

N-Methyl-2,2'-bipyridylium Complexes of the Zinc Group

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Abstract

N-Methyl-2,2'-bipyridylium halides, (bpyMe)X (X = Cl, Br, I), react with the zinc-group halides, MX₂ (M = Zn, Cd, Hg; X = Cl, Br, I), in ethanol to give the complexes M(bpyMe)X₃. Infrared spectroscopy indicates that the bpyMe⁺ ion is coordinated to the metal ion, and that the complexes are four-coordinate with nominal C_{3v} symmetry. The complexes behave as 1:1 electrolytes in acetonitrile; a dissociation to form (bpyMe)[M(MeCN)X₃] is suggested.

Introduction

Theoretically, 2,2'-bipyridyl (bpy) can coordinate to metal ions as a monodentate, chelating or bridging ligand, although in practice, only the chelating mode has been observed [1]. To our knowledge, the only exception is the two-coordinate methylmercury(II) complex [CH₃Hg(3,3'-dmbpy)]NO₃ (3,3'-dmbpy = 3,3'-dimethyl-2,2'-bipyridyl) in which the bipyridyl ligand is monodentate [2]. Ir(bpy)₃Cl₃·4H₂O, first prepared by Watts *et al.* [3], was originally believed to contain a monodentate bpy group. X-ray studies [4] have now shown that the complex is six-coordinate with two 'normal' N,N'-bpy ligands and one cyclo-metallated N,C^{3'}-bpy chelate.

Nonetheless, stopped-flow NMR [5] and Fourier-transform infrared [6] studies have shown that the intermediates in the formation of bpy chelates contain the monodentate ligand. Similarly, kinetic studies [7, 8] of the acid-catalysed aquation of tris(bpy) complexes provide further support for monodentate intermediates.

We have been investigating [9–11] the rational preparation of monodentate bpy complexes. One approach is to place bulky substituents in the 3,3'-positions of bpy, however, this does not prevent the ligand from forming chelates [10, 12] (except for the methylmercury complex mentioned above). Another approach is to block one of the nitrogen atoms of bpy by quaternisation with an alkyl group. We have shown [9, 11] that neither the positive charge nor the bulk of the resultant cation prevents coordination.

In this paper we describe some N-methyl-2,2'-bipyridylium complexes with metal ions of the zinc group.

Experimental

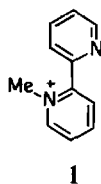
The metal halides and general reagents were obtained from B.D.H. Chemicals Ltd. and 2,2'-bipyridyl from the Aldrich Chemical Company.

Infrared spectra (4000–200 cm⁻¹) were recorded as nujol mulls (CsI plates) or as CsI discs on Perkin-Elmer 577 and 1430 spectrophotometers. Conductances were measured with a Toshniwal CL01/01A A.C. conductance bridge. Analytical grade acetonitrile was dried over 4 Å molecular sieves, then distilled from phosphorus pentoxide under dry nitrogen onto freshly-activated molecular sieves. Melting points were determined with a Kofler hot-stage microscope calibrated with appropriate standards.

Elementary microanalyses were determined by the Microanalytical Services at University College, London and the University of Queensland. Halide content (for Zn and Cd) was determined by a combination of the Mohr and Volhard methods [13]. Satisfactory end-points could not be obtained when an absorption indicator was used (see main text).

Preparation of (bpyMe)X (X = Cl, Br, I)

N-Methyl-2,2'-bipyridylium iodide, (bpyMe)I (1), was prepared by a modification of the method of Westheimer and Benfey [14].



A mixture of 2,2'-bipyridyl (5.0 g, 32 mmol) and iodomethane (4.7 g, 33 mmol) in 1-butanol (30 ml) was heated under reflux for 3 h. The orange solution was filtered hot to remove the small amount of

N,N'-dimethyl-2,2'-bipyridylium iodide (0.2 g) that had formed and cooled to crystallise (bpyMe)I (9.5 g), which was collected and washed with small portions of 1-butanol and ether.

The crude (bpyMe)I was recrystallised from the minimum amount of hot ethanol, washed with ether and dried *in vacuo* (melting point (m.p.) 149–150 °C, ref. 14 145–146 °C). A further crop can be isolated by adding ether to the mother liquor, but this usually contains a small amount of 2,2'-bipyridyl.

