Synthesis and Spectroscopic Properties of $[AsPh_4][MO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$ (M = Mo or W); *X*-Ray Crystal Structure of the Tungsten Complex†

Janusz Szklarzewicz* and Alina Samotus
Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland
Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL
Matthias Moll
Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, D 8520 Erlangen, Federal Republic of Germany

Reaction of $K_3Na[MO_2(CN)_4]\cdot6H_2O$ (M = Mo or W) with 2,2′-bipyridyl (bipy) in water–methanol solution (pH 8.4) affords the new compounds $[AsPh_4][MO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$. The structure of the tungsten complex was determined by *X*-ray analysis. Principal dimensions (ranges or means; estimated standard deviation 0.005 Å) are: W=O 1.735, W–C 2.129–2.149, W–N 2.149 and 2.307 Å. The crystals are triclinic, space group $P\bar{1}$, a = 10.035(3), b = 12.829(5), c = 15.732(5) Å, α = 76.00(3), β = 84.00(3), γ = 88.30(3)°, Z = 2, R = 0.069 for 6 104 observed $[I/\sigma(I) \geqslant 2.0]$ reflections. Tungsten is six-co-ordinated with oxygen and cyano ligands *trans* to the bidentate bipy. The structure contains 'free' bipy which links the complex anions in chains *via* hydrogen-bonded water molecules. The i.r. spectra of the solids are in agreement with this structure as are the n.m.r. (^1H and ^{13}C) spectra. The visible spectra in various organic solvents are dominated by metal-to-ligand charge-transfer bands with absorption maxima that are linearly dependent on the Gutmann acceptor number of the solvent.

In recent years Leipoldt and co-workers reported a series of 'mixed' complexes of molybdenum(IV) and tungsten(IV) derived from $[MO(OH_2)(CN)_4]^{2-}$ (M = Mo or W) by replacement of one ligand (H_2O) by various monodentate ligands [$L = N_3^-$, F^-, NCS^-, or pyridine (py)][1] or by replacement of two ligands (H_2O and CN^-) by bidentate ligands L′ [L′ = 1,10-phenanthroline (phen) or pyridine-2-carboxylate (pyca)].[2–4] Recently, we extended this series to L′ = 2,2′-bipyridyl (bipy), studying photochemical reactions of $[M(CN)_8]^{4-}$–bipy systems.[5] In this paper we report details of the synthesis of $[AsPh_4][MO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$ and the crystal structure of the tungsten complex. Much attention has been paid to the spectroscopic characterisation of the salts in the solid state and in organic solvents, because such mixed-ligand cyano–polypyridyl complexes of transition metals are very promising as light absorption sensitizers and electron-relay species in photochemical systems directed towards the conversion and storage of solar energy.[6]

Experimental

Starting Materials.—The compounds $K_3Na[MO_2(CN)_4]\cdot6H_2O$ were obtained as described earlier.[7] All other materials were produced commercially and used as supplied.

Preparation of $[AsPh_4][MoO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$ (**1**).—Solid $K_3Na[MoO_2(CN)_4]\cdot6H_2O$ (2.4 g, 5 mmol) was added to a solution of bipy (1.56 g, 10 mmol) in MeOH (60 cm^3). To this, water was added to dissolve the suspended solid. The pH was adjusted to 8.4 (HCl) and the solution was allowed to stand for 2 h. Excess of $AsPh_4Cl$ was then added and the resulting black crystals were filtered off and recrystallised from water–methanol (1:3). Yield *ca.* 90% (Found: C, 59.6; H, 4.2; N, 9.7. Calc. for $C_{42}H_{36}AsMoO_3$: C, 59.8; H, 4.3; N, 10.0%). I.r. (Nujol): ν(CN) 2 102vs, 2 116m, ν(M=O) 973vs, selected bands of bipy and cation 467m, 698s, 739s, 748s, 756s, 762s, 784s, 1 002m, 1 086m, 1 169m, 1 188m, 1 259m, 1 285m, 1 323m, 1 345m, 1 563m, and 1 584m cm^{-1}.

