

## Metal Complexes of Sulphur–Nitrogen Chelating Agents. III. 2-Aminocyclopentene-1-Dithiocarboxylic Acid Complexes of Cr(III), Fe(III), Co(III), Fe(II) and Co(II)

K. NAG and D. S. JOARDAR

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

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With 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) complexes of the type  $M(ACDA)_2 \cdot nH_2O$  (Co(II),  $n = 3$ ; Fe(II),  $n = 2$ ),  $Cr(ACDA)_3 \cdot 4H_2O$  and  $M(ACDA)_3$  (Fe(III) and Co(III)) have been prepared. The compounds have been characterized from their infrared and electronic spectra, magnetic moment and thermal analysis. The Co(II) complex is of square planar configuration. The i.r. spectra suggest that in the Fe(II) and Fe(III) complexes bonding take place from (N,S<sup>-</sup>) donor sites of the ligand and in the Co(II), Co(III) and Cr(III) complexes disulphur chelation occur. The electronic spectra of the latter two complexes support this view. The Fe(II) complex is probably polymeric in nature.

### Introduction

As a part of our investigations on the metal com-

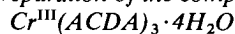
plexes derived from the skeletal unit  $NH_2-C=C-\overset{\overset{S}{\parallel}}{C}-S^-$ , 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) has been found to be a good chelating agent. This ligand is expected to show linkage isomerism, since bonding may take place through (N,S,S<sup>-</sup>), (N,S<sup>-</sup>) or (S,S<sup>-</sup>) coordination sites. The isolation and characterization of the ACDA complexes of Ni(II), Pd(II) and Pt(II)<sup>1</sup> and Rh(I), Cu(I) and Hg(II)<sup>2</sup> have been described earlier by us. In this paper we wish to report our observations on the Cr(III), Fe(III), Co(III), Fe(II) and Co(II) complexes. Pattnik *et al.*<sup>3</sup> made some limited investigation on the Co(II) and Fe(II) complexes. However, our findings on these compounds appear to be somewhat different.

### Experimental

Chemicals and solvents used were of reagent grade. Preparation of the ligand has been described earlier.<sup>1</sup> In the preparation of few metal complexes the ligand

ACDA was used as its ammonium salt, which in turn was obtained by grinding the calculated amount of ACDA with few drops of strong ammonia, the paste formed was then extracted with water and the solution was used after filtering.

#### Preparation of the complexes



An ethanolic solution of ACDA (6 mmol) was added dropwise with stirring to an ethanolic solution of chromium nitrate nonahydrate (2.2 mmol). The stirring was continued for ~1 hr and the initial volume of the solution (80 ml) was then reduced to about 20 ml under reduced pressure. A bluish-violet complex formed was collected and washed first with cooled water-ethanol (1:1) mixture and finally with small amount of ether. The compound was recrystallized from ethanol and was dried over calcium chloride. Yield 50%.



An aqueous solution of ferrous sulphate heptahydrate (2.1 mmol) was first reduced with few drops of aqueous sulphur dioxide solution, to it was then added an aqueous solution of the ammonium salt of ACDA (4 mmol) with stirring. The preparation was carried out in a nitrogen atmosphere. The greyish black compound formed was collected, washed with water and ethanol and dried over calcium chloride. Yield 90%.



To a stirred ethanolic solution of ACDA (6.2 mmol), 2 mmol of ferric chloride hexahydrate in ethanol was added dropwise. After stirring the solution for 15 min, part of the solvent was removed under suction. The black compound deposited was filtered and washed with ethanol and ether. The compound was dried *in vacuo*. Yield 90%.



An aqueous solution of the ammonium salt of ACDA (4 mmol) was allowed to drip slowly into a stirred

solution containing cobalt nitrate hexahydrate (2.1 mmol) and ammonium nitrate (2 gm) in a stream of nitrogen. The dark brown product separated was filtered through a fine porosity glass frit and was then washed successively with water, ethanol and ether. The recrystallization of the product was made from chloroform. The compound was dried and stored *in vacuo*. Yield 80%.

