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Tris(2,2′-bipyrimidine)M (M = Fe(II), Co(II), Ni(II)) Perchlorate Complexes. Spectroscopic Properties for Precursor Complexes in the Preparation of Polymetallic Systems

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Abstract

The synthesis, electronic spectrum, magnetic susceptibility and electrochemistry of the d^8 metal complex $[Ni(bpym)_3](ClO_4)_2$ (bpym = 2,2′-bipyrimidine) are reported here. Additionally, for the d^6, d^7, d^8 series of $M(bpym)_3{}^{2+}$ species, M = Fe(II), Co(II), Ni(II), electronic spectral assignments are made by comparison with the analogous $M(bpy)_3{}^{2+}$ (bpy = 2,2′-bipyridine) complexes. The relative position of the LUMOs and the relative amount of $d_M \rightarrow \pi_L{}^*$ backbonding in $M(bpy)_3{}^{2+}$ *vs.* $M(bpym)_3{}^{2+}$ is obtained from the frequency of the MLCT absorption for the series of $M(bpym)_3{}^{2+}$ complexes. Cyclic voltammetry of $Ni(bpym)_3{}^{2+}$ in acetonitrile shows the reduction potential ($E_{1/2}(3+/2+)$) is +0.4 V more positive than for $Ni(bpy)_3{}^{2+}$. A similar trend was also observed for the tris(2,2′-bipyrimidine)Fe(II) and -Co(II) complexes.

Introduction

Recent studies have demonstrated the utility of 2,2′-bipyrimidine (bpym), both as a stable bidentate ligand in monometallic complexes [1–11], as well as an effective bridge connecting metal centers in polymetallic systems (including mixed-metal complexes) [6, 8]. One of the areas of our recent interest has been the preparation of polymetallic systems in which a highly absorbing, non-reactive (antenna) fragment, such as $(NH_3)_4RuL^{2+}$ or $(CN)_{2n}FeL_{3-n}{}^{(2-2n)+}$ (L = bpym), may be bound to non-absorbing reactive fragments for the purpose of driving intramolecular energy transfer reactions. Previous studies indicate that the bidentate bpym ligand is more stable and allows more effective electronic communication between metal centers than do most monodentate bridges [12, 13]. We have now prepared a series of $M(bpym)_3{}^{2+}$ complexes (M = Fe(II), Co(II), Ni(II)) which, due to the open coordination site of the bpym ligand, could serve as precursor complexes in the synthesis of polymetallic complexes. Additionally, we are interested in the preparation and study of metal–metal interaction through delocalized bridging ligands.

We have previously reported the preparation of CN^- substituted derivatives of $Fe(bpym)_3{}^{2+}$ [10], and the interesting electrochemical properties of $Co(bpym)_3{}^{2+}$ [11]. We now wish to report the preparation, spectroscopy, magnetic susceptibility and electrochemistry of the d^8 metal complex $[Ni(bpym)_3](ClO_4)_2$. Additionally, for the d^6, d^7, and d^8 series of $M(bpym)_3{}^{2+}$ M = Fe(II), Co(II), Ni(II) complexes, we assign the ligand field (LF) and metal-to-ligand charge-transfer (MLCT) transitions by comparison with the analogous $M(bpy)_3{}^{2+}$ complexes. Electrochemical results for all $M(bpym)_3{}^{2+}$ complexes will be used to assess the amount of electron delocalization over the nitrogen heterocyclic ring system as compared to the analogous $M(bpy)_3{}^{2+}$ complexes.

Experimental

Materials

Analytical reagent grade compounds were used for all preparations described in this work. 2,2′-Bipyrimidine was obtained from Alfa Inorganics (U.S.A.) or Lancaster Syntheses (England). The acetonitrile used as solvent and the ammonium hexafluorophosphate used as a supporting electrolyte in the electrochemical experiments were obtained from Aldrich Chemical (U.S.A.). Elemental analyses were performed by Atlantic Microlab, Atlanta, Georgia (U.S.A.).

