Rare Earths

DOI: 10.1002/anie.201204452

Genuine Redox Isomerism in a Rare-Earth-Metal Complex**

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Dedicated to Professor Gleb A. Abakumov on the occasion of his 75th birthday

Redox isomerism, which is a reversible metal-to-ligand electron transfer, was first reported by Pierpont and Buchanan in 1980 for an *o*-benzoquinone complex of cobalt.[1] A few years later, a similar effect was observed by Abakumov, Nevodchikov, and Cherkasov in a copper complex.[2] To date, redox isomerism, which is also called valence tautomerism, is known for various d elements,[3] including Co, Ru, Cr, Ni, Mn, Fe, Rh, Cu, and Ir, in solution and in the solid state. In 2007, the occurrence of redox isomerism was claimed for a complex of an f element, [(dpp-dad)Yb(C_5Me_5)(thf)] (dpp-dad = 1,4-bis(2,6-diisopropylphenyl)diaza-1,3-butadiene).[4] Based on the solid-state magnetic susceptibility it was proposed that at 2 K the complex consists of Yb^{II} and a dpp-dad radical anion, while at 300 K it is present as Yb^{III} with a dpp-dad dianion. As far as we know, these redox preferences are opposite to almost all of the earlier reported cases,[5] where the low-temperature form is represented by the species with a more oxidized metal M^{n+1} and the high-temperature isomer has a reduced metal ion M^n. More precisely, as redox isomerism is an entropy-driven process, the isomeric forms with the shorter M–L bonds, that is, with the more oxidized metal ion M, are usually stabilized at lower temperatures. Herein we report the synthesis and a combined X-ray crystallography plus SQUID study of the new complex [{(dpp-bian)Yb(μ-Cl)(dme)}$_2$] (**1**; dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), which turns out to be the first rare-earth-metal complex that exhibits genuine thermally induced redox isomerism in the solid state. Similar to its bromine analogue, [{(dpp-bian)Yb(μ-Br)(dme)}$_2$],[6] complex **1** reveals intramolecular electron transfer between the metal and the dpp-bian ligand in solution as well; these data will be published elsewhere.

Dimeric [{(dpp-bian)Yb(μ-Cl)(dme)}$_2$] (**1**) can be prepared in two different ways: 1) reacting an excess of ytterbium (powder or pieces) with dpp-bian and $YbCl_3$ in 1,2-dimethoxyethane (dme) at reflux; or 2) by oxidation of [(dpp-bian)Yb(dme)$_2$] [6] in dme solution with chlorine-containing substances,[7] for example, 1,2-dichloroethane. A well-resolved ^{1}H NMR spectrum of complex **1** can be obtained at low temperature. In contrast, EPR spectroscopy is not useful for characterizing **1** owing to the presence of Yb^{III} species. To obtain X-ray-quality crystals of complex **1**, the crude product (92–96 % yield) left after evaporation of dme was dissolved at 110 °C in benzene in a sealed glass ampoule. The resulting solution was cooled down slowly and kept over several days at room temperature, affording crystals of **1** in moderate yield. Numerous X-ray diffraction studies of single crystals isolated from a series of experiments show the presence of three different modifications, **1A**–**1C**, in every crop. Whereas **1A** and **1B** are polymorphs, **1C** is a different solvate. The existence of different crystalline modifications of complex **1** may by itself indicate the presence of complex isomers, that is, redox isomers. However, as the intramolecular electron transfer in such systems is often thermally induced, determination of the structure of every modification at different temperatures was desired. The crystal data for **1A**, **1B**, and **1C** at different temperatures are presented in Table 1 (for selected atom distances and bond angles, see the Supporting Information, Table S1). Unit cell parameters of one of three modifications, namely **1B**, were found to vary significantly with temperature. The molecular structures of **1B** at two different temperatures are depicted in Figure 1. These are redox isomers in which the Yb–N bond lengths are quite different owing to the difference in bonding strength in the pairs [dpp-bian]$^{2-}$/[YbCl]$^{2+}$ and [dpp-bian]$^{1-}$/[YbCl]$^{1+}$.

