Charge-Transfer Complexes of Metal Dithiolenes, XV[1]

Ion Pair Charge-Transfer Complexes of Dithiolene Metalates with Diquaternary 2,2′-Biimidazoles[☆]

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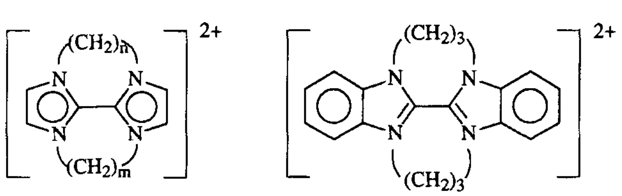
Cycloalkylated biimidazolium dications (A^{2+}) of reduction potentials from −0.4 to −1.4 V form ion pair charge-transfer complexes $\{A^{2+}[M(mnt)_2]^{2-}\}$ with dithiolene metalates, M = Zn, Ni, Pd, Pt, mnt^{2-} = maleonitrile-2,3-dithiolate. X-ray analyses of $\{P_2BBIm^{2+}[Ni(mnt)_2]^{2-}\}$ [P_2BBIm^{2+} = 1,1′,3,3′-bis(propane-1,3-diyl)bibenzimidazolium] and $\{B_2BIm^{2+}[Pd(mnt)_2]^{2-}\}$ [B_2BIm^{2+} = 1,1′,3,3′-bis(butane-1,4-diyl)biimidazolium] reveal that the solid-state structure is largely determined by the geometry of the acceptor. When the latter is strongly twisted, the usually observed mixed donor-acceptor columns are modified to a chain-like arrangement. In the case of the bibenzimidazolium dication P_2BBIm^{2+} the otherwise planar $[Ni(mnt)_2]^{2-}$ becomes tetrahedrally distorted. By the application of the Hush model a reorganization energy of about 67 kJ/mol is estimated for the thermal electron transfer from $[M(mnt)_2]^{2-}$ to A^{2+} when M = Ni, Pd, Pt, but considerable deviations from this model are observed when M = Zn. Irradiation of the free biimidazolium acceptors in the presence of EDTA affords the strongly reducing radical cations which reduce water to hydrogen in the presence of colloidal platinum. Attempts to sensitize this reaction by irradiating into the charge-transfer band of $\{A^{2+}[M(mnt)_2]^{2-}\}$ have failed until now. The molar absorptivity of one biimidazolium radical cation is measured by spectroelectrochemistry.

Ion-pair charge-transfer (IPCT) complexes consisting of redox-active components provide ideal conditions for the systematic investigation of supramolecular CT interactions[2,3]. The combination of dianionic transition metal dithiolenes $[ML_2]^{2-}$ with organic dicationic bipyridinium compounds (A^{2+}) leads to IPCT complexes of the type $\{A[ML_2]\}$ showing an IPCT band in their UV-Vis-NIR spectra[4]. Application of the "Hush model" affords thermodynamic and kinetic data about the relation between optical and thermal electron transfer in solution[5]. Flash photolysis reveals the formation of the primary redox products $A^{+\cdot}$ and $[ML_2]^-$ followed by a fast back-electron transfer[6]. Moreover, on the basis of the redox potential differences of the components the solid-state electrical conductivity can be quantitatively tuned[7].

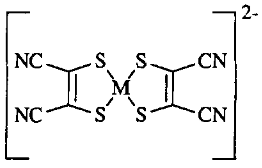
In the course of our previous investigations only bipyridinium compounds and closely related systems were used as acceptors. The first reduction potentials of these are found in the range of −0.4 to −0.8 V (MeCN, vs SCE). In the following we report on the chemical, structural, and spectroscopic properties of IPCT complexes containing biimidazolium acceptors R_2BIm^{2+} which have unusually low first reduction potentials from −1.1 down to −1.4 V. These potentials qualify them as excellent candidates in photoreduction reactions including the photoreduction of water. Additionally, four complexes containing a bibenzimidazolium acceptor P_2BBIm^{2+} of a moderate viologen-like reduction potential have been included for the purpose of comparison (Scheme 1).

