

A Novel Bis(imino)amine Ligand as a Result of Acetonitrile Coupling with the Diiodides of Dy(II) and Tm(II)

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The molecular diiodides of divalent neodymium, dysprosium, and thulium, the investigation of which has developed only in the last five years,¹ reveal in some cases a quite unusual chemical behavior. In particular, it has been established that the addition of aromatic compounds to solutions of LnI₂ in THF or DME causes LnI₃ formation and, judging on immediate solvent splitting, a dramatic increase in the reductive power of these salts.² To explain the observed transformations, a disproportionation of the diiodides into LnI₃ and LnI promoted by aromatic compounds was proposed. The generated monovalent species immediately attack the solvent with splitting of C–O, C–H, and C–C bonds. Here we report that the reactions of LnI₂ (Ln = Dy, Tm) with acetonitrile easily proceed without any additions, affording complexes with an imine-amine ligand of a novel type.³ Previously studied reactions of nitriles with organoyttrium^{4,5} and organoscandium⁶ complexes mainly yield insertion products containing the Ln(μ -N=CRR') fragments. Only in the case of the reactions of acetonitrile with the bis(benzamidinato)yttrium alkyls [PhC(NSiMe₃)₂]₂YR (R = CH(SiMe₃)₂, CH₂-Ph) was C–C bond formation observed providing the crotonitrile-amido complex {[PhC(NSiMe₃)₂]₂YNHCMe=CHCN}₂.⁷

The reactions of DyI₂ and TmI₂ with excess acetonitrile proceed with formation of yellow-brown (Dy) or brownish-yellow (Tm) solutions from which colorless rodlike crystals of the lanthanide triiodide complexes {[(HN=CMe)₂MeCNH₂ }Ln(MeCN)₆]I₃ (Ln = Dy (**1a**), Tm (**1b**)) were isolated with yields of 7 (**1a**) and 10% (**1b**), respectively.⁸ In these complexes, the lanthanide metals are coordinated by acetonitrile and by the C–C coupling product 2,4-diimino-3-methyl-3-aminopentane. Both complexes are unstable in air, soluble in acetonitrile and THF, but insoluble in benzene and hexane. Heating of the compounds to 100–120 °C under a dynamic vacuum causes the quantitative liberation of acetonitrile.

The structures of the ionic products **1a,b** were determined by X-ray diffraction analysis. Compound **1a** crystallizes in the orthorhombic space group *Pnma*.⁹ The unit cell consists of four {[(HN=CMe)₂MeCNH₂ }Dy(MeCN)₆]I₃³⁺ cations and 12 I[−] anions which are not in contact to each other. Additionally, the unit cell contains four noncoordinating MeCN solvent molecules, three of them being disordered about a mirror plane. The cation shows C_s symmetry (Figure 1). The Dy atom, two of the coordinating MeCN molecules, and the central carbon and nitrogen atoms of the 1,1'-bis(iminoethyl)ethylamine ligand are located on a crystallographic mirror plane. The cation of the Tm compound **1b** is isostructural with the cationic moiety of **1a**, but not isomorphous. The compound **1b** crystallizes in the triclinic space group *P-1* with two {[(HN=CMe)₂MeCNH₂ }Tm(MeCN)₆]I₃³⁺ cations, six I[−] anions, and two noncoordinating MeCN solvent molecules in the unit cell, one