According to the molecular structures of **1B** (Figure 1) in the solid state, the lowering of the temperature from 170 to 120 K causes a shortening of the Yb–N(av.) bond lengths in one half of the dimeric molecule (170 K: Yb1–N(av.) 2.20(1) Å, Yb2–N(av.) 2.44(1) Å; 120 K: Yb1–N(av.) 2.21(1) Å, Yb1′–N(av.) 2.21(1) Å). This reflects the transfer of an electron from Yb2 into the attached radical-anionic dpp-bian ligand, converting the latter into a dianion. Thus, at 170 K and above, crystalline **1B** is best described as a mixed-valence Yb^{III}/Yb^{II} compound that at lower temperatures transforms into the Yb^{III}/Yb^{III} isomer (Scheme 1). The similarity of the two Yb atoms in the low-temperature case is also supported by the observation that the structure at 120 K could be refined using only one crystallographically independent half of the molecule, which reduces the cell volume to approximately half of the value estimated at 170 K.

As the magnetic properties of di- and trivalent ytterbium ions are different (Yb^{2+} $4f^{14}$, diamagnetic; Yb^{3+} $4f^{13}$, $\mu_{eff} = 4.0$–

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[**] This work was supported by the Russian Foundation for Basic Research (10-03-00430). We thank Prof. Dr. G. K. Fukin for determination of the molecular structure of 1A.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.204452.

Table 1: Crystal data for the polymorphs **1A**, **1B**, and **1C** obtained at different temperatures.

	1A		**1B**		**1C**[a]		
temperature	100 K	298 K	120 K	170 K	120 K (I)	120 K (II)	170 K
formula	$C_{80}H_{100}Yb_2N_4O_4Cl_2 \cdot 2\,C_6H_6$		$C_{80}H_{100}Yb_2N_4O_4Cl_2 \cdot 2\,C_6H_6$		$C_{80}H_{100}Yb_2N_4O_4Cl_2 \cdot 3\,C_6H_6$		
M_r	1754.84		1754.84		1832.94		
crystal	monoclinic		triclinic		triclinic		
space group	$P2_1/n$		$P\bar{1}$		$P\bar{1}$		
a [Å]	12.68	12.58	12.16	12.25	15.20	11.85	11.88
b [Å]	18.83	18.89	12.33	18.01	17.54	14.17	14.22
c [Å]	17.60	18.35	13.70	18.90	19.11	14.36	14.40
α [°]	90	90	94.8	83.7	82.3	64.4	64.4
β [°]	96.5	95.4	92.5	86.9	68.8	83.4	83.2
γ [°]	90	90	93.3	88.0	65.5	85.9	85.8

[a] Two different cell choices (I and II) at 120 K; see the Supporting Information for details.