Preparation of $[AsPh_4][WO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$ (**2**).—The procedure was analogous to that for the molybdenum complex. The only difference was that the reacting solution was kept for 1 h at 40 °C (Found: C, 54.2; H, 4.4; N, 9.6. Calc. for $C_{42}H_{36}AsO_3W$: C, 54.2; H, 4.9; N, 9.0%). I.r. (Nujol): ν(CN) 2 093vs, ν(W=O) 971vs, selected bands of bipy and cation 467m, 697s, 733s, 748vs, 782vs, 1 002s, 1 085s, 1 167s, 1 188m, 1 248s, 1 270s, 1 320vs, 1 345vs, 1 562m, and 1 580m cm^{-1}.

Physical Measurements.—I.r. and electronic spectra were recorded as described previously,[8] ^1H and ^{13}C n.m.r. spectra on JEOL PMX 60 (^1H) and FT-JNM GX 270 (^1H and ^{13}C n.m.r.) spectrometers in $(CD_3)_2SO$.

Crystal Structure Analysis of $[AsPh_4][WO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$.—$C_{42}H_{36}AsO_3W$, M = 931.6, triclinic, space group $P\bar{1}$, a = 10.035(3), b = 12.829(5), c = 15.732(5) Å, α = 76.00(3), β = 84.00(3), γ = 88.30(3)°, U = 1 594(3) Å^3, D_c = 1.58 g cm^{-3}, Z = 2, λ = 0.710 69 Å, T = 290 K, μ = 39.1 cm^{-1}, lustrous black plates, crystal dimensions 0.083 × 0.22 × 0.35 mm.

Data were collected with a Syntex $P2_1$ four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ±1.0° (2θ) around the $K_{\alpha1}$—$K_{\alpha2}$ angles, scan speed 2—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. Three standard reflections were monitored every 200 reflections, showed only slight changes during data

---

† Tetraphenylarsonium (2,2′-bipyridyl)tricyano-oxotungstate(IV)–2,2′-bipyridyl (1/0.5) dihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

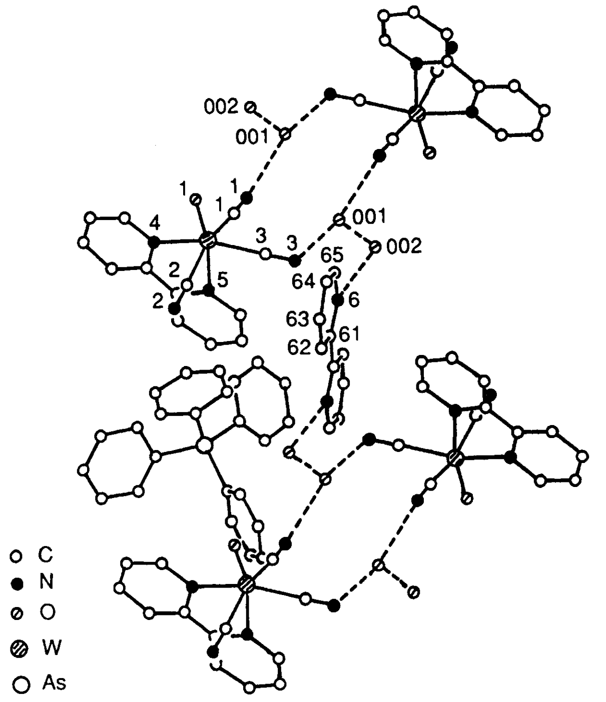


Figure 1. Partial projection of the structure of [AsPh$_4$][WO(bipy)(CN)$_3$]·0.5bipy·2H$_2$O onto the *xy* plane. Atoms numbered according to Table 1. Dashed lines are hydrogen bonds. For clarity only one tetraphenylarsonium ion is shown

