Charge-transfer Interactions between Bipyridinium Ions and Octacyano-molybdates and -tungstates *

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Investigation of the interaction between the 4,4′-bipyridinium(2+) cation (4,4′-H_2bipy^{2+}) and the octacyanometalates(IV) $[M(CN)_8]^{4-}$ (Mo or W) led to the isolation of $[4,4'\text{-}H_2bipy]_2[W(CN_8)]\cdot 4.5H_2O$ and its isomorphous molybdenum analogue. The spectroscopic properties of both and the X-ray structural characterization of the former [monoclinic, space group $P2_1/c$, $a = 11.281(5)$, $b = 9.198(5)$, $c = 30.113(24)$ Å, $\beta = 91.21(5)°$, $Z = 4$] are described. The $[W(CN)_8]^{4-}$ anion has an approximate square-antiprismatic D_{4d} configuration with average dimensions W–C 2.168, C–N 1.136 Å, W–C–N 177.0°. The structure consists of a three-dimensional hydrogen-bonded framework and cation–anion interaction occurs mainly through the water molecules. The intensely coloured solids (hydrated and anhydrous) and aqueous solutions are discussed in terms of the ion pairs which exhibit an outer-sphere electron transfer between adjacent redox sites. The correlation between the structures of the hydrated solids, the close contact ion pairs of the anhydrous salt and the solvent-separated ion pairs (solution) are discussed.

The alkali-metal salts of octacyano complexes of molybdenum(VI) and tungsten(IV) react with a number of bi- and trivalent cations to give stable compounds.[1–10] The formation of these complexes is often associated with a change of colour. This results from the simple sum of absorbances of the cations and octacyanides in combination with peaks arising from interaction between the cations and highly charged anions. Ion pairs which contain a reducing (Mo^{IV} or W^{IV}) and an oxidizing ($M = Cu^{II}$, Fe^{III}, Pt^{IV} or U^{VI}) metal centre show metal-to-metal charge-transfer (m.m.c.t.) bands in their absorption spectra.[7–10] Another explanation of colour changes is the formation of polynuclear complexes with bridging cyanide ligands leading to inner-sphere electron transfer.[9,10]

In our studies of the $Hbipy^+$–$[M(CN)_8]^{4-}$ (M = Mo or W, bipy = 2,2′-bipyridine) system,[11] we observed a new band at 490 nm which we assigned to outer-sphere charge transfer (o.s.c.t.) from the reducing centre, M^{IV}, to the oxidizing $Hbipy^+$ centre. In this work we report the spectroscopic properties of the new ion pairs of $[M(CN)_8]^{4-}$ (M = Mo or W) with the 4,4′-bipyridinium cation, 4,4′-H_2bipy^{2+}, as well as the synthesis and structure of solids formulated as $[4,4'\text{-}H_2bipy]_2[M(CN)_8]\cdot 4.5H_2O$ (M = Mo or W). The structures of the $[M(CN)_8]^{n-}$ (n = 3 or 4) ions are themselves of great interest and various investigations have been carried out to determine the geometries of these ions both in the solid state and in solution, often with contradictory results. X-Ray crystallographic studies have provided examples of square antiprismatic (D_{4d}), dodecahedral (D_{2d}) or bicapped trigonal prismatic (C_{2v}) configurations as well as structures intermediate between idealized polyhedra (see Table 1). The structure determination of $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot 4.5H_2O$ also contributes to the understanding of the factors influencing the stereochemistry of $[M(CN)_8]^{n-}$ ions.

Experimental

Materials.—The compounds $K_4[M(CN)_8]\cdot 2H_2O$ (M = Mo or W) were prepared according to published procedures.[23] 4,4′-Bipyridine (POCh) was of analytical grade. All other materials were of analytical grade (Aldrich) and used as supplied.

Analytical Methods and Physical Measurements.—Carbon, N, H, Mo and W were determined as described earlier.[11] The water content was determined by isothermal dehydration *in vacuo* over P_4O_{10} (*a*) and by thermal gravimetric analysis (*b*).

