Reactions of benzonitrile with diiodides of neodymium, dysprosium, and thulium

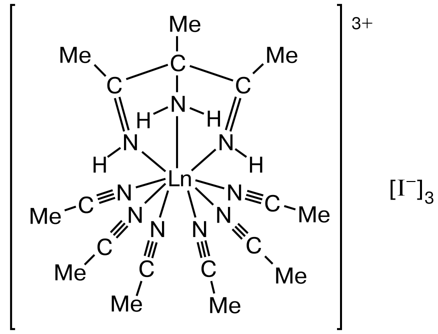
T. V. Balashova,[a] G. V. Khoroshenkov,[a] D. M. Kusyaev,[a] I. L. Eremenko,[b]
*G. G. Aleksandrov,[b] G. K. Fukin,[a] and M. N. Bochkarev[a]**

[a]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603950 Nizhny Novgorod, Russia,
Fax: +7 (831 2) 127497, E-mail: mboch@imoc.sinn.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences,*
31 Leninsky prosp., 119991, Moscow, Russian Federation,
Fax: +7 (095) 954 1279. E-mail: ilerem@igic.ras.ru

The reactions of LnI_2 (Ln = Nd, Dy, Tm) with benzonitrile are accompanied by disproportionation, resulting in the formation of triiodides $LnI_3(PhCN)_4$ and an intractable mixture of monoiodine derivatives LnI(R)R´. Hydrolysis of the mixture gives 2,4,6-triphenyl-1,3,5-tiazine, 2,3,5,6-thetraphenyl-1,4-pyrazine, and 2,4,5-triphenylimidazole. The reaction of dysprosium diiodide with acrylonitrile gives a metal-containing polymer with a molecular weight of 2700. Treatment of the polymer with water results in separation of $DyI_2(OH)(H_2O)_x$ to give metal-free polyacrylonitrile with a molecular weight of 2400.

Key words: acrylonitrile, benzonitrile, dysprosium, neodymium, thulium, triazine, pyrazine, imidazole.

It is known[1] that sodium readily reacts with nitriles inducing a series of transformations that end, after hydrolysis, in the formation of iminonitriles. The weaker reducing agent SmI_2 is inert toward to acetonitrile;[2] however, it promotes the ketone—nitrile reducing cross-coupling.[3] Recently, we found[4] that the diiodides LnI_2 (Ln = Nd (**1**), Dy (**2**), and Tm (**3**)) whose electrode potentials are comparable with those of alkali metals, also readily react with acetonitrile. The reactions produce C—C bonds to give rise to a tridentate ligand of a new type, 3-amino-2,4-diimino-3-methylpentane, which was isolated as cationic complexes with the iodide anion.



The structures of the dysprosium and thulium complexes were determined by X-ray diffraction. This study deals with the reactions of diiodides **1—3** with benzonitrile. Unlike MeCN, this reagent contains no active H atoms.

Results and Discussion

Diiodides **1**, **2**, and **3** readily react with PhCN at room temperature (Scheme 1). As soon as 5 min after mixing of the reactants, the solution acquires a typical dark-red-brown color and most of the starting LnI_2 dissolves. In the case of diiodides **2** and **3**, crystallization from the solution gave the corresponding triiodides coordinated with four benzonitrile molecules, $LnI_3(PhCN)_4$. The dysprosium benzonitrile complex $DyI_3(PhCN)_4$ (**4**), which crystallizes as a solvate with 0.5 PhCN molecules, was studied by single-crystal X-ray diffraction (Fig. 1). The Dy atom in the complex molecule forms a highly distorted pentagonal-bipyramidal coordination in which four N atoms of four benzonitrile groups (Dy—N distances are 2.438—2.475(6) Å) and the I(1) ligand (Dy—I(1), 3.001(5) Å) form the equatorial plane and the other two iodide ligands, I(2) and I(3), are in the axial positions (Dy—I distances are 3.021 and 2.940(5) Å, the Dy—I—Dy angle is 166.63°). The benzonitrile molecule of solvation has C_i crystallographic symmetry and contains a disordered nitrile group, which occupies two equivalent sites in the *para*-positions of the benzene fragment with populations of 0.5. In turn, the benzonitrile molecules of solvation, related to each other by crystallographic axis 2, form short intermolecular N...N contacts (1.55 Å) whose length is close to the length of the typical N—N single bond. Actually, the disorder of benzonitrile molecules

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 789—793, April, 2004.

