Inorganica Chimica Acta, 29 (1978) L181–L184
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On the Existence of Platinum(V) and Palladium(V) Dithiolene Complexes. An ESR Study

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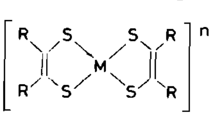
Received March 28, 1978

Dithiolene ligands are known to form an unusual series of palladium and platinum complexes (I) which contain the metal ion in the formal oxidation states +1, +2, +3, and +4 [1–3].



(I)

M = Pd, Pt
(Ia): R = CN
$n = -3, -2, -1$
(Ib): R = H, alkyl, aryl, CF_3
$n = -2, -1, 0$

Continuing our investigations on transition metal dichalcogeno complexes containing the metal ions in high formal oxidation states [4–8], we studied the reactions of several Pt(IV) and Pd(IV) dithiolene complexes (M = Pt, R = $i\text{-}C_3H_7$, $p\text{-}CH_3OC_6H_4$, C_6H_5, $p\text{-}Cl\text{-}C_6H_4$; M = Pd, R = $p\text{-}CH_3OC_6H_4$) with bromine by ESR. As a result unstable paramagnetic Pt and Pd complexes are formed which should contain the metal in the formal oxidation state "+5". In this paper we report the ESR spectra of the different complexes obtained. Furthermore, conclusions were made concerning the structures of these complexes.

Experimental

The complexes $[PtS_4C_4(i\text{-}C_3H_7)_4]$, $[PtS_4C_4(p\text{-}CH_3OC_6H_4)_4]$, $[PtS_4C_4(C_6H_5)_4]$, $[PtS_4C_4(p\text{-}Cl\text{-}C_6H_4)_4]$, and $[PdS_4C_4(p\text{-}CH_3OC_6H_4)_4]$ were prepared according to [9, 10]. For the ESR measurements calibrated $Br_2/CHCl_3$ solutions were added to the complexes dissolved in the same solvent at room temperature. Measurements were made immediately after mixing the reactants. ESR spectra were recorded at $295 \geq T \geq 130$ K in the X band (at 9.4 GHz) with a VARIAN "E-112" and a JEOL "JES-3BQ" spectrometer. The magnetic field was calibrated with NMR markers; g values were derived using DPPH as reference.

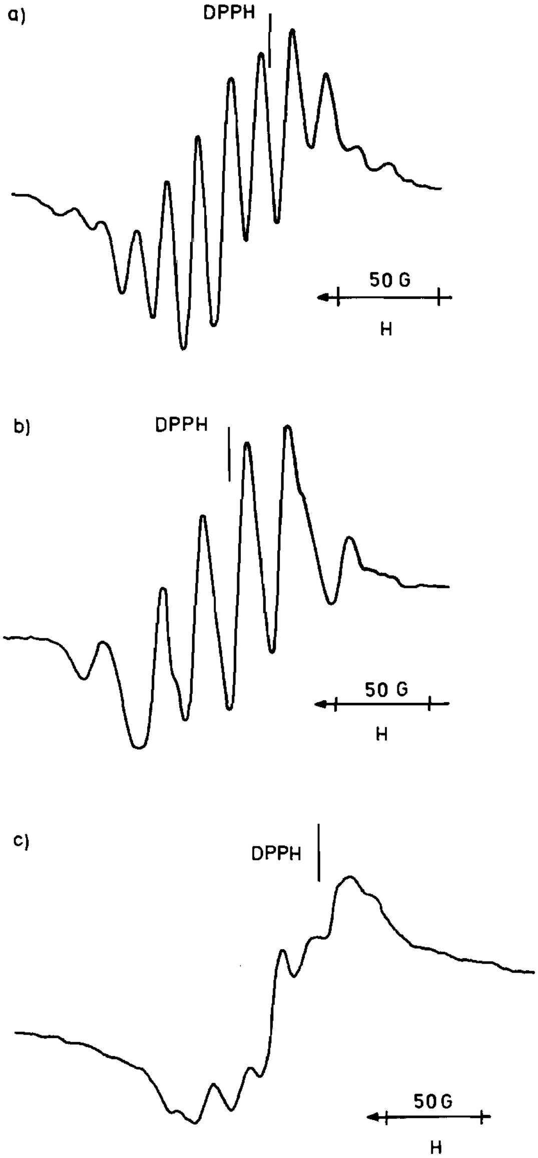


Figure 1. X band ESR spectra of (a) $[PtS_4C_4(i\text{-}C_3H_7)_4Br_2]^-$ at T = 295 K; (b) $[PtS_4C_4(C_6H_5)_4Br]$ at T = 295 K (Br_2:PtL_2 < 3:1); (c) the same mixture as for (b) at T = 253 K. All spectra were taken from $CHCl_3$ solutions.

