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PREPARATION AND CHARACTERIZATION OF NEW In(III), Re(III), AND Re(V) COMPLEXES WITH THENOYLTRIFLUOROACETONE AND SOME BIDENTATE HETEROCYCLIC LIGANDS

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PREPARATION AND CHARACTERIZATION OF NEW In(III), Re(III), AND Re(V) COMPLEXES WITH THENOYLTRIFLUOROACETONE AND SOME BIDENTATE HETEROCYCLIC LIGANDS

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ABSTRACT

New In(III), Re(III) and Re(V) complexes with the thenoyltrifluoroacetone ligand (HTTA) of the general formulae [In-(TTA)(H₂O)₄]SO₄, [Re(TTA)_n(H₂O)_x]Cl_{3-n} and [ReO(TTA)_n -(H₂O)_x]Cl_{3-n} (where n and x refer to the number of [TTA]⁻ moieties and H₂O molecules, respectively) have been prepared

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and characterized by spectroscopy, thermogravimetry, elemental analyses and X-ray diffraction. The charge densities on the ligand atoms were calculated via CNDO-SCF calculations. The newly prepared complexes $[In(TTA)(H_2O)_4]SO_2$ and $[ReO(TTA)(H_2O)_2]CL_2$ were employed as precursors for the synthesis of the mixed-ligand complexes [In(TTA)(HOCTA)₂], [In(TTA)(TZT)₂] and [ReO(TTA)(HOTCA)]Cl using R(-)-2oxothiazolidine 4-carboxylicacid (H₂OTCA) and 1H-1,2,4triazole-3-thiol (H₂TZT) as ligands. The synthesized mixedligand complexes were characterized by the conventional physical and chemical methods of analysis applied earlier for the characterization of the precursors. The investigated complexes are soluble in water, ethanol and acetonitrile, insoluble in non-polar solvents and could be of potential use for clinical studies. The antibacterial activity of the investigated complexes has been tested and evaluated.

INTRODUCTION

Metals offer many opportunities for designing radiopharmaceuticals by modifying the environment around the metal and allowing specific *in vivo* targeting to be incorporated into the molecule. The coordination compounds of certain transition metals have wide applications as pharmaceuticals and radiopharmaceuticals. Important considerations in the design and use of the complexes in biological systems were their stability and behavior in biological organs^{1–5}. Many ¹¹¹In and ¹⁸⁶Re chelates were successfully applied as radiodiagnostic and radiotherapeutic agents. For instance, ¹¹¹In-DTPA is used for radiographic cisternography studies (evalution of cerebral spinal fluid pathways)⁶, ¹¹¹In-Oxine (indium In 111 oxyquinoline solution, Amersham International) has been approved for the labeling of leukocytes (white blood cells) which are used for imaging sites of infections or inflammations⁷.

¹⁸⁶Re-DMSA displays selective uptake in tumors of kidney tissue analogous to that of the Tc species and offers the possibility of therapeutic treatment of this disease⁶. It has been, therefore, a great impetus for researchers to explore the synthesis of new indium and rhenium complexes using new classes of aliphatic or alicyclic ligands. In the present study new complexes of indium and rhenium have been prepared using thenoyltrifluoroacetone and other ligands containing NS or NO donor sites. The complexes were characterized using conventional physico-chemical

techniques of analysis and their antibacterial activity was tested. No previous work concerning the preparation of these complexes has been reported.

EXPERIMENTAL

Materials and Instrumentation

All chemical used were of analytical grade and were used without further purification. IR spectra were recorded in KBr pellets on a Perkin Elmer FT-IR spectrometer "Spectrum 1000". UV-Vis spectra in ethanolic solutions were recorded on a Cecil 599 spectrophotometer using 1 cm matched silica cells. ¹H and ¹³C NMR spectra were measured in DMSO-d₆ as solvent on a JEOL NMR 400 MHZ spectrometer. Elemental analyses were carried out on a Perkin Elmer 2400 CHNSO elemental analyzer. Indium contents in the investigated indium complexes were determined by the analytical laboratory at SABIC (R&D) (Saudi Arabia). TG measurements were carried out using a Netzsch STA-429 thermal analyzer. The weight loss was measured from ambient temperature up to 700 °C at a heating rate of 10 °C/min. X-ray diffraction patterns of the complexes were recorded using a XRD 5000 Siemens diffractometer with Cu-target.

General Method for the Preparation of $[Re(TTA)(H_2O)_4]Cl_2$ (1), $[Re(TTA)_2(H_2O)_2]Cl$ (2), $[ReO(TTA)(H_2O)_2]Cl_2$ (3), $[ReO(TTA)_2]Cl$ (4), and $[In(TTA)(H_2O)_4]SO_4$ (5)

The amounts in mmoles of ReCl_3 , ReCl_5 , $\text{In}_2(\text{SO}_4)_3$ (anhydrous) and HTTA required for the preparation of 1:1 and 1:2 metal:ligand molar rations complexes are listed in Table I.

