(CO) spectra of nujol mulls: (a) K[$Cr_2(CO)_{10}(\mu-H)$]; (1); (2); (3); (b) K[$HCr(CO)_5$].

with the analogous region of the starting chromium carbonyl hydrides [6,12] evidences the presence of a quite different chromium carbonyl skeleton in these products, which cannot be interpreted as an influence of packing phenomena in the crystal lattice. These are remarkable to a variable extent in the case of $[HCr_2(CO)_{10}]^-$ derivatives, depending on the counter ion associated [6–10]. The ν(CO) region of (**1**) exhibits three sharp bands at 2033 mw, 1938 vs, 1868 s cm^{-1}, known to be characteristic of presence of $Cr(CO)_5$ groups, and similar to the one of solutions of $[Cr_2(CO)_{10}(\mu-H)]^-$ in which its electron-deficient Cr–H–Cr system is linear [6–10] (whereas it is non-linear in the solid state [7–10]); only the 1880 s cm^{-1} band of the latter is shifted in (**1**) at 1868 cm^{-1}. The ν(CO) bands of (**2**) are detectable at 2066 w, 2032 m, 1937 s, 1876 mw cm^{-1}, whereas the ν(CO) region of (**3**), besides three bands at ca. 2035 w, 1938 m, 1902 vs, exhibits in the 1800–1700 cm^{-1} range two bands at ca. 1768 ms and 1728 ms, and a band at 1710 vw cm^{-1}; this known to indicate bridging CO groups. In Figs. 2 and 3 the IR regions of nujol mulls of the new compounds between 3800 and 3100 cm^{-1} with the characteristic broad band of H_2O molecules in the 3500–3200 cm^{-1} range, and be-

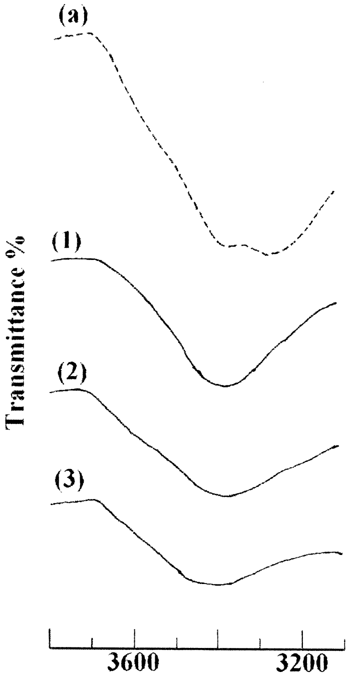

Fig. 2. The IR water region of nujol mulls: (a) $Yb(acac)_3 \cdot 3H_2O$; (1); (2); (3).

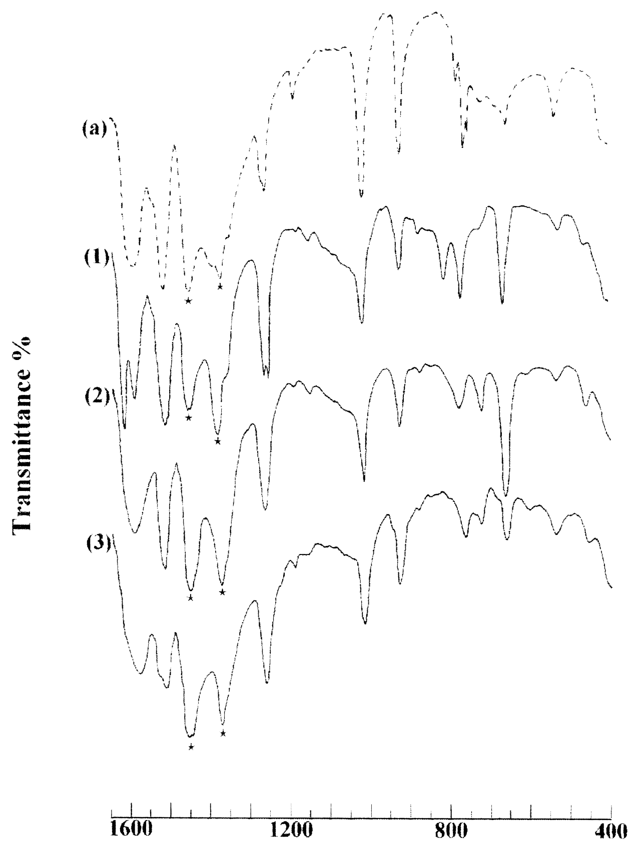

Fig. 3. The IR $acac^-$ region of nujol mulls: (a) $Yb(acac)_3 \cdot 3H_2O$; (1); (2); (3). ★ nujol bands.

tween 1650 and 400 cm^{-1} of the coordinated $acac^{-}$ ligand, are compared with the analogous ones of $Yb(acac)_3 \cdot 3H_2O$. It is possible to detect modifications in the range 720–780 cm^{-1}, splittings in (**1**) at 1620–1595 cm^{-1} and 1265–1257 cm^{-1}, and shifts as well as intensity changes of bands in all compounds.

IR spectra of nujol mulls of prepared mixtures further provided the evidence that these products are definite compounds. Their nature, definite nuclearity and linkages, requires X-ray studies. Attempts are in progress to obtain suitable crystals for such investigations.

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