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Metal-mediated and solvent dependent chlorination of the nitrosonaphtholato ligand †

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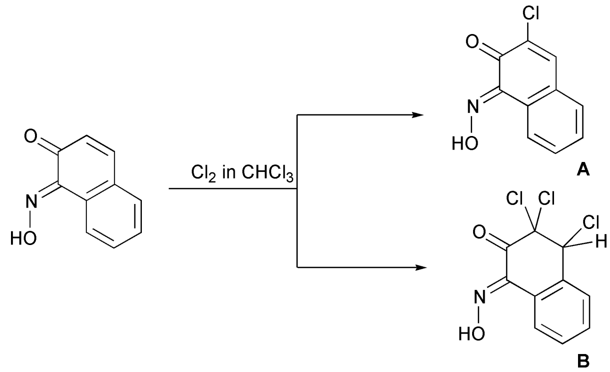
Reaction of K[PtCl$_3$(Me$_2$*S*O)] and 1,2-naphthoquinone-1-monoxime in water–dimethyl sulfoxide medium led to *cis*-(*S*,*N*)-[PtCl{2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] **1**. Chlorination of the latter in methanol readily generates, under mild conditions, the platinum(IV) compound *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_5$Cl$_2$(OMe)*N*O}(Me$_2$*S*O)] **2** with a chelating nitrosonaphtholato ligand bearing a new chiral atom due to concomitant chlorination and nucleophilic addition of a MeOH solvent molecule. The newly formed ligand was liberated from **2** by reaction with excess thiourea. The chlorination course is strongly dependent on the nature of solvent employed and in CHCl$_3$ also at room temparature the chlorination with either Cl$_2$ or NOCl brings about only oxidation of the metal center to achieve *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] **3**. All complexes were characterized by C, H, N, Cl and Pt elemental analyses, FAB$^+$ mass-spectrometry, IR and ^{1}H, ^{13}C{^{1}H} and ^{195}Pt NMR spectroscopies, and **2** and **3** by X-ray crystallography which indicates the chelating bidentate ligand adopts the nitroso form.

Introduction

Coordination of a substrate to a metal site usually makes the ligand more electrophilic and in a number of instances it becomes subject to a facile metal-mediated *nucleophilic* attack giving new, often fascinating, molecules.[1] Consequently, *electrophilic* reactions targeted to a coordinated ligand are rather rare although some examples of protonation, alkylation, halogenation, nitration and sulfonation[1–3] have been reported in the literature. As far as halogenation is concerned, attention should be drawn to the addition of chlorine to amines, with the sp^3-N atom bound to platinum giving chloroamides[4] or to ammonia in a ruthenium(II) complex giving ligated nitrosyl[5] and studies on bromination of azaheterocycles ligated to cobalt(III) or nickel(II) ions.[6,7] In the course of our on-going project directed towards, on the one hand, activation of substrates by their coordination to a metal center[8–10] and, on the other hand, organic syntheses involving metal complexes[11,12] we have investigated chlorination, by Cl$_2$, of the platinum(II) salicylaldoxime and salicylaldoximato(1−) complexes,[12] where—instead of the previously observed (for free oximes) Piloty reaction[13] or the formation of platinum(III) compounds[14] (for coordinated oximes)—we found both chlorination of the salicylaldoxime benzene ring and the oxidative addition of molecular chlorine to the platinum(II) center. The role of the metal center is, at least, dual. First, it is protecting the oxime nitrogen from the well-known oxidative deoximation[8] and second, the platinum site stabilizes the oxo(1−)-substituent in the benzene ring orienting the chlorination towards the *ortho* and *para* positions.

In continuation of the chlorination studies,[12] we attempted to extend the reaction to other aromatic oxime systems, *e.g.* involving coordinated 1,2-naphthoquinone-1-monoximato ($\rightleftharpoons$ nitrosonaphtholato) species. Zincke and Schmunk[15] have investigated chlorination of 1,2-naphthoquinone-1-monoxime by Cl$_2$ in chloroform and found its significant dependence on reaction conditions, *i.e.* under mild conditions the chlorination yielded 3-chloro-1,2-naphthoquinone-1-monoxime (**A** in Scheme 1), while at prolonged reaction times and strong excess of Cl$_2$ another product, **B** in Scheme 1, was isolated in good yield.



Scheme 1

We were interested to verify metal center control on the reactivity of 1,2-naphthoquinone-1-monoximato *ligand* as compared to free 1,2-naphthoquinone-1-monoxime. In the course of our studies we observed a remarkable solvent dependence in the chlorination and these results are reported in this article.

