

Synthesis and characterisation of palladium(II) complexes with 1,2-bis(N-methylbenzimidazolyl)benzene

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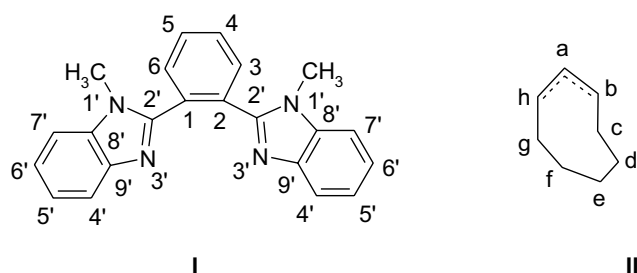
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Palladium(II) salts react with a bidentate N-heterocycle 1,2-bis(N-methylbenzimidazolyl)benzene (N–N) to yield complexes of the composition $\text{PdX}_2(\text{N–N})$ ($\text{X} = \text{Cl}, \text{Br}$ or ClO_4). A cationic complex, $[\text{Pd}(\text{cod})(\text{cotl})]\text{ClO}_4$ ($\text{cod} = 1,5\text{-cyclooctadiene}$, $\text{cotl} = \text{cyclooctenyl}$, $\text{C}_8\text{H}_{13}^-$) undergoes substitution of cod with N–N to produce $[\text{Pd}(\text{cotl})(\text{N–N})]\text{ClO}_4$. Dihalobridged binuclear complexes $[\text{PdX}(\text{cotl})]_2$ ($\text{X} = \text{Cl}$ or Br) react with N–N to give complexes of the types $[\text{Pd}_2\text{Cl}_2(\text{cotl})(\text{N–N})]\text{Cl}$ and $[\{\text{PdBr}(\text{cotl})\}_2(\text{N–N})]$.

Keywords: palladium, organopalladium complexes, N-heterocycle, spectroscopy

N-heterocycles represent an important class of ligands in coordination chemistry.¹

Transition metal complexes containing N-heterocycles are gaining significance because of their relevance to metallo-proteins and catalytic activity.^{2–8} A variety of transition metal complexes containing multidentate N-heterocycles has been reported from these laboratories.^{9–14} 1,3-bis(benzimidazolyl)benzene forms cyclometallated complexes with palladium and rhodium.^{12,15} Williams and coworkers¹⁶ have reported a dinuclear double helical copper(I) complex containing 2,6-bis(N-methylbenzimidazolyl)pyridine. Some palladium and platinum complexes containing N-heterocycles have been tested for cytotoxicity and antitumour activity.^{17,18} Herein, we describe the synthesis and characterisation of the N-heterocycle, 1,2-bis(N-methylbenzimidazolyl)benzene (**I**) and its reactions with palladium halides, palladium perchlorate and organopalladium complexes containing the cyclooctenyl group (**II**).



Experimental

Reagents

1,2-bis(N-methylbenzimidazolyl)benzene (N–N) was prepared following the literature methods given for related N-heterocycles.^{10,19–20} PdCl_2 was procured from Arora-Matthey Ltd. and 1,5-cyclooctadiene was obtained from Merck. PdBr_2 and $\text{Pd}(\text{ClO}_4)_2$ were made by dissolving $\text{Pd}(\text{OH})_2$ (obtained by treating PdCl_2 solution with Na_2CO_3) in 1:1 HBr and HClO_4 respectively. $[\text{Pd}(\text{cod})(\text{cotl})]\text{ClO}_4$ and $[\text{PdX}(\text{cotl})]_2$ ($\text{X} = \text{Cl}$ or Br) were prepared as described earlier.²¹ The solvents used were distilled prior to their use.

Measurements

Microanalysis of the metal complexes were carried out at CDRI Lucknow, India. IR (in nujol) and far-IR (in polyethylene powder) spectra were recorded on Shimadzu IR-435, Nicolet FT-IR and Bruker IFS 113V spectrometers respectively. Solid-state electronic spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. The molar conductivity measurements were determined using an Elico model CH-82T conductivity cell. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz FT NMR spectrometer with TMS as the internal reference. Mass spectra were recorded on a KRATOS MALDI-TOF mass spectrometer.