Synthesis

$[Ni(bpym)_3](ClO_4)_2$

Tris(2,2′-bipyrimidine)nickel(II) perchlorate was generated by modification of the method of Morgan and Burstall for the preparation of tris(2,2′-bipyridine)nickel perchlorate [14]. A solid sample

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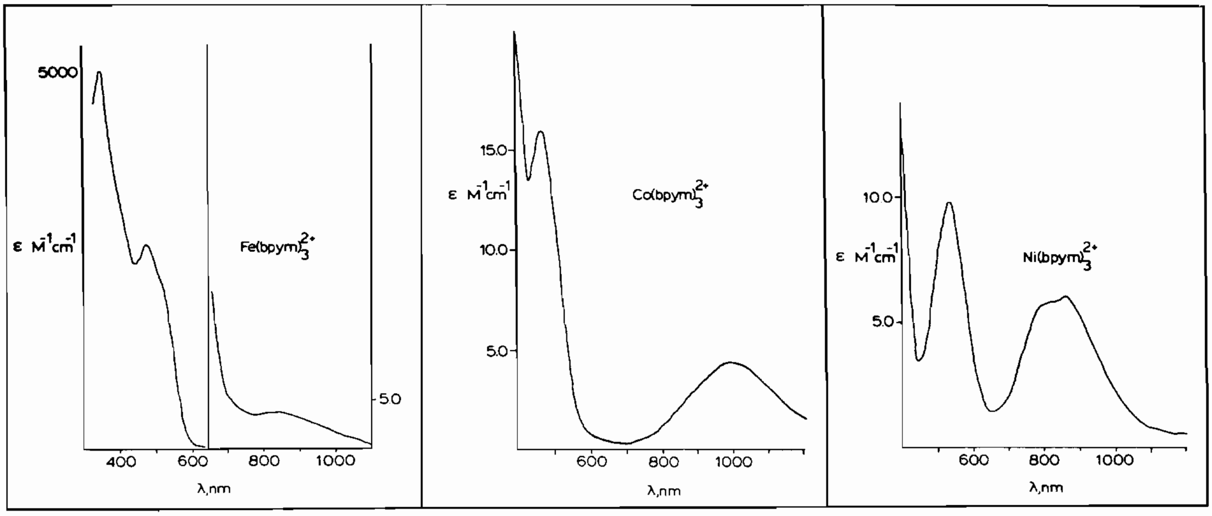

Fig. 1. Aqueous visible absorption spectra of $M(bpym)_3^{2+}$ (M = Fe(II), Co(II), Ni(II)).

of 0.10 g (0.42 mmol) $NiCl_2 \cdot 6H_2O$ was added to 20 ml of warm (35–40 °C) deoxygenated H_2O containing 0.25 g (1.58 mmol) 2,2′-bipyrimidine. The pink solution which formed on stirring was allowed to react for 45 minutes at 35–40 °C. Aqueous $NaClO_4$ was then added to the warm pink solution to precipitate the $[Ni(bpym)_3](ClO_4)_2$ complex. The precipitate was collected by vacuum filtration, washed with methanol to remove excess 2,2′-bipyrimidine and $NaClO_4$, dried with diethyl ether, and dried under vacuum. Yield 0.234 g (76%). *Anal.* Calcd for $NiC_{24}H_{22}N_{12}Cl_2O_{10}$: C, 37.50; H, 2.87; N, 21.88%. Found: C, 37.58; H, 2.91; N, 21.82%. The room temperature magnetic susceptibility was measured as μ = 3.03 B.M. and is typical for the paramagnetic d^8 species (Table II).

$[Fe(bpym)_3](ClO_4)_2$ and $[Co(bpym)_3](ClO_4)_2$

These were prepared as previously reported in the literature [8–10]. Magnetic susceptibilities were measured as μ = 0.6 B.M. and μ = 4.8 B.M., respectively. These values are typical for the low spin Fe(II) d^6 and high spin Co(II) d^7 complexes (Table II).

Instrumentation

Visible absorption spectra were recorded on a Bausch & Lomb Spectronic 2000 spectrophotometer. Near-infrared and ultraviolet spectra were recorded with matching quartz cells on a Cary Model 14 spectrophotometer.

Cyclic voltammograms were recorded on an IBM Instruments Inc. Model EC/225 Voltammetric Analyzer. The glassy carbon working electrode (5.0 mm diameter) was polished with alumina prior to each scan. Non-aqueous voltammograms were recorded in acetonitrile with 0.1 M NH_4PF_6 as a supporting electrolyte. Either a SCE or $Ag/AgNO_3$ (0.1 M Ag^+ in acetonitrile) reference electrode was used. All potentials are reported *vs.* SCE, and remain uncorrected for junction potential. All scans were recorded in deoxygenated solution with N_2 blowing over the top of the solution during the scan. Scan rates varied from 25–200 mV/s.

