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Synthesis and characterization of Li(I)–M(II) (M = Co, Ni) heterometallic complexes as molecular precursors for $LiMO_2$

Zhanna Dobrokhotova [a], Anna Emelina [b], Aleksei Sidorov [a], Grigory Aleksandrov [a], Mikhail Kiskin [a,*], Pavel Koroteev [a], Mikhail Bykov [b], Marat Fazylbekov [b], Artem Bogomyakov [c], Vladimir Novotortsev [a], Igor Eremenko [a]

[a] N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prosp. 31, 119991 Moscow, GSP-1, Russian Federation
[b] Department of Chemistry, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation
[c] Institute International Tomography Centre, Siberian Branch of the Russian Academy of Sciences, Institutskaya Str. 3a, 630090 Novosibirsk, Russian Federation

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ABSTRACT

Lithium-containing heterometallic complexes with cobalt ($Li_2Co_2(Piv)_6(2,4\text{-Lut})_2$ (**2**, Piv is the pivalate anion) and $Li_2Co_2(O_2CCH_2Bu^t)_6(2,4\text{-Lut})_2$ (**3**)) and with nickel ($Li_2Ni_2(Piv)_6(DME)_2$ (**4**) and $Li_2Ni_2(Piv)_6(2,2'\text{-bpy})_2$ (**5**)) were synthesized. The structures of the complexes were established by X-ray diffraction. The magnetic properties of complexes **2** and **4** were studied. The thermal behavior of compounds **2**, **3**, and **5** was investigated. It was shown that the compounds under study can be used as molecular precursors for the synthesis of lithium cobaltate and nickelate.

1. Introduction

It is only in the recent past that polynuclear coordination compounds have attracted attention of chemists working on the design of new materials. Investigations of the methods for the chemical assembly of target molecules of a particular composition and even the structures not only have a great potential for the solution of fundamental problems of chemistry and physics of this class of complex compounds but also provide a route to the design of new materials based on these compounds [1].

In the synthesis of complex oxide systems with the use of heterometallic coordination compounds, the composition of the target oxide and, probably, its properties, can be specified in the step of the formation of a molecular precursor yielding the oxide under rather mild conditions (at temperatures below 500 °C) after the removal of the "organic moiety" of the molecule. This approach has attracted particular attention. Thus, the thermal behavior of the coordination compounds $[Fe_2Ni(C_4H_4O_5)_{2.5}(OH)_2]NO_3{\cdot}5H_2O$, $[Fe_2Ni(C_4H_8O_3N_2)_4](NO_3)_8{\cdot}24H_2O$, and $(NH_4)[Fe_2Ni(C_4H_4O_5)_3(OH)_3]{\cdot}3H_2O$, which are formally potential precursors for nickel ferrite, was investigated [2]. Heteropolynuclear copper and zinc complexes with ethylenediamine [3] and the heterometallic Cu^{II}/Mn^{II} oxalate complex with ethylenediamine [4] are the starting compounds for the synthesis of inorganic ceramics, which are used as electrocatalysts for the reduction of oxygen. It was shown that mixed-metal Cu–Co and Ni–Cu oxide thin films can be prepared starting from molecular heterometallic cubane-type precursors [5].

An important requirement for heterometallic molecules used as the starting compounds for the generation of the target materials is that the ratio between metals should remain unchanged during thermolysis. The complexes $Li(H_2O)M(N_2H_3CO_2)_3]{\cdot}0.5H_2O$ (M = Co or Ni), whose thermolysis affords materials of the composition $LiMO_2$ [6], are of interest in this respect. Recently, we have shown that the thermal decomposition (400–500 °C) of the heterometallic coordination polymer $[Li_2Co_2(Piv)_6(\mu\text{-}L)_2]_n$ (**1**, L = 2-amino-5-methylpyridine, Piv is the pivalate anion) and the molecular complex $Li_2Co_2(Piv)_6(NEt_3)_2$, which were used as the starting precursors, gave $LiCoO_2$ [7] in almost quantitative yield.

The aim of the present study was to search for new molecular systems, which can be used as molecular precursors for lithium cobaltate and nickelate $LiMO_2$ in the mild thermolysis. It is necessary that the organic components of the selected heterometallic complexes should be easily eliminated with the ratio between metals remaining unchanged in the final product.

2. Experimental

2.1. Synthesis

Commercial reagents and solvents (MeCN, EtOH, THF, and DME) were used without additional purification. The starting complexes

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* Corresponding author. Tel.: +7 495 955 4817; fax: +7 495 952 1279.
E-mail address: mkiskin@igic.ras.ru (M. Kiskin).

