

## Metal Complexes of Sulphur–Nitrogen Chelating Agents. I. 2-Aminocyclopentene-1-Dithiocarboxylic Acid Complexes of Ni(II), Pd(II) and Pt(II).

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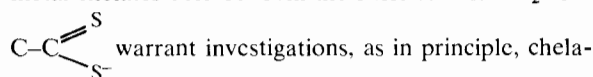
The Ni(II), Pd(II) and Pt(II) chelates of 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) are described. With each metal ions, two differently colored products having identical composition  $M(ACDA)_2$  are obtained when reactions are carried out with the acid itself and its ammonium salt. PMR spectra of ACDA indicates strong hydrogen bonding between one amino proton and thiocarbonyl sulphur atom. The nature of bonding in the complexes have been investigated from their i.r., pmr and electronic spectra, magnetic moment, thermal analysis and X-ray diffraction data. In all the chelates bonding with metal ions occur through amino nitrogen and deprotonated thiol sulphur. The stability constant of Ni-ACDA complex has been evaluated spectrophotometrically. Ni(ACDA)<sub>2</sub> forms a 1:2 adduct with pyridine. The color difference in the chelates probably arises due to geometrical isomerism.

### Introduction

The avid interest in studying many novel aspects of sulphur containing metal chelates has engendered large number of publications<sup>1-7</sup> during recent years. Of particular importance are the disulphur chelated species derived from (i) 1,1-dithiolates, viz., dithiocarbamates, dithiophosphates, dithioxanthates, dithiocarboxylates etc., (ii) 1,2-dithiolenes and (iii) 1,3-dithiolenes like dithio-β-diketone and dithio-β-keto esters. Another important topic of contemporary interest is the metal complexes derived from sulphur–nitrogen containing chelating agents, in many of which, both nitrogen and sulphur atoms are involved in bond formation, while in some others metal ions display preference for bond formation either with nitrogen or with sulphur. In this respect the bonding behavior in the complexes of hydrazine dithiocarboxylic acid and its derivatives have gained considerable importance due to recent studies by different groups of workers<sup>8-10</sup>. In as much as their interaction with nickel ion is concerned, while with hydrazine dithiocarboxylic acid and some of its substituted derivatives bond formation occurs through

terminal amino and thiol sulphur, with some other substituted acids disulphur chelation occur. Thus, chelating agents which are akin to this type of ligands would have a tendency to exhibit ambidentate nature.

In this context it appears to us that studies on metal chelates derived from the skeletal unit  $NH_2-C=$



tion may occur from either of the sites (N,S<sup>-</sup>,S), (N,S<sup>-</sup>) or (S,S<sup>-</sup>). With a view to explore such possibilities we have undertaken a systematic investigation on the metal complexes of 2-amino cyclopentene-1-dithiocarboxylic acid (heretofore referred as ACDA), and some of its derivatives. In this paper we wish to report our observations on Ni(II), Pd(II) and Pt(II) chelates.

Yokoyama *et al.*<sup>11</sup> described ACDA as the most sensitive color reagent for Ni(II) (visual sensitivity 20 ppb.) and alleged the formation of a tris-complex species in solution. Several metal complexes of ACDA including Ni(II) and Pt(II) were reported by Sen *et al.*<sup>12</sup>, though not studied in detail. Matolcsy *et al.*<sup>13</sup> related the antifungal behavior of ACDA to its ability to form metal chelates.

The highlight of the present study is that with each metal ions two differently colored species having identical composition are obtained. The nature of bonding in these differently colored compounds have been investigated from their i.r., electronic and <sup>1</sup>H nmr spectra, thermal analysis, magnetic moment and powder diffraction data.

### Experimental

#### Chemicals

Chemicals and solvents used were reagent grade. Na<sub>2</sub>PdCl<sub>4</sub> was prepared from PdCl<sub>2</sub>·xH<sub>2</sub>O (J. Matthey) and K<sub>2</sub>PtCl<sub>4</sub> from H<sub>2</sub>PtCl<sub>6</sub> (J. Matthey).

#### Preparation of the Ligand ACDA

The reagent was prepared following a modified procedure<sup>14</sup> of Takeshima *et al.*<sup>15</sup> The ammonium salt of

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the acid was prepared by stirring a mixture of cyclopentanone (25 g), carbon disulphide (30 g) and 28% aqueous ammonia (100 ml) below 0° C for eight hours. The yellow crude product was collected, washed with ether and dried over CaCl<sub>2</sub>; yield 26 g. In contrast to earlier observation<sup>15</sup> this ammonium salt could not be recrystallised from ethanol. The attempted recrystallisation causes substantial decomposition of the compound. The ammonium salt is not stable at room temperature, loses ammonia on standing. The acid was prepared by dissolving the crude product in water and slowly neutralizing with 2N HCl (avoiding excess) under ice-cooling. The yellow prismatic crystals were collected, washed with water and dried. The crude acid was dissolved in air free cold ethanol until saturation, an equal volume of water was added to the filtered solution and kept in an ice bath for half an hour. The shining yellow crystals were collected, washed with water-ethanol (1:1) and dried over CaCl<sub>2</sub>. It is recommended that the compound be preserved in a refrigerator. Yield 12 g, m.p 98° C (decomp).