Magnetic susceptibility measurements were made on solid samples using the Faraday method. A Cahn Model RG Automatic Electrobalance and Alpha Scientific 7500M electromagnet were used. $HgCo(SCN)_4$ was used as a calibrant [15]. Diamagnetic corrections were made using Pascal constants [16]. Room temperature was controlled at 21.5 ± 0.2 °C.

Results and Discussion

The aqueous electronic absorption spectrum of $Ni(bpym)_3^{2+}$ (Fig. 1a) shows ligand field bands quite similar in energy and intensity to $Ni(bpy)_3^{2+}$ (Table I). The $^3T_1(F) \leftarrow {}^3A_2$ transition for $Ni(bpy)_3^{2+}$ at 521 nm is shifted to slightly lower energy for $Ni(bpym)_3^{2+}$ at 539 nm. Lever [27, 28] has shown that Ni(II) complexes generally undergo little metal-to-ligand π-backbonding. Thus, a decrease in the energy of the lowest LF transition in $Ni(bpym)_3^{2+}$ is due primarily to weaker bpym σ-donor interaction with Ni(II) rather than π-acceptor changes. This result leads us to place bpym lower than bpy in the spectrochemical series for Ni(II).

There has been previous discussion of the assignments of the two lowest absorption bands of $Ni(bpy)_3^{2+}$. As pointed out by Jørgenson [17], this area of the spectrum corresponds to the energy crossover point of the $^3T_2$ and ^1E energy level. Initially, the shoulder at 860 nm for $Ni(bpy)_3^{2+}$ was assigned

TABLE I. Spectra of Some Tris Chelated Ni(II), Co(II) and Fe(II) Complexes in Aqueous Solution.

Complex	λ, nm	ε, M^{-1} cm^{-1}	Assignment	Ref.
$Ni(bpy)_3^{2+}$	862	5.7	$^3T_2 \leftarrow {}^3A_2$	[20, 21]
	787	7.1	$^1E \leftarrow {}^3A_2$	
	521	11.6	$^3T_1 \leftarrow {}^3A_2$	
	385	2.0×10^3	MLCT	[19, 28]
	318	4.0×10^4	$\pi-\pi^*$	[19]
	296	4.2×10^4	$\pi-\pi^*$	
	245	3.2×10^4	$\pi-\pi^*$	
$Ni(bpym)_3^{2+}$	870	6.0	$^3T_2 \leftarrow {}^3A_2$	
	790	5.8	$^1E \leftarrow {}^3A_2$	
	537	9.8	$^3T_1 \leftarrow {}^3A_2$	
	(370)	–	MLCT	
	243	3.2×10^4	$\pi-\pi^*$	
$Co(bpy)_3^{2+}$	910	8.0	$^4T_2(F) \leftarrow {}^4T_1(F)$	[18]
	(450)	(50)	$^4T_1(P) \leftarrow {}^4T_1(F)$	
	305	3.4×10^4	$\pi-\pi^*$	[24]
	294	3.7×10^4	$\pi-\pi^*$	
	243	3.0×10^4	$\pi-\pi^*$	
$Co(bpym)_3^{2+}$	990	5.2	$^4T_2(F) \leftarrow {}^4T_1(F)$	
	472	18.7	$^4T_1(P) \leftarrow {}^4T_1(F)$	
	242	4.7×10^4	$\pi-\pi^*$	
$Fe(bpy)_3^{2+}$	870	3.6	$^3T_1 \leftarrow {}^1A_1$	[18]
	523	8.6×10^3	MLCT	
	(495)	7.8×10^3	MLCT	
	(415)	2.4×10^3	MLCT	
	(387)	3.7×10^3	MLCT	
	351	6.5×10^3	MLCT	
	298	7.0×10^4	$\pi-\pi^*$	
$Fe(bpym)_3^{2+}$	890	3.8	$^3T_1 \leftarrow {}^1A_1$	
	(530)	2.7×10^3	MLCT	
	481	3.0×10^3	MLCT	
	363	5×10^3	MLCT	
	243	4.9×10^4	MLCT	

Shoulders in parentheses, a) this work.

to the $^1E \leftarrow {}^3A_2$ transition while the 790 nm transition was assigned as $^3T_2 \rightarrow {}^3A_2$ [18, 19]. Subsequent studies on a series of α-diimmine complexes with N-alkyl substituents showed the high energy absorption at 790 nm to remain unshifted and the lower energy absorption remain unshifted and the lower energy absorption varied with ligand substitution [20]. These results support the assignment of the $^1E \leftarrow {}^3A_2$ transition, which would be unaffected by *Dq*, at higher energy, while the lower energy absorption ($\tilde{\nu}$ = 10 *Dq*) is due to $^3T_2 \rightarrow {}^3A_2$. Later studies have assigned the $^3T_2 \leftarrow {}^3A_2$ transition at lower energy for bpy [21] and other pyridyl groups [22] as well.