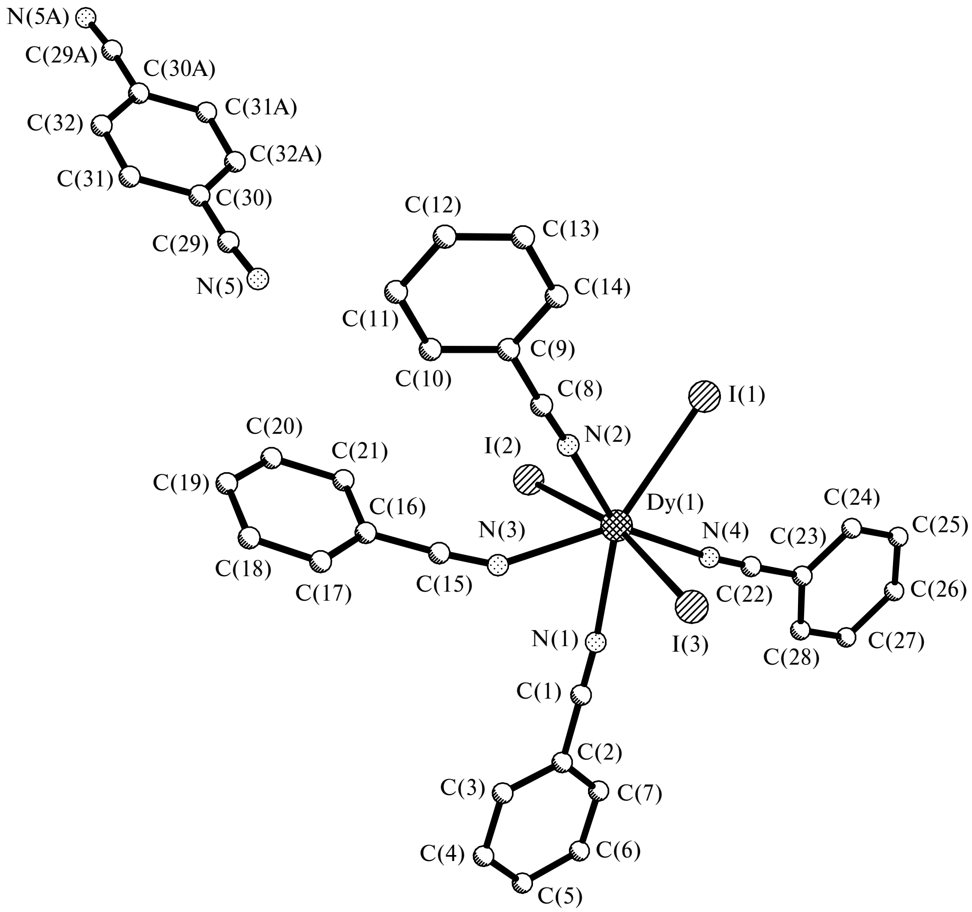
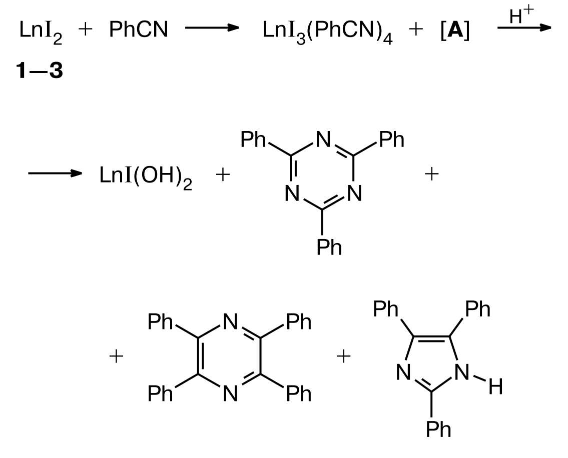


Fig. 1. Structure of complex **4**.

gives rise to the ......NCPhCN...NCPhCN...NCPhCN... chains in the crystal (Fig. 2).