Type of the Complexes	[HTTA] mmol (g)	[ReCl ₃] mmol (g)	[ReCl ₅] mmol (g)	$[In_2(SO_4)_3]$ mmol (g)
(1) $[Re(TTA)(H_2O)_4]Cl_2$ (2) $[Re(TTA)_2(H_2O)_2]Cl$ (3) $[ReO(TTA)(H_2O)_2]Cl_2$ (4) $[ReO(TTA)_2]Cl$	1 (0.222) 2 (0.444) 1 (0.222) 2 (0.444)	1 (0.292) 1 (0.292)	1 (0.363) 1 (0.363)	
(5) $[In(TTA)(H_2O)_4]SO_4$	1 (0.222)			1 (0.517)

Table I. Stoichiometric Amounts of the Reactants

The required amounts of metal salt were dissolved separately in 10 mL water and added dropwise to 10 mL of an ethanolic solution containing the corresponding amount of HTTA while stirring. The reaction mixture in each case was refluxed for about an hour while a few drops of acetate buffer (pH \approx 5) were added dropwise to the reaction mixture. A solid product in each case was precipitated. The solutions were rotary evaporated to about 1/3 of the total volume and these allowed to stand in air over night. The resulting solid products were collected and washed several times with diethyl ether.

General Method for the Preparation of [In(TTA)(HOTCA)₂] (6), [In(HTTA)(HTZT)₂] (7), and [ReO(TTA)(HOTCA)]Cl (8)

The stoichiometric molar amounts in mmoles of the precursors $[In(TTA)(H_2O)_4]SO_4$ (5), $[ReO(TTA)(H_2O)_2]Cl_2$ (3), the ligands H_2OTCA and H_2TZT required for the preparation of complexes (6), (7) and (8) are listed in Table II.

The calculated molar amounts of the precursors were dissolved separately in 10 mL water and added dropwise to the ethanolic solutions (10 mL) of the ligands while stirring. The reaction mixture was heated under reflux for an hour and the volumes were reduced to about 1/3 of the total volumes by rotatory evaporation. After standing over night solid products were precipitated, which were collected and washed with diethyl ether.

Comparison Experiments for Preparation of the Mixed Ligand Complexes

Comparison experiments were carried out for preparation of the complexes (6), (7), and (8) starting from the initial reagents, HTTA, H₂OCTA, H₂TZT, ReCl₅ and In₂(SO₄)₃. The stoichiometric amounts of

Type of the Complexes	H ₂ OTCA mmol (g)	H ₂ TZT mmol (g)	[In(TTA)(H ₂ O) ₄]SO ₄ mmol (g)	[ReO(TTA)- (H ₂ O) ₂]Cl ₂ mmol (g)
(6) [In(TTA)(HOTCA) ₂] (7) [In(TTA)(HTZT) ₂] (8) [ReO(TTA)- (HOTCA)]Cl	2 (0.3) 1 (0.15)	2 (0.2)	1 (0.53) 1 (0.53)	1 (0.53)

Table II. Stoichiometric Amounts of the Reactants

indium or rhenium salts were dissolved separately in 10 mL water. The amounts of HTTA/H₂OCTA or HTTA/H₂TZT in ethanol (10 mL) were added slowly with stirring to the aqueous metal ion solutions while stirring with the addition of few drops of acetate of few drops of acetate buffer solution of pH \approx 5. The reaction mixture was refluxed as previously to give solid products analogous to those obtained starting with the precursors [In(TTA)(H₂O)₄]SO₄ (5) and [ReO(TTA)(H₂O)₂]Cl₂ (3).

RESULTS AND DISCUSSION

The metal complexation reactions were carried out according to the following equations:

 $\text{ReCl}_3 + \text{HTTA} + 4\text{H}_2\text{O} \rightarrow [\text{Re}(\text{TTA})(\text{H}_2\text{O})_4]\text{Cl}_2 (1) + \text{HCl}$

 $\text{ReCl}_3 + 2\text{HTTA} + 2\text{H}_2\text{O} \rightarrow [\text{Re}(\text{TTA})_2(\text{H}_2\text{O})_2]\text{Cl}(2) + 2\text{HCl}$

$$ReCl_{5} + HTTA + 2H_{2}O + \frac{1}{2}O_{2} \rightarrow [ReO(TTA)(H_{2}O)_{2}]Cl_{2} (3) + HCl + Cl_{2}$$

$$ReCl_5 + 2HTTA + \frac{1}{2}O_2 \rightarrow [ReO(TTA)_2]Cl~(\textbf{4}) + 2HCl + Cl_2$$

$$In_2(SO_4)_3 + 2HTTA + 8H_2O \rightarrow 2[In(TTA)(H_2O)_4]SO_4 (5) + H_2SO_4$$

The microanalytical data of the investigated complexes are tabulated in Table III. Thenoyltrifluoroacetone molecule (HTTA) has the following tautomeric forms (Fig. 1)

The charge densities calculations were performed *via* CNDO-SCF calculations in the singlet electronic ground state configuration (Fig. 2). The calculations indicated that the oxygen atoms of the carbonyl group (atoms No. 10 and 14) exhibit higher values of electronic charge densities and would, accordingly, be favorable sites for coordination of In(III), Re(III), and Re(V) with the ligand⁸.