#### Preparation of the Metal Complexes

##### *Ni(ACDA)<sub>2</sub>*

**Method A.** An ethanolic solution of ACDA (0.64 g, 4 mmol) was added dropwise with stirring to an ethanolic solution of hydrated nickel chloride (0.50 g, 2.1 mmol). The stirring was continued for fifteen minutes. The dark chocolate precipitate was collected by filtration, washed with ethanol and dried *in vacuo*. Yield 90%.

**Method B.** An aqueous solution containing 4 mmol of ammonium salt of ACDA (this was prepared by grinding 0.66 g of the acid with few drops of strong ammonia, the resulting paste was then extracted with water and the solution was used after filtration) was added dropwise with constant stirring to an aqueous solution of nickel chloride (0.50 g, 2.1 mmol). The stirring was continued for an additional hour, then filtered through fine porosity glass frit. The reddish violet compound was thoroughly washed with water and dried *in vacuo* over H<sub>2</sub>SO<sub>4</sub>. Yield 95%.

##### *Pd(ACDA)<sub>2</sub>*

**Method A.** An ethanolic solution of sodium tetrachloropalladate(II) (0.60 g, 2 mmol) was added slowly with stirring to an ethanolic solution of ACDA (0.67 g, 4.2 mmol). The resulting orange red complex was filtered off, washed first with ethanol, then with water till chloride free, again with ethanol and dried *in vacuo*. Yield 70%.

**Method B.** Same procedure as in method A was followed, the difference being aqueous solution of the ammonium salt of ACDA was used. The compound is mustard colored. Yield 75%.

##### *Pt(ACDA)<sub>2</sub>*

**Method A.** Potassium tetrachloroplatinate(II) (0.32 g, 1 mmol) in acetone was added with stirring to an acetone solution of ACDA (0.33 g, 2.1 mmol). After stirring the mixture for 15 min, the dark red product was separated by filtration, washed first with acetone, then with warm water and finally with acetone. The compound was dried *in vacuo*. Yield 70%.

**Method B.** A bright red product was obtained in 70% yield by following the method B for Pd(ACDA)<sub>2</sub>.

**Method C.** By adopting a procedure of Sen *et al.*<sup>12</sup> a product in 60% yield was obtained. To an aqueous solution of potassium hexachloroplatinate(IV) (1 mmol) an aqueous solution of ammonium ACDA (2 mmol) was added with stirring. The precipitate was filtered, washed with water and dried *in vacuo*.

#### Analyses

Carbon, hydrogen were determined in the Micro Analytical Laboratory of this Institute, nitrogen by semimicro combustion analysis. Nickel and palladium were estimated gravimetrically by dimethylglyoxime after decomposition of the complexes with nitric-perchloric acid mixture. Sulphur content was determined by peroxide fusion of the sample, followed by gravimetric estimation in the form of BaSO<sub>4</sub>. Analytical data of the compounds are shown in Table I.

#### Electronic Measurements

The ultraviolet and visible spectra of the ligand and its complexes of Ni(II), Pd(II), Pt(II) were recorded in Hilger UV-spek or Spectro MOM 201 spectrophotometer in the concentration range 10<sup>-5</sup>–10<sup>-3</sup> M in dimethylsulphoxide or dimethylformamide and in the range 10<sup>-5</sup>–10<sup>-2</sup> M in pyridine. A saturated solution of Ni(ACDA)<sub>2</sub> (dark chocolate form) in acetone was also used for spectral measurement. The visible reflectance spectra for nickel complexes were recorded in Unicam SP-500 spectrophotometer using MgO as the reference material.

The composition of the nickel-ACDA complex was determined by the method of continuous variations for equimolar solutions of nickel nitrate and ACDA in acetone (5 × 10<sup>-5</sup> M) and measuring the optical density at 540 nm. The stability constant was determined by this method with non-equimolar solutions. The composition of pyridine adduct of Ni(ACDA)<sub>2</sub> was determined by the molar-ratio method; the initial Ni(ACDA)<sub>2</sub> concentration (in acetone) was 6 × 10<sup>-5</sup> M and the pyridine concentration (in acetone) was varied in the range 2 × 10<sup>-5</sup>–6 × 10<sup>-4</sup> M, optical density was measured at 530 nm.

#### Infra-red Spectra

The infra-red spectra were recorded in a Beckman

TABLE I. Analytical Data.

