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PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF 5-ACYL AND 5-ALKYLAMINO-1,2-BENZOQUINONE-2-OXIMES

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Abstract—Reaction of palladium(II) chloride and potassium tetrachloroplatinate(II) with 5-acylamino and 5-alkylamino-1,2-benzoquinone-2-oximes (qOH; 1) has led to complexes of the type $M(qo)_2$ (**2**). $Pd(qo)_2$ was also obtained by the nitrosation of the appropriate phenol in the presence of palladium(II) chloride. The complexes were characterised by elemental analysis, IR and NMR (^1H, ^{195}Pt) spectroscopy. These studies indicated that the ligands are bonded to the metals *via* the oxime nitrogen and the quinonoid carbonyl oxygen, while mass spectral analysis indicated that the complexes were monomeric. The complexes failed to react with 2,2-dipyridyl, pyridine, and dimethyl acetylenedicarboxylate though the palladium complex, $Pd(5\text{-}Acqo)_2$, reacted with triphenylphosphine to give the corresponding iminophosphoranyl complex. Copyright © 1996 Elsevier Science Ltd

Despite the extent of current interest in 1,2-quinone monooximes,[1] few reports on the complexes of these versatile ligands with the 2nd and 3rd row transition metals have been reported. In fact, with the exception of some reports from these laboratories,[2] most of the available reports deal with complexes of 1st row transition metals.[3] In the case of palladium(II) and platinum(II), only one report which summarised the analytical applications of their complexes with 1,2-naphthoquinone-1-oxime has been published.[4]

In contrast, numerous complexes of both palladium(II) and platinum(II) with other oxime type ligands have been reported.[5] In the case of dioximic ligands, it has been shown that the ligands are bonded to the metal through the oxime nitrogen.[6] Similarly, with mixed N, O donor ligands such as salicylaldoxime,[7] the metal is bonded *via* the oxime nitrogen and a neighbouring oxygen atom forming 5-membered chelate rings not dissimilar to that which has been observed in complexes of 1,2-quinone monooximes with 1st row transition metals.[8]

Previously we reported on the synthesis of complexes of 5-acetylamino-1,2-benzoquinone-2-oxime with copper(II), nickel(II), manganese(II), iron(II) and cobalt(III) ions.[9] As part of our ongoing interest in complexes of quinone monooximes, we report

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here on the synthesis of palladium(II) and platinum(II) complexes of 5-acetylamino-, (5-AcqoH), 5-butyrylamino- (5-BuqoH), 5-hexylamino- (5-HxqoH), and 5-ethylamino-4-methyl-1,2-benzoquinone-2-oxime (5-EtaqoH).

EXPERIMENTAL

Palladium(II) chloride and potassium tetracloroplatinate(II) were both provided by INCO Europe. The 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-oximes were obtained by ion exchange chromatography of the corresponding nickel (II) complex. The purity of these ligands was confirmed by NMR spectroscopy. The solvents used for spectroscopic studies were purified and dried by standard techniques. Palladium and platinum were determined by atomic absorption methods.

Physical measurements

Infra-red spectra in the range 4000–600 cm^{-1} were recorded on a Biorad FTS40 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-250 spectrometer while ^{195}Pt spectra were recorded at 296 K on a Bruker AM-80 machine. Chemical shifts were measured relative to K_2PtCl_4 in D_2O which was used as an external reference (−1764 ppm). LSIMS mass spectra were obtained in a 3-nitrobenzylalcohol matrix on a Kratos MS 50S double focusing mass spectrometer using a caesium ion source. Solution electronic spectra were recorded on a Shimadzu UV-2100 spectrophotometer.

Preparation of the complexes

Reaction of palladium(II) chloride and potassium tetrachloroplatinate(II) with 1,2-*benzoquinone*-2-*oximes*

To a solution of palladium(II) chloride (15 mmol) in water/dilute hydrochloric acid (100 cm^3), a methanolic solution of the free 1,2-benzoquinone-2-oximes (30 mmol) was added with stirring (24 h). Filtration afforded dark brown solids which were washed with water and ethoxyethane and dried *in vacuo* to give the complex. Yields and analytical data for the complexes prepared in this way are given in Table 1.

