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New Co(III), Ni(IV) and Cu(III) tellurato complexes

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ABSTRACT

The new telluric acid complexes in higher oxidation states, $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ and $K_5[Cu(TeO_4(OH)_2)_2]$ were prepared and their structures characterized on the bases of spectroscopic (IR, Raman, UV-vis), magnetic, X-ray diffraction and thermal measurement.

KEYWORDS

Telluric acid;
Copper;
Nickel;
Cobalt;
High oxidation state.

INTRODUCTION

Metal telluride, MTe (M = Zn, Cd, Hg), nanomaterials have been recognized as candidates for solar cells and bio-imaging applications[1-4]. Coordination chemistry of 2-telluropyridines is of interest possibly due to their use in synthesis of MTe nanoparticles[5].

We have early reported the preparation, structure investigation and oxidation reactions of periodato complexes; $Na_5[M(IO_5(OH))_2]$ (M(III) = Cu, Ag, Au), $Na_6[M((IO_5OH))_2(OH)_2]$ (M(IV) = Ni, Pd, Pt), $Na_6[MO_2(IO_5(OH))_2]$ (M (VI) = Ru, Os) and $K_5[IM_6O_{24}].6H_2O$ (M(VI) = Mo, W)[6,7]. The X-ray crystal structure of $Na_4K[Au(IO_5(OH))_2].KOH.15H_2O$ has also been reported[6]. The spectroscopic details and structural characterizations of the tellurato complexes, $Na_5[Cu(TeO_4(OH)_2)_2].nH_2O$ and $Na_7K[Mn(TeO_4(OH)_2)_3].3H_2O$ have been reported by Levason *et al*[8,9] as well as the X-ray crystal structures of the complexes, $Na_5[Cu(TeO_4(OH)_2)_2].16H_2O$[8], $K_6Na_2[Pt(OH)_2(TeO_5(OH))_2]. 12H_2O$[10] and $Na_8K_2H_4[Pd_2Te_4O_{24}H_2].20H_2O$[10].

In this report, the new tellurato complexes of Co(III), Ni(IV) and Cu(III) were prepared and their structural characterization is assigned. Their magnetic, X-ray diffraction and thermal stabilities are also discussed. In continuation of our research interest, the purpose of preparing these complexes, which contain transition metal ions in high oxidation states, is to apply them as oxidants to oxidize many organic substrates.

EXPERIMENTAL

Materials and methods

All manipulations were performed under aerobic conditions using materials and solvents as received. Telluric acid was obtained from BDH while $K_2S_2O_8$, $NiSO_4$, $Na_3[Co(NO_2)_6]$, $CuSO_4$ and KOH were of extra pure quality and obtained from sigma-Aldrich Chemie GmbH, Germany.

Instrumentation

Hydrogen was measured in the Micro Analytical Unit, Cairo University. IR spectra were measured as KBr discs on a Matson 5000 FT-IR spectrometer. Raman spectra were measured on an in-Via Renishaw spectrometer using 785-nm laser excitation. Metal analyses (Co, Ni, Cu, Te) were carried out on Perkin Elmer Atomic Absorption Spectrometer-2380. Electronic spectra were recorded using a Unicam UV_{2-100} U.V.-vis. spectrometer. Magnetic moments at 25° C were recorded using a Johnson Matthey magnetic susceptibility balance with $Hg[Co(SCN)_4]$ as calibrant. X-Ray powder diffraction patterns were determined using a Bruker diffractometer (Bruker D8 advance target); the scan rate was fixed at 8° C in 2θ min^{-1} for phase identification. The patterns were run with $CuK_{\alpha 1}$ radiation with a second monochromator ($\lambda = 0.1545$ nm) at 40 kV and 40 mA. Thermal analysis measurements were made in the 20 –800° C range at a heating rate of 10° C min^{-1}, using α-Al_2O_3 as a reference, on a Shimadzu Thermogravimetric Analyzer TGA-50.