Infrared (Brüker IFS 48), UV/VIS absorption (Zeiss M-40) and reflectance (Perkin Elmer Lambda 6)† spectra were recorded in a routine manner. Raman spectra were recorded in rotating KBr pellets in the short wavenumber range 2000–2400 cm^{-1} (to prevent decomposition of the samples) on a Cary 82 spectrometer‡ using a 514.5 nm excitation line. ESR spectra either in the solid state or in solution were recorded with a SE/X-25 spectrometer (Poland) using $[Hbipy]_3[W(CN)_8]\cdot H_2O$[11] as a standard to estimate the content of M^V in the M^{IV} complexes. The thermogravimetric (TGA) and differential thermal (DTA) analyses were performed under argon with a heating rate of 2 and 5 °C min^{-1} respectively on a Mettler thermoanalyser.‡ Potentiometric titrations were carried out with a model OP-211 Radelkis pH meter standardized in the usual way.

Preparation of Bis(4,4′-*Bipyridinium*) *Octacyanotungstate*(IV)–*Water* (2/9), $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot 4.5H_2O$ **1**.—To a solution of $K_4[W(CN)_8]\cdot 2H_2O$ (1.45 g, 2.48 mmol) in water (30 cm^3) was slowly added a solution of 4,4′-bipyridine (1.17 g, 7.49 mmol) in 0.5 mol dm^{-3} H_2SO_4 (50 cm^3). The solution turned yellow to orange and then dark violet crystals started to precipitate. Upon standing overnight the mixture was filtered, the precipitate washed three times with water and then EtOH, and dried in air. The salt was then recrystallized from hot water. Yield: 1.4 g (64%) (Found: C, 42.55; H, 3.80; N, 20.70; W, 23.40; H_2O, 9.90,[a] 10.10.[b] Calc. for $C_{28}H_{29}N_{12}O_{4.5}W$: C, 42.55; H, 3.65; N, 21.30; W, 23.30; H_2O, 10.25%).

Preparation of Bis(4,4′-*Bipyridinium*) *Octacyanomolybdate*(IV)–*Water* (2/9), $[4,4'\text{-}H_2bipy]_2[Mo(CN)_8]\cdot 4.5H_2O$ **2**.—The

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* *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

† Measurements were performed in the Department of Chemistry, University of Ferrara, Italy.

‡ Measurements were performed in the Regional Laboratory of Physicochemical Analyses and Structural Research of Jagiellonian University, Kraków, Poland.

Table 1 Selected crystal structure data and idealized geometries of $[M(CN)_8]^{3-/4-}$ (M = Mo or W) anions with various cations

Symmetry	Complex formula Mo	W	Average M–C (M–N)/Å	Ref.
D_{4d}	$Cd_2[Mo(CN)_8]\cdot 2N_2H_4\cdot 4H_2O$			12
	a	$H_4[W(CN)_8]\cdot 6H_2O$	2.180 (3.306)	13
		$H_4[W(CN)_8]\cdot 4HCl\cdot 12H_2O$	2.176 (3.323)	14
	$Ag_4[Mo(CN)_8]\cdot 5NH_3\cdot 1.5H_2O$		2.157 (3.308)	15
D_{2d}	$K_4[Mo(CN)_8]\cdot 2H_2O$	*a*	2.163 (3.314)	16
	$[NBu_4]_3(Mo(CN)_8]$		2.115 (3.275)	17
	$[C_6H_6NO_2]_4[Mo(CN)_8]$	*a*	2.159 (3.308)	18
	$Rb_4[Mo(CN)_8]\cdot 3H_2O$		2.149 (3.302)	19
$D_{2d} + D_{4d}$[b]	$[NH_4]_4[Mo(CN)_8]\cdot 0.5H_2O$		2.227 (3.353)	19
D_{4d}–D_{2d}[c]	*a*	$Na_3[W(CN)_8]\cdot 4H_2O$	2.139 (3.302)	20
C_{2v}	$Cs_3[Mo(CN)_8]\cdot 2H_2O$		2.17 (3.32)	21
D_{2d}–C_{2v}[c]	$[NHEt_3]_2[H_3O]_2[Mo(CN)_8]$	*a*	2.149 (3.304)	22