### $\text{Co}^{\text{III}}(\text{ACDA})_3$

To a stirred aqueous solution of hexaaminocobaltic nitrate (2 mmol), an aqueous solution of the ammonium salt of ACDA (6.4 mmol) was added dropwise. The stirring was continued for 10 min after which the precipitated brown product was filtered and washed thoroughly with water, then dried over calcium chloride. It was recrystallized from acetone. Yield 80%.

### Analysis

Cobalt was estimated gravimetrically by weighing in the form of  $\text{CoSO}_4$ . Chromium and iron were determined by usual volumetric procedures; nitrogen and sulphur contents were assayed as described earlier<sup>1</sup>.

Physical measurements were carried out as reported earlier<sup>1,2</sup>.

## Results and Discussion

The analytical data of the compounds shown in Table I indicate that bis-chelates are formed with Co(II) and Fe(II), while with the trivalent metal ions tris-chelates result. The Co(III) and Cr(III) complexes are fairly soluble in common organic solvents like methanol, ethanol, acetone, chloroform *etc.* and also in DMF and DMSO. The Co(II) complex is sparingly soluble in the alcohols, more soluble in acetone and chloroform and fairly soluble in DMF and DMSO. The Fe(III) complex is soluble only in the latter two solvents, but the Fe(II) is practically insoluble in all the solvents. In an earlier study Pattnaik *et al.*<sup>3</sup> reported

a Fe(II) complex of composition  $\text{NH}_4[\text{Fe}^{\text{II}}(\text{ACDA})_3]$  which was obtained by reacting the ammonium salt of ACDA with ferrous ammonium sulphate. Moreover, it was stated that  $\text{NH}_4[\text{Fe}(\text{ACDA})_3]$  on keeping turns to a pasty mass. Contrary to this, we find that  $\text{Fe}(\text{ACDA})_2 \cdot 2\text{H}_2\text{O}$  is quite stable and remains unchanged in composition for a fairly long period of storage.

The room temperature magnetic moments of the compounds are listed in Table I. As expected the Co(III) complex is of the spin-paired type. The moment observed for the Co(II) complex is 2.26 BM. On the basis of magnetic moment it is difficult to distinguish between low-spin octahedral and square planar complexes of Co(II), as in principle for both cases the moment should be close to the spin-only value for one unpaired electron. In practice, for very few known low-spin octahedral complexes of Co(II), the magnetic moments are close in the range 1.8–2.0  $\text{BM}^4$ , whereas for several Co(II) complexes having definite square planar configuration the values fall in the range 2.1–2.8  $\text{BM}^{4,5}$ . On this basis the ACDA complex of Co(II) appears to have a square planar geometry. The color of the Co(II) complex darkens on exposure to air for several days and is accompanied by an increase in magnetic moment. For a three months old compound the observed moment was 3.12 BM. We suspect this to be due to the absorption of oxygen by the compound, however this aspect has not been investigated at present. The earlier report<sup>3</sup> claims that the Co(II) complex is aerially oxidized to a Co(III) species as the compound becomes diamagnetic on keeping. The magnetic criterion is again difficult to apply in distinguishing between octahedral and tetrahedral Fe(II) complexes. The usually observed moments for the octahedral complexes are 5.3–5.5 BM and for the tetrahedral complexes the range is 4.9–5.2 BM. In the case of  $\text{Fe}(\text{ACDA})_2 \cdot 2\text{H}_2\text{O}$ , the observed moment (4.96 BM) would tend to categorize it as having tetrahedral configuration. Alternatively if the complex is polymeric in nature, an octahedral geometry

TABLE I. Analytical and Magnetic Moment Data.