Synthesis

1,2-bis(N-methylbenzimidazolyl)benzene (N–N): N-methyl-o-phenylenediaminedihydrochloride (1 mmol) dissolved in hot polyphosphoric acid (30 cm^3) was treated with phthalic acid (0.5 mmol). The mixture was stirred at 200°C on a sand bath for 4 h and was neutralised with 10% sodium carbonate solution. The resulting solid was recrystallised from methanol to yield a white crystalline solid (70%).

Preparation of the complexes

$[\text{PdX}_2(\text{N–N})]$: PdX_2 ($\text{X} = \text{Cl}, \text{Br}$ or ClO_4) (1 mmol) in THF (5 cm^3) was treated with the heterocycle, N–N (1 mmol) in THF (5 cm^3). The mixture was refluxed at room temperature for 4 h during which time a brown solid separated. The solid was washed with THF and dried *in vacuo*. Yield: 70%.

$[\text{Pd}(\text{cotl})(\text{N–N})]\text{ClO}_4$: To a suspension of $[\text{Pd}(\text{cotl})(\text{cod})]\text{ClO}_4$ (1 mmol) in THF (20 cm^3) was added the heterocycle, N–N (1 mmol) dissolved in THF (10 cm^3). The resulting mixture was refluxed for 2 h during which time a yellow solid separated. The solid was washed with THF and dried *in vacuo*. Yield: 65%.

$[\text{Pd}_2\text{Cl}_2(\text{cotl})(\text{N–N})]\text{Cl}$: $[\text{PdCl}(\text{cotl})]_2$ (0.05 mmol) in THF (10 cm^3) was treated with the heterocycle, N–N (0.05 mmol) in THF (10 cm^3). The mixture was stirred at room temperature for 24 h during which time a yellow compound separated. The solid was washed with THF and dried *in vacuo*. Yield: 35%.

$[\{\text{PdBr}(\text{cotl})\}_2(\text{N–N})]$: $[\text{PdBr}(\text{cotl})]_2$ (1 mmol) in THF (10 cm^3) was treated with the heterocycle, N–N (1 mmol) in THF (10 cm^3). The mixture was stirred at room temperature for 24 h during which time a yellow compound separated. The solid was washed with THF and dried *in vacuo*. Yield: 70%.

Results and discussion

The N-heterocycle, 1,2-bis(N-methylbenzimidazolyl)benzene (N–N), has been prepared by treating a mixture of N-methyl-o-phenylenediaminedihydrochloride in polyphosphoric acid with phthalic acid in 1:1 mole ratio, followed by workup. The product is obtained as white crystalline solid. It is soluble in common organic solvents. Palladium(II) salts, PdX_2 ($\text{X} = \text{Cl}, \text{Br}$ or ClO_4) in THF at refluxing temperature react with N–N to produce brown complexes of the composition $[\text{PdX}_2(\text{N–N})]$. The complexes are insoluble in common organic solvents but are soluble in DMF, in which they behave as non-electrolytes (Table 1).

$[\text{Pd}(\text{cod})(\text{cotl})]\text{ClO}_4$ in THF reacted with N–N to yield $[\text{Pd}(\text{cotl})(\text{N–N})]\text{ClO}_4$. It is soluble in DMF and the solution shows uni-univalent electrolytic behaviour of the complex.

$[\text{PdCl}(\text{cotl})]_2$ in THF reacts with N–N to give $[\text{Pd}_2\text{Cl}_2(\text{cotl})(\text{N–N})]\text{Cl}$, the bromo analogue in THF undergoes bromobridge cleavage with N–N to yield $[\{\text{PdBr}(\text{cotl})\}_2(\text{N–N})]$. Both chloro and bromo complexes are soluble in DMF, the solutions of which exhibit uni-univalent and non-electrolytic behaviour for the former and latter. Physical properties and analytical data of the complexes are listed in Table 1.