Preparation of complexes

(a) $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2].10H_2O$

$Na_3[Co(NO_2)_6]$ (0.4 g, 1.0 mmol) in water (5 mL) was added to basic aqueous solution (0.25M KOH, 20 mL) of telluric acid, $Te(OH)_6$, (0.46 g, 2.0 mmol). The reaction mixture was warmed with stirring for 4h. Upon standing overnight, a fine green precipitate was obtained. It was filtered off, washed with ice cold water and dried *in vacuo*. Anal. Calc. for $CoH_{28}K_5O_{24}Te_2$: Co, 6.4; K, 21.2; Te, 27.7; H, 3.0%. Found: Co, 6.2; K, 21.4; Te, 27.9; H, 2.8%.

(b) $K_5[Cu(TeO_4(OH)_2)_2].16H_2O$

Potassium persulfate (0.55 g, 2 mmol) was added to an aqueous solution of KOH (0.75 g, 13.4 mmol; 5 mL), the reaction mixture heated and stirred with the addition of $CuSO_4.5H_2O$ (0.5 g, 2 mmol). A blue-black precipitate was formed, which partially dissolved on adding $Te(OH)_6$ (1.84 g, 4 mmol). The resulting brown solution was heated and stirred for 15 min. It was left to cool and filtered to remove the excess of precipitate. A mixture of saturated KNO_3 solution and 1M KOH solution in water (10 mL) was added to the filtrate and the mixture was left to crystallize. A shiny brown precipitate was filtered off, washed with ice-cold water and dried *in vacuo*. Anal. Calc. for $CuH_{36}K_5O_{28}Te_2$: Cu, 6.4; K, 19.5; Te, 25.6; H, 3.6%; Found: Cu, 6.5; K, 19.9; Te, 26.4; H, 3.5%.

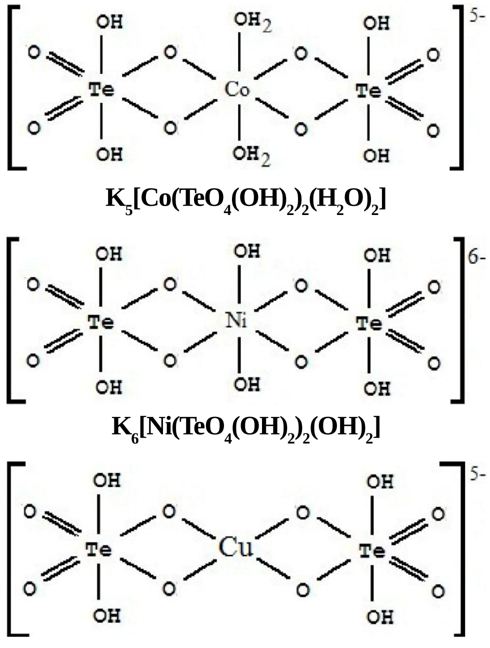
(c) $K_6[Ni(TeO_4(OH)_2)_2(OH)_2].12H_2O$

A similar method to that for the copper complex was used in which $K_2S_2O_8$ (1.10 g, 4 mmol) and $Ni(NO_3)_2.6H_2O$ (0.6 g, 2 mmol) was used to produce the pale brown precipitate. Anal. Calc. for $NiH_{30}K_6O_{26}Te_2$: Ni, 5.9; K, 23.5; Te, 25.7; H, 3.0%; Found: Ni, 5.7; K, 23.4; 25.3; H, 2.8%.

Potassium, copper, nickel, cobalt and tellurium were determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The highly hydrated complexes, $K_5[M(TeO_4(OH)_2)_2(H_2O)_n]$ (M(III) = Co, n = 10; M(III) = Cu, n = 16) and $K_6[Ni(TeO_4(OH)_2)_2(OH)_2].12H_2O$ (Figure 1) were prepared by the methods reported in the literature with some modification[8,11], which involve the addition of $Na_3[Co(NO_2)_6]$, $Ni(NO_3)_2$ or $CuSO_4$ to basic (KOH) solution of $K_2S_2O_8$ to oxidize Ni(II) or Cu(II) to Ni(IV) or Cu(III), respectively.