(bpyMe)I is slightly hygroscopic and was shown to be free from unreacted 2,2'-bipyridyl by treatment with ferrous ammonium sulphate. Any red coloration indicates the presence of 2,2'-bipyridyl.

The salts (bpyMe)X (X = Cl, Br) were prepared by stirring aqueous solutions of (bpyMe)I with Amberlite IRA400 (Cl, Br form respectively) and evaporating to dryness.

Preparation of the Complexes

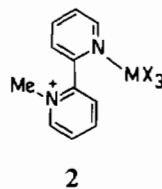
Hot ethanolic solutions of (bpyMe)X (X = Cl, Br, I; 1.1 mmol) and the anhydrous metal(II) halide* (M = Zn, Cd, Hg; X = Cl, Br, I; 1.0 mmol) were mixed with stirring. Upon cooling, the white crystals of M(bpyMe)X₃ were collected, washed with ethanol and dried *in vacuo*.

Typical yields and the elementary microanalyses are summarised in Table I. Although the compounds are not hygroscopic, they were stored over silica-gel.

Results

The mixing of hot ethanolic solutions of *N*-methyl-2,2'-bipyridylium halide, (bpyMe)X (X = Cl, Br, I) (1), and a metal(II) halide (MX₂; M = Zn, Cd, Hg; X = Cl, Br, I) yields, on cooling, white crystals of

M(bpyMe)X₃ (2) in good yield (Table I). The compounds are stable in dry air and soluble in polar solvents such as acetonitrile, nitromethane (*vide infra*) and water. By analogy with the first-row transition metal complexes, M(bpyMe)Cl₃ (M = Co, Ni, Cu) [9], the zinc-group complexes should dissociate completely in aqueous solution.



The halide content of the zinc and cadmium compounds was initially determined by titration with silver nitrate using an adsorption indicator [13] (dichlorofluorescein for chloride, eosin for bromide and iodide). This method was found to be unsatisfactory for two reasons. Firstly, the colour change at the equivalence point was indistinct due to pre-colouring of the silver halide precipitate. Secondly, the silver halide did not flocculate close to the equivalence point. These problems did not occur with identical titrations of the inorganic salts, NaCl, CdCl₂ and CdBr₂, which all gave clear end-points [13], whereas the titration of (bpyMe)I itself was unsatisfactory for the same reasons as those given for the complexes. It follows that the bpyMe⁺ ion is interfering with the equivalence point.

The methods of Mohr and Volhard gave good end-points and reproducible halide contents. Of these two methods that of Volhard is preferred; with the Mohr method it was difficult to match the colour of the blank with that of the titrate at the concentrations used (*ca.* 6 × 10⁻³ M in halide).

The Zn, Cd and Hg compounds all have high, and generally sharp, melting points, which are closely

*For CdCl₂ and CdBr₂ the hydrated salts were used.

TABLE I. Physical and Analytical Data for the Complexes

M(bpyMe)X ₃		Yield (%)	Melting point (°C)	Carbon (%)		Hydrogen (%)		Halogen (%)		Λ _M ^a
M	X			Found	Calc.	Found	Calc.	Found	Calc.	
Zn	Cl	75	291(dec)	38.0	38.5	3.2	3.2	29.9	31.0	1.40
Zn	Br	70	302–304(dec)	27.7	27.7	2.4	2.3	50.0	50.3	1.41
Zn	I	73	289(dec)	21.8	21.4	1.8	1.8	61.1	61.7	1.42
Cd	Cl	95	210.5	33.9	33.9	2.9	2.8	27.2	27.3	1.48
Cd	Br	87	230	25.5	25.3	2.2	2.1	45.8	45.8	1.63
Cd	I	85	211	20.1	19.9	1.7	1.7	56.7	57.3	1.46
Hg	Cl ^b	75	192–193	27.5	27.6	2.3	2.3	–	–	1.65
Hg	Br ^c	70	187–188	21.7	21.6	1.8	1.8	38.6	39.2	1.67
Hg	I ^d	78	145–147	17.5	17.6	1.4	1.5	50.8	50.6	1.67

^aMolar conductivity (Sm² mol⁻¹ × 10²), conc. *ca.* 1 × 10⁻³ in acetonitrile at 298 K. ^bNitrogen %: found 5.9, calc. 5.9. ^cNitrogen %: found 4.7, calc. 4.6. ^dNitrogen %: found 3.8, calc. 3.7.