Results and discussion

Synthesis and characterization of [PtCl{2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] (1), a starting material

Quinone monoximes in general and 1,2-naphthoquinone-1-monoxime in particular are classic chelating ligands and numerous of their transition metal complexes have been extensively described in the literature.[16] Despite that, quinone monoxime (ato) compounds of platinum are quite scarce and only

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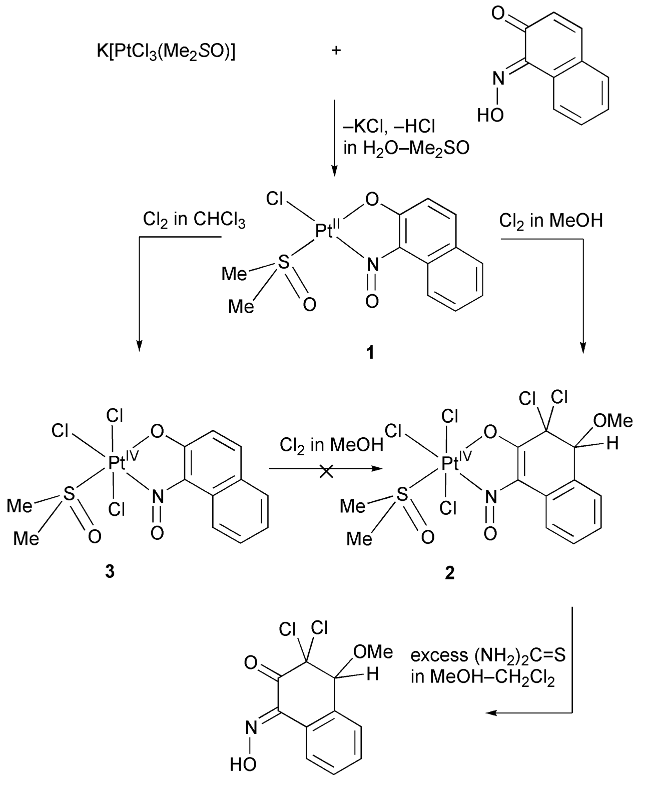
a few data, *i.e.* early publication on analytical applications of 1,2-naphthoquinone-1-monoxime in the chemistry of platinum(II)[17] and a rather recent synthetic work,[18] are known. It was reported in the latter article that treatment of $K_2[PtCl_4]$ with 5-*R*-1,2-benzoquinone-2-oxime brings about precipitation of [Pt(5-*R*-1,2-benzoquinone-2-oximato)$_2$] complexes which were characterized by elemental analyses, IR and ^{1}H and ^{195}Pt NMR spectroscopies but no X-ray structural characterization was performed.

As the starting material for preparation of the 1,2-naphthoquinone-1-monoxime platinum(II) complex we addressed K[PtCl$_3$(Me$_2$*S*O)][19] for the following two reasons: (i) S-coordinated dimethyl sulfoxide exhibits a strong *trans*-effect[20] thus facilitating substitution; (ii) a Pt(II)-bound dimethyl sulfoxide ligand with its characteristic spectral pattern[21] constitutes a good "internal" reference for ^{1}H NMR integration making easier the interpretation of spectral data. In addition, the position of methyl signals and the value of J_{PtH} are sensible to geometrical (*cis* or *trans*) arrangements of ligands and also to the oxidation state of the metal center.

In accord with our expectations, K[PtCl$_3$(Me$_2$*S*O)] reacts with 1,2-naphthoquinone-1-monoxime in a *ca.* 1 : 1 molar ratio to give a red-purple precipitate of [PtCl{2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] **1** in *ca.* 80% yield (Scheme 2).



Scheme 2

Chlorination of [PtCl{2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] (1)

Passage of excess Cl$_2$ through a chloroform solution of [PtCl{2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] **1** at 16–18 °C for 20–25 min results in *conventional* oxidative addition of chlorine to the metal center to give the appropriate platinum(IV) complex *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] (**3** in Scheme 2), while the nitrosonaphtholato ligand remains intact. The product **3** was also obtained by reaction of **1** and NOCl. The chlorination by Cl$_2$ proceeds differently—and in a *non-conventional* way—in methanol. In this case, we observed three processes operating together, *i.e.* chlorination of both the platinum center and the *meta*-position of the ring and methoxylation that occurs in the *para*-position, giving a chiral center on the newly formed nitrosoalkene species (**2** in Scheme 2).

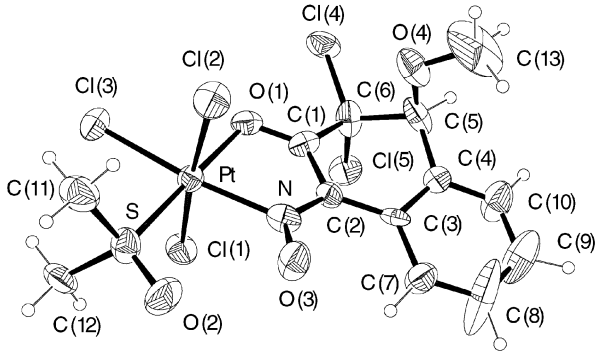


Fig. 1 ORTEP drawing of *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_5$Cl$_2$(OMe)*N*O}(Me$_2$*S*O)] **2** with atomic numbering scheme.

Our attempt to chlorinate the free 1,2-naphthoquinone-1-monoxime in methanol led to formation of a broad mixture of products from which we were able to isolate a material, in less than 3% yield, which—based on elemental analyses, FAB$^+$-MS, ^{1}H and ^{13}C{^{1}H} NMR spectra—was attributed to the free methoxylated ligand, 2-(O)C$_{10}$H$_5$Cl$_2$(OMe)NOH. In contrast to the latter reaction, chlorination/methoxylation of **1** proceeds smoothly and gives the product in 24% isolated yield along with separated unreacted starting material exhibiting poor solubility in MeOH. The yield difference in chlorination/methoxylation between free and coordinated ligand suggests that the methoxylation is metal-mediated. Moreover, treatment of **3** with Cl$_2$ in methanol for 1 h (Scheme 2) does not result in any further reaction (in particular, **2** is not formed). This observation allows us to assume that the chlorination/methoxylation is concerted with the oxidation of the platinum center.