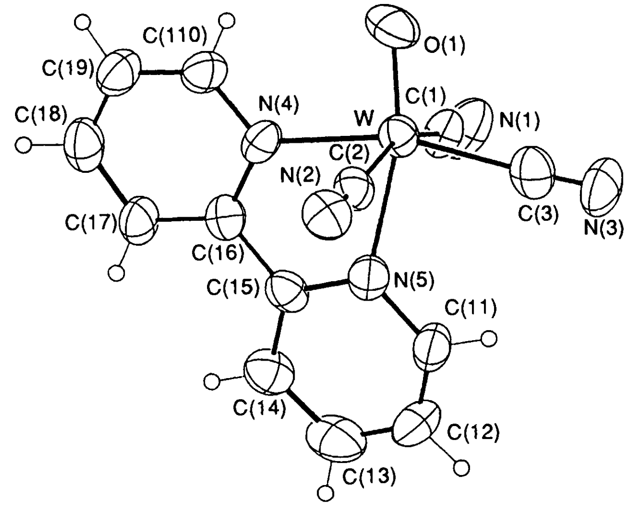


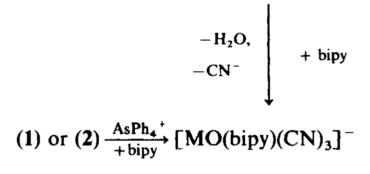
Figure 2. Structure of the anion [WO(bipy)(CN)$_3$]$^-$ in the salt (**2**), showing the atomic numbering; 50% probability ellipsoids

collections. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($20 < 2\theta < 22°$). Reflections were processed using profile analysis to give 6 908 unique reflections; 6 104 were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method: maximum and minimum transmission factors were 0.73 and 0.43. No systematic absences. The space group $P\bar{1}$ was assumed and confirmed by successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses, including 2H$_2$O and free bipy lying across an inversion centre. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07\text{A}^2$, inserted at calculated positions and not refined. Final refinement was on F by least-squares methods with 478 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height +8 and -2 e Å^{-3}, with all peaks >0.9 e Å^{-3} near W or As. These exceptionally high values are attributed to imprecision in the absorption correction for the platy crystal. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0012$ was used and shown to be satisfactory by weight analysis. Final $R = 0.069$, $R' = 0.075$. Maximum shift/error in final cycle 0.05. Computing was with SHELXTL PLUS[9] on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 10. Final atomic co-ordinates are given in Table 1, selected bond lengths and angles in Tables 2 and 3.

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

Results and Discussion

Synthesis and Characterisation of the Complexes.—Treatment of a water–methanol solution of the salt K$_3$Na[MO$_2$(CN)$_4$]·6H$_2$O (M = Mo or W) with bipy followed by the addition of AsPh$_4$Cl affords the black diamagnetic compounds, [AsPh$_4$][MO(bipy)(CN)$_3$]·0.5bipy·2H$_2$O (Scheme). This formulation was confirmed by *X*-ray crystallography of complex (**2**). The attempted synthesis of a solid without 'free' bipy (by lowering of the bipy:M ratio below 1:1, or *via* repeated recrystallisation) always gave the products of formula (**1**) or (**2**). The same products are also formed in the reaction of [MO(CN)$_5$]$^{3-}$ with bipy.[5]



$$\begin{tikzcd}
{[MO_2(CN)_4]^{4-}} \arrow[r, "pH\ 8.4", "+H^+"'] & {[MO(OH_2)(CN)_4]^{2-}} \arrow[d, "-H_2O,\ -CN^-"', "+\ bipy"] \\
{(1)\ or\ (2)} \arrow[r, "AsPh_4^+", "+bipy"'] & {[MO(bipy)(CN)_3]^-}
\end{tikzcd}$$

Scheme.

Complexes (**1**) and (**2**) show intense absorption in the characteristic ν(CN) stretching region around 2 100 cm^{-1} and ν(M=O) stretching region around 970 cm^{-1}. The spectra also contain bands typical for AsPh$_4$$^+$ and bipy but no difference between co-ordinated (*cis* conformation) and 'free' (*trans* conformation) bipy is seen. The spectra in this region are practically the same as for [AsPh$_4$]$_2$[W(bipy)(CN)$_6$]·4H$_2$O (**3**).[8] This supports the conclusion that the bipy bands are not sensitive to co-ordination.[11]

The complexes are relatively air-stable in the solid state and are insoluble in water, but soluble in various organic solvents. They are decomposed easily by alkalis and acids. Cyclic voltammetry measurements and potentiometric oxidation with Ce(SO$_4$)$_2$ in MeCN show irreversible oxidation to molybdate or tungstate.

Description of the Structure of Complex (**2**).—The structure consists of discrete tetraphenylarsonium cations and [WO(bipy)(CN)$_3$]$^-$ anions which form a hydrogen-bonded chain with water and bipy molecules (Figure 1).