Scheme 1



Ln = Nd (**1**), Dy (**2**), Tm (**3**)

After benzonitrile had been replaced by THF, additional amounts of triiodides were isolated from solutions as tetrahydrofuran complexes $LnI_3(thf)_3$. The overall yields of the triiodides were 42 and 50% (w/w) for **2** and **3**, respectively, indicating a high degree of disproportionation of LnI_2 into LnI_3 and LnI(R)R´. The neodymium derivatives are distinguished by much better solubility than the Dy and Tm analogs. Therefore, the benzonitrile triiodide $NdI_3(PhCN)_4$ has not been isolated upon the reaction with diiodide **1**; however, the tetrahydrofuran complex $NdI_3(thf)_3$ was obtained in a yield of 42% (w/w).

The attempts to isolate the monoiodide derivatives LnI(R)R´ (**A**) in a pure state failed. To identify the organic fragments, these compounds were treated with methanol and then with water. Chromatographic analysis showed that all three iodides are converted into the same set of products, which counts more than ten compounds. Three major compounds were isolated and identified. These were 2,4,6-triphenyltriazine, 2,3,5,6-tetraphenylpyrazine, and 2,4,5-triphenylimidazole. The inorganic part was found to contain hydroxy iodides $LnI(OH)_2(H_2O)_x$, whose molar yield corresponds to the half of LnI_2 taken, *i.e.*, this is in line with the disproportionation stoichiometry.

The yield of triazine decreases appreciably on passing from **1** to **2** and **3**, being equal to 13, 5, and 2 mol. % per

