Chlorination of Platinum-Bound Salicylaldoxime. The First Example of a Structurally Characterized Monodentate Salicylaldoxime-Type Ligand

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The reaction of $K_2[PtCl_4]$ and salicylaldoxime in an approximate 1:2 molar ratio in water resulted in the isolation of a mixture of four compounds from which $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$ (**1**) and $[PtCl(OC_6H_4CH{=}NOH)(HOC_6H_4CH{=}NOH)]$ (**2**) were isolated, whereas the other two were shown to be unstable and decomposed both in solution and on SiO_2 during chromatography. Chlorination of **1** and **2** with Cl_2 resulted in the oxidative addition of chlorine to the platinum(II) center and in the chlorination of the benzene ring, giving the platinum(IV) complexes $[PtCl_2(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)_2]$ (**3**) and $[PtCl_3(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)(3,5,2\text{-}Cl,Cl,HOC_6H_2CH{=}NOH)]$ (**5**), respectively, containing commercially unavailable 3,5-dichloro-2-hydroxybenzaldehye oxime. Alternatively, treatment of **1** with NOCl resulted only in the oxidation of the platinum(II) center to furnish $[PtCl_2(o\text{-}OC_6H_4CH{=}NOH)_2]$ (**4**), whereas the benzene rings of salicylaldoximato ligands remained intact. All complexes were characterized by C, H, N, Cl and Pt elemental analyses, FAB$^+$ mass spectrometry, IR and ^1H, $^{13}C\{^1H\}$ and ^{195}Pt NMR spectroscopy. Compounds **1**, **3** and **5** were analyzed by X-ray crystallography. In **1**, the salicylaldoximato ligands adopt a *trans* configuration and the hydrogen atoms of the OH groups are involved in intramolecular hydrogen bonding, forming five-membered rings. In **3**, every molecule of the complex forms the repeating unit for a self-assembly that produces infinite one-dimensional polymeric chains directed along the z axis held by hydrogen bonds. The complex **5** represents the first example of a structurally characterized metal complex with a monodentate salicylaldoxime-type ligand, although the conventional bidentate *N,O*-coordination mode is a classical topic in coordination chemistry.

Introduction

Although oximes (RR′C=NOH) display one of the most versatile modes of reactivity in metal-mediated processes, their conversions at a metal center have attracted attention only in the last decade.[1,2] Being involved in these studies for the last five years, we have been investigating some aspects of oxime ligand reactivity, in particular with respect to (*i*) the OH group, e.g. their facile deprotonation and the self-assembly of the oxime-oximato species formed,[3] addition to nitriles bound to Pt^{IV},[4,5] Re^{IV} [6] and Rh^{III} [7] ions, addition to ketones in a Pt^{IV} complex,[8] formation of metallacycles accompanied by the OH addition;[9] (*ii*) the N−OH group, e.g. its oxidative addition to an electron-rich rhenium(I) center,[10] (*iii*) the oxime N atom, e.g. its oxidation to give (nitrosoalkane)Pt complexes[11,12] or its reduction in a strongly acidic solution,[13] (*iv*) the C=N group, e.g. its metal-mediated hydrolysis[14] and the conversion into the nitrile group upon Ru-assisted dehydration of aldoximes.[15] Following these studies, we turned our attention to the reactions of *peripheral* R/R′ groups and have recently reported the chlorination, by molecular chlorine, of the platinum(II) salicylaldoxime, *trans*-(*S,N*)-$[PtCl_2(o\text{-}HOC_6H_4\text{-}CH{=}NOH)(Me_2SO)]\cdot H_2O$, and the salicylaldoximato(1$^-$), *trans*-(*S,N*)-$[PtCl(o\text{-}OC_6H_4CH{=}NOH)(Me_2SO)]$, complexes.[16] Instead of the Piloty reaction, which in the case of aldoximes leads to chloro oximes, RC(Cl)=NOH (*via* RCH(Cl)−N=O),[17] or to the formation of platinum(III) derivatives previously detected upon the chlorination of (*vic*-dioximato)platinum(II) compounds,[18] we observed both the chlorination of the salicylaldoxime benzene ring and the oxidative addition of Cl_2 to the platinum(II) center. Conclusions that can be derived from the latter work indicate that platinum acts as a protecting center for the oxime functionality and this allows for the formation of the chlorinated species, which cannot be synthesized by direct chlorination of the corresponding salicylaldoxime.

Our interest in the continuation of the chlorination experiments lied in at least three areas. Firstly, we wondered if the protection of the NOH group and the concomitant chlorination of the benzene ring was peculiar for the complexes being investigated or if the reaction could be extended to other salicylaldoxime platinum compounds. Secondly, it was expected to contribute to the almost unexplored chemistry of salicylaldoxime coordinated to plat-

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inum. Thirdly, our own observations[16] and also some earlier studies[19] indicated the possibility of *N-monodentate* coordination of classical *bidentate chelating* ligands such as salicylaldoxime and its derivatives. We therefore focused our efforts on the structural determination of previously uncharacterized monodentate species. In this paper we present the revisited synthesis (previously reported by Cox et al.[19]) of two salicylaldoxime complexes of platinum(II). We report the X-ray structure of one of the compounds, as well as the isolation of a new product, chlorination studies of the two platinum(II) compounds with Cl_2 and NOCl giving, in one case, a Pt^{IV}-based *monodentate* chlorinated salicylaldoxime that was successfully characterized by X-ray single-crystal diffraction. Furthermore, an unusual intermolecular hydrogen bonding was shown by an X-ray study of one of the Pt^{IV} products. This hydrogen bonding results in a self-assembly, forming infinite one-dimensional polymeric chains, and is significant in the developing field of self-assembly of metal complexes by hydrogen bonding, which has applications in crystal engineering and materials science.[3]