The [WO(bipy)(CN)$_3$]$^-$ anion (Figure 2) has a distorted octahedral structure with the bipy, oxygen, and one cyano ligand [C(3)–N(3)] in one plane containing W and the two other cyano ligands out of plane. The angles N(4)–W–O(1) and N(5)–W–C(3) are close to 90° but O(1)–W–C(3) and

Table 1. Atomic co-ordinates (× 10^4) for $[AsPh_4][WO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$

Atom	*x*	*y*	*z*
W	2 077.9(4)	2 076.8(3)	668.2(3)
As	8 595.6(9)	1 632.2(8)	3 436.2(6)
N(1)	976(11)	3 302(8)	−1 227(7)
N(2)	4 141(10)	995(8)	2 132(6)
N(3)	2 689(11)	4 397(8)	1 071(7)
N(4)	2 238(8)	620(6)	218(5)
N(5)	3 978(8)	2 144(7)	−305(6)
N(6)	6 760(12)	4 832(8)	4 879(7)
O(1)	570(8)	1 709(7)	1 303(5)
O(001)	8 950(10)	4 489(10)	7 755(7)
O(002)	8 267(14)	3 661(10)	6 368(9)
C(1)	1 399(11)	2 887(8)	−565(7)
C(2)	3 434(10)	1 402(8)	1 611(7)
C(3)	2 506(11)	3 610(9)	901(7)
C(11)	4 852(11)	3 028(8)	−584(7)
C(12)	5 833(12)	3 098(10)	−1 233(9)
C(13)	6 046(13)	2 312(11)	−1 668(8)
C(14)	5 205(11)	1 393(10)	−1 406(7)
C(15)	4 174(9)	1 327(8)	−716(6)
C(16)	3 242(10)	457(8)	−414(6)
C(17)	3 332(11)	−469(8)	−700(8)
C(18)	2 392(12)	−1 295(9)	−332(8)
C(19)	1 419(12)	−1 139(9)	301(9)
C(110)	1 361(10)	−212(9)	564(8)
C(21)	7 276(10)	1 316(8)	4 431(6)
C(22)	7 190(11)	314(9)	4 965(7)
C(23)	6 320(14)	126(11)	5 744(8)
C(24)	5 602(12)	955(12)	5 938(8)
C(25)	5 615(14)	1 907(12)	5 421(10)
C(26)	6 475(11)	2 153(10)	4 650(8)
C(31)	10 149(10)	2 202(8)	3 768(7)
C(32)	10 079(12)	2 461(10)	4 592(8)
C(33)	11 157(13)	2 912(12)	4 823(8)
C(34)	12 341(13)	3 044(11)	4 272(9)
C(35)	12 414(11)	2 793(11)	3 475(9)
C(36)	11 306(11)	2 336(10)	3 232(8)
C(41)	7 885(10)	2 665(8)	2 490(6)
C(42)	8 685(12)	3 415(9)	1 923(7)
C(43)	6 026(14)	3 277(11)	1 699(9)
C(44)	6 829(13)	4 044(9)	1 120(8)
C(45)	8 157(15)	4 108(9)	1 238(8)
C(46)	6 536(11)	2 569(9)	2 376(8)
C(51)	9 060(10)	309(8)	3 119(6)
C(52)	8 110(13)	−150(10)	2 731(8)
C(53)	9 639(16)	−1 629(10)	2 701(9)
C(54)	8 449(16)	−1 122(10)	2 501(9)
C(55)	10 538(13)	−1 185(10)	3 098(8)
C(56)	10 259(12)	−193(9)	3 293(8)
C(61)	5 582(11)	5 073(9)	4 632(7)
C(62)	5 331(15)	5 384(12)	3 761(9)
C(63)	6 437(20)	5 462(16)	3 125(10)
C(64)	7 647(17)	5 261(15)	3 371(12)
C(65)	7 797(13)	4 946(12)	4 251(12)

Table 2. Selected bond lengths (Å) with estimated standard deviations (e.s.d.s) in parentheses

W–N(4)	2 149(9)	W–N(5)	2 307(8)
W–O(1)	1.735(7)	W–C(1)	2.137(10)
W–C(2)	2.129(10)	W–C(3)	2.149(13)
N(1)–C(1)	1.165(15)	N(2)–C(2)	1.157(14)
N(3)–C(3)	1.130(17)	N(4)–C(16)	1.389(12)
N(4)–C(110)	1.373(13)	N(5)–C(11)	1.409(13)
N(5)–C(15)	1.359(15)	C(11)–C(12)	1.331(16)
C(12)–C(13)	1.349(21)	C(13)–C(14)	1.422(17)
C(14)–C(15)	1.407(14)	C(15)–C(16)	1.435(13)
C(16)–C(17)	1.366(16)	C(17)–C(18)	1.413(15)
C(18)–C(19)	1.367(17)	C(19)–C(110)	1.347(18)