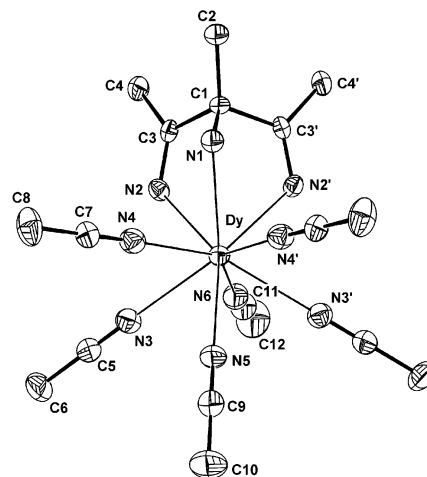


Figure 1. ORTEP drawing (50% probability thermal ellipsoids) of the structure of the cation $\{[(\text{HN}=\text{CMe})_2\text{MeCNH}_2]\text{Dy}(\text{MeCN})_6\}^{3+}$ of **1a**. The hydrogen atoms were not localized. Selected bond lengths (Å) and angles (deg): Dy–N(1) 2.512(6), Dy–N(2) 2.451(4), Dy–N(3) 2.530(5), Dy–N(4) 2.496(5), Dy–N(5) 2.534(7), Dy–N(6) 2.483(7), N(1)–C(1) 1.485(9), C(1)–C(2) 1.526(9), C(1)–C(3) 1.536(6), N(2)–C(3) 1.279(6), C(3)–C(4) 1.487(7), N(1)–Dy–N(2) 63.27(14), N(1)–Dy–N(3) 123.66(11), N(1)–Dy–N(4) 71.92(15), N(1)–Dy–N(5) 134.9(2), N(1)–Dy–N(6) 123.6(2), N(2)–Dy–N(3) 73.05(14), N(2)–Dy–N(4) 85.88(15), N(2)–Dy–N(5) 141.80(10), N(2)–Dy–N(6) 72.46(16), N(2)–Dy–N(2') 73.82(19), N(2)–Dy–N(3') 134.84(14), N(2)–Dy–N(4') 135.17(15), N(3)–Dy–N(4) 71.15(15), N(3)–Dy–N(5) 69.80(13), N(3)–Dy–N(6) 68.88(13), N(3)–Dy–N(3') 112.2(2), N(3)–Dy–N(4') 139.14(15), N(4)–Dy–N(5) 74.19(16), N(4)–Dy–N(6) 138.52(11), N(4)–Dy–N(4') 81.1(2), N(5)–Dy–N(6) 101.5(2), C(1)–N(1)–Dy 107.6(4), C(3)–N(2)–Dy 121.3(3), N(1)–C(1)–C(2) 113.6(6), N(1)–C(1)–C(3) 104.7(4), C(2)–C(1)–C(3) 113.3(4), C(3)–C(1)–C(3') 106.5(5), N(2)–C(3)–C(1) 115.2(4), N(2)–C(3)–C(4) 124.9(4), C(4)–C(3)–C(1) 119.9(5). Symmetry transformations used to generate equivalent atoms: (') $x, 0.5 - y, z$.

of the last being disordered about two positions.⁹ As in **1a**, the cations and anions are well separated without short intermolecular contacts.

The most interesting feature of both compounds is the C–C coupling product, 1,1'-bis(iminoethyl)ethylamine. The C–N bond lengths of the imino groups (**1a**, 1.28 Å; **1b**, 1.26, 1.27 Å) and the amino group (**1a,b**, 1.49 Å) are consistent with the typical interatomic distances estimated for such groups,¹⁰ except for the slight elongation of the latter by 0.01–0.02 Å. The C–C bond distances show values (1.49–1.54 Å) expected for carbon–carbon single bonds.¹⁰ All three nitrogen atoms of the tridentate (HN=CMe)₂MeCNH₂ ligand coordinate to the metal center. The Ln–N distances of the imino groups (**1a**, 2.45 Å; **1b**, 2.43 Å) are somewhat shorter than the Ln–N distance of the amino group (**1a**, 2.51 Å; **1b**, 2.49 Å). Because of the six additionally coordinating MeCN molecules, the coordination number of the Ln(III) atom

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increases to nine, and the coordination geometry around the metal atom corresponds to a distorted tricapped trigonal prism. The Ln–N (MeCN) distances (**1a**, 2.48–2.53 Å; **1b**, 2.42–2.51 Å) are comparable with those in the [(HN=CMe)₂MeCNH₂]_xLn fragment reported above and also with those estimated for, for example, [Cl₃Dy(MeCN)(μ-Cl)₂[PPh₄]₂ (2.46 Å),¹¹ [(Bu₂CHO)₃Dy(MeCN)₂] (2.54 Å),¹² and the tris(2-(salicylideneaminoethyl)amine dysprosium and thulium complexes (C=N(C)–Dy 2.48 Å; C=N(C)–Tm 2.45 Å).^{13,14} The differences in the Ln–N distances of **1a** and **1b** correspond to the difference in the ionic radii of Dy(III) and Tm(III) (approximately 0.03 Å).¹⁵ In both structure analyses, the hydrogen atoms were not localized due to the presence of the heavy metal atoms, but the existence of N–H groups in **1a,b** is strictly confirmed by the strong absorptions at 3150 cm⁻¹ in the IR spectra of the products.