Scheme 1



n = 2, m = 3 : $EPBIm^{2+}$
n = m = 3 : P_2BIm^{2+}
n = m = 4 : B_2BIm^{2+}

P_2BBIm^{2+}



	Zn	Ni	Pd	Pt
P_2BBIm^{2+}	**1a**	**1b**	**1c**	**1d**
$EPBIm^{2+}$	**2a**	**2b**	**2c**	**2d**
P_2BIm^{2+}	**3a**	**3b**	**3c**	**3d**
B_2BIm^{2+}	**4a**	**4b**	**4c**	**4d**

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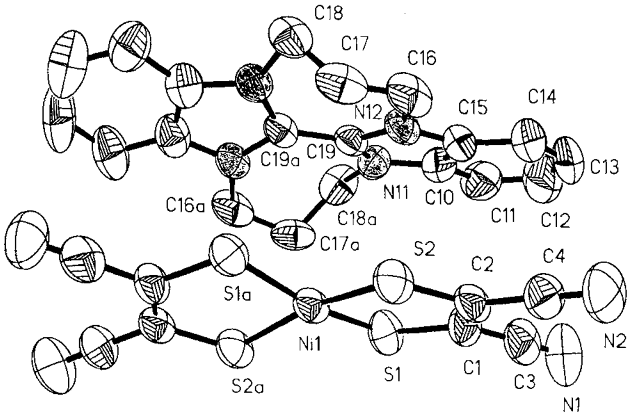
Results and Discussion

X-Ray Structural Investigations

In a series of IPCT complexes the electrical conductivity can be quantitatively tuned by variation of the redox potentials of the components[7] as long as two planar components are involved. In that case the solid-state structure contains mixed donor-acceptor stacks[1,8,9]. It is therefore of interest to investigate how the structure changes when non-planar biimidazolium acceptors of different torsion angles around the central C−C bond are introduced. The new compounds have been prepared as described recently[9].

Figure 1. Molecular structure of **1b**, ORTEP plot; bond lengths [pm]: Ni1−S1 217.3(4), Ni1−S2 217.6(4), Ni1−S1A 217.3(4), Ni1−S2A 217.6(4), S1−C1 173.1(7), S2−C2 174.1(11), C1−C2 138.1(10), C1−C3 144.9(16), C2−C4 143.2(10), C3−N1 112.3(16), C4−N2 113.2(9), C15−C14 141.6(12), C15−C10 140.3(10), C15−N12 139.6(14), C14−C13 137.0(21), C13−C12 138.5(15), C12−C11 134.1(17), C11−C10 139.3(18), C10−N11 137.8(12), N11−C19 136.4(11), N11−C18A 147.7(7), N12−C16 150.7(9), N12−C19 134.6(7), C16−C17 146.9(15), C17−C18 152.8(12), C18−N11A 147.7(7), C19−C19A 147.1(18), bond angles [°]: S1−Ni1−S2 91.8(1), S1−Ni1−S1A 168.7(2), S2−Ni1−S1A 89.4(1), S1−Ni1−S2A 89.4(1), S2−Ni1−S2A 167.8(2), S1A−Ni1−S2A 91.8(1), Ni1−S1−C1 103.9(3), Ni1−S2−C2 104.1(2), S1−C1−C2 120.8(8), S1−C1−C3 117.2(5), S2−C2−C1 119.4(6), C14−C15−C10 121.9(10), C14−C15−N12 130.4(8), C10−C15−N12 107.7(7), C15−C14−C13 114.1(8), C14−C13−C12 123.2(11), C13−C12−C11 123.4(15), C12−C11−C10 116.1(9), C15−C10−C11 121.3(8), C15−C10−N11 106.1(9), C11−C10−N11 132.6(6), C10−N11−C19 109.0(5), N11−C19−N12 109.4(7), N11−C19−C19A 123.5(6), N12−C19−C19A 127.1(9)



In the bibenzimidazolium complex **1b** the nickel atom is not found in the inversion center as it is usually the case[1,8,9,10] but on a twofold axis. The MS_4 core is no longer planar but has a torsion angle of 25°. The bibenzimidazolium system is likewise twisted around the central C−C bond by 27°. The deformation of the dithiolato core is most likely caused by steric effects as indicated by a short contact between the sulfur atoms S2 and propylene hydrogens H17 (Figure 1), vide infra. For **1b** and {MV[Ni(mnt)$_2$]}[8] the same angle between the perpendiculars of the least-squares planes of the donor (Ni1, S1, S2, C1, C2) and acceptor (N11, N12, C10, C15, C19) ions is found (4°). While the components of {MV[Ni(mnt)$_2$]} and {MV[Pd(mnt)$_2$]} are slipped by 150 pm relative to each other[1,8], the central bond of the bibenzimidazolium dication in **1b** lies exactly above the nickel atom. The packing behavior found for **1b** (Figure 2) compares well to that of {MV[Ni(mnt)$_2$]}[8] and {MV[Pd(mnt)$_2$]}[1] consisting of mixed donor-acceptor stacks. Shortest intrastack contacts are found between C3 and C11 (345 pm) and between S2 and H17/H18 (271 pm). The interstack contacts are shortest between N2 and C16 (324 pm) and between N2 and H16/H19 (243 pm).