Table 3. Selected bond angles (°) with e.s.d.s in parentheses

N(4)–W–N(5)	70.8(3)	N(4)–W–O(1)	93.5(4)
N(5)–W–O(1)	164.1(4)	N(4)–W–C(1)	89.0(4)
N(5)–W–C(1)	76.9(3)	O(1)–W–C(1)	101.3(4)
N(4)–W–C(2)	88.6(4)	N(5)–W–C(2)	82.6(3)
O(1)–W–C(2)	99.7(4)	C(1)–W–C(2)	159.0(4)
N(4)–W–C(3)	162.7(4)	N(5)–W–C(3)	92.0(4)
O(1)–W–C(3)	103.7(4)	C(1)–W–C(3)	89.1(4)
C(2)–W–C(3)	87.0(4)	W–C(2)–N(2)	177.1(9)
W–C(1)–N(1)	176.9(9)	W–C(3)–N(3)	175.9(10)

N(4)–W–N(5) are far from ideal for octahedral geometry at tungsten. The W–N bonds differ significantly, with the longer one *trans* to the strong W=O bond. All three cyanide ligands differ in bond distances by about 0.01 Å with the longest W–C(3) *trans* to the shorter W–N(4) bond. This bonding pattern is similar to that of $[WO(pyca)(CN)_3]^{2-}$ in $[AsPh_4]_2[WO(pyca)(CN)_3]\cdot2H_2O$ (W=O 1.669; W–C 2.042, 2.158, and 2.175 Å).[4] The bipy ligand is not abnormally distorted. Its configuration is similar to those reported for a number of complexes where bipy is bound to metal centres. The C(15)–C(16) bond length and the twist of 7.8(5)° of the two pyridine groups about the C(15)–C(16) axis are very similar to the values reported in these other systems.[12]

The outer-sphere bipy is in *trans* conformation, with typical bond lengths for free bipy.[12] The nitrogen atoms N(6) and N(6′) of bipy are hydrogen bonded to oxygen atoms of two water molecules [N(6)$\cdots$O(002) 2.99(2), 0(001)$\cdots$0(002) 2.80 (2) Å]. An oxygen atom is also hydrogen bonded to nitrogen atoms [N(1) and N(3)] of the cyanide ligands [0(001)$\cdots$N(1) 2.89(2), 0(001)$\cdots$N(3) 2.94(2) Å] (Figure 1).

The As atoms are tetrahedrally bonded to four carbon atoms of the four phenyl rings. The average As–C bond distance (1.916 Å) and C–As–C bond angle (109.5°) compare well with the 1.906 Å and 109.5° in $[AsPh_4]_2[WO(pyca)(CN)_3]\cdot2H_2O$.[4]

Electronic Absorption Spectra.—The remarkable properties of polypyridyl complexes of transition metals arise from the presence of long-lived, strongly reducing d-π^* metal-to-ligand charge transfer (m.l.c.t.) excited states. It is known that complexes containing a single M–bipy unit can exhibit most of the interesting properties of homoleptic M–bipy complexes.[13] The visible spectra of complexes (**1**) and (**2**) like previously described species (**3**)[8] are dominated by intense W–bipy m.l.c.t. bands (Figure 3). These bands are solvent dependent, shifting to longer wavelengths on going from water to acetone, with a linear dependence of $\nu_{max.}$ on the Gutmann acceptor number (AN) of the solvents[14] (Table 4). The pronounced solvatochromic effect [which is however, less than observed for (**3**)] has been explained by a model[15] in which the solvent is acting as an acceptor in s.s.d.a. (second-sphere donor-acceptor) interaction at the nitrogen end of the cyanide ligand. This finds support in the crystal structure of complex (**2**) (hydrogen bonding between cyano ligands and water molecules, Figure 1). However such strong solvent effects are observed only for mixed-ligand (*e.g.* cyano–polypyridyl) complexes in contrast to homoleptic (cyano or polypyridyl) species. This means that the entire molecular system (with donor properties of CN^- ligands and flexibility of the π-electron system of bipy) can adapt to the

