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A pyrazole-containing verdazyl radical ligand Meprv: structure of its precursor prvH₃ and its bis(2,2'-bipyridine)ruthenium(II) complex

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Abstract

Reaction between 1,1'-dimethyl carbonic dihydrazide and pyrazole-3-carboxaldehyde gave 1,5-dimethyl-3-(3'-pyrazolyl)-6-oxotetrazane (prvH₃), which crystallizes in the orthorhombic space group *Pca*₂₁, with *a* = 10.7745(4), *b* = 8.1745(2) and *c* = 10.6625(3) Å. Dehydrogenation of prvH₃ in methanol by 1,4-benzoquinone afforded the methylated radical 1,5-dimethyl-3-(1'-methyl-3'-pyrazolyl)-6-oxoverdazyl (Meprv), which reacted with *cis*-[Ru(bpy)₂Cl₂] and NaBPh₄ to yield the cation [Ru(bpy)₂(Meprv)]²⁺ as its BPh₄ salt. The absence of luminescence and the electrochemical behavior of this complex imply that the lowest ³MLCT (metal to ligand charge transfer) excited state is located on the electron-deficient Meprv ligand.

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Keywords: Verdazyl; Radical; Pyrazole; 2,2'-Bipyridine; Ruthenium(II); Crystal structures

1. Introduction

Transition metal complexes of radical ligands have received a great deal of attention, due to their interesting electronic structures, biological relevance and magnetic properties [1–5]. Of the numerous radical compounds, the family of verdazyls is unique for the neutrality and high stability of its members [6,7]. However, the first metal–verdazyl complex was not reported until 1997 [8]. Since then, several chelating verdazyl ligands, such as 1,5-dimethyl-3-(2'-pyridyl)-6-oxoverdazyl (pyv) [9], and their coordination compounds with Mn(II), Ni(II), Zn(II), Cd(II), Hg(II) and Cu(I) [10–16] have been described. The binding mode of the pyridyl-verdazyl ligands resembles to some extent that of the widely used didentate ligand 2,2'-bipyridine (bpy). The coordination chemistry of these chelating verdazyls deserves a more

thorough investigation. Herein, we report the syntheses of the new verdazyl-containing ligand, 1,5-dimethyl-3-(1'-methyl-3'-pyrazolyl)-6-oxoverdazyl (Meprv; Scheme 1) and its coordination compound with Ru(bpy)₂²⁺. The X-ray structure of the precursor molecule 1,5-dimethyl-3-(3'-pyrazolyl)-6-oxotetrazane (prvH₃) has also been determined.

2. Experimental

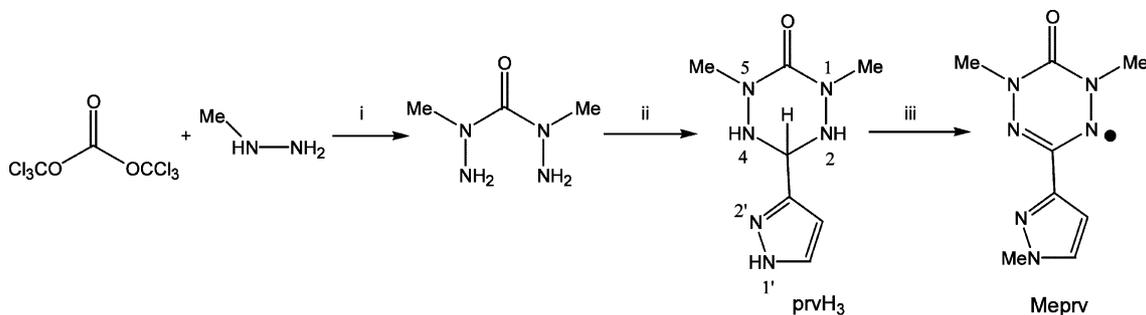
2.1. General methods

All reagents were purchased from commercial sources and used as received. All solvents were purified by regular methods. The syntheses were performed under an inert atmosphere of argon using standard Schlenk equipment. 1,1'-Dimethyl carbonic dihydrazide was prepared from triphosgene and methylhydrazine according to the literature method, with the exception that dichloromethane was used to replace toxic benzene as the solvent [9]. *cis*-[Ru(bpy)₂Cl₂]·2H₂O was prepared according to the literature [17]. UV–Vis spectra were