Figure 2. View of the structure of **1b** along the *y* axis. The propylene bridges between the nitrogen atoms of P_2BBIm^{2+} are omitted for the sake of clarity

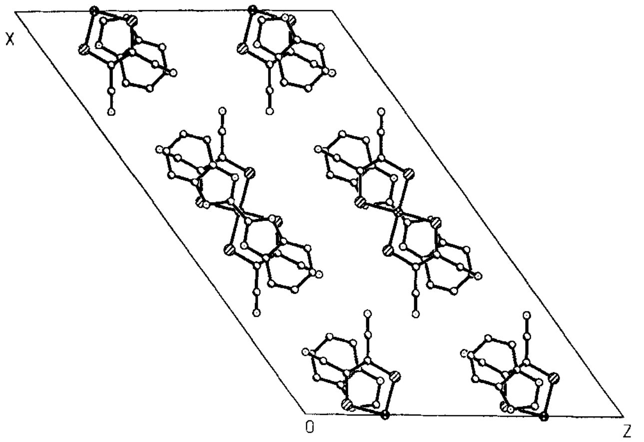
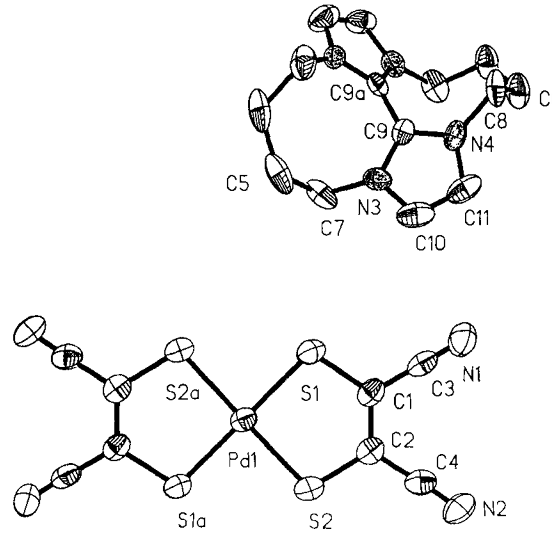
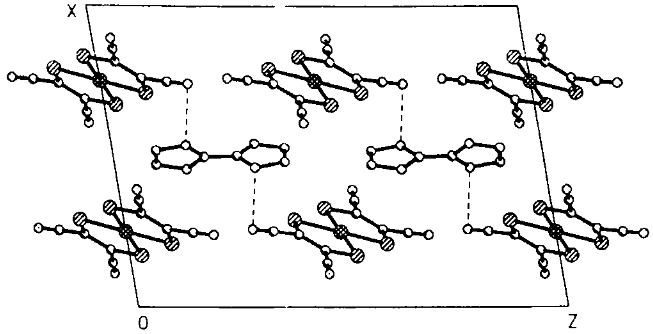


Figure 3. Molecular structure of **4c**, ORTEP plot; bond lengths [pm]: C5−C7 155.1(14), C5−C5A 158.8(24), C7−N3 149.3(11), C6−C8 153.5(13), C6−C6A 151.3(18), C8−N4 152.8(12), N3−C9 134.9(11), N3−C10 137.2(11), C9−N4 133.1(10), C9−C9A 147.4(16), N4−C11 139.5(12), C10−C11 133.9(17), bond angles [°]: C9−N3−C10 107.8(8), N3−C9−N4 109.2(7), N3−C9−C9A 125.1(6), N4−C9−C9A 125.6(7), C9−N4−C11 107.4(8), N3−C10−C11 108.0(9), N4−C11−C10 107.6(8)



In **4c** the MS_4 core of $[Pd(mnt)_2]^{2-}$ is planar but B_2BIm^{2+} is strongly twisted as indicated by an N−C−C−N torsion angle of 55° (Figure 3). Molecular mechanics calculations of the neutral monobridged compounds suggest torsion angles of 11, 39, and 41° for the ethylene-, propylene-, and butylene-bridged derivatives, respectively[11]. In the structure of **4c** no stacking is observed along any crystallographic axis. Instead, the packing rather consists of donor-acceptor chains than of columns (Figure 4). The chains are twisted in such a way that the perpendicular of the least-squares plane of the dithiolene part (Pd1, S1, S2, C1, C2) forms an angle of 25° with the adjacent imidazolium ring (C9, N3, C10, C11, N4). Short interionic contacts are observed between nitrile and imidazolium nitrogen atoms (N2···N3: 298 pm) and between C4 and C10 (343 pm). Calculated N···H contacts of 247 pm between nitrile nitrogen N1 and imidazolium hydrogen H10 and C3···H10 contacts of 268 pm are in the range of van der Waals distances[12]. The data for $[Pd(mnt)_2]^{2-}$ compare well to those reported for $\{MV[Pd(mnt)_2]\}$[1].

