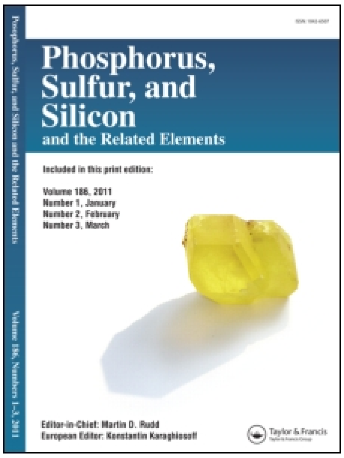

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TELLURITO COMPLEXES: BASIC METAL PYROTELLURITO COMPLEXES

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TELLURITO COMPLEXES: BASIC METAL PYROTELLURITO COMPLEXES

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The reaction between metal salts and $K_2TeO_2 \cdot xH_2O$ in aqueous ethanol yielded basic metal pyrotellurito complexes, $nMTe_2O_5 \cdot mM(OH)_2 \cdot xH_2O$ (M = Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and UO_2(VI); n, m and x are whole numbers) and $M_2(Te_2O_5)_3 \cdot mM(OH)_3 \cdot xH_2O$ (M = Cr(III) and Fe(III)). As the reaction medium was slightly alkaline basic pyrotellurites are formed instead of normal tellurites. The complexes are micro-crystalline, stable compounds and insoluble in all common solvents indicating their polymeric nature. FT-IR spectra of the complexes showed that the metal atoms are bridged through the terminal oxygen atoms of the pyrotellurito anions, $Te_2O_5^{2-}$, and the hydroxo groups of the accompanying metal hydroxides. The characteristic bending band of the hydroxo group appeared in all complexes. The electronic absorption spectra and magnetic moments of the d-elements showed that the compounds are high-spin and hexacoordinated.

Keywords: Tellurium complexes; I.R. spectra; high-spin

INTRODUCTION

The coordination chemistry of the tellurite ion, TeO_3^{2-}, is an area nearly devoid of research. The corresponding sulfite, SO_3^{2-}, and selenite, SeO_3^{2-}, ions were previously used as inorganic ligands where basic and normal salts and also mixed ligand complexes were synthesized(1–14).

In order to investigate the tellurite group in more detail, $K_2TeO_3 \cdot xH_2O$ in excess was reacted with some metal salts and basic octahedral metal pyrotellurito complexes were obtained. Their composition and structure were determined by chemical analyses, IR and visible spectra. Magnetic moments were also determined.

EXPERIMENTAL

Materials

In all preparative work, potassium tellurite $K_2TeO_3 \cdot xH_2O$ (Aldrich) was used without further purification. It was dried at 125°C for four hours and kept in a desiccator before use. Nickel(II), cobalt(II), zinc(II), cadmium(II), uranyl(VI), chromium(III), and iron(III) nitrates, and copper(II) acetate were reagent grade.

Preparation of the Basic Metal Pyrotellurites

Potassium tellurite was dissolved in a minimum amount of water and added slowly to a solution of the metal nitrate or acetate in 100 ml ethanol; the solution was stirred for two hours. The resulting precipitates were filtered and washed with water and ethanol, then air dried. The molar ratio of the metal nitrate or acetate to potassium tellurite was 1:2. The products were insoluble in all common solvents.

Physical Measurements and Analyses

Infra-red spectra (4000-400 cm^{-1}) of the basic metal pyrotellurites were recorded on an FT-IR Monson 4000 spectrometer using KBr discs. Electronic spectra were recorded on a JASCO V550 spectrophotometer using Nujol mulls. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson-Matthy Alfa Products, model no. MKI). Diamagnetic corrections were calculated from Pascal's constants.

Microanalysis of hydrogen was carried out at the Microanalytical Centre, Cairo University, Egypt. Analyses of the metals were carried out by dissolving the solid complexes in conc. HCl, the diluted solutions were neutralized by ammonia solution and metal cations were then titrated with EDTA.