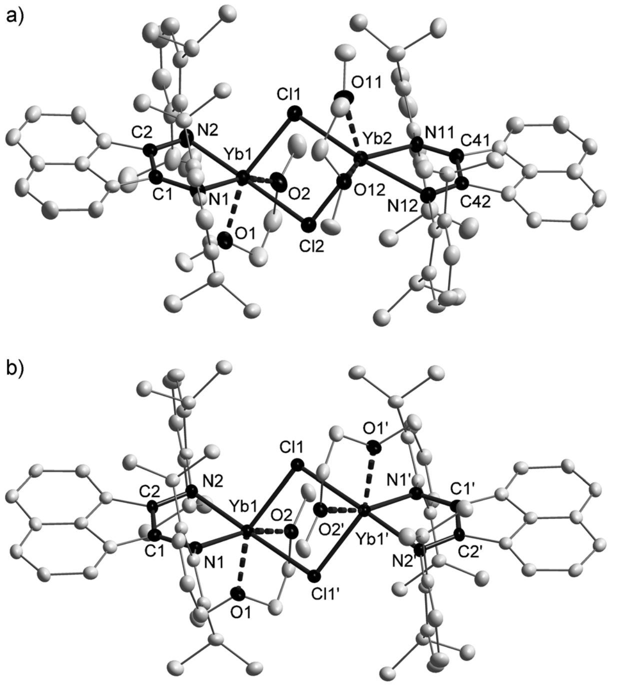
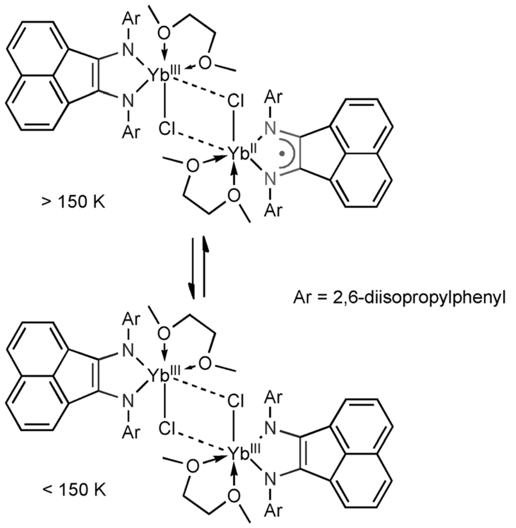


Figure 1. Molecular structure of **1B** at a) 170 and b) 120 K. Ellipsoids are set at 30% probability; solvent molecules and hydrogen atoms are omitted for clarity. Symmetry operation used to generate equivalent atoms: (′) 1−*x*, 1−*y*, 1−*z*.

4.5 μ_B),[8a] temperature-dependent magnetic susceptibility data should reflect the proposed electron-transfer process. A series of SQUID measurements using different samples of **1** each containing around a dozen of small crystals showed poor reproducibility, although the expected anomaly, namely a rise of the magnetic moment upon lowering the temperature owing to the transformation of Yb^{II} into Yb^{III}, was always observed. Note that the magnetic moment of even a mononuclear Yb^{III} species decreases upon lowering the temperature because of changes in the population of Kramers doublet states, which are produced by a non-cubic ligand field.[8]



Scheme 1. Redox isomerism in [{(dpp-bian)Yb(μ-Cl)(dme)}$_2$] (**1B**).

We therefore decided to determine the magnetic susceptibility of a single crystal of modification **1B**. The dependence of μ_{eff} on T (200–100 K) for a single crystal of **1B** is presented in Figure 2. Lowering the temperature from 270 to 147 K causes μ_{eff} to decrease monotonically, just as in many other Yb^{III} complexes, such as $[(C_5Me_5)_2Yb(L)]^+I^-$ (L = bipy or phen)[9a] and $[\{(C_5H_5)_2Yb(\mu\text{-}X)\}_2]$ (X = Cl, Br).[9b] However, at 147 K the magnetic moment (5.2 μ_B)[10] starts to increase abruptly, reaching 6.6 μ_B at 140 K. This value is close to the

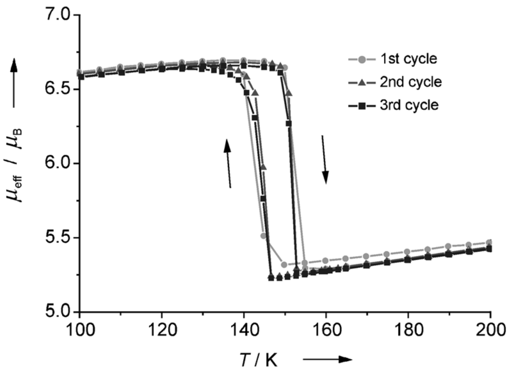


Figure 2. Plot of μ_{eff} vs. T (200–100 K) for a single crystal of **1B**.

calculated value (6.4 μ_B) if uncoupled spins of two Yb ions in the Yb^{III}/Yb^{III} isomer ($\mu_{\mathrm{eff}} = [(\mu_{\mathrm{eff(Yb1)}})^2 + (\mu_{\mathrm{eff(Yb2)}})^2]^{1/2}$) are assumed. From 140 down to 2 K, the magnetic moment of **1B** shows a further slight decrease with the same gradient as observed in the high-temperature range (270 to 147 K). Backward scans in heating mode reveal a pronounced thermal hysteresis loop for μ_{eff} ($\Delta T = 7$ K) until μ_{eff} returns to the initial value of 5.3 μ_B at 153 K.