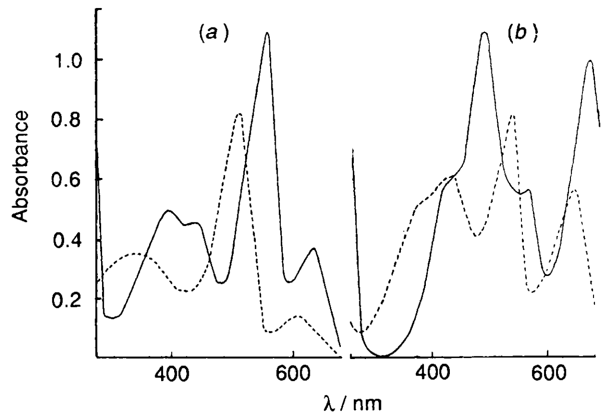


Figure 3. Absorption spectra of complexes (**1**) (1.96×10^{-4} mol dm^{-3}) (*a*) and (**2**) (1.75×10^{-4} mol dm^{-3}) (*b*) in acetone (——) and in methanol (- - -); path length 1 cm

Table 4. Absorption maxima ($\lambda_{max.}$/nm and $\nu_{max.}/10^3$ cm^{-1}) and molar absorption coefficients ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) of $[AsPh_4][MO(bipy)(CN)_3]\cdot0.5bipy\cdot2H_2O$ in various solvents

Solvent (AN)	(1)			(2)		
	$\lambda_{max.}$	($\nu_{max.}$)	$\varepsilon_{max.}$	$\lambda_{max.}$	($\nu_{max.}$)	$\varepsilon_{max.}$
Water[a]				385	(26.0)	*b*
(54.8)	455	(22.0)	1.89	495	(20.2)	*b*
	645	(15.5)	0.17	666	(15.0)	*b*
CH_3OH				401	(24.9)	3.06
(41.3)	367	(27.2)	1.89	432	(23.1)	3.53
	498	(20.1)	4.27	526	(19.0)	4.63
	642	(15.6)	0.78	684	(14.6)	3.23
C_2H_5OH				402	(24.9)	3.08
(37.1)	368	(27.2)	1.94	437	(22.9)	3.71
	506	(19.8)	4.43	531	(18.8)	4.56
	645	(15.5)	0.86	688	(14.5)	3.40
CH_3CN	379	(26.4)	2.20	418	(23.9)	3.48
(18.9)	400	(25.0)	2.17	455	(22.0)	4.92
	525	(19.0)	5.14	555	(18.0)	4.36
	655	(15.3)	1.22	711	(14.1)	4.76
dmf[c]	388	(25.8)	2.34	428	(23.4)	3.50
(16.0)	424	(23.6)	2.27	471	(21.2)	5.66
	541	(18.5)	5.43	558	(17.9)	3.77
	662	(15.1)	1.67	724	(13.8)	5.38
$(CH_3)_2CO$	393	(25.4)	2.53	433	(23.1)	3.52
(12.5)	431	(23.2)	2.32	477	(21.0)	6.28
	546	(18.3)	5.62	562	(17.8)	3.27
	666	(15.0)	1.86	737	(13.6)	5.68

[a] Data for aqueous solutions of complexes (**1**) and (**2**) taken from A. Samotus, W. Gług, A. Kanas, and J. Szklarzewicz, to be published. [b] Not determined. [c] Dimethylformamide.

environment in accordance with the Gutmann concept of molecular system organization.[16]

In contrast to cyano-bipy complexes of Ru^{II} the lowest excited state in (**1**) and (**2**) is metal-centred (m.c.) rather then m.l.c.t. in character. The complexes do not show luminescence even in the weak acceptor solvent acetone. The longest-wavelength band, which seems to be the superposition of a m.l.c.t. and a m.c. transition, is less sensitive to change of solvent than the other bands, suggesting a greater contribution of m.c. transition (in accordance with smaller crystal-field effects of oxide in comparison with cyanide).

