Letters to the Editor

Complexes of lanthanide(II) diiodides with isopropylamine

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All presently known molecular compounds of divalent neodymium, dysprosium, and thulium, whose chemistry has intensely been developed in the recent decade, contain THF or DME molecules as the coordinatively bound ligand.[1] The total number of these complexes is at most 17. They are mainly thulium derivatives,[2] and only four complexes, namely, $LnI_2(THF)_5$ and $LnI_2(DME)_3$, are the neodymium[2b,3,4] and dysprosium[2b,4] compounds. Attempts to synthesize the complexes with other ligands, such as NH_3,[2b] HMFA,[5] py,[6] MeCN,[7] and PhCN (see Ref. 8), were unsuccessful because of easy oxidation of the active bivalent metal with these compounds.

When studying the chemical behavior of LnI_2 (Ln = Nd, Dy, Tm) in different media,[2] we have unexpectedly found that isopropylamine, in spite of the presence of the reactive NH groups, forms stable complexes with these salts and their Sm, Eu, and Yb analogs. The dissolution of LnI_2 in isopropylamine gives colored solutions (violet for Nd and Dy, emerald-green for Sm and Tm, salad-green for Eu, and greenish-yellow for Yb). After the solvent was removed from these solutions *in vacuo* or under deep cooling, the $LnI_2(Pr^iNH_2)_x$ complexes (x = 4 (Sm, Eu, Dy, Tm, Yb); x = 5 (Nd)) were isolated as colored crystalline substances decomposing on heating in a sealed capillary at 68—74 °C (Nd), 131—132 °C (Sm), >90 °C (Eu), 125—127 °C (Dy), >115 °C (Tm), and >90 °C (Yb). The elemental analysis and IR spectroscopy data correspond to the proposed formulas. The X-ray diffraction analyses of $EuI_2(Pr^iNH_2)_4$ (**1**) and $TmI_2(Pr^iNH_2)_4$ (**2**) showed that both the complexes have structures of a tetragonal bipyramid. In a molecule of **2** the apical positions are occupied by the I^- ions (Tm—I bond lengths are 3.1325(3) and 3.1325(3) Å), whereas in a molecule of **1** these positions are occupied by the I^- ion and the N atom (Eu—I bond lengths are 3.2850(3) and 3.2860(3) Å). The divalent state of the metal in the complexes is confirmed by their UV-vis spectra containing bands characteristic of the corresponding Ln^{2+} ions, as well as by magnetic measurements (μ_{eff} (293 K)/μ_B = 2.7 (Nd); 3.4 (Sm); 7.4 (Eu); 4.1 (Tm); the Yb complex is diamagnetic) and chemical properties.

The solubility of LnI_2 in isopropylamine and stability of solutions are similar to the corresponding parameters of the solutions in THF. The decomposition of the solutions, *i.e.*, oxidation of metals with amine, resulting in the formation of amides $(Pr^iNH)LnI_2(Pr^iNH_2)_y$ (y = 4 (Nd), y = 3 (Dy)), is completed within 30 min at room temperature in the case of Nd, while for Dy this time is 1 day. The amide/amine complexes were characterized by elemental analyses and IR spectra. Solutions of other

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iodides are stable for infinitely long time. Other primary amines ($MeNH_2$, $PrNH_2$, Bu^tNH_2, $PhNH_2$) react rapidly with LnI_2, preventing the formation of the solutions and corresponding complexes. The found ability of lanthanide(II) diiodides to dissolve in isopropylamine without changing the oxidation state provide new challenges for their use in organic synthesis.

IR spectra of samples (as suspensions in Nujol between KBr plates) were recorded on a Specord M-75 instrument. Magnetic measurements were carried out using an earlier developed procedure.[9]

Diiodopentakis(isopropylamine)neodymium(II) was prepared by the dissolution of NdI_2 (0.15 g, 0.38 mmol) in isopropylamine (10 mL) at −30 °C. The solution was filtered and concentrated to 3 mL, removing the solvent *in vacuo*. The precipitated dark violet crystals of $NdI_2(Pr^iNH_2)_5$ were decanted and dried *in vacuo* at room temperature for 5 min. The yield was 0.11 g (42%), m.p. 68—74 °C (decomp.). IR (ν/cm^{-1}): 3464, 3166, 3084, 1569, 1488, 1395, 1208, 1156, 794, 460. Found (%): Nd, 20.79; I, 34.58. $C_{15}H_{45}I_2N_5Nd$. Calculated (%): Nd, 20.83; I, 34.80. μ_{eff} (293 K) 2.7 μ_B.

Diiodotetrakis(isopropylamine)dysprosium(II). Under the previous experimental conditions, $DyI_2(Pr^iNH_2)_4$ was prepared in a yield of 0.17 g (26%) from DyI_2 (0.42 g, 1.01 mmol) and isopropylamine (10 mL) as a finely crystalline dark violet substance with m.p. 125—127 °C (decomp.). IR (ν/cm^{-1}): 3470, 3170, 3085, 1584, 1569, 1206, 1016, 939, 809, 461.

Diiodotetrakis(isopropylamine)samarium(II) was synthesized by stirring of SmI_2 (1.24 g, 3.07 mmol) in isopropylamine (15 mL) at room temperature for 20 min. The dark green solution that formed was filtered and concentrated to 5 mL, and the precipitated powder was decanted and dried *in vacuo*. The yield of $SmI_2(Pr^iNH_2)_4$ was 0.21 g (11%), m.p. 131—132 °C (decomp.). IR (ν/cm^{-1}): 3477, 3165, 3073, 1585, 1567, 1487, 1394, 1206, 1156, 1010, 978, 940, 808, 795, 460. Found (%): Sm, 23.15; I, 39.81. $C_{12}H_{36}I_2N_4Sm$. Calculated (%): Sm, 23.47; I, 39.62. μ_{eff} (293 K) = 3.4 μ_B.