Besides **1a,b**, the reactions produce pale yellow crystals of LnI₃(MeCN)_x (*x* = 4 (Dy), 8 (Tm)) in 25 and 17% yield, respectively. After the isolation of **1a,b** and of the LnI₃(MeCN)_x derivatives and after the removal of all volatiles under vacuum, a dark yellow solid remains in both cases. The molar I/Ln ratio of these products varies from 1.23 to 1.5 depending on the kind of the lanthanide and the way of isolation. We suggest that these substances are mixtures of the respective lanthanide(III) monoiodides, triiodides, and probably diiodides coordinated respectively by dianionic, monoanionic, or neutral ligands generated from acetonitrile. The IR spectra of the mixtures display a set of bands characteristic for single, double, and triple carbon–nitrogen bonds and also for N–H groups. The separation, characterization, and chemical reactivity of these products as well as the reaction of acetonitrile with NdI₂, which according to preliminary studies proceeds similarly, are still under investigation.

Thus, we suggest that the interaction of DyI₂ and TmI₂ with MeCN is associated with the disproportionation of LnI₂ into LnI₃ and the extremely reactive LnI. The subsequent oxidation of LnI by acetonitrile will lead to the formation of a complex mixture of organometallic and organic products including the bis(imino)amine system. The latter coordinates to LnI₃ providing the complexes **1a,b**. It should be noted that (HN=CMe)₂MeCNH₂ is a new type of tridentate ligand, which seems promising for the preparation not only of imine-amine coordinated metal complexes, but as well of imide-amide compounds with metal–nitrogen σ-bonds.

