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Metal Complexes of Sulfur–Nitrogen Chelating Agents. IV. Complexes of Ni(II), Pd(II), Pt(II), and Rh(III) with Methyl Ester of 2-Amino-1-cyclopentene-1-carbodithioic Acid

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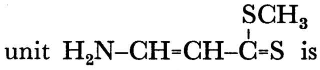
The methyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid (HE) acts both as an unidentate and a bidentate ligand. With Ni(II) and Pd(II) the deprotonated chelates of the ME_2 type are obtained readily, the corresponding Pt(II) complex being obtained on the addition of an equivalent amount of alkali. In these compounds, bond formation takes place from the nitrogen and the sulfur atoms and there is strong delocalization in the chelate ring. Unidentate bonding behavior of the ligand is observed in the complexes $Pt(HE)_2Cl_2$ and $Rh(HE)_3Cl_3$, where the bonding takes place through the nitrogen atom only.

Coordination compounds with ligands showing linkage isomerism are a topic of interest. We have shown[1-4] that in the complexes of 2-amino-1-cyclopentene-1-carbodithioic acid (ACDA) and its *N*-ethyl derivative the metal-ligand bonding takes place either from the amino nitrogen and the deprotonated thiol sulfur or from the dithiocarboxylic moiety depending on the type of a metal ion. The methyl ester of ACDA which contains the skeletal unit  $H_2N\text{-}CH{=}CH\text{-}\overset{SCH_3}{\underset{|}{C}}{=}S$ is also capable of forming linkage isomers with metal ions. There are several possibilities for the ligand to bind a metal ion, *e. g.* (i) through NH_2 and C=S, (ii) through NH_2 and the deprotonated thiol sulfur or through the deprotonated amino nitrogen and C=S, (iii) through NH_2 only, (iv) through C=S only, and (v) interaction of SCH_3 in combination with the other donor atoms.

We wish to report here the preparation and characterization of Ni(II), Pd(II), Pt(II), and Rh(III) complexes with the methyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid (hereafter abbreviated as HE).

Experimental

The ligand was prepared by the method of Bordás *et al.*[5] and recrystallized from (1 : 1) ethanol-water mixture (mp 75 °C, lit,[5] 77—79 °C). Satisfactory results in the elemental analysis of the compound were obtained (Table 1). Other chemicals used were of reagent grade.

Preparation of the Complexes. NiE_2: To an ethanolic solution of the ligand (4 mmol) was slowly added an ethanolic solution of hydrated nickel chloride (2 mmol) with stirring. The complex began to separate almost immediately, but to ensure the completion of reaction the mixture was stirred for 30 min. The olive green crystals were collected by filtration, washed with ethanol, and recrystallized from chloroform; yield 90%.

PdE_2: On slow addition of an ethanolic solution of the ligand (4 mmol) to an ethanolic solution of sodium tetrachloropalladate(II) (2 mmol), a brownish yellow compound was formed. This was filtered and washed first with ethanol and then with water till the filtrate showed negative test for chloride ion. The compound was recrystallized from chloroform; yield 80%.

$Pt(HE)_2Cl_2$: A mixture of potassium tetrachloroplatinite (II) (2 mmol) and HE (4 mmol) in acetone was stirred for 2 h. The brownish red product was filtered, washed with ethanol and warm water, and finally recrystallized from chloroform; yield 70%.

$PtE_2 \cdot H_2O$: To a solution of potassium tetrachloroplatinite (2 mmol) in acetone was added dropwise a mixture of 4 mmol of the ligand and 5 mmol of sodium hydroxide in ethanol. The brick red product was filtered and washed successively with petroleum ether, 1 : 1 aqueous ethanol, and warm water. The compound was recrystallized from chloroform; yield 70%.