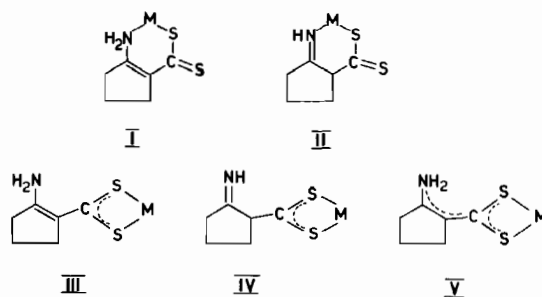
Compound	Color	%M		%N		%S		$\mu_{\text{eff}}$ B.M.
		Calc.	Found	Calc.	Found	Calc.	Found	
$\text{Fe}(\text{ACDA})_2 \cdot 2\text{H}_2\text{O}$	Greyish-black	13.69	13.71	6.86	6.95	31.38	31.02	4.96
$\text{Fe}(\text{ACDA})_3$	Charcoal-black	10.54	10.61	7.93	8.02	36.24	36.31	5.72
$\text{Cr}(\text{ACDA})_3 \cdot 4\text{H}_2\text{O}$	Bluish-violet	8.70	8.71	7.02	7.12	32.11	32.18	3.65
$\text{Co}(\text{ACDA})_2 \cdot 3\text{H}_2\text{O}$	Dark-brown	13.74	13.81	6.53	6.61	29.84	29.40	2.26
$\text{Co}(\text{ACDA})_3$	Brown	11.06	11.20	7.88	7.95	36.02	36.12	Diamagnetic

with reduced moment might result. Heiber *et al.*<sup>6</sup> pointed out that the tetrahedral assignment of Fe(II) complexes should be viewed with caution as the moment of an octahedral complex can be reduced by distortion from regular octahedral symmetry or electron delocalization on to the ligands. The observed moment of the Fe(III) complex is consistent with high-spin octahedral configuration. The value obtained for the Cr(III) complex is slightly below the spin-only value and perhaps this is due to some sort of exchange interaction in the complex.

The thermal analyses of the compounds were carried out to ascertain the nature of binding of the water molecules in the hydrated complexes and also to compare the relative thermal stabilities of the anhydrous compounds. The Cr(III) complex begins to lose water molecules at 60°C and the dehydration is complete at 150°C. From 160°C onward the anhydrous compound begins to decompose. The observed weight loss (12.5%) confirms the presence of four water molecules in the compound (calc. 12.1%). The Fe(II) complexes lose water molecules in the temperature range 50°–140°C. The rapid decomposition of the dehydrated product takes place from 160°C. The weight loss due to dehydration (8.9%) agrees well with the expected value (8.8%) for the loss of two water molecules. The removal of three water molecules from the Co(II) complex takes place between 50°–100°C (weight loss observed 12.3%, calc. 12.6%). The anhydrous compound does not show any change in weight between 100°–150°C. While the Co(III) complex is thermally stable up to 180°C and sharp decomposition takes place above this temperature, the Fe(III) complex on the other hand begins to decompose slowly from 50°C. The results of thermal analysis indicate that due to the relatively low temperature (50°–60°C)

required for the onset of dehydration, the water molecules in the hydrated complexes may be regarded as lattice water. Thus the square planar configuration of the Co(II) complex appears to be certain. The Fe(II) complex on this basis would indicate tetrahedral configuration, however the insoluble nature of the compound suggests it to be of a polymeric type.

The i.r. spectra of the Co(II) and Co(III) complexes were recorded in the range 4000–250 cm<sup>-1</sup> and the remaining compounds in the range 4000–650 cm<sup>-1</sup>. The infrared bands along with their probable assignments are shown in Table II. It may be noted that in the hydrated complexes as expected a broad band is observed in the range 3550 cm<sup>-1</sup>. The assignments of the other pertinent bands have been made on the basis of our previous studies<sup>1,2</sup>. The appearance of a strong band at ~1515 cm<sup>-1</sup> in the Cr(III), Co(III), and Co(II) complexes which is not observed in the Fe(II) and Fe(III) complexes and also in the Ni(II), Pd(II) and Pt(II) chelates<sup>1</sup> necessitates the consideration of the following modes of bonding (I–V).



In the case of  $d^8$  metal chelates bonding takes place in the way shown in (I). The appearance of the band

TABLE II. IR Data.

