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A New Approach to Functionalize an Organic Compound through the Influence of Metal Bis(dithiolene) Complexes Leading to Ion-Pair Compounds Exhibiting Strong Emission at Room Temperature in the Visible Region

Vedichi Madhu and Samar K. Das*

School of Chemistry, University of Hyderabad, Hyderabad 500046, India

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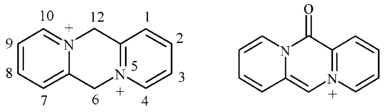
The facile oxidation of 6,12-dihydrodipyrido [1,2-α;1′,2′-d] pyrazidinium ($DDP^{2+} = [C_{12}H_{12}N_2]^{2+}$) chloride to cyclic quaternary ammonium monocation, 12-oxo-9*H*-dipyrido[1,2-α;1′,2′-d]pyrazin-5-ium ($ODP^{1+} = [C_{12}H_9N_2O]^{1+}$) is achieved when it reacts with $[M(mnt)_2]^{2-}$ ($M{=}Ni^{2+}$ and Cu^{2+}) resulting in the formation of the ion pair compounds $[ODP]_2[Ni(mnt)_2]$ (**1**) and $[ODP]_2[Cu(mnt)_2]$ (**2**), respectively (see Scheme 1 for the structures of $[ODP]^{1+}$ and $[DDP]^{2+}$). The nickel complex **1** exhibits intense emission at room temperature in the visible region, whereas, in the case of copper analogue **2**, the emission gets quenched. The oxo cation ODP (known to be an unstable species and never characterized unequivocally before) is stabilized in **1** and **2** by cation–anion interactions.

Introduction

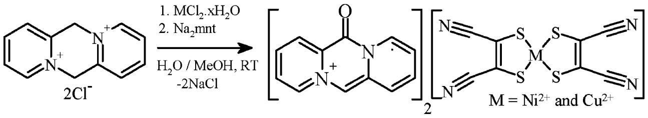
The design and the synthesis of metal bis(dithiolene) complexes are of continuing interest due to their potential applications as near-infrared (NIR) dyes,[1] conducting,[2] magnetic,[3] and nonlinear optical materials.[4] The scope of metal−dithiolene complexes has expanded to bioinorganic modeling because of the existence of metal−dithiolene moiety in many metalloenzymes.[5] Eisenberg and co-workers have extensively studied the emission properties of mixed-ligand M(II)−diimine−dithiolate complexes ($M = Ni^{2+}$, Pt^{2+}, and Pd^{2+}).[6] Both square planar and trigonal prismatic metal−(tris)dithiolenes, $M[S_2C_2R_1R_2]_3$ have been used as electrochemical catalysts in the context of photochemical charge separation.[7] More recent reports have described that the metal (mono) dithiolene complexes are very useful catalysts for organic synthesis of cyanofluoroamides.[8]

Scheme 1



DDP **ODP**

Scheme 2



However, there are not many reports on organic transformations that use a metal−bis(dithiolene) complex as a catalyst. We describe here an easy oxidation of a condensed heterocyclic system (which incorporate pyridinium cations) in a metal−(bis)dithiolene complex matrix. More specifically, when we add the chloride salt of DDP (an organic heterocyclic dication, see Scheme 1) to the aqueous methanol solution of $[Ni(mnt)_2]^{2-}$ [generated in situ from $NiCl_2{\cdot}6H_2O$ and Na_2mnt, see Scheme 2, ($mnt^{2-} = 1,2$-dicyanoethylene dithiolate)], instantaneous formation of an ion pair compound $[ODP]_2[Ni(mnt)_2]$ (**1**) (in which DDP dication is oxidized to ODP monocation with the addition of an oxo group, see Scheme 1) is observed. The synthesis of ODP bromide from DDP bromide had been achieved in 1960s,[9] which was carried out in two steps. In the first step, the Pd/C catalyst

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* To whom correspondence should be addressed.

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was used to dehydrogenate DDP, and the second step (oxidation) was performed using selenium dioxide (SeO_2) as an oxidizing agent to achieve $[ODP]^{1+}$ as bromide salt.[9]

Nevertheless, the keto analogue ODP had never been characterized unequivocally. There was a brief mention about IR spectroscopy,[9] but without any data, especially for C=O vibrations. We describe here the unambiguous crystallographic characterization of **1** besides its routine spectral (that include IR, NMR, and UV−visible) and elemental analysis.[10] Compound **2** was additionally characterized by ESR spectroscopy. Remarkably, compound **1** exhibits strong emission at room temperature in the visible region.