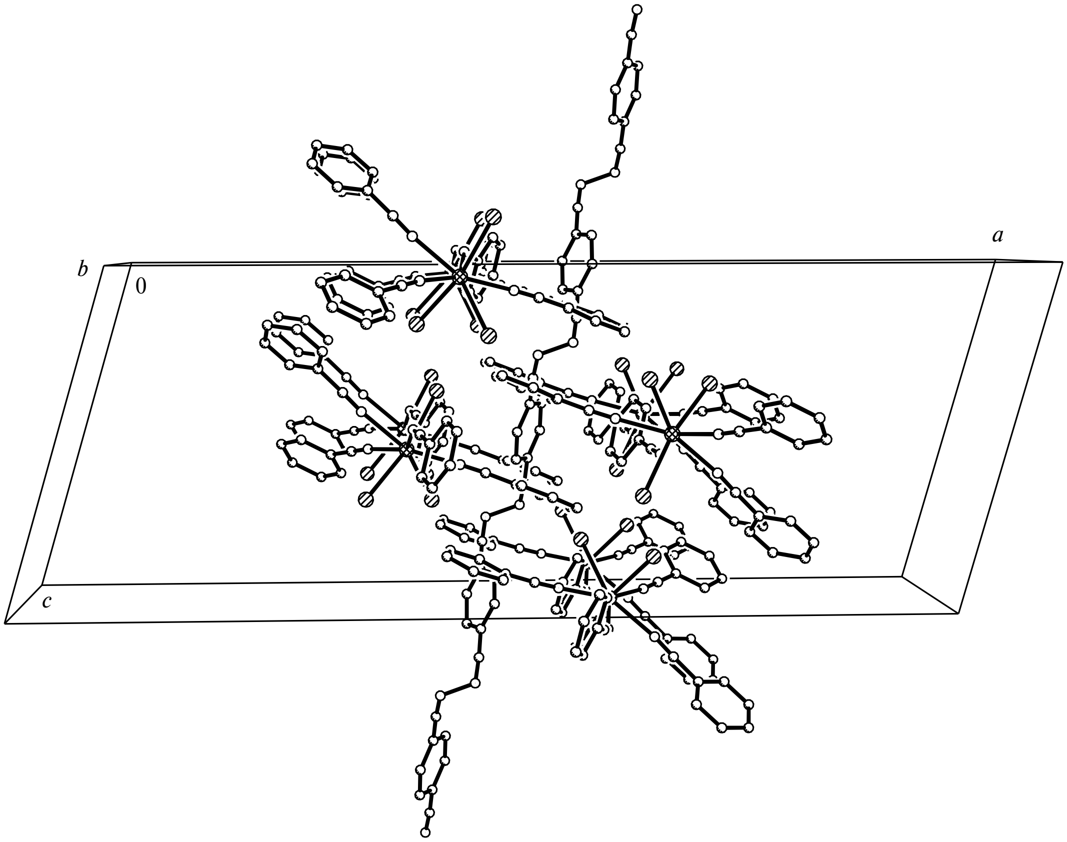


Fig. 2. Crystal cell of complex **4**.

mole of LnI_2, respectively. However, it should be borne in mind that, although the pathway to triazine as well as to other products remains obscure, the process is not catalytic, and with allowance for the most probable reaction stoichiometry (3 LnI_2 : 3 PhCN : $Ph_3C_3N_3$), the yields of triazine would be 39, 15, and 6%. The molar yield of pyrazine also decreases on passing from neodymium iodide (10%) to dysprosium (3%) and thulium salts (2%). Conversely, the highest yield of imidazole (9%) was obtained in the reaction with diiodide **3**. In the case of diiodides **1** and **2**, this product was obtained in 2.4 and 2.1% yields, respectively.

Attempted isolation of free bis(ethylimino)ethylamine from the above-mentioned dysprosium complex $[\{(HN=CMe)_2MeCNH_2\}Dy(MeCN)_6]I_3$ by hydrolysis of the THF complex, $[\{(HN=CMe)_2MeCNH_2\}Dy(thf)_x]I_3$, also resulted in tetramethyl-1,4-pyrazine, 2,3,5,6-$Me_4C_4N_2$, formed in a high yield. Analogous bis(imino)amine complexes might be the precursors of pyrazine in the reactions with benzonitrile.

It is known[5] that acrylonitrile (AN) is a monomer that readily undergoes anionic polymerization on treatment with alkali metals. The reaction of AN with iodide **2** at room temperature without a solvent also affords a polymer, which is liberated as a light-brown powder. Like polyacrylonitrile prepared by the traditional method, this polymer is virtually insoluble in organic solvents, except for DMF. Although the product contains metal chemically bound to the polymeric matrix, it remains unchanged during keeping in air for an indefinitely long time. This is seldom encountered for organic or coordination compounds of lanthanides. The hydrolysis of the polymer results in liberation of $DyI_2(OH)(H_2O)_x$ and the formation of metal-free polyacrylonitrile.

Thus, the study showed that the easily proceeding reactions of diiodides Nd^{II}, Dy^{II}, and Tm^{II} with benzonitrile give rise to nitrogen-containing heterocyclic compounds. Presumably, the reactions of these reducing agents with akyl- and arylnitriles can be successfully used for the synthesis of cyclic and acyclic nitrogen-containing compounds.

Experimental

All operations involved in the synthesis and isolation of the products up to hydrolysis were carried out *in vacuo* using conventional Schlenk equipment. Diiodides **1**, **2**, and **3** were prepared by burning a lanthanide metal and iodine according to a previously developed protocol.[6] The complex $[\{(HN=CMe)_2MeCNH_2\}Dy(MeCN)_6]I_3$ was synthesized as described previously.[4] Benzonitrile was distilled several times over P_2O_5 and, immediately prior to use, treated with a minor amount of NdI_2 (**1**). The required amounts were withdrawn by vacuum recondensation. Commercially available acrylonitrile was washed with dilute H_2SO_4 and then with dilute alkali, dried with $CaCl_2$, and fractionated.

