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LETTER

Photochemistry of the $[M(CN)_8]^{4-}$–2,2'-Bipyridyl System: a New Complex Ion $[MO(bpy)(CN)_3]^-$ (M = Mo, W)

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Photolysis of $[M(CN)_8]^{4-}$ (M = Mo, W) in neutral and alkaline solutions normally produces $[MO(OH_2)(CN)_4]^{2-}$ or $[MO(OH)(CN)_4]^{3-}$ (depending on the pH) [1]. Only under excess of cyanide, is the final photoproduct $[MO(CN)_5]^{3-}$ [2]. More recently, Ali and Murtaza [3, 4] reported that in the presence of 2,2'-bipyridyl (bpy) the $[M(OH)_3(bpy)_2(CN)]$ is formed via the photo-substitution process

$$[M(CN)_8]^{4-} + bpy \xrightarrow{h\nu} [M(OH)_2(bpy)(CN)_4]^{2-} + 2OH^- + 4HCN \quad (1)$$

$$[M(OH)_2(bpy)(CN)_4]^{2-} + bpy \xrightarrow{h\nu} [M(OH)_3(bpy)_2(CN)] + 2OH^- + 3HCN \quad (2)$$

We now report that the photolysis of octacyanometalates(IV) in the presence of bpy is, in fact, photo-aquation of cyanide ligands but not photo-substitution by bpy.

Figure 1 shows absorption spectra of the $[M(CN)_8]^{4-}$–bpy system upon irradiation. Although the experimental results are similar to those reported by Ali and Murtaza [3], none of the bands in Fig. 1 is attributable to the complexes proposed by the authors. Following precipitation procedure with CsCl [5], we have isolated $Cs_2Na[MO(CN)_5]$ having $\lambda_{max} = 645$ nm (Mo) and $\lambda_{max} = 615$ nm (W), thus proving that the main product of photolysis is the $[MO(CN)_5]^{3-}$ ion (as in the presence of cyanide [2]). In the dark this product decreases and another one, with a well-resolved maximum at $\lambda = 455$ nm (Mo) and $\lambda = 495$ nm (W) is formed (Fig. 2).

Thermal reaction of $[MO(CN)_5]^{3-}$ with bpy followed by precipitation with $AsPh_4^+Cl^-$ affords the black solid, $(AsPh_4)[MO(bpy)(CN)_3]\cdot\frac{1}{2}bpy\cdot 2H_2O$. The structure of the tungsten complex (after recrystallization from methanol) has been obtained by X-ray diffraction. Crystal data for $(AsPh_4)[WO(bpy)(CN)_3]\cdot\frac{1}{2}bpy\cdot 2H_2O$: triclinic $P\bar{1}$ with $a = 10.035(3)$, $b = 12.829(5)$, $c = 15.732(5)$ Å; $\alpha = 76.00(3)$, $\beta = 84.00(3)$, $\gamma = 88.30(3)^\circ$; $U = 1954(3)$ Å^3, $Z = 2$ for 6104 unique observed ($I/\sigma(I) \geq 2.0$) reflections. A perspective drawing together with selected bond lengths and angles is given in Fig. 3.

The same product can be obtained from the reaction of $[MO(OH_2)(CN)_4]^{2-}$ with bpy [6]. Its

