Trivalent Metal Complexes of 1,3,4-Thiadiazole Derivatives

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Abstract:

New derivatives 2,5-bis(2-amino pyrimidyl) -1,3,4thiadiazole (APMTD), and 2,5-bis(1- thiacarbazino)-1,3,4- thiadiazole(TCTD), and their complexes with trivalent metal ions; La^{+3} , Y^{+3} and Ce^{+3} were prepared and characterized using IR,UV-Visible, Atomic

Introduction:

Although 1,3,4-thiadiazole ring is classified as π -excessive¹, the presence of two nitrogen atom of pyridine type in the ring leave the carbon atoms with rather low electron density, and consequently no electrophilic substitution in the unsubstituted 1,3,4-thiadiazole ring have been recorded. Three toutomers of the ligand (I,II

absorption, Molar conductivity and Dissociation constant. These measurements suggest an octahedral geometry with ionic nature for all of the prepared complexes.

and III) had been reported^{2,3}. Infra-red spectra showed an absorption band near 2300 cm⁻¹ characteristic for SH group. The 2,5-dithio structure (I) is excluded by ultraviolet spectral evidence , while 2-mercapto-5-thion structure (II) had been established in CHCl₃ solution and the dithione form (III) predominate in ethanol solution⁴.



The synthesis of these heterocyclic has received considerable attention in recent years⁵⁻⁹. Aminothiadiazole were among the first heterocyclic been use to prepare a diazo components for disperse dyes ¹⁰. As an example 2-amino-1,3,4-thiadiazole derivatives were used to prepare such dyes derived from five-membered sulphur-containing heterocyclices¹¹⁻¹⁶



Physical Measurements:-

The following physical measurements were carried out for the synthesis ligands and their complexes .

- 1-Melting points were measured by Gallenkamp melting point apparatus.
- 2-Elemental analysis (C.H.N) were carried out using Carlo-Erba microanalyser .
- 3-Infra-red spectra were recorded in the 4000-200 cm⁻¹ region using a Pye-Unicom 200 infra-red spectrophotometer with KBr and CsI disc at Ibn Al-Bitar centre laboratories.
- 4-UV-Visible spectra were carried out in the region 190-800nm at Chem. Department College of Science Al-Mustanserya University.
- 5-Molar conductivity was measured on WTW F56 using Platinum electrode with cell constant 1.01 cm⁻¹.

Experimental:

The two new ligands and their complexes were prepared according to the following procedures:





1- 2,5-bis(2-amino pyrimidyl)-1,3,4-thiadiazole (APMTD)

To a solution of 2,5-dimetrcapto-1,3,4-thiadiazole (1.5g,10mmol) in 1,4-dioxane (25ml), a solution of 2amino pyrimidine (1.19g,20mmol) in 1,4-dioxane(25ml) was added. The resulting mixture was refluxed for 30minutes and solvent was evaporated under vacuum to the half of the original volume. A yellow precipitate was obtained on cooling, filtered off and washed with 1,4-dioxane and recrystallized from absolute ethanol to afford bright yellow crystals (2.25g,85%), scheme 1

2- 2,5-bis(1-thiacarbazino)-1,3,4-thiadiazole (TCTD)

A solution of 2,5-dimercapto-1,3,4-thiadiazole (1.5g,10mmol)in absolute ethanol (25ml) was added to a solution of thiosemicarbazide (1.8g,20mmol) in absolute ethanol (25ml). The resulting mixture was refluxed for six hours. The volume of solvent was reduced to half of the original volume. On cooling a yellow precipitate was obtained which was left for overnight, filtered off and recrystallized from hot absolute ethanol to afford a pale yellow crystals (2.5g,90%). Scheme 2.

3- Metal complexes of APMTD ligand

A solution of the ligand APMTD (0.272g,1mmol) in absolute ethanol (10ml) was added to a solution of the metal salt (1mmol) , ($YCl_3.6H_2O$, $LaCl_3.6H_2O$ and $CeCl_3.4H_2O$) in absolute ethanol(10ml). The mixture was refluxed for one hour . On cooling fine crystals were obtained , filtered off ,washed with distilled water and dried (Table 1).

4- Metal complexes of TCTD ligand

The complexes were prepared by mixing a solution of (0.264g, 1mmol) of the ligand in absolute ethanol (20ml) with a solution of the metal salt (1mmol), (YCl₃.6H₂O, LaCl₃.6H₂O and CeCl₃.4H₂O) dissolved in absolute ethanol (20ml). The resulting mixture was refluxed for two hours and solvent was evaporated under vacuum. The precipitate filtered off, washed with cold water and dried. Recrystallization from hot absolute ethanol afford fine crystals.