The solid-state IR spectra of the complexes are comparable with those of the uncoordinated N-heterocycle apart from minor shifts in the positions of the bands. The spectra of the complexes displayed bands around 1550 and 1620 cm^{-1} due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ respectively and another band around 1400 cm^{-1} due to the N–CH₃ deformation vibration. The perchlorate complexes, in addition to the heterocycle peaks, showed additional peaks due to the perchlorate group. The $[\text{Pd}(\text{OClO}_3)_2(\text{N–N})]$ complex displayed split bands around 1070 and 630 cm^{-1} (Table 1) and these are

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Table 1 Analytical and IR spectral data of the complexes

Complex	Colour	M.P./D.P.(°C)	Λ_m^b $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Found (calcd.%)				IR spectral data (cm^{-1})			
				C	H	N	Cl/Br	$\nu(\text{C}=\text{C})\&$ $\nu(\text{C}=\text{N})$	$\delta\text{ N-CH}_3$	$\nu(\text{ClO}_4)$	
N-N ^a											
[PdCl ₂ (N-N)]	White	250	—	78.1(78.1)	5.4(5.4)	16.1(16.6)	—	1545, 1616	1403	—	
[PdBr ₂ (N-N)]	Brown	>270	29	51.2(51.2)	3.4(3.9)	10.8(10.9)	14.1(13.7)	1548, 1610	1409	—	
[Pd(OCIO ₃) ₂ (N-N)]	Brown	>270	17	43.8(43.7)	3.1(3.3)	9.2(9.3)	25.4 (25.7)	1548, 1610	1409	—	
	Brown	>270	39	40.9(41.0)	2.9(3.1)	8.8(8.7)	—	1548, 1626	1403	1093, 1062	
										628, 623	
[Pd(cotl)(N-N)]ClO ₄	Yellow	>250	78	55.2(55.15)	5.1(5.1)	8.6(8.6)	—	1545, 1616	1398	1098, 628	
[Pd ₂ Cl ₂ (cotl)(N-N)]Cl	Yellow	226	68	47.2(47.0)	4.1(4.3)	7.5(7.3)	13.6(13.8)	1548, 1621	1409	—	
[{PdBr(cotl)} ₂ (N-N)]	Yellow	>250	3	48.5(49.1)	4.8(5.0)	7.5(6.0)	17.6(17.2)	1548, 1621	1409	—	

^aN-N = 1,2-bis(N-methylbenzimidazolyl)benzene^bMolar conductance of 10⁻³ M solution in dmf around 25°C

characteristic of coordinated perchlorates.¹³ The [Pd(cotl)(N-N)]ClO₄ complex exhibited bands at 1098 and 628 cm^{-1} due to ionic perchlorate group.²²

The far-IR spectra of the parent complexes [PdX(cotl)]₂ displayed bands at 270 and 157 cm^{-1} for $\nu(\text{Pd-Cl-Pd})$ and $\nu(\text{Pd-Br-Pd})$ respectively.²¹ The products, [Pd₂Cl₂(cotl)(N-N)]Cl and [{PdBr(cotl)}₂(N-N)] displayed peaks corresponding to bridged palladium-chloride stretches at 274 cm^{-1} and terminal palladium-bromide stretches at 179 cm^{-1} indicated the former has not undergone chlorobridge cleavage and latter has undergone bromobridge cleavage.^{15,23}

A comparison of the ¹H NMR spectra of the heterocycle, N-N, [Pd(cod)(cotl)]ClO₄, [PdX(cotl)]₂ (X = Cl or Br) with those of their reaction products revealed the presence of coordinated N-N in the latter. Further both positive and negative coordination induced shifts (c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$) have been observed. The spectrum of [Pd(cotl)(N-N)]ClO₄ showed resonances due to cotl and the N-heterocycle implying the displacement of cod in the precursor complex by N-N and thus a weaker coordination of cod and a stronger coordination of the cotl unit in the starting material. The proton resonances of the cotl unit in the product are observed in the range δ 1.75–3.60. The N-CH₃ resonance of the coordinated heterocycle is observed at *ca* δ 3.88. The resonances due to the benzimidazole unit and the benzene ring are in the observed range δ 7.14–8.72.