Nitrosation of 3-*acylaminophenols in the presence of palladium(II) chloride*

Palladium(II) chloride (3.0 g, 17 mmol) in water/dilute HCl (9 : 1, 100 cm^3) was added to a solution of 3-acetylaminophenol (5.0 g, 33 mmol), sodium ethanoate (1.2 g, 15 mmol), glacial ethanoic acid (15 cm^3) in water/methanol (1 : 4, 50 cm^3). To this mixture, a solution of sodium nitrite (4.3 g, 51 mmol) in water (25 cm^3) was added dropwise with stirring (24 h). Filtration gave a brown solid which was washed with water (3 × 25 cm^3) and extracted with dichloromethane to afford bis-(5-acetylamino-1,2-benzoquinone-2-oximato)palladium(II) as the residue in 65% yield. Concentration of the extract afforded 3-acetylamino-1,4-benzoquinone-4-oxime (15%) confirmed by comparative tlc.[9] Similarly, reaction of 3-butyrylaminophenol gave bis-(5-butyrylamino-1,2-benzoquinone-2-oximato) palladium(II) (80%) (see Table 1 for analytical data) and 3-butyrylamino-1,4-benzoquinone-4-oxime (12%). m.pt 176–178°C. Found: C, 57.6; H, 5.8; N, 13.4. Calc. for $C_{10}H_{12}N_2O_3$: C, 57.7; H, 5.8; N, 13.4%.

Nitrosation of 3-*acylaminophenols in the presence of potassium tetrachloroplatinate(II)*

The nitrosation of 3-acylaminophenols in the presence of potassium tetrachloroplatinate(II) as described above afforded black solids, multi-

Table 1. Physical and analytical data for $M(qo)_2$

			Analysis found (calc.) (%)			
Complex	(%) Yield	M.p. (°C)	C	H	N	M
$Pd(5\text{-}Acqo)_2$	53	250–255	41.4(41.1),	3.0(3.0),	12.1(12.1),	43.9(43.8)
$Pd(5\text{-}Buqo)_2$	60	270–273	46.2(46.2),	4.2(4.2),	10.8(10.8),	38.8(38.8)
$Pd(5\text{-}Hxqo)_2$	68	242–245	52.3(52.3),	6.2(6.2),	10.2(10.2),	31.3(31.3)
$Pd(5\text{-}Etaqo)_2$	87	235–237	45.8(46.0),	4.9(4.7),	11.6(11.9),	37.7(37.4)
$Pt(5\text{-}Acqo)_2$	65	230–233	34.7(34.7),	2.5(2.5),	10.1(10.1),	52.7(52.7)
$Pt(5\text{-}Buqo)_2$	47	240–245	39.4(39.4),	3.6(3.6),	9.2(9.2),	47.8(47.8)
$Pt(5\text{-}Hxqo)_2$	52	241–243	45.2(45.2),	5.2(5.3),	9.0(8.8),	40.6(40.7)
$Pt(5\text{-}Etaqo)_2$	53	233–235	39.1(39.1),	4.0(4.0),	10.1(10.1),	46.8(46.8)

component by tlc with a typical nitrogen content of 18%. Assignment of credible formulae for these solids was not possible.

Reaction of Pd(5-Acqo)$_2$ *with triphenylphosphine*

To a suspension of Pd(5-Acqo)$_2$ (1.16 g, 2.5 mmol) in dimethoxy ethane/water (8 : 2, 100 cm^3), triphenyl phosphine (0.72 g, 2.6 mmol) was added and the mixture gently refluxed (24 h). Filtration of the resulting mixture afforded a black residue which was washed with ethoxyethane (3 × 20 cm^3) and dried *in vacuo* to give bis-(5-acetylamino-2-triphenyl-phosphoranylidene-aminophenolato) palladium(II) (2.03 g, 85%); m.pt 250–253°C decomp. Found: C, 65.27; H, 4.60; N, 5.86; P, 6.49; Pd, 11.09. Calc. for $C_{52}H_{44}N_2O_4P_2Pd$: C, 67.80; H, 4.40; N, 5.64; P, 6.52; Pd, 11.25%.

RESULTS AND DISCUSSION

Nitrosation of 5-acetylaminophenol and 5-butyrylaminophenol with sodium nitrite/acetic acid in the presence of palladium(II) chloride gave bis-(5-acylamino-1.2-benzoquinone-2-oximato) palladium(II) and bis-(5-butyrylamino-1,2-benzoquinone-2-oximato)palladium(II) respectively, both in high yield. The same complexes were obtained by the direct reaction of acidified aqueous palladium(II) chloride with methanolic solutions of other 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-oximes.

In contrast, the reaction of the acylaminophenols with sodium nitrite in the presence of potassium tetrachloroplatinate(II) failed to give complexes of the type Pt(qo)$_2$. Instead, these reactions afforded black solids which could not be satisfactorily separated. However elemental analysis of these solids showed them to have nitrogen : metal ratios greater than 2 : 1. The failure to isolate Pt(qo)$_2$ complexes by this method is not surprising because of the well-known propensity of platinum to form nitrosyl complexes.[10]

All the complexes were stable at room temperature, sparingly soluble in common organic solvents like methanol, but highly soluble in dimethyl sulfoxide. Thermal gravimetric analysis showed that the complexes decomposed in a single step at temperatures between 220°C and 350°C.

