N-Methylbipyridylium Complexes: Synthetic Evidence for a Monodentate Intermediate in the Formation of Chelated 2,2′-Bipyridyl Complexes

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Received March 20, 1981

The ligand 2,2′-bipyridyl (bpy) can be considered to be intermediate in flexibility between 1,2-diaminoethane and 1,10-phenanthroline. Although there are numerous examples of 1,2-diaminoethane behaving as either a monodentate [1] or as a chelating ligand, there are no examples [2, 3] of a complex containing a monodentate bpy group. However, species containing a monodentate bpy have been postulated [4] as intermediates in the aquation of $[Fe(bpy)_3]^{2+}$ and such a species is observed in the reaction of bpy with $[Al(Me_2SO)_6]^{3+}$ [5].

Bpy can be converted into a potential monodentate ligand by quaternising one of the nitrogen atoms. The resulting cation should still be capable of coordination since it has been shown that neither the presence of a positive charge on a ligand [6] nor a bulky substituent in the 2-position of a pyridine (*e.g.* 8-methylquinoline [7]) prevents coordination to the appropriate metal ion.

We report the preparation of stable N-methylbipyridylium complexes of some of the first-row transition metals. These are the first complexes to unequivocally demonstrate that bpy is sterically capable of behaving as a monodentate ligand.

N-methylbipyridylium iodide, [bpyMe]I, was prepared by heating under reflux equimolar quantities of bpy and iodomethane in 1-butanol for 3 h. The monomethyl salt was separated from the N,N′-dimethyl salt, $[bpyMe_2]I_2$, and unreacted bpy by extraction into and subsequent recrystallisation from hot ethanol. [bpyMe]X (X = Cl, NO_3, ClO_4) were prepared by the appropriate metatheses.†

The mixture of hot ethanolic solutions containing Li_2MCl_4 (M = Co, Cu) (1 mol) and [bpyMe]Cl (2–3 mol) gives, on cooling, crystalline precipitates with the composition $M(bpyMe)Cl_3$. These compounds (where M = Co, Cu, Zn) can be prepared directly by mixing hot ethanolic solutions containing equimolar quantities of [bpyMe]Cl and the hydrated metal(II) chloride. $Co(bpyMe)X_3$ (X = I, NO_3) were prepared similarly from CoX_2 and [bpyMe]X. There was no precipitate with $NiCl_2 \cdot 6H_2O$ and the solution had to be evaporated to dryness to obtain $Ni(bpyMe)Cl_3$.

The compounds are stable in dry air, but slowly absorb moisture when exposed to the atmosphere except $Ni(bpyMe)Cl_3$ which is deliquescent. They are insoluble in non-polar solvents, soluble to varying degrees in acetonitrile and nitromethane and decompose in dimethylsulphoxide and water.

The infrared spectrum of the $[bpyMe]^+$ ion can be regarded as a composite of the spectra of a 2-substituted-pyridine and -N-methylpyridinium ion, $[pyMe]^+$, respectively. On complex formation the part due to the $[pyMe]^+$ ion should remain fairly constant while the part due to the pyridine moiety should show characteristic changes. These are [8] (a) a shift in the ring-stretching mode at 1578 cm^{-1} to 1600 cm^{-1} and (b) shifts of the bands at 601 and 403 cm^{-1} to higher wavenumbers.

The ring-stretching modes ($\nu_{C=C}$, $\nu_{C=N}$) of bpy are at 1578 and 1557 cm^{-1}. On mono N-methylation these change to 1628, 1578 (broad) and 1568 cm^{-1} as expected for a molecule containing both a pyridine (1578 ± 5, 1565 ± 5 cm^{-1}) [9] and a $[pyMe]^+$ (1632, 1581 cm^{-1}) [10] ring. In the spectra of the $M(bpyMe)X_3$ compounds (Table I) these bands remain relatively unaltered while the new band at 1600 cm^{-1} is indicative of complex formation through the pyridyl nitrogen atom.

