

Fabrication of heterojunctions and current-voltage characteristics of vanadium coordination compounds

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Current voltage (*I-V*) characteristics of the films of four vanadium complexes, VO₂(3-fl) (**1**) (3-fl = 3-Hydroxyflavone), VO(pbd)₂ (pbd = 1-Phenyl-1,3-butadione) (**2**), VO(dbm)₂ (dbm = Dibenzoylmethane) (**3**), and VO(acac)₂ (acac = Acetylacetonate) (**4**), have been investigated at room temperature. The films were grown on copper (Cu) and Aluminum (Al) substrates by using a centrifugal machine operated at 183, 733 and 1650 g values. *I-V* characteristics of all samples showed non-linear rectification behavior. All complexes exhibited higher conductivity for Cu than Al substrate indicating that Cu and V complex contact resistance is lower than that of Al. Press tablets of the samples exhibited p-type semiconductor behavior. In **1** and **4**, a switching effect from low conductance to high conductance states was observed. An abrupt increase in the current at threshold voltage may be related to switching effect from low to high conductivity state. At relatively low current the switching effect was reversible for both substrates, whereas at high current it was only reversible for Al. Heterojunction samples of Cu/1/TiO₂/Ga and Al/4/TiO₂/Ga (TiO₂ = titanium oxide) were also fabricated and they were found to be p-n aniso type.

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1. Introduction

Vanadium oxides and some of their complexes are known to exhibit semiconductor properties and have potential to be used in different kinds of sensors. It has been shown that vanadium dioxide thin films prepared by chemical vapor deposition from vanadium(III) acetylacetonate (V(acac)₃) exhibit optical and electrical switching behavior which strongly depends on film thickness [1]. Films comprised of nanowires of β-Na_xV₂O₅ prepared by using β-diketonato complex, **4**, as precursor are also reported [2]. Nanocrystalline TiO₂-organic photosensitizer based solar cells are investigated and their high performance is demonstrated [3,4]. This indicates the importance of the introduction of different metal based materials into existing technology which may lead to dramatic improvements in functionality and/or cost of organic-inorganic materials [5].

It is known that the structure and properties of organic semiconductors are highly dependent upon their fabrication technology [6,7,8]. Generally, the organic materials have large molecular weight and unique physical properties because of van der Waals intermolecular forces. For this reason, organic materials and particularly semiconductors are found suitable for centrifugal processing that has given interesting results for different kinds of materials [9-12].

For fabrication of the semiconductor devices, type of metal-semiconductor and hetero-junctions play very crucial role [13]. If metal-semiconductor junction is nonrectifying or ohmic, it is a low-resistance junction

providing current conduction in both directions and may be used as a contact material in the semiconductor devices and integrated circuits. A metal-semiconductor rectifying junction called a Schottky barrier diode may be used at different semiconductor devices as photo-electric sensors, solar cells, field effect transistors etc. In a number of organic semiconductor devices the space-charge-limited currents (SCLC) are reported, where current mostly takes place due to injection of charge carriers from electrode material into semiconductor. Current-voltage characteristics are non-linear and their behavior may be used practically in different devices [14,15]. In this work, we report the deposition of the films of four vanadium coordination compounds, **1-4**, by using centrifugation method and the investigation of their current-voltage characteristics. The heterojunction characteristics of vanadium complexes and TiO₂ are also reported.

2. Experimental details

2.1 Materials

Dibenzoylmethane (dbm), 3-hydroxyflavone (3-fl) and 1-Phenyl-1,3-butadione (pbd) were obtained from Sigma-Aldrich Chemical Company and were used as received. Complexes **1**, **2** and **3** were prepared using standard techniques [16] whereas **4** was obtained from Aldrich Chemical Company. Sodium acetate solution was prepared by dissolving 2.05g in 40 mL of H₂O.

2.2 Preparation of press tablets

Press-tablets of 13 mm diameter and 2 mm height were prepared from the powders of vanadium complexes at a pressure of 6×10^3 atmosphere. Complexes 1-4 were found to be *p*-type semiconductors as determined by hot probe methods [17].

2.3 Preparation of solutions

Solubility and stability of vanadium complexes were monitored in different polar and non-polar organic solvents like dimethylsulfoxide, benzene, methylene chloride, acetone and chloroform. Chloroform was chosen for our studies because of the high solubility and stability of most of the vanadium compounds used in this study.