ACDA	Fe(ACDA) <sub>2</sub> ·2H <sub>2</sub> O	Fe(ACDA) <sub>3</sub>	Cr(ACDA) <sub>3</sub> ·4H <sub>2</sub> O	Co(ACDA) <sub>2</sub> ·3H <sub>2</sub> O	Co(ACDA) <sub>3</sub>	Assignment
—	3600b	—	3520b	3550b	—	$\nu_{OH}$
3350b	3420b	—	—	3400bw	3420m	
—	—	3300m	3300sh	3300w	3300w	$\nu_{NH}$
3225sh	3250b	—	3210m	3210w	3210w	
2550m	—	—	—	—	—	$\nu_{SH}$
1610s	1615s	1615s	1615s	1620s	1615s	$\delta_{NH_2}$
—	—	—	1510s	1520s	1515s	$\nu_{C=N}$
1450s	1460s	1465m	1465m	1465m	1465s	$\delta_{CH_2} + \nu_{C=C}$
—	1410sh	1410sh	1420w	1420vw	1425sh	
1310s	1365m	1360w	1325m	1325m	1325s	$\nu_{C-N} + \nu_{C=S}$
1280s	—	1290m	1290m	1290m	1290m	$\nu_{C=S} + \nu_{C-N}$
—	945vw	—	940w	940vw	940vw	
—	900w	905m	915m	920sh	915vw	$\nu_{asym CSS}$
880m	865b	860w	875sh	875vw	875vw	
615b	605b	—	—	—	—	$\nu_{sym CSS}$
—	—	—	—	315vw	315w	$\nu_{M-S}$

at  $1515\text{ cm}^{-1}$  is difficult to be justified either with the structures I or II. In II one should expect to observe a band due to the C=N stretching which usually absorbs at  $\sim 1650\text{ cm}^{-1}$ . In the case of dithiocarbamates a strong band observed at  $\sim 1500\text{ cm}^{-1}$  is attributed to partial double bonded C-N as required by SS chelation<sup>7</sup>.



This analogy found successful application in distinguishing the (S,S<sup>-</sup>) and (N,S<sup>-</sup>) type chelation in the complexes of dithiocarbamic acid and its derivatives<sup>8,9</sup>. In the present case if the band at  $\sim 1515\text{ cm}^{-1}$  is similarly regarded as due to C=N stretching, the contribution of the resonating structures III and IV which in effect is more representative in V should be taken into consideration. Thus on the basis of the i.r. spectra we tentatively assume that in the Fe(II) and Fe(III) complexes bonding takes place from (N,S<sup>-</sup>) donor sites (structure I), whereas in the Co(II), Co(III) and Cr(III) complexes disulphur chelation occur. Further, in the dithiocarbamates and dithiocarbazates where asymmetric CSS stretching is observed at  $\sim 1000\text{ cm}^{-1}$ , in the case of disulphur chelation a single band is usually observed, whereas for unidentate sulphur coordination this band gets split<sup>8-10</sup>. In our earlier studies we noted that for the (N,S<sup>-</sup>) type of bonding the ligand band at  $880\text{ cm}^{-1}$  is symmetrically bifurcated at  $900\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$ . In the case of Fe(II) and Fe(III) complexes similar splitting of the ligand band can be observed but in the case of the other three complexes the pattern of splitting is not prominent. The band at  $315\text{ cm}^{-1}$  may be regarded as due to M-S stretching.