Compound	Color	%M		%N		%S		%C		%H	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ni(ACDA) <sub>2</sub>	Dark-chocolate	15.64	15.55	7.47	7.50	34.17	34.34	—	—	—	—
Ni(ACDA) <sub>2</sub>	Reddish-violet	..	15.56	..	7.42	..	34.27	—	—	—	—
Pd(ACDA) <sub>2</sub>	Orange red	25.19	24.95	6.63	6.70	30.30	30.15	—	—	—	—
Pd(ACDA) <sub>2</sub>	Mustard	..	24.92	..	6.58	..	30.41	—	—	—	—
Pt(ACDA) <sub>2</sub>	Dark red	—	—	5.48	5.50	—	—	28.18	28.23	3.13	3.30
Pt(ACDA) <sub>2</sub>	Bright red	—	—	—	5.53	—	—	..	28.27	..	3.25
ACDA	Yellow	—	—	8.80	8.75	40.22	40.15	45.28	45.40	5.70	5.75

IR-15 spectrophotometer. The spectra of the metal complexes were recorded in the range 4000–650 cm<sup>-1</sup> in KBr disc and in the range in 700–250 cm<sup>-1</sup> in nujol mull between thin polystyrene sheets. The ligand spectra were recorded in nujol, KBr and in chloroform solution.

#### <sup>1</sup>H Nmr Spectra

The proton magnetic resonance spectra of the ligand, its nickel and palladium chelates were recorded in a 100 MHz JELCO spectrometer at room temperature using TMS as the internal standard. The ligand spectra were recorded both in CDCl<sub>3</sub> and in DMSO-*d*<sub>6</sub> and the metal complex in the latter solvent.

#### Magnetic Measurements

Magnetic measurements were performed on solid samples at room temperature in a Guoy balance using Hg[Co(SCN)<sub>4</sub>] as the calibrant. All the metal complexes are diamagnetic. The pyridine solution of the nickel complexes in the concentration range 10<sup>-2</sup> M are found to be slightly paramagnetic (0.78 BM).

#### Thermal Analysis

Thermal analyses of nickel and palladium chelates were performed in a MOM Derivatograph. The compounds were heated in air atmosphere at the rate of 10° C/min.

#### X-ray Diffraction Data

The X-ray powder diffraction studies of the differently colored nickel and palladium complexes were carried out in a Philips PW 1051 Diffractometer using CuKα radiation.

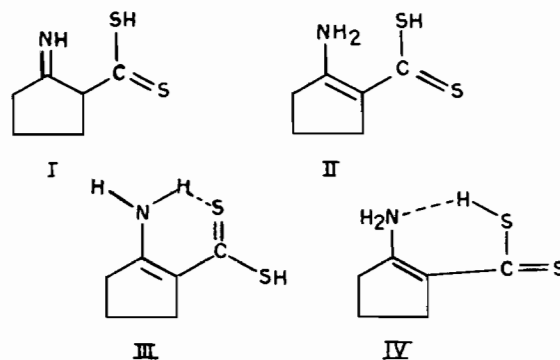
#### Results and Discussion

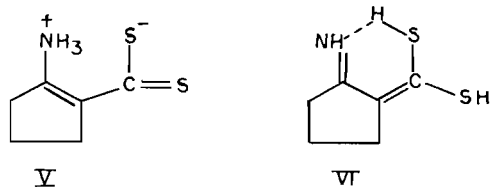
The method of preparation of the metal complexes and their analytical data as shown in Table I indicate that for each of the metal ions studied two differently

colored products having identical composition are obtained. The compounds, in general, have the composition M<sup>II</sup>(ACDA)<sub>2</sub>. All of them are insoluble in water and in common organic solvents, very slightly soluble in acetone and nitromethane, but fairly soluble in dimethylsulphoxide, dimethylformamide and pyridine. For any particular metal, the variety obtained from ACDA itself is slightly more soluble than the species obtained from the ammonium salt of ACDA. The compounds in general are fairly resistant toward the action of acids or alkalis. In particular the nickel chelate could be prepared in low yield from even 3–4 M HCl solution.

In our initial attempts to prepare the metal complexes from ammonium salt of ACDA or ACDA as obtained by the method of Takeshima *et al.*<sup>15</sup> we obtained impure products which could not be purified. The earlier report on the preparation of nickel and platinum complexes by Sen *et al.*<sup>12</sup> necessitated the use of ammonium salt of ACDA which was obtained by adopting this procedure. However, the ligand prepared by modified procedure as described here affords pure complexes.

Before proceeding to describe the nature of bonding in the complexes, it is necessary to establish the structure of the ligand as there existed some ambiguity over this. In principle, there may be six tautomeric forms of ACDA (I–VI) as shown below:





While from pmr spectra of ACDA in DMSO- $d_6$ , Takeshima *et al.*<sup>15</sup> proposed the structure I, Bordas *et al.*<sup>16</sup> assigned III as the structure for ACDA from pmr spectra in CDCl<sub>3</sub>. To find the correct answer, we redetermined the pmr spectra of ACDA both in CDCl<sub>3</sub> and in DMSO- $d_6$ . The results are shown in Table II.

