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The Relative Stability of Five and Six-Membered Chelate Rings in Palladium(II) Complexes Containing Bidentate Thioethers

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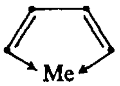
The equilibrium constants for the processes of the type:

$$Pd(L-L)I_2+2I^- \rightleftarrows PdI_4^{2-}+L-L$$

where L is a chelating thioether of the type R–S–(CH₂)ₙ–S–R (n = 2,3; R = phenyl, p*-chlorophenyl,* p*-tolyl,* m*-tolyl) have been measured in methanol at 25°C. The results show that the complexes with five-membered rings are more stable than those with six-membered rings and that the greater stability parallels a greater dependence of the equilibrium constant on the nature of the aryl radical R.*

Introduction

Mononuclear complexes formed from transition metals and bidentate ligands may be divided into two main classes. In the first the high stability of the chelate ring can be attributed to a resonance effect, often arising from the presence of conjugate double bonds and leading to a pseudo-aromatic ring of the type:



(Me = metal)

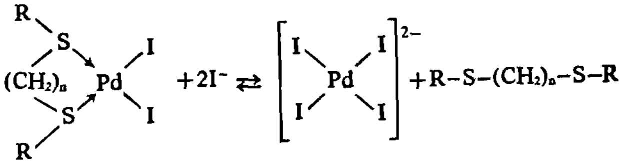
Complexes of this type are formed, for instance, by ligands such as α,α′-bipyridil, 1,10-phenanthroline, *o*-oxy-quinoline, acetylacetone etc. The second class includes compounds containing saturated bidentate ligands such as ethylendiamine, S-methyl-mercapto-acetic acid, etc.

In this second class it has been established[1] that the complexes with five-membered rings are, as a rule, more stable that the comparable complexes with six-membered rings. However, as far as this ring-size effect is concerned, the available data mainly originate from measurements carried out with metal ions of the first transition series, and it is reasonable to suppose that, on going from the first to the second and third transition series, the six-membered ring could become favoured owing to the greater size of the metal.

Some recent results concerning the displacement of bidentate thioethers from palladium(II) and platinum(II) complexes[2] showed that there is no significant difference between the lability of chelating thioethers forming either five or six-membered rings with the metal.

As a consequence, it seemed of interest to investigate the effect of ring size in the equilibria involving bidentate thioethers and palladium(II) species. It may also be noted that the covalent radii of palladium and platinum are almost the same (1.30 and 1.32 Å respectively).[3] From previous studies[4] on the reactivity of certain thioethers towards palladium(II) complexes it appears that in these cases no significant π bonding effects contribute to the S→Pd coordinate bond.

In this paper we report and discuss the values of the equilibrium constants relative to the processes



in methanol at 25° C, where n = 2,3 and R = phenyl, *p*-chlorophenyl, *p*-tolyl, *m*-tolyl. As the inductive effect of two methylene groups is different from that of three methylene groups we have also studied the effct of changing the radical R in order to estimate separately both the inductive effect and that of ring size.

Experimental Section

Materials. The complexes of the type $Pd(L-L)Cl_2$ where $L-L = C_6H_5-S-CH_2CH_2CH_2-S-C_6H_5$ and $C_6H_5-S-CH_2CH_2-S-C_6H_5$ were prepared according to methods reported in the literature.[5] The corresponding complexes with different ligands L–L were obtained by following the same general method, *i.e.* by adding a solution of the ligand in acetone to an aqueous solution of K_2PdCl_4 in the molar ratiol : 1. The products were filtered off in the form of yellow precipitates, whashed with water and recrystallized from acetone.

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(1) A. E. Martell and M. Calvin, « Chemistry of Metal Chelate Compounds », Prentice-Hall Inc., Third Edition, 1956 and references therein.

[2] G. Marangoni, S. Degetto and E. Celon, *Gazz. Chim. Ital.* 99, 816 (1969).

(3) F. G. Mann and H. R. Watson, *J. Chem. Soc.* 2772 (1958).

(4) L. Cattalini, G. Marangoni and M. Martelli, *Inorg. Chem.* 7, 1495 (1968).

(5) G. M. Bennet, A. N. Mosses and F. S. Statham, *J. Chem. Soc.* 1668 (1930).