2.4 Deposition of films

A table-top centrifugal machine was used for the deposition of films on the 10×10 mm² Cu or Al foil substrates at room temperature deposited from 0.5-1.0 wt.% solution of the vanadium complexes in chloroform at gravity conditions of 183 g, 733 g and 1650 g, where *g* is acceleration due to gravity. Thickness of the foil was 12 μm and 27 μm for copper and aluminum, respectively. The substrates were flattened properly because experimentally it was found that small bends on substrate affect the uniformity of the deposited films. The substrate was placed inside a flat-bottomed glass tube, which was mounted in the centrifugal machine. Internal diameter of 12 mm and length of 25 mm was found to be the optimal size of the centrifugal tube.

Centrifugal rotation speeds of 1000, 2000 and 3000 rpm were used. For every experiment, two tubes each containing 0.5mL of the solution were put in the centrifuge machine on opposite sides to keep the machine in mechanical balance. At the acceleration of 183 g, 733 g and 1650 g the processing time of 40-60 minutes, 30-50 minutes and 20-40 minutes, respectively, was the optimum time to completely evaporate the solvent. In several experiments, substrates were placed in the tube at an inclined angle of 3-6°, and it was found that thickness of deposited films was not uniform and it decreased to the clockwise direction of rotation. Experimental conditions for centrifugation such as the size of glass tube, the deposition time, rotation speed, kind of solvent and substrates (Al showed more stability and reversibility of the results than Cu) were optimized, and Al/1/Ga, Cu/1/Ga, Al/2/Ga, Cu/2/Ga, Al/3/Ga, Cu/3/Ga, Al/4/Ga, Cu/4/Ga, Cu/1/TiO₂/Ga and Al/4/TiO₂/Ga sandwich type samples were fabricated.

2.5 Determination of film thickness

For the determination of the thickness of the deposited films, the substrates were weighed before and after deposition and the mass (*m*) and area of the deposited film were determined. The thickness of the deposited film (*d*) was calculated by the expression where ρ is density, *A* is area and *m* is mass:

$$d = m / \rho A \quad (1)$$

The thickness of the films were in the range of 12 μm (deposited at 183 g) to 7 μm (deposited at 1650 g). As expected, the thickness of the films decreased with increasing acceleration or rotation speed of the centrifuge machine.

2.6 Deposition of vanadium films on TiO₂

TiO₂ films from 10 weight% of its aqueous suspension were deposited on predeposited films of vanadium complexes by drop deposition method. The thickness of the TiO₂ films was in the range of 10-15 μm. The droplets of liquid gallium of 2-3 mm diameter were deposited on the films of vanadium complexes or TiO₂ to provide a soft contact. The liquid gallium was used as a contact material to the substrate as well. Figure 1 shows a schematic view of the sandwich type samples.

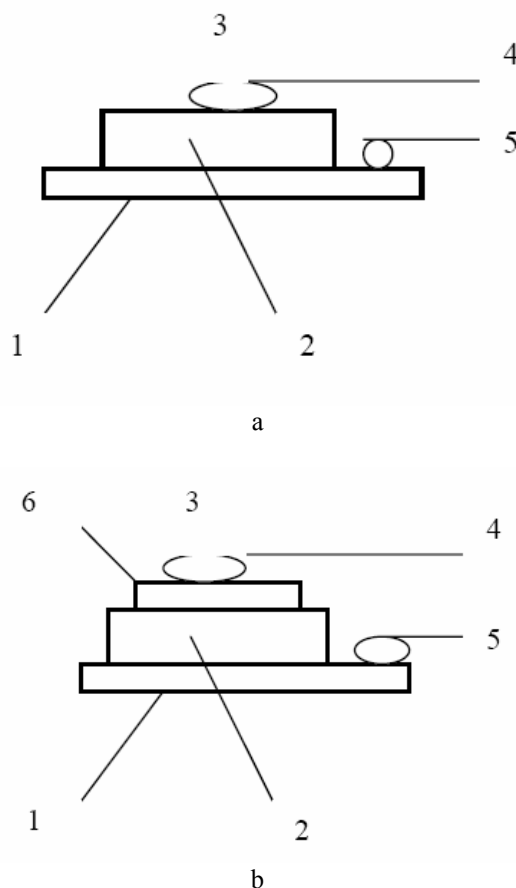


Fig. 1. Schematic diagrams of the metal/metal-organic complex/metal (a) and metal/heterojunction/metal (b) samples; 1 – substrate (Cu or Al), 2 – vanadium metal complex, 3 – drops of gallium, 4 and 5 – terminals, 6 – TiO₂.