$Rh(HE)_3Cl_3 \cdot 2H_2O$: A mixture of hydrated rhodium chloride (2 mmol) and the ligand (6.5 mmol) in acetone was stirred for 4 h. A brown compound precipitated slowly was collected on a glass frit, and washed with acetone and water. The compound was dried over fused calcium chloride but could not be recrystallized due to the lack of solvent; yield 50%.

Physical Measurements. Infrared spectra were recorded in nujol mulls on a Perkin-Elmer 457 spectrophotometer in the frequency range 4000—250 cm^{-1}. The NMR spectrum of the ligand in carbon tetrachloride was recorded on a Varian T 60 spectrometer using TMS as a reference. Electronic spectral measurements were made on a Hilger UV-spek spectrophotometer. Conductivity measurements were carried out using a Philips PR 9500 conductivity bridge. Magnetic measurements were performed on a Guoy balance. Thermal analysis was carried out in a Derivatograph (MOM). Molecular weight determination was made with a Mechrolab vapor phase osmometer.

Analyses. C and H were determined by micro combustion analysis, nitrogen by semimicro combustion analysis, and sulfur and metal ions as described earlier.[1]

Results and Discussion

The analytical data (Table 1) indicate that with HE two types of compounds are obtained, *viz.* (a) type ME_2(Ni, Pd, Pt) in which the ligand is in the deprotonated form, and (b) type $M(HE)_mX_n$(Pt, Rh) in which the ligand is in the uncharged form. With Ni(II) and Pd(II), compounds of the type $M(HE)_2Cl_2$ could not be prepared; NiE_2 is formed even in slightly acidic solution (pH≈2). Of the compounds, NiE_2 is soluble in chloroform, acetone, and DMF; PdE_2 in chloroform, nitrobenzene, and DMSO, $PtE_2 \cdot H_2O$ in chloroform and DMF, $Pt(HE)_2Cl_2$ in acetone, chloroform, and nitrobenzene, and $Rh(HE)_3Cl_3 \cdot 2H_2O$ in DMF. The diamagnetic nature of the compounds under investigation indicates the square planar configuration of Ni(II), Pd(II), and Pt(II) complexes and the octahedral configuration of the Rh(III) complex. Both $Pt(HE)_2Cl_2$ and $Rh(HE)_3Cl_3$ act as non-electrolytes (in nitro-

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TABLE 1. ANALYTICAL DATA

Compound	Decomposes at °C	%C		%H		%Cl		%M		%N		%S	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_7H_{11}NS_2$	75	48.56	48.48	6.36	6.28					8.09	8.20	37.00	36.81
$C_{14}H_{20}N_2S_4Ni$	250							14.58	14.61	7.01	6.94	31.71	31.65
$C_{14}H_{20}N_2S_4Pd$	240							23.62	23.54	6.22	6.30	28.42	28.31
$C_{14}H_{22}ON_2S_4Pt$	220	30.16	30.32	3.95	4.05					5.02	5.10		
$C_{14}H_{22}N_2S_4Cl_2Pt$	200	27.45	27.60	3.59	3.65	11.58	11.40			4.57	4.61		
$C_{21}H_{37}O_2N_3S_6Cl_3Rh$	250	32.97	33.12	4.32	4.45	13.67	13.51			5.50	5.43		