[a] Molybdenum or tungsten salts were found to be isomorphous. [b] Two different environments of molybdenum atoms. [c] The co-ordination polyhedron can be described as about half-way between the two idealized polyhedra.

preparation followed the same procedure as used for the synthesis of the tungsten analogue. The pure compound was obtained as dark violet crystals. Yield: 1.23 g (62%) (Found: C, 47.45; H, 4.00; Mo, 13.90; N, 23.65; H_2O, 11.20,[a] 11.80.[b] Calc. for $C_{28}H_{29}MoN_{12}O_{4.5}$: C, 47.90; H, 4.15; Mo, 13.65; N, 23.95; H_2O, 11.55%).

Crystal Structure Analysis of $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot 4.5H_2O$.—$C_{28}H_{29}N_{12}O_{4.5}W$, $M = 789.54$, monoclinic, space group $P2_1/c$, $a = 11.281(5)$, $b = 9.198(5)$, $c = 30.113(24)$ Å, $\beta = 91.21(5)°$, $U = 3124(3)$ Å^3, $D_c = 1.70$ g cm^{-3}, $Z = 4$, $\lambda = 0.710\,69$ Å, $T = 290$ K, μ(Mo-Kα) = 37.6 cm^{-1}, $F(000) = 1584$, flat plates, turquoise blue in transmitted light, crystal dimensions 0.49 × 0.35 × 0.04 mm.

Data were collected with a Siemens P3 four-circle diffractometer in ω–2θ mode. Maximum 2θ was 45° with scan range ±1.5° (2θ) around the $K_{\alpha 1}$, $-K_{\alpha 2}$ angles, scan speed 3–29° min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time; *hkl* ranges: 0–12, 0–9, −32 to 32. Three standard reflections were monitored every 200 reflections, and showed a slight decrease during data collection: the data were recalculated to account for this. Unit-cell dimensions and standard deviations were obtained by least-squares fitting to 15 reflections ($15 < 2\theta < 18°$). Reflections were processed using profile analysis to give 4098 unique reflections of which 3117 were considered observed $[I/\sigma(I) > 2.0]$ and used in refinement. They were corrected for Lorentz, polarization and absorption effects, the latter by the Gaussian method; maximum and minimum transmission factors were 0.875 and 0.337. The space group $P2_1/c$ was assigned from the systematic absences. Heavy atoms were located by the Patterson interpretation section of SHELXTL PLUS[24] and the light atoms then found on successive Fourier syntheses, including five water molecules, one of which showed low electron density and was assigned 0.5 occupancy. Anisotropic thermal parameters were used for all non-H atoms (except the 0.5 occupancy water). Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å^2, inserted in calculated positions and not refined. Final refinement was on F by cascaded least-squares methods refining 411 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height ±0.5 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0010$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.032$, $R' = 0.033$. Maximum shift/error in final cycle was 0.02. Computing was with SHELXTL PLUS on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 25. Final atomic coordinates are given in Table 2 and selected bond lengths and angles in Tables 3, 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

The unit cell of the corresponding molybdenum compound was established as monoclinic, with $a = 11.251(3)$, $b = 9.175(3)$, $c = 30.074(4)$ Å, $\beta = 91.11(2)°$. It is presumably isomorphous with the tungsten compound, but a full structure determination was not carried out.