Results and Discussion

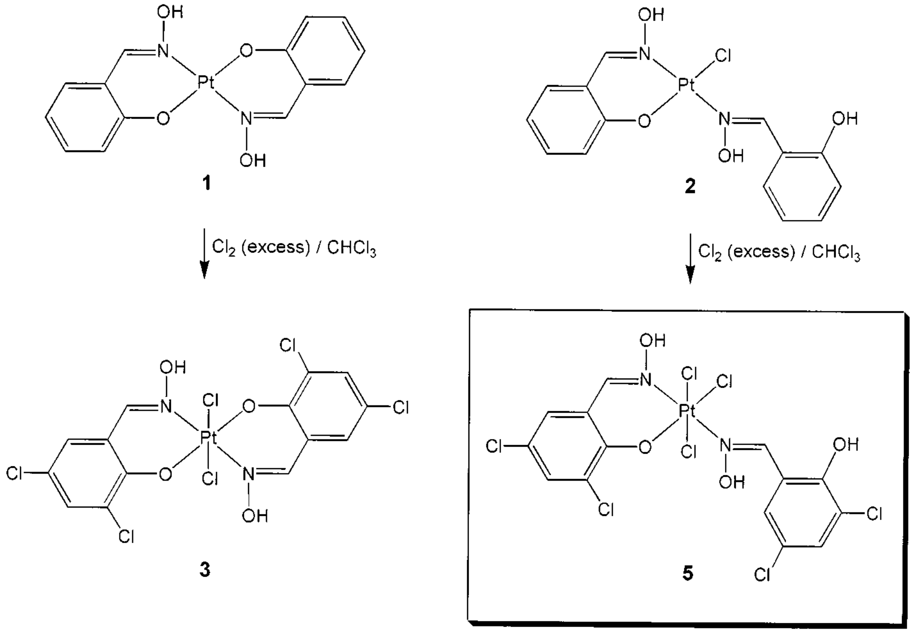
Synthesis of Platinum(II) Compounds with Salicylaldoxime(ato) Ligands

Cox and co-authors[19] reported the reaction of $K_2[PtCl_4]$ and salicylaldoxime in a molar ratio of approximately 1:2 in water, resulting in the isolation of a mixture of the *bis*-chelate $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$ and the complex $[PtCl_2(o\text{-}HOC_6H_4CH{=}NOH)_2]$ that contains, as had been suggested,[19] monodentate salicylaldoxime ligands. It was pointed out[19] that the latter complex is unstable in solutions and decomposes on standing.

The ^{195}Pt NMR spectrum of the crude mixture, prepared according to a known procedure,[19] showed four signals of similar intensities, and TLC showed four well-defined spots. The signal at $\delta = -1611$ (480 Hz) in the spectrum was assigned to $[Pt(o\text{-}OC_6H_4CH{=}NOH)_2]$ (**1**) and the peak at $\delta = -1842$ (360 Hz) was ascribed to $[PtCl(OC_6H_4CH{=}NOH)(HOC_6H_4CH{=}NOH)]$ (**2**) (both are depicted in Scheme 1). The former was isolated by following the method of Cox,[19] and the latter was separated from the mixture by chromatography, and both were characterized by C, H, N, Cl and Pt elemental analyses, FAB^+ mass spectrometry, IR and ^1H, $^{13}C\{^1H\}$ and ^{195}Pt NMR spectroscopy. Compound **1** was analyzed by X-ray crystallography. Our attempts to isolate two other compounds [^{195}Pt NMR: $\delta = -1999$ (500 Hz) and $\delta = -2064$ (250 Hz)] failed because of their decomposition both in solution and on SiO_2 during chromatography. Although the values of the chemical shifts for these yet unidentified species seem to be reasonable for *cis* and *trans* isomers of **1**, no further evidence in favor of these complexes was obtained.

Complex **1** was characterized by X-ray single-crystal diffractometry. The coordination polyhedron of the centrosymmetric compound is a slightly distorted square plane (Figure 1).

The salicylaldoximato ligands in the structure adopt a *trans* configuration and the hydrogen atoms of the OH groups are involved in intramolecular hydrogen bonding, forming a five-membered ring. Interestingly, these H atoms, found from the difference synthesis, are disordered by two positions with a 50% population at each one, i.e. at the oxime =NOH group and at the phenol OH group, thus indicating the existence of two solid tautomers. However, careful comparison of bond lengths in the chelated ring of **1** with (*i*) typical bond lengths in oxime/oximato compounds; (*ii*)



Scheme 1

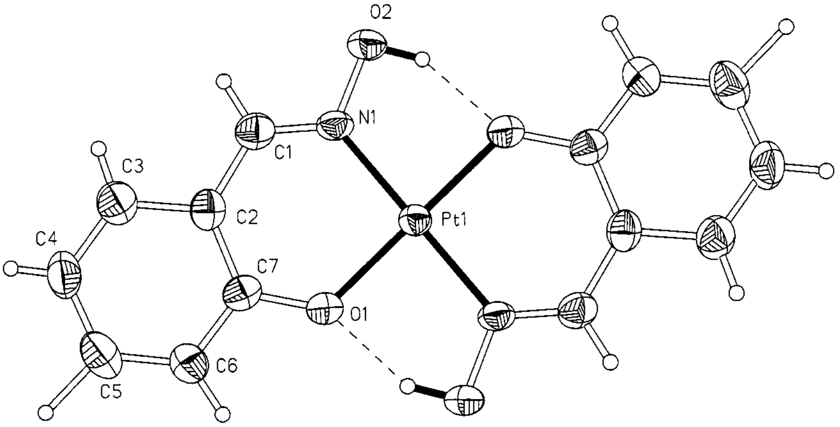


Figure 1. View of *trans-(N,N)*-[Pt(*o*-$OC_6H_2CH{=}NOH)_2$] (**1**) with atomic numbering

Table 1. Selected bond lengths for the (salicylaldoximato)Pt^{II} complexes and literature data

Complexes/bond lengths, Å	=N−O	C=N	C−C(H)=	C=C	C−O
[Pt(*o*-$OC_6H_4CH{=}NOH)_2$] (**1**)	1.385(8)	1.268(9)	1.434(11)	1.415(11)	1.327(9)
[$PtCl_2$(3,5,2-Cl,Cl,$OC_6H_2CH{=}NOH)_2$] (**3**)	1.367(7)	1.292(9)	1.452(10)	1.409(10)	1.331(8)
[$PtCl_3$(3,5,2-Cl,Cl,$OC_6H_2CH{=}NOH$)-(3,5,2-Cl,Cl,$HOC_6H_2CH{=}NOH$)] (**5**)					
monodentate ligand	1.390(16)	1.299(17)	1.44(2)	1.40(2)	1.36(2)
bidentate ligand	1.390(17)	1.270(19)	1.43(2)	1.41(2)	1.340(16)
ref. average[31,32]	1.402[a] 1.367−1.393[b]	1.281[c]	1.455[d]	1.397[e]	1.321[f]

[a] N−O in (C=)(CC_{sp^3})−C=N−OH oximes. − [b] N−O in oxime and oximato Pt^{II} complexes.[3] − [c] C=N in oximes. − [d] $C_{sp^3}{-}CC_{sp^2}$ conjugated. − [e] In substituted phenyl ring. − [f] Aryloxy complexes.

distances within both the chelated salicylaldoximato ring and the monodentate salicylaldoxime ligand in the two platinum(IV) complexes from both the current (see Table 1) and previous work;[16] and (*iii*) bond lengths in some other salicylaldoximato complexes,[20] does not give any further evidence in favor of the phenol tautomeric structure.