Although there were no crystallographic indications of any redox isomerism in modification **1C**, we decided to determine its magnetic susceptibility on a single crystal for comparison. The μ_{eff} data in the temperature range 295–2 K are shown in Figure 3 (black dots), together with the data for **1B**. In the high-temperature regime (295–147 K) the μ_{eff} curves are essentially congruent, but **1C** lacks the hysteretic step and continuous to decrease monotonically even below 147 K. Thus **1C** remains in the Yb^{III}/Yb^{II} state throughout, with radical character of the dpp-bian ligand at Yb^{II}. The more rapid decrease of μ_{eff} for **1C** below 25 K might possibly be explained by intermolecular antiferromagnetic coupling that is enhanced when spin density is found on the ligand, or by a more pronounced ligand-field effect.

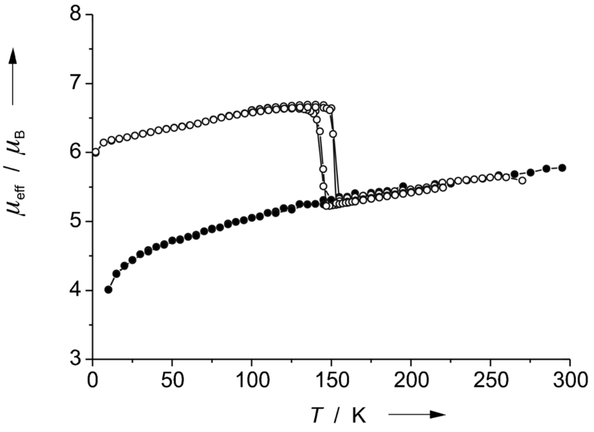


Figure 3. Plot of μ_{eff} vs. T for a single crystal of **1C** (180–10–295 K, solid dots) in comparison to **1B** (open dots).

In conclusion, we have observed for the first time redox-isomerism in a f-block metal complex, namely in the ytterbium complex of the non-innocent 1,2-diimine ligand dpp-bian. Another phenomenon recently found in ytterbium complexes of redox-active ligands, for example, [$(\mathrm{C_5Me_5})_2\mathrm{YbL}$] (L = dad or bipy), is the intermediate valence, which arises from a multiconfigurational ground state that has both an open-shell singlet $f^{13}(\pi^*)^1$ (π^* is the lowest unoccupied molecular orbital of the bipy or dad) and a closed-shell singlet f^{14} component.[11] A distinct feature of [$(\mathrm{C_5Me_5})_2\mathrm{YbL}$] systems is an attenuated temperature dependence of the ytterbium valence. As may be expected, the metal-to-ligand electron transfer in the solid state in our system is accompanied not only by significant Yb−N bond-length alterations but also by changes of the unit-cell parameters. In view of the fact that two of the three crystal modifications of complex **1**, namely **1A** and **1C**, do not show any redox isomerism, the crystal packing seems to play a crucial role for the observed phenomenon. The third hypothetical redox isomer of **1**, in which both Yb atoms are in their divalent state, should be present at temperatures much above 300 K. However, this could not be probed as compound **1** decomposes at such temperatures. As in d-block metal complexes, the low-temperature isomer in the ytterbium complex of dpp-bian features the more oxidized metal center.