Figure 4. View of the structure of **4c** along the *y* axis. The butylene bridges between the nitrogen atoms of B_2BIm^{2-} are omitted for the sake of clarity



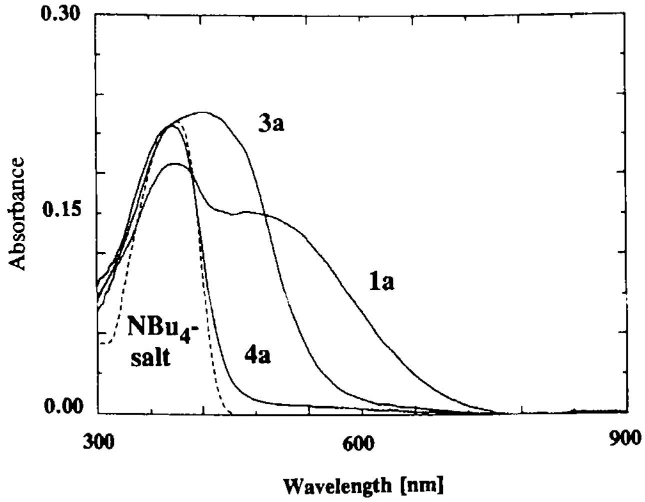
A closer look at the structure of $\{P_2BBIm[Ni(mnt)_2]\}$ (**1b**) reveals that the packing found here is a borderline case for ion pairs with less twisted acceptors. The $\{MV[Ni(mnt)_2]\}$ packing type is maintained but to optimize the arrangement the planarity of $[Ni(mnt)_2]^{2-}$ is given up to some extent. It is regained when P_2BBIm^{2+} in **1b** is replaced by the non-twisted $EPBIm^{2+}$ and P_2BIm^{2+}[13]. In cases of acceptors of larger torsion angles the $[M(mnt)_2]^{2-}$ remains planar, but the columns are now tilted towards a chain-like arrangement as in the case of **4c** and the isostructural **4b** and **4d**[13].

Electronic Spectra

The presence of charge-transfer bands is obvious from the colors of these substances. While $\{MV[Zn(mnt)_2]\}$ and **1a** are dark red and **2a** and **3a** are orange, **4a** has the same weakly yellow color as $(NBu_4)_2[Zn(mnt)_2]$. In Figure 5 the corresponding diffuse reflectance spectra of **1a**, **3a**, **4a**, and $(NBu_4)_2[Zn(mnt)_2]$ are shown. In the case of **1a** the IPCT band at 469 nm is clearly separated from the mnt band at 392 nm while it is hidden underneath as indicated by the distinct tailing in the case of **2a**, **3a**, and **4a**. The difference spectra show the IPCT maxima for these complexes to be located at 450, 448, and 435 nm, respectively. The overall sequence is in agreement with the variation of the first reduction potentials of the acceptors which are −0.49[15], −1.18, −1.12, and −1.39 V[11] for $(P_2BBIm)Br_2$, $(EPBIm)Br_2$, $(P_2BIm)Br_2$, and $(B_2BIm)Br_2$, respectively, as measured in acetonitrile vs. SCE. For the P_2BBIm complexes **1b** (730 nm), **1c** (745 nm), and **1d** (770 nm) the IPCT bands can be assigned by means of the difference spectra. Only broadening of the donor absorptions are likewise found in the spectra of all $\{R_2BIm[M(mnt)_2]\}$ (M = Ni, Pd, Pt).

According to the "high-temperature limit model" of Hush[2,14] the optical energy E_{op} (calculated from λ_{max}^{IPCT}) and the free enthalpy of the thermal electron transfer ΔG_{12} are connected with the reorganization energy χ by the equation $E_{op} = \chi + \Delta G_{12}$. ΔG_{12} can be estimated[5,7] as the difference of the redox potentials of the isolated components. Linear regression analysis (correlation coefficient: 0.97) for the series $\{[A][Zn(mnt)_2]\}$ (**1a**−**4a**) however reveals a slope of 0.2 which deviates strongly from unity. This suggests that the intrinsic barriers of electron transfer are not constant within this series. When A^{2+} is a 2,2′-bipyridinium acceptor, a similar plot for three zinc complexes affords a slope of 0.7 and a correlation coefficient of 0.98, as calculated from the data given in ref.[5]. For the bibenzimidazolium complexes **1b**−**d** no correlation between ΔG_{12} and E_{op} can be derived from the solid-state spectra.