Chlorination of [Pt(*o*-$OC_6H_4CH{=}NOH)_2$] (1)

Passage of excess Cl_2 through a chloroform solution of **1** for 20 min at room temperature resulted in the oxidative addition of chlorine to the platinum(II) center and in the chlorination of the benzene ring (Scheme 1). As a result of the overall process, the platinum(IV) complex [$PtCl_2$(3,5,2-Cl,Cl,$OC_6H_2CH{=}NOH)_2$] (**3**) (Scheme 1), containing commercially unavailable 2-hydroxy-3,5-dichlorobenzaldehyde oxime was isolated in 85% yield. The oxime 3,5,2-Cl,Cl,$HOC_6H_2CH{=}NOH$ was prepared earlier by the chlorination of salicylaldehyde to give 3,5,2-Cl,Cl,$HOC_6H_3CH{=}O$ and its subsequent condensation with hydroxylamine.[21] We have also observed that when nitrosyl chloride is used instead of molecular chlorine, only oxidation of the central ion is observed, to give [$PtCl_2$(*o*-$OC_6H_4CH{=}NOH)_2$] (**4**), and the benzene rings remain intact.

As already indicated,[16] chlorination of *free* salicylaldoxime under the same conditions as for the platinum(II) complexes gave a variety of products due to oxidative deoximation[1,2] and chlorination, with no dominant compound. The latter fact suggests that coordination affects the reaction by blocking and thus protecting the oxime N atom from oxidation, thus also making the chlorination selective.

The structure of **3** was determined by X-ray crystallography. In the centrosymmetric complex, the coordination polyhedron of platinum is a slightly distorted octahedron with the ligands in a *trans* configuration (Figure 2). All bonds around the Pt center have normal values. The chelate ring is in the envelope-like conformation where the Pt atom deviates from the organic unit by 0.256 Å.

The oxime group is involved in an unusual hydrogen bonding (Figure 3), e.g. the *intermolecular* − rather than *intramolecular* as in the case of [Pt(*o*-$OC_6H_4CH{=}NOH)_2$] (**1**) − O(2)−H···Cl(3) hydrogen bond [O(2)···Cl(3)(*x,y,z* − 1) = 3.155, H···Cl(3) 2.34 Å, angle O(2)−H···Cl(3) 161°]. According to Wells,[22] O···Cl^- distances in the range 2.95−3.4 Å are found for O−H···Cl^- hydrogen bonds (for Cl^-···H_3O^+ the distance is 2.95[22]). Every molecule of the complex forms the repeating unit for a self-assembly that produces infinite one-dimensional polymeric chains directed along the *z* axis held by H-bonds. It is worth noting that the study of self-assembly of metal complexes, in particular by hydrogen bonding, is a rapidly developing field

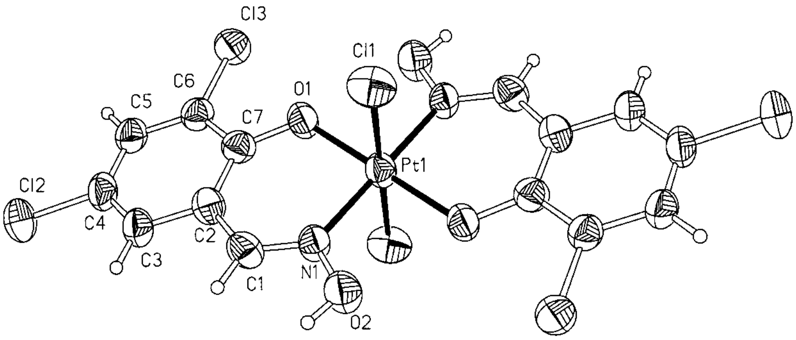


Figure 2. View of *trans-(N,N)*-[$PtCl_2(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)_2$] (**3**) with atomic numbering

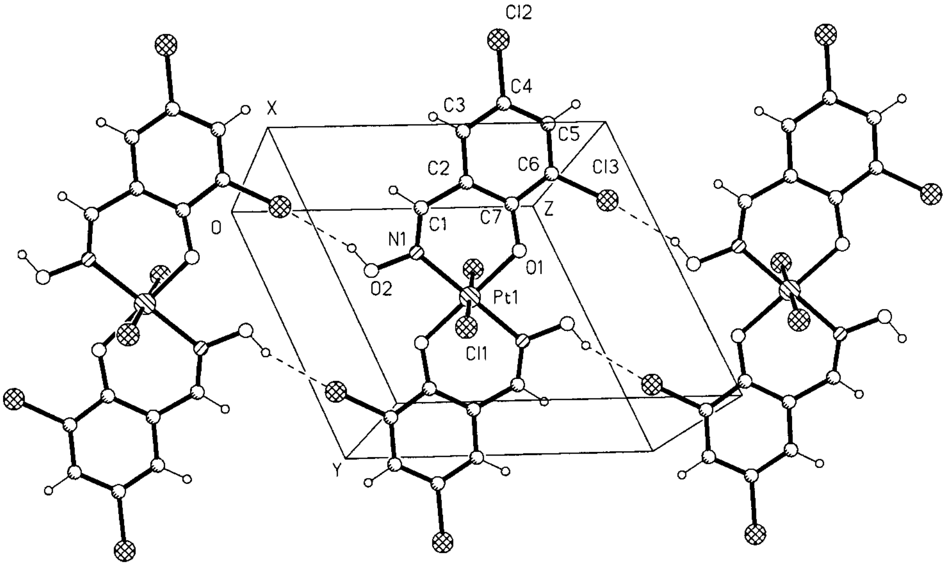


Figure 3. Packing diagram for *trans-(N,N)*-[$PtCl_2(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)_2$] (**3**) showing the hydrogen-bonding scheme

that is intrinsic for crystal engineering and materials science,[3] and from that point of view, it is likely that the observation of hydrogen bonding in the (salicylaldoximato)-Pt^{IV} compound deserves further investigation.

Chlorination of [$PtCl(OC_6H_4CH{=}NOH)(HOC_6H_4CH{=}NOH)$] (2) and Crystal Structure of *trans-(N,N)*-[$PtCl_3(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)(3,5,2\text{-}Cl,Cl,HOC_6H_2CH{=}NOH)$] (5)

The chlorination of **2** with molecular chlorine proceeded similarly to that described above for **1** (Scheme 1), but the reaction with NOCl gave a variety of products, which were not separated. In the former case, both monodentate and chelating ligands are chlorinated selectively at the 3- and 5-positions of the aromatic ring rather than at the oxime CH=N group, indicating that coordination of the phenolic oxygen has no influence on the course of the chlorination. However, the most interesting result from this part of the work is that the salicylaldoxime ligand maintains its monodentate coordination, which was unambiguously confirmed by X-ray study. In *trans-(N,N)*-[$PtCl_3(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)(3,5,2\text{-}Cl,Cl,HOC_6H_2CH{=}NOH)$] (**5**), the platinum exhibits a slightly distorted octahedral geometry with three meridian Cl ligands (Figure 4).

