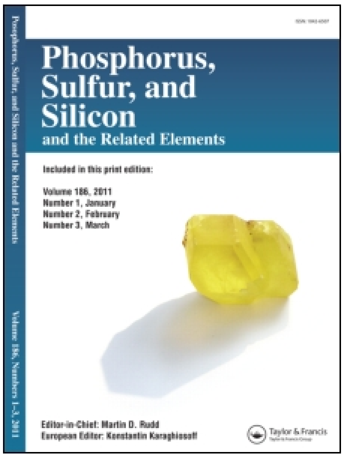

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TELLURITO COMPLEXES: MIXED LIGAND COMPLEXES OF COBALT(III)

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New tellurito complexes, [Co(en)$_2$TeO$_3$]Cl.2H$_2$O, [Co(1,2-pn)$_2$TeO$_3$]Cl.7H$_2$O, [Co(en)(1,2-pn)TeO$_3$]Cl$\cdot$5H$_2$O, and [Co(en)$_2$(NH$_3$)(TeO$_3$)$_{1/2}$]Br$_2\cdot\frac{1}{2}$KBr$\cdot 1\frac{1}{2}$H$_2$O where; en = ethylenediamine, pn = propylenediamine were synthesized. Infrared spectra of the tellurito complexes indicate that the tellurite ligand is coordinated exclusively through two of its oxygen atoms, i.e., in a bidentate form. Visible spectra and magnetic moments of the complexes show that they are low-spin and hexacoordinated. The molar conductances, λ_M, of these complexes in water show that the complexes are completely ionized.

Key words: Tellurium complexes, I.R. spectra, conductance, low-spin.

INTRODUCTION

Inorganic anions are commonly used as ligands in coordination chemistry.[1,2] The sulfite ion, SO$_3^{2-}$[3-11] and selenite ion, SeO$_3^{2-}$[12-13] were previously used as ligands in transition metal complexes. In continuation of our studies on the main group VI anions, we have found that very limited information is available about the tellurite anion as a ligand in coordination chemistry.

Attempts to synthesize basic tellurites of several transition metal cations have succeeded in our laboratory for copper(II), nickel(II), cobalt(II), iron(III), chromium(III) cations.[14]

A significant extension of the tellurite chemistry and in particular its coordination chemistry, has been achieved by the replacement of the halide ions, Cl$^-$ and Br$^-$, in Co(III) complexes with the TeO$_3^{2-}$ ligand. The present paper outlines the syntheses of some mixed tellurite-amine (and ammine)Co(III) complexes.

EXPERIMENTAL

Materials. In all preparative work, potassium tellurite, K$_2$TeO$_3\cdot x$H$_2$O (Aldrich) was used without further purification. It was dried at 125°C for four hours and kept in a desiccator before use. Ethylenediamine (Merck) was distilled over sodium hydroxide,[15] b.p. 117–118°C. 1,2-Propylenediamine was a Merck product and used without further purification. Cobalt(II) chloride hexahydrate and other chemicals used were reagent grade.

Preparation of Co(III) Complexes. The starting cobalt(III) complex, [Co(en)$_2$Cl$_2$]Cl, was prepared as described in the literature.[16] The [Co(1,2-pn)$_2$Cl$_2$]Cl and [Co(en)(1,2-pn)Cl$_2$]Cl complexes were prepared

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using the same method,[16] replacing ethylenediamine with other diamines or a mixture of them. $[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O$ was also prepared according to a literature procedure.[17]

The tellurito complexes, Table I, were prepared by reacting each of the four starting cobalt(III) complexes with $K_2TeO_3 \cdot xH_2O$, in the molar ratio 1:1 (2:1 for the latter complex), both dissolved in a minimum amount of water. For the three first complexes, the resultant solution was heated to 60°C for several minutes, then 100 ml of methanol were added. A red-purple precipitate was obtained. The precipitate was filtered and washed by methanol then air-dried. In case of the latter complex, the aqueous solution was heated to 60°C for 5 minutes then 100 ml of methanol was added and the solution was stirred for another 3 hours. The solution was evaporated on a water bath till near dryness and then kept in air till complete dryness. About 100 ml of ethanol was added to dissolve the resulting Co(III) complex. The KBr which formed was removed by filtration. Finally, the solid was obtained by the evaporation of the solvent, then air-dried. A bright red-purple solid was obtained in each case.