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$Co_2(Piv)_4(2,4\text{-Lut})_2$, $Ni_9(OH)_6(Piv)_{12}(HPiv)_4$, and $Ni_2(H_2O)(Piv)_4(2,2'\text{-bpy})_2$ were synthesized according to procedures described previously [8–10]. Commercial *tert*-butylacetic acid (Acros organics), LiOH (Alfa Aesar), 2,2′-dipyridyl (Alfa Aesar), and 2,4-lutidine (Acros organics) were used for the synthesis of new compounds.

2.1.1. $Li_2Co_2(Piv)_6(2,4\text{-Lut})_2$ (**2**)

Tetrahydrofuran (30 mL) was added to a mixture of $Co_2(Piv)_4(2,4\text{-Lut})_2$ (0.5 g, 0.68 mmol) and LiPiv (0.15 g, 1.35 mmol) (LiPiv was synthesized by the metathesis reaction of LiOH with HPiv). The reaction mixture was heated at 60 °C for 30 min. The resulting violet solution was filtered, concentrated to 10 mL, and cooled to room temperature. The violet crystals suitable for X-ray diffraction that precipitated after 24 h were separated from the solution by decantation, washed with cold THF, and dried in air. The yield of compound **2** was 0.62 g (95%). *Anal.* Calc. for $C_{44}H_{72}Co_2Li_2N_2O_{12}$ (%): C, 55.5; H, 7.6; N, 2.9. Found: C, 55.5; H, 7.5; N, 3.0%. IR (KBr, cm^{-1}): 2964 s, 2924 m, 2872 m, 1652 m, 1608 s, 1576 s, 1564 s, 1484 s, 1460 m, 1420 s, 1400 s, 1360 s, 1300 m, 1260 m, 1224 s, 1176 v.w, 1100 w, 1028 m, 928 w, 904 w, 892 w, 832 m, 792 s, 756 w, 668 v.w, 616 s, 576 m, 544 v.w, 472 s, 448 s, 432 s.

2.1.2. $Li_2Co_2(O_2CCH_2Bu^t)_6(2,4\text{-Lut})_2$ (**3**)

A solution of 2,4-lutidine (0.18 g, 1.68 mmol) in ethanol (50 mL) was added to a mixture of $CoCl_2{\cdot}6H_2O$ (0.4 g, 1.68 mmol) and $LiO_2CCH_2Bu^t$ (0.41 g, 3.36 mmol) ($LiO_2CCH_2Bu^t$ was synthesized by the metathesis reaction of LiOH with $HO_2CCH_2Bu^t$). The reaction mixture was heated at 80 °C for 40 min. The resulting green–blue solution was filtered and concentrated to dryness. Acetonitrile (30 mL) was added to the precipitate, and then $LiO_2CCH_2Bu^t$ (0.205 g, 1.68 mmol) was added. The reaction mixture was heated at 80 °C for 30 min. The resulting violet solution was filtered, concentrated to 20 mL, and cooled to room temperature. The violet crystals suitable for X-ray diffraction that precipitated after 24 h were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **3** was 0.69 g (80%). *Anal.* Calc. for $C_{50}H_{84}Co_2Li_2N_2O_{12}$ (%): C, 57.9; H, 8.2; N, 2.7. Found: C, 57.8; H, 8.0; N, 2.7%. IR (KBr, cm^{-1}): 2960 s, 2904 m, 2868 m, 1668 w, 1624 s, 1616 s, 1564 s, 1508 w, 1476 m, 1452 m, 1432 m, 1420 m, 1932 s, 1364 m, 1296 m, 1272 w, 1232 w, 1196 w, 1176 v.w, 1152 v.w, 1136 v.w, 1044 w, 1024 w, 928 v.w, 912 v.w, 836 w, 804 w, 736 w, 648 w, 632 w, 548 v.w, 464 m, 444 w, 416 v.w.

2.1.3. $Li_2Ni_2(Piv)_6(DME)_2$ (**4**)

Dimethoxyethane (20 mL) was added to a mixture of $Ni_9(OH)_6(Piv)_{12}(HPiv)$ (0.4 g, 0.17 mmol) and LiPiv (0.17 g, 1.54 mmol). The reaction mixture was heated at 80 °C for 30 min. The resulting green solution was filtered, concentrated to 10 mL, and cooled to room temperature. The green crystals suitable for X-ray diffraction that precipitated after 24 h were separated from the solution by decantation, washed with cold DME, and dried in air. The yield of compound **4** was 0.64 g (90%). *Anal.* Calc. for $C_{38}H_{74}Li_2Ni_2O_{16}$ (%): C, 49.7; H, 8.1. Found: C, 49.7; H, 8.0%. IR (KBr, cm^{-1}): 2956 s, 2928 m, 2864 m, 2836 w, 1684 w, 1664 m, 1624 s, 1584 s, 1572 s, 1536 s, 1484 s, 1460 m, 1412 s, 1356 s, 1280 w, 1228 s, 1196 w, 1168 v.w, 1120 m, 1096 s, 1076 s, 1028 m, 1016 m, 940 w, 908 m, 892 m, 868 s, 836 w, 812 w, 796 s, 612 s, 576 w, 536 w, 468 s, 428 s, 408 s.

