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Structure dependent charge transfer in bipyrimidinium–octacyanotungstate ion pairs

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ABSTRACT

Two solid state forms of the {$(bpymH_2)^{2+}$,$[W^{IV}(CN)_8]^{4-}$} charge-transfer ion pair have been obtained in the reaction between 2,2′-bipyrimidine (bpym) and octacyanotungstate(IV) in acidic solution and characterised in terms of structure and spectroscopic properties: $(bpymH_2)_2[W^{IV}(CN)_8]\cdot 4H_2O$ (**1**) and $(PPh_4)_2(bpymH_2)[W^{IV}(CN)_8]\cdot 10H_2O$ (**2**). In contrast to the yellow potassium salt, compound **1** is red and shows an outer-sphere charge-transfer (IPCT) band in the visible range of the electronic spectrum. In addition, due to thermal electron transfer *ca.* 0.3% of the diamagnetic W^{IV} centres is oxidised to paramagnetic W^{V}, as shown by the EPR spectra. In the yellow compound **2** the extent of the thermal charge separation increases to 16%, which can be rationalised by charge delocalisation through the π–π interactions between bpym and the phenyl rings of the additional PPh_4^+ cations.

1. Introduction

Supramolecular assemblies of redox-active metal complexes and organic cations that can act as electron acceptors have been widely studied as potential photocatalysts for organic reactions or hydrogen generation [1–5] as well as photochromic devices [6]. Bipyridine derivatives, have been employed in such systems in two ways: as ligands in chromophore complexes [1,2], and in the form of bipyridinium cations as electron transmitters in charge-transfer processes [3–6]. Apart from the classical assemblies containing Ru(II) complexes, [1,2] ion pairs based on different polycyanometallates and bipyridinium cations have been studied and proved to show interesting charge transfer properties [7]. For the $[M^{IV}(CN)_8]^{4-}$ anions (M = Mo or W), which exhibit reversible oxidation to $[M^{V}(CN)_8]^{3-}$, a series of ion pairs with bipyridinium cations have been characterised. They include salts of the diquaternary bipiridine derivatives paraquat (methyl viologen, 1,1′-dimethyl-4,4′-bipyridinium, pq^{2+}) and diquat (6,7-dihydrodipyrido[1,2-a:2,1-c]pyrazinediium, dq^{2+}): $(pq)_2[M(CN)_8]$ [9] and $(dq)_2[M(CN)_8]\cdot 5H_2O$, [10] as well as mono- and di-protonated bipyridines 2,2′-bipyridinium ($bpyH^+$ and $bpyH_2^{2+}$) and 4,4′-bipiridinium (4,4′-$bpyH_2^{2+}$): $(bpyH)_3(H_3O)[M(CN)_8]\cdot H_2O$, [11] $(bpyH_2)_2[W(CN)_8]\cdot 3H_2O$ [12] and $(4,4'\text{-}bpyH_2)_2[M(CN)_8]\cdot 4.5H_2O$ [13]. In all these assemblies both optical and thermal electron transfer was observed. The charge-transfer properties of these systems were shown to depend on the electron acceptor as well the presence of hydrogen bonds and the inter-ion distance. The effects of the cation conformation and the changeable geometry of the octa-coordinated anion were also noted. The charge separation was most effective in the di-protonated bpy salt, [12] where the amount of W^{V} was found to be of an order of magnitude higher than in the diquaternary bipyridinium salts [9,10].

The 2,2′-bipyrimidine (bpym) molecule is known to form a relatively stable mono-reduced radical of intense colour, and its reduction potential is very similar to those of bpy and 4,4-bpy [14]. Similarly to 2,2′-bipiridine, it was used to build chromophore metal complexes. With the additional asset of the second set of N-donor atoms it was also employed as a bridging ligand mediating the energy transfer [1,2]. Contrary to the bipyridinium cations, 2,2′-bipyrimidinium was scarcely used in the construction of supramolecular assemblies, although a recent report has shown the importance of the weak anion-π interactions in the modification of magnetic properties of rhenium(IV) halides [15].

In this work we present two structures of the $[W^{IV}(CN)_8]^{4-}$-based ion pairs with the $bpymH_2^{2+}$ cation and discuss how the outer-sphere charge-transfer in solid state is affected by the π–π interactions.

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2. Materials and methods

2.1. Syntheses

$K_4[W^{IV}(CN)_8]\cdot 2H_2O$ was prepared according to the published method [16]. All other reagents and solvents of analytical grade were used as supplied.

2.1.1. $(bpymH_2)_2[W^{IV}(CN)_8]\cdot 4H_2O$ (**1**)

To a solution of $K_4[W^{IV}(CN)_8]\cdot 2H_2O$ (0.2 mmol; 117 mg) and 2,2′-bipyrimidine (0.4 mmol; 64 mg) in 4 ml of water conc. HCl (130 μl) diluted in 0.5 ml of water was added. The red crystals of **1** developed within minutes. The product was filtered and dried in the air. Yield: 50%. *Anal.* Calc. for $C_{24}H_{24}N_{16}O_4W$: C, 36.75; H, 3.08; N, 28.57. Found: C, 36.57; H, 3.05; N, 28.11%. IR νCN: 2116vs, 2160vs.

2.1.2. $(PPh_4)_2(bpymH_2)[W^{IV}(CN)_8]\cdot 10H_2O$ (**2**)

To the orange-coloured filtrate obtained after the isolation of **1** solid PPh_4Cl (200 mg) was added. The resulting yellow precipitate was filtered, dried in the air and recrystallized from the MeOH–water mixture. The powder product was dissolved in 2 ml of MeOH, then 1 ml of water was added to the solution and it was left in an open beaker for slow evaporation. After one week the yellow crystals of **2** were collected by filtration and dried in the air. *Anal.* Calc. for $C_{64}H_{68}N_{12}O_{10}P_2W$: C, 54.47; H, 4.86; N, 11.91. Found: C, 54.14; H, 4.56; N, 11.85%. IR νCN: 2114vs, 2146vw.