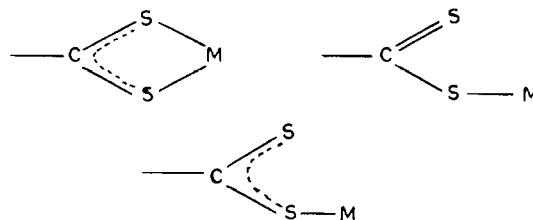
Among all the tautomeric structures of ACDA, the zwitterionic form V may be rejected on the ground as ACDA in chloroform (or in KBr) shows a sharp medium intensity band at  $\sim 2550\text{ cm}^{-1}$  (*vide infra*) which is due to S-H stretching frequency. From Table II, it appears that chemical shift values as obtained by us in DMSO- $d_6$  are in good agreement with those obtained by Takeshima *et al.*<sup>15</sup> As one should expect a triplet signal for the methine proton (C<sub>1</sub>-H) to account for the structure I, Takeshima *et al.* attributed the resonance at 3.40 ppm to C<sub>1</sub>-H, however, contrary to this we observed a rather broad signal at 3.34 ppm (integrated area indicates single proton) and we assign this to NH. Thus, as argued by Bordas *et al.*<sup>16</sup> who also did not observe the methine proton resonance, the structure I seems untenable. In the structures II and IV, the two amino protons should be equivalent, that is, one should have observed a two proton signal downfield, the integral trace line however indicates such is not the case. The two remaining structures III and VI are difficult to be distinguished. In VI the shielding effect on C<sub>3</sub> and C<sub>5</sub> methylene protons will be similar, while in III the corresponding chemical shift values should differ. From Table II it is apparent that in DMSO- $d_6$ , III is the major species, while in CDCl<sub>3</sub> VI will have some contribution.

All the metal complexes described here are diamagnetic in nature, that is, of square planar geometry. Moreover, as these are soluble in some polar solvents, the polymeric structure of the chelates seems less probable. It is evident therefore that in the bis-chelates, bonding has taken place either from (N,S<sup>-</sup>) or (S,S<sup>-</sup>) groupings.

The infrared bands of the ligand and the metal chelates are listed in Table III. The assignments of the pertinent bands which are important for metal-ligand bond formation have been made from a comparison of their spectra with those of dithiocarbazates<sup>8-10</sup>, dithiocarboxylates<sup>17,18</sup>, dithiocarbamates<sup>19,20</sup>, carbon disulphide complexes<sup>6</sup> and dithioesters<sup>21,22</sup>. The nature of assignments is incorporated in Table III.

It is clear from Table III that the band at  $\sim 2550\text{ cm}^{-1}$  in ACDA due to  $\nu\text{SH}$  is missing in all the metal complexes indicating metal-ligand bond formation through this site. The bands due to NH<sub>2</sub> stretching appear almost in the same region ( $3350\text{--}3100\text{ cm}^{-1}$ ) for the ligand and its complexes which at first sight would indicate non-involvement of the amino group in bond formation with metal ions. However, recalling the structure of ACDA (III) where strong intramolecular hydrogen bonding is present, one should expect little difference in the position of  $\nu\text{NH}_2$  bands in the ligand and its complexes bonded through the amino group. The presence of three bands in the range  $3350\text{--}3200\text{ cm}^{-1}$  in the complexes indicates that these are due to NH<sub>2</sub> stretching instead of NH stretching, which should have been the case had there been bonding through the ligand structure (I) (primary amines usually show two bands as against one for imines in the range  $3500\text{--}3400\text{ cm}^{-1}$ ). The NH<sub>2</sub> bending mode of vibration which is little affected due to chelation remain unaltered in the ACDA complexes. The strong band at  $\sim 1330\text{ cm}^{-1}$  in the ligand and its complexes appears to be due to a combination of  $\nu\text{CN}$  and  $\nu\text{C}\cdots\text{S}$ , and another strong band at  $\sim 1285\text{ cm}^{-1}$  due to mixing of  $\nu\text{C}\cdots\text{S}$  and  $\nu\text{CN}$ .

In the case of dithiocarboxylate metal complexes bonding may occur in the following way:



The question regarding the nature of sulphur chelation may be settled in the following light of observations.

TABLE II. Chemical Shift Values ( $\delta$ ) in ppm of ACDA.<sup>a</sup>

Solvent	CH <sub>2(4)</sub>	CH <sub>2(3)</sub>	CH <sub>2(5)</sub>	NH	SH	H(Chelated)
DMSO- $d_6$	1.84 (multiplet) [1.85 (multiplet)]	2.68 (triplet) 2.72 (triplet)	2.92 (triplet) 2.95 (triplet)	3.34 (b) 3.40 (triplet)	9.00 (b) 9.00 (singlet)	10.68 (b) 10.70 (multiplet)]
CDCl <sub>3</sub>	1.88 (multiplet)	2.66 (triplet)	2.76 (triplet)	4.82 (multiplet)	6.10 (very broad)	10.82 (very broad)

<sup>a</sup> Values in square bracket indicate results of Takeshima *et al.*<sup>15</sup> TMS was used as internal reference.

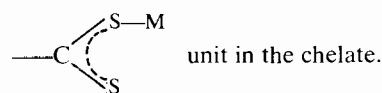
TABLE III. I. r. Data.