Scheme1

$$\frac{N-N}{S} + 2H_2N-NH + 2H_2N-NH + 2H_2N-NH + 2H_2N +$$

Scheme2

Т	able(1): Physical	properti	es of APN	MTD and	d TCTD lig	ands and	their comp	olexes
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Sequence			Yield %		Elemental analysis Found(calculated)%			
	Complex	m.p. ⁰C		Color	C	H	N	М
1	$C_{10}H_8N_8S$	185	85	Yellow	44.7 (44.2)	2.8 (2.9)	40.5 (41.0)	-
2	$[Y(C_{10}H_8N_8S)Cl]_2Cl_2$	199	42	Pale Yellow	25.3 (25.7)	1.65 (1.7)	23.4 (23.9)	19.9 (19.0)
3	$[La(C_{10}H_8N_8S)Cl]_2Cl_2$	195	70	Yellow	22.8 (23.2)	1.4 (1.5)	20.9 (21.7)	25.5 (25.9)
4	$[Ce(C_{10}H_8N_8S)Cl]_2Cl_2$	185	55	Bright yellow	22.7 (23.1)	1.4 (1.5)	20.8 (21.6)	26.11 (27.0
5	$C_4H_8N_8S_3$	145	90	Yellow	18.6 (18.2)	2.7 (3.0)	42.9 (42.4)	_
6	$[Y(C_4H_8N_8S_3)Cl]_2Cl_2$	161	50	Off-white	10.1 (10.4)	1.6 (1.7)	23.9 (24.4)	18.6 (19.3)
7	$[La(C_4H_8N_8S_3)Cl]_2Cl_2$	157	70	Yellow	8.9 (9.4)	1.3 (1.5)	21.3 (22.0)	26.9 (27.3)
8	$[Ce(C_4H_8N_8S_3)Cl]_2Cl_2$	153	60	Bright yellow	9.1 (9.4)	1.4 (1.6)	21.2 (21.9)	26.1 (26.4)

Result and Discussion:-

Infra- red spectra;-

Two strong bands for the two groups of (>NH) stretching for the two forms of the ligand (APMTD) were located at 3290 and 3190cm⁻¹, scheme 3. The stretching band for the methyl group (>CH) of the pyrimidine found on 2910cm⁻¹, while two bands attributed for the two (>C=N) were found at 1680 and 1640cm⁻¹ respectively.



Schem 3

For the ligand TCTD , two medium bands for the terminal (NH₂) stretching located on 3390 and 3330cm⁻¹, and one band for (>NH) group found at 3300cm⁻¹(VI). One strong band for each of (>C=N) stretching and (>NH₂) bending was found on 1679 and 1640cm⁻¹

respectively ^{17,18}. The characteristic ban for (N-C-N) and (HN-C=S) were located on 1550 and 460cm⁻¹ respectively ¹⁹ and another two bands for (C=S) stretching vibration were found at 1280 and 890cm⁻¹.



Metal complexes of the ligand (APMTD) showed a reasonable shift to a higher frequency for the two bands of (C=N) stretching for about 30-75cm⁻¹, which indicate a coordination occurrence , while the position of the

(NH) stretching did not affected . A new coordinated bands were observed at the region 380-498 and 215-265cm⁻¹ for M-N and M-Cl respectively.

A small shift $(15-30 \text{ cm}^{-1})$ was observed for (C=N) stretching in (TCTD) complexes with no shift for (NH_2) band . The new coordinated bands M-S and M-N were located at 370-420 and 505-550 cm⁻¹ respectively . The band for M-Cl bond appeared at 220-240 cm⁻¹.

Table(2):	Major Infra	-red and Electronic	c spectra absor	rption band	s(cm ⁻¹) and r	¹) and nm for ligands and c		
	Sequence							

Sequence	υ(C=N)	υ(M-N)	υ (M-S)	υ(M-Cl)	1(nm)	2(nm)
1	1680s,1640s	-	-	-	351	275
2	1710m,1755m	380,450	-	215	360	271
3	1718m,1758m	400,490	-	265	365	265
4	1715m,1745m	390,465	-	255	358	272
5	1640s,1670s	-	-	-	336	242
6	1655m	505	370	220	340	240
7	1635m	550	420	240	345	237
8	1650m	525	380	235	338	238

UV-visible spectra:

Two bands detected on 351 and 275nm attributed to the ligand APMTD, the first one was the conjugated system, while the second was for the heterocyclic ring aromaticity. In the metal complexes of this ligand a great splitting between these two bands were obtained with some shifting upward for the first band and downward for the other . This give us an indication for the occurrence of the coordination 20,21 , Table-2.