The values of the Pt−Cl bond lengths (Table 2) agree well with those of previously characterized platinum(IV) chloride compounds,[4,5] although the Pt−Cl(2) bond [2.316(4) Å] is slightly shorter that the other two [2.338(4) and 2.336(4) Å]. The most interesting feature of the structure is the presence of two different salicylaldoxime species, i.e. one is an unusual monodentate ligand and the other is the conventional *N,O*-salicylaldoximato chelate. Surprisingly, the corresponding bond lengths in the two types of salicylaldoximato ligands are the same within 3σ. Although the hydrogen atoms at the =NOH moieties were not found, the bond lengths indicated in Table 1 favor the oxime tautomeric structure in both cases.

IR and NMR Spectroscopic Characterization of 5

In IR spectra, only one band of ν(C=N) stretching vibrations appears for the *bis*-chelated species **1** and **3**, whereas complexes **2** and **5**, containing both chelating and monodentate ligands, display two ν(C=N) bands. ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **3** show only one set of signals for

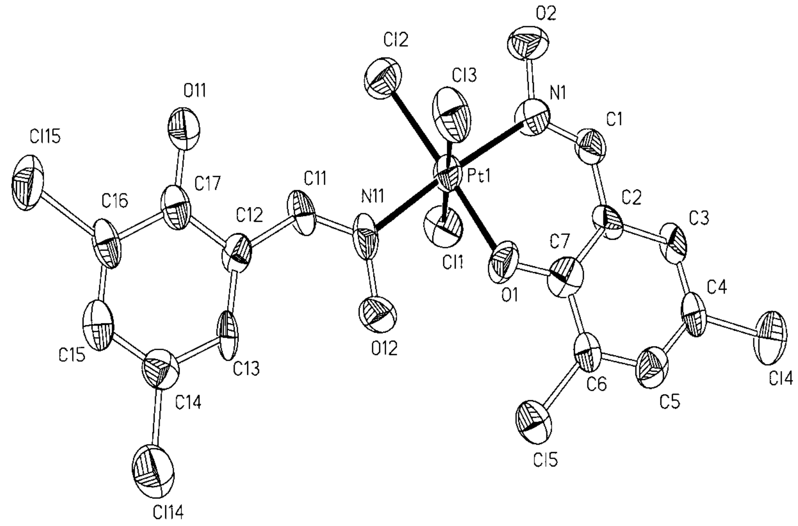


Figure 4. View of *trans-(N,N)*-[$PtCl_3(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)(3,5,2\text{-}Cl,Cl,HOC_6H_2CH{=}NOH)$] (**5**) with atomic numbering

Table 2. Bond lengths (Å) and bond angles (°) for **1**, **3** and **5**

Bond	Complex **1**	**3**	**5**
Pt(1)−O(1)	1.978(5)	1.980(5)	2.023(10)
Pt(1)−N(1)	1.974(6)	1.997(5)	2.032(13)
Pt(1)−Cl(1)		2.316(2)	2.338(4)
Pt(1)−Cl(2)			2.316(4)
Pt(1)−Cl(3)			2.336(4)
Pt(1)−N(11)			2.030(12)
Cl(1)−Pt(1)−Cl(2)			90.54(15)
Cl(1)−Pt(1)−Cl(3)			178.77(15)
Cl(1)−Pt(1)−O(1)		89.9(2)	89.5(3)
Cl(1)−Pt(1)−O(1)*		90.1(2)	
Cl(1)−Pt(1)−N(1)		90.6(2)	91.5(4)
Cl(1)*−Pt(1)−N(1)		89.5(2)	
Cl(1)−Pt(1)−N(11)			89.6(3)
Cl(2)−Pt(1)−Cl(3)			90.07(15)
Cl(2)−Pt(1)−O(1)			177.8(3)
Cl(2)−Pt(1)−N(1)			90.2(4)
Cl(2)−Pt(1)−N(11)			94.3(3)
Cl(3)−Pt(1)−O(1)			89.9(3)
Cl(3)−Pt(1)−N(1)			89.6(4)
Cl(3)−Pt(1)−N(11)			89.3(3)
O(1)−Pt(1)−N(1)		93.6(2)	92.0(5)
O(1)−Pt(1)−N(1)*		86.4(2)	
O(1)−Pt(1)−N(11)			83.5(4)
N(1)−Pt(1)−N(11)			175.4(5)

the salicylaldoximato-type ligands, while two sets are observed for **2** and **5**. Full assignment of the ^1H NMR peaks for **1−3** and **5** was made by means of one-dimensional homodecoupling and NOE experiments. By measuring NOE interactions between the oxime CH=N proton and the proton at the 6-position of the aromatic ring, one might distinguish between signals arising from the chelating and the monodentate ligands. In the chelate, in which the conformation of the ligand is fixed, the CH=N and 6-H protons are held at a distance of approximately 2.47 Å, as confirmed by the X-ray analysis of **5** (see above). This distance is sufficiently short to give rise to a NOE signal, and indeed this peak was observed for the *bis*-chelated complex [Pt(*o*-$OC_6H_4CH{=}NOH)_2$] (**1**) (δ = 8.51 to 7.50). The monodentate ligand, however, has more conformational freedom and, consequently, the average distance between the corresponding protons is much larger than in the chelated ligand. Therefore, one would expect a much weaker or even no observable NOE signal for the monodentate ligand. In agreement with this hypothesis, in both compounds **2** and **5**, only one CH=N proton revealed a strong NOE interaction with the 6-H proton (δ = 8.44 to 7.53 for **2**, δ = 8.64 to 7.76 for **5**), whereas irradiation of the second CH=N proton (δ = 8.84 for **2** and δ = 9.03 for **5**) did not show any NOE interaction. Furthermore, a comparison of the chemical shift and the coupling constants $^3J_{PtH}$ of the CH=N protons of the two ligands shows that, for the monodentate ligand, the δ value is higher (δ = 8.84−9.03 vs. δ = 8.44−8.77 for the chelate), while the $^3J_{PtH}$ value is smaller (23−30 Hz vs. 35−45 Hz for the chelate).

^1H NMR spectroscopic experiments with **2** or **5** also showed that the monodentate ligands do not interconvert into chelating ligands. For **2**, slow decomposition occurs upon prolonged storage (3 weeks at 20−25 °C) or on heating (3 d at 56 °C) to give a mixture of unidentified products. In contrast, **5** is stable and even after storage at room temperature for two months or on heating at 56 °C for 4 d in the presence of pyridine, neither transformation into the corresponding *bis*-chelated complex **3**, substitution of the monodentate ligand for pyridine, or decomposition were observed.