ACDA	Ni(ACDA) <sub>2</sub> Dark-chocolate	Ni(ACDA) <sub>2</sub> Reddish-violet	Pd(ACDA) <sub>2</sub> Orange-red	Pd(ACDA) <sub>2</sub> Mustard	Pt(ACDA) <sub>2</sub> Dark red	Pt(ACDA) <sub>2</sub> Bright red	Pt(ACDA) <sub>2</sub> <sup>a</sup> Brownish red	Assignments
3350b	3360m	3360m	3360m	3360m	3360m	3360m	3300sh	$\nu$ N-H
3225b	3270w	3270m	3270m	3270m	3270w	3270m	3280m	
-	3195w	3200w	3190w	3195w	3200w	3190w	-	
-	-	-	-	-	-	-	2940w	
2800w	-	-	-	-	-	-	-	
2550m	-	-	-	-	-	-	-	$\nu$ S-H
1610s	1615s	1615s	1610s	1610s	1615s	1610s	1610s	$\delta$ NH <sub>2</sub>
1450s	1468vs	1465vs	1465s	1465s	1465s	1460s	1460s	$\delta$ CH <sub>2</sub> + $\nu$ C=C
-	-	1405w	1405w	1405w	1405w	1405w	1410w	
1310s	1330m	1330s	1330s	1330s	1330s	1330s	1330s	$\nu$ C-N + $\nu$ C-S
1280s	1285m	1285s	1285s	1285s	1285s	1285s	1280m	$\nu$ C-S + $\nu$ C-N
1130sb	1160wb	1160wb	1160w	1160w	1160wb	1160wb	1150wb	
1040w	-	-	-	-	-	-	-	
970w	-	-	-	-	-	-	945w	
-	900m	900m	900w	900m	900w	900w	900w	$\nu$ <sub>Assym</sub> CSS
880m	860m	855m	860m	860m	860w	860w	-	
800w	-	-	-	-	-	-	810w	
-	-	-	-	715w	715m	720m	-	
-	-	-	-	-	-	-	770w	
615b	670m	660sh	660w	655w	650w	660w	655w	$\nu$ <sub>Sym</sub> CSS
500vw	560s	560s	555s	550s	560s	560s	560m	
475m	480s	475s	475s	475s	480s	480s	-	
-	465w	460s	460s	460s	450s	440s	430m	$\nu$ M-N
-	450s	445s	445s	450s	425s	420s	-	
412s	420m	410w	410sh	410sh	400sh	400sh	-	
385sh	380m	370m	-	-	-	-	-	
-	350w	345sh	325s	330s	330m	330w	-	$\nu$ M-S
325s	320s	310s	310s	-	310m	310w	-	
-	275w	270w	-	-	-	300w	-	

<sup>a</sup> Prepared according to Ref. 12.

In dithiocarbamates, where assymmetric CSS stretching is observed at  $\sim 1000\text{ cm}^{-1}$ <sup>19</sup>, in the case of disulphur chelation a single band is usually observed, whereas, for unidentate sulphur coordination this band is split. This criterion found successful application in distinguishing the types of sulphur bonding in metal dithiocarbazates<sup>9</sup> also. In the case of Vanadium(IV) complexes of aryl dithiocarboxylates which involve disulphur chelation, Piovesana *et al.*<sup>18</sup> attributed the band in the region  $1020\text{ cm}^{-1}$  due to  $\nu_{\text{assym}}\text{CSS}$  and at  $950\text{ cm}^{-1}$  due to  $\nu_{\text{sym}}\text{CSS}$ . On the other hand Fackler *et al.*<sup>17</sup> in their studies with aryl dithiocarboxylic acid complexes and some of their sulphur addition products, assigned the bands in the range  $1035$  to  $900\text{ cm}^{-1}$  to C=S and other modes of CS stretching frequencies. While in ACDA or its metal complexes no band in the region  $1000\text{ cm}^{-1}$  is observed, a strong band at  $\sim 880\text{ cm}^{-1}$  in the ligand is symmetrically bifurcated at  $900\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$  in the complexes. We attribute this to  $\nu_{\text{assym}}\text{CSS}$ , and formation of two bands in the chelates may be inferred due to unidentate sulphur bonding in them. A band at  $\sim 615\text{ cm}^{-1}$  in the ligand

which is displaced to higher frequency range  $\sim 670\text{ cm}^{-1}$  in the complexes is tentatively assigned either to  $\nu_{\text{sym}}\text{CSS}$  or to  $\nu\text{C-S}$ . We also relate the displacement of  $\nu_{\text{sym}}\text{CSS}/\nu\text{C-S}$  to higher energy to the presence of



A medium intensity band appeared in the region  $450\text{ cm}^{-1}$  in the complexes is possibly due to M-N stretching. A new band at  $350\text{ cm}^{-1}$  in the nickel complexes seems to be due to MS stretching, in the palladium and platinum chelates, this occurs at  $330\text{ cm}^{-1}$ .

It is important at this stage to invoke the assistance of i. r. spectra in distinguishing the two differently colored complexes for each metal ion. Apparently the color difference may arise to (i) *cis-trans* isomerism, (ii) variation in the mode of bonding. Foregoing discussion has made it clear that in ACDA complexes bonding takes place from (N,S<sup>-</sup>) co-ordination sites, hence variation in the nature of bonding in the chelates may arise due to complexation from the ligand structure

(I) and (III). However, since the i.r. spectra of the 'color isomers' are very similar and since the spectral assignments favor bonding through the ligand structure (III), color difference cannot be attributed to the variation in the mode of bonding. Among the two geometrical isomers, the *cis* variety should exhibit more i.r. active bands<sup>22</sup>. However, Table III does not indicate much difference in the number of bands.