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Supporting Information Available: Synthesis of **1b**, characteristics of the products (PDF). ORTEP drawing of the [(HN=CMe)₂MeCNH₂]-Tm(MeCN)₆]³⁺ cation of **1b**, packing diagrams of **1a,b**, crystallographic files for **1a,b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *35*, 133–134. (b) Bochkarev, M. N.; Fagin, A. A. *Chem.-Eur. J.* **1999**, *5*, 2990–2992. (c) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749–11759. (d) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 3176–3178. (e) Evans, W. J.; Allen, N. T. *J. Am. Chem. Soc.* **2000**, *122*, 2118–2119. (f) Fedushkin, I. L.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Chem.-Eur. J.* **2001**, *7*, 3558–3563.
- (2) (a) Bochkarev, M. N.; Fagin, A. A. *Abstracts, 85th CSC Conference*; Vancouver, 2002; p 421. (b) Bochkarev, M. N.; Fagin, A. A.; Khoroshenkova, G. V. *Russ. Chem. Bull. (Russ.)* **2002**, *10*, 1757–1762; *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 1909–1914.
- (3) Concerning novel types of ligands formed from MeCN, we refer to the complex [Me₂Al(HNCMe₂)₂C(CN)] obtained from AlMe₃ and MeCN in the presence of cesium halides, which contains a bidentate anionic ligand system generated from MeCN: Kopp, M. R.; Neumüller, B. Z. *Anorg. Allg. Chem.* **1999**, *625*, 739–745.
- (4) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.
- (5) Den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509–1514.
- (6) Bercaw, J. E.; Davies, D. L.; Wolczauski, P. T. *Organometallics* **1986**, *5*, 443–450.
- (7) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291–2302.
- (8) Synthesis of **1a** (**1b** is prepared in the same manner). Using an evacuated Schlenk system, we added 30 mL of acetonitrile to DyI₂ prepared from 1.63 g (10 mmol) of Dy metal and 1.19 g (4.69 mmol) of I₂ as described earlier.^{1b} The mixture was stirred for 10 h at ambient temperature. The yellow-brown solution formed was filtered through a glass filter, and one-half of the MeCN was evaporated under vacuum. Within 1 d, colorless crystals of **1a** separated, which were isolated by decantation, washed with cold acetonitrile, and dried under vacuum. Yield 0.173 g, 7%; mp 95–100 °C. Anal. Calcd for C₁₈H₃₁DyI₃N₆: Dy, 17.73; I, 41.54. Found: Dy, 17.60; I, 41.41. IR (Nujol): 3150 s (N–H), 2720 w, 2300 m, 2280 s (C=N), 1650 m (C=N), 1120 s (C–N), 1030 s, 930 m, 800 m, 620 m. Removal of all volatiles from the mother solution afforded 1.9 g of a dark yellow solid containing 27.65% of Dy and 28.73% of iodine (I/Dy molar ratio 1.23). IR (Nujol): 3200 m, 3150 m, 2300 m, 2800 s, 2190 s, 1650 m, 1590 s, 1150 w, 1120 w, 1030 m, 930 w, 800 m, 640 w, 550 w. The solid was extracted with 20 mL of THF, and the extract was concentrated to 5 mL and allowed to stand at room temperature. Within 1 d, 0.35 g of a light yellow microcrystalline solid was formed containing Dy (22.41%) and I (17.50%) in a molar ratio of 1:1. IR (Nujol, cm⁻¹): 2180 m, 1660 w, 1580 m, 1350 w, 1020 w, 1000 s, 910 w, 850 s, 840 sh, 680 m. The dark brown solid remaining on the glass filter was extracted with acetonitrile at 80 °C. Within 8 h at room temperature, 0.64 g (25%) of light-yellow rhombic crystals precipitated from the extract. The content of metal and iodine of these crystals answers the formula DyI₃(CH₃CN)₄. Anal. Calcd for C₈H₁₂DyI₃N₄: Dy, 22.97; I, 53.81. Found: Dy, 22.81; I, 53.91. IR (Nujol): 2700 w, 2300 m, 2270 s, 1140 w, 1600 w, 1020 s, 930 m, 590 w.
- (9) Crystallographic data: **1a**, *T* = 173 K, colorless, orthorhombic, *Pnma*, *a* = 20.3218(3) Å, *b* = 13.8313(1) Å, *c* = 15.4992(1) Å, *V* = 4356.47(8) Å³, *Z* = 4, ρ_{calcd} = 1.648 g/cm³, *R*₁ = 0.0419 (*I* > 2σ(*I*)), *wR*₂ = 0.0995 (all data), GOF(*F*²) = 1.052. Three of the four noncoordinating MeCN in **1a** are disordered about a mirror plane. The atoms of the disordered parts were refined isotropically. **1b**, *T* = 173 K, colorless, triclinic, *P*-1, *a* = 10.7188(3) Å, *b* = 13.7619(5) Å, *c* = 14.0021(5) Å, α = 69.641(1)°, β = 89.732(1)°, γ = 73.989(1)°, *V* = 1851.75(11) Å³, *Z* = 2, ρ_{calcd} = 1.803 g/cm³, *R*₁ = 0.0499 (*I* > 2σ(*I*)), *wR*₂ = 0.1061 (all data), GOF(*F*²) = 1.016. One of the two noncoordinating MeCN in **1b** is disordered about two positions, with occupancy factors of 0.67(2) and 0.33(2). The atoms of the disordered part were refined isotropically. The 1,2 and 1,3 distances of both parts were restrained to be equal.
- (10) Allen, F. H.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. In *International Tables For Crystallography*; Wilson, A. C. S., Prince, E., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1999; Vol. C, pp 782–803.
- (11) Crisci, G.; Meyer, G. Z. *Anorg. Allg. Chem.* **1998**, *624*, 927–928.
- (12) Herrmann, W. A.; Anwander, R.; Scherer, W. *Chem. Ber.* **1993**, *126*, 1533–1539.
- (13) Kanesato, M.; Yokoyama, T. *Anal. Sci.* **2000**, *16*, 335–336.
- (14) Kanesato, M.; Yokoyama, T. *Chem. Lett.* **1999**, 137–138.
- (15) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

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