Tellurium(IV) was reduced to elemental tellurium by potassium sulfite and the precipitated tellurium was filtered and estimated gravimetrically.

Uncorrected melting points of the complexes were measured. They were found to be greater than 260°C, except for the iron(III) complex, its color changed from yellow to brown upon heating to 200°C.

The chemical analyses of the basic metal pyrotellurito complexes together with their uncorrected melting points are listed in Table I.

TABLE I Analytical data of the basic metal pyrotellurito complexes

Complex and M. wt.	*Colour*	*Yield (%)*	*M.P. (°C)*	*Found (Calcd.) %*		
				M	Te	H
(1) $6NiTe_2O_5 \cdot 2Ni(OH)_2 \cdot 15H_2O$ (2819.0)	lemon green	90.7	>260	16.40 (16.66)	52.00 (54.32)	2.00 (1.22)
(2) $5CoTe_2O_5 \cdot Co(OH)_2 \cdot 8H_2O$ (2207.7)	brick red	75.0	>260	16.22 (16.02)	57.92 (57.80)	1.00 (0.82)
(3) $4CuTe_2O_5 \cdot Cu(OH)_2 \cdot 3H_2O$ (1746.6)	green	80.9	>260	19.2 (18.19)	58.71 (58.45)	1.12 (0.46)
(4) $3ZnTe_2O_5 \cdot Zn(OH)_2 \cdot 3H_2O$ (1355.1)	white	87.6	>260	18.90 (19.3)	56.20 (56.50)	1.10 (0.60)
(5) $4CdTe_2O_5 \cdot Cd(OH)_2 \cdot 4H_2O$ (2008.9)	white	80.6	>260	27.41 (28.00)	50.65 (50.82)	0.95 (0.50)
(6) $3UO_2Te_2O_5 \cdot UO_2(OH)_2 \cdot 2H_2O$ (2155.8)	yellow	93.9	>260	50.30 (50.10)	36.00 (35.51)	1.09 (0.47)
(7) $Cr_2(Te_2O_5)_3 \cdot 2Cr(OH)_3 \cdot 8H_2O$ (1459.6)	green	77.1	>260	14.60 (14.25)	54.00 (52.45)	2.10 (1.52)
(8) $Fe_2(Te_2O_5)_3 \cdot 3Fe(OH)_3 \cdot 8H_2O$ (1581.9)	yellow	83.4	changes to brown at 200	17.8 (17.65)	48.00 (48.39)	2.20 (1.59)

RESULTS AND DISCUSSION

The addition of potassium tellurite solution to metal salt solutions yielded basic metal pyrotellurito complexes instead of simple metal tellurites. This could be attributed to the fact that the reaction medium was slightly alkaline. The formation of basic metal pyrotellurites is not a surprise since similar basic metal pyroselenites were recently reported(15).

FT-IR spectra of the basic metal pyrotellurito complexes, Table II, show stretching and bending frequencies of both the two terminal TeO_2 and the bridging Te-O-Te groups of the pyrotellurite ion, $Te_2O_5^{2-}$. The bands of the terminal TeO_2 groups appear at 760–600 and 490–400 cm^{-1}, respectively, while those of

TABLE II FT-IR frequencies of the basic metal pyrotellurites (cm^{-1})(a)