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Scheme 1. Synthetic route to Meprv: (i) MeCN/dry ice, CH_2Cl_2 ; (ii) pyrazole-3-carboxaldehyde, MeOH, reflux; (iii) 1,4-benzoquinone, MeOH, reflux.

obtained on a Perkin–Elmer Lambda 900 spectrophotometer. X-band EPR spectra were recorded on a JEOL RE2 \times electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the diffuse reflectance technique ($4000\text{--}300\text{ cm}^{-1}$, resp. 4 cm^{-1}). C, H and N determinations were performed on a Perkin–Elmer 2400 Series II analyzer. Cyclic voltammetry measurements were performed with an Autolab PGSTAT10 cyclic voltammeter, using a Pt working electrode, a Pt counter electrode and an Ag/AgCl reference electrode in acetonitrile (10^{-3} M), with tetrabutylammonium hexafluorophosphate as the supporting electrolyte, at a scan rate of 0.2 V s^{-1} . NMR spectra were recorded on a JEOL JNM FX-200 (200 MHz) instrument. Mass spectrometry experiments were performed on a Finnigan MAT TSQ-700 equipped with a custom-made electrospray interface (ESI). Luminescence was monitored on a Perkin–Elmer LS50B luminescence spectrometer.

2.2. Synthesis

2.2.1. 1,5-Dimethyl-3-(3'-pyrazolyl)-6-oxotetrazone

To a solution of 1,1'-dimethyl carbonic dihydrazide (1.5 g, 12.7 mmol) in 80 ml of methanol was added dropwise 80 ml of a hot ($50\text{ }^\circ\text{C}$) methanolic solution of pyrazole-3-carboxaldehyde (1.22 g, 12.7 mmol). The mixture was then refluxed for 24 h. The solvent was removed under reduced pressure. Diethyl ether was used to transfer and wash the white product, yield 1.13 g (5.86 mmol, 45%). Recrystallization from a mixture of methanol and ethyl acetate yielded colorless crystals suitable for X-ray analysis. Anal. Calc. for $\text{C}_7\text{H}_{12}\text{N}_6\text{O}$: C, 42.85; H, 6.16; N, 42.83. Found: C, 42.67; H, 5.86; N, 42.64%. ^1H NMR (^6d -DMSO): δ (ppm): 7.60 (d, 5'-H, 1H, $J = 2.0$ Hz), 6.26 (d, 4'-H, 1H, $J = 2.0$ Hz), 5.55 (br, 2,4-H, 2H), 4.87 (s, 3-H, 1H), 2.92 (s, CH_3 , 6H). IR: ν (cm^{-1}) 3238, 3189, 1582, 1531, 1389, 1198, 1126, 1053, 980, 949, 856, 774, 726, 684, 619, 536, 381.

2.2.2. 1,5-Dimethyl-3-(1'-methyl-3'-pyrazolyl)-6-oxoverdazyl

To a solution of prvH₃ (0.102 g, 0.52 mmol) in 2 ml of methanol and 12 ml of toluene was added 0.090 g (0.83 mmol) of 1,4-benzoquinone. Immediately, the solution turned to yellow and then dark brown in color. After 6 h, the resulting dark brown precipitate was collected. To the filtrate was added diethyl ether, and more precipitate was obtained. The combined hygroscopic product weighed 0.070 g. MS (ESI, MeOH): m/z 207.5 (Meprv⁺ 207.2, 100%). Anal. Calc. for $\text{C}_8\text{H}_{11}\text{N}_6\text{O} \cdot 0.4\text{C}_6\text{H}_6\text{O}_2(\text{dihydroquinone}) \cdot 2.5\text{H}_2\text{O}$: C, 42.16; H, 6.26; N, 28.36. Found: C, 41.60; H, 5.76; N, 27.92%. IR: ν (cm^{-1}) 3138, 3042, 1772, 1622, 1512, 1446, 1405, 1210, 843, 608, 522.