It is also worth mentioning that chlorination of the mixture of (salicylaldoxime)Pt^{II} complexes, prepared according to the method of Cox and co-authors,[19] gave, besides [$PtCl_2(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)_2$] (**3**) and [$PtCl_3$-$(3,5,2\text{-}Cl,Cl,OC_6H_2CH{=}NOH)(3,5,2\text{-}Cl,Cl,HOC_6H_2$-$CH{=}NOH)$] (**5**), a purely organic material, i.e. 3,5,2-$Cl,Cl,HOC_6H_2C(Cl){=}NOH$. The latter is, at least formally, derived from both the Piloty reaction and the chlorination of the benzene ring. Since this compound was not observed in the course of the chlorination of salicylaldoxime itself,[16] and furthermore, chlorination of the individual platinum(II) complexes does not give 3,5,2-

Cl,Cl,HOC_6H_2C(Cl)=NOH, we anticipate that the chlorination occurs in the benzene ring of coordinated ligand followed by liberation of the chlorinated species. An investigation of this reaction is underway in our group.

Experimental Section

Materials and Apparatus: Salicylaldoxime (Aldrich) and solvents were obtained from commercial sources and used as received. Cl_2 for chlorination was obtained from the reaction of $KMnO_4$ and HCl by a standard procedure.[23] Traces of HCl were removed by bubbling through water and dried over H_2SO_4. Nitrosyl chloride was obtained by the reaction of an aqueous solution of $NaNO_2$ with concentrated HCl. Residues of HCl were removed over $NaNO_2$, and NO_2 was removed by treatment with moist KCl. The nitrosyl chloride was finally dried over $CaCl_2$.[24] − Melting points were determined on a Kofler table. For TLC, Silufol UV 254 SiO_2-plates were 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 the data-system acquisition was achieved using CsI. EI-MS of 3,5,2-Cl,Cl,HOC_6H_2C(Cl)=NOH was measured on the same mass spectrometer. − 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 obtained on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are reported relative to aqueous $K_2[PtCl_4]$ = −1630 ppm, half-height line widths are given in parenthesis.

Synthetic Work and Characterization

Preparation of (Salicylaldoximato)Pt^{II} Complexes: The complexes were prepared by treatment of $K_2[PtCl_4]$ with salicylaldoxime as described by Cox et al.[19] Complex [PtCl(OC_6H_4CH=NOH)(HOC_6H_4CH=NOH)] (**2**) was separated from the other species by TLC on SiO_2 (Silica gel L 5/40 μ, CHEMAPOL) with $CHCl_3$ as eluent (R_f [Pt(*o*-OC_6H_4CH=NOH)$_2$] (**1**) = 0.62, R_f [PtCl(OC_6H_4CH=NOH)(HOC_6H_4CH=NOH)] (**2**) = 0.29, while other species remain on the baseline). [PtCl(OC_6H_4CH=NOH)(HOC_6H_4CH=NOH)] (**2**) was then desorbed with acetone, and the solvent was removed in vacuo at room temperature. The residue was crystallized over a layer of cold water (5−10 °C). The *bis*-chelate [Pt(*o*-OC_6H_4CH=NOH)$_2$] (**1**) was obtained in according to a published method[19] and recrystallized from acetone.

[PtCl(OC_6H_4CH=NOH)(HOC_6H_4CH=NOH)] (2): − $C_{14}H_{13}N_2ClO_4Pt$: calcd. C 33.38, H 2.60, N 5.56, Cl 7.04, Pt 38.72; found C 33.78, H 2.91, N 5.71, Cl, 6.60, Pt 38.94. − FAB$^+$ MS; *m/z*: 504 $[M]^+$. − M.p. 197−198 °C (dec.). − TLC, R_f = 0.58 (eluent $Me_2CO/CHCl_3$, 1:8, v/v). − IR (KBr, selected bands): $\tilde{\nu}$ = 3488 m, br ν(OH), 1627 mw and 1601 vs ν(C=N) +ν(C=C), 1458 vs and 1475 vs br. δ(O−H), 1198 ms ν(C−O), 912 ms ν(N−O), 742 s δ(C−H) cm^{-1}. − ^1H NMR ([D$_6$]acetone): δ = 6.99 (t, J_{HH} = 7.5 Hz, 1 *H*), 7.05 (d, J_{HH} = 8.1 Hz, 1 *H*), 7.44 (t, J_{HH} = 7.5 Hz, 1 *H*), 8.44 (d, J_{HH} = 8.0 Hz, 1 *H*) (phenyl H), 8.84 (s + d, $^3J_{PtH}$ = 30.0 Hz, 1 *H*, =C(H)−, monodentate ligand), 6.83 (t, J_{HH} = 7.5 Hz, 1 *H*), 7.18 (d J_{HH} = 8.7 Hz, 1 *H*), 7.44 (t, J_{HH} = 7.5 Hz, 1 *H*), 7.53 (d, J_{HH} = 8.5 Hz, 1 *H*, phenyl H), 8.44 (s + d, $^3J_{PtH}$ = 40.0 Hz, 1 *H*, strong NOE to the signal at δ = 7.53, =C(H)−, bidentate ligand), 9.67 (br, OH), 10.12 (s, OH), 12.16 (br., OH). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 116.8, 119.0, 119.4, 120.6, 133.1, 133.9, 134.9, 135.4 (aromatic CH's), 146.1 (J_{PtC} not observed) and 148.1 (J_{PtC} not observed, N=CH), 158.3 and 158.9 (quaternary C's, two signals were not detected). − ^{195}Pt NMR ([D$_6$]acetone): δ = −1842 (360 Hz).

[Pt(*o*-OC_6H_4CH=NOH)$_2$] (1): − $C_{14}H_{12}N_2O_4Pt$: calcd. C 35.98, H 2.59, N 5.99, Pt, 41.74; found C 35.96, H 2.61, N 5.95, Pt, 41.97. − FAB$^+$-MS, *m/z*: 467 $[M]^+$. − M.p. 255 °C (melting with concomitant sublimation), 276 °C (melting of the sublimed compound). − TLC, R_f = 0.57 (eluent $CHCl_3/CCl_4$ 1:1, v/v). − IR spectrum in KBr (selected bands) cm^{-1}: $\tilde{\nu}$ = 1645 m-w ν(C=N), 1599 m-s ν(C=C), 1188 m ν(C−O), 741 δ(C−H). − ^1H NMR ([D$_6$]acetone): δ = 6.76 (ddd, J_{HH} = 8.1 Hz, 7.2 Hz, 1.2 Hz, 1 *H*), 7.16 (d, 8.4 Hz, 1 *H*), 7.39 (ddd, J_{HH} = 8.7 Hz, 6.9 Hz, 1.8 Hz, 1 *H*), 7.50 (dd, J_{HH} = 7.8 Hz, 1.8 Hz, 1 *H*, phenyl H), 8.51 [s + d, $^3J_{PtH}$ = 45.5 Hz, 1 *H*, strong NOE to the signal at δ = 7.50, =C(H)−], 10.91 (s, $^3J_{PtH}$ = 23.6 Hz, 1 H, OH). − $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 118.3, 120.4, 134.0, 134.3 (aromatic CH's), 144.8 (broad, N=CH), quaternary C's not observed. − ^{195}Pt NMR ([D$_6$]acetone): δ = −1611 (480 Hz).