The ¹H NMR spectra of [Pd₂Cl₂(cotl)(N-N)]Cl and [{PdBr(cotl)}₂(N-N)] complexes also exhibit resonances due to cotl and benzimidazole units. The resonances due to the benzene ring protons of the N-heterocycle display a downfield shift on complexation. The N-CH₃ resonance is observed around δ 3.9. The benzimidazole ring proton resonances observed in the spectra of the complexes exhibit both positive and negative c.i.s. The resonances due to the a, b, h protons (see **II**) of the cotl unit in the N-N containing complexes show upfield shifts as compared to those of the precursor complexes. The proton resonances of cotl corresponding to c,g,d,e and f have positive c.i.s. According to Orellana *et al.*,²⁴ the c.i.s. arise due to electron donation from the ligand to the metal via the σ -bond, metal electron π -back donation to the ligand, van der Waals interaction and magnetic anisotropy of ring currents. The ¹H NMR spectral data of the N-heterocycle and the complexes are listed in Table 2.

The ¹³C NMR spectra of [PdX₂(N-N)] complexes exhibit signals in the chemical shift range 110 to 150 ppm for the coordinated N-heterocycle, except for the N-CH₃ carbon whose signal is around 32 ppm. Negative c.i.s. for the carbon resonances may arise due to greater metal-to-ligand π -back donation, and positive c.i.s. due to ligand-to-metal σ -donation.²⁵ The carbons of the coordinated N-heterocycle in [Pd(cotl)(N-N)]ClO₄ and [Pd₂Cl₂(cotl)(N-N)]Cl complexes, resonate in the range 110–151 ppm. The resonances corresponding to the coordinated cotl are located in the range 21–115 ppm. The resonance due to the N-CH₃ carbon is observed at *ca* δ 31. The cotl signals have both positive and negative c.i.s. on complexation. The resonances corresponding to C-4' to C-9' of the benzimidazole unit (see **I**) and C-1 to C-6 of benzene unit show downfield shifts, except for C-4,5 of the chloro complex.

The ¹³C NMR spectrum of the [{PdBr(cotl)}₂(N-N)] complex display peaks due to cotl unit and the N-heterocycle. The carbon-a resonance of cotl in the complex has a negative shift whereas those due to other cotl and heterocycle carbons have both positive and negative c.i.s. The N-CH₃ resonance is observed at *ca* δ 33. The ¹³C NMR spectral data of the N-heterocycle and metal complexes are compiled in Table 3.

The electronic spectra of the N-heterocycle, and palladium(II) complexes in nujol mull have been recorded and the spectra exhibit an intense band at *ca* 33300 cm^{-1} . The band is assigned to metal-to-ligand charge transfer transition.²⁶

The FAB-mass spectrum of [Pd₂Cl₂(cotl)L]Cl (L = N-N) support its binuclear nature. The molecular ion peak corresponding to the dimer (*m/z*, 767) is absent. However peaks due to association product Pd₂Cl₃(cotl)(L-3H) (*m/z*, 764), and fragmentation products Pd₂Cl₂(cotl)(L-CH₃) (*m/z*, 716), Pd₂(cotl)L (*m/z*, 660), Pd₂Cl(L-CH₃) (*m/z*, 572), PdCl₂L (*m/z*, 516), PdCIL (*m/z*, 480) are observed. In addition, a peak is observed at 711 and this is probably due to the association of fragments to produce Pd₂Cl₂(L-CH₃) + 2H. The mass spectrum of [{PdBr(cotl)}₂L] complex (L = N-N) also support its binuclear nature. The spectrum displays a weak molecular ion peak at *m/z* 847 and this corresponds to Pd₂Br(cotl)(L-3H). Additional peaks are observed at *m/z* 894, 725, 524 and 445

Table 2 ^1H NMR spectral data of the N-heterocycle and complexes in DMSO- d_6 (δ in p.p.m)^a