Spectroscopic Measurements

The investigated complexes were subjected to extensive spectroscopic investigations using a combination of spectroscopic techniques.

		I		ſ		щ	ound (C	alculated	<u> </u>
Complex	Empirical Formula	Formula Weight	Yield	Decom. Temp	Colour	С	Н	z	In
(1) [Re(TTA)(H ₂ O) ₄]Cl ₂	$\mathrm{C_8H_{12}Cl_{12}F_3O_6ReS}$	550	61	>300	White	17.88	2.06	I	I
(2) $[Re(TTA)_2(H_2O)_2]CI$	$C_{16}H_{12}Cl\ F_6O_6ReS_2$	700.10	50	>300	White	27.65	1.49	I	Ι
(3) [ReO(TTA)(H ₂ O) ₂]Cl ₂	$C_8H_8Cl_2F_3O_5ReS$	530.41	43	>550	White	(27.42) 18.47 (18.47	(6/-1) 1.76 (5.53	I	Ι
(4) [ReO(TTA) ₂]Cl	$C_{16}H_8ClF_6O_5ReS_2$	680.06	42	>280	White	(10.12) 28.13 (20.75)	(2011) 1.26 1.18	I	Ι
(5) [In(TTA)(H ₂ O) ₄]SO ₄	$\mathrm{C_8H_{12}F_3InO_{10}S_2}$	504.12	49	>270	Reddish	(20.20) 18.88 10.000	(1.10) 2.23	I	28.03
(6) [In(TTA)(HOTCA) ₂]	$\mathrm{C}_{16}\mathrm{H}_{12}\mathrm{F}_{3}\mathrm{InN}_{2}\mathrm{O}_{8}\mathrm{S}_{3}$	628.29	52	>300	white White	(19.06) 30.72 (30.58)	(2.39) 1.78 1.01)	4.58	(////) 18.11 (18.27)
(7) [In(TTA)(HTZT) ₂]	$\mathrm{C_{12}H_9F_3InN_6O_2S_3}$	537.19	50	>300	White	(80.06) 27.12 (50.92)	(16.1) 1.81 (0)	(4.40) 15.32	(18.27) 21.58 (21.28
(8) [ReO(TTA)(HOTCA)CI]	$C_{12}H_8CIF_3NO_6ReS_2$	604.98	45	>300	White	(20.83) 23.57 (23.82)	(1.69) 1.48 (1.33)	(15.04) 2.59 (2.31)	(/?.12) -

vaccous/memun(μ1) unotude, [NeV(11A)/Π2O/2U-2, pis(aquo)pis(menoyitrinuoroacetone/monooxornenum(V) chloride; [ReU-(TTA)₂Cl₂, bis(thenoyltrifluoroacetone)monooxorhenium(V) chloride; [In(TTA)(H₂O)₄SO₄, tetraaquothenoyltrifluoroacetonein-dium(III) sulphate, [In(TTA)(HOTCA)₂], bis(oxothiazolidine-4-carboxylic acid)thenoyltrifluoroacetone indium(III)complex; [In(TTA)(TZT)₂], bis(triazole-3thiol)thenoyltrifluoroacetoneindium(III) complex, [ReO(TTA)(HOTCA)]Cl, oxothiazolidine-4-carboxylic acid thenoyltrifluoroacetonerhenium(V) chloride.

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Figure 1. Tautomeric forms of HTTA.

The v(C=O) IR band for the free HTTA ligand which provide evidence for the mode of attachment of the ligand to the metal ion is recorded at 1654 cm⁻¹. This band was shifted to lower wave lengths in the investigated complexes. This shift can be considered as evidence for the complexation through oxygen atoms. A sharp split band in the range 3443–3420 cm⁻¹ was observed in the IR spectra of the investigated complexes (1)–(4) and is assigned to coordinated water in the structures of the complexes. In case of the Re(V) complexes, the band due to v(Re=O) was recorded at 923 cm⁻¹ and 920 cm⁻¹ for [ReO(TTA)(H₂O)₂]Cl₂ (3) and [ReO(TTA)₂]Cl (4), respectively⁹. ¹H NMR spectral data and thermal analyses further verify the presence of coordinated water molecules. The ¹H NMR spectrum of [In(TTA)(H₂O)₄]SO₄ (5) shows signals at δ 6.62 ppm and



Figure 2. HTTA Molecule.

at 3.45 ppm relatives to TMS which are assigned to the =CH (enolic) protons and coordinated water, respectively. The signal at δ 3.7 ppm was assigned to the CH₂ ketonic protons. The signals due to the thiophene ring protons were observed in the range δ 7.23–7.99 ppm. The ¹³C NMR spectrum of [In(TTA)(H₂O)₄]SO₄ (5) shows a signal due to C=O in the range 189–191 ppm. The signals due to the thiophene ring and CF₃ carbon atoms were observed in the range δ 144–129 ppm. No NMR signals were recorded for the investigated rhenium complexes, which provide an evidence for the paramagnetic properties of the complexes. It is worthwhile to mention that high-spin behaviour is rarely observed in the 4d and 5d series of transition metals.