<sup>1</sup>H nmr spectra are occasionally used<sup>24</sup> to characterize *cis-trans* isomers. Unfortunately the nickel chelates do not have enough solubility in DMSO-*d*<sub>6</sub> for meaningful interpretation of data; the palladium chelates are somewhat better in this respect. The chemical shifts for the different protons in the two palladium chelates and the pattern of the signals are quite similar, which do not support different modes of bonding in the chelates or the *cis-trans* isomerism. As expected due to metal-

amino group bonding, the NH<sub>2</sub> proton resonance suffers large downfield shift ( $\delta = 8.35$  ppm). The resonance for CH<sub>2(4)</sub> protons which are little affected due to chelation appears at  $\delta = 1.78$  ppm. as against 1.84 ppm in the ligand. Due to proximity of the NH<sub>2</sub> group, CH<sub>2(3)</sub> resonance also suffers a downfield shift ( $\delta = 3.40$  ppm), whereas CH<sub>2(5)</sub> protons are somewhat shielded ( $\delta = 2.68$  ppm).

In Table IV, the band position, extinction values and the nature of transitions for each colored variety of Ni(II), Pd(II) and Pt(II) complexes are summarized.

For the two varieties of Ni complexes the electronic spectra in DMSO are almost similar, the absorption maxima occur in the same wavelength regions, the extinction values differ slightly. Of the three bands, *viz.* at  $\sim 35,000$ ,  $27,000$  and  $19,000$  cm<sup>-1</sup>, the first two are due to internal ligand transitions which occur in

TABLE IV. Electronic Absorption Spectra of Metal Chelates.

Compound	Color	Solvent	cm <sup>-1</sup>	log $\epsilon$	Assignment
Ni(ACDA) <sub>2</sub>	Dark-chocolate	DMSO	35,500	4.19	L → L*
			27,000	4.67	L → L* + ( <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub> )?
			18,700	4.39	CT + ( <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> )?
Ni(ACDA) <sub>2</sub>	Reddish-violet	DMSO	35,100	3.17	L → L*
			27,400	4.54	L → L* + ( <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub> )?
			19,000	4.13	CT + ( <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> )?
Ni(ACDA) <sub>2</sub>	Dark-chocolate	Pyridine	26,700	4.64	L → L*
			18,400	4.17	CT
			10,300	1.30	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>
			8,900	1.15	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>
Ni(ACDA) <sub>2</sub>	Reddish-violet	Pyridine	26,300	4.70	L → L*
			18,700	4.07	CT
			10,100	1.28	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>
			8,800	1.16	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>
Pd(ACDA) <sub>2</sub>	Orange-red	DMF	33,500	4.18	L → L*
			29,500	4.53	CT
			26,300	4.26	CT
			22,500	4.90	L → L*
Pd(ACDA) <sub>2</sub>	Mustard	DMF	29,500	4.53	CT
			26,300	4.30	CT
			22,500	4.90	L → L*
			37,500	4.18	CT
Pt(ACDA) <sub>2</sub>	Dark red	DMF	31,500	4.29	L → L*
			28,000	4.19	CT
			25,000	3.98	CT
			20,700	4.84	L → L*
			37,500	4.21	
Pt(ACDA) <sub>2</sub>	Bright red	DMF	31,500	4.27	L → L*
			28,100	4.13	CT
			25,000	4.04	CT
			20,700	4.84	L → L*
			37,500	4.15	
Pt(ACDA) <sub>2</sub> <sup>a</sup>	Reddish brown	DMF	37,500	4.15	
			34,400	4.00	
			30,500	4.25	
			25,600	4.06	
			20,800	4.26	

<sup>a</sup> Prepared according to Ref. 12.

the range 33,000 and 25,000  $\text{cm}^{-1}$  for ACDA. The band in the region 19,000  $\text{cm}^{-1}$  is possibly due to ligand to metal charge transfer, since it is known<sup>25</sup> that the ligand to metal charge transfer energies decrease as the ligand becomes more readily oxidisable, which is the case with ACDA. The ligand ACDA is easily oxidised by Cu(II), Pt(IV), Rh(III) *etc.* The Ni(II) complexes in DMSO do not exhibit any absorption beyond 800 nm which means the nonexistence of hexacoordinated solvent adduct. The dark chocolate variety for which spectrum was recorded in acetone from 300–1000 nm exhibits two bands, one at 18,500  $\text{cm}^{-1}$  and the other at 27,000  $\text{cm}^{-1}$ . The visible reflectance spectra of both the varieties of Ni(II) complexes shows one band at 18,000  $\text{cm}^{-1}$ . The high intensity of the bands in Ni(II) complexes indicates that the bands due to *d-d* transitions are overlapped with the ligand bands and charge transfer band. For square-planar Ni(II) complexes the  $\nu_2$  band due to  $^1A_{1g} \rightarrow ^1A_{2g}$  transition which occurs normally in the range 20,000  $\text{cm}^{-1}$  is probably merged with the CT band at 19,000  $\text{cm}^{-1}$  and the  $\nu_3$  band due to  $^1A_{1g} \rightarrow ^1B_{1g}$  coincides with the ligand band at 27,000  $\text{cm}^{-1}$ .