IR spectra were recorded on Specord M-80 and Perkin—Elmer 577 instruments for suspensions in mineral oil, and ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-200 spectrometer. The chromatographic analysis was performed on a Milichrom 1A chromatograph using a 2×64 mm stainless-steel column, and a hexane—THF or $MeOH—H_2O$ mixture as the eluent. The molecular weight of polyacrylonitrile was determined by viscosimetry at 25 °C in DMF. X-ray diffraction analysis of tetraphenylpyrazine was carried out on a Bruker AXS Smart Apex diffractometer.

Reaction of diiodide 1 with benzonitrile. Benzonitrile (20 mL, 0.2 mol) was added with stirring to a powder of compound **1** (3.77 g, 9.5 mmol). Within 5 min, the solution acquired a red-brown color. The solution was concentrated to half its volume, PhCN being removed by condensation *in vacuo*, and 15 mL of THF was added. The finely crystalline bluish-colored precipitate formed after 1 h was separated by decantation, washed with cold THF, and dried *in vacuo* to give 2.56 g (3.45 mmol) of $NdI_3(thf)_3$ (identified by elemental analysis and IR spectroscopy). From the red-brown mother liquor, THF was completely removed and 10 mL of MeOH was added. The resulting crystalline precipitate of 2,4,6-triphenyl-1,3,5-triazine was collected on a sintered funnel, washed with MeOH, and dried in air to give 0.39 g (1.25 mmol) of $C_{21}H_{15}N_3$, m.p. 233 °C (*cf.* Ref. 7: m.p. 233 °C). The structure of the triazine was confirmed by a structural study whose results coincided with published data.[8] After 20 h at ~20 °C, crystals of 2,3,5,6-tetraphenylpyrazine precipitated from the mother liquor. The crystals were separated by filtration, washed with MeOH, and dried to give 0.36 g (0.92 mmol) of $C_{28}H_{20}N_2$, m.p. 252 °C (*cf.* Ref. 9: m.p. 245—246 °C). The structure of the pyrazine was confirmed by a structural study whose results coincided with published data.[10] Methanol was completely removed from the solution and 10 mL of H_2O was added to give a white precipitate. The precipitate was separated by centrifuging and dried to give 2.31 g (5.85 mmol) of $NdI(OH)_2(H_2O)_5$. Found (%): I, 31.78; Nd, 36.79. $H_{12}INdO_7$. Calculated (%): I, 32.12; Nd, 36.50. After 20 h at ~20 °C, crystalline 2,4,5-triphenylimidazole precipitated. The product was collected on a filter, washed with ether, and dried to give 0.07 g (0.23 mmol) of $C_{21}H_{16}N_2$, m.p. 275 °C (*cf.* Ref. 11: m.p. 277 °C). IR (Nujol), ν/cm^{-1}: 1600 m, 1500 w, 1490 m, 1415 w, 1325 w, 1129 m, 1070 w, 1030 w, 969 m, 919 w, 840 w, 765 s, 735 w, 697 s, 495 w. ^1H NMR (200 MHz, THF-d_8), 27 °C, δ: 7.02—7.42 (m, 11 H, PhH); 7.55 (d, 2 H, *J* = 7.1 Hz); 7.93 (d, 2 H, *J* = 7.3 Hz). ^{13}C NMR (50 MHz, THF-d_8, 27 °C), δ: 124.6; 125.6; 126.8; 127.0; 127.2; 127.3; 127.9; 128.0; 128.1; 130.7; 131.8; 135.4; 137.5; 145.4. The ^1H and ^{13}C NMR signals were assigned using a database.[12]