The band at 601 cm^{-1} for pyridine is replaced by a band at 647 cm^{-1} for the $[pyMe]^+$ ion. However, the two bands observed for the $[bpyMe]^+$ ion (648, 607 cm^{-1}) cannot be regarded unequivocally as the summation of these two bands since bpy also shows two bands (655, 618 cm^{-1}) in this region. The latter band is sensitive to complex formation and shifts to higher frequency in the $[bpyMe]^+$ complexes, as does the corresponding band in both pyridine [8] and bpy complexes [11].

The two bands for the $[bpyMe]^+$ ion at 448 and 407 cm^{-1} appear to be the composite of the single bands for pyridine and $[pyMe]^+$ at 406 and 446 cm^{-1} respectively since bpy only shows one band at 406 cm^{-1}. The band at 407 cm^{-1} shows the expected shift to higher frequency on coordination, while the band at 448 cm^{-1} is hardly affected (see Table I). The metal–chloride stretching modes are

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†X = Cl^-, ion-exchange chromatography with Amberlite IRA400 (chloride form); X = NO_3^-, treatment with $AgNO_3$ in water; X = ClO_4^-, treatment with $LiClO_4$.

0020-1693/82/0000-0000/$02.75

observed at approximately 300 cm^{-1}. Either two or three modes are expected depending on the approximation (C_{3v}, Cs, C_1) used for the symmetry of the complex. Two distinct bands are present together with a number of shoulders, except for the copper complex which shows only one broad band. There is also a medium-intensity band at 285 cm^{-1} in the spectra of the chloro complexes. The cobalt–oxygen stretching modes in $Co(bpyMe)(NO_3)_3$ are assigned to the broad bands in the region 300–280 cm^{-1}.

In the reaction of the $[MCl_4]^{2-}$ ions with bpy a reactive intermediate with a monodentate bpy group, *i.e.* $[M(bpy)Cl_3]^-$, is presumably formed prior to the ring-closure to give $M(bpy)Cl_2$. The structure of this intermediate should be similar to that of the $M(bpyMe)Cl_3$ complexes. The latter compounds, apart from being inorganic Zwitter-ions can be thought of as trapped intermediates in the familiar reaction of bpy with metal ions to give chelated complexes.

TABLE I. Properties of the MLX_3[a] Complexes.

Compound	Colour	Infrared Spectrum[b]									
		Selected $[bpyMe]^+$ bands (cm^{-1})								ν_{M-X} (cm^{-1})	
L[c]	white	1627s	–	1578m	1567m	648w	607w	448w	407wm	–	–
$CoLCl_3$	bright blue	1633s	1602s	1583m	1570m	652m	643m	443m	427s	332sh	320s
$NiLCl_3$	deep blue	1627s	1600s	1583s	1570m	650wm	643m	443m	425m	327s	308s
$CuLCl_3$	yellow	1627s	1600s	1583m	1571m	651wm	646s	442m	427w	–	305s,br
$ZnLCl_3$	white	1632s	1600s	1583m	1570m	651wm	640s	443m	423s	318s	303s
$CoLI_3$	green	1629s	1600s	1583s	1570m	652wm	643m	442m	423m	–	–
$CoL(NO_3)_3$[d]	purple	1630s	1602s	1587s	1572m	652w	643s	443m	426s	*ca.* 300s	

[a] L = N-methylbipyridylium cation, $[bpyMe]^+$. All the complexes give satisfactory elemental analyses. [b] s = strong, m = medium, w = weak, br = broad, sh = shoulder. [c] Iodide and perchlorate salts. [d] The complex shows the bands for coordinated nitrate: 1480s, *ca.* 1300s ($[bpyMe]^+$ bands interfere), 1024s, *ca.* 790 ($[bpyMe]^+$ bands interfere), 745 ms, 700 w(?) cm^{-1}.

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