TABLE II. Selected Infrared Bands for Pyridine and Derivatives

Compound	Assignment ^a						
	8a	8b	19a	19b	6b	6a	16b
bpy	1578	1557	1448	1410	651	618	398
py	1578	1570	1478	1436	650	601	403
pyMe ⁺	1632	1581	1501	1486	647	534	446
bpyMe ⁺	1631, 1577 ^b	1580 ^b , 1570	1518, 1472	^c 1434	648	617, 530	448, 407
Zn(bpyMe)Cl ₃	1632, 1600	1583, 1570	1520, 1486	1458, 1436	651	640, 531	443, 423

^aAssignments are based on the work of Wilmshurst and Bernstein [17], Gill *et al.* [15] and Spinner [20], using the notation of Kline and Turkevich [19]. All figures are in cm⁻¹. *Italic numerals indicate the vibrations sensitive to coordination.* ^bThese modes overlap to give a broad composite band. ^cSpectrum has a band at 1450 cm⁻¹, assignment is uncertain, see text.



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followed by a series of complex decompositions*. The Zn(bpyMe)X₃ compounds form an unidentified sublimate on melting.

The bpyMe⁺ ion can be regarded as a pyridine (py) substituted at C² by an *N*-methylpyridinium ion (pyMe⁺) (3). The infrared spectrum of bpyMe⁺ will to a first approximation be the composite of the spectra of py and pyMe⁺ respectively (Table II). Infrared spectroscopy can therefore be used to determine whether bpyMe⁺ forms complexes or salts such as (bpyMe)₂[MCl₄] because well-characterised changes occur in the vibrations of the pyridine ring on coordination to a metal ion (*vide infra*) [15, 16]. We have not attempted to assign** all the bands for bpyMe⁺ and we shall consider only those bands that indicate complex formation.

Pyridine [15, 17] (and similarly bpy [18]) exhibits four ring-stretching modes (8a, 8b, 19a, 19b) [19] in the region 1650–1400 cm⁻¹ (see Table II). Quaternisation (*i.e.* pyMe⁺, 3) results in the shift of these four modes to higher frequency [20]. Of the eight ring-stretching modes expected for bpyMe⁺, those between 1650 and 1500 cm⁻¹ (8a, 8b, 19a) can be clearly assigned (Table II). Vibration 8a for the py ring and 8b for the pyMe⁺ ring are close in frequency, producing a broad band. Below 1500 cm⁻¹ there are bands at 1472, 1450 and 1436 cm⁻¹. The bands at 1472 and 1436 cm⁻¹ are assigned as py vibrations 19a and 19b respectively. The band at 1450 cm⁻¹ may be vibration 19b for pyMe⁺. However, a methyl

bending mode for pyMe⁺ and 2-methylpyridine [21] also occurs around this frequency.

The coordination-sensitive modes 6a (in-plane ring deformation) [16] at 601 cm⁻¹ and 16b (out-of-plane ring deformation) [16] at 403 cm⁻¹ for py are shifted to 534 and 446 cm⁻¹ respectively for pyMe⁺. All four vibrations can be identified in the spectrum of bpyMe⁺.

Upon the formation of a pyridine complex the following changes occur in the infrared spectrum [15, 16]: (i) ν_{8a} shifts from 1578 to *ca.* 1600 cm⁻¹, (ii) ν_{6a} shifts from 601 to 620–40 cm⁻¹, (iii) ν_{16b} shifts from 403 to 410–40 cm⁻¹, (iv) a weak band appears between 1235–1250 cm⁻¹.

Selected bpyMe⁺ bands for the complexes M(bpyMe)Cl₃ (M = Zn, Cd, Hg; X = Cl, Br, I) are presented in Table III and Zn(bpyMe)Cl₃ is included in Table II. The band in the region 1600–1590 cm⁻¹ (ν_{8a} for the py ring) is a clear indication that bpyMe⁺ is coordinated to the metal ion. This is accompanied by a sharpening of the composite band at 1582–77 cm⁻¹. The bands at 640–30 cm⁻¹ (ν_{6a} , py ring) and 423–08 cm⁻¹ (ν_{16b} , py ring)[†], together with the appearance of a new absorption at 1240 cm⁻¹, also confirm the formation of a bpyMe⁺ complex.

A steady decrease in frequency in the order Zn > Cd > Hg and Cl > Br > I is observed for vibrations 8a, 6a and 16b (py ring).