Complex(b),(c)	*νO-H* *(H_2O)*	*δO-H* *(H_2O)*	*νTe-O-Te* *(Te_2O_5)*	*νTe-O* *(Te_2O_5)*(d)	*δTe-O-Te* *(Te_2O_5)*	*δTe-O* *(Te_2O_5)*(d)
(1) Ni	3435vs,br	1638 s,sh	863.6m,sh	736 s	500 m	482 m
	3218vs,br	1461 w,br		682 vs		464 m
	2926m,br			627m,sh		
	2857m,br					
(2) Co	3346vs,br	1661 s	846 m,sh	755vs,br	518m,sh	464 s,sh
	3216vs,br			674vs,br		446 s
	2930vs,br			609 s,sh		
(3) Cu	3393vs,br	1654 s,sh	846 m,sh	758vs,sh	518 s,sh	481 s
	2926m,br	1455 w,sh		678vs,br		423 s,sh
	2856 s,br			655vs,sh		418 s,sh
(4) Zn	3370vs,br	1642 s,sh	833 m,sh	764vs,br	509m,sh	473 m
	3200 s,br	1472m,br		716vs,br		446m,br
	2930m,br			693vs,br		409 m
(5) Cd	3447vs,br	1654 s	806 m,sh	746vs,sh	500 m	482 m
	3180 s,br	1476m,br		685vs,br		445 m
	2926 s,br			618m,sh		427 m
	2857 s,br			582m,sh		
(6) UO_2	3435vs,br	1683vs,sh		764 s,sh		476m,sh
	2930 s,br	1546 s,br		682vs,br		428 m
		1450m,br				
(7) Cr	3408vs,br	1638 s	809 s,sh	773 s,sh	508 s,br	482 s,sh
	3236 s,br			689vs,br		427m,br
	2945m,br					
	2873m,br					
(8) Fe	3412vs,br	1642 s,sh	809 s,sh	782 s,sh	518 s,sh	450 s,br
	2926m,br	1455 w,sh		746 s,sh		437 s,sh
	2857m,br			674vs,br		409 s,sh

(a) s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad

(b) see Table I for characterization of the complexes

(c) M-OH band in all complexes appeared at 1387 cm^{-1}

(d) the stretching and bending vibrations are those of the terminal TeO_2 group of the $Te_2O_5^{2-}$

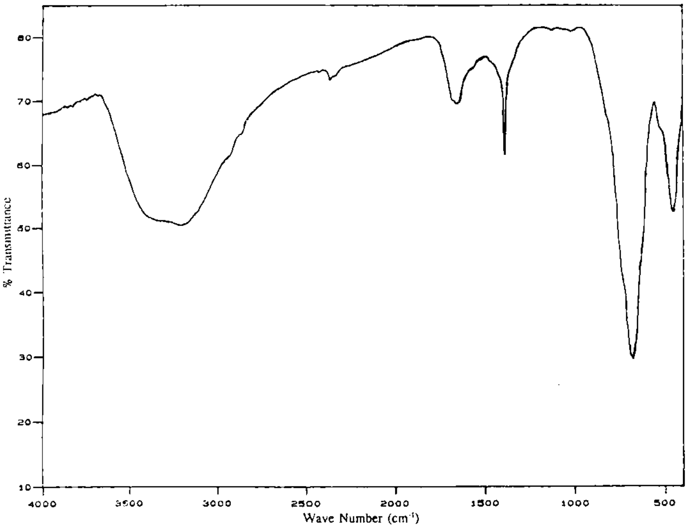

FIGURE 1 FT-IR spectrum of the complex [$5CoTe_2O_5 \cdot Co(OH)_2 \cdot 8H_2O$]

the bridging Te-O-Te group occur at 870–809 and 518–500 cm^{-1}, respectively. Vibrational assignments are based on comparison with those of the pyroselenite group, $Se_2O_5^{2-}$(16), and taking into account the differences in atomic weights of selenium and tellurium. The reported values for the pyroselenite group, for the compound $CoSe_2O_5$, are 870, 830 and 760 cm^{-1} for the stretching vibrations of the two terminal SeO_2 groups; 475 and 450 cm^{-1} for its bending vibrations. The stretching and bending vibrations of the bridging Se-O-Se group occur at 911–940 and 565–585 cm^{-1}, respectively.

