

PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH PYRAZINE *N*-OXIDE, PYRIDAZINE *N*-OXIDE, AND BENZOFURAZAN *N*-OXIDE

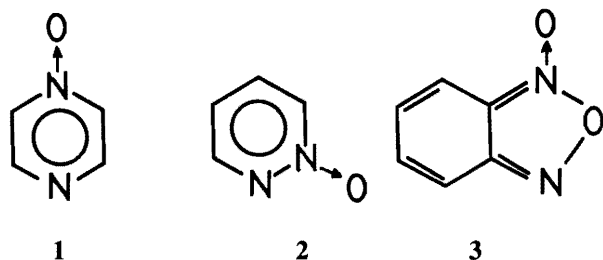
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INTRODUCTION

Metal complexes of pyrazine [1] and pyridazine [2] have been extensively studied. However, reactions of aromatic diazine mono-*N*-oxides with metal cations have received limited attention. Some pyrazine *N*-oxide (Pyz-O) metal complexes have been synthesized and characterized [3], but no studies have been done on the complexes of pyridazine *N*-oxide (Pdz-O). Concerning the related benzofurazan *N*-oxide (BFO), only its copper and nickel chelates have been proposed as intermediates in the transformation of ψ -*o*-dinitroso aromatic compounds into *o*-nitroarylamines [4].

This paper describes an investigation into the preparation and characterization of some palladium(II) and platinum(II) complexes with Pyz-O (1), Pdz-O (2) and BFO (3).



The availability of two potential coordination sites in these compounds allows them to act as unidentate ligands or as bidentate bridging ligands [5, 6]. Bonding of these heterocyclic *N*-oxides through the unoxidized nitrogen gives compounds that could be viewed as oxygen-atom transfer systems that might

readily oxidize certain sulfur compounds. In addition, complexes of BFO are used as intermediates in organic synthesis [4].

EXPERIMENTAL

All chemicals used were of GR grade and were dried and purified as required. K_2PdCl_4 , K_2PtCl_4 , $PdCl_2$, and $Pd(NO_3)_2$ were purchased from BDH and were used without further purification. IR spectra were obtained on a Perkin-Elmer Model 577 spectrometer as nujol mulls between KBr plates or polyethylene plates. Microanalyses were carried out by E. Pascher Microanalytical Laboratory (Bonn, W. Germany). Conductivity measurements were made with $10^{-3}M$ DMF or water solutions using digital conductivity meter model PW 9527. The proton NMR spectra were recorded with a Bruker WM-250 spectrometer in acetonitrile- d_3 .

Pyrazine *N*-oxide and pyridazine *N*-oxide were prepared [7] by the reaction of pyrazine or pyridazine with hydrogen peroxide, and were characterized by their melting points and IR spectra [8]. Benzofurazan *N*-oxide [9], and $Pd(PhCN)_2Cl_2$ [10] were prepared by literature methods.

Preparation of *cis*- $M(Pyz-O)_2Cl_2$ and *trans*- $M(Pdz-O)_2Cl_2$ ($M = Pd, Pt$)

To a filtered solution of K_2MCl_4 (1.0 mmol) in water (10 ml) was added a filtered solution of the diazine *N*-oxide (3.0 mmol) in water (10 ml). The solution was stirred on a steam bath for 1 h. The solution changed color from red to yellow with the

slow formation of a yellowish precipitate. The precipitate was filtered, washed with water, ethanol, and diethyl ether, and then dried under vacuum at 50°C.

Preparation of *cis*-Pd(Pyz-O)₂Cl₂ and *trans*-Pd(Pdz-O)₂Cl₂ from Pd(PhCN)₂Cl₂

To a filtered solution of Pd(PhCN)₂Cl₂ (0.38 g, 1.0 mmol) in dichloromethane (10 ml) was added a filtered solution of the diazine *N*-oxide (0.29 g, 3.0 mmol) in dichloromethane (10 ml). The mixture was refluxed for 1 h, during which time a small amount of a yellow powder separated. Petroleum ether (50 ml) was added to complete precipitation. The product was filtered, washed with diethyl ether, and then dried under vacuum at 50°C. These palladium complexes are identical with those isolated in the preceding procedure, as shown by their decomposition points and I.R. spectra.