$K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$

$K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$

$K_5[Cu(TeO_4(OH)_2)_2]$

Figure 1 : Structures of $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ and $K_5[Cu(TeO_4(OH)_2)_2]$

Vibration spectra

The IR and Raman spectra of the tellurato complexes $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ and $K_5[Cu(TeO_4(OH)_2)_2]$ are similar, suggesting the same molecular structure of the anion $(TeO_4(OH)_2)^{4-}$. TABLE 1 represents the IR and Raman spectral data of the reported complexes.

TABLE 1 : Vibrational spectra* of $[Co(TeO_4(OH)_2)_2(H_2O)_2]^{5-}$, $[Cu(TeO_4(OH)_2)_2]^{5-}$ and $[Ni(TeO_4(OH)_2)_2(OH)_2]^{6-}$

Co(III)		Cu(III)		Ni(IV)		Assignments
IR	R	IR	R	IR	R	
3500 vs-		3500 vs-		3200 vs-		ν(OH)
3000 b		3000 b		3000 vs		ν(OH)
2295 m		2300 m		2300 w		δ(TeOH)
1673 sh		1668 sh		1652 sh		δ(HOH)
1081 m		1075 m		1125 m		δ(TeOH)
			1200		*1108*	δ(TeOH)
739 s		732 s		741 s		ν_{as}(Te=O)
621 s		630 s		609 s		ν_{as}(Te=O)
				578 s		ν_{as}(Te=O)
	750		*752*			ν_s(Te=O)
						ν_s(Te=O)
	640		*638*			ν_s(Te=O)
	595		*592*		*596*	ν_s(Te=O)
					582	ν_s(Te=O)
	490		*494*			ν_s(MO)/ ν_s(TeO)
						ν_s(MO)/ ν_s(TeO)
	380		*382*		*380*	ν_s(MO)/ ν_s(TeO)
	276		*232*		*300*	ν_s(MO)/ ν_s(TeO)
				511 s		ν_{as}(MO)/ ν_{as}(TeO)
399 m		392 m		419 s		ν_{as}(MO)/ ν_{as}(TeO)
350 s		364 s		370 s		ν_{as}(MO)/ ν_{as}(TeO)

***Raman data in Italics, vs = very strong, b = broad, s = strong, m = medium, w = weak, sh = sholder**

The symmetric octahedral telluric acid, $Te(OH)_6$ (Figure 2), has vibration mode of $\nu_1(A_{1g})$ symmetric stretch, $\nu_2(E_g)$ and $\nu_3(F_{1u})$ asymmetric stretch, $\nu_4(F_{1u})$ asymmetric bending and $\nu_5(F_{2g})$ symmetric bending; ν_3 and ν_4 are IR active. Also, there are stretching and deformation modes due to Te(OH) units[12]. The IR spectra of the tellurato complexes (Figure 3), show strong broad bands near 3300 cm^{-1} assigned to ν(OH). The broad bands near 1640 cm^{-1} may assign to δ(HOH) of lattice and coordinated water[13]. The bands near 1075 cm^{-1} of moderate intensities arise from the overtones of δ(TeOH)[13]. A comparison of the IR spectral data of $K_5[Cu(TeO_4(OH)_2)_2]$ and $Na_5[Cu(TeO_4(OD)_2)_2]$ (M(III) = Cu, Ag, Au) showed that δ(TeOH) vibration near 1075 cm^{-1} are replaced by δ(TeOD) near 900 cm^{-1}[8]. The strong IR bands in the 750 – 600 and 550 – 450 cm^{-1} regions are attributed to ν_{as}(Te=O); the same feature was observed in the IR assignments of $K_2[TeO_2(OH)_4]$[13]. In addition, extra bands are observed in 450 - 250 cm^{-1} region may arise from M-O and Te-O stretches[13].