All complexes showed a band at 1387 cm^{-1} characteristic of the M-OH bond in metal hydroxides(2), indicating that the metal complexes contain both the hydroxy and pyrotellurito groups. The metal hydroxides in the complexes would be produced through the dissociation of water molecules to hydrogen ions, which transfer to the tellurite ions forming hydrogentellurite ions and consequently the pyrotellurite ions, and hydroxide ions which form the metal hydroxides as indicated in the following equations

$$2MTeO_3 \cdot xH_2O \rightleftharpoons M(HTeO_3)_2 \cdot M(OH)_2 \cdot (2x - 2)H_2O$$

$$\downarrow -H_2O$$

$$MTe_2O_5 \cdot M(OH)_2 \cdot (2x - 2)H_2O$$

TABLE III Magnetic moments and electronic spectra of the high-spin six-coordinated basic metal pyrotellurito complexes

Complex	$\mu_{compl.}{}^{(a)}$ *(B.M.)*	$\mu_{eff.}{}^{(b)}$ *(B.M.)*	*Electronic spectra* ν_1	ν_2	ν_3
(1) Ni	7.71	2.73	${}^3A_{2g} \rightarrow {}^3T_{2g}$ 8100	${}^3A_{2g} \rightarrow {}^3T_{1g}$ 13227 14700	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ 23925
(2) Co	9.86	4.03	${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ 7580	${}^4T_{1g} \rightarrow {}^4A_{2g}$ 15120	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ 18800
(3) Cu	3.14	1.33		${}^2E_g \rightarrow {}^2T_{2g}$ 14044	
(4) Zn	–	–	–	–	–
(5) Cd	–	–	–	–	–
(6) UO_2	–	–			23000
(7) Cr	6.11	3.06	${}^4A_{2g} \rightarrow {}^4T_{2g}$ 14300 16100	${}^4A_{2g} \rightarrow {}^4T_{1g}$ 22470	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ –
(8) Fe	8.37	3.74		no spin allowed transition	

(a) $\mu_{compl.}$ is the total magnetic moments of all cations in the complex.

(b) $\mu_{eff.}$ is the magnetic moment of one cationic species in the complex.

Broad bands appear at 3435–2867 and 1661–1461 cm^{-1} and are attributed to the stretching and bending vibrations of the coordinated water molecules and water of crystallization. Splitting of the stretching vibrations to three or four bands and the bending ones to two bands are observed. The presence of the lower stretching and bending bands indicate H-bonding between water molecules and the oxygen atoms of the tellurito anions. This H-bonding would facilitate the transfer of hydrogen ions to the tellurite groups as indicated by the equation above. However, the absence of lower IR bands for the OH vibrations of the $HTeO_3^-$ anion, corresponding to those observed for $HSeO_3^-$ anion(15,16) at 2430–2400 and 1256–1137 cm^{-1} and which are characteristic of the stretching and bending vibrations of the OH group, suggests that the $HTeO_3^-$ anions are not present in equilibrium with the $Te_2O_5^{2-}$ anions. The dioxouranium (VI) complex showed an extra strong band at 882 cm^{-1} due to ν_3 (UO_2) stretching vibration(17). The FT-IR spectrum of the cobalt (II) complex is shown in Fig. 1 as an example of the IR spectra of these complexes.

Electronic spectra of the complexes, Table III, show that the nickel (II), cobalt (II), copper (II) and chromium (III) complexes are octahedral. The nickel (II) complex show splitting of the ν_2 band. This would be due to spin-orbit coupling(18) or the $^3A_{2g} \rightarrow {}^1E_g$ forbidden transition which gain intensity through configurational interaction with the $^3T_{1g}(F)$ level(19,20). The uranyl complex exhibit a broad charge transfer band at 23000 cm^{-1}(21).

The magnetic moments of the complexes, Table III, are lower than expected for magnetically normal octahedral complexes, this would be attributed to antiferromagnetic exchange between adjacent transition metal ions in a chain-like, ligand-bridged, polymeric structure.

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