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Synthesis, crystal structure and properties of a new lanthanide-transition metal carbonyl cluster

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A new type heterobimetallic complex containing lanthanide and transition metal carbonyl cluster (Ln–M carbonyl cluster), $Sm_2\{OOCCCo_3(CO)_9\}_2\{OOCCF_3\}_4\{(CO)_9Co_3CCOOH\}_4$, has been synthesized by reaction of $(CO)_9Co_3CCOOH$ with $Sm(OOCCF_3)_3(H_2O)_2$, and structurally characterized by single-crystal X-ray diffraction. Application of the complex as a catalyst precursor for hydrogenation of carbon monoxide (Fischer–Tropsch reaction) was explored, and the thermogravimetric behavior and magnetic properties of the compound were examined as well. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: Ln–M carbonyl cluster; crystal structure; CO hydrogenation; activity; selectivity

Introduction

There has been significant interest in heterobimetallic complexes containing lanthanide and transition metals (Ln–M), since they have potential uses as precursors to new materials, such as catalysts,[1] electroceramic and chemical sensors,[2] magnetic[3] and fluorescent[4] materials. Over the last three decades, numerous Ln–M carbonyl compounds have been synthesized, and most of them have been structurally characterized.[5–9] Research has been focused on the elucidation of the interaction between the two metals, and little is known concerning the application of these compounds as catalytic and magnetic materials, although it was suggested that complexes containing Ln–M carbonyls offer the possibility of functioning as catalyst precursors[10–13]. Until now, the determination of the structural relationship between the two metals has revealed three possible structure types of Ln–M complexes:[14] ion pairs (I), isocarbonyl linkages (II) and Ln–M direct bonds (III), for example, $[Ln_9(OH)_{10}(acac)_{16}][HCr_2(CO)_{10}]$ (Ln = Sm, Eu, Gd, Dy, Yb) (I),[15] $[Yb(THF)_6][Co(CO)_4]_2$ (I),[16] $[(THF)_4I_2Sm(\mu\text{-}OC)Mo(CO)_2(C_5H_5)]$ (II),[17] $[(Pry)_4Yb\{(\mu\text{-}OC)_2-Co(CO)_2\}_2]_\infty$ (II),[14] $\{[(CH_3CN)_3YbFe(CO)_4]_2CH_3CN\}_\infty$ (III)[18] and $[(NH_3)_3YbFe(CO)_4]$ (III).[19] However, these assorted Ln–M interactions influence the assembly of the compounds, the distance between lanthanide and transition metal is not easy to control and discrete molecules or polymeric arrays were encountered.[14]

In light of their potential applications and their diverse structural motifs, we are interested in synthesizing a new type of heterobimetallic carbonyl compounds, which contains organic functional groups as bridging ligands. The carbonyl cluster fragment we have chosen is the well-known capped tricobalt $(CO)_9Co_3C$, which is both a versatile electronic donor and acceptor,[20] while the functional group we have chosen is $[-COO]^-$, which has the ability to coordinate to Ln(III) cores. The advantages of this type of Ln–M carbonyl compounds are that the interaction between the two metals could not influence the assembly of the compounds, as well as that the synthetic process is simpler than that of the above structure styles.

Herein, we report a new Ln–M carbonyl complex which is bridged by an organic functional ligand between the different metals. Application of the complex as a catalyst precursor for hydrogenation of carbon monoxide was investigated, and the thermogravimetric behavior and magnetic properties of the compound were examined as well.

Experimental

General details

$Co_2(CO)_8$ and CF_3COOH were purchased from Aldrich and used as received. Samarium metal (99.9%) was dissolved in aqueous CF_3COOH (50%) and the clear solution was slowly evaporated to yield white crystals of $Sm(OOCCF_3)_3(H_2O)_2$. $(CO)_9Co_3CCOOH$ was prepared as described previously[21] with a minor modification. The stage of the hydrolysis in concentrated sulfuric acid was shortened to 12 h to increase the $(CO)_9Co_3CCOOH$ yield. All the solvents used were dried and distilled under argon just before use. The reactions were performed under nitrogen on a Schlenk line using standard air free methods.