TABLE 2. SOME STRUCTURALLY IMPORTANT INFRARED BANDS IN THE DEPROTONATED CHELATES OF HE

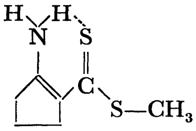
HE	NiE_2	PdE_2	$PtE_2 \cdot H_2O$	Assignments
3240(b, w)	3260(m)	3255(w)	3280(b, w)	ν(N-H)
1595(s)	1580(s)	1585(s)	1585(m)	δ(N-H) + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1410(w)	1420(m)	1420(m)	1410(w)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$
1305(w)	1305(w)	1310(w)	1310(w)	$\nu(\mathrm{S{-}CH_3})$
1260(w, b)	1290(w) 1255(m) 1225(w)	1290(w) 1245(b)	1290(w) 1245(w) 1215(w)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
1155(w, b)	1130(w)	1140(w)	1130(w)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$
970(m)	980(m) 965(m)	975(w) 960(w)	980(w)	CH_2 rocking
905(m)	910(s) 860(w)	900(s) 840(w)	915(s) 860(w)	assym($CSSCH_3$)
610(m)	630(w)	630(w)	630(w)	sym($CSSCH_3$) or ν(C-S)
—	490(w)	520(m) 490(w)	500(w)	ν(M-N)
—	380(m)	350(m)	355(w)	ν(M-S)

benzene) which indicate the unidentate behavior of the ligand in these compounds.

In order to confirm the coordination sites involved in bond formation, the structure of the ligand itself requires prior consideration. The PMR spectrum of the ligand has the following characteristics: 4-CH_2 (δ 1.78 ppm; quintet), SCH_3 (δ 2.50 ppm; singlet), 3,5-CH_2 (δ 2.33—2.93; multiplet), NH (δ 5.66 ppm; broad, slowly exchanged with D_2O). The above assignments are compatible with structures I and II, excluding other structures which could be envisaged. The hydrogen bonded structures are also supported by the IR spectra of the ligand (in the solid state and in chloroform) which show the presence of a weak broad band due to ν(N-H) at 3240 cm^{-1}, and the absence of a band due to ν(S-H). It appears that both the tautomeric forms coexist in solution.

In the ME_2 type chelates bond formation may take place as in III or IV. If the bond type is III, bands due to C=C and C=S stretching should be expected in the IR spectra. In the bond type IV both ν(C=C) and ν(C=N) vibrations will be observed but no band due to ν(C=S). For substituted cyclopentenes ν(C=C) is observed in the range 1670—1620 cm^{-1}, and for non-conjugated systems ν(C=N) is usually observed in the range 1690—1640 cm^{-1}. For a series of esters of carbodithioic acid Bellamy and Rogasch[6)] reported ν(C=S) in the range 1200—1170 cm^{-1}. Thus, a band around 1650 cm^{-1} is expected in both III and IV. However, if a delocalized chelate ring (V) results from the conjugation of 1,3-double bonds present in III and IV, bond orders of C=C, C=N, and C=S will decrease to a great extent. As a result, the stretching vibrations will be observed at lower frequencies. This was actually the case as shown in Table 2. It can be seen that the ν(N-H) band of the ligand at 3240 cm^{-1} remains almost in the same position as in the chelates. The lowering of ν(N-H) frequency in the ligand is shown to be due to hydrogen bonding and in the chelates the lowering of this band to a similar extent is also justified with the bond type (V). Two new bands appearing at 500 cm^{-1} and in the 380—350 cm^{-1} range are assigned to ν(M-N) and ν(M-S) respectively. In Table 2 assignments, based on observations made in several other related systems,[1—4,6—9)] have been made to several other vibrations which are structurally important.

Bond formation may take place either as VI or VII in $Pt(HE)_2Cl_2$ and in $Rh(HE)_3Cl_3$ where the unidentate nature of the ligand has been indicated. If bond formation takes place through the thione sulfur atom, ν(N-H) should be expected to occur in the 3500—3300 cm^{-1} range (the usual range for primary amines), whereas bond formation through the amino nitrogen atom would result in its displacement to lower frequency. In the Pt(II) complex two weak bands appear at 3220 and 3150 cm^{-1}, and in the Rh(III) complex these two bands are observed at 3240 and 3140 cm^{-1}. The presence of two bands and their shift to lower frequency indicates bond formation through the nitrogen atom. The band due to (N-H) deformation appears as a shoulder in the Pt(II) complex and as a band of medium intensity in the Rh(III) complex at 1580 cm^{-1}. In these two compounds a new band observed at 1630 cm^{-1} is absent in the ligand as well as in the deprotonated chelates. On the basis of the preceding arguments we assign this band due to ν(C=C). Moreover, a band due to ν(C=S) as required in VI is observed in the expected range, *viz.* at 1200 cm^{-1} in the Pt(II) complex and at 1215 cm^{-1} in the Rh(III) complex. Although ν(M–N) appears in both compounds at 500 cm^{-1}, ν(M–Cl) which is usually observed at 350—300 cm^{-1} probably gets merged with the ligand band at 320 cm^{-1}. Except for these bands no other significant variation in the spectral features of these compounds from the deprotonated chelates could be observed.