Results and Discussion

Description of the Structure.—The structure consists of discrete $[W(CN)_8]^{4-}$ anions and 4,4′-bipyridinium cations which form a three-dimensional framework stabilized by strong hydrogen bonds between the nitrogen atoms of the cyanide ligands, nitrogen atoms of $4,4'\text{-}H_2bipy^{2+}$ and water molecules (Fig. 1). Molecules $H_2O(1)$ and $H_2O(4)$ serve as links between two $[W(CN)_8]^{4-}$ polyhedra and $4,4'\text{-}H_2bipy^{2+}$ cations (Fig. 1 and Table 3). The water molecule $H_2O(2)$ also forms a bridge to $H_2O(3)$ which is itself hydrogen bonded to a cyanide and to a

Table 2 Atom coordinates (× 10^4) for $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot4.5H_2O$ **1**

Atom	*x*	*y*	*z*
W	2 579.1(2)	1 980.2(3)	1245.9(1)
O(1)	757(5)	−2 903(6)	2 310(2)
O(2)	−1 798(5)	2 470(6)	151(2)
O(3)	6 079(5)	1 089(7)	5 318(2)
O(4)	4 242(5)	7 290(7)	2 238(2)
O(5)*	623(18)	4 402(23)	4 750(7)
N(1)	−142(6)	2 028(9)	833(3)
N(2)	2 659(6)	4 175(8)	379(2)
N(3)	3 521(7)	5 169(8)	1 625(2)
N(4)	869(6)	2 956(8)	2 074(3)
N(5)	2 632(7)	−330(8)	411(3)
N(6)	5 371(6)	1 827(9)	941(3)
N(7)	4 254(6)	1 205(10)	2 130(3)
N(8)	1 550(7)	−1 107(8)	1 645(3)
N(11)	4 847(6)	−7 893(8)	4 629(2)
N(21)	1 810(6)	−4 769(8)	2 855(2)
N(31)	6 909(6)	3 885(8)	2 184(3)
N(41)	10 471(6)	6 503(7)	515(2)
C(1)	768(7)	2 053(10)	979(3)
C(2)	2 608(7)	3 408(9)	673(3)
C(3)	3 191(7)	4 084(9)	1 484(3)
C(4)	1 449(7)	2 645(8)	1 780(3)
C(5)	2 651(7)	433(9)	701(3)
C(6)	4 401(7)	1 869(9)	1 045(3)
C(7)	3 661(7)	1 425(9)	1 821(3)
C(8)	1 917(7)	−77(10)	1 489(3)
C(11)	4 098(8)	−6 838(10)	4 709(3)
C(12)	3 496(8)	−6 190(10)	4 367(3)
C(13)	3 666(7)	−6 650(8)	3 937(3)
C(14)	4 462(7)	−7 777(10)	3 868(3)
C(15)	5 031(8)	−8 383(10)	4 224(3)
C(21)	2 998(6)	−5 998(9)	3 552(3)
C(22)	1 922(7)	−5 317(10)	3 612(3)
C(23)	1 357(8)	−4 693(10)	3 255(3)
C(24)	2 830(8)	−5 416(10)	2 790(3)
C(25)	3 458(7)	−6 052(10)	3 137(3)
C(31)	6 712(8)	3 418(10)	1 775(3)
C(32)	7 387(7)	3 901(10)	1 428(3)
C(33)	8 267(6)	4 909(9)	1 515(3)
C(34)	8 435(7)	5 421(9)	1 945(3)
C(35)	7 739(8)	4 860(11)	2 270(3)
C(41)	9 039(6)	5 491(8)	1 158(3)
C(42)	8 593(7)	5 701(9)	731(3)
C(43)	9 344(7)	6 208(10)	411(3)
C(44)	10 927(7)	6 309(10)	919(3)
C(45)	10 215(7)	5 806(9)	1 251(3)

* Occupancy 0.5.

Table 3 Selected hydrogen bond distances (Å) for $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot4.5H_2O$ **1** (e.s.d.s all 0.10 Å)

O(1) ··· N(4)	2.753	O(2) ··· N(41)	2.699
O(1) ··· N(8)	2.759	O(3) ··· N(6)	2.809
O(1) ··· N(21)	2.641	O(3) ··· N(11)	2.644
O(2) ··· O(3)	2.793	O(4) ··· N(3)	2.795
O(2) ··· N(1)	2.778	O(4) ··· N(7)	2.713
O(2) ··· N(5)	2.749	O(4) ··· N(31)	2.639