Complex ^b	Benzimidazole ring				Benzene ring			Cotl unit			
	H-4'	H-5'	H-6'	H-7'	N-CH ₃	H-3,6	H-4,5	H-a	H-b,h	H-c,g	H-d,e,f
[Pd(cod)(cotl)]ClO ₄	-	-	-	-	-	-	-	5.60	5.17	1.85	1.48
[PdCl(cotl)] ₂	-	-	-	-	-	-	-	5.65	4.97	2.35	1.43
[PdBr(cotl)] ₂	-	-	-	-	-	-	-	5.64	3.75	1.92	1.45
N-N	7.50d	7.20t	7.14t	7.47d	3.48 s	7.80 m	7.80 m	-	5.09	2.37	-
[PdCl ₂ (N-N)]	8.28	7.42	7.42	7.70	3.78	8.24	8.07	-	3.37	1.93	-
[PdBr ₂ (N-N)]	8.27	7.40	7.40	7.70	3.77	8.25	8.05	-	-	-	-
[Pd(OCIO ₃) ₂ (N-N)]	8.25	7.37	7.30	7.15	3.88	8.25	8.05	-	-	-	-
[Pd(cotl)(N-N)]ClO ₄	7.80	7.38	7.28	7.15	3.88	8.70	8.40	-	-	-	-
[Pd ₂ Cl ₂ (cotl)(N-N)]Cl	8.25	8.06	7.78	7.70	3.89	8.72	8.40	3.60	3.48	2.20	1.75
[PdBr(cotl)] ₂ (N-N)]	8.25	8.20	7.75	7.43	3.88	8.71	8.41	(-2.0)	(-1.69)	(0.35)	(0.32)
	(0.75)	(1.00)	(0.61)	(-0.04)	(0.40)	(0.91)	(0.61)	(-1.85)	(-1.78)	(0.13)	(0.49)

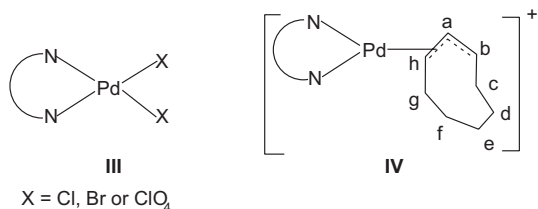
^aValues in parentheses are coordination induced shifts, c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$.^bs = singlet, d = doublet, t = triplet, m = multiplet**Table 3** ^{13}C NMR spectral data of N-heterocycle and complexes in DMSO- d_6 (δ in p.p.m)

Complex	Benzimidazole ring						Benzene ring						Cotl unit			
	C-2'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	N-CH ₃	C-1,2	C-3,6	C-4,5	C-a	C-b,h	C-c,g	C-d,f	C-e
[Pd(cod)(cotl)]ClO ₄	-	-	-	-	-	-	-	-	-	-	-	113.40	86.00	31.70	26.30	23.80
[PdCl(cotl)] ₂	-	-	-	-	-	-	-	-	-	-	-	116.92	88.36	35.74	30.69	27.84
[PdBr(cotl)] ₂	-	-	-	-	-	-	-	-	-	-	-	116.92	88.36	35.74	30.69	27.84
N-N	152.18	118.96	122.20	121.65	110.30	135.60	142.38	30.63	130.75	131.33	129.82	-	-	-	-	-
[PdCl ₂ (N-N)]	149.32	119.37	124.41	123.69	111.78	134.68	138.58	32.64	127.10	132.34	131.47	-	-	-	-	-
[PdBr ₂ (N-N)]	(-2.86)	(0.41)	(2.21)	(2.04)	(1.48)	(-0.92)	(-3.80)	(2.01)	(-3.65)	(1.01)	(1.65)	-	-	-	-	-
[Pd(OCIO ₃) ₂ (N-N)]	148.20	115.53	125.72	125.72	112.25	133.39	138.85	31.73	124.83	132.58	132.03	-	-	-	-	-
	(-3.98)	(-3.43)	(3.52)	(4.07)	(1.95)	(-2.21)	(-3.53)	(1.10)	(-5.92)	(1.25)	(2.21)	-	-	-	-	-
[Pd(cotl)(N-N)]ClO ₄	149.39	116.28	124.94	129.94	112.03	133.92	138.60	31.61	126.28	131.91	131.91	-	-	-	-	-
	(-2.79)	(-2.68)	(2.74)	(3.29)	(1.73)	(-1.68)	(-3.78)	(0.98)	(-4.47)	(0.58)	(2.09)	-	-	-	-	-
[Pd ₂ Cl ₂ (cotl)(N-N)]Cl	150.62	119.00	122.30	121.72	110.38	135.64	142.41	30.70	130.77	131.41	129.90	112.26	81.26	31.92	21.36	21.30
	(-1.56)	(0.04)	(0.10)	(0.07)	(0.38)	(0.04)	(0.03)	(0.07)	(0.02)	(0.08)	(0.08)	(-1.14)	(-4.74)	(0.22)	(3.06)	(-2.50)
[PdBr(cotl)] ₂ (N-N)]	150.50	119.00	121.20	121.70	110.30	135.64	142.40	31.32	130.65	131.40	129.80	114.90	85.6	33.4	88.03	25.62
	(-1.68)	(0.04)	(0.00)	(0.05)	(0.00)	(0.04)	(0.02)	(0.89)	(0.10)	(0.07)	(-0.02)	(-1.49)	(-2.76)	(-2.34)	(-2.66)	(-2.22)
	150.63	115.26	125.06	124.94	112.93	134.62	137.40	33.25	126.81	133.00	132.90	114.30	90.66	38.65	32.90	29.38
	(-1.55)	(-3.70)	(2.86)	(3.29)	(2.62)	(-0.98)	(-4.98)	(2.62)	(-3.94)	(1.67)	(3.08)	(-2.62)	(2.30)	(2.91)	(2.21)	(1.54)