Figure 5. Diffuse reflectance spectra of **1a**, **3a**, **4a**, and $(NBu_4)_2[Zn(mnt)_2]$

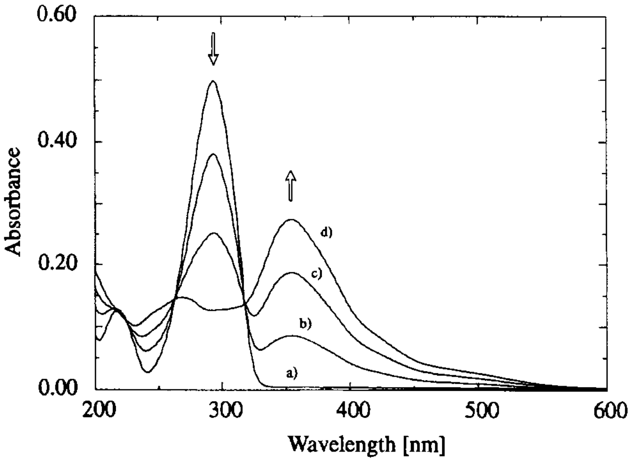


In solution IPCT absorptions can only be observed at considerably high concentrations using tandem cuvettes. From the difference spectra of the bibenzimidazolium complexes **1a**−**d** in DMSO/THF (1:1, v:v) weak and broad bands at 488, 749, 650, and 804 nm, respectively, can be derived. These values correspond to the variation of the donor potentials ($E_{1/2}^{-/2-}$ (Acetonitrile, SCE) $(NBu_4)_2[Zn(mnt)_2]$ +1.00 $V^{irrev.}$[16], $(NBu_4)_2[Ni(mnt)_2]$ +0.23 V, $(NBu_4)_2[Pd(mnt)_2]$ +0.46 V and $(NBu_4)_2[Pt(mnt)_2]$[17] +0.21 V. In the case of the d^8 complexes **1b**−**d** the plot of E_{op} vs. ΔG_{12} has a slope of 1.3 (correlation coefficient: 0.96) and affords an apparent reorganization energy of 67 kJ/mol. This corresponds well to the values of 60 to 70 kJ/mol found for analogous ion pairs with 2,2′- and 4,4′ bipyridinium acceptors[5]. In contrast to the solid-state spectra, in solution the biimidazolium complexes **2a**−**4d** only show tailing of dithiolato absorptions as compared to the corresponding tetrabutylammonium salts, but no maximum of the IPCT band can be assigned in the difference spectra. The pronounced negative first reduction potentials lead to a strong blue shift, and the bands cannot be separated from intense intracomponent absorptions.

Spectroelectrochemistry

While radical cations of methylviologen and related bipyridinium dications are well characterized, no physical properties apart from the redox potentials have been reported for the biimidazolium redox systems. We have obtained the electronic spectra of the reduced monocationic forms by spectroelectrochemical measurements[18]. Figure 6 shows the UV-Vis spectra of $P_2BIm(PF_6)_2$ during a 5-minutes reduction at the three indicated potentials.

Figure 6. Potentiostatic reduction of $P_2BIm(PF_6)_2$ in acetonitrile. a) 0 V, b) −1.10 V, c) −1.15 V, d) −1.20 V vs. SCE



The radical cation $P_2BIm^{+\bullet}$ is obviously stable during the reduction process [λ = 354 nm (ε = 13000 M^{-1} cm^{-1}) and 490 (sh) (1400)] whereas the neutral species generated by further reduction undergoes a subsequent unknown reaction so that an absorption spectrum cannot be recorded.

Thermal and Photochemical Reactivity of the Biimidazolium Metalates

In the absence of light and air all compounds are stable in the solid state and in solution. In the presence of air the diffuse reflectance spectra of the d^8 complexes show a characteristic time dependence while this is not the case for the d^{10} compounds. Additional absorptions indicating the formation of the monoanionic $[M(mnt)_2]^-$ appear at 850, 1110, and 870 nm for Ni, Pd, and Pt, respectively. The reaction does also happen in the case of the solid d^8 metal $(NBu_4)_2[M(mnt)_2]$ while it is absent in the dissolved state. It occurs already in a few minutes and is a thermal oxidation by dioxygen (air) since iodine vapour induces indentical spectral changes[19].

In solution the platinum complexes **1d**, **2d**, **3d**, and **4d** show a marked light-dependent sensitivity to oxygen resulting in the formation of the monoanionic $[Pt(mnt)_2]^-$ at λ = 870 nm. The reaction does not occur when $(NBu_4)_2[Pt(mnt)_2]$ or $\{MV[Pt(mnt)_2]\}$ are irradiated under identical conditions (DMSO, polychromatic irradiation, λ > 570 nm). Laser flash photolysis shows that the first reaction step involves optical electron transfer affording $R_2BIm^{+\bullet}$ and $[Pt(mnt)_2]^-$. Accumulation of the monoanion is made possible by a fast electron transfer from $P_2BIm^{+\bullet}$ to molecular oxygen[20].