Table 4 Selected bond lengths (Å) for 4,4′-bipyridine molecules

	4,4′-$Hbipy^{+a}$	4,4′-H_2bipy^{2+b}	4,4′-H_2bipy^{2+c}	4,4′-H_2bipy^{2+d}	
				A	B
N(21)–C(24)	1.347(7)	1.344(5)	1.35(3)	1.314(11)	1.321(11)
N(21)–C(23)	1.317(7)	1.336(6)	1.36(3)	1.320(12)	1.331(10)
C(24)–C(25)	1.388(8)	1.386(8)	1.46(5)	1.380(12)	1.376(12)
C(25)–C(21)	1.393(7)	1.380(6)	1.37(2)	1.365(11)	1.380(10)
C(21)–C(22)	1.411(7)	1.395(5)	1.36(4)	1.382(11)	1.387(11)
C(22)–C(23)	1.404(8)	1.368(8)	1.42(5)	1.364(13)	1.378(12)
N(11)–C(11)	1.320(8)			1.313(11)	1.319(12)
N(11)–C(15)	1.342(7)			1.322(12)	1.318(11)
C(11)–C(12)	1.364(7)			1.357(12)	1.378(13)
C(12)–C(13)	1.407(6)			1.381(12)	1.380(12)
C(13)–C(14)	1.396(7)			1.390(12)	1.387(12)
C(14)–C(15)	1.392(6)			1.356(13)	1.369(12)
C(21)–C(13)	1.480(6)	1.513(7)	1.68(7)	1.494(11)	1.497(11)

[a] Ref. 26. [b] Ref. 27*a*. [c] Ref. 27*b*. [d] This work: molecule A, atom labels as indicated; molecule B, atom labels, plus 20.

Table 5 Bond lengths (Å) and angles (°) for the $[W(CN)_8]^{4-}$ ion

W–C(1)	2.180(8)	W–C(2)	2.170(9)
W–C(3)	2.171(8)	W–C(4)	2.162(9)
W–C(5)	2.176(9)	W–C(6)	2.156(8)
W–C(7)	2.159(8)	W–C(8)	1.168(9)
N(1)–C(1)	1.108(10)	N(2)–C(2)	1.133(11)
N(3)–C(3)	1.143(11)	N(4)–C(4)	1.147(11)
N(5)–C(5)	1.118(12)	N(6)–C(6)	1.146(11)
N(7)–C(7)	1.153(11)	N(8)–C(8)	1.139(11)
W–C(1)–N(1)	176.6(8)	W–C(2)–N(2)	177.6(7)
W–C(3)–N(3)	177.5(7)	W–C(4)–N(4)	177.4(7)
W–C(5)–N(5)	176.1(8)	W–C(6)–N(6)	179.1(7)
W–C(7)–N(7)	176.4(8)	W–C(8)–N(8)	175.1(7)
C(1)–W–C(2)	73.6(3)	C(1)–W–C(3)	112.5(3)
C(2)–W–C(3)	73.3(3)	C(1)–W–C(4)	72.8(3)
C(2)–W–C(4)	116.1(3)	C(3)–W–C(4)	72.0(3)
C(1)–W–C(5)	78.0(3)	C(2)–W–C(5)	78.1(3)
C(3)–W–C(5)	144.7(3)	C(4)–W–C(5)	141.1(3)
C(1)–W–C(6)	142.1(3)	C(2)–W–C(6)	77.0(3)
C(3)–W–C(6)	80.6(3)	C(4)–W–C(6)	143.3(3)
C(5)–W–C(6)	72.9(3)	C(1)–W–C(7)	144.3(3)
C(2)–W–C(7)	139.8(3)	C(3)–W–C(7)	77.0(3)
C(4)–W–C(7)	78.6(3)	C(5)–W–C(7)	114.9(3)
C(6)–W–C(7)	71.8(3)	C(1)–W–C(8)	79.9(3)
C(2)–W–C(8)	144.0(3)	C(3)–W–C(8)	140.8(3)
C(4)–W–C(8)	77.4(3)	C(5)–W–C(8)	72.7(3)
C(6)–W–C(8)	113.0(3)	C(7)–W–C(8)	73.4(3)