Results and Discussion

Depending on the ratio Br_2:PtL_2 (L = dithiolene ligand) the oxidation of the platinum(IV) chelates yields two different paramagnetic complex species (II), (III) at room temperature, whose ESR spectra (recorded at T = 295 K) are shown in Figure 1. Adding small amounts of Br_2 (Br_2:PtL_2 < 3:1) the formation of the complex species (II) is favoured. Higher Br_2 concentrations produce complex (III)

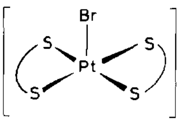
TABLE I ESR Parameter for Pt(V) Dithiolene Complexes $[PtL_2Br]$ (II) and $[PtL_2Br_2]^-$ (III) Coupling Constants in 10^{-4} cm^{-1}

L		$S_2C_2(C_6H_5)_2^{2-}$	$S_2C_2(p\text{-}CH_3OC_6H_4)_2^{2-}$	$S_2C_2(i\text{-}C_3H_7)_2^{2-}$	$S_2C_2(p\text{-}Cl\text{-}C_6H_4)_2^{2-}$
(II)	g_o^a	1 999			2 001
	a_o^{Pt}	56 2	–[b]	–[b]	59 0
	a_o^{Br}	21 2			20 0
(III)	g_o	1 989	1 988	1 987	
	a_o^{Pt}	63 3	64 2	66 0	–[b]
	a_o^{Br}	15 5	15 0	16 6	
	$g_\parallel{}^c$	1 930	1 934	1 928	
	$g_\perp$	2 014	2 012	2 012	[b]
	$A_\parallel^{Pt\ d}$	34 0	40 6	34 4	–
	$A_\perp^{Pt}$	78 1	76 0	81 8	
	$A_\parallel^{Br}$	20 0	19 7	20 6	

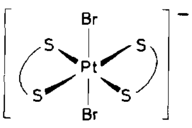
[a] Isotropic parameters derived at T = 295 K, $g_o \pm 0\ 002$, a_o^{Pt}, $a_o^{Br} \pm 0\ 5$ [b] Formation of these complexes is not observed (see text) [c] Experimental errors $g_\parallel, g_\perp \pm 0\ 003$, $A_\perp^{Pt} \pm 1\ 0$, $A_\parallel^{Br} \pm 1\ 0$ [d] Obtained from the relation $A_\parallel^{Pt} = 3a_o^{Pt} - 2A_\perp^{Pt}$

in the most cases In particular, oxidation of $[PtS_4C_4(p\text{-}Cl\text{-}C_6H_4)_4]$ results in the formation of complex (II) only, the oxidation of $[PtS_4C_4(i\text{-}C_3H_7)_4]$ and $[PtS_4C_4(p\text{-}CH_3OC_6H_4)_4]$ yields complex (III) even for the lowest Br_2 concentrations In general, the type of ligand influences strongly the oxidation behaviour As expected, the oxidability increases as the sulfur ligands become less electron-withdrawing, in the order R = $p\text{-}Cl\text{-}C_6H_4 < C_6H_5 < p\text{-}CH_3\text{-}OC_6H_4 < i\text{-}C_3H_7$

In the spectra of (II) each line of the Pt triplet (the outer lines of this triplet are caused by the ^{195}Pt isotope having a nuclear spin I = ½, natural abundance ≈ 33 7%) is split into a quartet of equally spaced hyperfine lines due to the interaction with one Br nucleus ($^{79,81}Br$, I = 3/2) indicating the coordination of one Br atom in the first coordination sphere The spectra obtained for (III) show $^{79,81}Br$ hfs caused by two magnetically equivalent Br atoms The g_o values as well as the hyperfine coupling constants are listed in Table I. The ESR spectra can be explained assuming the following structures for the complexes in which the Br atoms are axially coordinated



(II)



(III)