2.2.3. $[\text{Ru}(\text{bpy})_2(\text{Meprv})](\text{BPh}_4)_2$

A mixture of *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (66.6 mg, 0.128 mmol) and 1 equiv. Meprv (38.8 mg) in 30 ml of ethanol and 10 ml of water was refluxed for 6 h, then concentrated to nearly dryness using a rotary evaporator. The residue was dissolved in a small amount of water and filtered. The filtrate was loaded onto a Sephadex C-25 (Na^+ type) column and eluted with gradient solutions of sodium chloride. The fraction obtained with 0.2 M sodium chloride contained the desired complex. The solvent was reduced using a rotating evaporator. After filtration, a saturated solution of sodium tetraphenylborate was added to the filtrate. The brown precipitate, which formed immediately, was collected and washed thoroughly with water followed by diethyl ether, yield 75.2 mg (46%). Anal. Calc. for $\text{C}_{76}\text{H}_{67}\text{B}_2\text{N}_{10}\text{ORu} \cdot \text{H}_2\text{O}$: C, 71.48; H, 5.45; N, 10.97. Found: C, 71.07; H, 5.27; N, 10.92%. IR: ν (cm^{-1}) 3221, 3054, 1700, 1684, 1654, 1578, 1560, 1464, 1444, 1424, 1267, 1154, 1031, 846, 762, 730, 703, 611, 489, 463, 328, 302.

2.3. Structure determination of prvH₃

Intensity data for a single crystal were collected using graphite-monochromated Mo K α radiation, on a Nonius KappaCCD diffractometer with a rotating anode.

An absorption correction was considered unnecessary. The structure was solved by direct methods using SHELXS97, and was refined on F^2 by least-squares procedures using SHELXL97 [18]. Although the prvH_3 molecule crystallizes in a chiral space group ($Pca2_1$), since no heavy elements are present, anomalous dispersion effects were not large enough to allow the absolute structure to be established; therefore, Friedel-pair reflections were merged. All non-hydrogen atoms were refined freely, with anisotropic displacement parameters. All hydrogen atoms were positively identified in a difference map. The positions of hydrogen atoms bound to nitrogen were refined with a restraint on the N–H distances. Hydrogen atoms bound to carbon were constrained to idealized geometries and allowed to ride on their carrier atoms. All hydrogen atoms were refined with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure validation and molecular graphics preparation were performed with PLATON package [19]. The crystallographic data are summarized in Table 1.

3. Results and discussion

The chair-like molecular structure of prvH_3 is shown in Fig. 1. Selected bond lengths and angles are presented in Table 2. The pyrazole ring is strictly planar; the deviations of the relevant atoms from the average plane range from $-0.003(3)$ to $0.003(3)$ Å. The tetrazane ring, on the other hand, is puckered, with maximum deviations from the least-squares plane of $-0.311(2)$ and $0.280(2)$ Å; the geometries of N2, C3 and N4 are sp^3 -hybridized, while N1, N5 and C6 seem to adopt sp^2 -hybridized geometries. The pyrazole and tetrazane rings are nearly perpendicular; the dihedral angle between their average planes being $87.62(12)^\circ$. The prvH_3

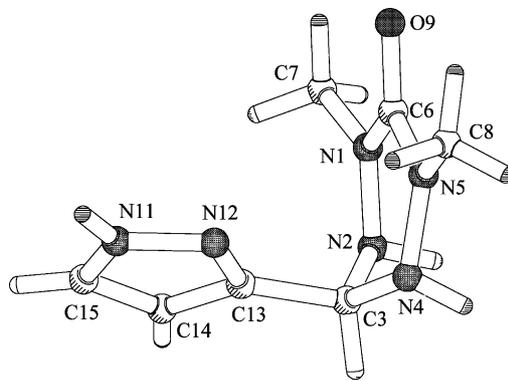


Fig. 1. Molecular structure of prvH_3 .

molecules are linked into two-dimensional nets parallel to the ac plane by intermolecular hydrogen bonding involving the three N–H donors: $\text{N}2 \cdots \text{N}12$ ($3/2-x, y, -1/2+z$), $3.069(3)$ Å; $\text{N}4 \cdots \text{O}9$ ($1/2+x, 1-y, z$), $3.040(3)$ Å; $\text{N}11 \cdots \text{O}9$ ($1-x, 1-y, 1/2+z$), $2.796(3)$ Å.