We could isolate[11] compounds **1** and **2** by a one-pot synthesis described in Scheme 2 (see Supporting Information for synthesis details). IR spectra of compounds **1** and **2** show four characteristic bands [1667 m for (C=O); 1636 m for intraring (C=N); 1464 m for (−C=C−) and 2190 s for (C≡N) groups] besides other bands (see Supporting Information).

The asymmetric unit in the crystal structure[12] of compound **1** consists of one $[ODP]^{1+}$ cation and half of a $[Ni(mnt)_2]^{2-}$ anion. Thus, the formula unit of **1** consists of a full $[Ni(mnt)_2]^{2-}$ anion and two ODP cations, as presented in Figure 1.

The classical inorganic complex $[M(mnt)_2]^{2-}$ anions are known to be a versatile π-conjugated acceptors that are frequently employed in $\pi-\pi$ interactions with π-conjugated donors.[13] In the present systems, two $[ODP]^{1+}$ cations interact with one $[Ni(mnt)_2]^{2-}$ anion through $\pi-\pi$ interactions, in which the average distance between anion and cation is 3.786 Å, as shown in Figure 2. Analysis of the crystal structure of **1** reveals that $[ODP]^{1+}$ cations generate a one-dimensional chain that is formed by weak intermolecular C−H···O hydrogen-bonding interactions (Figure 3). Two such parallel chains (that run along crystallographic *b* axis) are laterally attached by the square planar $[Ni(mnt)_2]^{2-}$ complex anions ($\pi-\pi$ interactions, Figure 2), as if a chain of $[Ni(mnt)_2]^{2-}$ complex anions intervene the parallel chains of ODP cations, as shown in Figure 3.

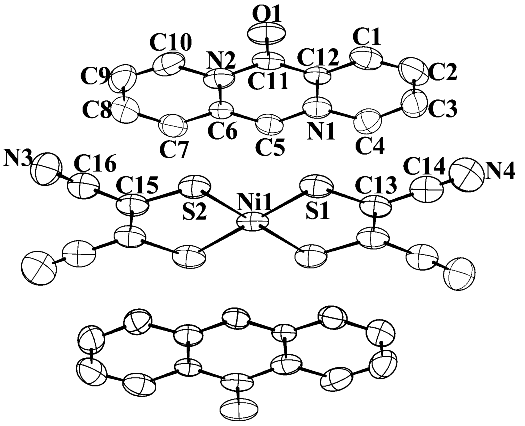

Figure 1. Thermal ellipsoidal plot of **1** (30% probability). Hydrogen atoms are not shown for clarity.

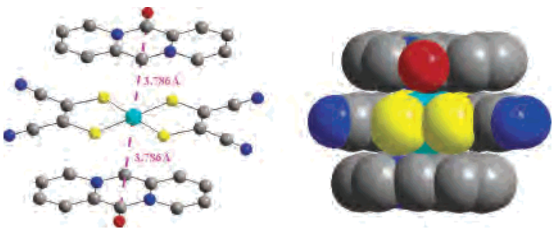

Figure 2. View of the interaction between ODP cations and the $[Ni(mnt)_2]^{2-}$ complex anion. Ball and stick view (left) and space filling view (right). Color code: C, medium gray; N, blue; O, red; S, yellow; Ni, cyan.

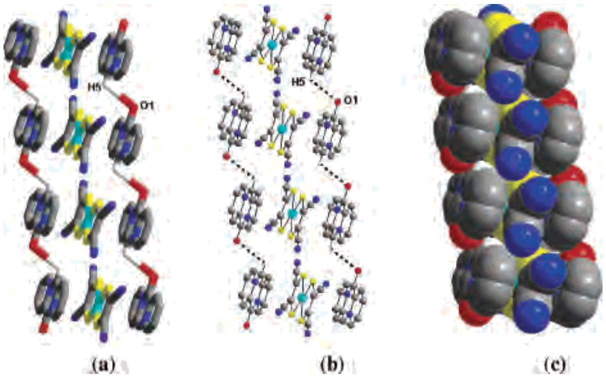

Figure 3. View of (a) wire frame, (b) ball and stick and (c) space filling representation of C−H···O hydrohen-bonding interactions between ODP cations (2.74(4) Å) resulting two zigzag chains, $[Ni(mnt)_2]^{2-}$ anions staying in between layers. Color code: C, medium gray; N, blue; O, red; S, yellow; Ni, cyan.