Chlorination of [Pt(*o*-OC_6H_4CH=NOH)$_2$] (1) by Cl_2: Molecular chlorine was passed through a lemon-yellow solution of **1** (0.136 g, 0.29 mmol) in $CHCl_3$ (80 mL) for 20 min at 20−25 °C. A cherry-brown solution formed, and was left to evaporate at 14−18 °C in an open 100-mL beaker to ca. 10 mL. Transparent, glittering rhombic-like brownish crystals of *trans-(N,N)*-[PtCl$_2$(3,5,2-Cl,Cl,OC_6H_2CH=NOH)$_2$] (**3**) were separated by filtration, washed with a Me_2CO/CCl_4 mixture (1:2, v/v, 3 × 3 mL), diethyl ether (3 × 3 mL) and dried in a vacuum-desiccator at room temperature over $CaCl_2$. Yield: 0.167 g, 85%.

***trans-(N,N)*-[PtCl$_2$(3,5,2-Cl,Cl,OC_6H_2CH=NOH)$_2$] (3):** − $C_{14}H_8N_2Cl_6O_4Pt$: calcd. C 24.85, H 1.18, N 4.14, Cl 31.46, Pt 28.85; found C 24.60, H 1.26, N 3.94, Cl 32.00, Pt 28.52. − FAB$^+$-MS, *m/z*: 606 $[M - 2Cl]^+$, 588 $[M - 2Cl - OH]^+$, 571 $[M - 2HCl - 2OH]^+$. − M.p. 238 °C. − TLC, R_f = 0.48 (eluent $CHCl_3$). − IR (KBr, selected bands): $\tilde{\nu}$ = 1645 mw ν(C=N), 1596 s ν(C=C), 1422 s, br. δ(O−H), 1189 ms ν(C−O), 912 s ν(N−O), 358 ms ν(Pt−Cl) cm^{-1}. − ^1H NMR ([D$_6$]acetone): δ = 7.82 and 7.84 (two d, 2.2 Hz, 1*H* each, phenyl H), 8.91 [s + d, $^3J_{PtH}$ = 37.9 Hz, 1 *H*, =C(H)−], 11.00 (s, 1 *H*, NOH). − $^{13}C\{^1H\}$ and ^{195}Pt NMR spectra were not measured even at high acquisition time owing to the low solubility of the complex in common deuterated solvents.

Chlorination of [PtCl(OC_6H_4CH=NOH)(HOC_6H_4CH=NOH)] (2) by Cl_2: Complex **2** (0.034 g, 0.068 mmol) was dissolved in $CHCl_3$ (10 mL) and molecular chlorine was passed through this solution for 20 min at 18−20 °C. The color of the reaction mixture turned from lemon-yellow to dark red during the chlorination. The reaction mixture was transferred to a long narrow tube, the solvent was evaporated at room temperature and cherry-red crystals of *trans-(N,N)*-[PtCl$_3$(3,5,2-Cl,Cl,OC_6H_2CH=NOH)(3,5,2-Cl,Cl,HOC_6H_2CH=NOH)] (**5**) were collected from the bottom part of the tube (0.015 g, 29%). A brownish material was collected from the upper part of the tube. Stirring this brownish material in heptane gave an additional amount of less pure **5** (0.021 g, 41%).

***trans-(N,N)*-[PtCl$_3$(3,5,2-Cl,Cl,OC_6H_2CH=NOH)(3,5,2-Cl,Cl,HO-C_6H_2CH=NOH)] (5):** − $C_{14}H_9N_2Cl_7O_4Pt$: calcd. C 23.58, H 1.26, N 3.93, Cl 34.83, Pt 27.38; found C 23.85, H 1.28, N 3.87, Cl 35.00, Pt 27.52. − FAB$^+$-MS, *m/z*: 643 $[M - 2Cl + H]^+$, 603 $[M - 3HCl]^+$. − M.p. 211 °C (dec.). − TLC, R_f = 0.62 (eluent acetone/ chloroform 1:2, v/v). − IR spectrum (KBr, selected bands): $\tilde{\nu}$ = 1655 w and 1635 w ν(C=N) and ν(C=C), 1187 m ν(C−O), 357 m and 347 m ν(Pt−Cl) cm^{-1}. − ^1H NMR ([D_6]acetone): δ = 7.83 (d, J_{HH} = 2.7 Hz, 1 *H*, phenyl H), 8.47(d, J_{HH} = 2.7 Hz, 1 *H*, phenyl H), 9.03 [s + d, $^3J_{PtH}$ = 23.4 Hz, 1 *H*, = C(H)−, monodentate ligand], 7.76 (d, J_{HH} = 2.7 Hz, 1 *H*, phenyl H), 7.79 (d, J_{HH} = 2.7 Hz, 1 *H*, phenyl H), 8.64 [s + d, $^3J_{PtH}$ = 35.7 Hz, 1 H strong NOE to the signal at δ = 7.76, =C(H)−, bidentate ligand], 10.94 (br., OH). − $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 131.0, 132.7, 135.8 and 136.0 (aromatic CH's), 149.1 (J_{PtC} = 28 Hz) and 151.4 (J_{PtC} not observed)(N=CH), 118.7 (J_{PtC} = 22 Hz), 119.8 (J_{PtC} = 25 Hz), 122.0, 123.5, 124.8, 125.6, 132.0 and 136.7 (quaternary C's). − ^{195}Pt NMR ([D_6]acetone): δ = +252 (440 Hz).