The metal–halogen stretching modes for M(bpyMe)X₃ (M = Zn, Cd, Hg; X = Cr, Br) are summarised in Table III. The two absorptions are consistent with four-coordinate complexes of C_{3v} symmetry [16].

The complexes M(bpyMe)X₃ are slightly soluble in aprotic dipolar solvents such as acetonitrile and nitromethane. The conductivities in acetonitrile (Table I)

*Thermogravimetric analysis for Zn(bpyMe)Cl₃ shows that weight loss begins at the same temperature as the melting point.

**The infrared spectrum of the bpyMe⁺ ion does not appear to have been reported.

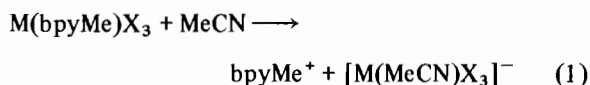
[†]The spectra of the complexes show a weak band at *ca.* 650 cm⁻¹ due to ν_{6b} . This mode is insensitive to coordination and is present in the spectra of py, pyMe⁺ and bpyMe⁺.

TABLE III. Infrared Spectra^a of the M(bpyMe)₃ Complexes

M(bpyMe) ₃		Pyridyl ring bands ^b			M-X stretch
M	X	8a	6a	16b	
Zn	Cl	1600s, 1240w	640s	423s	318vs, 303vs
Zn	Br	1598s, 1239w	640s	421ms	237vs, 230sh
Zn	I	1597s, 1240w	638s	417ms	<200
Cd	Cl	1596s, 1240w	638ms	415m	274vs, 262s
Cd	Br	1594s, 1240w	637ms	413m	ca. 200
Cd	I	1592s, 1239w	634s	410m	<200
Hg	Cl	1590s, 1239w	631s	411m	261s, 250sh
Hg	Br	1590s, 1240w	631s	408m	<200
Hg	I	1586m, 1239w	626ms	403m	<200

^aAll frequencies in cm⁻¹; s, strong; m, medium; sh, shoulder; v, very. ^bOnly bands due to the pyridyl ring of bpyMe⁺ and indicative of coordination are included.

are typical of 1:1 electrolytes [22, 23]. Solvolysis of bpyMe⁺ as shown in eqn. (1)



is favoured as the principal ionisation over substitution of halide, because the analogous cobalt complexes Co(bpyMe)₃ (X = Cl, Br) [24] and [Co(PR₃)₃X₃]⁻ (R = Buⁿ, Ph; X = Cl, Br) [25] dissolve in acetonitrile with complete substitution of bpyMe⁺ and the phosphine respectively to yield [Co(MeCN)₃X₃]⁻. The solubility of the bpyMe⁺ complexes is too low to enable satisfactory solution infrared spectra to be obtained.

Discussion

The bpyMe⁺ ion consists of a ligand portion (py moiety) and a cation portion (pyMe⁺ moiety) and this property, on treatment with divalent metal halides, gives four-coordinate zwitterionic complexes of the type M(bpyMe)₃ (X = halide). Pyridine itself (and related ligands) forms the analogous complexes [M(py)₃X₃]⁻ (M = Zn [26], Co [27]) where the counter ion is frequently a quaternised pyridinium ion. Galinos and coworkers [28] have prepared a series of such complexes where the cation is [(py)₂H]⁺.

The M-X stretching frequencies for Zn(bpyMe)₃ (X = Cl, Br) are slightly higher than those for the [Zn(py)₃X₃]⁻ anions [26, 29] (which also show two ν(M-X) bands) and are intermediate between those for Zn(py)₂X₂ [30] and [ZnX₄]²⁻ [16] (see Table IV). It is suggested that the bpyMe⁺ and the monopyridine complexes have the same structure. This is in agreement with the crystal structures of [Zn(py)Br_{3/2}Cl_{3/2}]⁻ [31] and the zwitterion

TABLE IV. Comparison of ν(Zn-X) Values for Tetrahedral Compounds of the Type [ZnL_nX_{4-n}]^{x-} (n = 0-2; x = 0-2)

Compound ^a	ν(M-X) (cm ⁻¹)		Reference
	X = Cl	X = Br	
[ZnX ₄] ²⁻	277	205	16
[Zn(α-pic)X ₃] ⁻	290, 284	216, 199	26
[Zn(py)X ₃] ⁻	296, 284	223	26
Zn(bpyMe) ₃	318, 303	237, 230	this work
Zn(py) ₂ Cl ₂	329, 296	254, 220	30

^aα-pic, 2-methylpyridine.

