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New Complexes of Palladium(II) with Dithiooxamide and N,N-Dimethyldithiooxamide

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During the course of our investigation on metal complexes of thioamides, we already studied compounds of primary [1] and tertiary thioamides [2, 3]. Extending this investigation, we report now on some complexes of dithiooxamide (H_2DH_2) and N,N-dimethyldithiooxamide (Me_2DH_2). With these compounds it is possible to study coordination through the nitrogen atom, which is very rare for simple thioamides. Dithioamides, as dithiooxamide and dithiomalonamide, however, can coordinate through both the sulphur and the nitrogen atoms [4, 5].

As indicated by the metal analyses and the conductivity measurements (Table I) neither of the ligands lose a proton on coordination. In that case, planar dithiooxamides give S,N coordination [4], while the non-planar N,N,N',N'-tetrasubstituted derivates are S,S coordinated [6]. The vibrational spectra (Table II) substantiate this for our compounds. In $[Pd(H_2DH_2)_2]Cl_2$ most of the bands are split. The ν(CN) peaks are shifted to a higher and lower frequency, compared to the ligand, in agreement with a S,N coordination. Simultaneously the ν(CS) bands are also found at a higher and lower frequency. We must also take into account the symmetry lowering of the ligand on coordination ($C_{2h} \rightarrow C_s$). However, as the I.R. and Raman active bands are very close to each other, in the case of the ν(CN) and ν(CS) vibrations [7], the symmetry change do not cause difficulties for the assignment. The ν(PdN) is assigned at 401 cm^{-1} and the ν(PdS) at 322 cm^{-1}. The 1ν(MN) + 1ν(MS) pattern indicates a *trans* configuration.

Me_2DH_2 is a twisted molecule [8, 9] and at first sight, both S,N and S,S coordination are possible. However, from previous studies we know that in such case S coordination is preferred to N coordination [10]. This is made clear by the spectra of $[Pd(Me_2DH_2)_2]X$ (X = Cl or ClO_4), which show a frequency increase of the ν(CN) bands of both the primary and the tertiary thioamide. Bands with ν(CS) character show a frequency decrease consistent with

TABLE I. Analytical Data of the Pd(II) Complexes with HDH_2 and Me_2DH_2.

Compound	Colour	%M	(calc.)	%S	(calc.)	Λ_M/Ω^{-1} mol^{-1} cm^2
$[Pd(H_2DH_2)_2]Cl_2$	red	25.3	(25.47)	30.1	(30.73)	145[a]
$[Pd(Me_2DH_2)_2]Cl_2$	orange	21.9	(22.45)	26.4	(27.08)	200[b]
$[Pd(Me_2DH_2)_2](ClO_4)_2$	orange	17.5	(17.67)	21.3	(21.34)	260[b]
$Pd(Me_2DH_2)Cl_2$	brown	31.8	(32.67)	20.3	(19.72)	diss.

[a] 10^{-3} *M* in MeOH. [b] 10^{-4} *M* in MeOH.

TABLE II. Important Infrared Bands of the Pd(II) Complexes with H_2DH_2 and Me_2DH_2.

Compound		Vibration				
		δ(NH_2)	ν(CN)	ν(CS)	ν(PdN)	ν(PdS)
H_2DH_2 [7]	I.R.	1585 vs	1428 s	832 s		
	R.		(1440)	832(3)		
$[PdL_2Cl_2$	I.R.	1693 m 1600 m	1485 vs 1315 sh	1016 s 820 ms	400 vw	325 w
	R.		1491(10) 1321 (3)	1016(9) 815(2)		

		ν(CN) (tert)	ν(CN) (prim)	ν_s(RNR) + ν(CS) (prim) + ν(CS) (tert)			ν(PdS)	
Me_2DH_2 [11]	I.R.	1546 vs	1403 s	929 m	851 m	667 sh		
$[PdL_2](ClO_4)_2$[a]	I.R.	1577 vs	1480 m	920 w	824 mw		331m	302 mw
$[PdL_2]Cl_2$	I.R.	1595 s 1578 s	1490 m	915 m	817 m	663 w	340m	315 mw
$PdLCl_2$[b]	I.R.	1539 vs	1477 ms	917 w	812 ms	679 w	343 m	

[a] ν(ClO_4) at 1133 sh, 1110 vs, 1088 s, 936 vw, 635 m, 627 s, 460 vvw. [b] ν(PdCl) at 312 s and 285 mw.