IR spectra were recorded on a Bruker 120 HR FTIR spectrophotometer in KBr pellets. Elemental analyses (C, H) were performed

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on an Elementar Var III type analyzer. Metal analyses were carried out using a Perkin-Elmer ICP spectrometer.

Preparation of $Sm_2\{\mu\text{-}OOCCCo_3(CO)_9\}_2\{\mu\text{-}OOCCF_3\}_4-\{(CO)_9Co_3CCOOH\}_4$, 1

A 500 mg (1.029 mmol) aliquot of the cluster ligand $(CO)_9Co_3CCOOH$ was dissolved in 20 ml of Tetrahydrofuran (THF), the portion was added slowly to a THF solution of 120 mg (0.228 mmol) $Sm(OOCCF_3)_3(H_2O)_2$ with stirring. After mixing at 30 °C for 1 h, the solvent was removed under vacuum. The solid was extracted with hot toluene, and the resulting solution was filtered and kept at room temperature for 2 days. Well-formed crystals of **1** were isolated in 82% yield based on samarium (300 mg, 0.082 mmol). IR (KBr, cm^{-1}): 2111(w), 2054(vs), 1700(m), 1674(m), 1645(m), 1617(m), 1479(w), 1378(w), 1338(w), 1264(w), 1205(m), 1158(w), 1061(w), 862(w), 844(w), 780(w), 720(w), 503(m). Elemental analysis for $C_{74}H_4Co_{18}F_{12}O_{74}Sm_2$: C 24.62, H 0.35, Co 28.06, Sm 7.98%. Calcd: C 24.24, H 0.11, Co 28.93, Sm 8.20%.

Structure determination

Crystals of **1** suitable for X-ray diffraction were grown from a saturated toluene solution at room temperature for 2 days. A black plate-like crystal with dimensions 0.15 × 0.15 × 0.10 mm was mounted on a glass fiber and data were collected with a Bruker CCD APEX diffractometer equipped with a graphite crystal monochromated Mo $K\alpha$ X-radiation ($\lambda = 0.71073$ Å) source. The structure was solved by direct methods and was refined in full-matrix least-squares on F^2 using the SHELXL-97 crystallographic program package.[22]

Thermogravimetric Analysis

Thermogravimetric behavior was recorded under nitrogen on a Netzsch apparatus, model STA 449C. The sample temperature was increased linearly from room temperature to 450 °C at 2 °C/min in nitrogen (100 ml/min). The electronics of the electrobalance were purged with flowing argon. All the gases used were ultra-high purity (99.999%), and further purified by moisture traps incorporated into the lines. The mass loss was recorded as a function of the temperature. To identify the species evolving from the complex during the pyrolysis, the exhaust gas stream was analyzed by an FTIR (EQUINOX 55) apparatus equipped with a fast response continuous inlet system.

Magnetic Measurement

Temperature dependence of the magnetic susceptibility of the solid sample was measured with a Quantum Design MPMS-7 SQUID magnetometer in the temperature range from 2 to 300 K at external magnetic field of 0.1 T, with powders (23.80 mg complex **1**) placed in gelcap sample holders. Susceptibility values were corrected for the sample diamagnetic contribution according to Pascal's constants[23] as well as for the sample holder diamagnetism. The θ values were obtained from extrapolations from curve fitting between 50 and 300 K.

CO Hydrogenation Tests

The γ-Al_2O_3 support was calcined in air at 500 °C for 10 h to dehydroxylate the surface prior to use. The bimetallic catalysts, all containing 5.0 wt% Co and 1.4 wt% Sm, were prepared by incipient wetness impregnation on the support. $CoSm/Al_2O_3$ was prepared by impregnation from a THF solution with the $Sm_2\{OOCCCo_3(CO)_9\}_2\{OOCCF_3\}_4\{(CO)_9Co_3CCOOH\}_4$ precursor under nitrogen and then dried slowly under vacuum at room temperature. A reference catalyst with the same metal loading, designated as $(Co + Sm)/Al_2O_3$, was also prepared for comparison purposes by impregnation of γ-Al_2O_3 with a THF solution containing a mixture of $(CO)_9Co_3CCOOH$ and $Sm(OOCCF_3)_3(H_2O)_2$ using a procedure similar to that of Johnston.[24]