protonated 4,4′-bipyridine. The water molecule $H_2O(5)$ and a close centrosymmetry-related equivalent (2.3 Å) must represent alternative occupation positions in a void in the structure. There is also a short cation–anion contact between N(6) and the π-electron system of the pyridine ring [mean distance from N(6) to C(11–15)N(11) 2.89 Å]. The bond distances and angles of the 4,4′-H_2bipy^{2+} cations are similar to those of other bipyridinium salts[26,27] but they lie between the values characteristic for mono- and di-protonated forms (Table 4). It appears possible that in the solid state the proton is transferred to a water molecule. The potentiometric titration of a solution of the compound with potassium hydroxide confirmed, however, the presence of diprotonated cations (only one potential jump due to the small difference between the acid dissociation constants).[28,29] The pyridine rings [C(21–25)N(21) and C(31–35)N(31)] in adjacent molecules lie approximately parallel (12.6°) above each other, but the N–N axes of the two 4,4′-H_2bipy^{2+} molecules are almost at 90° to each other. The ring–ring distance is 4.30 Å and indicates that there is no interaction between aromatic pyridine rings of the type characteristic of graphite-type interactions of polypyridyls.[30]

The W atom is bonded to eight CN ligands with co-ordination geometry close to antiprismatic (D_{4d}) (Fig. 2 and Table 5). The mean W–C (2.168 Å) and C–N distances (1.136 Å) are in good agreement with the values found for other octacyano complexes, especially those of D_{4d} structure (Table 1).

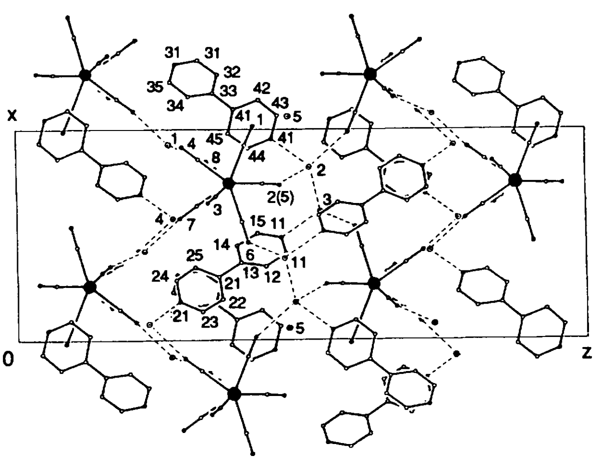

Fig. 1 Partial projection of the structure of $[4,4'\text{-}H_2bipy]_2[W(CN)_8]\cdot4.5H_2O$ onto the *xz* plane. Atoms numbered according to Table 2. Dashed lines are hydrogen bonds; ● W, ⊙ O, · N, ○ C

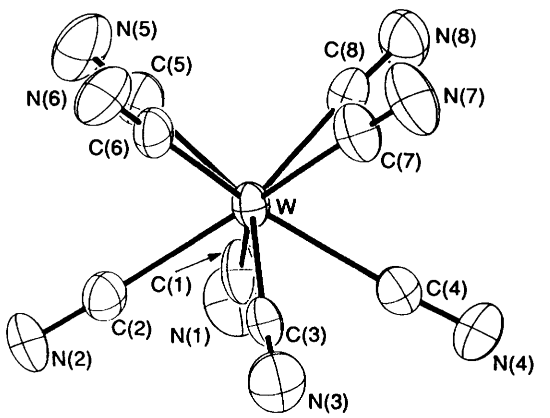

Fig. 2 Structure of the anion $[W(CN)_8]^{4-}$ in the salt **1** showing the atomic numbering; 50% probability ellipsoids

The W–C≡N chains are nearly linear, the W–C≡N bond angle departing no more than 5° from 180°. All the cyanide ligands [except N(2)] are hydrogen bonded to water molecules with distances ranging from 2.713 [O(4) · · · N(7)] to 2.809 Å [O(3) · · · N(6)] (Table 3).