Table 5. Proton n.m.r. data[a] for the ligand and metal complexes

Compound	*T*/°C	$H^{6,6'}$	$H^{5,5'}$	$H^{4,4'}$	$H^{3,3'}$
bipy	22	8.63 (d, 2)	7.36 (t, 2)	7.86 (t, 2)	8.37 (d, 2)
(**1**)	22	8.68 (d, 1)[b]	7.40 (m, 2)[b,c]	*d*	8.38 (d, 1)[b]
		9.43 (d, 1)[c]		*d*	8.48 (d, 1)[c]
		8.60 (d, 1)[e]	7.20 (t, 1)[e]	*d*	8.27 (d, 1)[e]
(**2**)	22	8.67 (t, 1)[b,e]	7.43 (m, 2)[b,c]	*d*	8.37 (d, 1)[b]
		8.95 (d, 1)[c]		*d*	8.50 (d, 1)[c]
			7.26 (t, 1)[e]	*d*	8.23 (d, 1)[e]
	60	8.67 (d, 1)[b]	7.38 (m, 2)[b,c]	*d*	8.37 (d, 1)[b]
		8.95 (d, 1)[c]		*d*	8.44 (d, 1)[c]
		8.59 (d, 1)[e]	7.21 (t, 1)[e]	*d*	8.28 (d, 1)[e]
	90	8.67 (d, 1)[b]	7.37 (m, 2)[b,c]	*d*	8.38 (m, 3)[b,c,e]
		8.95 (d, 1)[c]		*d*	
		8.56 (d, 1)[e]	7.18 (t, 1)[e]	*d*	

[a] Chemical shifts (δ) relative to $SiMe_4$ in $(CD_3)_2SO$. d = Doublet, t = triplet, and m = multiplet; numbers in parentheses show relative integrated intensities. [b] For 'free' bipy. [c] For the ring N(4)–C(16)–C(110) of co-ordinated bipy. [d] Resonances obscured by those of $AsPh_4^+$. [e] For the ring N(5)–C(15)–C(11) of co-ordinated bipy.

Table 6. ^{13}C N.m.r. data[a] for the ligand and metal complexes.

Compound	$C^{2,2'}$	$C^{3,3'}$	$C^{4,4'}$	$C^{5,5'}$	$C^{6,6'}$	CN^-
bipy	155.28	124.11	137.22	120.44	149.23	
(**1**)	155.18[b]	124.19[b]	137.29[b]	120.39[b]	149.24[b]	151.46
	153.97[c,d]	124.54[c]	138.73[c]	122.18[c]	149.47[c]	151.32
		123.15[d]	138.10[d]	121.02[e]	148.93[d]	146.88
(**2**)	155.20[b]	124.22[b]	137.32[b]	120.42[b]	149.27[b]	151.09
	154.11[c,d]	122.29[c]	137.70[c]	*f*	149.42[c]	148.15
		f	136.87[d]	121.05[e]	148.93[d]	145.90

[a] Chemical shifts in p.p.m. relative to $SiMe_4$ in $(CD_3)_2SO$. [b] For 'free' bipy. [c] For the ring N(4)–C(16)–C(110) of co-ordinated bipy. [d] For the ring N(5)–C(15)–C(11) of co-ordinated bipy. [e] Resonance superimposed on that of $AsPh_4^+$. [f] δ 121.77 p.p.m. is the sum of the C^3 and $C^{5'}$ resonances.

Proton and ^{13}C *N.M.R. Spectra.*—The n.m.r. spectra of complexes (**1**) and (**2**) (Tables 5 and 6) reflect their structural features as found by *X*-ray analysis. The presence of unco-ordinated bipy was clearly revealed by the position of H and C signals typical for free bipy.[17] In the spectroscopic pattern for co-ordinated bipy, due to the low symmetry of the complex anion (Figure 2), the aromatic rings are no longer equivalent and a line splitting occurs. The characteristic feature of the ^1H n.m.r. spectra (Table 5) is that a shift to higher field is observed for the protons of ring N(4)–C(16)–C(110) whereas the opposite effect is seen for the protons of the other ring [N(5)–C(15)–C(11), numbering as in Figure 2] relative to free bipy. The different shift of the complexed bipy protons can be explained by increased π back bonding in M–N(4) causing decreased electron density in the aromatic ring (short bond distance 2.149 Å) and concurrently decreased π back bonding in M–N(5) (long bond distance 2.307 Å) as O^{2-} competes effectively for electron density (O^{2-} being a better π acceptor than CN^-). With increasing temperature this effect is enhanced (except that the 3,3′ protons tend to become equivalent). Experiments at elevated temperature with complex (**2**) established also that the multiplet signal of $H^{6,6'}$ (δ 8.67) is associated with two doublets (Table 5).

