

Metal Complexes of Sulphur-Nitrogen Chelating Agents : Part IX— Nickel(II), Palladium(II) & Cobalt(II) Complexes of (2-Aminocyclopentene-1-dithiocarboxy)-S-acetic Acid

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The reaction between 2-aminocyclopentene-1-dithiocarboxylic acid and chloroacetic acid leads to the formation of the title ligand (H_2ACDSA). In the nickel(II) complex, $(NH_4)_2[Ni(ACDSA)_2] \cdot 2H_2O$, the ligand binds the metal atom through the amino nitrogen and deprotonated thiol sulphur whereas the carboxyl group in ionized form remains uncoordinated. In the palladium(II) complex, $Pd(HACDSA)_2 \cdot 2H_2O$, although the same donor sites are involved in bond formation, the carboxylic acid does not undergo dissociation. The amino nitrogen, thioether sulphur and carboxyl groups are all bound to the cobalt(II) atom in $Co(HACDSA)(OAc)$.

STUDIES on metal complexes of sulphur containing amino acids have aroused considerable interest^{1,2} as they are considered as models of metal sulphur proteins³⁻⁵. For quite sometime we have been investigating nature of bonding and stereochemical aspects of metal complexes derived from 2-aminocyclopentene-1-dithiocarboxylic acid and its derivatives⁶⁻¹². As a part of our continued interest in this area we recently reported the syntheses of the title ligand and its binuclear $Cu(II)$ - $Cu(I)$ mixed-valence species¹³. Here we wish to report variation in the donor sites involved in the formation of nickel(II), palladium(II) and cobalt(II) complexes with this ligand.

Materials and Methods

Preparation of the ligand (H_2ACDSA) — 2-Amino cyclopentene-1-dithiocarboxylic acid⁶ (12.7 g, 0.08 mol) in methanol (150 ml) was neutralized with potassium hydroxide (4.5 g, 0.08 mol) dissolved in 1 : 1 methanol-water mixture (50 ml). Similarly, monochloroacetic acid (7.6 g, 0.08 mol) in methanol (50 ml) was neutralized separately by adding an equivalent amount of potassium hydroxide. The two solutions were mixed together and refluxed for 1 hr on a steam-bath. On cooling at 0°C potassium chloride crystals separated out which were removed by filtration. The filtrate was reduced to a small volume in a rotary evaporator while further quantity of potassium chloride which precipitated out was filtered off. The filtrate was diluted to 500 ml with water, filtered, and neutralized with 2N HCl under ice cooling. The yellow prismatic crystals deposited were collected, washed with water and recrystallized from 1 : 1 methanol-water; yield 12 g (80%); m.p. 150–51°. (Found : C, 44.18; H, 5.10; N, 6.51. $C_8H_{11}NO_2S_2$ requires C, 44.24; H, 5.07; N, 6.45%.)

Preparation of the metal complexes : $(NH_4)_2[Ni(ACDSA)_2] \cdot 2H_2O$ — The ligand (0.88 g, 4 mmol) was

dissolved in ethanol (40 ml) and ammonium acetate (2 g) added to it and the solution filtered. To the filtrate was added a solution of nickel chloride hexahydrate (0.48 g, 2 mmol) in ethanol (15 ml) with stirring. The solution turned deep green and within a few minutes a green crystalline compound separated out. The compound was collected, washed several times with ethanol and recrystallized from methanol; yield 0.69 g (60%). (Found : C, 34.20; H, 5.44; N, 9.98; Ni, 10.51. $C_{16}H_{20}N_4O_6S_4Ni$ requires C, 34.13; H, 5.34; N, 10.03, Ni 10.44%.)

$Pd(HACDSA)_2 \cdot 2H_2O$ — Sodium tetrachloropalladate (0.6 g, 2 mmol) dissolved in methanol (15 ml) was added slowly with constant stirring to a methanolic solution (30 ml) of the ligand (0.88 g, 4 mmol). An orange-yellow compound formed was filtered, washed repeatedly with water and ethanol till a negative test for chloride ion was obtained, and recrystallized from methanol; yield 0.3 g (50%). (Found : C, 33.56; H, 4.12; N, 4.95; Pd, 18.62. $C_{16}H_{24}N_2O_6S_4Ni$ requires C, 33.43; H, 4.18; N, 4.87; Pd, 18.53%.)