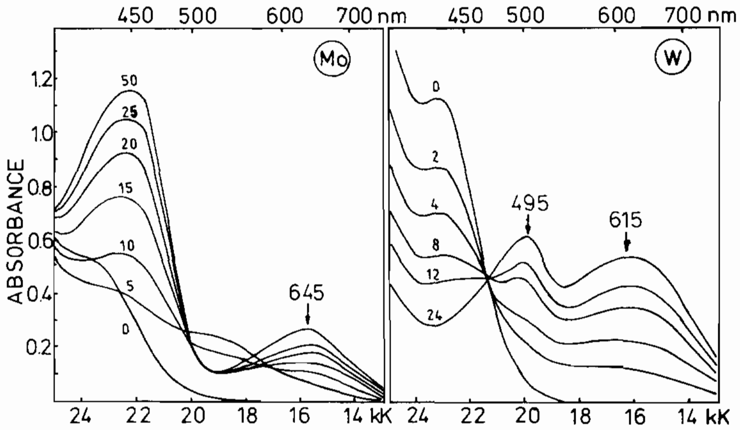

Fig. 1. Changes in the electronic spectra of an aqueous solution of 0.01 M $[M(CN)_8]^{4-}$ in 0.01 M bpy under irradiation (HBO-200 UV lamp). Numbers indicate the time of irradiation (t_{ir}) in s (M = Mo, d = 0.5 cm) or in min (M = W, d = 1 cm).

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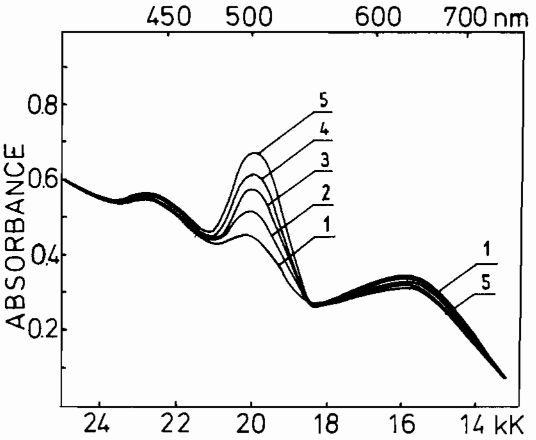

Fig. 2. Changes in the electronic spectra of irradiated (t_{ir} = 8 min) 0.01 M $[W(CN)_8]^{4-}$ in 0.01 M bpy in the dark. Curves 1–5 correspond to t = 0, 4, 9, 16 and 22 min respectively.

geometry conforms to that of an anion such as $[MO(phen)(CN)_3]^-$ [7] and $[WO(Pic)(CN)_3]^{2-}$ (Pic = 2-picolinate) [8]. The characteristic features of the $[MO(bpy)(CN)_3]^-$ anion are the intense metal-to-ligand charge-transfer bands at 455 and 645 nm (Mo) and at 495 and 633 nm (W) [6].

Finally, the results of this investigation clearly demonstrate that the photolysis of the $[M(CN)_8]^{4-}$–bpy system is a photo-aquation leading to $[MO(CN)_5]^{3-}$ followed by a relatively slower thermal substitution of two cyano groups by bpy.

Acknowledgements

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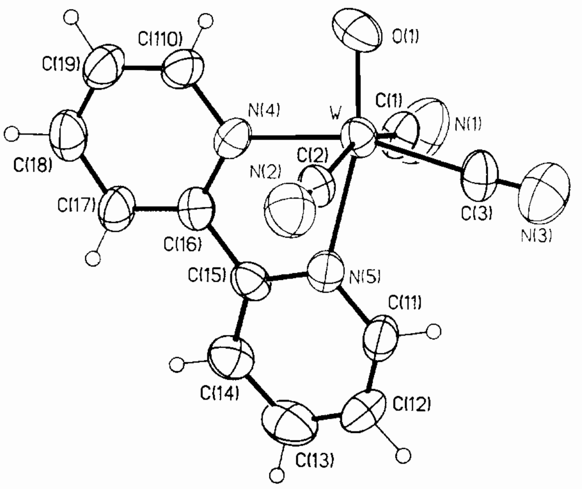

Fig. 3. View of the anion $[WO(bpy)(CN)_3]^-$ in crystalline $(AsPh_4)[WO(bpy)(CN)_3]\cdot\frac{1}{2}bpy\cdot 2H_2O$. Selected distances are: W–O, 1.735(7); W–C(1), 2.137(10); W–C(2), 2.129(10); W–C(3), 2.149(13); W–N(4), 2.149(9); W–N(5), 2.307(8) Å. Selected angles are: O–W–C(1), 101.3(4); O–W–C(2), 99.7(4); O–W(C(3), 103.7(4); O–W–N(4), 93.5(4); O–W–N(5), 164.1(4)°.

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