Electronic absorption spectra of the complexes were measured at ambient temperature in ethanolic solutions. The solutions of the complexes exhibit $\pi - \pi^*$ intraligand transition bands with absorption maxima (λ_{max}) in the range of 212–213 nm. Another absorption band due to a $n-\pi^*$ intraligand transition with λ_{max} in the range of 260–267 nm was observed in the spectra of the complexes. The electronic spectra of the Re(III) complexes show some d-d transitions with 336 nm and 335 nm absorption maxima for $[Re(TTA)(H_2O)_4]Cl_2$ and $[Re(TTA)_2(H_2O)_2]Cl$, respectively. Since HTTA is a relatively weak-field ligand, and distorted octahedral Re(III) complexes are high-spin and the d-d transition for [Re(TTA)2(H2O)2]Cl and $[\text{Re}(\text{TTA})(\text{H}_2\text{O})_4]\text{Cl}_2$ (1) could be assigned to the ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$ transition ${}^{10-12}$. The distorted square-pyramidal structure for the $[ReO(TTA)(H_2O)_4]Cl_2$ (1) and [ReO(TTA)]Cl (4) complexes show also some d-d transition band attributed to the ${}^{5}T_{1g} \rightarrow {}^{3}T_{2g}$ transition similar to [VO(acac)₂] (bisacetylacetonatovanadyl) where acac is acetylaceton. A feature of square-pyramidal structures is that there is the possibility of an additional ligand occupying the vacant axial site to produce six-coordinate complexes. This possibility has been tested by the small variations that have been observed in the electronic spectra of both [ReO(TTA)(H₂O)₂]Cl₂ (3) and [ReO(TTA)₂]Cl (4) in different solvents that are believed to be caused by a solvent molecule being weakly binding at the sixth coordination site. There is evidence that good donor solvents sometimes also introduce a ligating atom cis to the rhenyl oxygen¹³.

A ligand to metal charge transfer band (LMCT) at λ_{max} 336 nm was recorded for [In(TTA)(H₂O)₄]SO₄. This charge transfer band could be assigned to transition from the weakly bonding π orbitals on the ligand to the anti bonding t_{2g}^* or e_g^* orbitals of the metal ion. It should be mentioned that the change of solvent influences the position of the charge transfer band. This influence may be attributed to some inherent polarity for the asymmetric geometry of the complex. The UV-Vis spectrum of the investigated complex [In(TTA)(H₂O)₄]SO₄ (5) was compared with that of the free ligand in order to distinguish between the charge transfer band of the complex and the intraligand band. The spectroscopic data of the prepared complexes are summarized in Tables IV–VI.

Thermogravimetric Analysis

Thermal decomposition behaviour of the investigated complexes was followed using thermogravimetric (TG) and differential thermogravimetric (DTG) techniques. The decomposition occurred in one or more steps depending on the type of the complexes investigated. Table VII summarized the results of thermal decomposition of the investigated complexes. The decomposition ends with the formation of the metal oxides In_2O_3 or Re_2O_3 .

Determination of Reaction Order of the Decomposition

The Horowitz and Metzger equation, $Cs = (n)^{1/1-n}$ where Cs is the weight fraction of the substance present at the DTG peak temperature, Ts, is given as

$$Cs = (W_s - W_f)/(W_i - W_f)$$
⁽¹⁾

was applied for the determination of the reaction order(n) of the decomposition. Here W_s stands for the weight remaining at a given temperature T_s , *i.e.*, the DTG peak temperature W_i and W_f are the initial and final weights

Table IV. UV-Vis Spectroscopic Data of the Investigated Complexes^a

Complex	λ_{m}	UV-Vis ax (ϵ , L mol ⁻¹ cm ⁻¹	¹) ^a
(1) $[\text{Re}(\text{TTA})(\text{H}_2\text{O})_4]\text{Cl}_2$	212 (250)	264 (510)	336 (510)
(2) $[Re(TTA)_2(H_2O)_2]Cl$	212 (410)	265 (820)	335 (800)
(3) $[\text{ReO}(\text{TTA})(\text{H}_2\text{O})_2]\text{Cl}_2$	212 (410)	260 (810)	336 (950)
(4) $[\text{ReO}(\text{TTA})_2]$ Cl	213 (380)	267 (720)	33 (950)
$(5) [In(TTA)(H_2O)_4]SO_4$	264 (710)	336 (950)	
(6) $[In(TTA)(HOTCA)_2]$	205 (320)	225 (700)	340 (300)
(7) [In(TTA)(HTZT) ₂]	202 (470)	263 (350)	337 (220)
(8) [ReO(TTA)(HOTCA)]Cl	203 (390)	263 (710)	330 (900)

^a ε are in the range of 10^2 – 10^3 for six-coordinate complexes of low symmetry (spinallowed, Laporte-forbidden).