It is worthwhile to mention two important issues. First, alkoxylation of coordinated ligands, *e.g.* coordinated organonitriles,[22] polypyridine[23] or even nitrosonaphtholato ligands,[24] although it is known, usually requires harsh reaction conditions, usage of a base-catalyzed route or application of highly nucleophilic alkoxides, RO$^-$. For instance, to perform methoxylation, the (1-nitroso-2-naphtholato)Cu complex and NaOMe were refluxed in anhydrous MeOH for 3 h to give the appropriate (4-methoxy-1-nitroso-2-naphtholato)Cu compound.[24] In our system, the methoxylation is facile and proceeds under mild conditions. Furthermore, the ligand formed in the course of Cl$_2$/MeOH addition was easily liberated with excess thiourea (Scheme 2), a typical reagent for the Kurnakov test,[2,25] and isolated in individual form after extraction and column chromatography. Hence, coherency and driving forces for metal-mediated chlorination and methoxylation of organic substrates should be explored further. Second, we found that the alkoxylation occurs only in MeOH but does not proceed in higher alcohols. Indeed, in ethanol or *n*-butanol as solvents for the chlorination, oxidation of the platinum center proceeds concurrently with oxidation of the solvent and, as a result, only [PtCl$_3${2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] **3** was isolated.

X-Ray structural determination of *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_5$Cl$_2$(OMe)*N*O}(Me$_2$*S*O)] (2) and *cis*-(*S*,*N*)-[PtCl$_3${2-(O)C$_{10}$H$_6$*N*O}(Me$_2$*S*O)] (3)

In both platinum(IV) complexes, the platinum exhibits a slightly distorted octahedral geometry with three meridional Cl ligands (Figs. 1 and 2).

The values of the Pt–Cl bond distances (Tables 1 and 2) [2.288(7)–2.313(8) Å for axial Cl and 2.331(7)–2.340(8) Å for equatorial Cl atoms] agree well with those of previously characterized platinum(IV) chloride compounds.[9] The S–O bond lengths [1.40(2) Å for **2** and 1.425(14) Å for **3**] are shorter than that found in a variety of Pt(II) sulfoxide complexes [*av.* 1.466(2) Å][26] but agree with the previously observed S–O distances for the other two (dimethyl sulfoxide)Pt(IV) complexes with

Table 1 Bond lengths (Å) and bond angles (°) for *cis*-(*S*,*N*)-[$PtCl_3$-{2-(O)$C_{10}H_5Cl_2$(OMe)*N*O}(Me_2*S*O)] (**2**)

Pt–Cl(1)	2.288(7)	C(2)–C(3)	1.44(3)
Pt–Cl(2)	2.313(8)	C(3)–C(4)	1.39(3)
Pt–Cl(3)	2.340(8)	C(3)–C(7)	1.43(3)
Pt–S	2.278(8)	C(4)–C(5)	1.50(3)
Pt–O(1)	2.069(1)	C(4)–C(10)	1.38(3)
Pt–N	2.07(2)	C(5)–C(6)	1.54(3)
S–O(2)	1.40(2)	C(5)–O(4)	1.44(3)
S–C(11)	1.76(3)	C(6)–Cl(4)	1.80(3)
S–C(12)	1.77(3)	C(6)–Cl(5)	1.76(3)
N–O(3)	1.21(2)	C(7)–C(8)	1.34(4)
C(1)–O(1)	1.28(3)	C(8)–C(9)	1.37(5)
C(1)–C(2)	1.43(3)	C(9)–C(10)	1.35(5)
C(1)–C(6)	1.52(3)	C(13)–O(4)	1.42(5)
C(2)–N	1.34(2)		
Cl(1)–Pt–Cl(2)	174.5(3)	O(1)–C(1)–C(6)	120.6(19)
Cl(1)–Pt–Cl(3)	92.4(3)	C(2)–C(1)–C(6)	115.2(18)
Cl(1)–Pt–S	91.4(3)	N–C(2)–C(1)	111.4(17)
Cl(1)–Pt–O(1)	87.8(4)	N–C(2)–C(3)	124.7(18)
Cl(1)–Pt–N	87.7(5)	C(1)–C(2)–C(3)	123.8(18)
Cl(2)–Pt–Cl(3)	91.5(3)	C(2)–C(3)–C(4)	117.7(18)
Cl(2)–Pt–S	92.6(3)	C(2)–C(3)–C(7)	126.4(18)
Cl(2)–Pt–O(1)	88.2(5)	C(4)–C(3)–C(7)	115.8(19)
Cl(2)–Pt–N	87.9(5)	C(3)–C(4)–C(5)	120.5(20)
Cl(3)–Pt–S	88.0(3)	C(3)–C(4)–C(10)	121.0(21)
Cl(3)–Pt–O(1)	92.7(4)	C(5)–C(4)–C(10)	118.5(22)
Cl(3)–Pt–N	172.1(5)	C(4)–C(5)–C(6)	109.4(19)
S–Pt–O(1)	179.0(5)	C(4)–C(5)–O(4)	112.8(20)
S–Pt–N	99.9(5)	C(6)–C(5)–O(4)	101.4(18)
O(1)–Pt–N	79.4(6)	Cl(4)–C(6)–Cl(5)	108.8(12)
Pt–S–O(2)	113.6(9)	Cl(4)–C(6)–C(1)	110.2(15)
Pt–S–C(11)	108.7(9)	Cl(4)–C(6)–C(5)	111.2(16)
Pt–S–C(12)	108.7(9)	Cl(5)–C(6)–C(1)	106.5(15)
O(2)–S–C(11)	108.5(12)	Cl(5)–C(6)–C(5)	109.3(16)
O(2)–S–C(12)	113.8(12)	C(1)–C(6)–C(5)	110.6(18)
C(11)–S–C(12)	102.8(12)	C(3)–C(7)–C(8)	122.0(26)
Pt–O(1)–C(1)	110.1(13)	C(7)–C(8)–C(9)	119.9(35)
Pt–N–O(3)	120.8(14)	C(8)–C(9)–C(10)	120.5(33)
Pt–N–C(2)	114.3(13)	C(4)–C(10)–C(9)	120.5(27)
O(3)–N–C(2)	124.8(18)	C(5)–O(4)–C(13)	114.3(2)
O(1)–C(1)–C(2)	124.2(19)		