Table I. Analytical data for the complexes of the type $Pd(R{-}S{-}(CH_2)_n{-}S{-}R)I_2$

R	n	% C Calcd.	 Found	% H Calcd.	 Fuond	% S Calcd.	 Found
phenyl	2	27.8	27.9	2.3	2.3	10.5	10.4
p-tolyl	2	30.26	30.3	2.83	3.1	10.1	10.08
m-tolyl	2	30.26	31.2	2.83	2.95	10.1	10.1
p-chlorophenyl	2	24.88	24.9	1.78	1.8	9.49	9.52
phenyl	3	29.04	28.9	2.59	2.6	10.33	10.3
p-tolyl	3	31.43	31.5	3.08	3.1	9.89	9.85
m-tolyl	3	31.43	31.9	3.08	3.07	9.89	9.91

Table II. Molar absorption coefficients at 338 mμ in CH_3OH at 25°C.

Complex	ε_{338} mμ
PdI_4^{2-}	20500±50
$Pd(C_6H_5{-}S{-}CH_2CH_2{-}S{-}C_6H_5)I_2$	9850±50
$Pd(pCH_3{-}C_6H_4{-}S{-}CH_2CH_2{-}S{-}C_6H_4{-}pCH_3)I_2$	9280±50
$Pd(mCH_3{-}C_6H_4{-}S{-}CH_2CH_2{-}S{-}C_6H_4{-}mCH_3)I_2$	10800±50
$Pd(pCl{-}C_6H_4{-}S{-}CH_2CH_2{-}S{-}C_6H_4{-}pCl)I_2$	11790±50
$Pd(C_6H_5{-}S{-}CH_2CH_2CH_2{-}S{-}C_6H_5)I_2$	9500±50
$Pd(pCH_3{-}C_6H_4{-}S{-}CH_2CH_2CH_2{-}S{-}C_6H_4{-}pCH_3)I_2$	11400±50
$Pd(mCH_3{-}C_6H_4{-}S{-}CH_2CH_2CH_2{-}S{-}C_6H_4{-}mCH_3)I_2$	12820±50

The various complexes of the type $Pd(L{-}L)I_2$ were prepared by methatetical exchange with iodide ion (slightly in excess) from the corresponding chloride complexes in a 1 : 1 methanol-acetone solution. The complexes were characterized by elemental analysis (the data are summarized in Table 1) and I.R. spectra.

The solvent methanol was purified by refluxing and distillation over $(CH_3O)_2Mg$ before use. The iodide ion was introduced in the reaction mixture as the tetrabutylammonium salt (C. Erba product, reagent grade).

Equilibrium measurements. The equilibrium constants of various systems were determined spectrophotomertically, by measuring the optical density of methanolic solutions of the appropriate complex and tetrabutylammonium iodide at 338 mμ, corresponding to the maximum in the absorption spectrum of the PdI_4^{2-} anion.

Preliminary measurements showed that all the neutral complexes obey Beer's law in methanol under these experimental conditions. The low solubility of the neutral complexes made it possible to prepare solutions having a concentration of the order of magnitude of 10^{-5} mole/l. It was possible, from a series of repeated runs, to measure the molar absorption coefficients at 338 mμ of the various species considered. The values are reported in Table II. The same was done for the tetraiodopalladate(II) anion in the presence of excess I^- (which also prevents solvolysis). The value of the molar absorption coefficient at 338 mμ is constant over a range of I^- concentrations from 10^{-3} to 10^{-1} mole/l.

By following the change with time of spectrum of a solution of a given complex and iodide ion it was possible to establish when the system reached equilibrium. The experiments were carried out with thermostated solutions in the thermostated compartment of an Optica CF4R recording spectrophotometer (25± 0.05° C). In every run the concentration of the iodide ion was in large excess as compared to the concentration of the palladium complex.

The equilibrium constant is given by

$$K = x^2/(c_{Pd}-x)(c_I-2x)^2$$

where x = equilibrium concentration of PdI_4^{2-} = equilibrium concentration of organic ligand and c_{Pd}–c_I are the initial concentrations of the palladium complex and halide ion respectively.

Since, under our conditions, $c_I \gg 2x$,

$$K = x^2/(c_{Pd}-x)(c_I)^2$$

The optical density at 338 mμ of the starting solution and of the solution at equilibrium, D_o and D_e are respectively:

$$D_o = \varepsilon_1 c_{Pd}$$

$$D_e = \varepsilon_1(c_{Pd}-x)+\varepsilon_2 x$$

where ε_1 and ε_2 are the molar absorption coefficients of the starting complex and PdI_4^{2-} respectively.