Dehydrogenation of prvH_3 by 1,4-benzoquinone led to the abstraction of three hydrogens per molecule and, thus, to the formation of a radical. The mass spectrum clearly indicates that a methyl group was introduced into the molecule, which must have come from the methanol solvent and it must be connected to the pyrazole N1' atom. We were unable to completely remove the dihydrobenzoquinone byproduct to isolate the product Meprv in its pure form. Similar problems were reported for syntheses of the related pyv radical: in one case, pyv was obtained as a 1:1 complex with dihydroquinone [9]; in another case, involving the use of potassium ferricyanide as the oxidant, ferrocyanide was found present in the product [11].

Table 1
Crystallographic data for prvH_3

Empirical formula	$\text{C}_7\text{H}_{12}\text{N}_6\text{O}$
Formula weight	196.23
Crystal system	orthorhombic
Space group	$Pca2_1$ (No. 29)
V (Å ³)	939.11(5)
Z	4
D_{calc} (g cm^{-3})	1.388
Unit cell dimensions	
a (Å)	10.7745(4)
b (Å)	8.1745(2)
c (Å)	10.6625(3)
T (K)	150
μ (mm^{-1})	0.101
λ (Å)	0.71073
R, wR_2, S ($w = [\sigma^2(F_o^2) + (0.0396P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$)	0.0341, 0.0741, 1.08

Table 2
Bond lengths (Å) and angles ($^\circ$) for prvH_3

Bond lengths			
N(1)–N(2)	1.419(3)	N(2)–C(3)	1.469(3)
N(4)–C(3)	1.456(3)	N(4)–N(5)	1.437(3)
N(5)–C(6)	1.359(3)	N(1)–C(6)	1.352(3)
N(1)–C(7)	1.452(3)	C(3)–C(13)	1.515(3)
N(5)–C(8)	1.447(3)	O(9)–C(6)	1.255(3)
N(11)–N(12)	1.361(3)	N(12)–C(13)	1.331(3)
C(13)–C(14)	1.396(4)	C(14)–C(15)	1.369(3)
N(11)–C(15)	1.332(3)		
Bond angles			
N(2)–N(1)–C(6)	121.51(19)	N(1)–N(2)–C(3)	108.63(17)
N(2)–C(3)–N(4)	113.0(2)	N(5)–N(4)–C(3)	111.02(19)
N(4)–N(5)–C(6)	123.32(19)	N(1)–C(6)–N(5)	117.8(2)
N(2)–N(1)–C(7)	114.77(18)	C(6)–N(1)–C(7)	123.2(2)
N(2)–C(3)–C(13)	109.0(2)	N(4)–C(3)–C(13)	111.70(19)
N(4)–N(5)–C(8)	112.5(2)	C(6)–N(5)–C(8)	121.32(19)
O(9)–C(6)–N(1)	121.7(2)	O(9)–C(6)–N(5)	120.5(2)
N(12)–N(11)–C(15)	112.2(2)	N(11)–N(12)–C(13)	104.2(2)
N(12)–C(13)–C(14)	111.5(2)	C(13)–C(14)–C(15)	104.8(2)
N(11)–C(15)–C(14)	107.3(2)	N(12)–C(13)–C(3)	120.7(2)
C(3)–C(13)–C(14)	127.8(2)		

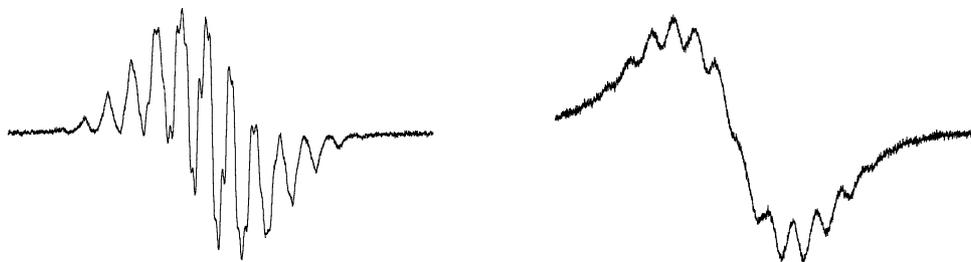


Fig. 2. EPR spectra of (a) Meprv in methanol/toluene (1/2), (b) $[\text{Ru}(\text{bpy})_2(\text{Meprv})](\text{BPh}_4)_2$ in acetonitrile/toluene (1/1) at room temperature. The total spectral width is 100 G.