The spectra of the two nickel complexes in pyridine show the ligand bands and the charge transfer band almost at the same wavelength with similar extinction values as observed in DMSO. In addition, two new bands at 10,000  $\text{cm}^{-1}$  and 8800  $\text{cm}^{-1}$  appear. This is evidently due to the formation of hexacoordinated species Ni(ACDA)<sub>2</sub>(Py)<sub>2</sub>. It is well known<sup>26</sup> that geometric distortion and/or non identical donor atoms cause departure from O<sub>h</sub> symmetry. Due to lowering of symmetry the  $\nu_1$  band is resolved into two components. The two bands in the pyridine adduct may be assigned in D<sub>4h</sub> symmetry to the transition  $^2B_{1g} \rightarrow ^2B_{2g}$  (10,000  $\text{cm}^{-1}$ ) and  $^2B_{1g} \rightarrow ^2E_g$  (8500  $\text{cm}^{-1}$ ). The susceptibility measurement of Ni(ACDA)<sub>2</sub> solution in pyridine ( $\sim 10^{-2}M$ ) indicates weak paramagnetism (0.78 BM). The attempt to isolate the pyridine adduct however was not met with success. The weak paramagnetic behavior of the pyridine solution coupled with the failure in isolating the adduct may be due to either or both of the following reasons. (i) The equilibrium constant of the reaction  $\text{NiA}_2 + 2\text{Py} \rightleftharpoons \text{NiA}_2\text{Py}_2$  is small, hence concentration of the paramagnetic species is low. (ii) In the hypothetical solid adduct NiA<sub>2</sub>Py<sub>2</sub>, the Ni–Py bond distance is large which causes significant tetragonal distortion in the molecule (hence magnetic behavior as with planar configuration) and due to large dissociation pressure of pyridine the solid adduct will be unstable. The formation of 1:2 adduct of Ni(ACDA)<sub>2</sub> with pyridine has also been verified by the molar-ratio method. It is important to mention here that the existence of tris-ACDA complex of nickel in solution as claimed by Yokoyama *et al.*<sup>11</sup> could not be verified. On the other hand, the composition of the complex as determined by the method of continuous

variations confirmed that the *bis*-chelate is the highest complex species in solution. Molecular weight determination of both the varieties of the nickel complex in DMF [Calc. 375; found 390 (reddish violet), 385 (dark chocolate)] also supported this view. The equilibrium constant for the reaction:  $\text{Ni}^{2+} + 2 \text{HACDA} \rightleftharpoons \text{Ni}(\text{ACDA})_2 + 2\text{H}^+$  (LogK = 12.02  $\pm$  0.12 at 25 °C) indicates very high stability of the chelate.

In the spectral range 270–500 nm, the two palladium complexes exhibit practically identical spectral behavior in DMF. In all, four bands are observed of which the bands at 33,500  $\text{cm}^{-1}$  and 22,500  $\text{cm}^{-1}$  are due to ligand. The high intensity of the other two bands indicate they are charge-transfer type.

For the two differently colored platinum chelates also the spectral behavior and band intensities are very similar in DMF. In this case, apart from the two ligand transition bands at 31,500  $\text{cm}^{-1}$  and 20,700  $\text{cm}^{-1}$ , there are three charge-transfer bands. The question whether these are M→L or L→M type could not be ascertained properly. Gray *et al.*<sup>27</sup> attributed a separation of  $\sim 10,000 \text{ cm}^{-1}$  in two CT bands in various 1,2-dithiolene Pt(II) complexes as due to M→L type charge-transfer. In the Pt–ACDA chelates two CT bands which appear at 37,500  $\text{cm}^{-1}$  and 28,000  $\text{cm}^{-1}$  may similarly be assigned due to M→L type charge-transfer.

For the electronic spectra of metal complexes the rule of average environment has often been used to assign the type of chromophores in metal complexes and also their stereochemistry<sup>28–30</sup>. Unfortunately in the metal chelates described here the electronic spectra exhibited a number of intense charge-transfer bands which have masked the bands due to ligand field splitting, thus rendering the spectra unsuitable to ascertain donor sites involved in bond formation and also the stereochemistry of the species. From the very similar spectral behavior of each pair of colored species of Ni(II), Pd(II) and Pt(II) chelates, however, it may be inferred that similar chromophores are present in the chelates.

