Letters to the Editor

Synthesis of lutetium octaalkylthiotetraazaporphyrin complexes

V. N. Nemykin, N. A. Kostromina, and S. V. Volkov*

Institute of General and Inorganic Chemistry,
32-34 prosp. Palladina, 252680 Kiev-142, Ukraine.
Fax: +7 (044) 444 3070

Tetraazaporphyrins are aza-analogs of porphyrins and attract significant interest as catalysts and semiconductors.[1] However, although significant numbers of papers has been devoted to the chemistry of tetraazaporphyrins and their metallocomplexes, until the present time, except for the synthesis of lutetium bis(octaoctyltetraazaporphyrinate),[2] there has been no information on lanthanide complexes with tetraazaporphyrin ligands. At the same time, the nearest analogs of tetraazaporphyrins, *viz.*, phthalocyanine complexes of lanthanides (which exist as complexes with a metal to ligand ratio of 1:1 or 1:2), are widely used in electrochromic devices.[3] Starting from the corresponding metal-free tetraazaporphyrin,[4] we have synthesized lutetium monooctaalkylthiotetraazaporphyrinates $TAP(RS)_8Lu(OAc)$ (**1a**,**b**), where R = Et (**a**) and $C_{10}H_{21}$ (**b**), using a scheme previously applied by us to the synthesis of monophthalocyanine complexes of lanthanides.[5] The prepared compounds were synthesized by the reaction of metal-free tetraazaporphyrin and lutetium acetate (molar ratio 1:3) in the presence of a strong base in DMSO at ambient temperature for 30 min. Then the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was separated, dried over sodium sulfate, and chromatographed on a column of alumina using sequential elution with benzene and ethanol. The ethanol fraction was pooled and evaporated. The yields were *ca.* 80 %.

The synthesized compounds are green crystals, readily soluble in many organic solvents. It is known[6] that in the long-wave region of the electronic absorption spectra (EAS) of metal-free octaalkylthiotetraazaporphyrins in toluene three bands at 709, 637, and 515 nm (inten-

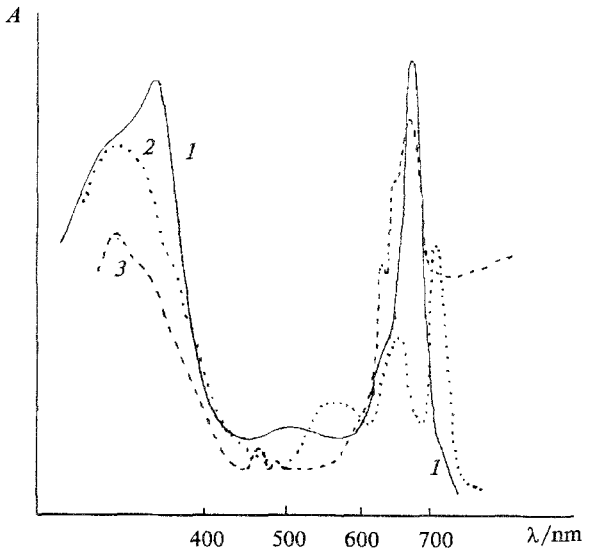

Fig. 1. EAS of **1a** (*1*) and the corresponding metal-free compound (*2*) (in hexane), and the bis-complex from Ref. 2 (*3*) (in cyclohexane).

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sity ratios 1.9:1.33:1.0) are observed. Like in the case of the well-studied phthalocyanine compounds, the formation of the complex with the lutetium ion leads to a dramatic change in the long-wave region of EAS. Instead of the bands at 709 and 637 nm, bands at 672 (**a**) and 673 (**b**) nm, respectively, arose; this fact, is probably related to degeneration of the HOMO in the complex due to the change in symmetry of the ligand from D_{2h} to D_{4h}. The bands have vibrational satellites at 608 and 610 nm, respectively. The band at 515 nm undergoes a hypsochromic shift and is observed at 495 and 497 nm, respectively. The ratio of band intensities also changes significantly (2.56:1.0:0.5 (**a**) and 3.25:1.0:0.44 (**b**)). The EAS of complex (**a**) and those of the original metal-free compound and the previously prepared lutetium bis(octaoctylthioporphyrinate)[2] are presented in Fig. 1. The absence of a signal in the ESR spectra (in comparison to the bis-complex, which has a signal with $g = 2.0033$), and the presence of the acetate group (IR and NMR data) along with the described synthetic route (which assists mono-complex formation) suggest the proposed formulae for the synthesized compounds.