	Table	V. IR	Spectrosco	pic Data	of the In	vestigated	l Comple	exes			
					II	(cm^{-1})					
Complex	(HN)	V _{str} (H ₂ O)	v(C=O) str.	vC(=O) ₂ asym.	(O-M)v	v(M-N)	v(M-S)	v(OH) bending	v(C-O) str.	v(Re=O)	v(SH)
(1) [Re(TTA)(H ₂ O) ₄]Cl ₂	T	3431 s	1560 s	I	529 m	I	T	I	Т	I	T
(2) $[Re(TTA)_2(H_2O)_2]CI$	I	3441 s	1563 m	I	525 m	I	ļ	Ι	I	Ι	I
(3) $[ReO(TTA)(H_2O)_2]Cl_2$	I	3431 m	1582 m	I	522 m	Ι	I	Ι	I	923 s	Ι
(4) $[ReO(TTA)_2]CI$	Ι	Ι	1581 s	I	518 w	I	I	Ι	Ι	920 s	I
(5) $[In(TTA)(H_2O)_4]SO_4$	I	3411 s	$1570\mathrm{s}$	I	528 m	I	ļ	Ι	I	Ι	I
(6) [In(TTA)(HOTCA) ₂]	3440 s	Ι	1578 m	$1416{ m m}$	619 w	463 w	Ι	1422 s	$1320 \mathrm{s}$	Ι	Ι
(7) $[In(TTA)(HTZT)_2]$	Ι	Ι	$1580\mathrm{s}$	Ι	644 m	549 w	400 w	Ι	Ι	Ι	2360 w
(8) [ReO(TTA)(HOTCA)]CI	$3410\mathrm{s}$	I	1597s	1412 m	581 m	462 m	I	1411 m	1355s	909 s	Ι

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		¹ H NMR (ppm)			13.0.00
Complex	δ(CH) enolic	ô thiophene ring	δ (H ₂ O)	δ (CH) ketonic	δ (C=O)
(5) $[In(TTA)(H_2O)_4]SO_4$	6.62 s	7.23 (t, $J = 4 Hz$), 7.99 (t, $J = 4 Hz$)	3.45 s	3.7 s	190 s
(6) $[In(TTA)(HOTCA)_2]$	6.61 s	7.24 (t, $J = 4 Hz$), 7.98 (t, $J = 4 Hz$)	I	3.71 s	191 s
(7) $[In(TTA)(HTZT)_2]$	6.63 s	7.24 (t, $J = 4 Hz$), 7.97 (t, $J = 4 Hz$)		3.69 s	192 s

Table VI. ¹H and ¹³C NMR Data of the Investigated Indium Complexes^a

^{a1}H NMR of the free ligand show two signals at δ 6.76 and 6.94 ppm(s, CH enolic). The thiophene ring protons appears at δ 7.35 (t, J = 4 Hz) and 8.29 (q, J = 5 Hz).

In(III), Re(III), AND Re(V) COMPLEXES

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	Decomposit Behaviour	tion	Pe Decon	rcent nposition						
Complex	Steps range	Temp. (°C)	Calc.%	(Found)%	$\mathop{\rm E_a}_{kJmol^{-1}}$	$\underset{K^{-1}Jmol^{-1}}{\overset{S*}{}}$	H* kJmol ⁻¹	G* kJmol ⁻¹	$\underset{min^{-1}}{lnA}$	R
(1) [Re(TTA)(H ₂ O) ₄]Cl ₂	First Second	100-200 450-530	13 53	15 57	130 220	-11.5 -10.3	55.2 80.2	60.6 90.9	8.79	0.988
(2) $[Re(TTA)_2(H_2O)_2]CI$	First	100-230	ŝ	9	110	-10.2	29.5	34.4	7.52	0.987
(3) [ReO(TTA)(H,O),]Cl,	Second First	400-540 120-220	63	65 8	230 120	-19.8 -10.7	81.2 30.2	91.9 35.1	16.21 8.21	0.985 0.987
	Second	430-520	44	43	240	-19.5	80.7	91.3	14.56	0.997
(4) [ReO(TTA) ₂]Cl	One major	250-450	72	73	285	-19.1	95.2	105.9	15.81	0.985
	step	000		t T	001	c c		-	2	
(5) [In(11A)(H ₂ U) ₄]SU ₄	First Second	130-200 340-450	14 75	51 77	100 235	-19.7 	28.2	33.1 91.2	16.21	0.985 0.985
(6) [In(TTA)(HOTCA) ₂]	First	280–360	47	48	160	-15.2	60.8	65.2	9.21	0.998
	Second	400 - 510	35	37	230	-19.8	81.2	91.9	16.21	
$(7) [In(TTA)(HTZT)_2]$	First	260-350	38	39	155	-14.4	59.1	63.5	8.75	0.995
	Second	410-520	41	43	240	-20.9	61.3	66.2	9.32	
(8) [ReO(TTA)(HOTCA)]CI	First	290-400	24	25	150	-14.5	54.2	63.6	8.75	0.997
	Second	450–580	45	44	220	-19.3	80.2	90.9	15.21	

Table VII. Thermal Data of the Investigated Complexes

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of substance, respectively. The calculated values of Cs are in range 0.3-.04 which indicates that the decomposition follows first order kinetics for both the dehydration and the main decomposition steps¹⁴.

