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Tetrazoles as Ligands, Part II.
The Unexpected Formation of Transition Metal(II) Salts of 5-Carbamyltetrazole

PETER L. FRANKE and WILLEM L. GROENEVELD

Department of Coordination Chemistry, Gorlaeus Laboratoria, Rijksuniversiteit Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Transition metal(II) ions and 5-cyanotetrazole give salts of 5-carbamyltetrazole. Comparable compounds can be obtained directly from 5-carbamyltetrazole. For each metal ion two 5-carbamyltetrazole anions are present. The compounds were characterized and identified by chemical analyses, infrared and ligand field spectra. The salts are considered to be polynuclear. The ligands act as tridentates.

Introduction

In a previous communication [1], transition metal(II) salts and complexes of 5-cyanotetrazole (CNHTe) were reported. These compounds could be obtained from various solvents. In refluxing acetone however, we obtained different products, salts of 5-carbamyltetrazole (CAHTe) (Fig. 1), *viz.*, M(CATe)$_2$ with M^{2+} = Mn^{2+}, Co^{2+},Ni^{2+}, Cu^{2+}, and Zn^{2+}. Related compounds were obtained from metal(II) nitrates and CAHTe in water. The salts were obtained as microcrystalline solids, with a very low solubility in most solvents, which prevented, for the time being, the preparation of single crystals and structure determinations by X-ray analyses were not possible.

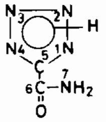


Fig. 1. 5-Carbamyltetrazole.

To obtain information on the coordination and some structural aspects, we. investigated the infrared and ligand field spectra.

Experimental

Transition metal(II) nitrates were used as the comercially available hydrates, recrystallized from water.

TABLE I. Metal(II) Salts of 5-Carbamyltetrazole, Their Colours, Preparation Methods and Analytical Data (%).

No.	Compound	Colour	Prep. meth.	Analyses							
				found				calculated			
				M	C	H	N	M	C	H	N
1.	Mn(CATZ)$_2$	white	A	20.0				19.7			
2.	Mn(CATZ)$_2$2H$_2$O	white	B	17.3				17.5			
3.	Co(CATZ)$_2$	orange	A	20.9	17.0	1.6	48.7	20.8	17.0	1.4	49.5
4.	Co(CATZ)$_2$2H$_2$O	orange	B	18.4	15.0	2.6	44.0	18.5	15.0	2.5	43.9
5.	Ni(CATZ)$_2$	purple	A	20.4	16.9	2.0	49.4	20.6	17.0	1.4	49.5
6.	Ni(CATZ)$_2$3H$_2$O	purple	B	16.9	14.3	3.5	41.5	17.4	14.3	3.0	41.6
7.	Cu(CATZ)$_2$	blue	A	22.1	16.0	1.7	47.8	21.9	16.7	1.4	48.6
8.	Cu(CATZ)$_2$2H$_2$O	blue	B	19.8				19.6			
9.	Zn(CATZ)$_2$	white	A	22.2				22.6			
10.	Zn(CATZ)$_2$2H$_2$O	white	B	20.1				20.1			

TABLE II. Some Important Infrared Absorption Bands (cm^{-1}) of CAHTZ and Its Metal Salts.[a]

CAHTZ	Mn	Co	Ni	Cu	Zn	Assignment
3368 s	3450 s,b	3450 s,b	3450 s,b	3400 s,b	3420 s,b	ν NH_a
3259 s	3350 sh	3350 sh	3370 s,b	3325 s,b	3370 sh	ν NH_a
3191 m	3250 m,b	3200 sh	3185 m	3230 m,b	3190 sh	ν NH_a
3150 sh	–	–	–	–	–	ν NH_r
1690 vs	1690 s	1685 s	1695 vs	1680 vs	1685 vs	ν CO_a
1609 m	1635 s,b	1625 s	1605 s	1610 s	1610 m,b	δ NH_a

[a] vs = very strong, s = strong, m = medium, b = broad, sh = shoulder. ν = stretching vibration, δ = in plane bending vibration, a = amide, r = ring.

TABLE III. Ligand Field Absorption Bands (cm^{-1}) and Some Calculated Ligand Field Parameters.

No.	Compound	Ligand Field Bands			Dq	B	Dq/B
3.	$Co(CATZ)_2$	21100	20000(sh)[a]	11100	1205	745	1.62
4.	$Co(CATZ)_2 2H_2O$	21080	–	11100	1200	740	1.62
5.	$Ni(CATZ)_2$	28600	18000	11700	1170	765	1.53
6.	$Ni(CATZ)_2 3H_2O$	28300	18100	11600	1160	775	1.50
7.	$Cu(CATZ)_2$			15200	1520		
8.	$Cu(CATZ)_2 2H_2O$			15150	1515		

[a] sh = shoulder.