Preparation of [M(Pyz-O)₄]X₂ (M = Pd, Pt; X = NO₃, PF₆)

To a boiling suspension of *cis*-M(Pyz-O)₂Cl₂ (1.0 mmol) in water (20 ml) was added dropwise a filtered solution of AgNO₃ or AgPF₆ (2.0 mmol) in water (20 ml). The mixture was further boiled for 10 min, and then filtered into a flask containing Pyz-O (4.0 mmol) in water (10 ml). The solution was cooled in an ice bath, and a microcrystalline product was precipitated. This product was filtered, washed with ice-cold water and then dried under vacuum at 50°C.

Preparation of [Pd(Pyz-O)₄](NO₃)₂ from Pd(NO₃)₂

To a filtered solution of Pd(NO₃)₂ (0.23 g, 1.0 mmol) in water (20 ml) was added a filtered solution of Pyz-O (0.48 g, 5.0 mmol) in water (10 ml). The mixture was stirred on a steam bath for 1 h and then filtered while hot. The yellow filtrate was cooled in an ice bath until crystallization seem complete. The pale yellow microcrystals were collected, washed with ice-cold water and then dried under vacuum at 50°C.

Preparation of Pd(BFO)Cl₂

To a filtered solution of BFO (0.28 g, 2.0 mmol) in dry THF (10 ml) was added a filtered solution of Pd(PhCN)₂Cl₂ (0.40 g, 1.0 mmol) in dry THF (20 ml). A brown-red precipitate separated upon mixing. The mixture was refluxed with stirring for

1 h. The very fine brown precipitate was filtered, washed with dry THF, and diethyl ether and then dried under vacuum at 50°C.

Oxidation of Dimethyl Sulfoxide via Pd(BFO)Cl₂

A sample of freshly distilled DMSO (5.0 ml) was added dropwise to a solid sample of Pd(BFO)Cl₂ (0.63 g, 2.0 mmol). Upon addition of the first drops of DMSO, a fast and highly exothermic reaction started. The reaction mixture was left to cool and excess DMSO was removed under vacuum. The black residue was sublimed at 80°C under hard vacuum. Dimethyl sulfone was obtained as colorless crystals and was identified by its m.p. 109°C (lit [11] 107°C), IR and mass spectrometry (M⁺ = 94).

RESULTS AND DISCUSSION

Pyrazine *N*-oxide and pyridazine *N*-oxide react with K₂PdCl₄ (or Pd(PhCN)₂Cl₂) and K₂PtCl₄ to give compounds with the formula ML₂Cl₂ (M = Pd, Pt; L = Pyz-O, Pdz-O). This formulation and the geometrical assignments are based on their analytical data (Table 1) and infrared stretching vibrations (Table 2). These square planar complexes are thermally stable up to 150°C, and are non-electrolytes, as shown by their electrical conductance in DMF. They are soluble in hot DMF, slightly soluble in hot water, and practically insoluble in acetone, ethanol, chloroform, or diethyl ether.

By comparison of the IR spectra of the ML₂Cl₂ complexes with those of the ligands involved (Table 2), it is observed that $\nu_{N=O}$ is shifted by about 20 cm⁻¹ to higher wavenumber region upon coordination. Such shift indicates metal-binding through the unoxidized ring nitrogen atom, rather than to the oxygen of the N–O group [3, 6]. This mode of bonding is further confirmed by proton NMR spectroscopy. For example, the proton NMR spectrum of Pt(Pyz-O)₂Cl₂ in deuterioacetonitrile shows a complex multiple at 7.4–8.8 ppm due to the Pyz-O protons. Two satellite doublets $J(^{195}\text{Pt}-\text{H}) = 32.0$ Hz were observed for the signal at 8.8 ppm as a result of the ¹⁹⁵Pt–N–C–H coupling. The *cis*-geometry for M(Pyz-O)₂Cl₂ complexes is supported by the presence of two ν_{M-Cl} bands in the region 365–305 cm⁻¹ and two ν_{M-N} bands in the region 270–240 cm⁻¹ (Table 2). On the other hand, M(Pdz-O)₂Cl₂ complexes show only one band for ν_{M-Cl} at about 340 cm⁻¹ and one for ν_{M-N} at about 270 cm⁻¹, indicating a *trans*-geometry for these complexes. Attempts to isolate the *cis*-M(Pdz-O)₂Cl₂

Table 1. Colors, Melting Points, and Elemental Analyses of the Complexes.

