

Synthesis of 5-Isothiocyanato-1,10-phenanthroline

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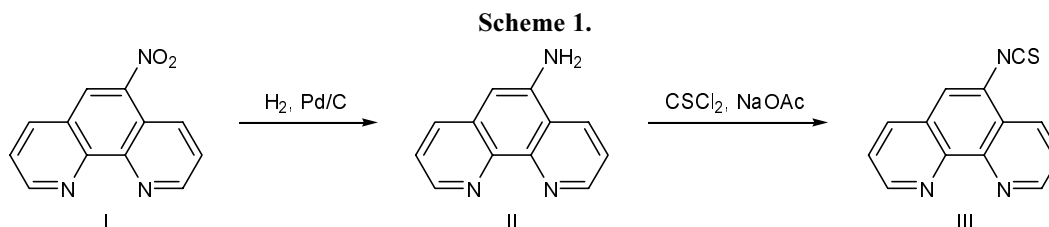
Abstract—Reduction of 5-nitro-1,10-phenanthroline with hydrogen over Pd/C, followed by the treatment of 1,10-phenanthroline-5-amine with thiophosgene in the presence of sodium acetate, gave 5-isothiocyanato-1,10-phenanthroline which is a thermally stable highly reactive ligand capable of quantitatively forming covalently bonded nanohybrid structures in a system transition metal complex–silica under mild conditions.

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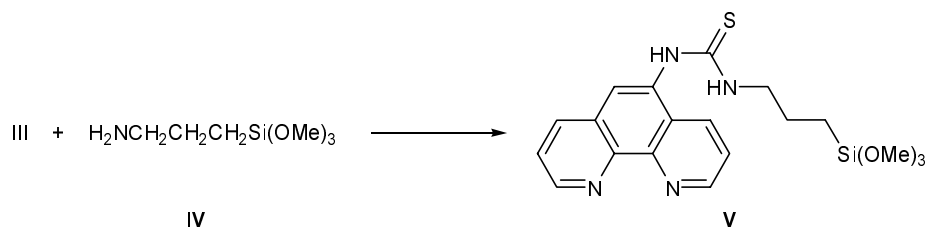
Most transition metals with 1,10-phenanthroline form thermally and chemically stable complexes [1]. Diversity of electron transitions in transition metal compounds (due to accessibility of their *d* and *f* electron shells) in combination with the conjugated π -electron system of 1,10-phenanthroline gives rise to a number of interesting photophysical, photochemical, and electrochemical properties of such complexes [2–4]. Practical applications of these complexes imply their immobilization on a polymeric organic or inorganic matrix. The stability of films, coatings, fibers, sol–gel glasses, and other optical materials is determined exclusively by the possibility of chemical bonding between the components, i.e. formation of a covalent bond by the ligands (or one ligand) with the matrix [5, 6]. Therefore, synthesis of 1,10-phenanthroline derivatives having reactive substituents in positions 3–8 becomes important. At present, the most promising is the reduction of 5-nitro-1,10-phenanthroline (**I**) to 1,10-phenanthroline-5-amine (**II**). Condensation of the latter at the amino group with alkoxy-silyl isocyanates or acryloyl chlorides gave rise to a series of composite materials in the systems consisting

of phenanthroline transition metal complex and silica [7–9] or poly(acrylamide) [10]. However, the reliability of the reported results casts some doubt. On the one hand, the stability of amine **II** is not obvious; at least, we failed to isolate it from solution in the pure form. Analogous results were obtained previously by other authors [11]. On the other hand, amine **II** is a very weak base, and replacement of both hydrogen atoms in the amino group via reactions with weakly active aliphatic isocyanates to give bis-urea derivatives [7, 8, 12] seems to be improbable.

Taking the above state into account, we have developed a procedure for the synthesis of 5-isothiocyanato-1,10-phenanthroline (**III**) which is a thermally stable heterocyclic isothiocyanate possessing enhanced reactivity. Unfortunately, we failed to reproduce with an acceptable yield the described synthesis of amine **II** via reduction of nitro derivative **I** with tin(II) chloride [13] or hydrazine hydrate in the presence of palladium catalyst [8, 14]. Therefore, we performed catalytic hydrogenation of compound **I** over Pd/C in dimethylacetamide. Amine **II** thus obtained was brought into subsequent transformation without isolation. Its struc-



Scheme 2.



ture was confirmed by the ¹H NMR spectrum; for this purpose, a sample of 5-nitro-1,10-phenanthroline (**I**) was hydrogenated in dimethylformamide-*d*₇.