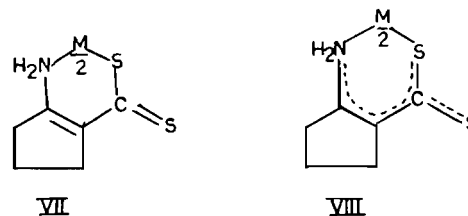
It is important at this stage to mention the difference of our finding on the platinum chelate obtained by the methods described here with the species obtained by a method described by Sen *et al.*<sup>12</sup> (See Experimental). The spectrum of the Pt(II) chelate obtained by this method, while not differing much in the band positions, however differs greatly in the intensities. The analytical data of this species is also unsatisfactory. It is quite likely that Pt(IV) which was used for preparation of the complex has oxidised ACDA to its dimer while getting itself reduced to Pt(II) stage and perhaps excess of unoxidised ACDA formed complex with Pt(II). The ready oxidation of thiol groups by metal ions is well known and in fact the dimer of ACDA has been isolated by Takeshima *et al.*<sup>15</sup> The electronic and i.r. spectra of the dimer exhibit similar band positions as ACDA. However, the dimer being insoluble

in common organic solvents it might have contaminated the chelate.

The thermal analysis of the two forms of nickel and palladium chelates were carried out to find the thermal stability of each species. The two forms of nickel compounds have almost similar thermal stability—while the reddish violet form is stable up to 250°C, the dark chocolate compound decomposes above 230°C. Both the compounds show sharp loss in weight above these temperatures. The thermal study rules out the possibility in color difference to any kind of hydrate formation and moreover the high thermal stability of the nickel chelates may be regarded as quite unusual for sulphur containing chelates, and this indicates that the compounds are highly stabilized in planar configuration. Both varieties of palladium chelates do not show any loss in weight below 100°C, though slight loss in weight (less than 2%) occurs up to 280°C and above this temperature rapid decomposition starts.

Finally to find the reason of such color difference, the X-ray diffraction patterns of the nickel and palladium compounds were recorded. The spacings and relative intensity values are shown in Table V. It is apparent from a comparison of the values in Table V that both the varieties of nickel and palladium chelates are isomorphous and the similarity in intensity values also indicates that they are isostructural. Preliminary computation of the diffraction data by Ito's method<sup>31</sup> indicates triclinic cell for these compounds.

The nature of bonding in the complexes thus appears to be (VII); however, due to delocalisation in the molecule (VIII) seems more probable:



The remaining possibilities for the difference in color may be due to (i) difference in grain size, (ii) defect in the crystal lattice. As the compounds retain color difference even on prolonged grinding reason (i) may be precluded. In absence of crystal structure studies as the defects in the lattices cannot be located the question then still remains why this happens for all the metal ion studied.

As mentioned earlier, apart from (N,S<sup>-</sup>) type, (S,S<sup>-</sup>) type of bonding can also occur in principle in the metal chelates of ACDA. In an attempt to isolate such species reactions of ACDA were carried out with nickel acetylacetonato, ethylenediamine and triphenylphosphine complexes: in all the cases either of the two forms of Ni(ACDA)<sub>2</sub> were obtained. While reaction with aqueous solution of ethylenediamine complex

TABLE V. X-ray Diffraction Data.

Ni(ACDA) <sub>2</sub> Reddish-violet		Ni(ACDA) <sub>2</sub> Dark-chocolate		Pd(ACDA) <sub>2</sub> Mustard		Pd(ACDA) <sub>2</sub> Orange-red	
$d_{hkl}$ Å	I/I <sub>0</sub>	$d_{hkl}$ Å	I/I <sub>0</sub>	$d_{hkl}$ Å	I/I <sub>0</sub>	$d_{hkl}$ Å	I/I <sub>0</sub>
6.606	58.61	6.646	58.75	6.628	75.70	6.685	86.50
6.212	52.78	6.278	48.75	6.277	55.00	6.157	48.38
5.925	67.36	5.916	61.87	5.916	67.89	5.907	67.74
5.112	34.72	5.122	35.00	5.170	31.65	5.229	30.64
4.304	27.78	4.297	28.75	4.301	28.44	4.268	23.22
—	—	4.032	23.12	—	—	—	—
3.911	27.78	3.915	26.25	3.899	27.06	3.915	19.35
—	—	3.866	24.75	—	—	—	—
3.678	100	3.715	100	3.697	100	3.670	100
—	—	3.496	24.50	—	—	3.528	19.35
3.239	31.25	3.258	41.00	3.255	26.00	3.266	14.51
2.522	33.33	2.514	42.50	2.535	29.81	2.539	27.42
2.353	27.78	2.353	57.25	2.374	27.52	2.374	21.93
2.201	24.72	2.175	27.75	—	—	—	—
1.977	25.00	1.973	30.62	—	—	1.960	17.74
1.926	26.39	1.920	31.25	—	—	1.929	16.77
—	—	1.856	30.62	—	—	—	—
—	—	1.752	28.75	—	—	—	—
—	—	1.635	27.50	—	—	—	—
—	—	1.551	27.75	—	—	—	—



afforded the reddish violet variety, from the other two reactants in chloroform or in acetone the dark chocolate variety was obtained. One common point emerges from these observations, that is, the color difference is independent of the substrates, but depends on whether reactions were carried out in aqueous or in organic solvents. It seems plausible to us that the product obtained in aqueous medium is a pure geometrical isomer (probably *trans*) and that obtained in organic solvent is a mixture of *cis* and *trans* (the latter in excess). In fact powdered diffraction data of the latter type of compounds contained few more lines.

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