References

1. *Phthalocyanines: Properties and Application*, Ed. C. C. Leznoff and A. B. P. Lever, VHC. New-York, 1989, **1**, **2**.
2. G. Ricciardi, F. Leij, and F. Bonosi, *Chem. Phys. Lett.*, **215**, 541.
3. K. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, 1980, **32**, 67.
4. C. J. Schram and B. M. Hoffman, *Inorg. Chem.*, 1980, **19**, 383.
5. N. B. Subbotin, L. G. Tomilova, N. A. Kostromina, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1986, **56**, 297 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
6. G. P. Shaposhnikov, V. I. Kulinich, and R. P. Smirnov, *Khim. Geterosikl. Soedin.*, 1986, 603 [*Chem. Heterocycl. Compd.*, 1986 (Engl. Transl.)].

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Palladium catalyzed cross coupling of diaryliodonium salts with copper acetylide

E. V. Luzikova, L. I. Sukhomlinova, T. P. Tolstaya, N. A. Bumagin, and I. P. Beletskaya*

M. V. Lomonosov Moscow State University, Department of Chemistry,
119899 Moscow, Vorobjovy gory.
Fax: +7 (095) 939 0220

The reaction of copper acetylides with aryl halides needs rather drastic conditions (prolonged refluxing in pyridine or DMF).[1,2] This reaction proceeds at a high rate at ambient temperature in the presence of Pd complexes and sodium iodide in acetone.[3]

We found that copper phenylacetylide reacts with bis(*m*-nitrophenyl)iodonium salts in DMF or acetone in the presence of NaI and Pd complexes. It should be noted that this reaction may also be carried out in aqueous media using $NaI \cdot 2H_2O$. At the first stage, the reaction of copper phenylacetylide with diaryliodonium salt rapidly affords *m*-nitrotolan and *m*-iodonitrobenzene:

$$(m\text{-}NO_2C_6H_4)_2IHSO_4 + PhC{\equiv}CCu \xrightarrow{i} PhC{\equiv}CC_6H_4NO_2\text{-}m + m\text{-}NO_2C_6H_4I$$

98% 96%

i. $PdCl_2$, $NaI \cdot 2H_2O$, 20 °C, 15 min.

At the second stage, copper phenylacetylide reacts somewhat more slowly with *m*-iodonitrobenzene:

$$m\text{-}NO_2C_6H_4I + PhC{\equiv}CCu \xrightarrow{i} PhC{\equiv}CC_6H_4NO_2\text{-}m$$

i. $PdCl_2$, $NaI \cdot 2H_2O$, 20 °C, 1 h.

It was shown independently that copper phenylacetylide reacts quantitatively with *m*-iodonitrobenzene in the presence of $PdCl_2(PPh_3)_2$ and $NaI \cdot 2H_2O$ in aqueous acetone at ambient temperature within 1 h.

$(m\text{-}NO_2C_6H_4)_2IOCOCF_3$ (0.5 mmol) was dissolved in acetone (2 mL) under Ar in a flask equipped with a magnetic stirrer and a reflux condenser. Copper phenylacetylide (1.05 mmol), $NaI \cdot 2H_2O$ (1.05 mmol), and a 0.1 *M* aqueous solution of $PdCl_2$ (0.1 mL, 0.01 mmol) were added to the solution. The reaction mixture was stirred at 20 °C for 1 h, then it was ex-

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