The other ligand TCTD showed two absorption bands located on 336 and 242nm for the conjugated system (thiadiazole ring). Again a small shift recorded for these two bands in the metal complexes, upward for the first and downward for the second. A high absorption intensity band for the ligand(ϵ :molar extension coefficient >14,000mole⁻¹. l.cm⁻¹) and higher than that for the complexes even a concentration of 10⁻⁵M was used and this could be due to the presence of the conjugated system for the ligand and the increasing of electron density at the coordination atoms (N and S). For that reason we were not able to identify the charge transfer and ligand transition bands $(\pi - \pi^*)$ and $(n - \pi^*)$ because a possible overlapping of the band with the transition bands and a broad bands were recorded for all the complexes(Fig. 1).



Fig. 1: Electronic spectra for Y(APMTD) Molar conductivity:

A continuous variation method was used to obtain the molar ratio between the ligand and the metal ion with the concentration of 10^{-3} M using DMSO as a solvent . Data result were agree with 1:1 molar ratio(Fig.2) while the molar conductivity for the metal complexes with 10^{-3} M in DMSO as a solvent showed a high molar conductance corresponding to two chloride ions not coordinated directly to the metal ion^{22,23} (Table-3) . When plotting the values of molar conductivity against the square root of the concentration , a slop line for a weak electrolyte was determined (Fig.3). The presence of the chloride ion outside the coordinated sphere was approved by using silver nitrate solution.

complex	1×10^{-3}	0.5×10^{-3}	0.37×10^{-3}	0.25×10^{-3}	0.2×10^{-3}	K _d
La(TCTD)	101	116	135	204	287	1.5x10 ⁻⁴
Ce(TCTD)	112	140	164	206	259	1.8x10 ⁻⁴
Y(TCTD)	118	151	171	203	236	2.1x10 ⁻⁴
La(APMTD)	126	157	175	201	269	2.5x10 ⁻⁴
Ce(APMTD)	137	163	178	212	291	3.8×10^{-4}
Y(APMTD)	141	168	183	210	301	4.6×10^{-4}

Table (3): Variation of Λ_M with the concentration using DMSO as a solvent



F.g.(2): Molar ratio of La(APMTD) complex



Fig. 3: Molar conductivity of La(APMTD) complex Dissociation constant measurements:

Dissociation constant(K_d) for the metal complexes were measured by using a Cruze rearrangement which derived from Ostwald equation of dilution²⁴.

$$K = K_d \Lambda_o \frac{1}{\Lambda_M} - K_d \Lambda_o^2$$

By using the results observed for the molar conductivity with the different concentration for the metal complexes , and when plotting specific constant (K) against $(1/\ \Lambda_M)$ "molar conductivity", a straight line was obtained

(Fig.4). The intercept of that line with X and Y axis (1/ Λ_o) " conductivity at infinite dilution", - $K_d \; {\Lambda_o}^2 \;$ can be observed and then K_d can be calculated . The low values for the K_d of the metal complexes approved the good stability at normal condition.



Fig. 4: Molar conductivity of La(APMTD) and La(TCTD) complexes Conclusion:

The data observed from physical measurements (infrared, UV-visible spectra, atomic absorption, molar conductivity and dissociation constant) suggest an octahedral geometry with ionic nature for all the metal complexes as shown in Fig. 5 and 6.



 $M = La^{+3} or Y^{+3} or Ce^{+3}$

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معقدات ثلاثية التكافؤ لمشتقات ١،٣،٤ – ثايادايازول

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الملخص:

تم تشخيص المعقدات المحضرة باستخدام طرق الفحص ؛ الاشعة فوق البنفسجيةوالمرئية ، الاشعة تحت الحمراء ، المطياف الذري ، التوصيلية المولارية وحساب ثابت التفكك. وقد افترحت تلك الطرق ان تكون جميع الاشكال الهندسية ثمانية السطوح ذات طبيعة ايونية. تم تحضير مركبين جديدين من مشتقات ٢، ٢، ٣- ثايادايازول [٢،٥- بس (٢- امينو بيريميدايل)-١،٣،٤ - ثايادايازول (APMTD) و ٢٠٥ - بس (١- ثاياكاربازينو)-١،٣،٤ - ثايادايازول (TCTD) والحصول على معقدات جديدة لهذه المشتقات مع بعض العناصر الفلزية ثلاثية التكافؤ ((۲۰۰ - ۲۰