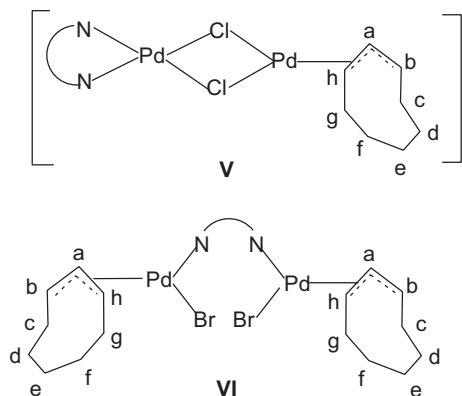
Values in parentheses are coordination induced shifts, c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$

and these may be due to fragmentation products like $\text{Pd}(\text{cotl})(\text{L}_2-2\text{H})$, $\text{Pd}_2\text{Br}_2(\text{L}-\text{CH}_3) + \text{H}$, PdBrL and PdL respectively.^{13,26,27}

The analytical data, molar conductance, IR and ^1H and ^{13}C NMR spectral results indicate that the heterocycle, halide and cotl groups are coordinated to the palladium ion. Molecular models suggest that the N-heterocycle can act as chelating or bridging bidentate in the complexes. In the case of the $\text{PdX}_2(\text{N}-\text{N})$ complexes, the tertiary nitrogen of each benzimidazole unit and the halides are coordinated to palladium. The N-heterocycle being a chelating or bridging bidentate four-electron donor serves as a good nucleophile to displace cod in $[\text{Pd}(\text{cot})(\text{cod})]\text{ClO}_4$. Based on the above results, $\text{PdX}_2(\text{N}-\text{N})$ and $[\text{Pd}(\text{cot})(\text{N}-\text{N})]^+$ complexes are suggested to have four (III) and pseudo-three co-ordinate (IV) geometries respectively.



$[\text{Pd}(\text{cotl})\text{X}]_2$ (X = Cl or Br) reacts with N-N to form complexes of the types $[\text{Pd}_2\text{Cl}_2(\text{cotl})(\text{N}-\text{N})]\text{Cl}$ and $[\{\text{PdBr}(\text{cotl})\}_2(\text{N}-\text{N})]$. During the course of the reaction, N-N displaces one of the cotl units in the dichloro-bridged complex, it cleaves the bromo bridge of the dimer $[\text{Pd}(\text{cotl})\text{Br}]_2$ and subsequently the heterocycle forms the bridge in the product. Thus N-N acts as chelating bidentate in one chloro-complex and bridging bidentate in another bromo-complex. The ^1H and ^{13}C NMR spectra of the complexes indicate the coordination of the N-heterocycle via the tertiary nitrogens of the benzimidazole moiety. Based on the above results, the complexes $[\text{Pd}_2\text{Cl}_2(\text{cotl})(\text{N}-\text{N})]^+$ and $[\{\text{PdBr}(\text{cotl})\}_2(\text{N}-\text{N})]$ are proposed to have four (V) and pseudo coordinate (VI) geometry respectively around each metal ion.^{13,16,26}



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