The highly reducing $R_2BIm^{+\bullet}$ can also be obtained by continuous irradiation of $R_2BIm(PF_6)_2$ in solution in the presence of sacrificial donors like Na_2EDTA. Due to overlapping bands its formation can be monitored only indirectly by addition of MV^{2+}, PQ^{2+}, or BQ^{2+} *after* irradiation (see Experimental), which causes the characteristic colors of $MV^{+\bullet}$ (blue), $PQ^{+\bullet}$ (orange) and $BQ^{+\bullet}$ (orange-red) immediately to appear. Irradiation of $(R_2BIm)Br_2$ in the presence of Na_2EDTA and colloidal platinum in water leads to the formation of molecular hydrogen in amounts comparable to the standard $MVCl_2/Na_2EDTA$ under identical conditions.

Attempts to sensitize the photoreduction of the acceptors by irradiation into the IPCT band were conducted with $\{R_2BIm[M(mnt)_2]\}$. Excitation of $\{R_2BIm[Zn(mnt)_2]\}$ ($\lambda^{IPCT} \approx$ 440 nm) in the presence of $MV(PF_6)_2$ with wavelengths longer than 400 nm gives no $MV^{+\bullet}$. However this occurs when ligth of λ < 375 nm is employed. The formation of $MV^{+\bullet}$ thus seems not to follow an IPCT mechanism. More likely is a thermal reduction of methylviologen[21] by free mnt^{2-} nucleophiles produced by photodecomposition of $[Zn(mnt)_2]^{2-}$[22]. Accordingly, Na_2mnt reduces MV^{2+} in the dark at room temperature to $MV^{+\bullet}$.

In order to prevent the photodecomposition of the donor component, the photostable platinum analogues $\{R_2BIm[Pt(mnt)_2]\}$ are irradiated under similar conditions. However, in the absence or presence of a sacrificial reducing agent as Na_2EDTA or triethylamine formation of $R_2BIm^{+\bullet}$ or reduced $MV^{+\bullet}$ has never been observed. Moreover, all attempts to accomplish the reduction of water to dihydrogen in the presence of colloidal platinum have failed until now. This lack of reactivity of the $\{R_2BIm[Pt(mnt)_2]\}$ complexes most likely originates from a fast back-electron transfer due to the high exergonicity (150 kJ/mol) of this reaction.

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Experimental

All reactions were conducted under nitrogen by using nitrogen-saturated solvents. $(NBu_4)_2[Zn(mnt)_2]$, $(NBu_4)_2[Ni(mnt)_2]$, $(NBu_4)_2[Pd(mnt)_2]$, $(NBu_4)_2[Pt(mnt)_2]$[19], $(EPBIm)Br_2$, $(P_2BIm)Br_2$, $(B_2BIm)Br_2$[11], and $(P_2BBIm)Br_2$[23] were prepared as described in the literature. Addition of ammonium hexafluorophosphate to solutions of the acceptor dibromides in water led to the corresponding bishexafluorophosphates in yields generally higher than 90%.

The new complexes were precipitated from solutions of the corresponding $(NBu_4)_2[M(mnt)_2]$ and $(R_2BIm)(PF_6)_2$ or $(P_2BBIm)(PF_6)_2$ compounds. They are soluble only in a few dipolar aprotic solvents like dimethyl sulfoxide, propylene carbonate, dimethylformamide, or acetonitrile. Moreover, all dithiolene zincates tend to form oversaturated solutions. A tpyical synthesis procedure consists of dropwise addition of 0.2 mmol of the acceptor bishexafluorophosphate in 40 ml of acetone to a well-stirred solution containing 0.2 mmol of $(NBu_4)_2[M(mnt)_2]$ in 30 ml of acetone. The resulting suspension is stirred for 30 min, then the solid is filtered off by suction, washed with 5 ml of acetone and 5 ml of methanol and dried in vacuo. All the zincates are soluble in pure acetone and should only be washed with methanol.

1,1′:3,3′-Bis(propane-1,3-diyl)-2,2′-bibenzimidazolium Bis(cis-1,2-dicyanoethene-1,2-dithiolato)zincate(II) (**1a**): After mixing of the components 20 ml of 2-propanol was added. The product crystallized on standing at −30°C for 2 d. Red crystalline powder (42%). – $C_{28}H_{20}N_8S_4Zn$ (662.2): calcd. C 50.79, H 3.04, N 16.92, S 19.37; found C 51.01, H 3.13, N 16.94, S 18.95.

Nickel Complex **1b**: Yellowish brown powder (76%). – $C_{28}H_{20}N_8NiS_4$ (655.5): calcd. C 51.31, H 3.08, N 17.09, S 19.57; found C 51.28, H 3.03, N 17.18, S 19.31.