Experimental Section

All manipulations were carried out under vacuum or nitrogen using Schlenk techniques. The magnetic susceptibilities were determined using a SQUID MPMS-5 (Quantum Design) at 5 kOe. For **1A** the crystallographic data were collected on a Bruker SMART APEX diffractometer, for **1B** and **1C** on a STOE IPDS II diffractometer.[12] CCDC 885277 (**1A** at 100 K), 885278 (**1A** at 298 K), 885279 (**1B** at 120 K), 885280 (**1B** at 170 K), 885281 (**1C** at 120 K I), 885282 (**1C** at 120 K II), and 885283 (**1C** at 170 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [$\{(\text{dpp-bian})\mathrm{Yb}(\mu\text{-Cl})(\mathrm{dme})\}_2$] (**1**): A mixture of dpp-bian (0.5 g, 1.0 mmol) and $\mathrm{YbCl_3}$ (0.093 g, 0.33 mmol) in dme (40 mL) was added into an evacuated glass ampoule supplied with a Teflon stopcock and containing 4.5 g of ytterbium metal (99.9% CHEMPUR). This mixture was refluxed at 90 °C for 3 h. A dark-red microcrystalline suspension formed was than decanted under vacuum into a glass ampoule. The residual metal was washed with dme (2 × 30 mL). All of the solvent was removed under reduced pressure. Benzene (40 mL) was added to the microcrystalline solid that was left after evaporation of the solvent. The ampoule was sealed off and then heated to 110 °C in an oil bath for 3 h, and the bath was then slowly cooled down to ambient temperature. After 5 days, the ampoule was opened under vacuum and the mother liquor was decanted from the dark, almost black crystals of compound **1**. Yield 0.31 g (35%). M.p. > 150 °C (decomp); ^{1}H NMR ([D$_8$]thf, 400 MHz, 193 K): δ = 22.8 ppm (s, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 12.2 (s, 2H, $\mathrm{C}H(\mathrm{CH_3})_2$), 11.6 (s, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), 10.3 (s, 1H, CH arom.), 9.7 (s, 1H, CH arom.), 7.6 (s, 6H, $\mathrm{C_6}H_6$), 6.1 (s, 2H, CH arom.), 3.6 (s, 4H, $\mathrm{C}H_2$(dme)), 3.4 (s, 6H, $\mathrm{C}H_3$(dme)), −14.8 (s, 2H, CH arom.), −15.6 (s, 2H, CH arom.), −25.2 (s, 2H, CH arom.), −26.7 (s, 1H, CH arom.), −35.8 (s, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), −50.1 (s, 6H, $\mathrm{CH}(\mathrm{C}H_3)_2$), −105.7 ppm (s, 2H, $\mathrm{C}H(\mathrm{CH_3})_2$); UV/Vis (293 K, dme): λ = 691 nm; IR (Nujol): $\tilde{\nu}$ = 1579w, 1574m, 1508w, 1430m, 1410s, 1365m, 1340w, 1315m, 1303m, 1246m, 1219w, 1205w, 1185s, 1160w, 1143w, 1113w, 1101w, 1081w, 1060m, 1038m, 1009w, 937w, 923w, 917w, 886w, 860m, 845w, 836w, 819w, 801w, 788w, 773w, 765m, 753w, 677s, 604w, 538w cm^{-1}. Anal. calcd (%) for $\mathrm{C_{80}H_{100}Yb_2N_4O_4Cl_2 \cdot 2\,C_6H_6}$ (1754.84): C 62.97, H 6.43; found: C 62.56, H 6.26.

Received: June 8, 2012
Revised: July 26, 2012

Keywords: magnetochemistry · redox-active ligands · redox isomerism · structure elucidation · ytterbium

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[10] The magnetic contribution of the radical-anionic dpp-bian ligand in complex **1B** at $T > 150$ K will be largely temperature-independent. The value of the magnetic moment of 5.2 μ_B at 147 K is somewhat higher than the calculated value for the upper isomer shown in Scheme 1, $\mu_{eff} = [(4.5)^2 + (1.73)^2]^{1/2} = 4.8\,\mu_B$. This can be explained either by a small admixture of the other morphologies of complex **1**, or by partial oxidation of the sample in the course of its preparation.

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