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NOTE

Oxotitanium (IV) Complexes with 4-Salicylideneamino-3,5-dimercapto-1,2,4-triazoles

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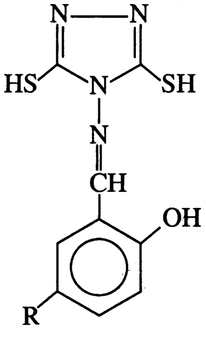
Oxotitanium(IV) complexes have been prepared by reacting oxotitanium(IV) perchlorate with salicylideneamino-3,5-dimercapto-1,2,4-triazoles in ethanol medium. The complexes are orange yellow in colour. These complexes have been characterised by elemental analysis and spectral data. Five-coordinated trigonal bipyramidal structure has been proposed for these complexes.

In our attempt to design a new series of ligands for synthesizing metal complexes, we have prepared a series of organic compounds by condensing 4-amino-3,5-dimercapto-1,2,4-triazoles with substituted salicylaldehyes. These ligands can be compared with 3-substituted-4-salicylalideneamino-5-mercapto-1,2,4-triazoles and their complexes which have been reported from our laboratory.[1–3] The difference between these two ligands is that these new series possess one —SH group in the third position of the triazole ring.

The literature on such condensation products is not much, and therefore it is thought to probe into some spectral properties of these derivatives. In this paper the synthesis and spectral studies of the following 4-salicylideneamino-3,5-dimercapto-1,2,4-triazoles and their complexes with oxotitanium (IV) have been made.



I = H
II = CH_3
III = Cl
IV = OCH_3

All the chemicals used for preparing ligands were of reagent grade. Oxotitanium(IV) perchlorate was prepared by the method reported in the literature.[4] The substituted salicylaldehydes were prepared by Duff's Method.[5]

4-Amino-3,5-dimercapto-1,2,4-triazole was prepared according to the method reported in the literature.

To prepare the complexes, oxotitanium(IV) perchlorate (0.01 mol) in ethanol was refluxed with the ligand (0.01 mol) for 3 h. About 2 g of sodium acetate was added and refluxion was continued for an hour. The complex was precipitated by adding water, filtered and washed and dried over fused calcium chloride.

The complexes were analysed for titanium, nitrogen and sulfur contents by standard methods. The IR spectra of the ligands and complexes were recorded in nujol mull on a Perkin-Elmer 297 spectrophotometer in the region 4000–200 cm^{-1} and Hitachi 150 spectrophotometer.

Oxotitanium(IV) complexes of dimercapto-triazoles are orange yellow in colour. The elemental analysis (Table-1) agrees well with stoichiometry TiOL. These complexes are soluble to limited extent in DMF and DMSO. The molar conductance values are too low to account for any dissociation, and hence, regarded as non-electrolytes.

The important infrared frequencies of these complexes are listed in Table-1.

TABLE-1

ANALYSIS AND IR SPECTRAL DATA (cm^{-1}) OF OXOTITANIUM (IV) COMPLEXES

Empirical formula	% Analysis, Found (Calcd.)			ν(C=N)	Phenolic ν(C—O)	ν(Ti = O)
	Ti	N	S			
$(C_9H_7N_4S_2O)TiO{\cdot}OH$ (Ligand-I)	14.61 (14.43)	16.69 (16.87)	19.52 (19.28)	1605s	1305m	980m
$(C_{10}H_9N_4S_2O)TiO{\cdot}OH$ (Ligand-II)	14.01 (13.85)	15.96 (16.91)	18.82 (18.50)	1610s	1610s	990w 970w
$(C_9H_6N_4S_2OCl)TiO{\cdot}OH$ (Ligand-III)	13.29 (13.07)	15.11 (15.28)	17.70 (17.47)	1600m	1300sh	980brw
$(C_{10}H_9N_4S_2O_2)TiO{\cdot}OH$ (Ligand-IV)	13.14 (13.24)	15.24 (15.47)	17.86 (17.68)	1610m	1295m	940m

A broad weak band with fine structure which appears in the region 2675–2630 cm^{-1} for ligands disappears in complexes. The shifting of phenolic ν(C—O) to the higher frequency suggests the coordination to the metal moiety through oxygen *via* deprotonation. The shifting of the bond due to ν(C=N) to the lower frequency (1620–1600 cm^{-1}) makes one to corroborate that ν(C=N) groups of ligands have coordinated to the metal through nitrogen.

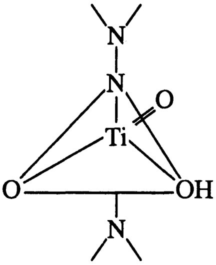
The literature reports[7] that TiO group in the complexes gives a sharp band in the region 1100–900 cm^{-1} indicating the multiple oxygen bonded stretching. In the TiO complexes of tetradentate Schiff bases[8] this band is located at 1090 cm^{-1}. In TiO aldoximes[9] the band has been found in the 1040–1000 cm^{-1}. In view of these observations a medium intensity band around 980 cm^{-1} is assigned to Ti = O stretching.

The assignments of ν(M—N), ν(M—O) are based on the available literature[1-11]. Considering the previous assignments the bands appear in the region

530–415 cm^{-1} for ν(M—N) vibration. The bands in the region 310–270 cm^{-1} have been suggested for ν(M—O) vibrations.

Oxotitanium(IV) does not form coordination bond with sulfur atoms as it is a hard acceptor.

The complexes analyse for the stoichiometry of the type TiOL. The spectral observations suggest the involvement of C═N and —OH groups in the bond formation. All these observations suggest that these oxotitanium(IV) complexes have coordination number five. On the basis of previous literature[12] a trigonal bipyramidal structure of the following type has been proposed for these complexes.



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