3,5,2-Cl,Cl,$HOC_6H_2C(Cl)$=NOH: This purely organic material was formed by the chlorination of a mixture of salicylaldoxime complexes, prepared in agreement with Cox et al.,[19] and was separated mechanically upon fractional crystallization of the products of the reaction from an acetone/toluene (3:1, v/v) mixture. Colorless needles. − $C_7H_4NCl_3O_2$: calcd. C 34.94, H 1.66, N 5.83, Cl 44.29; found C 34.45, H 2.10, N 5.65, Cl 45.10. − EI-MS, *m/z:* 241 $[M]^+$, 203 $[M - HCl]^+$. − M.p. 141 °C [vs. *ref.* m.p. 194−195 °C for 3,5-Cl,Cl-C_6H_3CH=NOH[21]). − TLC, R_f = 0.67 (eluent: chloroform). − IR (KBr, selected bands): ṽ = 3423 vs ν(O−H), 1651 mw and 1605 mw ν(C=N) and ν(C=C), 1180 m ν(C−O) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.48 (d, 1 *H*, J_{HH} = 2.2 Hz), 7.76 (d, 1 *H*, J_{HH} = 2.6 Hz), 9.02 (s, 1 *H*, C−OH), 10.64 (s, 1 *H*, oximic OH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 132.01 (CH), 127.34 (CH) quaternary carbons were not observed owing to the low solubility of the compound.

Chlorination of [Pt(*o*-OC_6H_4CH=NOH)$_2$] (1) by NOCl: Nitrosyl chloride was passed through a lemon-yellow solution of **1** (0.13 g, 0.28 mmol) in a mixture of CCl_4 (10 mL) and $CHCl_3$ (50 mL) for 20 min at 5 °C. A cherry-brown solution was formed and left to evaporate at 14−18 °C in an open 100-mL beaker to ca. 10 mL. Transparent, glittering rhombic-like brownish crystals of **4** were separated by filtration, washed with a Me_2CO/CCl_4 mixture (1:2, v/v, 3 × 3 mL), diethyl ether (3 × 3 mL), and dried at room temperature in a vacuum-desiccator over $CaCl_2$. Yield: 0.11 g, 73%.

***trans-(N,N)*-[$PtCl_2$(*o*-OC_6H_4CH=NOH)$_2$] (4):** − $C_{14}H_{12}N_2Cl_2O_4Pt$: calcd. C 31.24, H 2.25, N 5.20, Cl 13.17, Pt 36.24; found C 30.99, H 2.30, N 5.11, Cl 13.69, Pt 35.8. − FAB^+-MS, *m/z*: 538 $[M]^+$. − M.p. 149−152 °C (dec.). − IR (KBr, selected bands): ṽ = 1652 m ν(C=N), 1597 s ν(C=C), 912 s ν(N−O) cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 6.82 (t, J_{HH} = 7.7 Hz, 1 *H*), 7.29 (d, J_{HH} = 9.2 Hz, 1 *H*), 7.45 (t, J_{HH} = 7.2 Hz, 1 *H*), 7.56 (d, J_{HH} = 7.2 Hz, 1 *H* each *o*-phenyl H), 8.77 [s + d, $^3J_{PtH}$ = 34.8 Hz, 1 *H*, =C(H)−], 11.78 (s, br, 1 *H*, NOH). Solubility of the complex in [D_6]DMSO was insufficient to allow for the accumulation of either $^{13}C\{^1H\}$ or ^{195}Pt NMR spectra, even with long acquisition times.

X-ray Crystal Structure Determinations

(*i*) Dark yellow prismatic crystals of **1** were grown by the slow evaporation of a solution in CCl_4 at room temperature. Diffraction data were collected on an Enraf−Nonius CAD 4 diffractometer. Diffractometer data were processed by the program PROFIT,[25] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based on the Pt-atom coordinates obtained from the Patterson synthesis using SHELXTL package.[26] All non-hydrogen atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction was applied. Lorentz, polarization and absorption corrections were made.[27]

(*ii*) Transparent, glittering rhombic-like brownish crystals of **3** were obtained directly from the reaction mixture. The crystallographic measurements were performed on an Enraf−Nonius CAD-4 CCD diffractometer using the technique described in ref.[28] The structure was solved by direct methods and refined anisotropically for non-hydrogen atoms and isotropically for H atoms using SHELXL-97.[29] Positions of hydrogen atoms bonded to carbons were calculated based on known atom geometry. These hydrogen atoms were allowed to ride on their neighboring carbons during the refinement.

Table 3. Crystal data and structure refinement for **1**, **3** and **5**

Empirical formula	$C_{14}H_{12}N_2O_4Pt$	$C_{14}H_8N_2Cl_6O_4Pt$	$C_{14}H_9N_2Cl_7O_4Pt$
Formula weight	467.34	676.0	712.5
Space group	monoclinic	triclinic	triclinic
Crystal system	$P2_1/n$ (No 14)	$P\bar{1}$	$P\bar{1}$
a [Å]	4.5410(10)	6.9940(8)	9.559(4)
b [Å]	25.007(5)	8.2560(7)	10.266(5)
c [Å]	5.847(10)	9.1310(11)	10.565(3)
α [°]	90	66.026(6)	93.64(3)
β[°]	97.65(3)	77.142(5)	93.45(3)
γ [°]	90	89.253(7)	97.82(4)
V [Å^3]	658.1(2)	467.91(9)	1023(3)
Z	2	1	2
D_c [Mg/m^3]	2.358	2.399	2.314(3)
F(000)	440	318	672
μ(Mo−K_α) [mm^{-1}]	10.679	8.378	8.148
$2\theta_{max}$ [°] and sinθ/λ for data collection	51.9	52.0	59.94 and 0.703
Refinement method	full-matrix (anisotropic for all non-H atoms) least squares on F^2 for **1** and **3**, and based on *F* for **5**		
Crystal size, mm	0.18 × 0.42 × 0.52	0.30 × 0.10 × 0.10	0.3 × 0.2 × 0.1
Index ranges	$-5<h<5$ $-0<k<30$ $0<l<7$	$0<h<8$ $-10<k<10$ $-10<l<11$	$0<h<12$, $-7<k<7$ $-7<l<7$
Collected reflections	1365	1834	2024
Unique reflections	802 [$I \leqslant 2\sigma(I)$]	1834 [$I \leqslant 2\sigma(I)$]	1800 [$F(hkl) \geq 4\sigma(F)$]
Refinement parameters	118	125	327
Extinction coefficient	0.003(6)	0.032(3)	−
Goodness-of-fit on *F*	1.093	1.014	1.101
R	0.0227	0.0389	0.0373
wR	0.0590	0.0411	0.0353

Their thermal parameters were assigned the value of 1.2 times the initial equivalent isotropic thermal parameters of their neighboring carbons and were not refined. The oxime H atom was located by difference Fourier synthesis and refined with restraints to maintain the geometry derived from the difference map. Its thermal parameter was assigned the value of 1.5 times the initial equivalent isotropic thermal parameter of its neighboring oxygen and was not refined. The final *R*-value was 0.0389 for 1779 reflections with $I = 2\sigma(I)$.