For a first order process the following Coats-Redforn and Horowitz-Metzger equations were applied for determination of activation energy E_a and Arrhenius constant, A, of the decomposition^{14,15}.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \frac{-E_a}{RT} + \ln\frac{AR}{\phi E_a}$$
(2)

$$\ln[-\ln(1-\alpha)] = \frac{E(T-T_s)}{RT_s^2}$$
(3)

where α is the fraction decomposed at time t and is given by

$$\alpha = \frac{m_o - m_t}{m_o - m_f}$$

(m_o is the mass at the beginning of the decomposition step, m_t is the mass at time t, m_f is the mass at the end of the decomposition step), E_a , A, R, ϕ and T_s are activation energy of decomposition, Arrhenius constant gas constant, heating rate and temperature at the DTG peak, respectively. The kinetic parameters were calculated from the plots of the left hand side of eqs. (2) and (3) versus 1/T and (T-T_s), respectively. The correlation coefficient r (>0.95) is computed using the least-square method for eqs. (2) and (3). The activation entropy, S*, the activation enthalpy H* and the free energy of activation G* were calculated using the following equations.

$$\mathbf{S}^* = 2.303 \, \left(\log \frac{\mathrm{Ah}}{\mathrm{KT}} \right) \mathbf{R} \tag{4}$$

$$\mathbf{H}^* = \mathbf{E}^* - \mathbf{R}\mathbf{T} \tag{5}$$

$$\mathbf{G}^* = \mathbf{H}^* - \mathbf{T}_{\mathbf{s}} \mathbf{S}^* \tag{6}$$

K and h are the Boltzman and Planck constants, respectively. The temperature T involved in the calculations was selected as the temperature at the end of the decomposition step. The calculated kinetic and thermodynamic value are reported in Table VII for the various decomposition steps. The kinetic parameters, especially E_a and S^* , are helpful in assigning the strength of the bonding of both water molecules and ligand moieties with the metal ion. The values of the major decomposition step of the studied compounds *i.e.*, the stages of the decomposition to volatile products are in the range 220–285 kJmol⁻¹ which indicates that the ligand is strongly bound to the metal ion. The activation energy for the dehydration step of the complexes lies in the range 100–130 kJ/mol. These values are comparable of the generally accepted values of activation energy for coordinated water¹⁶. The negative values indicate that the activated complexes have a more ordered structure than the reactants and that the complexation reactions are slower than normal¹⁷.

Two of the prepared complexes, $[In(TTA)(H_2O)_4]SO_4$ (5) and $[ReO(TTA)(H_2O)_2]Cl_2$ (3), were employed as precursors for the preparation of mixed-ligand complexes using the following ligands in Fig. 3.



R(-)-2-Oxothiazolidine-4-carboxylic acid (H₂OTCA)



1H-1,2,4-Triazole-3-thiol (H₂TZT)

Figure 3. Ligands for the mixed-ligand complexes.

Ligand atoms charge density calculations indicated that for the free ligand H_2OTCA the more attractive sites for coordination with In and Re atoms are the oxygen atoms of carboxylate ion (atoms No. 11 and 12). The favorable coordination sites of the H_2TZT ligand are suggested to be nitrogen atoms (atoms No. 2 and 9). It was found that both [In(TTA)- $(H_2O)_4$]SO₄ (5) and [ReO(TTA)($H_2O)_2$]Cl₂ (3) could undergo ligand exchange reactions according to the following equations.

$$\begin{split} [In(TTA)(H_2O)_4]SO_4 + 2H_2OCTA &\rightarrow & [In(TTA)(HOCTA)_2] \ (6) \\ &+ 4H_2O + H_2SO_4 \\ \\ [In(TTA)(H_2O)_4]SO_4 + 2HTZT &\rightarrow & [In(TTA)(TZT)_2] \ (7) + 4H_2O \\ &+ H_2SO_4 \end{split}$$

$$\begin{aligned} \text{ReO}(\text{TTA})(\text{H}_2\text{O})_2]\text{Cl} + \text{H}_2\text{OCTA} \rightarrow & [\text{ReO}(\text{TTA})(\text{HOTCA})]\text{Cl} \ (\textbf{8}) \\ & + 2\text{H}_2\text{O} + \text{HCl} \end{aligned}$$

The microanalytical, spectroscopic and thermal data of the investigated mixed ligand complexes are tabulated in Tables III–VII, respectively.

X-Ray Powder Data of [ReO(TTA)₂]Cl (4)

Complex (4) was subject to a preliminary XRPD study. A Siemens D5000 X-ray powder diffractometer, powered at 40 kV and 35 mA, was used for data collection. Data were measured by using CuK_{α} radiation ($\lambda = 1.54056$ Å). The data were collected by the continuous scanning mode with a step width of 0.04 and a step time of 2 s. The intensity of the diffraction lines was measured as peak heights and expressed in percentage of the strongest line. The source of the initial cell parameters was the indexing program DICVOL91 [$M_{20} = 36, F_{20} = 58.4(0.0023, 148)$]¹⁸. The cell was checked and refined by the CHECKCELL program¹⁹. a = 22.8091(3), b = 10.5554(1), c = 10.9527(1) Å, $\beta = 115.786(1)^{\circ}$, V = 2374.40 Å³. Possible space groups are the monoclinic $P2_1$ or $P2_1/m$. The X-ray powder diffraction data are presented in Table VIII.