No.	Complex	Color (Yield)	Melting* Point (°C)	%C		%H		%N	
				Found	Calc.	Found	Calc.	Found	Calc.
1	<i>cis</i> -Pd(Pyz-O) ₂ Cl ₂	Lemon Yellow (92%)	300	26.29	26.00	2.11	2.19	15.15	15.17
2	<i>cis</i> -Pt(Pyz-O) ₂ Cl ₂	Bright Yellow (87%)	175	20.63	20.96	1.66	1.76	11.86	12.23
3	<i>trans</i> -Pd(Pdz-O)Cl ₂	Orange Yellow (89%)	190	26.33	26.00	2.17	2.19	14.98	15.17
4	<i>trans</i> -Pt(Pdz-O)Cl ₂	Yellow (85%)	150	21.11	20.96	1.75	1.76	11.97	12.23
5	[Pd(Pyz-O) ₄](NO ₃) ₂	Pale Yellow (75%)	275	30.99	31.25	2.43	2.63	22.67	22.79
6	[Pt(Pyz-O) ₄](NO ₃) ₂	Pale Yellow (65%)	310	26.92	27.31	2.17	2.30	19.51	19.91
7	[Pd(Pyz-O) ₄](PF ₆) ₂	Off-White (72%)	265	24.41	24.61	1.98	2.07	14.41	14.36
8	[Pt(Pyz-O) ₄](PF ₆) ₂	Off-White (65%)	280	21.88	22.10	1.89	1.86	12.88	12.89
9	Pd(BFO)Cl ₂	Dark Brown (95%)	>360	23.36	22.99	1.41	1.29	8.88	8.94

*Melting with decomposition.

Table 2. Infrared Data (cm⁻¹)* and Conductivity Measurements of the Ligands and Their Complexes

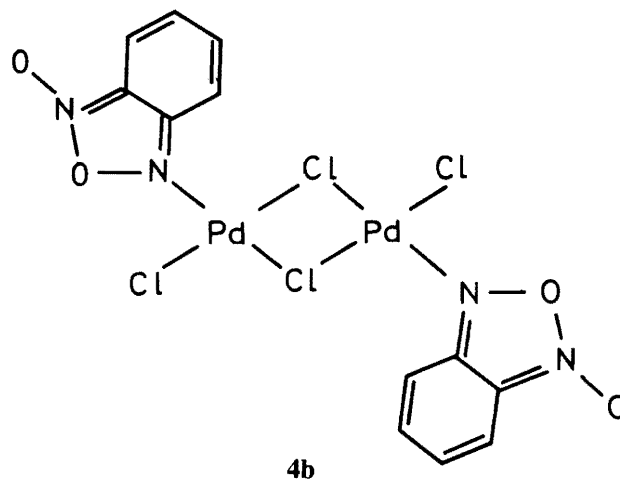
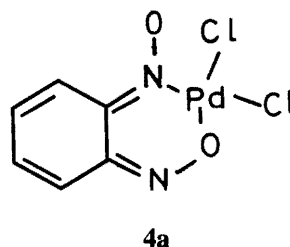
Complexes	ν C=N	ν N-O	ν M-Cl	ν M-N	ν PF ₆ ⁻ or ν NO ₃ ⁻	Λ_M (solvent) (ohm ⁻¹ cm ² mol ⁻¹)
Pyz-O	1595(s)	1310(s)	—	—	—	—
Pdz-O	1580(s)	1310(s)	—	—	—	—
BFO	1630(s)	1360(s)	—	—	—	—
<i>cis</i> -Pd(Pyz-O)Cl ₂	1615(s)	1330(s)	365(s), 305(m)	265(m), 245(m)	—	Non-electrolyte
<i>cis</i> -Pt(Pyz-O)Cl ₂	1610(s)	1330(s)	350(s), 320(s)	270(s), 240(w)	—	„
<i>trans</i> -Pd(Pdz-O) ₂ Cl ₂	1590(s)	1330(s)	335(s)	260(s)	—	„
<i>trans</i> -Pt(Pdz-O) ₂ Cl ₂	1590(s)	1325(s)	335(s)	265(m)	—	„
[Pd(Pyz-O) ₄](NO ₃) ₂	1610(s)	1325(s)	—	260(m)	1760(w) 1380(s)	297(H ₂ O)
[Pt(Pyz-O) ₄](NO ₃) ₂	1620(s)	1330(s)	—	290(m)	1770(w) 1375(s)	262(H ₂ O)
[Pd(Pyz-O) ₄](PF ₆) ₂	1620(s)	1320(s)	—	275(m)	830(s) 755(w) 560(s)	138(DMF)
[Pt(Pyz-O) ₄](PF ₆) ₂	1620(s)	1320(s)	—	295(m)	835(s) 755(w) 570(s)	133(DMF)
Pd(BFO)Cl ₂	1585(s)	1340(s)	350(m), 320(m)	—	—	—

*s = Strong, m = Medium, w = Weak.