2.1.4. $Li_2Ni_2(Piv)_6(2,2'\text{-bpy})_2$ (**5**)

2.1.4.1. Method A. Acetonitrile (30 mL) was added to a mixture of $Li_2Ni_2(Piv)_6(DME)_2$ (**4**) (0.5 g, 0.54 mmol) and 2,2′-dipyridyl (0.17 g, 1.08 mmol). The reaction mixture was heated at 80 °C for 30 min. The resulting green solution was filtered, concentrated to 10 mL, and cooled to room temperature. The green crystals suitable for X-ray diffraction that precipitated after 24 h were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **5** was 0.51 g (90%). *Anal.* Calc. for $C_{50}H_{70}Li_2N_4Ni_2O_{12}$ (%): C, 57.2; H, 6.7; N, 5.3. Found: C, 57.2; H, 6.5; N, 5.2%. IR (KBr, cm^{-1}): 2960 s, 2928 m, 2868 m, 1608 s, 1560 s, 1536 m, 1484 s, 1476 s, 1460 m, 1444 m, 1432 s, 1416 s, 1372 m 1356 m, 1312 w, 1284 v.w, 1224 s, 1172 w, 1156 w, 1104 v.w, 1056 w, 1024 w, 908 m, 888 m, 816 w, 796 m, 768 s, 736 m, 656 m, 636 w, 604 s, 564 w, 536 v.w, 464 s, 448 s, 416 s.

2.1.4.2. Method B. Acetonitrile (35 mL) was added to a mixture of $Ni_2(H_2O)(Piv)_4(2,2'\text{-bpy})_2$ (0.4 g, 0.55 mmol) and LiPiv (0.12 g, 1.1 mmol). The reaction mixture was heated at 80 °C for 30 min. The resulting green solution was filtered, concentrated to 15 mL, and cooled to room temperature. The green crystals suitable for X-ray diffraction that precipitated after 24 h were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **5** was 0.52 g (90%). *Anal.* Calc. for $C_{50}H_{70}Li_2N_4Ni_2O_{12}$ (%): C, 57.2; H, 6.7; N, 5.3. Found: C, 57.1; H, 6.6; N, 5.2%. IR (KBr, cm^{-1}): 2960 s, 2928 m, 2868 m, 1608 s, 1560 s, 1536 m, 1484 s, 1476 s, 1460 m, 1444 m, 1432 s, 1416 s, 1372 m 1356 m, 1312 w, 1284 v.w, 1224 s, 1172 w, 1156 w, 1104 v.w, 1056 w, 1024 w, 908 m, 888 m, 816 w, 796 m, 768 s, 736 m, 656 m, 636 w, 604 s, 564 w, 536 v.w, 464 s, 448 s, 416 s.

2.2. Methods

The spectra were measured on a Specord M-80 IR spectrometer in KBr pellets. The elemental analysis was carried out on a Carlo Erba instrument. The magnetochemical measurements were performed on a Quantum Design MPMS-5S SQUID magnetometer in the temperature range of 2–300 K in a magnetic field of up to 5 kOe. The calculated molar magnetic susceptibility χ was corrected for the diamagnetic contribution. The effective magnetic moment was calculated by the formula $\mu_{\text{eff}} = (8\chi T)^{1/2}$.

2.3. X-ray data collection

The X-ray data sets for complexes **2** and **3** were collected on a Bruker SMART APEX II diffractometer equipped with a CCD camera and a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å) [11]. The X-ray diffraction study of complexes **4** and **5** was carried out on an Enraf Nonius CAD-4 diffractometer (graphite monochromator, λ = 0.71073 Å, ω-scanning technique, the scan step was 0.3°, the exposure time per frame was 10 s) according to a standard technique [12]. Semi-empirical absorption corrections for all complexes were applied [13]. The structures were solved by direct methods and using Fourier techniques and were refined by the full-matrix least squares against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The *tert*-butyl substituents at the carboxylate groups in **4** and **5** are partially disordered. The positions of all methyl carbon atoms in the disordered CMe_3 fragments were located in difference Fourier maps and refined with occupancies of 0.660(9) and 0.340(9) for the *tert*-butyl group at the atom C(2) and 0.611(5) and 0.389(5) at the atom C(7) for **4** and with occupancies of 0.809(7) and 0.191(7) for the *tert*-butyl group at the atom C(7) for **5**. The hydrogen atoms of the carbon-containing ligands in compounds **2**–**5** were positioned geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX97 program package [14]. The crystallographic parameters and the refinement statistics are given in Table 1.

The X-ray powder diffraction analysis of the solid products of the decomposition in air was carried out on a G670 (HUBER) Guinier camera using Cu Kα1 radiation. The X-ray powder diffraction analysis of the solid products of the decomposition under an inert