Amine **II** was converted into isocyanate **III** according to a novel procedure by treatment with thiophosgene in the presence of sodium acetate (Scheme 1). Isothiocyanate **III** is stable up to 200°C and is quite reactive toward nucleophiles. For example, it quantitatively reacted at 0°C with primary and secondary aliphatic and aromatic amines. The reaction of **III** with 3-(trimethoxysilyl)propanamine (**IV**) (which is widely used in sol-gel chemistry) under mild conditions gave the corresponding stable trimethoxysilyl 1,10-phenanthroline derivative, *N*-(1,10-phenanthrolin-5-yl)-*N'*-(3-trimethoxysilylpropyl)thiourea (**V**) (Scheme 2).

Joint hydrolytic polycondensation of tetramethoxysilane with transition metal complexes including molecule **V** as a ligand could give rise to covalently bonded organic-inorganic hybrids in the system phenanthroline transition metal complex-silica.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were measured on a Bruker DPX-300 instrument at 300.13 and 75.5 MHz, respectively, using tetramethylsilane as internal reference. The elemental compositions were determined on a Hewlett-Packard 185-B CHN analyzer. The reaction mixture was analyzed, and the purity of the product was checked, by TLC on Silica gel 60_{F254} plates. Palladium on activated carbon (10% of Pd), thiophosgene, and 3-(trimethoxysilyl)propan-1-amine were commercial products (from Aldrich). 5-Nitro-1,10-phenanthroline (**I**) was synthesized by nitration of 1,10-phenanthroline according to the procedure described in [15].

Reduction of 5-nitro-1,10-phenanthroline (I). A suspension of 2.00 g (8.89 mmol) of compound **I** in 20 ml of dimethylacetamide was subjected to hydrogenation under stirring at room temperature under atmospheric pressure over 400 mg of 10% Pd/C. When the theoretical amount of hydrogen was absorbed

(2 days), the catalyst was filtered off, and the yellow-orange solution was diluted with two volumes of water and was used in further synthesis without isolation of 1,10-phenanthrolin-5-amine (**II**). ¹H NMR spectrum (DMF-*d*₇), δ, ppm: 3.85 br.s (NH₂, H₂O), 7.04 s (1H, 6-H), 7.54 d.d and 7.76 d.d (1H each, 3-H, 8-H, *J*₁ = *J*₂ = 6 Hz), 8.09 d.d and 8.80 d.d (1H each, 4-H, 7-H, *J*₁ = 8, *J*₂ = 1.5 Hz), 8.75 d.d and 9.11 d.d (1H each, 2-H, 9-H, *J*₁ = 5, *J*₂ = 1.5 Hz).

5-Isothiocyanato-1,10-phenanthroline (III). The solution of amine **II** in aqueous dimethylacetamide (see above) was cooled to -5°C, a solution of 1.46 g (17.78 mmol) of sodium acetate in 5 ml of water was added, and a solution of 1.02 g (8.89 mmol) of thiophosgene in 5 ml of acetone was then added dropwise over a period of 10 min under vigorous stirring. After 5 min, the precipitate was filtered off and dried under reduced pressure. The crude product was Soxhlet extracted with methylene chloride overnight. The extract was filtered through a layer of silica gel, the sorbent was washed with CH₂Cl₂-acetone (3:1), and the eluate was evaporated under reduced pressure. The residue was sublimed at 80°C and a residual pressure of 0.01 mm. Yield 1.18 g (56% on the initial nitro compound **I**), pale yellow crystals, mp 182-183°C. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 7.83 d.d and 7.95 d.d (1H each, 3-H, 8-H, *J*₁ = *J*₂ = 7.5 Hz), 8.27 s (1H, 6-H), 8.48 d.d and 8.51 d.d (1H each, 4-H, 7-H, *J*₁ = 8, *J*₂ = 1.5 Hz), 9.12 d.d and 9.22 d.d (1H each, 2-H, 9-H, *J*₁ = 4.5, *J*₂ = 1.5 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 151.6, 151.3 (C², C⁹); 146.8, 145.4, 138.2 (C=S, C^{10a}, C^{10b}); 135.9, 131.9 (C⁴, C⁷); 128.0, 126.7, 125.3 (C^{4a}, C⁵, C^{6a}); 124.1, 123.95, 123.4 (C³, C⁶, C⁸). Found, %: C 65.46, 65.85; H 3.27, 3.02; N 17.77, 17.90. C₁₃H₇N₃S. Calculated, %: C 65.82; H 2.95; N 17.72.