Studies of palladium and platinum complexes with ligands which are structurally related to 1,2-benzoquinone monooximes have shown that there are two possible modes of bonding. Thus, for the palladium and platinum complexes of violuric acids, spectroscopic evidence suggests that the ligand is bonded to the metal *via* the oxime nitrogen and an adjacent quinonoid carbonyl oxygen. Though this structure has not been confirmed crystallographically, the spectroscopic similarities between these compounds and their ruthenium analogue, the structure of which has been established by X-ray crystallography,[11] was taken as evidence of 5-membered chelate ring formation. By contrast, the X-ray crystal structure of the platinum(II) complex of 4-isonitroso-3-(R)-isoxazol-5-one shows the ligand to be bonded *via* the oximic group only.[12]

By analogy to previously reported M(qo)$_2$ complexes, the IR spectra of the complexes prepared during this study contained bands assignable to the quinonoid νCO at between 1620 cm^{-1} and 1600 cm^{-1}. In all cases, these bands occurred at lower frequency than for the corresponding bond in the IR spectrum of the free ligands.[13] This finding is consistent with the formulation of the complexes as bis-chelates in which the quinonoid carbonyl and oxime groups are both involved in bonding. In this respect, they show similarities with the ruthenium violurate complexes[11] but contrast sharply with the platinum isoxazolone complex.[12] The room temperature magnetic moment of all the complexes show them to be diamagnetic as is expected for four coordinate, planar, d^8 systems.[14]

The solution electronic spectra of both the palladium(II) and platinum(II) complexes in DMSO showed bands at approximately 890 nm and 450 nm. Though the unambiguous assignment of the bands in the spectra was not possible, these bands are believed to be due to *d–d* transitions. Molar absorptivities for the bands in the spectra of Pd(5-Buqo)$_2$ and Pt(5-Etaqo)$_2$ are given in Table 2. The spectra also showed absorption bands in the same region as the free ligands including a strong ligand band at 260 nm. The latter was blue shifted with respect to the free ligand (320–310 nm), and is consistent with strong metal–ligand interaction. Similar shifts have been observed in the electronic

Table 2. Observed electronic transition data for Pt(5-Etaqo)$_2$ and Pd(5-Buqo)$_2$

Complex	λ_{max} nm (cm^{-1})	ε M^{-1} m^{-2}
Pt(5-Etaqo)$_2$	883(11325)	1
(3.28 × 10^{-5} mol dm^{-3})	423(23640)	192
	260(38462)	161
Pd(5-Buqo)$_2$	894(11186)	4
(8.0 × 10^{-6} mol dm^{-3})	455(21978)	588
	258(38760)	345

spectra of related copper(II) and nickel(II) complexes.[15]

The ^1H, ^{106}Pd, and ^{195}Pt NMR spectra of the complexes prepared during this study were recorded in DMSO. The very broad nature of the Pd signal meant that no significant structural information could be derived from the spectra of the palladium complexes. In the case of the platinum(II) complexes, the ^{195}Pt NMR spectra (e.g. Fig. 1) contained a singlet between −1650 and −1750 ppm assignable to ^{195}Pt. The position of the signals suggests that there is little electron donation from the ligands to the metal. The downfield shift of the platinum nucleus compared to that reported for the starting material, K_2PtCl_4, −1764 ppm[16] confirms the change in the coordination environment of the metal and is within the range expected for an N_2O_2 coordination environment.[17] Further, the presence in the spectra of only one signal due to Pt confirms the symmetry, isomeric purity and monomeric nature of the complexes in solution.

The ^1H NMR spectra of the complexes displayed resonances for all ligand hydrogens. Importantly, these spectra provided no evidence of the coupling of ^{195}Pt to ^1H of the amino or the amido groups confirming that the metal in these complexes is bonded *via* the oxime nitrogen and the quinonoid oxygen only. In view of the proposed formulation of the complexes, such coupling would have required a four bond pathway which is generally not significant for ^{195}Pt–^1H interactions.

The LSIMS mass spectra (e.g. Fig. 2) of both the palladium(II) and platinum(II) complexes contained prominent molecular ion peaks. However in contrast to their nickel(II) and copper(II) analogues, the spectra contained no bimetallic species and thus confirmed the complexes as being monomeric in solution.

In contrast to the nickel(II) and copper(II) analogues, the palladium(II) and platinum(II) complexes failed to react with DMAD, pyridine or 2,2-dipyridyl. This was not surprising, since adduct formation would necessitate the expansion of the coordination sphere of the palladium and platinum nuclei. The latter is however not possible with ligands of the type considered in this study. The palladium(II) complexes reacted with triphenyl phosphine to give the iminophosphoranyl complex. This type of reaction was observed previously with complexes of first-row transition metal nuclei.[18]

The facile precipitation of palladium(II) and platinum(II) ions by reaction with 5-acylamino- and 5-alkylamino-1,2-benzoquinone-2-oximes affords a possible route to recovery of these metals from solution. Moreover, the apparent stability of the alkylamino substituted ligands in acid[19] offers some hope of ligand recycling from such a separation system.