The direct assignment of the corresponding low energy absorptions of $Ni(bpym)_3^{2+}$ at 790 nm and 870 nm can be made by analogy. As demonstrated, the shift to lower energy of the $Ni(bpym)_3^{2+}$ $^3T_1(F) \leftarrow {}^3A_2$ transition places the $10Dq/B$ position to the lower side of $Ni(bpy)_3^{2+}$ in a Tanabe-Sugano diagram for d^8 complexes. Consideration of the direction of this shift can only further lower the energy of the $^3T_2$ state of $Ni(bpym)_3^{2+}$ with respect to the ^1E state. We therefore assign the absorption at 870 nm as being $^3T_2 \leftarrow {}^3A_2$ and the shoulder at 790 nm as $^1E \leftarrow {}^3A_2$.

A shift to lower energy for the ligand field bands of $M(bpym)_3^{2+}$ *vs.* $M(bpy)_3^{2+}$ for M = Co(II) and Fe(II) is also observed (Table I and Fig. 1b, 1c). The aqueous spectrum of $Co(bpy)_3^{2+}$ has been assigned [23], and the observed transitions correlate with energy levels predicted from theory [19]. By analogy, we assign the lowest energy absorption at

990 nm as ${}^4T_2(F) \leftarrow {}^4T_1(F)$ and the 472 nm absorption as ${}^4T_1(P) \rightarrow {}^4T_1(F)$. The ${}^4T_1(P) \leftarrow {}^4T_1(F)$ transition appears as a distinct peak for $Co(bpym)_3{}^{2+}$, rather than a shoulder as is the case for $Co(bpy)_3{}^{2+}$. This appears to be a result of the ${}^4T_1(P)$ state lying at lower energy for $Co(bpym)_3{}^{2+}$, as well as the π—π^* intraligand absorption for bpym being at higher energy than for bpy.

Large MLCT bands obscure most of the ligand field absorptions for the low spin d^6 $Fe(bpy)_3{}^{2+}$ [18, 21] and $Fe(bpym)_3{}^{2+}$ complexes. Only the lowest energy ${}^3T_1 \leftarrow {}^1A_1$ transition at 870 nm for $Fe(bpy)_3{}^{2+}$ has been observed [18]. We assign the transition observed at 890 nm for $Fe(bpym)_3{}^{2+}$ as ${}^3T_1 \leftarrow {}^1A_1$.

The metal—ligand charge transfer (MLCT) absorption band for $Ni(bpym)_3{}^{2+}$ appears as a shoulder at about 370 nm on the side of a more intense intraligand (π—π^*) transition. This is comparable to MLCT absorptions for $Ni(bpy)_3{}^{2+}$ or $Ni(phen)_3{}^{2+}$ at 385 nm and $Ni(bpz)_3{}^{2+}$ (where bpz = 2,2′-bipyrazine) at 362 nm [25, 26, 28]. Such a small change in MLCT energy is typical of Ni(II) complexes, which Lever has pointed out undergo little π-backbonding [27, 28]. A more distinct comparison of π^* levels of bpy *vs.* bpym occurs for the Fe(II) complexes. The lower energy of the $Fe(bpym)_3{}^{2+}$ *vs.* $Fe(bpy)_3{}^{2+}$ MLCT band suggests that the $d\pi$—$p\pi^*$ transition for bpym is lower in energy than for bpy. Qualitatively, this fits into the previously-established pattern of lowering the MLCT transition energy as electron withdrawing groups (*i.e.*, N is substituted for C—H) are incorporated into the aromatic heterocyclic ring [1, 29–31]. These results are not surprising since molecular orbital calculations indicate the bpym π^* LUMO lies lower in energy than the corresponding bpy LUMO in the free ligands [32].