The identity of the bulk samples of **1** and **2** was confirmed by PXRD (Figs. S1 and S2).

2.2. X-ray crystallography

The single-crystal diffraction data were collected on a Nonius Kappa CCD equipped with a Mo Kα radiation source (fine focus sealed tube) and a graphite monochromator. The structures were solved by direct methods using SIR-97 [17]. Refinement and further calculations were carried out using SHELXL [18]. The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. The C–H H-atoms positions were calculated from geometrical conditions and refined isotropically using constraints. The H-atoms of water molecules were found from the difference Fourier map. The measurement for **1** was performed at room temperature, and since the quality of the structure solution was satisfactory it was not repeated at 100 K. Graphics were created with Mercury 3.3 [19].

2.3. Measurements

Elemental analyses were performed on an ELEMENTAR Vario Micro Cube CHNS analyser. Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA 851e equipped with a QMS Thermostar GSD 300 T Balzers detector in a temperature range of 35–350 °C with a heating rate of 2 K/min, under Ar atmosphere. Powder XRD patterns were measured at room temperature between 3° and 70° 2θ angle on a PANalytical X'Pert PRO MPD diffractometer with a capillary spinning add-on using Cu Kα radiation ($\lambda = 1.54187$ Å). Powdered samples were sealed in 0.5 mm glass capillaries. The reference powder patterns were generated using Mercury 3.3 software [19]. Diffuse-reflectance solid state electronic spectra were measured in the range of 1000–200 nm on a Perkin-Elmer Lambda 35 UV–vis spectrometer equipped with a 50 mm integrating sphere. IR spectra in the 4000–500 cm^{-1} range were measured on a Thermo Scientific Nicolet iS5 spectrometer with iD5 ATR-Diamond add-on. EPR spectra were recorded at both ambient temperature and 77 K with an X-band Bruker ELEXSYS-II E580 spectrometer, operating at 100 kHz field modulation. The modulation amplitude of 0.2 mT and microwave power of 5 mW were applied. EPRsim32 software was used for spectra simulations [20]. The number of spins was determined by comparison of the integral signal intensity of the investigated samples with that of the primary $VOSO_4 \times 5H_2O$ standard diluted with diamagnetic K_2SO_4 containing 5×10^{19} paramagnetic centers/g. The content of W^V was determined from the EPR spectra with the precision of about ±20% [21]. Continuous Shape Measure analysis for the coordination spheres of the eight-coordinated W centres was performed using SHAPE software ver. 2.1 [22].

3. Results and discussion

3.1. Synthesis

The yellow water solution containing the $[W^{IV}(CN)_8]^{4-}$ anions and bpym in 1:2 ratio turns red upon acidifying with HCl. The change of colour is similar to those in the related bipyridinium salts [9,10,12,13] and reflects the formation of an ion pair, in which optical charge-transfer from the metal complex anion to the aromatic protonated cation takes place (Eq. (1)).

$$\left\{(bpymH_2)^{2+},\ [W^{IV}(CN)_8]^{4-}\right\} \leftrightarrow \left\{(bpymH_2)^{+*},\ [W^{V}(CN)_8]^{3-}\right\} \tag{1}$$

The red crystals of the $(bpymH_2)_2[W^{IV}(CN)_8]\cdot 4H_2O$ (**1**) salt develop within minutes or days depending on the concentration of the reactants. When the orange filtrate remaining after isolation of **1** is treated with saturated solution or solid PPh_4Cl another salt of the formula $(bpymH_2)(PPh_4)_2[W^{IV}(CN)_8]\cdot 10H_2O$ (**2**) can be obtained. Compound **2**, in which the anion to the protonated 2,2-bipyrimidinium cation ratio is 1:1, is of intense yellow colour. We have originally observed formation of salt **2** as a by-product in an attempted thermal substitution of the CN ligands in octacyanotungstate(IV) by bpym using compound **1** as a starting material.

Table 1
Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{24}H_{24}N_{16}O_4W$	$C_{64}H_{68}C_{l0}N_{12}O_{10}P_2W$
Formula weight	784.44	1411.09
T (K)	293(2)	100(2)
Crystal system	tetragonal	monoclinic
Space group	$P4_22_12$	$C2/c$
a (Å)	10.175(5)	19.8810(4)
b (Å)	10.175(5)	16.1120(3)
c (Å)	14.784(5)	20.0330(3)
α (°)	90	90
β (°)	90	96.5250(10)
γ (°)	90	90
V (Å^3)	1530.6(16)	6375.5(2)
Z	2	4
D_{calc} (Mg m^3)	1.702	1.470
Absorption coefficient (mm^{-1})	3.833	1.930
F(000)	772	2880
Crystal size (mm)	0.40 × 0.40 × 0.36	0.215 × 0.200 × 0.195
θ (°)	2.755 to 27.462	2.528 to 27.481
Reflections collected	26350	22748
R_{int}	0.1051	0.0284
Independent reflections	1767	7283
Parameters	116	446
Goodness-of-fit (GOF) on F^2	1.000	1.071
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0215$ $wR_2 = 0.0492$	$R_1 = 0.0227$ $wR_2 = 0.0560$
R indices (all data)	$R_1 = 0.0309$ $wR_2 = 0.0529$	$R_1 = 0.0267$ $wR_2 = 0.0578$