Compound **2** is isostructural with compound **1**, as is evidenced by its unit cell parameters.[12]

Further structural details are given in Supporting Information. The oxo group (of the ketone function) formed after oxidation is not only evidenced in the IR spectra of compounds **1** and **2** (an IR response in the range of 1664−1668 cm^{-1}), but also is confirmed in the crystal structure of **1** that exhibits the relevant C=O bond distance of 1.221(4) Å. The formation of this C=O bond is additionally supported by ^{13}C NMR spectroscopy (see Supporting Information).

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(10) Selected data for **1** and **2** are provided in the Supporting Information.

(11) Synthesis of $[DDP]Cl_2 \cdot 2H_2O$: 2-Picolylchloride hydrochloride was dissolved in water and neutralized with K_2CO_3 and extracted with dichloromethane. The organic layer was separated and dried with Na_2SO_4, and then the CH_2Cl_2 solution was kept at room temperature after complete evaporation of solvent pale yellow crystals was formed. Synthesis of **1**: 0.118 g of $NiCl_2 \cdot 6H_2O$ (0.5 mmol) was dissolved in 10 mL of a $MeOH/H_2O$ (1:1) mixture. To this solution, 0.186 g of Na_2mnt (1 mmol) was added and it was then stirred for 10 min at room temperature. This reaction mixture was treated with an aqueous solution of $[DDP]Cl_2 \cdot 2H_2O$ (0.145 g and 0.5 mmol), whereby a red precipitate was immediately formed, which was separated by filtration. The precipitate was washed with ether and dried in air. It was then crystallized from dimethylformamide (DMF) by slow ether diffusion. The crystals of **1** were separated and washed with ether and dried at room temperature. Yield 0.187 g (51 %). Synthesis of **2**: This was synthesized by the same preparation as described for compound **1** (see Supporting Information for details).

(12) Crystal data of **1**: $C_{32}H_{18}N_8NiO_2S_4$, $M = 733.49$ g mol^{-1}, monoclinic, space group $C2/c$, $a = 24.980(4)$ Å, $b = 6.4802(10)$ Å, $c = 21.104(3)$ Å, $\beta = 118.107(2)°$, $U = 3013.2(8)$ $Å^3$ $Z = 4$, $D_C = 1.617$ g cm^{-3}, $\mu = 0.969$ mm^{-1}, $F(000) = 1496$, crystal size $= 0.44 \times 0.12 \times 0.08$ mm^3. 13 804 measured with 2660 unique reflections ($R_{int} = 0.0309$), of which 2120 ($I > 2\sigma(I)$) were used for the structure solution. Final R1 = 0.0671, 218 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −0.196 and +0.433 e $Å^{-3}$. Unit cell parameters for compound **2**: monoclinic, $a = 24.866(5)$ Å, $b = 6.412(10)$ Å, $c = 21.322(14)$ Å, $\beta = 117.17(3)^o$, $U = 3025.1$ (11) $Å^3$

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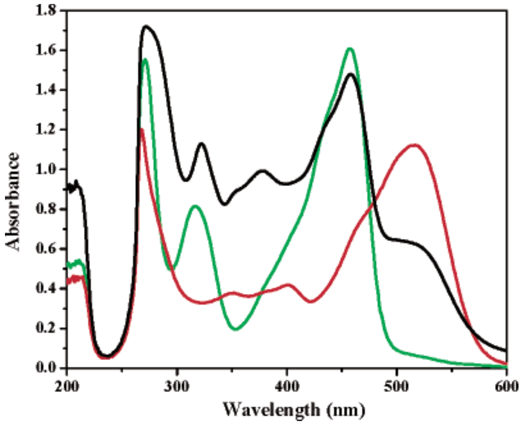

Figure 4. Absorption spectra of $[DDP]Cl_2$ (red), **1** (green) and **2** (black) in DMF solvent, concentration, 1×10^{-5} M for all three.