Reaction of diiodide 2 with benzonitrile. Under conditions of the previous experiment, benzonitrile (20 mL, 200 mmol) was added to a powder of compound **2** (4.57 g, 11 mmol). The resulting red-brown solution was concentrated to half its volume, benzonitrile being removed *in vacuo*. After 24 h, colorless rectangular crystals precipitated. These were separated by decantation, washed with benzonitrile, and dried to give 1.8 g (1.88 mmol) of $DyI_3(C_6H_5CN)_4$, m.p. 202 °C. Found (%): Dy, 16.98; I, 39.69. $C_{28}H_{20}DyI_3N_4$. Calculated (%): Dy, 17.0; I, 39.84. IR (Nujol), ν/cm^{-1}: 2250 s, 1590 w, 1290 w, 755 s, 685 s, 550 s. Tetrahydrofuran (15 mL) was added to the red-brown mother liquor. After 1 h, a bluish finely crystalline precipitate was formed. The solution was decanted and the residue was washed with cold THF and dried *in vacuo* to give 1.94 g (2.56 mmol) of $DyI_3(thf)_3$ (identified by elemental analysis and IR spectroscopy). From the red-brown decanted solution, THF was completely removed and 10 mL of MeOH was added. The crystalline precipitate of 2,4,6-triphenyl-1,3,5-triazine (0.17 g, 0.56 mmol) was collected on a filter, washed with MeOH, and dried. The melting point of the product was 233 °C; its IR spectrum was identical to the spectrum of triazine obtained in the previous experiment. On storage of the mother liquor for 24 h at ~20 °C, colorless crystals of 3,5,6-tetraphenylpyrazine precipitated. The crystals were separated by filtration, washed with MeOH, and dried to give 0.03 g (0.37 mmol) of $C_4(C_6H_5)_4N_2$, m.p. 252 °C. The IR and ^1H and ^{13}C NMR spectra of the compound coincide with the corresponding characteristics of the pyrazine obtained in the experiment with diiodide **1**. Metanol was completely removed from the solution, and 10 mL of H_2O was added to the residue. The white-colored precipitate that formed was separated by centrifuging, washed with ether, and dried to give 3.25 g (6.71 mmol) $DyI(OH)_2(H_2O)_{11}$. Found (%): Dy, 31.14; I, 24.22. $H_{24}DyIO_{13}$. Calculated (%): Dy, 31.17; I, 24.34. After 20 h, crystalline 2,4,5-triphenylimidazole precipitated from the organic layer. The precipitate was collected on a filter, washed with ether, and dried to give 0.07 g (0.23 mmol) of $C_{21}H_{16}N_2$, m.p. 275 °C; the IR and ^1H and ^{13}C NMR spectra of the product were similar to those described above. A poorly soluble polymeric product (0.3 g) was isolated from the organic layer. This product could not be identified.

Reaction of diiodide 3 with benzonitrile. The reaction and the isolation and identification of the products were carried out as in the experiment with compound **2**. The reaction of $TmI_2(thf)_5$ (2.0 g, 2.56 mmol) and 15 mL of benzonitrile gave $TmI_3(PhCN)_4$ (0.71 g, 0.74 mmol), $TmI_3(thf)_3$ (0.52 g, 0.68 mmol), 2,4,6-triphenyl-1,3,5-triazine (0.02 g, 0.05 mmol), 2,3,5,6-tetraphenyl-1,4-pyrazine (0.02 g, 0.05 mmol), $TmI(OH)_2(H_2O)_5$ (0.45 g, 1.07 mmol), and 2,4,5-triphenylimidazole (0.07 g, 0.23 mmol).

The complex $TmI_3(PhCN)_4$, m.p. 204 °C. Found (%): Tm, 17.49; I, 39.68. $C_{28}H_{20}I_3N_4Tm$. Calculated (%): Tm, 17.56; I, 39.57. IR (Nujol), ν/cm^{-1}: 2250 s, 1590 w, 1290 w, 755 s, 685 s, 550 s.

The complex $TmI(OH)_2(H_2O)_5$. Found (%): I, 30.74; Tm, 40.19. $H_{12}IO_7Tm$. Calculated (%): I, 30.23; Tm, 40.23. As in the reaction with diiodide **2**, an unidentified polymer (0.2 g) was isolated from the organic layer.