$Co(HACDSA)(OAc)$ — Cobalt acetate hexahydrate (0.57 g, 2 mmol) dissolved in methanol (15 ml) was added dropwise with stirring to a methanolic solution (30 ml) of the ligand (0.88 g, 4 mmol). The mixture was stirred for 30 min and the compound that precipitated out was filtered off and washed several times with methanol; yield, 0.55 g (75%). Recrystallization of this compound could not be accomplished due to its poor solubility in common organic solvents. (Found : C, 35.85; H, 3.96; N, 4.12; Co, 17.58. $C_{10}H_{13}NO_4S_2Co$ requires C, 35.94; H, 3.89; N, 4.19; Co, 17.65%.)

Physical measurements — Infrared spectra of the compounds were recorded in KBr matrix on a Beckman IR-20A spectrophotometer, electronic spectra on a Cary 17D spectrophotometer and the PMR spectra on a Varian 90 MHz spectrometer. Solution

conductivity measurements were made with a Philips PR 900 conductivity bridge. Magnetic measurements at room temperature were performed on a Guoy balance.

Results and Discussion

The reaction between 2-aminocyclopentene-1-dithiocarboxylic acid and monochloroacetic acid in principle can generate either **1** or **2** having the empirical composition $C_8H_{11}NO_2S_2$.

The mass spectrum of the ligand shows three prominent peaks at m/z 217 (M^+), 158 and 126, of which the last one is most intense. Fragmentation of the molecular ion could account for the various peaks (see structure **1**).

The PMR spectrum (chemical shifts in δ ppm) of the ligand is also consistent with structure (**1**). The two-proton multiplet at 1.83 has been assigned to 4- CH_2 , another five-proton multiplet at 2.68 to 3- CH_2 , 5- CH_2 and NH, the two-proton singlet at 4.07 to S- CH_2 ; two more protons observed at downfield (~ 11.1) are due to COOH and N-H...S. However, IR spectrum of **1** shows the absence of free COOH since the band expected at 3500 is absent. This could be either due to zwitterionic structure or due to the formation of a dimeric planar ring by

intramolecular hydrogen bonding between two COOH groups. The appearance of a strong band at 3330 and a weaker one at 3120 rules out, the presence of $-NH_3^+$ due to zwitterion formation.

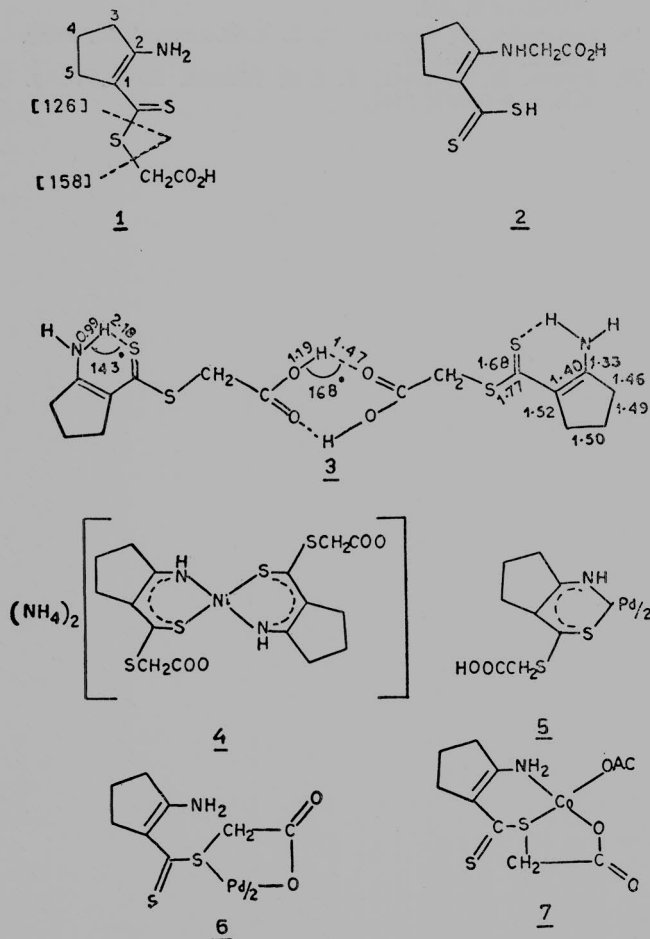
The ligand also shows two weak bands at 2680 and 2580 and medium bands at 1490, 1300 and 925, thereby indicating a dimeric structure as reported by McAuliffe¹⁴ and Hadzi *et al.*^{15,16} Two strong bands observed at 1710 and 1595 may be taken as due to $\nu(C=O)$ and $\delta(NH) + \nu(C \cdots C)$ respectively. The close resemblance in IR and PMR spectra of **1** with those of the methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid⁹ leads to the conclusion that in this case also there is intramolecular hydrogen bonding between $-NH_2$ and C=S groups. In fact X-ray crystallographic study of the ligand has confirmed¹⁷ structure **3**.