It was suggested previously[21] that in octacyano complexes small cations (H^+, Na^+) favour square-antiprismatic geometry possibly with some distortion whereas larger cations pack better with dodecahedra (K^+) or even 4,4-bicapped trigonal prisms (Cs^+). It seems, however, that the geometry of the $[M(CN)_8]^{4-}$ ions is determined to a large extent by hydrogen bonding. The more symmetrical the system of hydrogen bonding the more likely is the anion to show higher symmetry. The presence of at least four water (or ammonia) molecules per mole of compound gives a chance for such a symmetric system to form and the higher (D_{4d}) geometry of the complex anion is adopted (see Table 1). The influence of the non-spherical cation on the negative charge distribution of M–C≡N bonds was postulated also to explain the low symmetry of $[NHEt_3]_2[H_3O]_2[Mo(CN)_8]$.[22]

Characterization of the Complexes.—In contrast to the yellow octacyanometalates(IV) of alkali metals, complexes **1** and **2** are dark violet solids scarcely soluble in cold water but with higher solubility in hot water, from which they can be recrystallized. They are insoluble in common organic solvents. Both salts are light sensitive as solids and in solution, but in the dark (or in diffuse light) they remain unaltered in air for long periods. The isothermal dehydration *in vacuo* over P_4O_{10}, when all 4.5 molecules of water are released, changes the colour to metallic green (**1**) or to turquoise-blue (**2**). In a wet atmosphere the original colour and composition return. The bathochromic shift for anhydrous salts indicates that after the loss of water molecules the cation–anion interaction is stronger, probably due to direct hydrogen bonding between $4,4'\text{-}H_2bipy^{2+}$ and the cyano ligands (see below). The thermograms of polycrystalline samples show that dehydration takes place in two separate steps. In the first with T_{max} (DTA peaks maximum temperature) of 122 °C the weight-loss measurements indicate that 3.5 H_2O per mol of the complex are liberated. In the next step at 132 (**1**) or 130 °C (**2**) the last strongly bonded water molecule is lost. Taking into consideration that of the five different water molecules $H_2O(4)$ has the shortest hydrogen bonding distance (Table 3) this could be the one released in the second step. At higher temperature decomposition of the compounds occurs also in two separate steps. In the first with T_{max} 190 (**1**) or 192 °C (**2**) only HCN (five HCN per mol of the complex) is released whereas in the last step at 361 (**1**) or 264 °C (**2**) complete decomposition occurs. The characteristic feature is that the temperature of complete decomposition of the tungsten compound is about 100 °C higher than that of the molybdenum analogue.

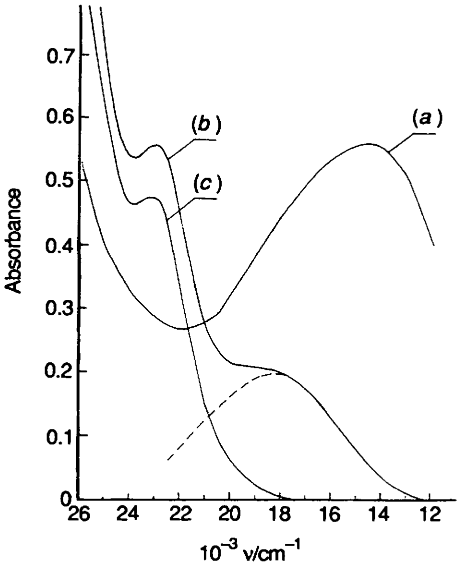

Fig. 3 Reflectance spectrum of complex **1** (*a*) and absorption spectrum of a 2 × 10^{-3} mol dm^{-3} solution of **1** (*d* = 2 cm) (*b*) in comparison with the spectrum of $K_4[W(CN)_8]$ of the same concentration (*c*). The differential spectrum [(*b*) − (*c*)] is shown by the dashed line