The dispersion measurements of Co metal particles of the activated catalysts were performed by the carbon monoxide pulse chemisorption method, using an AutoChem2910 instrument. The BET-surface areas of the activated catalysts were measured using a Micromeritics ASAP2020 analyzer, based on nitrogen adsorption at the temperature of liquid nitrogen, after degassing the samples at 300 °C for 1 h under a nitrogen stream.

Hydrogenation of carbon monoxide was carried out with a fixed-bed reactor equipped with an on-line GC system consisting of two Shimadzu GC-8A series gas chromatographs. The outlet gases with H_2, CO, CH_4 and CO_2 were analyzed by on-line gas chromatography on a Shimadzu GC-8A equipped with a TDX-01 carbon molecular sieve column and a TCD detector. Hydrocarbon products with carbon numbers lower than 5 were analyzed by on-line gas chromatography on a Shimadzu GC-8A provided with a Porapack-Q column and a FID detector, and those with larger carbon numbers (C_{5+}) were collected by a cold trap at 12 h intervals and analyzed by gas chromatography on a Shimadzu GC-2014 equipped with a capillary column (HP-1, 30m) and an FID detector.

The catalyst (3 g) was loaded into the reactor, and activated *in situ* by heating to 300 °C at 2 °C/min in Ar then switching to H_2 for 2 h. After activation, the catalyst was slowly cooled to 190 °C under H_2 flow. Then, the reactor was pressurized to the desired reaction pressure, and was gradually changed to syngas to prevent overheat by the fresh catalyst.

The composition of the synthesis gas was $H_2/CO/Ar = 10:5:1$, and argon was used as an internal standard for the calculation of CO conversion. The reaction pressure was kept constant at 2.0 MPa and the typical reaction temperature was 220 °C. The gas hourly space velocity (GHSV) was kept constant at 500 h^{-1}.

Results and Discussion

Crystal Structure of Complex 1

X-ray single-crystal analysis revealed **1** to be a monoclinic space group *P*2(1)/*c*, with two molecules of **1** in the unit cell. Crystallographic data and experimental details for **1** are collected in Table 1. Table 2 gives the selected bond lengths and angles. An ORTEP drawing of **1** with numbering is depicted in Fig. 1.

As seen in Fig. 1, complex **1** consists of an unusual dimeric Sm(III) system with two asymmetrical chelating cluster carboxylates $[Co_3(CO)_9CCOO]^-$ and four asymmetrical bridge linking $[CF_3COO]^-$ ligands. Each $[CF_3COO]^-$ ligand bridges the two Sm(III). Additionally, two $(CO)_9Co_3CCOOH$ carboxylates coordinate to each Sm(III) center. Each Sm ion is eight-coordinated with a square antiprism coordination geometry, surrounded by eight carboxylic oxygen atoms, four from bridging $[CF_3COO]^-$ ligands with Sm(1)–O(7,8,9,10) averaging 2.415 Å (range 2.385–2.472 Å), the other four from carbonyl cluster carboxylates ligands with Sm(1)–O(1,2,3,5) averaging 2.476 Å (range 2.416–2.599 Å). There

Table 1. Summary of data collection and structure refinement for complex **1**

Empirical formula	C_{74} Co_{18} F_{12} O_{74} Sm_2
Formula weight	3662.18
Crystal system	Monoclinic
space group	*P*2(1)/*c*
F(000)	3516
Unit cell dimensions	
a (Å)	13.241(5)
b (Å)	24.848(11)
c (Å)	18.378(8)
β (deg)	99.654(7)
V (Å^3)	5961(4)
Z	2
$D_{calc.}$ (g/cm^{-3})	2.043
Absorption coefficient (mm^{-1})	3.518
Radiation (Mo Kα) (Å)	0.71073
Temperature (K)	293(2)
Θ range (deg)	1.39–26.01
Reflections collected	27 374
Independent reflections	11 722 [*R*(int) = 0.0802]
Goodness-of-fit on F^2	0.983
Data/restraints/parameters	11722/0/867
R_1, ωR_2 ($I > 2\sigma(I)$)^a	0.0597, 0.1328
R_1, ωR_2 (all data)	0.1147, 0.1646
Largest difference peak and hole (e Å^{-3})	1.981 and −1.733