Palladium Complex **1c**: Brown powder (85%). – $C_{28}H_{20}N_8PdS_4$ (703.2): calcd. C 47.83, H 2.87, N 15.94, S 18.24; found C 47.61, H 2.90, N 15.78, S 18.22.

Platinum Complex **1d**: Dark red powder (88%). – $C_{28}H_{20}N_8PtS_4$ (791.9): calcd. C 42.47, H 2.55, N 14.15, S 16.20; found C 42.43, H 2.58, N 13.85, S 16.21.

1,1′-(Ethane-1,2-diyl)-3,3′-(propane-1,3-diyl)-2,2′-biimidazolium Bis(cis-1,2-dicyano-ethene-1,2-dithiolato)zincate(II) (**2a**): A solution of 0.2 mmol of $EPBIm(PF_6)_2$ in 30 ml of acetone was allowed to react with 0.2 mmol of $(NBu_4)_2[Zn(mnt)_2]$ in 20 ml of acetone. After stirring for 30 min 60 ml of methanol and 40 ml of 2-propanol were added. Orange powder (79%). – $C_{19}H_{14}N_8S_4Zn$ (548.0): calcd. C 41.64, H 2.57, N 20.45, S 23.40; found C 41.74, H 2.52, N 20.49, S 23.53.

Nickel Complex **2b**: Red powder (88%). – $C_{19}H_{14}N_8NiS_4$ (541.3): calcd. C 42.16, H 2.60, N 20.70, S 23.69; found C 42.17, H 2.50, N 20.52, S 23.35.

Palladium Complex **2c**: Yellowish green powder (85%). – $C_{19}H_{14}N_8PdS_4$ (589.0): calcd. C 38.74, H 2.40, N 19.02, S 21.77; found C 38.59, H 2.40, N 18.72, S 21.69.

Platinum Complex **2d**: Red powder (78%). – $C_{19}H_{14}N_8PtS_4$ (677.7): calcd. C 33.67, H 2.08, N 16.53, S 18.92; found C 33.80, H 2.03, N 16.56, S 19.06.

1,1′:3,3′-Bis(propane-1,3-diyl)-2,2′-biimidazolium Bis(cis-1,2-dicyanoethene-1,2-dithiolato)zincate(II) (**3a**): Procedure as described for **2a** by using 60 ml of acetone. After mixing of the components 17 ml of methanol was added, the product crystallized after 5 d at room temp. Orange crystalline powder (29%). – $C_{20}H_{16}N_8S_4Zn$ (562.0): calcd. C 42.74, H 2.87, N 19.94, S 22.82; found C 42.66, H 2.79, N 19.89, S 22.47.

Nickel Complex **3b**: Red powder (90%). – $C_{20}H_{16}N_8NiS_4$ (555.3): calcd. C 43.25, H 2.90, N 20.18, S 23.09; found C 43.55, H 2.89, N 20.32, S 23.17.

Palladium Complex **3c**: Green powder (83%). – $C_{20}H_{16}N_8PdS_4$ (603.1): calcd. C 39.83, H 2.67, N 18.58, S 21.27; found C 39.72, H 2.67, N 18.42, S 21.38.

Platinum Complex **3d**: Red powder (69%). – $C_{20}H_{16}N_8PtS_4$ (691.8): calcd. C 34.73, H 2.33, N 16.20, S 18.54; found C 34.99, H 2.35, N 16.31, S 18.62.

1,1′:3,3′-Bis(butane-1,4-diyl)-2,2′-biimidazolium Bis(cis-1,2-dicyanoethene-1,2-dithiolato)zincate(II) (**4a**): A solution of 70 mg of $ZnCl_2$ in 10 ml of MeOH was added to a solution of 190 mg of Na_2mnt[8] in 10 ml of MeOH. The resulting yellow solution was stirred for 30 min. After addition of 200 mg of $B_2BIm(Br)_2$ in 10 ml of MeOH a yellow precipitation formed which was filtered off by suction upon standing for 12 h at room temp. The product was washed with MeOH until the filtrate was colorless and dried in vacuo (210 mg, 71%). The crude product was dissolved in 50 ml of acetonitrile, the solution was filtered, and 70 ml of 2-propanol was added to the filtrate. Crystallization occured during standing of the mixture for 14 d at −30°C. Yellow crystalline powder (21%). – $C_{22}H_{20}N_8S_4Zn$ (590.1): calcd. C 44.78, H 3.42, N 18.99, S 21.73; found C 44.43, H 3.44, N 19.03, S 21.29.

Nickel Complex **4b**: Red needles (69%). – $C_{22}H_{20}N_8NiS_4$ (583.4): calcd. C 45.29, H 3.46, N 19.21, S 21.98; found C 45.56, H 3.42, N 19.26, S 21.98.