(*iii*) Dark cherry-red prismatic crystals of **5** were obtained after the slow evaporation of a solution in acetone/toluene (3:1, v/v) in a long (150 mm) narrow (5 mm) tube. Diffraction data were collected on a Syntex $P2_1$ diffractometer. An extinction correction was not made. Before anisotropic refinement, an absorption correction was made using DIFABS[30] program. The contributions of hydrogen atoms were included at fixed calculated positions, based on geometrical requirements. All experimental data processing, solving and refinement were performed using the CSD[27] program. Crystal data for **1**, **3** and **5** are given in Table 3.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144573 (**1**), CCDC-144575 (**3**) and CCDC-144574 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] V. Yu. Kukushkin, D. Tudela, A. J. L. Pombeiro, *Coord. Chem. Rev.* **1996**, *156*, 333.

[2] V. Yu. Kukushkin, A. J. L. Pombeiro, *Coord. Chem. Rev.* **1999**, *181*, 147.

[3] V. Yu. Kukushkin, T. Nishioka, D. Tudela, K. Isobe, I. Kinoshita, *Inorg. Chem.* **1997**, *36*, 6157 and references therein.

[4] V. Yu. Kukushkin, T. B. Pakhomova, Yu. N. Kukushkin, R. Herrmann, G. Wagner, A. J. L. Pombeiro, *Inorg. Chem.* **1998**, *37*, 6511.

[5] V. Yu. Kukushkin, T. B. Pakhomova, N. A. Bokach, G. Wagner, M. L. Kuznetsov, M. Galanski, A. J. L. Pombeiro, *Inorg. Chem.* **2000**, *39*, 216.

[6] G. Wagner, A. J. L. Pombeiro, N. A. Bokach, V. Yu. Kukushkin, *J. Chem. Soc., Dalton Trans.* **1999**, 4083.

[7] V. Yu. Kukushkin, I. V. Ilichev, G. Wagner, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1999**, 3047.

[8] V. Yu. Kukushkin, V. K. Belsky, D. Tudela, *Inorg. Chem.* **1996**, *35*, 510.

[9] M. F. C. Guedes da Silva, C. M. P. Ferreira, E. M. P. R. P. Branco, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. A. Michelin, U. Belluco, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, V. Yu. Kukushkin, *Inorg. Chim. Acta (Topical Volume on Platinum Chemistry)* **1997**, *265*, 267.

[10] C. M. P. Ferreira, M. F. C. Guedes da Silva, V. Yu. Kukushkin, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **1998**, 325.

[11] V. Yu. Kukushkin, D. Tudela, Yu. A. Izotova, V. K. Belsky, A. I. Stash, *Inorg. Chem.* **1996**, *35*, 4926.

[12] V. Yu. Kukushkin, V. K. Belsky, E. A. Aleksandrova, V. E. Konovalov, G. A. Kirakosyan, *Inorg. Chem.* **1992**, *31*, 3836.

[13] M. F. C. Guedes da Silva, Yu. A. Izotova, A. J. L. Pombeiro, V. Yu. Kukushkin, *Inorg. Chim. Acta* **1998**, *277*, 83.

[14] V. Yu. Kukushkin, I. V. Ilichev, M. A. Zhdanova, G. Wagner, A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.* **2000**, 1567.

[15] Yu. N. Kukushkin, M. V. Bavina, A. V. Zinchenko, V. K. Belsky, V. Yu. Kukushkin, *Polyhedron* **1997**, *16*, 2429.

[16] Yu. N. Kukushkin, V. K. Krylov, S. F. Kaplan, M. Calligaris, E. Zangrando, A. J. L. Pombeiro, V. Yu. Kukushkin, *Inorg. Chim. Acta* **1999**, *285*, 116.

[17] [17a] O. Piloty, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 452. − [17b] O. Piloty, A. Stock, *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 3093. − [17c] J. G. Aston, D. F. Menard, *J. Am. Chem. Soc.* **1935**, *57*, 1920. For reviews on the Piloty reaction see: N. Boyer, in *The Chemistry of the Nitro and Nitroso Groups*, (Ed.: H. Feuer), Interscience, New York, Part 1, **1969**, p. 235; H. Metzger, in *Houben−Weyl. Methoden der Organischen Chemie*, vol. X, Part 4, Georg Theime Verlag, Stuttgart, **1968**, p. 98 and 239.

[18] L. A. M. Baxter, G. A. Heath, R. G. Raptis, A. C. Willis, *J. Am. Chem. Soc.* **1992**, *114*, 6944.

[19] E. G. Cox, F. W. Pinkard, W. Wardlaw, K. C. Webster, *J. Chem. Soc.* **1935**, 459.

[20] [20a] R. C. Srivastava, E. C. Lingafelter, P. C. Jain, *Acta Crystallogr.* **1967**, *22*, 922. − [20b] M. Lalia-Kantouri, M. Hartophylles, P. D. Jannakoudakis, G. P. Voutsas, *Z. Anorg. Allg. Chem.* **1995**, *621*, 645. − [20c] G. P. Voutsas, K. G. Keramidas, M. Lalia-Kantouri, *Polyhedron* **1996**, *15*, 147. − [20d] C. E. Pfluger, R. L. Harlow, S. H. Simonsen, *Acta Crystallogr., Sect. B* **1970**, *26*, 1631. [20e] P. L. Orioli, E. C. Lingafelter, B. W. Brown, *Acta Crystallogr.* **1964**, *17*, 1113. − [20f] M. A. Jarski, E. C. Lingafelter, *Acta Crystallogr.* **1964**, *17*, 1109.

[21] H. Biltz, K. Stepf, *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 4022.

[22] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, **1986**, pp. 357, 692.

[23] [23a] G. Graebe, *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 645.[23b] G. Graebe, *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 43.

[24] J. R. Morton, H. W. Wilcox, *Inorg. Synth.* **1953**, *4*, 48.

[25] V. A. Strel′tsov, V. E. Zavodnik, *Kristallografia* **1989**, *34*, 1369.

[26] G. M. Sheldrick, *SHELXTL* User Manual, Revision 3; Nicolet XRD Corp.: Cupertino, CA, **1981**.

[27] L. G. Axelrud, Yu. N. Grin, P. Yu. Zavalii, V. K. Pecharsky, V. S. Fundamensky, CSD-universal program package for single crystal and/or powder structure data treatment. Collected Abstracts, *XII-th European Crystallographic Meeting*, Moscow, August **1989**; USSR Academy of Sciences, Moscow, **1989**, p 155.

[28] Z. Otwinowski, Denzo-SMN − Programs Denzo and Scalepack developed Z. Otwinowski. Copyright **1994−1997** by Texas Southwestern Medical Center at Dallas.

[29] G. M. Sheldrick: *SHELXL97. Program for crystal structure refinement*, University of Göttingen, Germany.

[30] N. Walker, D. Stuart, *Acta Crystallogr., Series A* **1983**, *39*, 158.

[31] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, *S1*.

[32] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, *S1*.

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