The nickel (II) complex, $(NH_4)_2[Ni(ACDSA)_2] \cdot 2H_2O$ is soluble in polar organic solvents like methanol, DMF, DMSO, nitrobenzene etc. This compound is diamagnetic and its electrical conductivity ($55 \text{ ohm}^{-1} \cdot \text{cm}^2 \text{ mol}^{-1}$) measured in nitrobenzene shows it to be a 1 : 2 electrolyte. The electronic spectrum is a typical of square planar nickel(II) complexes having N, S bondings^{9,11} and is very similar to that of nickel(II) complexes of the methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid. The band at 16260 is assigned to the transition ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and another $\sim 23000 \text{ cm}^{-1}$ is a charge transfer band.

The IR spectrum of the complex shows a broad band at 3500 assignable to non-coordinated water molecules. Thermal analysis also reveals that dehydration takes place between 80° – 100° . A medium intensity band at 3280 may be due to coordinated NH_2 group, although in the presence of NH_4^+ ion this is not a definite evidence. A shoulder at 1590 may be considered as due to free COO^- group¹⁸⁻²⁰. Moreover, the complex shows close resemblance to several other bands observed in Ni(II) complex^{9,11} of methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid. On the basis of these data structure (**4**) can be proposed for the Ni(II) complex.

The palladium (II) complex, $Pd(HACDSA)_2 \cdot 2H_2O$ is a nonelectrolyte in nitrobenzene, ($\Delta_M 2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The two water molecules in the complex occupy lattice positions as evidenced from thermal analysis. Since composition and stereochemistry of the palladium complex indicate monoprotic and bidentate nature of the ligand, there remain two possibilities, viz. **5** and **6** in which metal-ligand binding may take place.

The IR spectrum shows a medium intensity band at 3300 which is indicative of amino group coordination. Similar to the ligand, the complex also shows a broad and weak band at ~ 2600 . The presence of unionized COOH is indicated by two strong bands at 1700 and 1670. Also like the nickel(II) species band due to $\delta(NH) + \nu(C \cdots C)$ appears at 1580. The appearance of a satellite band at 2600 and two weak bands at 1410 and 1300 indicate that the free COOH groups in the complex are probably associated in the dimeric form.



Support in favour of (N, S⁻) type bonding is available from the electronic spectrum of the complex in DMSO which shows the presence of a charge transfer band at 24,700. It may be mentioned that in the corresponding compounds with methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid⁹ and N,N'-ethylene-bis(methyl 2-amino-1-cyclopentene-dithiocarboxylate)¹¹ where metal-ligand binding occurs as in **5**, the charge transfer bands appear in the region 24,000-15,000. The PMR spectrum of the complex in DMSO-d₆ shows that the S-CH₂ singlet (4.05) appears in the same position as in the ligand and therefore precludes the bonding sites as shown in **6** because in such case there would have been considerable down-field shift of S-CH₂ proton. On the other hand, down-field shift of 4-CH₂ (1.93) and 3,5-CH₂ (2.63 at the centre of gravity) with respect to the ligand is in conformity with **5**. The water molecules in the complex appear as a broad peak at 3.5.

The Co(II) complex, Co (HACDSA) (OAc) is also a nonelectrolyte in nitrobenzene. The room temperature magnetic moment of the compound (4.28 B.M.) indicates a tetrahedral geometry. The absence of a band at 1700 in its IR spectrum indicates the absence of free COOH group. The ν_{as} (COO⁻) at 1580 indicates that COO⁻ is either coordinated or free. The latter may be rejected on the basis of electro-neutrality of the compound. The band at 3270 shows coordinately bound amino group. Plausible binding sites involved in the complex are shown in **7**.

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