Palladium Complex **4c**: Green needles (81%). – $C_{22}H_{20}N_8PdS_4$ (631.1): calcd. C 41.87, H 3.19, N 17.75, S 20.32; found C 41.53, H 17.56, N 17.56, S 20.60.

Platinum Complex **4d**: Red needles (90%). – $C_{22}H_{20}N_8PtS_4$ (719.8): calcd. C 36.71, H 2.80, N 15.57, S 17.82; found C 36.82, H 2.77, N 15.41, S 18.00.

All UV-Vis-NIR spectra were recorded with a Shimadzu UV 3101PC spectrometer. For diffuse reflectance measurements the substances were spread on a corundum carrier which also served as reflectance standard. Solution spectra were obtained before and after mixing of $5 \cdot 10^{-3}$ M solutions of the components in DMSO/THF (1:1, v:v) in tandem cuvettes (Hellma). Optical spectra of the one-electron-reduced acceptors were measured by reduction of the corresponding $R_2BIm(PF_6)_2$ salts in acetonitrile using a spectroelectrochemical cell as described previously[18]. Irradiations were conducted in water-cooled quartz cuvettes (d = 1 cm) on an optical bench equipped with a xenon lamp (Xe-150W/S) and cut-off filters. Concentrations were in the range of $5 \cdot 10^{-3}$ M for $(NBu_4)_2[M(mnt)_2]$, a tenfold excess of acceptor hexafluorophosphate was applied (DMSO, DMF, DMSO/H_2O, and DMF/H_2O, 4:1, v:v). For the indirect detection of $P_2BIm^{+\bullet}$ and $B_2Bim^{+\bullet}$ $5 \cdot 10^{-4}$ M solutions of the acceptor dibromides in methanol were irradiated (Xe lamp without filters) in the presence of 100 mg of Na_2EDTA. After irradiation 10 mg of $MVCl_2$ [methylviologene dichloride (Fluka)], $(PQ)Br_2$ (propane-1,3-diyl-2,2′-bipyrdidinium dibromide), or $(BQ)Br_2$ (butane-1,4-diyl-2,2′-bipyridinium dibromide) was added. The same reactivity was found in methanol/acetone mixtures (1:1, v:v) when the corresponding acceptor hexafluorophosphates were used. Hydrogen evolution was examined in aqueous solutions containing $R_2BIm(Br)_2$ and Na_2EDTA (Fluka) in 10^{-3} and $5 \cdot 10^{-2}$ M concentrations, respectively. Platinum sol was prepared by thermal reduction of H_2PtCl_6 (Fluka) with trisodium citrate dihydrate (Fluka) in water. Excess citrate was removed with Amberlite MB-3 (Merck) ion exchange resin[24], no protective agent was applied. Hydrogen gas, typically 10–100 µl, was detected with a Pye Unicam PU 4500 gas chromatograph (nitrogen carrier gas, thermal conductivity detector).

X-Ray Crystallographic Determination: Crystals of **1b** and **4c** were prepared by diffusion of methanol into saturated solutions of the compounds in DMSO. Powder diffraction diagrams of crystallized **1b** revealed that two modifications are formed, yet only one modification could be characterized by single-crystal structure analysis.

$C_{28}H_{20}N_8NiS_4$ **1b** (655.5), black needles, crystal size 0.80 × 0.40 × 0.30 mm, monoclinic crystal system, space group $C2/c$, a =

2717.6(20), b = 743.0(6), c = 1765.7(18) pm, β = 126.03(6)°, V = 2.883(5) nm^3, $d_{\text{calc.}}$ = 1.51 g/cm^3 (Z = 4). R = 0.059, R_w = 0.051, 186 parameters refined.

$C_{22}H_{20}N_8PdS_4$ **4c** (631.1), green prisms, crystal size 0.30 × 0.30 × 0.20 mm, monoclinic crystal system, space group $C2/c$, a = 1315.3(4), b = 1028.2(3), c = 1890.8(7) pm, β = 99.74(2)°, V = 2.520(1) nm^3, $d_{\text{calc.}}$ = 1.66 g/cm^3 (Z = 4). R = 0.061, R_w = 0.052, 161 parameters refined.

Structure analysis was carried out on a automatic four-circle goniometer (Siemens P4) at 293 K using Mo-K_α radiation (graphite monochromator). The structure was solved by direct methods by using the SHELXTL-PLUS[25] program. For the refinement all non-hydrogen atoms were included with anisotropic temperature factors; the hydrogen positions were determined by difference Fourier analysis and included into the refinement with fixed coordinates and temperature factors[26].

☆ Dedicated to Professor Dr. *Heinz Dürr* on the occasion of his 60th birthday.

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