Some of the lower frequency bands may be due to the vibrations or librations of molecules of water of crystallization, since all the complexes studied here are highly hydrated. Raman spectra of the tellurato complexes (Figure 4) show typically triplet of bands centered near 730 cm^{-1} which may arise from ν_s(Te=O) while that near 600 cm^{-1} are assigned to ν_{as}(Te=O) stretches[14]. Raman bands in the 490 – 300 cm^{-1} are probably due to M-O and Te-O stretches[14].

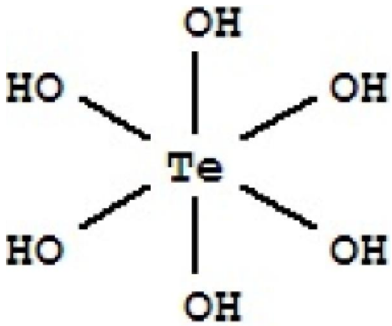


Figure 2 : Octahedral telluric acid

Electronic spectra

The diamagnetic complex, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ shows absorption UV-vis bands suggest distorted octahedral geometries around the Ni(IV) ions. The electronic spectrum of this complex exhibits band at 407 nm probably arising from the charge transfer from Ni(IV) t_{2g} to ligand orbital[15].

The electronic spectrum of the diamagnetic complex, $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$, illustrates a low spin octahedral environment around Co(III) ion. In the visible region, the ground state is $^1A_{1g}$ and the excited states corresponding to $^1T_{1g}$, $^1T_{2g}$, $^3T_{1g}$ and $^3T_{2g}$ in order of decreasing energy. This complex exhibits band at 390 nm arising from $^1A_{1g} \rightarrow {}^1T_{2g}$ transition[16].

In addition, the electronic spectrum of the diamagnetic complex, $K_5[Cu(TeO_4(OH)_2)_2]$ (Figure 5), shows absorption bands at 402 nm assigned to ligand (π) → metal d_{x2-y2} transition[7,8] while the band at 270 nm is due to ligand (σ) → metal d_{x2-y2} transition, since Cu(III) d^8 has $d_{xz}^2\, d_{xy}^2, d_{z2}^2, d_{xy}^2, d_{x2-y2}^0$ configuration[7,8].

Crystallography (XRD)

It have been reported that the successful catalysts that containing Te(VI) should present strong Bragg reflection at 2θ near 22.0, 28.0, 36.0, 45.0, and 50.0[17,18]. From the XRD patterns of the complexes, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ and $K_5[Cu(TeO_4(OH)_2)_2]$ (Figure 6), it is clear that the introduction of the metal ions affect the crystallinity[18,19]. The reported XRD patterns of the complexes show sharp peaks indicating the high crystallinity of the complexes, which may be attributed to the deformation of the strong hydrogen bonding[20].