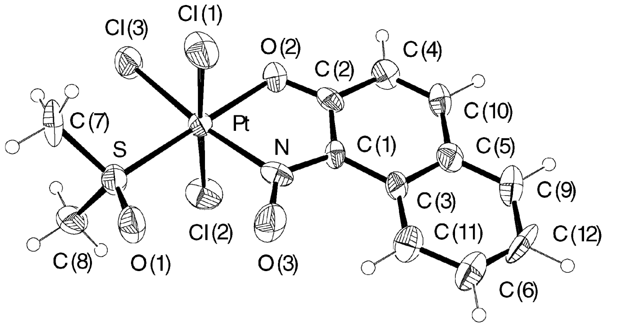
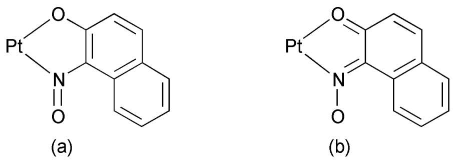


Fig. 2 ORTEP drawing of *cis*-(*S*,*N*)-[$PtCl_3${2-(O)$C_{10}H_6$*N*O}(Me_2*S*O)] **3** with atomic numbering scheme.

Table 2 Bond lengths (Å) and bond angles (°) for *cis*-(*S*,*N*)-[$PtCl_3$-{2-(O)$C_{10}H_6$*N*O}(Me_2*S*O)] (**3**)

Pt–Cl(1)	2.305(7)	C(1)–C(3)	1.44(2)
Pt–Cl(2)	2.302(7)	C(2)–O(2)	1.30(2)
Pt–Cl(3)	2.331(7)	C(2)–C(4)	1.42(2)
Pt–S	2.298(6)	C(3)–C(5)	1.42(2)
Pt–O(2)	2.039(12)	C(3)–C(11)	1.41(3)
Pt–N	2.04(2)	C(4)–C(10)	1.29(3)
S–O(1)	1.425(14)	C(5)–C(9)	1.39(3)
S–C(7)	1.75(2)	C(5)–C(10)	1.45(3)
S–C(8)	1.75(2)	C(6)–C(11)	1.37(3)
N–O(3)	1.26(2)	C(6)–C(12)	1.34(3)
N–C(1)	1.33(2)	C(9)–C(12)	1.40(3)
C(1)–C(2)	1.44(2)		
Cl(1)–Pt–Cl(2)	177.1(3)	Pt–N–O(3)	122.4(12)
Cl(1)–Pt–Cl(3)	91.8(2)	Pt–N–C(1)	116.1(11)
Cl(1)–Pt–S	89.4(2)	O(3)–N–C(1)	121.5(15)
Cl(1)–Pt–O(2)	88.7(4)	N–C(1)–C(2)	112.0(14)
Cl(1)–Pt–N	90.1(5)	N–C(1)–C(3)	126.5(15)
Cl(2)–Pt–Cl(3)	90.6(2)	C(2)–C(1)–C(3)	121.4(14)
Cl(2)–Pt–S	92.2(2)	O(2)–C(2)–C(1)	120.3(14)
Cl(2)–Pt–O(2)	89.6(4)	O(2)–C(2)–C(4)	120.2(15)
Cl(2)–Pt–N	87.3(5)	C(1)–C(2)–C(4)	119.4(15)
Cl(3)–Pt–S	90.0(2)	C(1)–C(3)–C(5)	115.9(15)
Cl(3)–Pt–O(2)	91.7(4)	C(1)–C(3)–C(11)	126.0(15)
Cl(3)–Pt–N	170.5(5)	C(5)–C(3)–C(11)	118.1(15)
S–Pt–O(2)	177.4(4)	C(2)–C(4)–C(10)	119.2(16)
S–Pt–N	99.3(5)	C(3)–C(5)–C(9)	118.5(16)
O(2)–Pt–N	79.0(6)	C(3)–C(5)–C(10)	119.5(15)
Pt–S–O(1)	114.3(6)	C(9)–C(5)–C(10)	122.0(17)
Pt–S–C(7)	109.9(8)	C(11)–C(6)–C(12)	122.3(21)
Pt–S–C(8)	110.3(7)	C(5)–C(9)–C(12)	121.7(19)
O(1)–S–C(7)	109.4(9)	C(4)–C(10)–C(5)	124.5(17)
O(1)–S–C(8)	110.9(9)	C(3)–C(11)–C(6)	120.6(18)
C(7)–S–C(8)	101.3(10)	C(6)–C(12)–C(9)	118.7(21)
Pt–O(2)–C(2)	112.5(10)		