Physical Measurements and Analyses

Infrared spectra (4000–400 cm^{-1}) of the tellurito complexes were recorded on an FT-IR Monson 4000 spectrometer using KBr discs. Electronic spectra were recorded on a Perkin-Elmer 550 spectrophotometer using aqueous solutions of the complexes. Molar conductances of the complexes in water (10^{-3} M) were measured using a Model LBR 40A conductivity meter from Wissenschaftlich-Technische Werkstatten, D 8120 Weilheim, Germany.

Microanalyses for carbon, hydrogen, nitrogen and halogen were carried out at the Microanalytical Centre, Cairo University, Giza, Egypt. Attempts to estimate Co(III) in the tellurite complexes either by EDTA titrations or by atomic spectrophotometry failed to give good results, and this may be attributed to tellurium interference. Tellurium(IV) was reduced to elemental tellurium by potassium sulfite and the precipitated tellurium was filtered and estimated gravimetrically. The chemical analyses of the complexes together with uncorrected melting points are listed in Table I.

RESULTS AND DISCUSSION

New tellurite complexes of Co(III) with different diamine ligands were prepared. The tellurite anion may act either as a bidentate chelate or bridging ligand. This is accomplished by the replacement of two chloride ligands coordinated to the central cobalt(III) cation by the tellurite group as in the case of $[Co(en)_2TeO_3]Cl \cdot 2H_2O$, $[Co(1,2\text{-}pn)_2TeO_3]Cl \cdot 7H_2O$ and $[Co(en)(1,2\text{-}pn)TeO_3]Cl \cdot 5H_2O$, or the replacement of one bromide ligand to form bridging tellurite as in the case of $[Co(en)_2(NH_3) \cdot (TeO_3)_{1/2}]Br_2 \cdot \frac{1}{2}KBr \cdot 1\frac{1}{2}H_2O$. The Co(III) complexes are soluble in water without any change in their colour. The solubility of the complexes in water supports their ionic formulae.

Attempts to prepare $[Co(NH_3)_xTeO_3]^+$; (x = 4 or 5) by replacing the CO_3^{2-} group with TeO_3^{2-} in $[Co(NH_3)_xCO_3]^+$ were unsuccessful. However, basic Co(II) tellurite, $CoTeO_3 \cdot Co(OH)_2 \cdot nH_2O$, was obtained in both cases. This was confirmed by elemental analyses and IR spectra. In contrast, we have succeeded[13] in synthesizing $[Co(NH_3)_xSeO_3]^+$ by replacing CO_3^{2-} with SeO_3^{2-} in $[Co(NH_3)_xCO_3]^+$; (x = 4 or 5). A Russian group[18–20] has previously studied the interaction of the $[Co(NH_3)_5Cl]^{2+}$ complexes with SeO_3^{2-}, CO_3^{2-} and TeO_3^{2-} anions. They found that the stability of the complexes decreases in the order $SeO_3^{2-} > CO_3^{2-} > TeO_3^{2-}$. The formation of basic Co(II) tellurite may be due to the hydrolysis of potassium tellurite and the subsequent formation of an intermediate metal hydroxide complex. Then tellurite anions can then replace hydroxyl groups possibly via a mechanism previously suggested by Stranks *et al.*[21]

IR spectra are consistent with the formation of tellurito-amine (or ammine) Co(III) complexes in the solid state. The IR spectra of the complexes are compared with those of the starting cobalt(III) diamine complexes. The spectra show strong simi-

TABLE I

Analytical data of the tellurito complexes

Complex	Colour	Yield	M.P.	Found (Calcd.)%				
		(%)	(°C)	Te	C	H	N	Halogen
(1) $[Co(en)_2TeO_3]Cl.2H_2O$	Red purple	79	200 decomp.	30.1	11.9	4.7	10.0	7.8
				(29.9)	(11.3)	(4.7)	(13.2)	(8.3)
(2) $[Co(1,2\text{-}pn)_2TeO_3]Cl.7H_2O$	Red purple	84	185 decomp.	24.3	12.9	6.4	10.0	7.8
				(23.8)	(13.5)	(6.4)	(10.5)	(7.8)
(3) $[Co(en)(1,2\text{-}pn)TeO_3]Cl.5H_2O$	Red purple	85	220 decomp.	25.9	12.3	4.1	10.3	6.3
				(25.8)	(12.2)	(5.7)	(11.3)	(7.2)
(4) $[Co(en)_2(NH_3)(TeO_3)_{1/2}]Br_2.\frac{1}{2}KBr.1\frac{1}{2}H_2O$	Red purple	81	225 decomp.	13.3	9.1	4.4	13.6	38.8
				(12.8)	(9.1)	(4.2)	(13.2)	(37.7)