TABLE IV. Far Infrared Absorption Bands (cm^{-1}).

Mn	Co	Ni	Cu	Zn
239 s	288 s	341 m, 338 sh	348 m	348 s
214 s	245 sh, 223 s	305 s	310 s	248 vs
198 s	202 s	245 m	290 s	200 s,b
			250 s	

CNHTe was prepared according to the method described by Henry [2]. CAHTe was prepared by hydrolysis of CNHTe in concentrated hydrochloric acid (35%) similar to the preparation of amides from cyanides by acidic hydrolysis. Commercially available acetone (H_2O content 1%) was used as solvent. The salts have been listed in Table I, with their colours, analytical data and preparation methods.

Preparation Method A

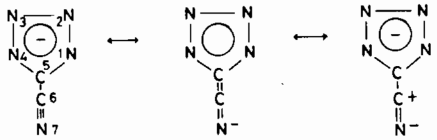
5 mmol of metal salt were dissolved in 10 ml acetone and added to a solution of 16 mmol CNHTe in 50 ml of boiling acetone. After refluxing the reaction mixture for 30 minutes, the solution was cooled to room temperature. The salts were obtained as fine precipitates, were washed with ethanol and ether and dried *in vacuo* at 90 °C for several hours.

Preparation of 5-Carbamyltetrazole ($C_2H_3N_5O$)

10 g of CNHTe were dissolved in 50 ml concentrated hydrochloric acid (35%). This solution was refluxed for 30 minutes and slowly cooled to room temperature. CAHTe separated as a finely divided crystalline solid. The yield was 10.6 g (89.1%) of a white compound that decomposes at 235–240 °C to a reddish brown liquid. *Anal.* Found: 21.1 %C, 2.6 %H, 62.0 %N. Calculated: 21.2 %C, 2.7 %H, 62.0 %N.

Preparation Method B

5 mmol of metal salt were dissolved in 10 ml water and added to a solution of 11 mmol CAHTe



I II III

Fig. 2. Mesomeric structures of CNTe$^-$.

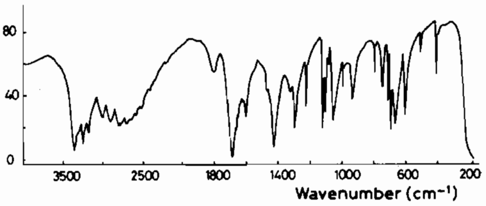


Fig. 3. Infrared spectrum of CAHTe.

in 10 ml water. After a few hours the salts precipitated, were obtained by filtration, washed with ethanol and ether and dried *in vacuo* at 90 °C for several hours.

Elemental analyses of carbon, hydrogen and nitrogen were carried out by Dr. Pascher [3], the metal contents were determined complexometrically after prior decomposition with concentrated nitric acid.

Infrared measurements were carried out on a Perkin-Elmer model 580 Spectrophotometer in the region of 4000–180 cm^{-1}. The samples were measured as KBr pellets and as emulsions in nujol between KRS-5 windows; for the region below 500 cm^{-1} polyethene windows were used. The ligand field spectra were recorded on a Beckman DK$_2$A UV–Vis. Spectrophotometer in the region of 2000–350 nm.

Table II gives the position of some important ir absorption bands for CAHTe and its salts. Table III gives the ligand field data and the calculated ligand field parameters (assuming regular octahedral symmetry). In Table IV far ir data have been listed.

Discussion

In part I of this investigation [1] we described the existence of some important mesomeric structures of the CNTe$^-$ ion (Fig. 2). From ir spectra evidence was gained that the CNTe$^-$ ion exists partly as structure III. The exocyclic carbon atom (Fig. 2) is slightly positively charged, providing ideal conditions for hydrolysis of the CNTe$^-$ ion in the salts with CNTe$^-$ ligands.

We suggest the following mechanism, first the proton is removed from CNHTe to form the metal tetrazolate, then a water molecule attacks at the positive carbon atom (Fig. 2) and hydrolysis of the CN group takes place. Apparently, in refluxing acetone ideal conditions are created; pure and sharply characterized compounds are formed. In refluxing ethanol (96%) or water hydrolysis also occurs, but impure and poorly characterized substances were the result.

We also studied the metal dependence of the reaction by weighing the precipitates, obtained after 30 minutes of the reaction, and plotting the yields in mmol against the metals used. The differences were very small and no significant results could be obtained.