(M = Pd, Pt) were unsuccessful. The *cis*-geometry of Pdz-O complexes is probably disfavored due to the steric effect caused by the proximity of the N–O group to the adjacent coordination site.

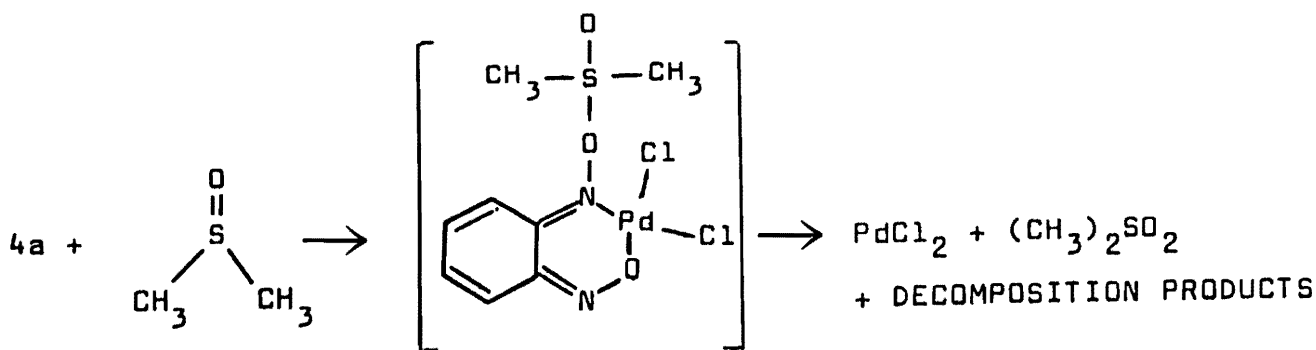
In an attempt to prepare complexes with the formula $[ML_4]Cl_2$ (M = Pd, Pt; L = Pyz-O, Pdz-O), excess ligand was added to a boiling water suspension of the corresponding ML_2Cl_2 complexes. No reaction was observed after 6 hours of reflux. This is not surprising in view of the weak coordination ability of these ligands. The presence of the strong electron-withdrawing N–O group makes these diazine *N*-oxides weaker ligands than pyridine or their unoxidized parent diazines [3]. However, use of halogen-abstracting reagents such as $AgPF_6$ or $AgNO_3$, allows the isolation of only $[M(Pyz-O)_4]X_2$ (M = Pd, Pt; X = NO_3 , PF_6). In general, these ionic compounds are more soluble and have higher decomposition points than the corresponding neutral $M(Pyz-O)_2Cl_2$ compounds. Their IR spectra show absorptions due to ionic PF_6^- or ionic NO_3^- and the characteristic bands of N-bonded ligands (Table 2). Conductivity measurements on $[M(Pyz-O)_4](NO_3)_2$ in water and on $[M(Pyz-O)_4](PF_6)_2$ in DMF (Table 2) are in good agreement with 2:1 electrolytes [12].

Benzofurazan *N*-oxide reacts with $Pd(PhCN)_2Cl_2$ in THF to give a compound formulated as $Pd(BFO)Cl_2$ on the basis of analytical data (Table 1). The IR spectrum of the complex shows $\nu_{C=N}$ and $\nu_{N=O}$ at 1580 cm^{-1} and 1340 cm^{-1} , respectively. Both absorptions are shifted to lower wavenumber region as compared with free BFO. It also shows two ν_{M-Cl} at 350 cm^{-1} and 320 cm^{-1} . Based on the above data, structure (4a) was proposed for this complex in which BFO acts as a bidentate ligand [4]. Another likely possible structure, that cannot be ruled out, is the halo-bridged dimer (4b).