Zn(EtOpy-py)Cl₃ (EtOpy-py⁺ = N-(4'-pyridyl)-4-ethoxypyridinium) [32] in which both complexes are four-coordinate with tetrahedral geometry. Steffen and Palenik [32] concluded that the ligand EtOpy-py⁺ has about the same pK_b as pyridine and consequently the cationic site on the second pyridine ring has virtually no effect on the donor properties of the ligand.

Treatment of cadmium and mercury halides (M'X₂, X = Cl, Br, I) with alkali (M⁺ = K, Rb, Cs) and ammonium (M⁺ = NR₄, R = H, Me, Et etc.) halides yields complexes of the type M[M'X₃]. A variety of structures have been observed [33, 37] for these complexes, viz: (a) polymeric based on [MX₆] octahedra (M⁺ = K, Rb, Cs, NH₄⁺) [34, 38], (b) polymeric based on [MX₄] tetrahedra (M⁺ = Me₂NH₂) [35], (c) dimeric with halide bridging (M⁺ = NPr₄ⁿ, NBu₄ⁿ) [36-38], (d) monomeric (M⁺ = NMe₄, SMe₃) [36], (e) trigonal bipyramidal (related to d).

The principal structure types can be distinguished by their infrared spectra [34, 36, 38, 39]. For the [HgCl₃]⁻ system one infrared-active asymmetric (Hg-Cl) stretching mode (terminal) is observed for each structure type at a distinct frequency: polymer (a) 309-20 cm⁻¹, dimer 280-90 cm⁻¹, monomer 250-60 cm⁻¹. The cadmium system has been studied [34, 38] to a lesser extent than mercury. Polymeric [CdCl₃]⁻ ions show one asymmetric ν(Cd-Cl) (terminal) band at 247 cm⁻¹ while the dimer** has bands at 280, 287 cm⁻¹.

For the Hg(bpyMe)₃ (X = Cl, Br, I) compounds, it can be argued that they are salts of the type (bpyMe)[HgX₃] because of the low frequencies of the coordination-sensitive vibrations of bpyMe⁺ (i.e. 8a, 6a and 16b, Table III). If this were the case, the most likely structure for the [HgX₃]⁻ ion is the dimer,

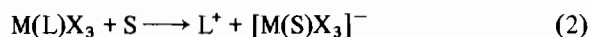
*The structure of NH₄[HgCl₃] consists of infinite sheets of [HgCl₆] octahedra, while that of NH₄[CdCl₃] consists of double chains of linked [CdCl₆] octahedra.

**Apparently monomeric [CdX₃]⁻ ions are unknown. NMe₄[CdCl₃] has a polymeric structure, isomorphous [40] with the nickel analogue [41] with chains of octahedra linked by opposite faces.

as this is formed in salts with large cations, such as tetraalkylammonium and metal complexes [42]. However, for X = Cl the Hg-Cl stretching frequencies (261, 250 cm⁻¹) suggest a monomeric [HgCl₃]⁻ unit. Furthermore, the coordination of the bpyMe⁺ ion to the [HgX₃]⁻ (X = Cl, Br, I) is evidenced by the band at 1240 cm⁻¹, which is diagnostic of coordinated pyridine, and is in agreement with two ν(M-Cl) absorptions. Thus, there seems to be no reason for regarding the mercury compounds as being different to the other complexes.

We are aware of only one study [43] involving cationic-ligand complexes of mercury. The N-benzylpiperazinium ion (bzpipz⁺) reacts with HgX₂ (X = Cl, Br) to give (bzpipz)Hg₂X₅, which is polymeric with halide bridges. The bromo complex can be cleaved with extra ligand to form (bzpipz)HgBr₃ which was assigned a tetrahedral structure based on the two observed Hg-Br stretching bands.

Most zwitterions of the type M(L)X₃ (M²⁺ = Mn-Zn; L⁺ = cationic ligand; X = halide) are slightly soluble in the aprotic dipolar solvents acetonitrile, nitromethane [44-47] and dimethylformamide [48], with solubilities increasing in the order Cl < Br < I. These solutions have appreciable conductivities with values often in the range expected for 1:1 electrolytes. The general reaction in these solutions is the substitution given in eqn. (2) (S = MeCN, MeNO₂)



For transition metal complexes the electronic spectra in solution are also indicative of this substitution.

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