***N*-(1,10-Phenanthrolin-5-yl)-*N'*-(3-trimethoxysilylpropyl)thiourea (V).** A solution of 200 mg (0.84 mmol) of isothiocyanate **III** in 3 ml of anhydrous methylene chloride was added to a solution of 160 mg (0.90 mmol) of amine **IV** in 30 ml of anhydrous pentane under stirring at 0°C. The mixture was stirred

for 10 min at 0°C, and the precipitate was filtered off and washed with 10 ml of anhydrous pentane with protection from atmospheric moisture. Yield quantitative, colorless crystals, mp 169–171°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 0.54 t (2H, CH₂Si, *J* = 7.5 Hz), 1.70 q (2H, CH₂, *J* = 7.5 Hz), 3.39 s (9H, OCH₃), 3.66 q (2H, CH₂N, *J* = 7.5 Hz), 6.56 br.t (1H, CH₂NH, *J* = 7.5 Hz), 7.67 d.d (2H, 3-H, 8-H, *J*₁ = *J*₂ = 1.5 Hz), 8.20 d and 8.45 d (1H each, 4-H, 7-H, *J* = 8 Hz), 8.25 br.s (1H, 5-NH), 9.17 d (2H, 2-H, 9-H, *J* = 7 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 6.7 (CH₂Si); 22.5 (CH₂); 48.1 (CH₂N); 51.0 (OCH₃); 123.7, 123.9, 125.6 (C³, C⁶, C⁸); 126.8, 128.2, 131.9 (C^{4a}, C⁵, C^{6a}); 132.4, 136.4 (C⁴, C⁷); 145.4, 146.7 (C^{10a}, C^{10b}); 150.7, 150.8 (C², C⁹); 182.0 (C=S). Found, %: C 55.07, 54.84; H 6.06, 5.93; N 13.68, 13.27. C₁₉H₂₄N₄O₃SSi. Calculated, %: C 54.81; H 5.77; N 13.46.

REFERENCES

1. Kermak, V. and McKeil, D., *Heterocyclic Compounds*, Elderfield, R.C., Ed., New York: Wiley, 1960, vol. 7. Translated under the title *Geterotsiklicheskie soedineniya*, Moscow: Inostrannaya Literatura, 1965, vol. 7, chap. 4, p. 287.
2. Lo, K.K.-W., Chan-Ming Ng, D., and Chung, C.-K., *Organometallics*, 2001, vol. 20, p. 4999.
3. Tyson, D.S. and Castellano, F.N., *Inorg. Chem.*, 1999, vol. 38, p. 4382.
4. Lo, K.K.-W., Chung, C.-K., and Zhu, N., *Chem. Eur. J.*, 2003, vol. 9, p. 475.
5. Shavaleev, N.M., Moorcraft, L.P., Pope, S.J.A., Bell, Z.R., Faulkner, S., and Ward, M.D., *Chem. Eur. J.*, 2003, vol. 9, p. 5283.
6. Khimich, N.N., Semov, M.P., and Chepik, L.F., *Dokl. Ross. Akad. Nauk*, 2004, vol. 394, p. 636.
7. Kloster, G.M. and Watton, S.P., *Inorg. Chim. Acta*, 2000, vol. 297, p. 156.
8. Binnemans, K., Lenaerts, P., Drisen, K., and Gürller-Walrand, C., *J. Mater. Chem.*, 2004, vol. 14, p. 191.
9. Li, H.R., Lin, J., Fu, L.S., Guo, J.F., Meng, Q.G., Liu, F.Y., and Zhang, H.J., *Micropor. Mesopor. Mater.*, 2002, vol. 55, p. 103.
10. McNamara, K.P., Li, X., Stull, A.D., and Rosenzweir, Z., *Anal. Chim. Acta*, 1998, vol. 361, p. 73.
11. Gelewitz, E.W., Riedeman, W.L., and Klotz, I.M., *Arch. Biochem.*, 1954, vol. 53, p. 411.
12. Li, H.R., Fu, L.S., Lin, J., and Zhang, H.J., *Thin Solid Films*, 2002, vol. 416, p. 197.
13. Crean, C.W., Kavanagh, Y.T., O'Keefe, C.M., Lawler, M.P., Stevenson, C., Davies, R.J.H., Boyle, P.H., and Kelly, J.M., *Photochem. Photobiol. Sci.*, 2002, vol. 1, p. 1024.
14. Lecomte, J.-P., Mesmaeker, A.K.-D., Demeunynck, M., and Lhomme, J., *J. Chem. Soc., Faraday Trans.*, 1993, vol. 89, p. 3261.
15. Smith, C.F. and Cogle, F.W., Jr., *J. Org. Chem.*, 1947, vol. 12, p. 781.