The bands observed in the electronic spectra of the complexes along with the nature of transitions are summarized in Table III. In the Cr(III) complex, the

first two spin allowed transitions,  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (F), are observed at 15.4 kK and 18.9 kK respectively. These two bands have high extinction values. Another band observed in the higher energy range is possibly due to the combination of charge transfer bands and internal ligand transition bands. The 10 Dq value for the complex turns out to be 15.4 kK, and due to the absence of the third spin allowed transition the  $\beta_{35}$  value could not be calculated accurately. However, by using the relation  $B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2) / (15\nu_2 - 27\nu_1)$ , an approximate value of  $\beta_{35}$  (0.34) is obtained. Battistoni *et al.*<sup>11</sup> compared the 10 Dq values for a large number of complexes containing the chromophores  $[\text{CrS}_6]$  and  $[\text{CrN}_3\text{S}_3]$  and on the basis of these values established the donor groups involved in the bond formation in Cr(III) dithiocarbazates. In the (S,S<sup>-</sup>) bonded complexes 10 Dq values lie in the range 15–16 kK, whereas in the (N,S<sup>-</sup>) bonded type the corresponding range is 17–18 kK. The value 15.4 kK in the Cr(III)–ACDA complex therefore justifies the contention of disulphur chelation as proposed from i.r. spectra. Moreover, the usually observed range of  $\beta_{35}$  in the  $[\text{CrS}_6]$  chromophore is 0.4–0.5 and 0.6–0.75 in the  $[\text{CrN}_3\text{S}_3]$  chromophores. Our  $\beta_{35}$  value also indicates disulphur chelation. The remarkable increase in the intensity of absorption bands in the Cr(III) complexes with sulphur containing ligands has been attributed partly to the covalency of the metal–ligand bond and partly to the lowering of symmetry of the complexes<sup>12</sup>. In the Co(III) complex, while the first band is due to the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition, the second band is presumably due to the charge transfer transition coupled with  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition. In this case, the 10 Dq value could not be evaluated. However, the occurrence of the first spin allowed transition in the  $[\text{CoS}_6]$  chromophore in the range 15–16 kK in a large number of complexes as against the corresponding band in the range 17.5–18.5 kK in the  $[\text{CoN}_3\text{S}_3]$  complexes<sup>10</sup> indicates that in  $\text{Co}(\text{ACDA})_3$  bonding

TABLE III. Electronic Absorption Spectra of Metal Chelates.

Compound	Solvent	$\lambda$ , $\text{cm}^{-1}$	Loge	Assignment
$\text{Co}(\text{ACDA})_2 \cdot 3\text{H}_2\text{O}$	DMF	23,260	4.24	CT + ${}^1A_{1g} \rightarrow {}^1T_{1g}$ $L \rightarrow L^*$
		26,320	4.38	
$\text{Co}(\text{ACDA})_3$	Acetone	15,870	2.67	CT + ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ${}^1A_{1g} \rightarrow {}^1T_{2g}$ $L \rightarrow L^*$
		22,220	4.61	
		26,670	4.83	
$\text{Cr}(\text{ACDA})_3 \cdot 4\text{H}_2\text{O}$	DMF	15,380	2.45	CT + ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F) $L \rightarrow L^*$
		18,870	3.10	
		23,530	4.88	
		30,300	4.22	
$\text{Fe}(\text{ACDA})_3$	DMF	10,990	1.43	CT + ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ( $4G$ ), $L \rightarrow L^*$ CT
		25,000	4.16	
		30,300	4.22	
ACDA	DMF	25,510	4.19	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
		32,790	3.78	

takes place from (S,S<sup>-</sup>) donor sites. There is little information available on the electronic spectra of square planar Co(II) complexes. In the low spin complexes with the [CoO<sub>2</sub>N<sub>2</sub>] chromophore a narrow band near 8.5 kK and a stronger broad band at 20 kK ( $\epsilon$ , 300 l cm<sup>-1</sup> mol<sup>-1</sup>) have been observed<sup>13</sup>. Other square planar complexes also exhibit a band in the region 23–20 kK<sup>14,15</sup>. In the Co(II)–ACDA complex, the lower energy band in DMF could not be detected. Due to high extinction value, the band at 23 kK can appropriately be treated as a combination of *d–d* and charge transfer transitions. The lower energy band observed in the Fe(III) complex at 11 kK may be ascribed to the <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (4G) transition in a pseudo octahedral geometry.

The bonding behavior of ACDA thus appears to be interesting. It can stabilize both the lower and higher valency states of cobalt and iron. The phenomenon of linkage isomerism is also exhibited by the ligand.

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