Synthesis of $[\{(HN=CMe)_2MeCNH_2\}Dy(thf)_{3.5}]I_3$. Tetrahydrofuran (50 mL) was added to the light-yellow crystals of $[\{(HN=CMe)_2MeCNH_2\}Dy(MeCN)_6]I_3$ (0.91 g, 0.99 mmol) and the mixture was heated for 1 h at 80 °C. The solid partially dissolved and was converted into a white powder, which was separated centrifugation followed by decantation, washed with cold THF (2×10 mL), and dried *in vacuo* at ~20 °C to give 0.73 g (79.36%) of $[\{(HN=CMe)_2MeCNH_2\}Dy(thf)_{3.5}]I_3$. Found (%): Dy, 17.54; I, 36.05. $C_{28}H_{20}DyI_3N_4$. Calculated (%): Dy, 17.0; I, 39.84. The IR spectrum (Nujol, ν/cm^{-1}) exhibits bands for the $(HN=CMe)_2MeCNH_2$ ligand (3210, 3180, 1660, 1580, 1470, 1390, 1210, 1170, 1110, 870, 860, 800, 720, and 610)[4] and THF (1270, 1090, 1020, and 930), but no absorption bands for the C≡N groups at 2100—2300 cm^{-1}, which were present in the spectrum of the initial complex.

Attempted isolation of $(HN=CMe)_2MeCNH_2$ from $[\{(HN=CMe)_2MeCNH_2\}Dy(thf)_{3.5}]I_3$. The complex $[\{(HN=CMe)_2MeCNH_2\}Dy(THF)_{3.5}]I_3$ (0.68 g, 0.74 mmol) was heated for 1 h in a dynamic vacuum with gradual increase in the temperature from 20 to 195 °C. After heating the sample, the absorption bands of bis(imino)amine were retained in the IR spectrum, and the relative absorption intensity of THF sharply decreased. Water (3 mL) was added to the resulting light-yellow powder, and the mixture thus formed was extracted with ether (2×5 mL). The ether was evaporated under reduced pressure and the residue was sublimed *in vacuo* (0.1 Torr) at 50—60 °C to give 0.03 g (66%) of 2,3,5,6-tetramethyl-1,4-pyrazine, m.p. 84—86 °C (*cf.* Ref. 13: m.p. 86 °C). ^{1}H NMR (200 MHz, C_6D_6), δ: 2.24 (s, Me). ^{13}C NMR (50 MHz, C_6D_6), δ: 21.1 (Me); 148.0 (CN).

The reaction of diiodide 2 with acrylonitrile. Acrylonitrile (50 mL) was added with stirring to a powder of compound **2** (0.616 g, 1.48 mmol). After 16 h, a yellow solid precipitated. The unreacted acrylonitrile was removed by condensation *in vacuo*. The precipitate was washed with THF and dried *in vacuo* to give 1.03 g of a metal-containing polyacrylonitrile as a light-yellow powder, which decomposed on heating above 100 °C. The elemental composition of the product corresponded to the formula $DyI_2(CH_2CHCN)_5(thf)$. Found (%): C, 30.0; H, 3.45; Dy, 22.02; I, 34.63. $C_{19}H_{23}DyI_2N_5O$. Calculated (%): C, 30.26; H, 3.05; Dy, 21.56; I, 33.68. IR (Nujol), ν/cm^{-1}: 3250 s, 2260 w, 1615 s, 1090 w, 970 m, 730 s, 675 w. The molecular weight was 2700. Treatment of the polymer with water resulted in the liberation of $DyI_2(OH)(H_2O)_x$ and the formation of metal-free polyacrylonitrile with a molecular weight of 2400.