The Meprv radical is very stable. No change was observed after storage for months at room temperature as judged by EPR. Its EPR spectrum in solution is shown in Fig. 2(a). The g value of the radical is located at 2.0036. The observed hyperfine structure arises from the coupling of the unpaired electron to the four verdazyl ring nitrogens and the six methyl protons, as has been reported for other similar verdazyl radicals [7,9,11]. Simulation of EPR spectrum afforded the hyperfine coupling constants $a(\text{N}2, 4) = 9.4$ G, $a(\text{N}1, 5) = 7.3$ G and $a(\text{H}) = 6.2$ G.

It was our intention to synthesize the mixed-ligand manganese(II) complex $[\text{Mn}(\text{bpy})_2(\text{Meprv})]^{2+}$, but regardless of whether the reaction mixture of $[\text{Mn}(\text{bpy})_2\text{Cl}_2]$ and Meprv was heated or not, the product isolated always appeared to be $[\text{Mn}(\text{bpy})_3](\text{BPh}_4)_2$ (NaBPh₄ was used to crystallize the product), as was revealed by X-ray diffraction and IR spectroscopy [20]. This observation implies that the ligand exchange rate for Mn(II) is quite high and that the coordinating ability of Meprv is much lower than that of bpy. Since ligand exchange rates for Ru(II) are generally much lower, $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ was subsequently utilized as the reactant, and the desired product $[\text{Ru}(\text{bpy})_2\text{Meprv}]^{2+}$ was indeed obtained as its BPh₄ salt.

The complex $[\text{Ru}(\text{bpy})_2\text{Meprv}]^{2+}$ appears to retain the radical EPR signal, as can be seen in Fig. 2(b). Unfortunately, due to the solubility limitations, clearer hyperfine structures could not be resolved.

$[\text{Ru}(\text{bpy})_2\text{Meprv}]^{2+}$ displays a strong (molar extinction: $2.5 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$) ¹MLCT (metal to ligand charge transfer) electronic absorption band in solution at approximately 441 nm, as is characteristic for $[\text{Ru}(\text{bpy})_2(\text{NN})]^{2+}$ -type complexes [22]. Excitation at this wavelength, however, does not result in the luminescence response observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ and the majority of $[\text{Ru}(\text{bpy})_2(\text{NN})]^{2+}$ -type complexes [21,22]. This observation implies that the lowest ³MLCT excited state is not located on bpy, but on the Meprv ligand. Since Meprv is a tetraaza-based radical, its electron deficiency makes it an electron withdrawing ligand, which inhibits the luminescent transition from ³MLCT to the metal-centered ground state [21,22].

The excited state distribution is further confirmed by cyclic voltammetry measurements for $[\text{Ru}(\text{bpy})_2(\text{Meprv})]^{2+}$. By comparing the results with those for other $[\text{Ru}(\text{bpy})_2(\text{NN})]^{2+}$ -type complexes [21], it was determined that of the three didentate ligands of $[\text{Ru}(\text{bpy})_2(\text{Meprv})]^{2+}$, Meprv is the most easily reduced. Meprv is irreversibly reduced at -0.055 V (versus Ag/AgCl), while the two bpy ligands are reduced at -0.720 and -1.648 V, successively. Meprv is oxidized at 0.870 V, while oxidation of Ru(II) to Ru(III) occurs at 2.08 V. The redox behavior of the Meprv ligand is consistent with the tendency of a radical to form a closed-shell structure.

The electron deficiency of Meprv could account for the fact that, as mentioned above, its coordinating ability is weaker than that of bpy. Of course, the presence of the methyl groups adjacent to the coordinating nitrogen atoms of the verdazyl and the pyrazole rings, clearly are steric factors that also will hamper the coordination of Meprv.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 204494. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or [www:http://www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)).

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