In frozen solutions (T ≈ 130 K) complicated ESR spectra were observed Figure 2 shows the low-temperature ESR spectrum obtained from a solution containing $[PtS_4C_4(p\text{-}CH_3OC_6H_4)_4]$ and Br_2 in the ratio 1 5 These spectra can be described by the following spin-Hamiltonian

$$\hat{\mathcal{H}}_{sp} = \beta_e \vec{H}\,\tilde{g}\,\hat{\vec{S}} + \hat{\vec{S}}\,\tilde{A}^{Pt}\,\hat{\vec{I}}^{Pt} + \sum_{i=1}^{2} \hat{\vec{S}}\,\tilde{A}^{Br}\,\hat{\vec{I}}^{Br},$$

the experimentally derived parameters of which are collected in Table I In the high-field region of the spectrum, *e g*, for H ‖ $g_\parallel$, $A_\parallel^{Pt}$, $^{79,81}Br$ hfs is observed due to two magnetically equivalent Br atoms Some of these lines are overlapped by the more intense lines of the central part of the spectrum From the Br hfs we conclude that in frozen solutions mainly complexes of the type (III) are present The weak line found in the low-field region of the spectra (Figure 2) indicates the presence of a small amount of another paramagnetic complex The low-temperature spectrum observed for $[PtS_4C_4(p\text{-}ClC_6H_4)_4]$ could not be explained unambiguously either for small or for high Br_2 PtL_2 ratios, more than one paramagnetic complex is present

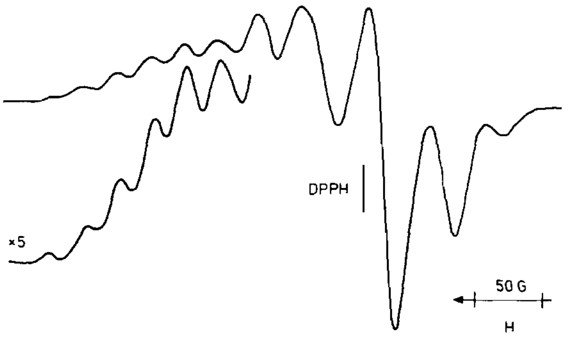


Figure 2 X band ESR spectrum of $[PtS_4C_4(p\text{-}CH_3OC_6H_4)_4Br_2]^-$ in $CHCl_3$ at T = 130 K

Whilst this work was in progress, Larin *et al.* [11] published a paper describing the oxidation of $[PtS_4C_4(C_6H_5)_4]$ with Br_2. The liquid solution spectra (at T = 295 K) obtained by him are in agreement with those found by us apart from the isotropic ^{195}Pt hfs constant of complex (II) which we found to be considerably smaller. However, there are some striking differences concerning the spectra in frozen solutions. In contrast to us Larin *et al.* found two different ESR spectra attributed to the complexes $[PtS_4C_4(C_6H_5)_4Br]$ and $[PtS_4C_4(C_6H_5)_4Br_2]^-$. With the exception of $[PtS_4C_4(p\text{-}Cl\text{-}C_6H_4)_4]$ in all attempts made by us only the spectrum of (III) could be observed as suggested by the $^{79,81}Br$ hfs which appeared in the high-field part of the spectrum. No Br hfs is described by Larin *et al.* for the frozen solution spectra. In order to clarify the differences we studied the temperature-dependence of the ESR spectrum obtained from a solution of $[PtS_4C_4(C_6H_5)_4]$ containing a small amount of Br_2 only. As can be seen from Figure 1b the spectrum observed at room temperature is that expected for a complex with one Br atom in the coordination sphere. For temperatures lower than T = 273 K this spectrum disappears and another spectrum is observed showing the main features typically of $[PtS_4C_4(C_6H_5)_4Br_2]^-$ (Figure 1c). Obviously, at low temperatures a second Br atom does coordinate in *trans*-position to the other one in the complex. The same is observed for the other Pt complexes studied.