Measurement of current-voltage (*I-V*) characteristics was carried out using a digital voltmeter and ammeter at room temperature. External series resistor, connected to the voltage supply, that limits the value of the current

passing through the sample, was equal to 1 M Ω . Room temperature conductivity of the samples and the metal-semiconductor and hetero-junction's parameters as rectification ratio, threshold voltage, and junction resistance were determined.

3. Results and discussion

3.1 Vanadium complexes used in this study

Structures of four different vanadium complexes, **1-4**, used in this study are depicted in Fig. 2. In these

complexes, vanadium is in +5 oxidation state in **1** whereas it is in +4 oxidation state in all other compounds. Vanadium compounds in +4 oxidation state have one electron in low energy d-orbitals whereas, vanadium complex in +5 oxidation state have empty d orbitals. Presence of an electron in V(IV) complexes exhibit electron transitions in visible and infrared regions which may exhibit useful electronic properties and make it suitable for sensor devices. However, our studies (*vide infra*) indicate little effect of the oxidation state of vanadium on their current-voltage (*I-V*) characteristics of the deposited films. This indicates that d electrons may not be participating in current-voltage characteristics.

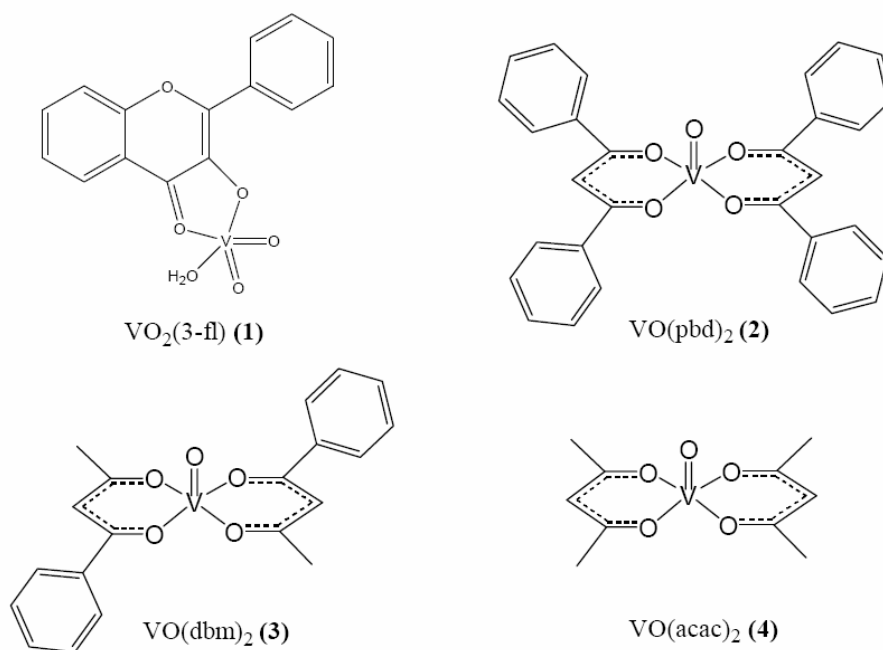


Fig 2. Molecular structures of complexes 1-4.

3.2 *I-V* Characteristics

Table 1 shows experimental data on conductivity, junction resistance, rectification ratio, non-linearity

coefficient, and type of conductance data obtained for all investigated vanadium complexes and their heterojunction samples.

Table 1. Electric properties of vanadium coordination complexes and their heterojunction samples.