TABLE II

Observed IR frequencies of the tellurite group and the electronic spectra of the complexes

Tellurito Complexes	Absorption frequencies (cm^{-1})						Electronic Spectra (cm^{-1})	
	$\nu_1(A')$	$\nu_2(A')$	$\nu_3(A')$	$\nu_4(A')$	$\nu_5(A'')$	$\nu_6(A'')$	$\nu_1\ {}^1A_{1g} \longrightarrow {}^1T_{1g}$	$\nu_2\ {}^1A_{1g} \longrightarrow {}^1T_{2g}$
(1)	839	768	593	523	685	482	19200	26300
(2)	857	768	601	554	685	469	19100	25800
(3)	848	773	585	554	685	469	19700	26900
(4)	804	714	598	525	624	462	19000	25250
Uncoordinated tellurite ion	$\nu_1(A_1)$		$\nu_2(A_1)$	$\nu_3(E)$	$\nu_4(E)$			
TeO_3^{2-} (a)	830		540	740	460			
$K_2TeO_3.xH_2O$ (b)	830		550	740, 670	460			

(a) Raman spectral data in aqueous solution, from Ref. 22.

(b) IR spectral data recorded in the solid state.

larities between the two types of complexes. In addition, high intensity absorption bands of the tellurite group are present.

The free tellurite anion, TeO_3^{2-}, has C_{3v} symmetry and absorbs in the region 460 –850 cm^{-1}. There are six fundamental modes of vibration, two pairs of which are degenerate, giving rise to four fundamental frequencies $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$ and $\nu_4(E)$ which are infrared active. Table II shows the fundamental frequencies of the free TeO_3^{2-} anion as determined by the Raman spectrum determined in solution.[22]

If the tellurite ion coordinates with a metal centre through the tellurium atom, then the C_{3v} symmetry of the tellurito group would be retained and four fundamental frequencies should be observed. On the other hand, if the tellurite ion coordinates through either one or two of its oxygen atoms, then the C_{3v} symmetry would be lowered to C_s and six fundamental frequencies, three stretching and three bending, should be observed.

Vibrational assignments were aided by comparison with the vibrational frequencies of the TeO_3^{2-} anion in K_2TeO_3, and with the related complexes with SO_3^{2-} and SeO_3^{2-}.[8–13] The six fundamental stretching and bending frequencies of TeO_3^{2-} were observed in the lower frequency range, 460–860 cm^{-1}.

The infrared vibrations of the tellurite group in the tellurito complexes showed six absorption bands, which indicate that the tellurite ligands are coordinated through oxygen atoms. Table II lists the stretching vibrations of the TeO_3^{2-} groups in Co(III) complexes. In these complexes, the TeO_3^{2-} ions can be regarded as bidentate chelate ligands, as all the six distinct bands were observed. Also, in the case of the complex $[Co(en)_2(NH_3)(TeO_3)_{1/2}]Br_2 \cdot \frac{1}{2}KBr \cdot 1\frac{1}{2}H_2O$, where the tellurite group acts as a bridging bidentate ligand to two Co(III) cations, six absorption bands are also observed. However, in the latter case the stretching vibrations occur at lower frequencies than those of the free TeO_3^{2-} and the other complexes.

The electronic spectra of the complexes are shown in Table II. The electronic spectra of the Co(III) complexes show two absorption bands of about equal intensities and correspond to the spin allowed transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ states. The first transition is broader and occurs in the visible region, in the range 19000–19700 cm^{-1}. The other transition has its band in the range 25250–26900 cm^{-1}. The two spin forbidden bands to the triplet states, $^3T_{1g}$ and $^3T_{2g}$ are not observed. The visible spectra of these complexes are consistent with low-spin complexes of Co(III) and thus these complexes are diamagnetic.[23]

The molar conductance, λ_M, of these complexes in water (10^{-3} M) are 220 $ohm^{-1} \cdot cm^3 \cdot mole^{-1}$ for $[Co(en)_2(NH_3)(TeO_3)_{1/2}]Br_2 \cdot \frac{1}{2}KBr \cdot 1\frac{1}{2}H_2O$ and 174 $ohm^{-1} \cdot cm^3 \cdot mole^{-1}$ for the rest of the complexes, at room temperature. This would be due to the formation of 2.5:1 and 1:1 electrolytes, respectively.

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