TABLE III. Electronic Spectra[a] of the Pd(II) Complexes.

Compound	d–d		Other bands		
$[Pd(H_2DH_2)_2]Cl_2$	17.7 sh	20.8	19.6	25.9 sh	
$[Pd(Me_2DH_2)_2]Cl_2$	19.2 sh	23.0 sh	25.1		
$[Pd(Me_2DH_2)_2](ClO_4)_2$	18.7 sh	22.2	26.0		
$Pd(Me_2DH_2)Cl_2$	19.8	21.7	23.9 sh	25.5	27.1

[a] $\bar{\nu} \times 10^{-3}$ cm^{-1}; nujol mulls on filter paper.

S,S coordination. In $Pd(Me_2DH_2)Cl_2$ the ν(CN) of the tertiary function shows a small downward shift. However, such anomalous behaviour has already been observed in some tertiary thioamide complexes [2]. The ν(CS) vibrational frequencies, however, decrease, indicating S,S coordination. In the $[Pd(Me_2DH_2)_2]X_2$ (X = Cl or ClO_4) compounds, two ν(PdS) vibrations are observed at 331–340 cm^{-1} and at 302–315 cm^{-1}, respectively, as a moderately intense and a weak band. In $Pd(Me_2DH_2)Cl_2$ only one ν(PdS) band could be detected, the other probably being overlapped by the strong ν(PdCl) vibration at 312 cm^{-1}. A second ν(PdCl) band is found at 285 cm^{-1}. The observation of two ν(PdCl) bands is in agreement with the *cis*-structure.

The lower bands in the electronic spectra (Table III) can be assigned to d–d transitions. The frequencies of the bands are in good agreement with those of other S,N or S,S coordinated dithiooxamides [4, 6].

Experimental

H_2DH_2 was purchased from Merck (*p.a.*); Me_2DH_2 was prepared according to Persson and Sandström [9]. $PdCl_2$ was delivered by UCB.

$[Pd(H_2DH_2)_2]Cl_2$

50 ml of a 5 × 10^{-3} *M* solution of $PdCl_2$ in 2*M* HCl was added slowly to 200 ml of a 5 × 10^{-3} *M* solution of the ligand in a MeOH/HCl (37%) mixture. The concentration of HCl in the latter solution was also 2*M*. After one hour the complex was filtered off, washed with small quantities of MeOH and dried *in vacuo*.

$[Pd(MeDH_2)_2]Cl_2$

$PdCl_2$ was dissolved in an ethanolic (96%) LiCl solution and added to an excess of ligand in EtOH. After filtration, the complex was washed with EtOH and dried *in vacuo*.

$Pd(MeDH_2)Cl_2$

The same procedure as for $[Pd(Me_2DH_2)_2]Cl_2$, but the ligand solution was added to the metal solution in a 1:1 molar ratio.

$[Pd(Me_2DH_2)_2](ClO_4)_2$

$Pd(OH)_2$, precipitated upon neutralization of a $PdCl_2$ solution in HCl with aqueous KOH, was dissolved in an $EtOH/HClO_4$ (70%) mixture (9:1 ratio). This solution was added to an excess of ligand in EtOH. The complex was filtered off, washed with EtOH and dried *in vacuo*. The analyses were performed by standard techniques. The physical methods [1, 2] have been reported earlier.

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