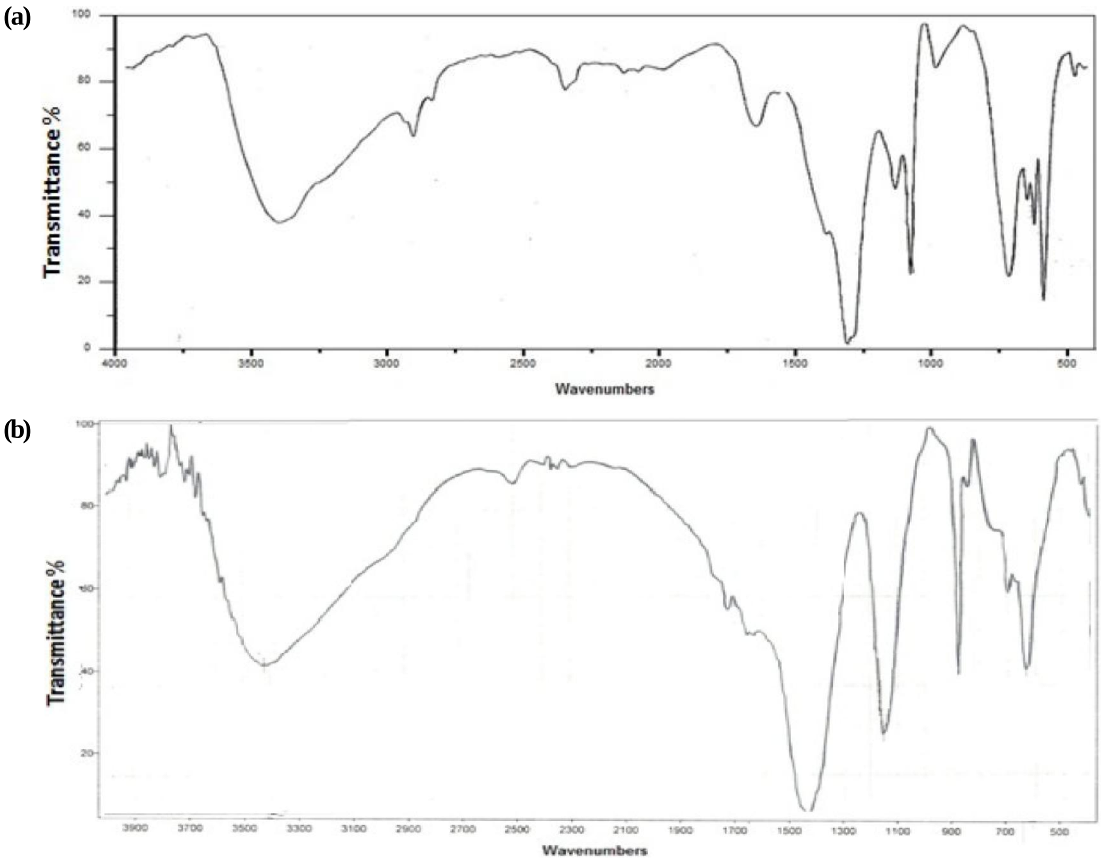


Figure 3 : IR spectra of $K_5[Cu(TeO_4(OH)_2)_2]$ (a), $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ (b)