Reaction of $Pd(BFO)Cl_2$ with DMSO

Oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone is known to proceed with strong oxidants and at elevated temperatures [13]. It is also reported [14] that pyridine *N*-oxide reacts with DMSO at 195°C to form dimethyl sulfone and pyridine. Herein, we find that $Pd(BFO)Cl_2$ decomposes in DMSO at room temperature in a very exothermic and vigorous reaction leading to the formation of dimethyl sulfone:



The reaction can be rationalized by a mechanism in which the oxygen atom of the N–O group in the complexed BFO (activated by Pd-bonding) attacks the sulfur atom of the DMSO-forming intermediate (5). The latter decomposes to give dimethyl sulfone, PdCl₂ and unidentified decomposition products. No such reaction was observed between DMSO and free BFO or any of the Pyz-O or Pdz-O complexes under the same conditions. Reactions between DMSO and suspensions of Pd(BFO)Cl₂ or ML₂Cl₂ (M = Pd, Pt; L = Pyz-O, Pdz-O) in THF gave the substitution product, Pd(DMSO)₂Cl₂, as characterized by its analytical and spectral data [15]. It is concluded that Pd-coordination could activate furazan N-oxide systems and thus facilitate the loss of the N-oxygen atom.

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REFERENCES

- [1] M. Goldstein, F. B. Taylor, and W. D. Unsworth, "Infrared Spectra, Electronic Spectra, and Magnetic Properties of Dihalogenobis(Pyrazine) Complexes of Cobalt(II) and Nickel(II) a Structural Re-assignment", *Journal of the Chemical Society, Dalton Transactions*, (1972), p. 418; G. A. Foulds and D. A. Thorton, "The Infrared Spectra of the Complexes *cis*- and *trans*-Pt(Pyrazine)₂-X₂ (X = Cl, Br, I, NO₂)", *Spectrochimica Acta*, **37A** (1981), p. 917.
- [2] J. R. Allan, G. A. Barnes, and D. H. Brown, "Some Transition Metal Complexes of Pyridazine, Phthalazine and 3,4-Benzocinnoline", *Journal of Inorganic and Nuclear Chemistry*, **33** (1971), p. 3765.
- [3] N. M. Karayannis, A. N. Specca, D. E. Chason, and L. L. Pytlewski, "Coordination Complexes of the N-Oxides of Aromatic Diimines and Diazines", *Coordination Chemistry Reviews*, **20** (1976), p. 37.
- [4] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, and F. Sahhar, "The Transformation of ψ -O-Dinitroso Aromatic Compounds into o-Nitroaryl Amines", *Journal of the American Chemical Society*, **77** (1955), p. 5688.
- [5] P. F. Huffman and J. E. House, Jr., "Silver Complexes Containing Pyrazine N-Oxide as Ligands", *Journal of Inorganic and Nuclear Chemistry*, **36** (1973), p. 2618.
- [6] A. N. Specca, N. M. Karayannis, and L. L. Pytlewski, "Transition Metal Perchlorate Complexes with Pyrazine N-Oxide", *Journal of Inorganic and Nuclear Chemistry*, **35** (1973), p. 3113.
- [7] C. F. Koelsch and W. H. Gumprecht, "Some Diazine-N-Oxides", *Journal of Organic Chemistry*, **23** (1958), p. 1603.
- [8] B. Klein and J. Berkowitz, "Pyrazines. I. Pyrazine-N-Oxide. Preparation and Spectral Characteristics", *Journal of the American Chemical Society*, **81** (1959), p. 5160.
- [9] F. B. Mallory, "Benzofurazan Oxide", *Organic Synthesis*, **37** (1957), p. 74.
- [10] J. R. Doyle, P. E. Slade, and H. B. Jonassen, "Metal Diolefin Coordination Compounds", *Inorganic Syntheses*, **VI** (1960), p. 216.
- [11] D. T. McAllan, T. V. Gullum, R. A. Dean, and F. A. Fidler, "The Preparation and Properties of Sulfur Compounds Related to Petroleum. I. The Dialkyl Sulfides and Disulfides", *Journal of the American Chemical Society*, **73** (1951), p. 3627.
- [12] W. J. Geary, "The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds", *Coordination Chemistry Reviews*, **7** (1971), p. 81.
- [13] H. H. Szmant, in *Organic Sulphur Compounds*. ed. M. Kharasch, vol. 1. London: Pergamon, 1961, ch. 16.
- [14] M. E. C. Biffin, J. Miller, and D. B. Paul, "Concerning the Mechanism of Reduction by Dimethyl Sulphoxide: Deoxygenation of Pyridine N-Oxide", *Tetrahedron Letters*, 1969, p. 1015.
- [15] J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, "Palladium(II) and Platinum(II) Alkyl Sulfoxide Complexes. Examples of Sulfur-Bonded, Mixed Sulfur- and Oxygen-Bonded, and Totally Oxygen-Bonded Complexes", *Inorganic Chemistry*, **11** (1972), p. 1280.

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