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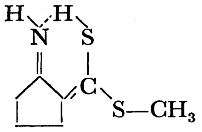

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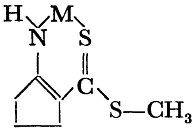

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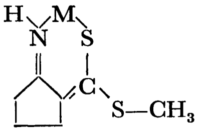

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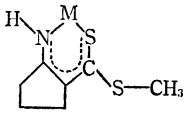

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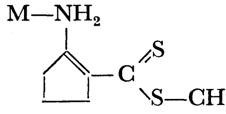

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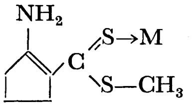

VII

The electronic spectra of the compounds proved to be less useful in confirming the bond types because of the presence of high intensity ligand bands in the UV region. In methanol, the ligand shows the presence of two bands at 25840 and 32050 cm^{-1} with the extinctions (log ε) 4.38 and 4.10, respectively (in chloroform these bands are shifted slightly to lower energy). The spectra of the complexes were measured in chloroform solution except for the Rh(III) compound for which a dimethylformamide solution was used. In the nickel complex the lowest energy band at 15870 cm^{-1} (log ε=1.98) is the ν_1 band ($^1A_{1g} \rightarrow {}^1A_{2g}$) of the square planar complexes. The next higher energy band observed at 22730 cm^{-1} (log ε=3.72) appears to be the ν_2 band ($^1A_{1g} \rightarrow {}^1B_{1g}$), but the high extinction indicates that it is mixed with the ligand band in this region. A third band at 33560 cm^{-1} (log ε=4.68) arises due to internal ligand transition. It is interesting to note that in complexes containing the chromophore [NiS_4], the ν_1 band is observed in the range 14500—16000 cm^{-1},[10] whereas for[NiN_2S_2] chromophore, it is usually observed at 18000 cm^{-1}.[11,12] The energy of the ν_1 band in our complex (15870 cm^{-1}) on this basis would indicate disulfur chelated species. However, molceular weight determination in chloroform established the monomeric nature of the complex and the infrared data showed that chelation takes place from the nitrogen and the sulfur atoms. There are increasing evidences[13,14] to show that in [NiN_2S_2] chromophores having strong delocalization in the chelate ring the energy range for the ν_1 band is 15500—16500 cm^{-1}.

No band due to d-d transition could be noted in the Pd(II), Pt(II), and Rh(III) complexes. This is not unexpected since the energy range at which such transitions occur is masked by the ligand band. The Pd(II) complex shows two bands at 24510 cm^{-1} (log ε=3.93) and 32680 cm^{-1} (log ε=4.38) due to the ligand, however a band at 41150 cm^{-1} (log ε=4.55) appears to be due to charge transfer transition. Similar is the case with $PtE_2 \cdot H_2O$ whose bands are located at 26320 cm^{-1} (log ε=3.87), 31250 cm^{-1} (log ε=4.25) and 41150 cm^{-1} (log ε=4.24). $Pt(HE)_2Cl_2$ shows only two bands at 30770 cm^{-1} (log ε=4.33) and 41490 cm^{-1} (log ε=4.34). In the Rh(III) complex also only the ligand bands at 25840 cm^{-1} (log ε=4.28) and 36360 cm^{-1} (log ε=4.59) are observed.

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