(a) (b)

Fig. 3

reported[12] X-ray structures. Concurrently, the Pt(IV)–S bond distance [2.278(8) Å for **2** and 2.298(6) Å for **3**] is markedly longer than the Pt(II)–S bond distances [*av.* 2.226(3) Å],[26] thus suggesting the lack of any significant π bonding contribution in the Pt(IV)–S bond.

It is well-documented that free 1,2-naphthoquinone-1-monoximes exist in the quinonemonoxime form,[27] while their deprotonation and coordination to copper,[28] nickel,[29] ruthenium[30] and iridium[31] centers result in stabilization of the nitrosonaphtholato form in the complexes. In complete accord with those observations, in our platinum(IV) compounds **2** and **3** the coordinated bidentate ligands also adopt the nitroso form [Fig. 3(a)] rather than the quinonemonoxime one [Fig. 3(b)].

Indeed, the N–O distances [1.21(2) Å for **2** and 1.26(2) Å for **3**] are, on the one hand, similar to those in nitrosoalkanes bound to a Pt(II) center [1.21(2)–1.24(4) Å][32,33] and, on the other hand, shorter than the average N–O bond lengths in both free (*av.* 1.394 Å)[34] and coordinated oximes (*av.* 1.393 Å).[34] At the same time, the C–O bonds [*av.* 1.30(2) for **2** and 1.28(3) Å for **3**] are intermediate between typical C–O distances, *e.g.* in phenols (*av.* 1.362 Å),[35] and the mean C=O double bond (1.192 Å)[35] but closer to the former ones.

Concluding remarks

The current work is a meeting point of four of our projects, *i.e.* (i) activation of substrates by their ligation to a metal center;[3,9,10] (ii) organic syntheses involving metal complexes;[11] (iii) reactivity of oxime species,[8] and (iv) generation of nitroso-*C* species bound to a platinum center.[32] The results obtained from this study are of significance for at least the four following points which deserve further investigation. First, formation of a chiral center on selective addition of Cl_2/MeOH at the oxime ligand of the sulfoxide-containing platinum(II) complex suggests a study of the degree of asymmetric induction by the coordinated enantiomerically pure *S* or *R* sulfoxides, *e.g.* Me-(*p*-tolyl)S=O. The potential of chiral sulfoxides as asymmetric inductors and/or resolving agents in platinum(II) complexes has recently been clearly demonstrated.[36] Second, in the course of concerted chlorination and methoxylation we observed formation of the stable *nitrosoalkene* ligand. This reaction, if proved to be of general applicability, may represent a route to nitroso-*C* species whose platinum chemistry is poorly investigated. Third, the possibility of liberation from the metal center of the nitrosonaphtholato ligand opens up a convenient metal-mediated route for functionalised chiral ligands with a carbonyl monoxime moiety which otherwise cannot be obtained. Fourth, in addition to the synthetic works performed, we were interested in the preparation of sulfoxide–oxime platinum complexes for biological studies. Our interest in these systems is based on discoveries by Farrell and Van Beusichem[37,38] who have reported that (i) although a *cis*-geometry is usually necessary for the antitumor activity of Pt(II) amino complexes,[39] planar ligands such as pyridine enhance dramatically the cytotoxicity of the *trans*-complexes in comparison to that of both their *cis*-isomers and *trans*-$[PtCl_2(NH_3)_2]$;[37] (ii) mixed sulfoxide/N-donor ligands complexes exhibit antitumor propreties.[38] Bearing in mind that the C=N double bond gives planarity to oxime ligands, our sulfoxide/N-donor ligand systems might be logical candidates for biological studies and this project is underway.

Experimental

Materials and apparatus

Complex $K[PtCl_3(Me_2SO)]$ was obtained according to the published method.[19] 1,2-Naphthoquinone-1-monoxime (Reakhim) and solvents were obtained from commercial sources and used as received. Cl_2 for chlorination was obtained from $KMnO_4$ and HCl by a standard procedure[40] and then purified from HCl bubbling through water and dried over H_2SO_4. Nitrosyl chloride was obtained by reaction of a saturated aqueous solution of $NaNO_2$ with concentrated HCl and purified from HCl over $NaNO_2$, from NO_2 over moist KCl and then dried over $CaCl_2$.[41] Melting points were determined on a Kofler table. For TLC, Silufol UV 254 SiO_2-plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets, while spectra in the range 400–140 cm^{-1} were measured on a Hitachi FYS-3 spectrometer in polyethylene pellets. ^1H, $^{13}C\{^1H\}$ and ^{195}Pt NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ by using aqueous $K_2[PtCl_4]$ ($\delta = -1630$) as a standard, and the half height line width is given in parentheses.