No	Samples	RR*	B	R _j , M Ω	Type	σ 10 ⁻¹¹ Ω^{-1} cm ⁻¹
1.	Cu/ 4 /Ga	27	--	23	p	5
2.	Cu/ 1 /Ga	29	--	34	p	4
3.	Cu/ 2 /Ga	2	1.6	140	p	1
4.	Al/ 4 /Ga	10	2.3	64	p	2
5.	Al/ 1 /Ga	7	3.4	59	p	3
6.	Al/ 3 /Ga	1.5	2.3	285	p	0.4
7.	Al/ 4 /TiO ₂ /Ga	5	2	73	--	--
8.	Cu/ 1 /TiO ₂ /Ga	8	2.1	216	--	--

*RR was determined at voltages of 5; 3.2; 2.8; 2.8; 20; 20; 10 and 20 V, respectively.

Fig. 3 shows I - V characteristics of Al/4/Ga and Cu/4/Ga films deposited at 183 g at room temperature. Polarity of voltage shown in the I - V characteristics was matched with the polarity of applied voltage to the substrate (Cu or Al) for the forward and reverse bias. Both characteristics show rectification behavior. Fig. 3a shows non-linear continuous growth of forward bias current with increase of voltage. Non-linear forward bias current (I_f) dependence on the voltage, (V) is given by [18]:

$$I_f = cV^B \quad (2)$$

where c is proportional factor and B is a non-linearity coefficient that may be determined from the following expression:

$$B = \frac{(\ln I_2 - \ln I_1)}{(\ln V_2 - \ln V_1)} \quad (3)$$

where I_1 and I_2 are currents measured at voltages V_1 and V_2 , respectively.

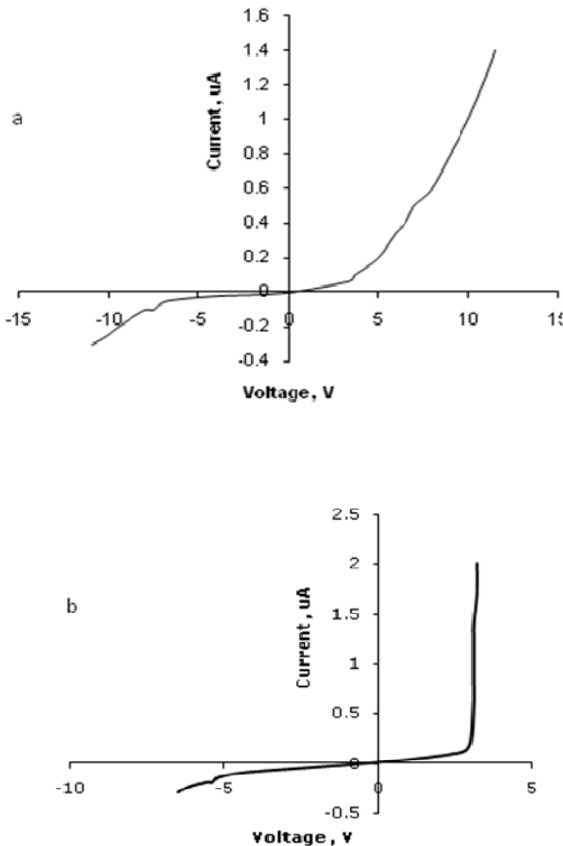


Fig. 3. Current-voltage characteristic of (a) Al/4/Ga and (b) Cu/4/Ga at room temperature.

For the I - V characteristics of Al/4/Ga heterojunction as shown in Figure 3a exhibited B value of 2.3 indicating a non-linear behavior. This shows the importance of these materials in their applications in electric devices like rectifier, modulator and voltage regulators.

The rectification ratio (RR) which gives a ratio of forward and reverse bias currents at the same voltage was determined. In the case of Al/4/Ga and Cu/4/Ga samples the RR values were equal to 10 and 27, and junction resistances ($R_j = dV/dI$, at $V=0$) of 64 and 23 M Ω , respectively. From the value of R_j the room temperature conductivity (σ) of the Al/4/Ga and Cu/4/Ga samples was determined to be $\sigma = 2 \times 10^{-11} \Omega^{-1}\text{cm}^{-1}$ and $5 \times 10^{-11} \Omega^{-1}\text{cm}^{-1}$, respectively. It shows that in the case of copper substrate conductivity is higher than aluminum indicating that Cu/4 contact resistance is lower than Al/4. It may be due to the presence of Al_2O_3 on the surface of aluminum foil. Therefore, for the design of practical devices copper substrate seems more preferable than aluminum substrates. The conductivity is also dependent upon the type of vanadium complex. Complexes **2** and **3** exhibited low conductivity compared to other compounds. The structure of these two compounds is similar to **4** with respect to their coordination environment. However, in **2** and **3** the phenyl rings ($-\text{C}_6\text{H}_5$) attached to diketo unit are more non-polar than methyl groups of **4**, which may be responsible for the high resistivity.