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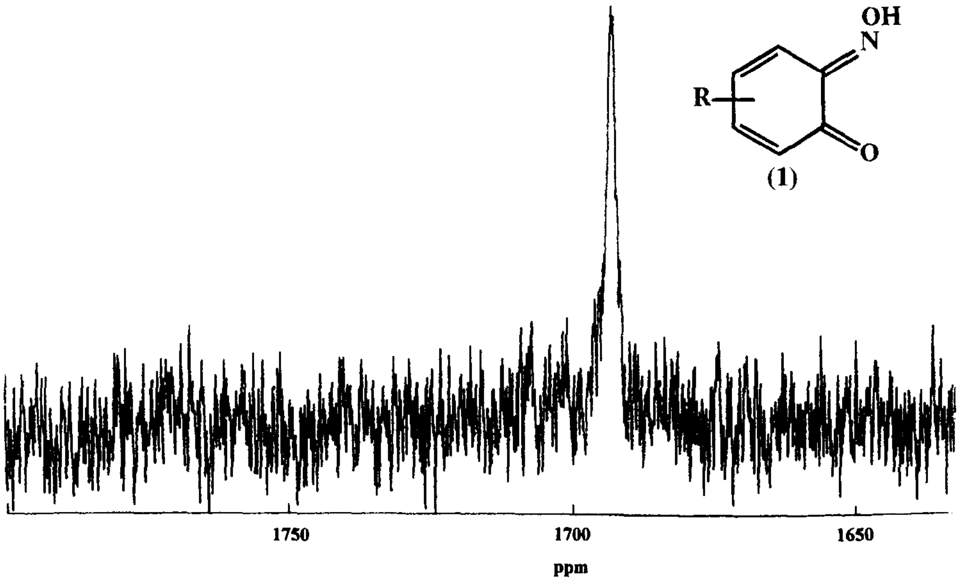

(1)

Fig. 1. ^{195}Pt NMR spectrum of $Pt(5\text{-}Etaqo)_2$ in DMSO.

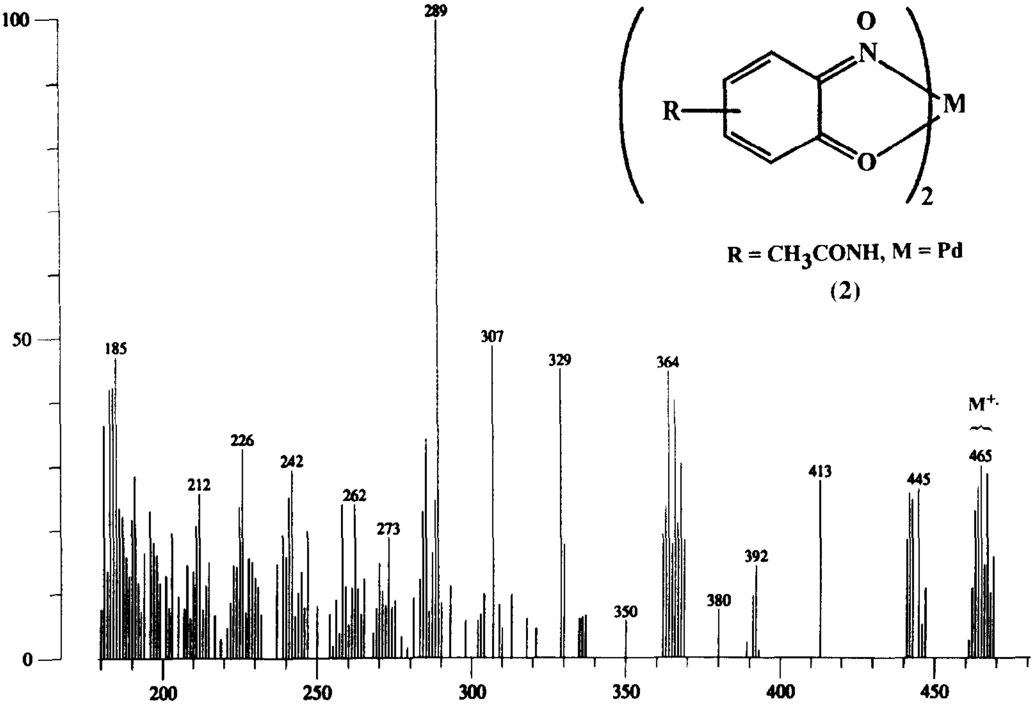

Fig. 2. LSIMS mass spectrum of Pd (5-Acqo)$_2$.

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