When obtaining extinction coefficient values for the $Fe(bpym)_3{}^{2+}$ MLCT absorptions in deoxygenated aqueous solutions, it was noted that at concentrations $<1 \times 10^{-3}$ M, an equilibrium for the dissociation of the $Fe(bpym)_3{}^{2+}$ complex occurs [10]. Assuming the overall equilibrium to be

$$Fe^{2+} + 3bpym \rightleftharpoons Fe(bpym)_3{}^{2+}$$

the formation constant K was calculated as 1×10^7 in aqueous solution. Subsequent synthetic steps using $Fe(bpym)_3{}^{2+}$ will require relatively high concentrations of the complex and/or free ligand or the use of non-aqueous solvents. Similar dissociation was not observed for the Co(II) or Ni(II) analogs.

The cyclic voltammetry of the $Ni(bpym)_3{}^{2+}$ was recorded in acetonitrile, despite low solubility, because of the large positive value of the $Ni(bpym)_3{}^{3+/2+}$ reduction potential. Ammonium hexafluorophosphate was used as a supporting electrolyte due to the decreased solubility of perchlorate salts of all $M(bpym)_3{}^{2+}$ complexes in acetonitrile. The results for $Ni(bpym)^{3+/2+}$ show a single irreversible wave with a peak to peak separation of 140–170 mV at 25 mV/s when scanned from +1.0 V to +2.40 V *vs.* SCE (Table II, Fig. 2a). The equality of the anodic and cathodic peak currents as a measure of reversibility is difficult to determine, as it is obscured by the onset of solvent oxidation. Plots of $\nu^{1/2}$ (where ν = scan rate in V/s) *vs.* the cathodic wave peak height are non-linear and indicate irreversibility [39].

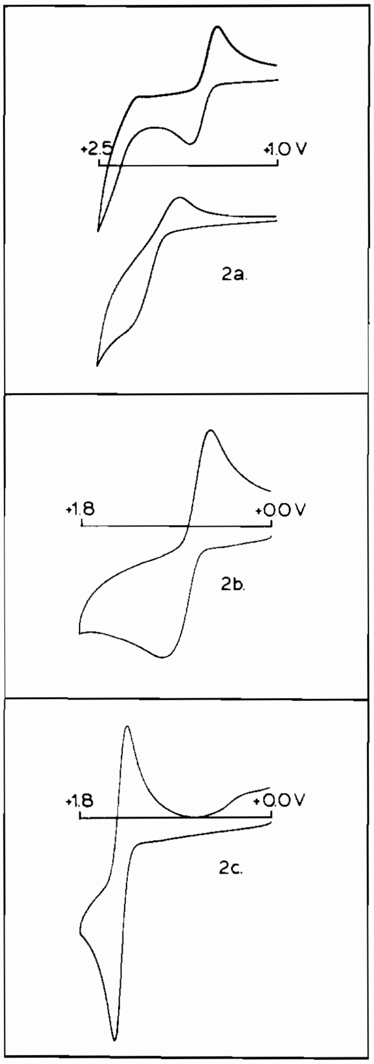

Fig. 2. Cyclic voltammograms of 2a) $Ni(bpy)_3{}^{2+/3+}$ top; $Ni(bpym)_3{}^{2+/3+}$ bottom; 2b) $Co(bpym)_3{}^{2+/3+}$; 2c) $Fe(bpym)_3{}^{2+/3+}$ in acetonitrile 0.1 M NH_4PF_6 *vs.* SCE.

The $Ni(bpym)_3{}^{3+/2+}$ reduction potential is 0.4 V more positive than the $Ni(bpy)_3{}^{3+/2+}$ complex which has an $E_{1/2}$ of +1.70 V [37, 38], which indicates that the removal of an electron from the metal complex becomes more difficult when electron-withdrawing groups are inserted in the ligands. An increased

TABLE II. Potentials for the 3+/2+ Reduction, and Magnetic Moments for the Perchlorate Salts of Tris bpy and bpym Complexes of Fe(II), Co(II) and Ni(II).