The ^{13}C n.m.r. spectra (Table 6) are also in agreement with the solid-state structure. The resonances showing major shifts are again those for the ring N(4)–C(16)–C(100) as for the ^1H n.m.r. spectra. Separate resonances are observed for three inequivalent cyano groups {^{13}CN chemical shifts range from 145.90 to 151.46 p.p.m.; in $[W(CN)_8]^{4-}$, 146.9 p.p.m.[18]}.

The present study leads us to believe that the chemistry of these new complexes in solution can be interpreted from their solid structure.

Acknowledgements

This work was supported by the Polish Academy of Sciences (Project CPBP 01.12.9.5), by the British Council, and by the S.E.R.C.

References

1 S. S. Basson, J. G. Leipoldt, I. M. Potgieter, and A. Roodt, *Inorg. Chim. Acta*, 1985, **103**, 121; J. G. Leipoldt, S. S. Basson, A. Roodt, and I. M. Potgieter, *S. Afr. J. Chem.*, 1986, **39**, 179; A Roodt, J. G. Leipoldt, S. S. Basson, and I. M. Potgieter, *Transition Met. Chem.*, 1988, **13**, 336; I. M. Potgieter, S. S. Basson, A. Roodt, and J. G. Leipold, *ibid.*, p. 209.

2 S. S. Basson, J. G. Leipoldt, and I. M. Potgieter, *Inorg. Chim. Acta*, 1984, **87**, 71.

3 S. S. Basson, J. G. Leipoldt, and I. M. Potgieter, *Inorg. Chim. Acta*, 1984, **90**, 57.

4 J. G. Leipoldt, S. S. Basson, A Roodt, and I. M. Potgieter, *Transition Met. Chem.* (*Weinheim, Ger.*), 1986, **11**, 323.

5 A. Samotus, J. Szklarzewicz, and N. W. Alcock, *Inorg. Chim. Acta*, 1990, **172**, 129.

6 C. A. Bignozzi, C. Chiorboli, M. T. Indelli, M. A. Rampi-Scandola, G. Varani, and F. Scandola, *J. Am. Chem. Soc.*, 1986, **108**. 7872; A. Juris, F. Barigelletti, V. Balzani, P. Belser, and A. von Zelewsky, *J. Chem. Soc., Faraday Trans. 2*, 1987, 2295.

7 A. Samotus, M. Dudek, and A. Kanas, *J. Inorg. Nucl. Chem.*, 1975, **37**, 943.

8 J. Szklarzewicz and A. Samotus, *Transition Met. Chem.*, 1988, **13**, 69.

9 G. M. Sheldrick, SHELXTL PLUS, User Manual, Nicolet XRD Corporation, Madison, Wisconsin, 1983.

10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

11 A. A. Schilt, *Inorg. Chem.*, 1964, **3**, 1323.

12 B. Durham, S. R. Wilson, D. J. Hodgson, and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 600.

13 P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger, and W. H. Woodruff, *J. Am. Chem. Soc.*, 1981, **103**, 7441; P. S. Braterman, A. Harriman, G. A. Heath, and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1983, 1801; S. J. Milder, J. S. Gold, and D. S. Klinger, *J. Phys. Chem.*, 1986, **90**, 548.

14 V. Gutmann, *Electrochim. Acta*, 1976, **21**, 177.

15 J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1369; V. Balzani, N. Sabbatini, and G. Scandola, *Chem. Rev.*, 1986, **86**, 319; F. Scandola and T. Indelli, *Pure Appl. Chem.*, 1988, **60**, 973; N. Kitamura, M. Sato, H. B. Kim, R. Obata, and S. Tazuke, *Inorg. Chem.*, 1988, **27**, 651.

16 V. Gutmann and G. Resch, *Monatsh. Chem.*, 1985, **116**, 1107.

17 G. Nord and B. V. Agarwala, *Acta Chem. Scand., Ser. A.* 1981, **35**, 231; S. Kitagawa, M. Munakata, and N. Miyaji, *Inorg. Chem.*, 1982, **21**, 3842.

18 M. Hirota, Y. Koike, H. Ishizuka, A. Yamasaki, and S. Fujiwara, *Chem. Lett.*, 1972, 853.

Received 22*nd March* 1990; *Paper* 0/01266A