Synthetic work and characterization

$[PtCl\{2\text{-}(O)C_{10}H_6NO\}(Me_2SO)]$ (1). $K[PtCl_3(Me_2SO)]$ (0.748 g, 1.8 mmol) was dissolved in water (3 mL) at 60 °C, cooled to 30 °C and a solution of 1,2-naphthoquinone-1-monoxime (0.300 g, 1.7 mmol) in dimethyl sulfoxide (4 mL, 51.7 mmol) was added. The purple slurry formed was stirred for 12 h, whereupon a red-purple precipitate was collected by filtration, washed with ten 10 mL portions of water, three 5 mL portions of ethanol and three 8 mL portions of diethyl ether and dried in air at 85–90 °C. Yield 0.702 g, 81%.

Anal. calc. for $C_{12}H_{12}NClO_3PtS$: C, 29.97; H, 2.52; N, 2.91; Cl 7.37; Pt 40.57; S, 6.67. Found: C, 30.17; H, 2.5; N, 3.0; Cl 7.61; Pt 40.38; S, 6.58%. FAB$^+$-MS, *m/z* (*I*, %): 482 $[M + H]^+$ (50), 446 $[M - Cl]^+$ (33). The compound has no characteristic mp; on heating it decomposes at 195–200 °C. TLC, $R_f = 0.62$ (acetone : chloroform 1 : 4, v/v). IR spectrum in KBr, selected bands/cm^{-1}: 1510 ms and 1590 ms ν(N=O), 1131 s ν(S=O), 430 s and 378 s γ(CSO), 351 ms and 338 ms ν(Pt–Cl). ^1H NMR in acetone-d_6: δ 3.58 (s + d, $^3J_{PtH}$ 23.88 Hz, 6H, Me_2SO), aromatic protons: 7.19 [d, J_{HH} 9.7 Hz, 1H, C(3)H], 9.10 [d, J_{HH} 8.4 Hz, 1H, C(4)H], 8.19 [d, J_{HH} 9.2 Hz, 1H, C(5)H], 7.65 [t, J_{HH} 7.5 Hz, 1H, C(6)H], 7.76 [t, J_{HH} 7.7 Hz, 1H, C(7)H] and 7.92 [d, J_{HH} 8.0 Hz, 1H, C(8)H]. ^1H NMR in $CDCl_3$: δ 3.55 (s + d, $^3J_{PtH}$ 24.0 Hz, 6H, Me_2SO), aromatic protons: 7.18 (d, J_{HH} 9.6 Hz, 1H), 7.56 (td, J_{HH} 7.5 Hz, J_{HH} 2.1 Hz, 1H), 7.67 (t, J_{HH} 7.8 Hz, 1H), 7.69 (d, J_{HH} 7.8 Hz, 1H), 7.89 (d, J_{HH} 9.6 Hz, 1H) and 9.12 (d, J_{HH} 8.0 Hz, 1H). ^{13}C NMR in $CDCl_3$: δ 44.9 (Me_2SO); 121.3, 123.7, 128.0, 130.2, 133.8, 147.6 (CH aryl), quarternary carbons were not detected even after 18 h accumulation time. ^{195}Pt NMR in $CDCl_3$: δ −2822 (300 Hz).

***cis*-(*S*,*N*)-$[PtCl_3\{2\text{-}(O)C_{10}H_6NO\}(Me_2SO)]$ (3).** Molecular chlorine was passed through a suspension of $[PtCl\{2\text{-}(O)C_{10}H_6NO\}(Me_2SO)]$ (0.207 g) in $CHCl_3$ (45 mL) at 16–18 °C for 20–25 min until the brown suspension transformed into a red solution. The solution thus formed was left to evaporate to *ca.* 4 mL at room temperature, giving a bright red precipitate which was filtered off, washed with 3–4 mL of cold (0 °C) chloroform and dried in a vacuum dessicator over KOH. Yield 0.204 g, 86%. The same product is formed when EtOH or *n*-BuOH is used instead of chloroform or when NOCl is passed through a suspension of **3** (0.20 g) in $CHCl_3$ (45 mL) at 16–18 °C for 40–45 min. Yields are *ca.* 30%.