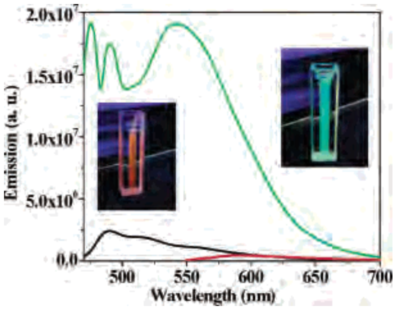

Figure 5. Emission spectra of $[DDP]Cl_2$ (red: excited at 535 nm), compound **1** (green solid line: excited at 470 nm), and compound **2** (black solid line: excited at 470 nm). Concentration = 1×10^{-5} M in DMF for all.

From a synthetic point of view, it is worth mentioning that the transition metal complexes, $[M(mnt)_2]^{2-}$, are generated in situ by using free dithiolene ligand (Na_2mnt) and the chloride salt of respective transition metals, MCl_2. The role of free mnt ligand cannot be ignored in such organic functionalization reaction (conversion of $[DDP]^{2+}$ to $[ODP]^{1+}$), because mnt^{2-} is also a redox-active species. To ensure this ambiguity, we performed the same synthesis without adding MCl_2, whereby a yellowish-brown solid was isolated. The IR spectrum of this compound (see Supporting Information, S-Figure 8) does not show the characteristic band for C═O group as are shown in the IR spectra of both compounds **1** and **2** (vide supra). Thus, the role of transition metal ion/metal−dithiolene complex anion, $[M(mnt)_2]^{2-}$ in this oxidation of $[DDP]^{2+}$ to $[ODP]^{1+}$, is significant. In order to gain some idea about the mechanism for this “oxo-insertion” reaction, we performed solution ESR studies by taking the same reaction mixture as was used for the synthesis of nickel compound. However, we did not observe any characteristic ESR signal for Ni(III) species (the solution remained ESR silent). Therefore, the mechanism for the oxidation of $[DDP]^{2+}$ to $[ODP]^{1+}$ is not clear at this stage.

The electronic absorption spectrum of $[DDP]Cl_2$ in DMF exhibits strong visible band at 516 nm with other three bands in the UV region (Figure 4). This peak shows a blue-shift to 458 nm, on its oxidation to $[ODP]^{1+}$, as shown in the electronic absorption spectra of compounds **1** and **2** (Figure 4).

The chloride salt of $[DDP]^{2+}$ (an organic heterocyclic dication) shows weak (red) emission at around 590 nm, as shown in Figure 5. When it is oxidized to $[ODP]^{1+}$ in compound **1**, there is a band shift and tremendous increase in fluorescence intensity (Figure 5).

The fluorescence intensity at 540 nm is ca. 42 times that of the $[DDP]Cl_2$ at 590 nm (Figure 5), which clearly indicates that **1** is a highly emissive compound. This is in contrast to the fact that the emission of $[ODP]^{1+}$ in compound **2** is quenched as shown in Figure 5. The paramagnetic copper complex (a d^9 system) associated with $[ODP]^{1+}$ cation (via noncovalent interaction) seems to be responsible for this quenching[14] (see Supporting Information for emission details).

In conclusion, we have demonstrated an easy one-pot room-temperature keto-group insertion (method) into a heterocyclic cationic ring in an inorganic coordination complex matrix, which otherwise needs two different steps (reduction followed by oxidation with respective reductant and oxidant). Amazingly, this oxidation from $[DDP]^{2+}$ to $[ODP]^{1+}$ in **1** enhances the emission enormously at room temperature in the visible region. On the other hand, this emission is drastically quenched in compound **2**. The present system represents a new type of synthetic strategy for organic oxidation in the matrix of classical coordination complexes. Compound **1** is a rare example of a metal−dithiolene system that causes an otherwise difficult oxidation at one of its component (cation) and exhibits emission in the visible region at room temperature.

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Supporting Information Available: Text depicting synthetic, spectroscopic (UV−vis, emission, IR, ESR, etc.) and crystallographic details, a complete X-ray crystallographic file in CIF format, and simulated X-ray powder diffraction patterns of compounds **1** and **2** from their respective crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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