In order to obtain similar salts of CAHTe with non transition metals, we refluxed solutions of CNHTe in acetone with the nitrates of Mg, Al and K. No salts were obtained from this reaction mixture and ir measurements of the residue after evaporation of the acetone did not show the characteristic ν(CO) at 1690 cm^{-1} of the amide. We arrive at the conclusion that hydrolysis takes place only with transition metal ions. The CNTe$^-$ salts are easily formed and will be quickly hydrolysed as was pointed out before. Pure compounds are obtained in refluxing acetone and probably some similar solvents. The formation of the CATe$^-$ salts is easily recognized in the ir spectrum as the CN stretching vibration of CNHTe [1] at 2284 cm^{-1} has disappeared and is replaced by several new bands (Table II). These new bands are characteristic for amides [4–6]. To obtain ir spectra of CAHTe and for the preparation of salts directly from CAHTe (type B), we prepared CAHTe from CNHTe by acidic hydrolysis. Alkaline hydrolysis leads to the formation of alkali salts of tetrazole-5-carboxylic acid.

The transition metal salts, prepared from CAHTe (type B) are almost identical to the salts obtained from CNHTe (type A) except for the water content in the crystals. The ir spectra of the type B salts do not show distinct OH or HOH vibrations because they are obscured by the ligand NH stretching vibration bands. Therefore the ir spectra of type B salts do not differ from spectra of type A salts. Attempts to remove the water from the type B salts failed and from non-aqueous solvents no CATe$^-$ salts could be obtained directly from CAHTe.

Infrared Spectra

In the region of 4000–1500 cm^{-1} the ir spectrum of CAHTe (Fig. 3) (Table II) shows some characteristic bands of amides, the $\nu(\mathrm{NH})_{\mathrm{asym.}}$ at 3368 cm^{-1}, the $\nu(\mathrm{NH})_{\mathrm{sym.}}$ at 3259 cm^{-1} and at 3191 cm^{-1} a ν(NH) due to H-bond formation [4–6]. The shoulder at 3259 cm^{-1} belongs to the ν(NH) of the tetrazole ring [1]. Compared to spectra of a range of other amides [4–6] the NH stretches have shifted to lower frequencies, due to H-bonds of the amide protons and the ring nitrogen atoms. The amide I absorption band, mainly ν(CO), is present at 1690 cm^{-1} and the amide II absorption, consisting of δ(NH) and ν(CN), occurs at 1609 cm^{-1}. We shall consider only this region of the spectrum in relation to the compounds.

The ir spectrum of the salts (Table II) shows the same number of vibrations in this area, except for the shoulder at 3150 cm^{-1} in the spectrum of CAHTe. Because the ring proton is removed this $\nu(NH)_r$ has disappeared. Except for the ν(CO) all amide bands have shifted to higher frequencies, probably due to cleavage of the amide-ring H-bonds, caused by coordination at the ring and the amide group. Although it is not obvious that the amide group takes part in the coordination, this seems unavoidable for sterical reasons.

Ligand Field Spectra

The ligand field spectra (Table III) show a pattern that is usually found for octahedrally surrounded transition metal ions. We assume therefore that the symmetry of the chromophore is approximately O_h. The ligand field parameters have been calculated assuming octahedral symmetry. The Dq values are high, standing for a ligand ranking high in the spectrochemical series (higher than *e.g.* ethylenediamine). Therefore the metal ions are surrounded by six nitrogen donor atoms and from the stoichiometry of the compounds the conclusion is legitimated that the $CATe^-$ ion acts as a tridentate ligand.

From models that were built we draw the conclusion that only two possibilities of tridentate coordination can occur. The amide nitrogen atoms must take part in the coordination in both cases. The first possibility involves nitrogen atoms 2 and 3, the second, nitrogen atoms 1 and 3 [2, 4] (Fig. 1). It is not possible to decide which of these possibilities is the most likely. The ir spectra cannot be used for this purpose because in both models C_s-symmetry is present and all vibrations are ir active, so there will be no significant difference between the spectra of 2,3 and 1,3 ring coordinating ligands. One conclusion can be drawn, in both cases the compounds must be three dimensional polynuclear.

Far Infrared Spectra

In order to obtain some information about the nature and strength of the metal ligand bonds, far ir spectra (Table IV) were recorded. The absorptions follow the Irving–Williams sequence and are found in the region common for nitrogen donor ligands. The occurrence of several different M–L absorption bands, three or four, suggests the existence of different M–L bonds, probably due to coordination by different nitrogen atoms. This is an indication that coordination is more probable by the nitrogen atoms 1,3 and 7 [2, 4, 7] as these atoms are all different. In a structure with the coordination 2,3 and 7 a simple pattern is expected for the M–L vibration bands in the ir spectrum. From X-ray diffraction measurements no information could be obtained.

Conclusions

1) 5-Cyanotetrazole and transition metal(II) ions can react with H_2O under special conditions in refluxing acetone, resulting in the formation of 5-carbamyltetrazole salts.

2) This reaction is found to progress only with transition metal(II) ions.

3) The 5-carbamyltetrazolate ions act as tridentates in the salts and coordinate probably by nitrogen atoms 1,3 and 7 [2, 4, 7].

4) The salts possess three dimensional polynuclear structures.

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