By using the experimentally determined values of D_o, D_e, ε_1, ε_2, it is possible to calculate the equilibrium constants, since:

$$R = D_e/D_o = \frac{c_{Pd}-x}{c_{Pd}} + \frac{\varepsilon_2}{\varepsilon_1}\cdot\frac{x}{c_{Pd}}$$

$$x = \frac{R-1}{(\frac{\varepsilon_2}{\varepsilon_1}-1)}\cdot c_{Pd}$$

and therefore

$$K = \frac{(R-1)^2}{(\frac{\varepsilon_2}{\varepsilon_1}-1)(\frac{\varepsilon_2}{\varepsilon_1}-R)}\cdot\frac{c_{Pd}}{c_I^2}$$

The form of the expression for the equilibrium constant has been confirmed by determining the dependence of the position of quilibrium on the iodide ion

Table III. Equilibrium constants, K, for the processes (1) in methanol at 25°C.

R	σ	n	n° of runs	K, M^{-1}	probable error
p-tolyl	-0.17	2	8	0.011	± 0.0005
m-tolyl	-0.07	2	7	0.059	± 0.004
phenyl	0.00	2	10	0.19	± 0.05
p-Cl-phenyl	$+0.23$	2	7	4.73	± 0.2
p-tolyl	-0.17	3	8	5.95	± 0.4
m-tolyl	-0.07	3	10	10.9	± 0.7
phenyl	0.00	3	8	15.3	± 0.6

concentration. One example is reported in Figure 1, where the values of

$$\log \frac{(R-1)^2 \, . \, D_o}{(\frac{\varepsilon_2}{\varepsilon_1} - R)}$$

determined in each experimental run, in the case of the complex with $C_6H_5-S-CH_2CH_2CH_2-S-C_6H_5$, have been plotted against the corresponding values of log C_I. As expected, the experimental data fit a straight line having a slope = 2.

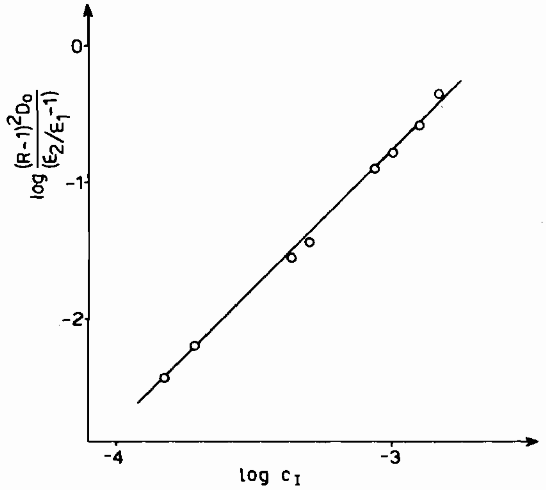

Figure 1. Second order dependence of the equilibrium constant from the iodide ion concentration for the complex containing the ligand $C_6H_5-S-CH_2CH_2CH_2-S-C_6H_5$.

Results and Discussion

The values of the equilibrium constants are summarized in Table III, together with the probable error The values of σ reported on the same Table are the Hammet constants,[6] *i.e.* a measure of the inductive effect of the radical R bonded to the sulphur donor atom.

In Figure 2 the values of log K are plotted against the values of σ. The present discussion will be developed with reference to Figure 2 which summarized all the results obtained during this work.

The first point to be considered is that in all the systems examined the complexes with five-membered rings are more stable than those with six-membered rings. The difference in stability depend on the nature of the chelating molecule. These differences are significant in all cases and show that the tendency to form five better than six-membered rings does not markedly depend on the size of the central metal.