Anal. calc. for $C_{12}H_{12}NCl_3O_3PtS$: C, 26.12; H, 2.20; N, 2.54; Cl, 19.28; Pt, 35.36; S, 5.81. Found: C, 26.3; H, 2.1; N, 2.5; Cl, 19.6; Pt, 35.2; S, 5.9%. FAB$^+$-MS, *m/z* (*I*, %): 551 $[M]^+$ (65), 516 $[M - Cl]^+$ (65). mp 240–241 °C (dec.). TLC, $R_f = 0.64$ (acetone : chloroform 1 : 6, v/v). IR spectrum in KBr, selected bands/cm^{-1}: 2915 m, 3004 m and 3026 ms ν(C–H), 1586 s ν(C=C), 1553 ν(N=O), 1166 ν(S=O), 1020 ms ν(C–O), 430 s γ(CSO). ^1H NMR in acetone-d_6: δ 3.88 (s + d, $^3J_{PtH}$ 17.1 Hz, 6H, Me_2SO), 7.44 (d, J_{HH} 9.6 Hz, 1H) and 8.31 (d, J_{HH} 9.6 Hz, 1H) (substituted aryl ring), 7.81 (td, J_{HH} 7.5 Hz, J_{HH} 1.2 Hz, 1H), 7.92 (td, J_{HH} 7.8 Hz, J_{HH} 1.5 Hz, 1H), 8.04 (d, J_{HH} 7.5 Hz, 1H) and 8.89 (d, J_{HH} 7.8 Hz, 1H) (unsubstituted aryl ring). ^{13}C NMR in acetone-d_6: δ 43.9 ($^2J_{PtC}$ 32.7 Hz, Me_2SO); 122.1, 124.7, 131.1, 132.6, 135.7, 151.2 (C–H), quarternary carbons were not detected even after 18 h accumulation time. ^{195}Pt NMR in acetone-d_6: δ −387 (300 Hz).

***cis*-(*S*,*N*)-$[PtCl_3\{2\text{-}(O)C_{10}H_5Cl_2(OMe)NO\}(Me_2SO)]$ (2).** Molecular chlorine was passed through a suspension of $[PtCl\{2\text{-}(O)C_{10}H_6NO\}(Me_2SO)]$ (0.168 g) in MeOH (50 mL) at 16–18 °C for 20–25 min. The reaction mixture was filtered off from undissolved starting material (0.101 g), and the filtrate was then saturated with Cl_2 at 18 °C and left to evaporate to *ca.* 10 mL. The dark red crystals formed were collected by filtration, washed with two 3 mL portions of cold (0–5 °C) methanol and dried in air at room temperature. Yield 0.054 g, 24%.

Anal. calc. for $C_{13}H_{14}NCl_5O_4PtS$: C, 23.92; H, 2.17; N, 2.15; Cl, 27.16; Pt, 29.89; S, 4.91. Found: C, 24.2; H, 2.3; N, 1.9; Cl, 27.3; Pt, 29.7; S, 4.9%. FAB$^+$-MS, *m/z* (*I*, %): 652 $[M - H]^+$ (48), 581 $[M - 2Cl]^+$ (100). mp 164 °C (dec.). TLC, $R_f = 0.44$ (acetone : chloroform 2 : 1, v/v). IR spectrum in KBr, selected bands/cm^{-1}: 3009 m, 2956 vw, 2918 m and 2828 vw ν(C–H), 1550 ms ν(N=O), 1113 s ν(S=O), 1077 ms ν(C–O), 1023 s ν(C–O) in the chelate ring, 736 ms ν(C–Cl), 457 ms γ(CSO). ^1H NMR in acetone-d_6: δ 3.45 (s, 3H, OMe), 3.96 (s + d, $^3J_{PtH}$ 19.4 Hz, 3H, Me_2SO), 3.98 (s + d, $^3J_{PtH}$ 18.6 Hz, 3H, Me_2SO) [nonequivalency of methyl groups of coordinated Me_2SO has previously been observed],[42] 5.11 [s, 1H, C(4)H], 7.64 (td, J_{HH} 7.8 Hz, J_{HH} 2.1 Hz, 1H), 7.68 (td, J_{HH} 7.5 Hz, J_{HH} 1.8 Hz, 1H), 7.79 (dd, J_{HH} 6.6 Hz, J_{HH} 2.1 Hz, 1H), 8.44 (dd, J_{HH} 7.5 Hz, J_{HH} 1.8 Hz, 1H) (aryl). ^{13}C NMR in acetone-d_6: δ 45.1 (s + d, $^2J_{PtC}$ 34.8 Hz, Me_2SO), 45.4 (s + d, $^2J_{PtC}$ 36.6 Hz, Me_2SO), 59.2 (OMe), 86.8 [C(4)H]; 126.2, 130.6, 131.0, 131.8 (CH aryl); 125.6, 132.9 (quarternary C, aryl); C–NO and C–O were not detected. ^{195}Pt NMR in acetone-d_6: δ −401 (300 Hz).

Liberation of the ligand $2\text{-}(O)C_{10}H_5Cl_2(OMe)NOH$. A solution of thiourea (0.146 g, 1.92 mmol) in a mixture of CH_2Cl_2–MeOH (3 : 1 v/v, 9 mL) was added to a solution of $[PtCl_3\{2\text{-}(O)C_{10}H_5Cl_2(OMe)NO\}(Me_2SO)]$ (0.103 g, 0.16 mmol)

Table 3 Crystal data and structure refinement for [$PtCl_3${2-(O)$C_{10}H_5Cl_2$(OMe)*N*O}(Me_2*S*O)] (**2**) and [$PtCl_3${2-(O)$C_{10}H_6$*N*O}(Me_2*S*O)] (**3**)