Spectroscopic Data.—Fig. 3 gives the electronic spectra of the reagents and the products in the visible region for the tungsten system. In dilute solutions for both the Mo and W systems ($c \leqslant 10^{-4}$ mol dm^{-3}) the spectra are typical for $[M(CN)_8]^{4-}$ since $4,4'\text{-}H_2bipy^{2+}$ is transparent. In more concentrated solution ($c > 10^{-3}$ mol dm^{-3}) a new band is found at 550 (**1**) or 480 nm (**2**) assigned to o.s.c.t. within the ion pair. The dependence of absorbance on concentration (up to saturated solution) at 20 °C suggests that only one species is formed, with a rather small formation constant.[31] In the solid state the band is shifted towards higher wavelength [700 (**1**) or 590 nm (**2**)] in accordance with the stronger association (and protonation of cyanide ligands). Changes in the same direction are observed after dehydration (see above). In the ultraviolet region, the spectra are essentially a simple sum of absorbances of cation and anion.

Both complexes are diamagnetic in solution as expected for d^2 metal complexes of D_{4d} symmetry. In the solid state, however, an ESR signal typical for a d^1 species[32] is observed which indicates that stronger cation–anion interaction stimulates to some extent electron shift from the metal centre to the aromatic cation and its delocalization onto the pyridine rings.

Table 6 Selected IR (Raman) spectral data (cm^{-1}) of complexes **1** and **2**

Complex	ν_{CN}[a]	Cation
1	2105vs (2100) 2117(sh) (2117)	1633s, 1491s, 1240w, 997s, 813vs, 724vs, 613s, 563w
1[b]	2109(sh), 2098s 2081s	1635m, 1625m, 1603s, 1592m, 1506w, 1486s, 1228w, 1201w, 1031w, 1001w, 959w, 799vs, 721w, 713w, 668vw, 615vw, 559vw, 513vw
2	2120(sh) (2110) 2108vs (2090)	1633s, 1491s, 1241w, 998s, 813s, 724s, 613m, 563m
2[b]	2110(sh), 2102m 2087m	1635s, 1623s, 1603s, 1592s, 1506w, 1486s, 1231m, 1201m, 1031m, 1001m, 959w, 800vs, 720w, 713m, 668w, 615w, 559w, 516w

[a] Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder. [b] Data for anhydrous salts.

We have observed similar phenomena previously for 2,2′-bipy–$[M(CN)_8]^{4-}$ systems.[11] The content of paramagnetic M^V is *ca.* 0.89 (**1**) and 2.88% (**2**) and increases upon dehydration (up to 6.77% for the tungsten complex) in accordance with increasing tendency to ion-pair formation.

The infrared and Raman spectra are consistent with the antiprismatic structure of $[M(CN)_8]^{4-}$ [33] and with a protonated 4,4′-bipy cation (Table 6). In contrast to $[M(CN)_8]^{4-}$ of D_{2d} symmetry[34] the spectra in the ν_{CN} range (2000–2120 cm^{-1}) are simple [the expected number of allowed fundamentals for D_{4d} symmetry is 2(IR) and 3(Raman) without coincidences]. Dehydration increases the number of bands in this region suggesting a decreased symmetry of the complex anion. On the other hand the shift of ν_{CN} towards lower wavenumbers as well as the presence of bands characteristic for mono- rather than diprotonated 4,4′-bipy[35] indicate significant shift of the proton from the cation to the nitrogen atom of a cyanide ligand.

Conclusion

The study of the 4,4′-H_2bipy^{2+}–$[M(CN)_8]^{4-}$ system in solution and in the solid state offers the opportunity to observe changes in ion-pair formation upon decreasing the distance between the aromatic cation and the complex anion. In aqueous solution a 1:1 association complex is formed, which shows an o.s.c.t band of rather low intensity, due to solvation of the ions and thus increasing distance between the donor and acceptor. In the hydrated solid which is formally a 2:1 association complex a bathochromic shift of the o.s.c.t band is observed and its intensity increases. To some extent a real electron shift from the d^2 metal to the pyridine ring takes place. In the anhydrous salts, IR and ESR spectra indicate a direct shift of protons from the protonated 4,4′-bipy cation to the nitrogen atoms of the cyanide ligands and appreciable shift of the charge in the reverse direction.

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