Complex	$E_{1/2}$, V[a]	μ, B.M.
$Fe(bpy)_3{}^{2+}$	+1.04 +1.03[b,c]	0.62 0.6–0.7[b,d]
$Fe(bpym)_3{}^{2+}$	+1.41	0.62
$Co(bpy)_3{}^{2+}$	+0.26 +0.25[b]	4.5 4.3–4.8[e]
$Co(bpym)_3{}^{2+}$	+0.80	4.6
$Ni(bpy)_3{}^{2+}$	+1.69 +1.71[b]	3.1 3.03[b,d]
$Ni(bpym)_3{}^{2+}$	+2.10	3.04

[a] Vs. SCE. [b] Reference 37. [c] Reference 38. [d] Reference 36. [e] References 33–35.

amount of delocalization of electron density over ligands orbitals was also previously observed as an increased reduction potential for $Ni(bpz)_3{}^{3+/2+}$ *vs.* the bpy complex [28]. The trend toward more positive reduction potentials is also observed for $Fe(bpym)_3{}^{3+/2+}$ *vs.* $Fe(bpy)_3{}^{3+/2+}$ ($\Delta E_{1/2}$ = 0.37 V), and $Co(bpym)_3{}^{3+/2+}$ *vs.* $Co(bpy)_3{}^{3+/2+}$ ($\Delta E_{1/2}$ = 0.54 V) (Table II, Fig. 2b, 2c), as well as other metal systems [1]. The asymmetrical shape of the oxidation wave for $Co(bpym)_3{}^{3+/2+}$ couple suggests some chemical reaction following oxidation. The product has not been conclusively identified, however solvent substitution seems most probable. The $Fe(bpym)_3{}^{3+/2+}$ couple appears to be totally reversible. The cyclic voltammograms for $M(bpym)_3{}^{2+}$ M = Fe(II) and Co(II) complexes also have scan rate dependent peak-to-peak separation values $\geqslant$0.059 V.

The observed order of increasingly more positive reduction potential of $Ni(bpym)_3{}^{3+/2+}$ > $Fe(bpym)_3{}^{3+/2+}$ > $Co(bpym)_3{}^{3+/2+}$ may best be interpreted by consideration of the ground state electron configuration, and simple molecular orbital considerations. Assuming constant bpy or bpym π^* and σ^* orbital energy for interaction with the metal dπ orbitals, the metal dπ $\rightarrow$ pπ^* interaction should stabilize the dπ and destabilize the pπ^* molecular orbitals most for $Fe(bpym)_3{}^{2+}$ and least for $Ni(bpym)_3{}^{2+}$ (Fig. 3) [27, 28].

Electrochemical oxidation of the low spin d^6 $Fe(bpym)_3{}^{2+}$ complex removes electron density from the predominately metal d bonding molecular orbital. Oxidation of the $Co(bpym)_3{}^{2+}$ (high spin d^7) complex requires removal of electron density from a highest occupied molecular orbital(HOMO), which is predominately metal dσ^* in character, and lies at a higher energy than the $Fe(bpym)_3{}^{2+}$ HOMO. Although oxidation of d^8 $Ni(bpym)_3{}^{2+}$ also removes electron density from a HOMO that is predominately dσ^* bonding in character, metal d orbital contraction across the periodic table lowers the $Ni(bpym)_3{}^{2+}$ dσ^* HOMO below the $Fe(bpym)_3{}^{2+}$ dπ HOMO energy level.

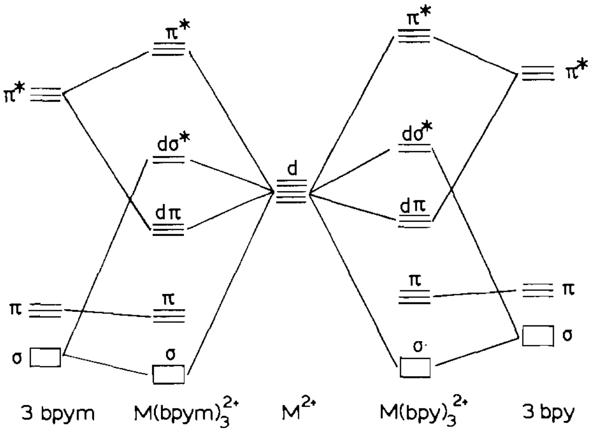

Fig. 3. General molecular orbital diagram for bpym–metal and bpy–metal interaction.

Summary

Owing to the potential coordination site of the bpym ligand on $M(bpym)_3{}^{2+}$ complexes, these complexes could serve as precursor complexes for polymeric molecules. The comparatively positive reduction potentials of the M(II) complexes could additionally impart thermal stability to polymetallic systems.

The paramagnetic Co(II) and Ni(II) complexes with 2,2'-bipyrimidine as bridging ligands to other paramagnetic systems also afford opportunities to study M–M interactions through the highly delocalized bpym bridging ligand. We have recently undertaken work in this area.

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