	2	**3**
Empirical formula	$C_{13}H_{14}NCl_5O_4PtS$	$C_{12}H_{12}NCl_3O_3PtS$
Formula weight	652.7	551.7
Space group	*Pbca*	$P\bar{1}$
Crystal system	Orthorhombic	Triclinic
a/Å	13.799(5)	7.227(2)
b/Å	12.217(4)	10.020(3)
c/Å	24.197(7)	11.877(5)
α/°	90	72.80(3)
β/°	90	91.18(3)
γ/°	90	101.06(2)
V/Å^3	4079(4)	806(1)
Z	8	2
D_c/Mg m^{-3}	2.125(2)	2.274(3)
$F(000)$	2480	520
μ(Mo-Kα)/mm^{-1}	8.01	9.78
$2\theta_{max}$/°, sin θ/λ for data collection	60.02, 0.704	59.18, 0.695
Refinement method	Full-matrix (anisotropic for all non-H atoms) least-squares based on F	
Crystal size/mm	0.45 × 0.23 × 0.19	0.2 × 0.1 × 0.01
Index ranges	$0 < h < 14, 0 < k < 14, 0 < < 14$	$0 < h < 8, -7 < k < 7, -7 < l < 7$
No. collected reflections	2602	1619
No. unique reflections [$F(hkl) \geq 4\sigma(F)$]	2253	1473
No. refinement parameters	282	238
Extinction coefficient	—	—
Goodness-of-fit on F	1.410	1.101
R	0.0401	0.0379
wR	0.0520	0.0345

in dichloromethane (20 mL) and the reaction mixture was refluxed for 30 min with stirring, whereupon it was cooled to 0 °C and the yellow precipitate formed was removed by filtration. The filtrate was evaporated to dryness in vacuum at 18–25 °C and extracted with three 3 mL portions of diethyl ether. The extract was evaporated to dryness in vacuum at room temperature and the residue formed was dissolved in chloroform (1 mL) and purified by column chromatography on silica gel (Silicagel L 40/100 µm, CHEMAPOL; chloroform : acetone 3 : 1, v/v), collecting the second colourless fraction.

2-(O)$C_{10}H_5Cl_2$(OMe)NOH. Anal. calc. for $C_{11}H_9NCl_2O_3$: C, 48.20; H, 3.32; N, 5.11. Found: C, 47.63; H, 3.09; N, 5.02%. FAB$^+$-MS, *m*/*z*: 274 [M + H]$^+$. mp 169 °C (dec.). TLC, $R_f = 0.65$ (acetone : chloroform 1 : 4, v/v). ^{1}H NMR in acetone-d_6: δ 3.42 (s, 3H, OMe), 4.97 [s, 1H, C(4)H], 7.60 [m, 2H, C(6 and 7)H], 7.70 (d, J_{HH} 4.6 Hz, 1H) and 8.72 [d, J_{HH} 4.6 Hz, 1H, C(5 and 8)H], 12.8 (s, br, 1H, NOH). ^{13}C NMR in acetone-d_6: δ 58.1 (OMe), 65.4 [C(3)Cl_2], 87.0 [C(4)H], 129.7, 130.3, 130.8, 131.4, [C(5,6,7,8)H, aryl], 126.8, 134.4 [quarternary carbons C(9), C(10)]; quarternary carbons C=O and C=NOH were not detected.

Chlorination of 1,2-naphthoquinone-1-monoxime in MeOH. Molecular chlorine was passed through a suspension of 1,2-naphthoquinone 1-monooxime (1.3 g) in MeOH (50 mL) at 15–20 °C for 20–25 min. The reaction mixture was left to stand overnight whereupon the solvent was removed *in vacuo*. The oily residue formed was dissolved in chloroform (10 mL) and the solvent was evaporated to *ca.* ¼ of the initial volume to give colourless crystals of 2-(O)$C_{10}H_5Cl_2$(OMe)NOH which were mechanically separated from product **B** depicted in Scheme 1. The yield was less than 3% by NMR integration of the crude reaction mixture.

X-Ray crystal structure determinations

Red needles of **3** were obtained by slow evaporation of the reaction mixture with added toluene (1 : 1, v/v) in a long (100 mm) and narrow (Ø 4 mm) tube at 16–18 °C, while dark red prismatic crystals of **2** were obtained directly from the reaction mixture. The cell dimensions and symmetry of crystals were defined in a Weissenberg camera. Diffraction data were collected on a Syntex $P2_1$ diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å), ω-scan method with variable scan rate (2–29.3° min^{-1}). Weak reflections were neglected. The intensities of three standard reflections were measured every 50 reflections and showed practically no change with time (±1%). After Lorentz and polarization correction both structures were solved by the heavy atom method and, following Fourier synthesis, refined by full-matrix (anisotropic for all non-hydrogen atoms and isotropic for hydrogen atoms) least-squares methods based on F using 1473 (**2**) and 2253 (**3**) unique reflections [$F(hkl) \geq 4.0\sigma(F)$] to a final R factor 0.0379, R_w 0.0345 for **2** and final R factor 0.0401, R_w 0.0520 for **3**. The extinction correction was not made. Before anisotropic refinement absorption correction was made using the DIFABS[43] program. Hydrogen atoms were included at fixed calculated positions, based on geometrical requirements. All experimental data processing, structure solution and refinement was executed using the CSD[44] program. Molecular graphics were obtained using the ORTEP III program.[45] Crystal data are given in Table 3, bond distances and angles are presented in Tables 1 and 2.

CCDC reference numbers 166156 and 166157.

See http://www.rsc.org/suppdata/dt/b1/b103000k/ for crystallographic data in CIF or other electronic format.

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