Diiodotetrakis(isopropylamine)thulium(II) (2) was prepared similarly from TmI_2 (0.99 g, 2.33 mmol) as dark green crystals. The yield was 1.015 g (80%), m.p. > 115 °C (decomp.). IR (ν/cm^{-1}): 3465, 3161, 3073, 1587, 1569, 1488, 1394, 1261, 1207, 1155, 1031, 938, 807, 460. Found (%): Tm, 25.09; I, 38.78. $C_{12}H_{36}I_2N_4Tm$. Calculated (%): Tm, 25.55; I, 38.39. μ_{eff} (293 K) = 4.1 μ_B.

Diiodotetrakis(isopropylamine)europium(II) (1). Compound **1** (0.46 g, 83%) was prepared from EuI_2 (0.35 g, 0.86 mmol) and isopropylamine (15 mL), m.p. 90—95 °C (decomp.). IR (ν/cm^{-1}): 3477, 3161, 3074, 1585, 1569, 1488, 1394, 1261, 1205, 1156, 1048, 1022, 979, 941, 802, 458. Found (%): Eu, 23.60; I, 38.99. $C_{12}H_{36}EuI_2N_4$. Calculated (%): Eu, 23.66; I, 39.52. μ_{eff} (293 K) = 7.4 μ_B.

Diiodotetrakis(isopropylamine)ytterbium(II). Greenish-yellow diamagnetic crystals of $YbI_2(Pr^iNH_2)_4$ were prepared from YbI_2 (0.412 g, 0.972 mmol) and isopropylamine (7 mL) in a yield of 0.24 g (37 %). At 200 °C the crystals turn yellow. IR (ν/cm^{-1}): 3473, 3161, 3073, 1584, 1570, 1488, 1394, 1208, 1158, 1015, 938, 809, 462. Found (%): Yb, 26.12. $C_{12}H_{36}I_2N_4Yb$. Calculated (%): Yb, 26.09.

Synthesis of the $(Pr^iNH)DyI_2(Pr^iNH_2)_3$ complex. A solution of $DyI_2(Pr^iNH_2)_4$ in isopropylamine (9 mL) was stored for 2 days at room temperature. The solution turned colorless. The solution was filtered, the solvent was removed *in vacuo*, and the remaining colorless crystals were dried *in vacuo* for 5 min. The yield was 0.34 g (75%), m.p. 132—136 °C (decomp.). IR (ν/cm^{-1}): 3281, 3219, 1562, 1160, 1030, 940, 811, 530, 478. Found (%): Dy, 25.09. $C_{12}H_{35}DyI_2N_4$. Calculated (%): Dy, 24.93.

Synthesis of the $(Pr^iNH)NdI_2(Pr^iNH_2)_3$ complex. A solution of $NdI_2(Pr^iNH_2)_5$ (0.19 g, 0.48 mmol) in isopropylamine (11 mL) was stirred for 50 min at room temperature until the solution turned light blue. The solution was filtered, volatiles were removed *in vacuo*, and the remaining light blue oil was dried *in vacuo* for 10 min at 30—40 °C and washed with hexane. The yield of $(Pr^iNH)NdI_2(Pr^iNH_2)_4$ was 0.24 g (73%), m.p. 55 °C (decomp.). IR (ν/cm^{-1}): 3280, 3217, 1562, 1245, 1160, 1030, 940, 807, 525, 478. Found (%): Nd, 21.03. $C_{15}H_{44}I_2N_5Nd$. Calculated (%): Nd 20.83. μ_{eff} (293 K) = 3.6 μ_B.

X-ray diffraction study. Crystals of compounds **1** and **2** were prepared by slow evaporation of the solvent *in vacuo* at room temperature. X-ray diffraction studies were carried out on a Smart Apex diffractometer (graphite monochromator, Mo-Kα radiation, φ-ω scan mode). Absorption was applied by the SADABS program.[10] The structures were solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms using the SHELXTL program.[11] Hydrogen atoms were placed in geometrically calculated positions and refined isotropically by the riding model.

Crystals of complex **1**, $C_{12}H_{36}EuI_2N_4$, at 100 K are orthorhombic, space group $P2(1)2(1)2(1)$, a = 12.4537(6) Å, b = 12.7147(6) Å, c = 14.3394 Å, V = 2270.6(2) Å^3, Z = 4, d_{calc} = 1.879 g cm^{-3}, μ = 5.479 mm^{-1}, 16393 measured reflections of which 3555 reflections (R_{int} = 0.0219) were independent with $I > 2\sigma(I)$, R_1 = 0.0142 against $I > 2\sigma(I)$, wR_2 = 0.0340 for all data; the absolute structure parameter was 0.005(10).

Crystals of complex **2**, $C_{12}H_{36}I_2N_4Tm$, at 100 K are monoclinic, space group $P2(1)/c$; a = 6.9397(6) Å, b = 15.925(1) Å, c = 10.0311(8) Å, β = 93.783(2)°, V = 1106.2(2) Å^3, Z = 2, d_{calc} = 1.979 g cm^{-3}, μ = 6.798 mm^{-1}, 5463 measured reflections of which 1732 reflections (R_{int} = 0.0249) were independent with $I > 2\sigma(I)$, R_1 = 0.0266 against $I > 2\sigma(I)$, wR_2 = 0.0729 for all data.

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