Figs. 4 shows I - V characteristics of Al/1/Ga (a), Cu/1/Ga (b), Cu/2/Ga (c) and Al/3/Ga (d) samples. All characteristics show rectification behavior however, their RR are very different. The switching effect in the Cu/1/Ga took place at threshold voltages of 2.8 V and 0.7 V for the thick (12 μm) and thin (7 μm) films deposited at 183g and 1650g, respectively. In the case of Cu/2/Ga and Al/3/Ga samples the effect of the substrates was not observed at 183g. I - V characteristics behavior was approximately same for Al and Cu substrates. Organic ligands in complexes **2** and **3** exhibit similar polarity and planarity of phenyl rings which may make their current voltage characteristics similar.

Fig. 4b depicts abrupt increase of current at threshold voltage ($V_{\text{Th}} = 3$ V) indicating a switching effect from low to high conducting state [19,20]. The threshold voltage is found to be proportional to the thickness of the films. The value of maximum current at switching process depends upon external series resistor of the circuit and the kind of substrate. It was higher for Cu than Al substrate which may be attributed to the presence of Al_2O_3 on the surface of Al. At relatively low currents, switching effect was reversible for both substrates. At large currents it reversed (or recovered) at 1-5 min in the case of Al whereas it was irreversible with Cu substrate.

I - V characteristics of the Al/4/TiO₂/Ga (a) and Cu/1/TiO₂/Ga (b) heterojunction samples are depicted in Fig. 5 in which films were deposited at 183 g. Both samples show rectification behavior. These heterojunctions are p-n aniso-type which is expected because TiO₂ is known to be an n-type semiconductor with very large band gap (3.2 eV) [3,4].

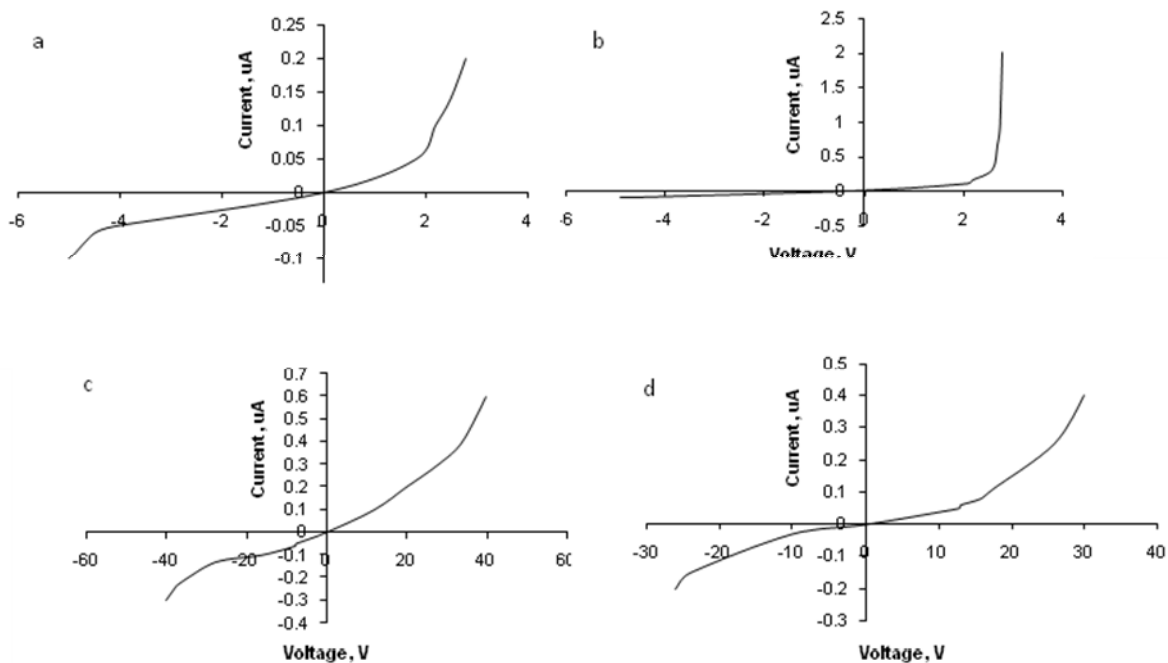


Fig. 4. Current-voltage characteristic of (a) Al/1/Ga, (b) Cu/1/Ga, (c) Cu/2/Ga, (d) Al/3/Ga at room temperature.

