Inorganica Chimica Acta, 77 (1983) L51–L52

Electron Spin Resonance Spectra of Dithiobis(π-cyclopentadienyl)tantalum(IV) Complexes, $(\pi\text{-}C_5H_5)_2Ta(SR)_2$

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Received March 15, 1983

The ESR spectrum of $(\pi\text{-}C_5H_5)_2TaCl_2$ has recently been interpreted in terms of molecular orbital parameters involved in bonding in this molecule [1]. The unpaired electron lies essentially in the $5d_{x^2-y^2}$ metal-ion orbital and it is partially delocalised on to the chloride ligands. It is of interest to compare the effects of changing chloride by thiol ligands on the bonding parameters and we therefore report the ESR, UV, and Visible absorption spectra of Dithiobis(π-cyclopentadienyl)tantalum(IV).

Experimental

The dithio-derivatives $(\pi\text{-}C_5H_5)_2Ta(SR)_2$, where R = Me or Ph were prepared by reacting NaSR with a suspension of $(\pi\text{-}C_5H_5)_2TaCl_2$ in ethanol and the purple crystalline products were isolated as described earlier [2, 3].

The ESR spectra were recorded using a Varian E-109 Spectrometer at 298 K and at 77 K. Typical spectrum recorded at 77 K for $(\pi\text{-}C_5H_5)_2Ta(SCH_3)_2$ is shown in Fig. 1. Optical spectra were recorded on a Beckman DB-G Spectrophotometer, and the position of the absorption maxima are summarised in Table I.

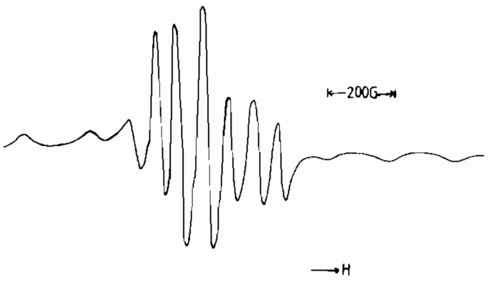

Fig. 1. ESR spectrum of $(\pi\text{-}C_5H_5)_2Ta(SCH_3)_2$ in chloroform at 77 K.

TABLE I. ESR and Optical Data for Dithiocomplexes of Tantalum in $CHCl_3$. All Hyperfine Tensors Components and ΔE are in Units of cm^{-1}.

Complex	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	$\Delta E(A_2^*)$	$\Delta E(A_2)$	$\Delta E(B_2^*)$ and $\Delta E(B_1^*)$	$\Delta E(B_2)$ and $\Delta E(B_1)$
$(\pi\text{-}C_5H_5)_2Ta(SCH_3)_2$	1.9850	1.9882	1.9430	−0.00730	−0.00705	−0.01705	13000	14500	22500	30000
$(\pi\text{-}C_5H_5)_2Ta(SC_6H_5)_2$	1.9860	1.9887	1.9425	−0.00725	−0.00695	−0.01655	12000	15000	23000	30000

0020-1693/83/$3.00

TABLE II. Bonding Parameters for Metallocene Complexes of Tantalum.

Complex	K	|a|	|b|	$(\alpha^*)^2$	$P_{md}(B_2^*)$	$P_{md}(B_1^*)$	$P_{md}(A_2^*)$
$(\pi\text{-}C_5H_5)TaCl_2$	0.88	0.999	0.001	0.86	0.428	0.442	0.428
$(\pi\text{-}C_5H_5)Ta(SCH_3)_2$	0.83	0.999	0.035	0.74	0.425	0.422	0.415
$(\pi\text{-}C_5H_5)_2Ta(SC_6H_5)_2$	0.81	0.999	0.025	0.72	0.425	0.410	0.408

Results and Discussion

The ESR spectra at 77 K of the complexes could all be interpreted in terms of a species having one unpaired electron moving in nearly axial symmetric orbital. Therefore the magnetic data could be fit to the usual Spin-Hamiltonian [4] and analysed by using method already described [1]. The Spin-Hamiltonian parameters calculated by this method are listed in Table I.