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$, $\omega R_2 = \{\sum \omega[(F_0)^2 - (F_c)^2]^2 / \sum \omega [(F_0)^4]\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**^{a}

Bond lengths		Bond angles	
Sm(1)–O(1)	2.416(5)	O(1)–Sm(1)–O(2)	52.91(18)
Sm(1)–O(2)	2.444(5)	O(1)–Sm(1)–O(3)	101.12(19)
Sm(1)–O(3)	2.599(5)	O(1)–Sm(1)–O(5)	74.2(2)
Sm(1)–O(5)	2.444(5)	O(1)–Sm(1)–O(7)	145.4(2)
Sm(1)–O(7)	2.472(6)	O(2)–Sm(1)–O(3)	70.12(18)
Sm(1)–O(8)$^{\#1}$	2.411(5)	O(2)–Sm(1)–O(3)	102.6(2)
Sm(1)–O(9)	2.385(5)	O(2)–Sm(1)–O(3)	142.62(19)
Sm(1)–O(10)$^{\#1}$	2.391(5)	O(5)–Sm(1)–O(3)	70.33(17)
		O(5)–Sm(1)–O(7)	71.82(19)
		O(5)–Sm(1)–O(9)	78.25(18)
		O(7)–Sm(1)–O(3)	73.40(19)
		O(7)–Sm(1)–O(9)	83.8(2)
		O(9)–Sm(1)–O(1)	83.1(2)
		O(9)–Sm(1)–O(2)	132.31(18)
		O(9)–Sm(1)–O(3)	145.53(17)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, -y+2, -z+1$.

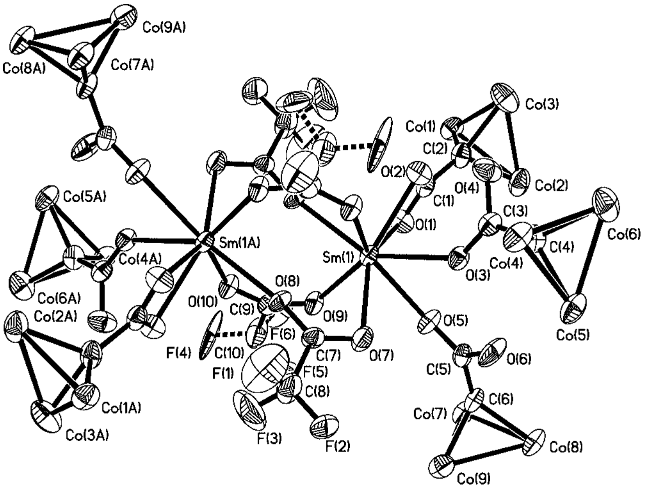
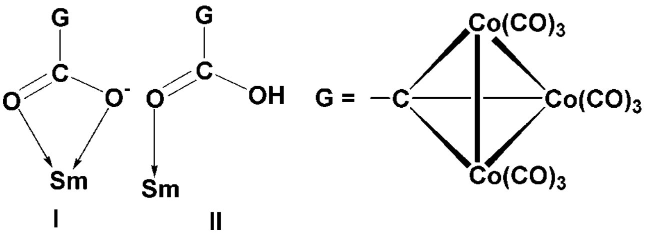


Figure 1. Molecular structure of complex **1**.