Based on the foregoing discussion the following structures are plausible for the investigated complexes as seen in Fig. 4.

No.	$2\theta_{obs}$	d _{obs}	I/I_0	h	K	1	$2\theta_{obs}{-}2\theta_{cal}$
1	8.075	10.9400	20.8333	-1	0	1	-0.0008
2	8.959	9.8624	100.0000	0	0	1	-0.0003
3	11.640	7.5962	32.5000	-1	1	1	-0.0006
4	12.930	6.8411	10.0000	-3	0	0	0.0093
5	16.553	5.3510	6.6667	-1	0	2	0.0042
6	17.118	5.1756	20.0000	2	1	1	0.0001
7	17.726	4.9995	27.5000	-4	1	1	0.0002
8	18.253	4.8563	30.8333	-2	1	2	-0.0002
9	19.246	4.6079	26.6667	-2	2	1	0.0045
10	22.721	3.9104	23.3333	4	0	1	0.0002
11	23.139	3.8407	28.3333	2	0	2	0.0001
12	24.163	3.6802	6.6667	-4	2	0	0.0001
13	25.262	3.5225	10.0000	-4	2	2	-0.0009
14	25.826	3.4469	3.3333	-3	1	3	-0.0032
15	26.595	3.3489	42.5000	-1	3	1	0.0044
16	27.014	3.2979	10.0000	-2	3	1	-0.0014
17	28.125	3.1701	29.1667	-3	3	1	-0.0007
18	29.897	2.9862	46.6667	-2	2	3	-0.0004
19	31.856	2.8068	10.8333	5	2	1	0.0002
20	32.791	2.7289	11.6667	-3	0	4	-0.0020
21	33.237	2.6933	9.1667	-5	0	4	-0.0014
22	33.831	2.6474	14.1667	-4	1	4	-0.0006
23	35.577	2.5213	60.0000	6	2	1	0.0001
24	36.825	2.4387	15.8333	-5	3	3	-0.0007
25	37.331	2.4068	10.0000	-9	1	1	0.0002
26	38.371	2.3439	9.1667	4	0	3	0.0006
27	41.171	2.1908	6.6667	2	0	4	0.0007
28	41.826	2.1579	11.6667	-8	2	4	0.0060
29	42.718	2.1149	4.1667	-2	0	5	-0.0004
30	43.254	2.0900	5.8333	-6	4	0	-0.0009
31	44.763	2.0229	11.6667	-9	3	1	-0.0068

Table VIII. X-Ray Powder Diffraction Data of [ReO(TTA)₂]Cl (4)

Antibacterial Activity

The antibacterial activity of the free HTTA ligand and its complexes were tested against various gram-positive and gram-negative bacterial cultures by using the agar diffusion method²⁰. The antibacterial activities of the investigated complexes and the free ligand were tested against various kinds of bacteria listed in Table VIII. The bacterial strains were grown in Mueller-



M = Re(III) or In(III) (1) and (5)

,0,

2+



 OH_2

Re [´]

<u>,</u>O,

ò

О.

0



Re

 H_2O











Figure 4. Suggested structures of the investigated complexes. $\binom{0}{0}$, $\binom{0}{0}$ and $\binom{N}{N}$ refer to TTA⁻, HOTCA⁻ and HTZT⁻, respectively.

+

		Actual]	Inhibition Zor	e Diameter in	ı (mm)	
Organism	HTTA	(1)	(2)	(3)	(4)	(5)
Gram-negative Escherichia coli ATCC25922	14	13.5	14.5	13.5 0.7	15 2 2	14
Yersinia Pseudetuberculosis ATCC10275	13	10	6	6.8	5.6	13
Y. enterocolitica ATCC23715	12	10	9.5	10.5	6	12
Shigella sonnei KKUH ⁹³⁴	6	9.25	10	9.25	10	6
Salmonella typhi KKUH ₁₀₁₂	8	Trace	8.5	9.5	8	8
Gram-positive Staphylococcus aureus	Trace	Trace	Trace	8	8	Trace
S. epidermidis	0.0	0.0	0.0	Trace	0.0	0.0
Streptococcus faecalis NCTC370	Trace	8	Trace	8	Trace	Trace
Bacillus megaterium CBSC 15-4900A	9.5	8.5	8.5	8	8	9.5
Bacillus cereus CBSC 15-4870A	9.5	8	8	8.5	Trace	9.5

nd Its Complexes ^a	
Activities of HTTA a	
Antibacterial .	
Table IX.	

^aTrace: inhibition zone is less than 8 mm in diameter.