The oxidation of $[PdS_4C_4(p\text{-}CH_3OC_6H_4)_4]$ with Br_2 in $CHCl_3$ yields also a low-spin complex containing the metal in the formal oxidation state "+5". However, the ESR spectrum can be observed only if small amounts of Br_2 were used. Higher concentrations of bromine decrease the signal intensity strongly indicating that the Pd(V) complex is much more unstable than the Pt(V) complexes. The principal values of the g tensor derived from the ESR spectra are $g_1 = 1.986$, $g_2 = 2.020$, $g_3 = 2.029$, and $\langle g \rangle = 2.012$. In contrast to the Pt complexes no $^{79,81}Br$ hfs is observed. Therefore, the Br atoms are not or only weakly coordinated. This is supported by the fact that the average $\langle g \rangle$ value of the Pd(V) complex is higher than those obtained for the Pt(V) complexes. Coordination of Br atoms is expected to cause a considerable shift of the g values to lower ones because the ratio of the spin–orbit coupling constants (λ_{Br}/λ_m) is much greater for M = Pd than for M = Pt.

Larin *et al.* suggested a d_{xz} ground state for the unpaired electron in the low-spin chelates $[PtS_4C_4(C_6H_5)_4Br]$ and $[PtS_4C_4(C_6H_5)_4Br_2]^-$ [11]. However, for this π-type ground state we would expect that the tensor parameters of the spin-Hamiltonian be more dependent on the nature of the different substituents R of the sulfur ligands than we observed experimentally.

The isotropic $^{79,81}Br$ hfs can be employed to obtain an estimate of the Br 4s contribution to the ground-state MO. The isotropic $^{79,81}Br$ splitting is given by the familiar expression

$$a_o(^{79,81}Br) = 8/3\pi g_e\, g_N\, \beta_e\, \beta_N\, |\psi_{4s}(0)|^2\, c_s^2$$

where c_s is the coefficient of the Br 4s orbital in the MO containing the unpaired electron and $|\psi_{4s}(0)|^2$ is the 4s electron density at the nucleus. The evaluation of c_s^2 is accomplished [12] by taking the ratio of the observed isotropic ^{79}Br splitting (^{81}Br hfs is not resolved), a_o^{obsd}, to that calculated, a_o^{calcd}, for an unpaired electron residing in a Br 4s orbital, i.e.,

$$c_s^2 = a_o^{obsd}/a_o^{calcd} = \frac{a_o^{obsd}}{7800\ [G]}$$

For the complexes of type (II) c_s^2 was estimated to be 0.0028 and for those of type (III) 0.0021. The values estimated are small and make a d_{xy} ground state more likely than d_{xz} for which more spin density would be expected to be transferred to Br nuclei. Single-crystal ESR studies are needed to clarify this question in detail. However, all attempts made to isolate any of the Pt(V) complexes were unsuccessful and, unfortunately, suitable host complexes are not available for preparing diamagnetically diluted single-crystals.

It should be noted that Pt(V) dithiolene chelates were obtained also using dilute chlorine solutions instead of bromine. However, these reactions are much more complicated than those observed for the bromine oxidation. Attempts with iodine were without success.

Finally, it is interesting to point out that the oxidation of Ni(IV) dithiolene complexes does not result in the formation of complexes containing the metal in the oxidation state "+5" [13]. In this case ligand radicals are formed as oxidation products.

References

1 J. A. McCleverty, *Progr. Inorg. Chem.*, *10*, 49 (1968).
2 E. Hoyer, W. Dietzsch and W. Schroth, *Z. Chem.*, *11*, 43 (1971).
3 W. E. Geiger, C. S. Allen, Th. E. Mines and F. C. Senftleber, *Inorg. Chem.*, *16*, 2003 (1977).
4 R. Kirmse, W. Windsch and E. Hoyer, *Z. anorg. allg. Chem.*, *386*, 213 (1971).
5 R. Kirmse and W. Dietzsch, *J. Inorg. Nucl. Chem.*, *38*, 255 (1976).
6 R. Kirmse, W. Dietzsch and B. V. Solovev, *J. Inorg. Nucl. Chem.*, *39*, 1157 (1977).

7 W. Dietzsch, R. Kirmse, E. Hoyer, I. N. Marov and V. K. Belyaeva, *Inorg. Chem.*, in press.
8 J. Stach, W. Dietzsch and R. Kirmse, *Z. Chem.*, in press.
9 D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc.*, *88*, 4876 (1966).
10 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, *87*, 1483 (1965).
11 G. M. Larin, G. A. Svereva and R. N. Schtscholokov, *Dokl. Akad. Nauk SSSR*, *237*, 1107 (1977).
12 P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, New York (1967) pp. 20–22.
13 G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.*, *92*, 5796 (1970).