Scheme 1. The coordination mode of carbonyl cluster ligand in complex **1**.

are no significant structural differences among the six tricobalt clusters surrounding the Sm(III) core. The structure of the tricobalt cluster remains invariant within experimental error. Two coordination modes (Scheme 1), $[Co_3(CO)_9CCOO]^-$ chelate and $Co_3(CO)_9CCOOH$ unidentate ligand, were observed in the structure of complex **1**. Moreover, the two $(CO)_9Co_3CCOOH$ carboxylates coordinated to each Sm(III) center also form hydrogen bond to the oxygen atoms of the chelating carboxylates. The structural features of the complex **1** are very similar to those in published structures,[25] except that the Sm–O(3) bond (2.599(5) Å) is longer than the reported Sm–O distance for $[Sm_2\{OOCCCo_3(CO)_9\}_2\{OOCCF_3\}_4\{(CO)_9Co_3CCOOH\}_2(THF)_2]$ (2.467(5) Å), which is attributed to the difference of the ligand volume between $(CO)_9Co_3CCOOH$ and THF and the substantial steric bulk of the coordinated carbonyl cluster. Actually, the complex we obtained is a substitutional analog of the reported compound.

Thermogravimetric analyses of complex 1

Figure 2 shows the mass loss for the title complex between room temperature and 450 °C. Looking at the structural feature of complex **1**, one can suppose at first sight that the molecule may lose carbon monoxide upon heating. It has been shown that thermal decomposition of $M_4O\{OOCCCo_3(CO)_9\}_6$ (M = Co, Zn) occurs in more than one step beginning from 100 °C, the first stage to the loss of part carbonyl groups as carbon monoxide, and the second stage to the loss of the remaining carbonyl ligands and carbon dioxide moieties from the carboxylate ligands.[26] Similar results are observed for the thermal decomposition of compound **1**. The first mass loss of 35.17% (observed) between 100 and 190 °C corresponds to the loss of 46 carbonyl groups (calculated, 35.13%) as gaseous CO as shown by TGA–FTIR measurement (Supporting Material Fig. S1), and the following mass loss of 18.77% (observed) from 190 to 350 °C can be related to the loss of the remaining carbonyl groups and carboxyl groups (calculated, 18.87%). The thermal decomposition plot reaches a constant mass (observed, 46.06%) zone near 350 °C, where almost all the volatile groups

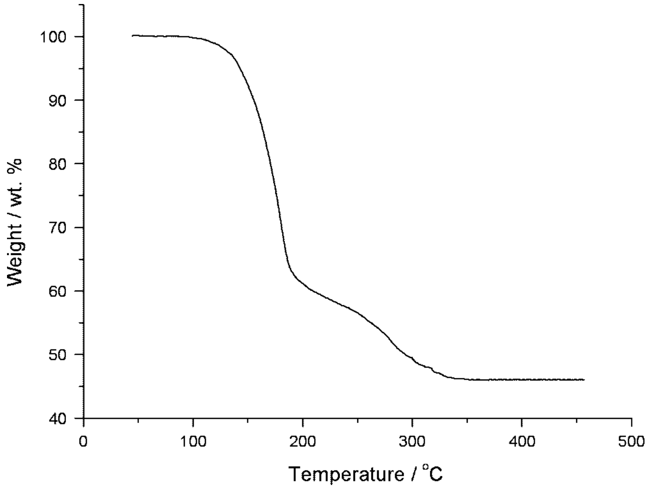


Figure 2. TGA trace of the thermal decomposition of complex **1**.

have been lost and a solid phase with high cobalt and samarium content is left.

Magnetic Property of Complex 1

The variable-temperature magnetic susceptibility of complex **1** in the temperature range of 2–300 K at an applied field of 1 T was measured; the $1/\chi_m$ and $\chi_m T$ vs T plots for the compound are presented in the Supporting Material (Fig. S2). There is no indication of long-range magnetic ordering down to 2 K.

The $\chi_m T$ value at 300 K is 1.81 emu K mol^{-1}, which decreases smoothly with decreasing temperature, reaching a minimum value of 0.65 emu K mol^{-1} at 2 K. Values of $1/\chi_m$ decrease gradually from 166 to 43 emu^{-1} mol as temperature is lowered from 300 to 50 K, and the onset of downward curvature below 50 K may be due to the large anisotropy effects for the lanthanide ions.[27] The observed susceptibility data obey the Curie–Weiss law [$\chi_m = C/(T - \theta)$], with Weiss constant $\theta = -42$ K and $C = 2.055$ emu K mol^{-1}, in the temperature range 50–300 K. The complex has negative values of θ, which indicates antiferromagnetic interactions between lanthanide cations.