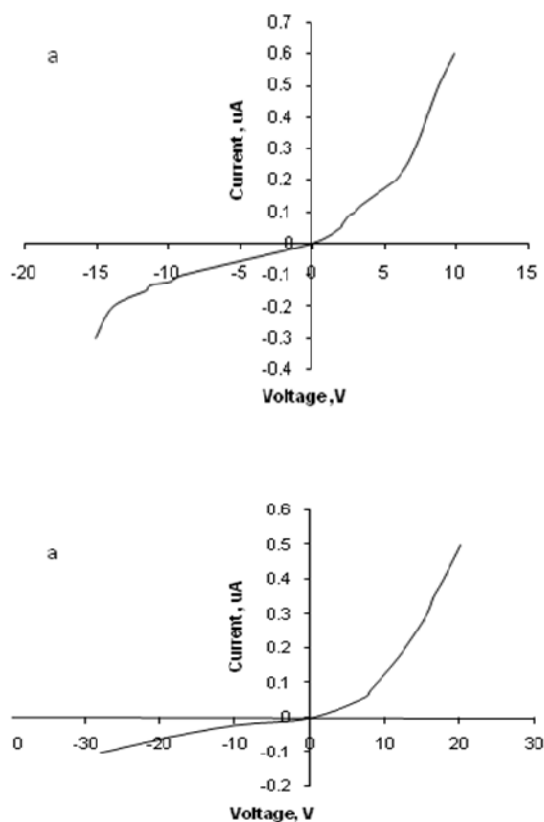


Fig. 5. Current-voltage characteristic of the (a) Al/4/TiO₂/Ga, (b) Cu/1/TiO₂/Ga heterojunction samples at room temperature.

The nonlinearity of I - V characteristics observed in this study may be caused by several factors such as, (i) increase of semiconductor's conductance by current's heating ("thermistor effect"), (ii) space-charge-limited current (SCLC), and (iii) the effect of electric field and others [6,7,13,18]. Contribution of thermistor effect may be estimated only if resistance-temperature relationships in the samples is investigated. The effect of electric field in conductance process, especially in switching effect, is visible, because the value of electric field in thin films was about 10^4 V/cm. This usually may increase mobility of charges by decrease of the barriers between potential wells promoting hopping and/or their tunneling. The SCLC approach application in this case is attractive as these semiconductors have relatively low conductance and conduction process may take place due to injection of electrons from metallic electrodes. The experimental study and modeling of the SCLC for the poly-N-epoxypropylcarbazole-p-Si junction were done and reasonable conformity was obtained [21]. The non-linearity coefficient (B) was equal to 3 in the case of poly-N-epoxypropylcarbazole [22]. All samples in this study exhibit value of B in the range of 1.6-3.4 which indicates that SCLC approach for our samples is acceptable.

Rectification behavior of the metal-complex type sample may be explained by SCLC approach for the case of electrodes made from different metals [23]. The work functions of Cu (4.65 eV) and Al (4.28 eV) with respect to Ga (4.2 eV) are different and asymmetric behavior of I - V characteristics may be due to different concentrations of injected charges from electrodes at forward and reverse bias. In the case of investigated heterojunction samples the rectification behavior may be result of work function

differences of the complexes and TiO₂, as well as of metallic electrodes (Cu and Ga, and Al and Ga).

4. Conclusion

Films of vanadium complexes, **1-4**, were deposited from solutions of different concentrations in chloroform at gravity conditions of 183g, 733g and 1650g. All samples show non-linear rectification behavior. This behavior is dependent upon the type of substrate, vanadium compounds, film thickness and centrifugation conditions. In the films of **1** and **4**, switching effect from low conductance to high conductance states was observed. By hot-probe method, press-tablets of the samples were found to be p-type semiconductors. It is proposed that SCLC approach may be used to explain the *I-V* characteristics behavior of the complexes reported here.

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