The optical spectra for the two compounds are almost similar and consisted of two weak absorption bands centered around 12000 and 15000 cm^{-1} which are ascribed to d–d transitions and two intense charge-transfer bands at about 23000 and 30000 cm^{-1}. These bands are fully assigned as shown in Table I.

The Spin-Hamiltonian parameters listed in Table I for all compounds could only be accomodated by placing the unpaired electron in an $\psi^*(A_1)$ molecular orbital which is mainly $d_{x^2-y^2}$ of the central metal-ion, although the very small deviation from axial symmetry in both g and A tensors show that the contribution of the metal-ion d_{z^2} orbital to $\psi^*(A_1)$ is very small.

More precise information can be obtained about electron distribution within these complexes if their Spin-Hamiltonian parameters are equated with the coefficients in appropriate linear combinations of atomic orbitals. The complexes are treated as belonging to the point group C_{2v}, and the explicit form of the magnetically important molecular orbitals appropriate to this symmetry are similar to those given in ref. [1]. Relationships connecting the coefficients of these molecular orbitals and the Spin-Hamiltonian parameters are also given in ref. [1]. The methods for evaluating the bonding parameters from the magnetic and optical data are given in detail in ref. [1] and the calculated values of these parameters for the complexes studied here together with the reported values [1] for $(\pi\text{-}C_5H_5)_2TaCl_2$ are listed in Table II.

The calculated values of $(\alpha^*)^2$, which reflect the degree of delocalisation of the unpaired electron onto the two sigma bonded ligands, for all complexes listed in Table II shows that in each case the unpaired electron lies mostly on the metal-ion orbitals and delocalised onto the thiol or chloride orbitals. However, in the case of thiocomplexes there appears to be much more electron delocalisation onto the thiol ligands since $(\alpha^*)^2 \sim 0.72$ compared with $(\alpha^*)^2 = 0.86$ for the corresponding complex containing chloride ligands. The change in the value of $(\alpha^*)^2$ due to the substitution of chloride by thiol ligand proves that this parameter reflects mainly the contribution of σ-bonded ligands and not the contribution of the $C_5H_5^-$ ring to the molecular orbital containing the unpaired electron. It is also noteworthy that the degree of covalency depends on the type of thiol ligands. $C_5H_5S^-$ seems to be more pulling the unpaired electron away from the metal than CH_3S^- ligand presumably due to mesomeric effect.

The values of the coefficients a and b of the $d_{x^2-y^2}$ and d_{z^2} metal-ion orbitals for all complexes listed in Table II show that the unpaired electron lies in a molecular orbital composed primarily of $d_{x^2-y^2}$ orbital mixed with a very small amount of the corresponding metal-ion d_{z^2} orbital. Also it can be seen that the values of a and b are affected very little by the nature of the σ-ligands in the complexes.

The values of $P_{md}(B_2^*)$ and $P_{md}(B_1^*)$ are a measure of the bonding strength between the metal-ion d_{yz} orbital and the π-cyclopentadienide ring and between the metal-ion d_{xz} orbital and σ-ligand orbitals respectively. These values are all showing a high degree of covalency, with the bond to cyclopentadienide rings being the more covalent. Also it can be seen that the values of $P_{md}(B_2^*)$ are, as expected, fairly constant for all complexes, whereas the values of $P_{md}(B_1^*)$ vary with the nature of the σ-bonded ligands, the bonding to the thiol ligands being stronger than that to the chloride ligands.

The values of $P_{md}(A_2^*)$, which reflect the bonding strength between the metal-ion d_{xy} orbital and the π-ligand orbitals, also show a high degree of covalency and that the bonding in the thiocomplexes is stronger than that in the analogous chloride derivatives.

References

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