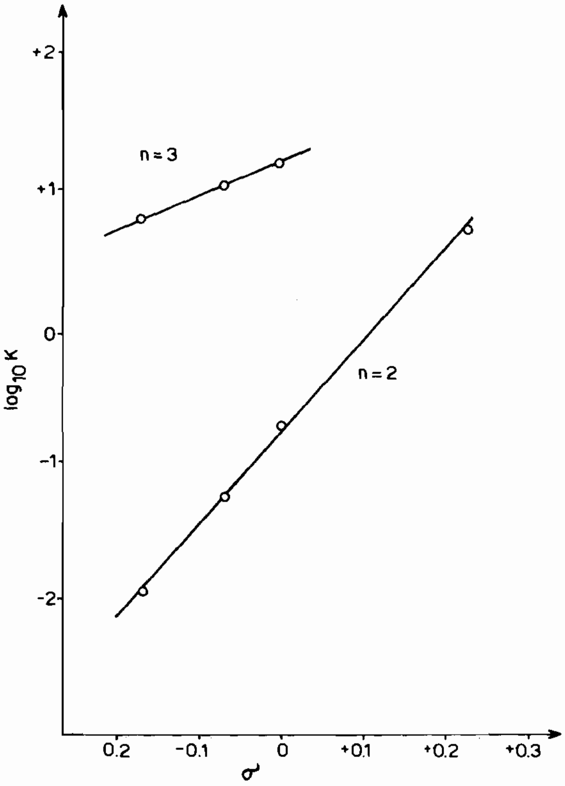

Figure 2. Linear relationships between the values of log K and the Hammet σ constants relative to the radical R bounded to the sulphur atom in the molecule $R-S-(CH_2)_n-S-R$.

A possible comparison can be made, for instance, with the typical equilibria:

$$Cu^{2+} + en \rightleftarrows Cu(en)^{2+} \qquad (\log \beta = 10.72)$$

$$Cu^{2+} + tn \rightleftarrows Cu(tn)^{2+} \qquad (\log \beta = 9.98)$$

where en = ethylendiamine and tn = 1,3-diaminopropane.[7] In this case the difference is smaller than in the systems reported in this paper even though the copper ion is significantly smaller than the palladium ion.

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(6) Jaffe, *Chem. Revs.* 53, 191 (1963).

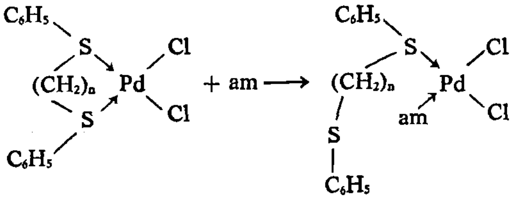
(7) F. A. Cotton and G. Wilkinson, « Advanced Inorganic Chemistry », Interscience Pub., 1962, pag. 546.

Another example is seen in the copper(II) complexes of alanine and β-alanine, where the values of log K are 8.40 and 7.15 respectively.[1]

The data reported in Table III and in Figure 2 show clearly that the different stabilities are due to the ring size and not to the changing inductive effect resulting from the presence of different numbers of $-CH_2-$ groups in the chelate molecules. In fact, the variation arising from the different inductive effects of the radicals R do not change the generally greater stability of the five-membered rings as compared to the six-membered ones. On the other hand, on increasing the tendency to induce negative charge on the sulphur atom (as happens on introducing an extra methylene in the chelate ring) the difference in stability of the two types of cycles increases (in the case of R = *p*-tolyl the values of log K differ by nearly three orders of magnitude).

The different slopes of the lines in Figure 2 indicate that the effect of the nature of the radical R is larger in the case of the five-membered ring, the slope being 6.9 when n = 2 and 2.5 when n = 3.

These observations can be used in discussing the mechanism of reaction of the complexes discussed above. For example, in the reactions of the type



in which the chelate ring is opened it was found[2] that there is no significant difference in the labilities of the complexes with five- and with six-membered rings. In the present equilibrium experiments it appears that the two sets of complexes (with n = 2 or 3) have different ground state energies and that this difference arises mainly from the difference in ring-size. As the difference in labilities is negligible, the difference in the transition state energies for the two kinds of complex must be roughly equal to the difference in their ground state energies. It seems improbable that this equality results from a coincidental balance between the ring-size and inductive effects in the transition states of the complexes with five- and six-membered rings. We therefore assume that the same factors are operative in determining both the ground state and the transition state energies. This implies, as has already been suggested tentatively,[2] that the similarity in lability is due to the associative nature of the displacement processes at palladium(II) planar complexes, so that the chelate ring is almost as completely bound in the transition state as it is in the ground state.

The present results are also relevant to the data obtained by Bjerrum in the reactions of chelation of ethylendiamine or 1,3-diaminopropane to platinum(II).[8] Also in this case the results were interpreted in therms of a greater stability of the five-membered ring as compared to the six-membered one.

Aknowledgments. This work has been carried out with the financial support of the Italian Council for Research (C.N.R. - Rome) through the contract No. 69/00383/115/2893.

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(8) O. Mønsted and J. Bjerrum, « Proceedings of the XI I.C.C.C. », Haifa and Jerusalem, 1968, pag. 103.