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Hinton agar (Merck) plates at 37 °C for 18 h, and then were diluted to a final concentration of approximately 10⁶ CFU/mL. 0.1 mL of each bacterial suspension was spread over the surface of the Mueller-Hinton agar plates. 10 µL of 10 mg/mL of each compound, HTTA and the investigated complexes, was absorbed onto a sterilized filter paper disk of 6 mm diameter. The sterilized filter paper disks were dried under sterile condition and then immediately placed on the surface of Mueller-Hinton agar plates after their inoculation with the test bacterium. The plates were incubated at 37 °C for 24 h and the diameter (mm) of the inhibition zone was recorded. The results presented in Table IX show that the free ligand showed higher toxicity towards the growth of gram-negative bacteria, more than gram-positive bacteria. Upon complexation with In(III), Re(III) and Re(V) metal ions a reduction in inhibitory power towards Y. Pseudetuberculosis and Y. enterocolitica was observed. This reduction in inhibitory power also appeared towards S. aureus upon complexation with In(III). Salmonella typhi (gram negative) is the most resistant bacteria towards complexation with Re(III) as $[Re(TTA)(H_2O)_4]Cl_2$. The effect of the ligand and its complexes on S. aureus, S. epidermidis and streptococcus faceless is equal and nearly negligible.

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REFERENCES

- Thunus, L.; Lejeune, R. Overview of Transition Metal and Lanthanide Complexes as Diagnostic Tools. Coord. Chem. Rev. 1999, 184 (1), 125–155.
- Weiner, R.E.; Thakur, M.L. Metallic Radionuclides: Applications Diagnostic and Therpeutic Nuclear Medicine. Radiochim. Acta 1995, 70/71, 273–287.
- 3. Jurisson, S.; Berning, D.; Wei Jia; Dangshe, Ma. Coordination Compounds in Nuclear Medicine. Chem. Rev. **1993**, *93*, 1137–1156.
- 4. Gopal B. Saha. *Fundamentals of Nuclear Pharmacy*: 3th Edn. Springer-Verlag: New York, Inc. 1992.
- Martell, A.E. Ed.; *Inorganic Chemistry in Biology and Medicine* ACS Symposium Series 140. American Chemical Society: Washington, DC, 1980.

- Dilworth, J.R.; Parrott, S.; In *Directions in Radiopharmaceutical Research and Development Mather*, S, Ed.; Kluwer: Netherlands, 1996; 1 and other articles there-in.
- Chilton, H.M.; Burchiel, S.W.; Waston, N.E., Jr. In *Pharmaceuticals in Medical Imaging*; Swanson, D.P., Chilton, H.M., Throll, J.H., Eds.; Macmillan Publishing Co: New York, 1990; 569–598.
- 8. Pople, J.A.; Beveridge, D.L. *Approximate Molecular Orbital Theory*; McGraw Hill: New York, 1970.
- Baluka, M.; Hanuza, J.; Jezowska-Trzebia, T.B. Infrared and Electronic Spectra of the Technetium Oxy-Compounds. Bull. Acad. Polon. Sci. Ser. Sci. Chim. 1972, 20 (3), 271–278.
- Figgis, B.N. Introduction to Ligand Fields; Wiley-Interscience: Newyork, 1966; 253.
- Figgis, B.N. Ligand Field Theory in Comprehensive Coordination Chemistry; Wilkinson, G., Gillard, R.D., McCleverty, J.A., Eds.; Pergamon Press: Elmsford, New York, 1987; Vol. 1. 243.
- 12. Miessler, G.L.; Tarr, D.A. Inorganic Chemistry; 2nd Edn. 1999, 352.
- Kettle, S.F.A. *Physical Inorganic Chemistry*; Oxford University Press: 1998; 37.
- Horowitz, H.H.; Metzger, A. New Analysis of Thermogravimetric Traces. Anal Chem. 1963, 35, 1464–1468.
- Coats, A.W.; Redfern, J.P. Kinetic Parameters from Thermogravimetric Data. Nature 1964, 201, 68–69.
- Garcice, J.; Molla, M.C.; Borras, J.; Escriva, E. Thermal Study of Mepirizol Complexes with Co(II), Ni(II), Cu(II) and Zn(II). Thermochim. Acta 1986, 106, 155–162.
- 17. Moeller, T. International Reviews of Science; Inorg. Chem. Series 1, VII, Bagnal, K.W., Ed.; 2, 1972; 282.
- Al-Farhan, K.A. FARHAN-a Qualitative and Quantitative PC Program for X-Ray Powder Diffraction. Powder Diffraction 1999, 14 (1), 16–21.
- Boultif, A.; Louër, D. Indexing of Powder Diffraction Patterns for Low Symmetry Lattices by the Successive Dichotomy Method. J. Appl. Cryst. 1991, 24, 987–993.
- 20. Patel, V.H.; Patel, A.K. Synthesis, Spectroscopic Studies and Antimicrobial Activities of Eu(III), Dy(III) and Tm(III) Heterochelates with 2,2'-Bipyridyl, Amine + Catechol. Synth. React. Inorg. Met.-Org. Chem. **1998**, 28 (7), 1207–1219.

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