CO Hydrogenation Studies

Complex **1** was used as a catalyst precursor for the hydrogenation of carbon monoxide. The catalytic activities and the product distributions over $CoSm/Al_2O_3$ and $(Co + Sm)/Al_2O_3$ catalysts are presented in Table 3.

As seen in Table 3, the CO conversion increased by 5%, CH_4 and C_{2-4} selectivity decreased by about 50%, and the C_{5+} selectivity dramatically increased to 8 times the reference catalyst. It is clear that the bimetallic catalyst derived from molecular cluster precursor showed higher activity and remarkably higher selectivity than the reference catalyst prepared by the conventional technique with a coimpregnation of the two metals on the support surface. Similar results were observed for silica supported CoRu, (Co + Ru), CoRh and (Co + Rh) catalysts derived from the transition metal carbonyl clusters.[28] The increase in CO conversion could be due to the intimate contact of lanthanide Sm and metal Co that helps uniformly disperse the particles of the decomposed product over the support, since the dispersion of $CoSm/Al_2O_3$ is higher than that of $(Co + Sm)/Al_2O_3$ (Table 4). Such a structure could be more effective in heterogeneous catalytic reactions with cobalt serving as the principal catalyst and lanthanide functioning as a catalyst promoter.[13,29] An explanation toward the significant improvement of C_{5+} selectivity for $CoSm/Al_2O_3$ catalyst may be attributed to the unique structure framework derived from the precursor structure, while the metal Co and Sm in $(Co + Sm)/Al_2O_3$ catalyst were largely separated from each other at random. As a result, introducing lanthanide promoter into the catalyst in the form of the molecule precursor is a more effective way of improving catalytic activity and selectivity for the FT reaction.

Table 3. Effect of the precursor $Co{-}Sm/Al_2O_3$ catalysts on the catalytic activity and product distribution in hydrogenation of carbon monoxide reaction[a]

Catalyst (5.0 wt% Co)	Conversion (%)	C_1(C%)	$C_2{-}C_4$(C%)	C_{5+} (C%)
$(Co + Sm)/Al_2O_3$	11	71	22	7
$CoSm/Al_2O_3$	16	37	9	54

[a] Reaction conditions: $H_2/CO = 2$; pressure = 2.0 MPa, $T = 220\,^\circ C$; GHSV = 500 h^{-1}.
$Co + Sm = (CO)_9Co_3CCOOH + Sm(OOCCF_3)_3(H_2O)_2$; $CoSm = Sm_2\{OOCCCo_3(CO)_9\}_2\{OOCCF_3\}_4\{(CO)_9Co_3CCOOH\}_4$.

Table 4. The characteristics of the $Co{-}Sm/Al_2O_3$ catalysts

Catalyst (5.0 wt% Co)	CO uptake (µmol/g)	Dispersion (%)	Active particle size (nm)	BET (m^2/g)
$(Co + Sm)/Al_2O_3$	0.6	10	10	208
$CoSm/Al_2O_3$	1.7	27	4	219

$Co + Sm = (CO)_9Co_3CCOOH + Sm(OOCCF_3)_3(H_2O)_2$; $CoSm = Sm_2\{OOCCCo_3(CO)_9\}_2\{OOCCF_3\}_4\{(CO)_9Co_3CCOOH\}_4$.

Conclusions

In summary, a new Ln–M carbonyl compound has been synthesized by employing $(CO)_9Co_3CCOOH$ cluster as a ligand. Moreover, it was a specific example that an Ln–M carbonyl complex was used as a catalyst precursor toward hydrogenation of carbon monoxide reaction. Furthermore, introducing lanthanide promoter by the organo-bimetallic precursor method is a more effective way for improving catalytic activity and selectivity for the FT reaction.

Supporting information

Supporting information may be found in the online version of this article.

Acknowledgments

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