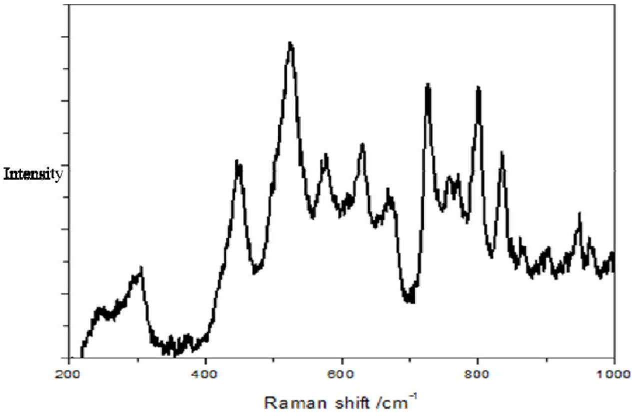


Figure 4 : Raman spectrum of $K_5[Cu(TeO_4(OH)_2)_2]$

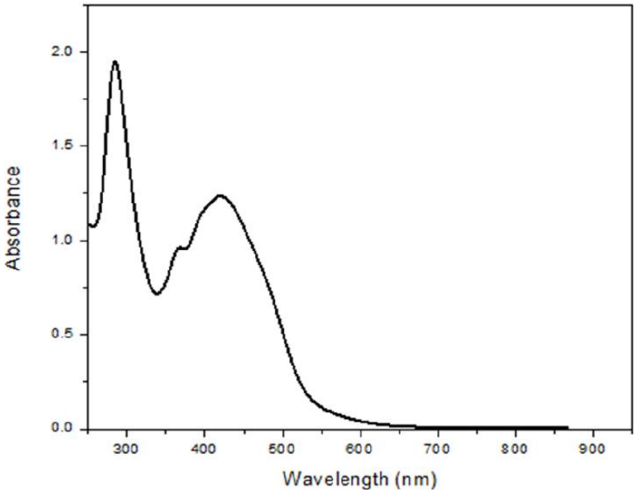


Figure 5 : UV-vis spectrum of $[Cu(TeO_4(OH)_2)_2]^{5-}$

Thermal measurements

The thermal stability and degradation behaviour of $Te(OH)_6$ was studied using the thermo-gravimetric (TG) technique. The TGA curve of $Te(OH)_6$ shows the first weight loss between 250 and 350° C, attributed to the loss of $3H_2O$ (Calcd. 23.5, Found 22.9%), leaving

TeO_3 at 550° C representing (Calcd. 76.5, Found 75.4%)[21].

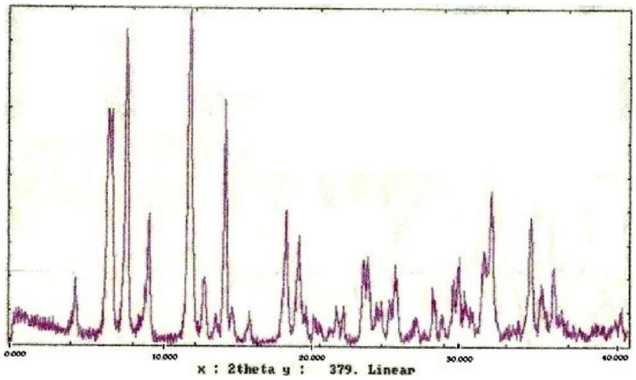


Figure 6 : XRD of $K_5[Cu(TeO_4(OH)_2)_2]$

The TGA curves of the complexes, $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2].10H_2O$ (Figure 7), $K_6[Ni(TeO_4(OH)_2)_2(OH)_2].12H_2O$ and $K_5[Cu(TeO_4(OH)_2)_2].16H_2O$ show abrupt weight loss in the temperature range 30 – 110° C with endothermic peaks, may be due to water of hydration[22]. The hydration temperatures of the complexes are almost the same, possibly due to the presence of the same constituents, $(TeO_4(OH)_2)^{4-}$ moieties. The peaks within the temperature ranges, 130 – 180, 270 – 350 and 650 – 750° C, can be attributed to the release of coordinated water, (O_2 and H_2O), leaving TeO_3 and the corresponding metal oxide.

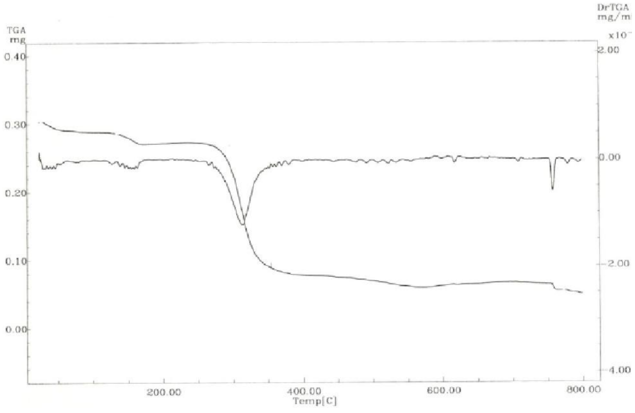


Figure 7 : TGA of $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2].10H_2O$

CONCLUSION

New hydrated tellurato complexes, $K_5[Co(TeO_4(OH)_2)_2(H_2O)_2]$, $K_6[Ni(TeO_4(OH)_2)_2(OH)_2]$ and $K_5[Cu(TeO_4(OH)_2)_2]$ were prepared. Their spectroscopic (IR, Raman, UV-vis), magnetic, crystallinity and thermal stability were discussed.

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