X-ray diffraction analysis of $DyI_3(PhCN)_4 \cdot 0.5(PhCN)$. The X-ray diffraction experiment was carried out by the conventional procedure[14] on a Bruker AXS SMART-1000 diffractometer equipped with a CCD detector (λ-Mo, graphite monochromator, T = 110 K, ω-scan mode, scan steps 0.3°, time per frame 30 s, $2\theta_{max} = 60°$). The crystals of **4** are monoclinic; at T = 110 K, a = 38.492(7), b = 12.174(2), c = 14.855(3) Å, β = 106.190(17)°, space group $C2/c$, Z = 8, d_{calc} = 2.002 g cm^{-3}, μ = 5.033 cm^{-1}, V = 6685(2) Å^3. Altogether 17567 reflections were collected, of which 8212 were independent reflections. A semiempirical absorption correction was applied.[15] The structure was solved by the direct method using the SHELXS97 program package[16] and refined using the SHELXL97 program package[17] by the least-squares method in the full-matrix anisotropic approximation (the positions of H atoms were fixed with U_H = 0.08 Å^2) to R_1 = 0.0411, $R_w(F_0^2)$ = 0.0939 for 4977 reflections with $F_0^2 > 4\sigma(F_0)$. The atom coordinates are deposited with the Cambridge Structural Data Base.

This work was financially supported by President of the Russian Federation (Russian Scientific Schools, Project NSh-58.2003.03), the Russian Foundation for Basic Research (Project No. 04-03-32093), and the American Civil Research and Development Foundation for Independent States of the Former USSR (CRDF, Project RC1-2322-NN-02).

The authors are grateful to the Head and the staff of the X-ray Diffraction Center (Institute of Organoelement Compounds of the RAS) for providing the opportunity for collecting experimental data on a Smart diffractometer (Russian Foundation for Basic Research, Project No. 00-03-32807).

References

1. E. N. Zil'berman, *Reaktsii nitrilov* [*Reactions of Nitriles*], Khimiya, Moscow, 1972, p. 208 (in Russian).
2. A. N. Kamenskaya, *Zh. Neorgan. Khim.*, 1984, 439 [*J. Inorg. Chem.*, 1984, **29**, 415 (Engl. Transl.)].
3. (a) R. Yoneda, *J. Org. Chem.*, 1991, **56**, 1827; (b) C. N. Wolfe, *J. Org. Chem.*, 1998, **63**, 9031.
4. M. N. Bochkarev, G. V. Khoroshenkov, H. Schumann, and S. Dechert, *J. Am. Chem. Soc.*, 2003, **125**, 2894.
5. F. C. Foster, *J. Am. Chem. Soc.*, 1952, **74**, 2299.
6. (a) M. N. Bochkarev and A. A. Fagin, *Chem. Eur. J.*, 1999, **5**, 2990; (b) M. A. Katkova, G. K. Fukin, A. A. Fagin, and M. N. Bochkarev, *J. Organomet. Chem.*, 2003, **682**, 218.
7. H. Tada, K. Yasuda, and R. Okawara, *J. Organomet. Chem.*, 1969, **16**, 215.
8. S. V. Lindeman, V. E. Shklover, Yu. T. Struchkov, L. M. Mitina, and V. A. Pankratov, *Zh. Strukt. Khim.*, 1984, 180 [*J. Struct. Chem. (USSR)*, 1984, **25**, 169 (Engl. Transl.)].
9. A. A. Bakibaev, A. Yu. Yagovkin, and V. D. Filimonov, *Zh. Org. Khim.*, 1991, 1512 [*J. Org. Chem. USSR*, 1991, **27**, 1497 (Engl. Transl.)].
10. R. Bartnik, R. Faure, and K. Gebicki, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, 1034.
11. M. Rogalski, U. Domannska, D. Czyrny, and D. Dyczko, *Chem. Phys.*, 2002, **285**, 355.
12. O. Yamamoto, K. Someno, N. Wasada, J. Hiraishi, K. Hayamizu, K. Tanabe, T. Tamura, and M. Yanagisawa, *Anal. Sci.*, 1988, **4**, 233.
13. *Beilstein Handbuch der Organischen Chemie*, Springer, Berlin, 1954, **23II**, 84.
14. *SMART (Control) and SAINT (Integration) Software*, version 5.0, Bruker AXS Inc., Madison, WI, 1997.
15. G. M. Sheldrick, *SADABS, Program for Scaling and Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany, 1997.
16. G. M. Sheldrick, *SHELXS-97. Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
17. G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

Received October 30, 2003;
in revised form December 16, 2003