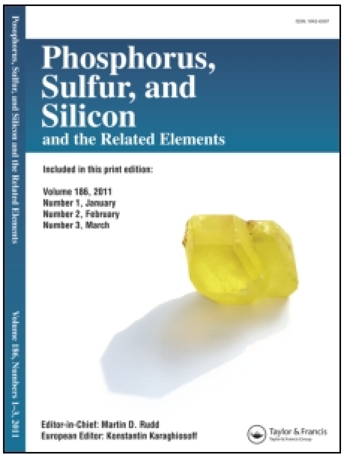

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Synthesis and Characterization of Some Mixed Ligand-Selenito and Tellurito Chromium(III) Complexes

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SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGAND-SELENITO AND TELLURITO CHROMIUM(III) COMPLEXES

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New mixed ligand Cr(III) complexes were prepared where diamine or oxalato ligands are coordinated together with either tellurito, selenito, or hydrogenselenito ions to form nine octahedral complexes. The complexes were characterized by chemical analyses, IR and UV-visible spectra, magnetic, and conductivity measurements. The tellurito and selenito ligands act as monodentate ligands, coupled with the bidentate diamine ligands. On the other hand, they act as bidentate chelate ligands when coordinated together with the oxalate ligand. However, hydrogenselenite ion act as a monodentate ligand coupled with the oxalate ligand. IR spectra indicated that the inorganic ligands are coordinated to the Cr(III) ion through their oxygen atoms. One of the bulky diamine molecules, 1,2-pn or 1,3-pn, was freed from the coordination sphere of Cr(III) on the addition of the bulky inorganic anions and was replaced by two water molecules.

Keywords: Conductance; electronic spectra; IR spectra; tellurium and selenium Cr(III) complexes

INTRODUCTION

The coordination chemistry of the tellurite ion, TeO_3^{2-}, is a new area of research where few publications have appeared.[1,2] On the other hand, the corresponding sulfite SO_3^{2-} [3–11] and selenite, SeO_3^{2-},[12–16] ions were previously used as inorganic ligands. Only two publications from our laboratory deal with the reactions of the tellurite ion with transition and non-transition metals. We found that $K_2TeO_3.xH_2O$ reacted with some di- and trivalent metal salts to yield basic pyrotellurito complexes, $nMTe_2O_5.mM(OH)_2.xH_2O$, and $nM(Te_2O_5)_3.mM(OH)_3.xH_2O$, where n

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and m are whole and variable numbers.[1] Also, the tellurite ion was found to react with mixed halogenoamine Co(III) complexes where it replaced the halogen ions and yielded the corresponding telluritoamine complexes.[2]

EXPERIMENTAL

Materials

Sodium selenite pentahydrate, $Na_2SeO_3.5H_2O$, sodium hydrogen selenite, $NaHSeO_3$, potassium tellurite, K_2TeO_3, were BDH products and were used without further purification. Ethylenediamine(en),1,2 propylenediamine(1,2-pn) and 1,3-propylenediamine(1,3-pn) were Merck products. Ethylenediamine was distilled over sodium hydroxide,[17] b.p. 117–118°C. The other diamines were used without further purification. Chromium(III) chloride hexahydrate, potassium dichromate, oxalic acid dihydrate and the organic solvents used were all reagent grade.

Preparation of Cr(III) Complexes

The parent Cr(III) complex, $[Cr(en)_2Cl_2]Cl.1.15H_2O$ was prepared as described in the literature.[18] The other diamine complexes, $[Cr(1,2\text{-}pn)_2Cl_2]Cl$ and $[Cr(1,3\text{-}pn)_2Cl_2]Cl$ were prepared similarly. The Cr(III) bis (oxalate) complex, $K[cis\text{-}Cr(C_2O_4)_2(H_2O)_2].{}^1\!/_2H_2O$ was also prepared according to a literature procedure.[19] The selenito and tellurito complexes (Table I) were prepared by dissolving $Na_2SeO_3.5H_2O$ or K_2TeO_3 mixed with the diamine complex in the molar ratio 1:1 in the minimum amount of water then the mixture was warmed to 60°C. To complete dissolution, 50 ml of methanol was added and the solution was stirred for 1 h. 10 ml of acetone was then added to precipitate the product. The precipitate was filtered, washed with acetone, then air-dried. In case of the reactions with the parent bis (oxalato) complex, the reactants were simply dissolved in the minimum amount of water and stirred for 1 h. The precipitate formed was filtered, washed with acetone, then air-dried. The reaction of the bis(oxalato) complex with $NaHSeO_3$ was carried out similarly, but in the molar ratio 1:2.

Physical Measurements and Analyses

Infrared spectra (4000-400 cm^{-1}) of the complexes were recorded on an FT-IR Monson 4000 spectrometer using KBr discs. Reflectance spectra (190–1100 nm) of the solid complexes as $BaSO_4$ discs were recorded

TABLE I Analytical Data of the Selenito and Tellurito Chromium(III) Complexes

Complexes	Color	Yield (%)	m.p. (°C)	Chemical analyses found (calcd.) %								
				C	H	N	Se	Te	Cr	K	Na	Halogen
(**1**) $[Cr(C_2N_2H_8)_2SeO_3Cl].NaCl.{}^1/_2CH_3OH$	purple	60	>230	12.9	4.4	13.6	19.3	—	13.0	—	5.6	16.9
$NaCrC_{4^1/_2}H_{18}N_4O_{3^1/_2}SeCl_2$				(13.2)	(4.4)	(13.7)	(19.3)	—	(12.7)	—	(5.6)	(17.3)
(**2**) $[Cr(C_2N_2H_8)_2TeO_3(OH_2)]\ Cl.3H_2O$	purple	71	>230[c]	10.2	5.3	12.3	—	28.0	11.4	—	—	7.8
$CrC_4H_{24}N_4O_7TeCl$				(10.6)	(5.3)	(12.3)	—	(28.0)	(11.4)	—	—	(7.8)
(**3**) $[Cr(C_3N_2H_{10})^aSeO_3(OH_2)_2Cl].3H_2O$	grayish green	60	>230	9.4	5.3	7.4	20.7	—	13.5	—	—	9.3
$CrC_3H_{20}N_2O_8SeCl$				(9.5)	(5.3)	(7.4)	(20.9)	—	(13.7)	—	—	(9.4)
(**4**) $[Cr(C_3N_2H_{10})^aTeO_3(OH_2)_2Cl].8H_2O$	green	77.5	>230[d]	7.0	5.7	5.4	—	24.5	9.9	—	—	6.8
$CrC_3H_{30}N_2O_{13}TeCl$				(7.0)	(5.9)	(5.4)	—	(24.7)	(10.1)	—	—	(6.9)
(**5**) $[Cr(C_3N_2H_{10})^bSeO_3(OH_2)_3]Cl.H_2O.{}^1/_2CH_3OH$	green	69	200[e]	10.9	5.3	7.1	20.9	—	14.0	—	—	9.4
$CrC_{3^1/_2}H_{20}N_2O_{7^1/_2}SeCl$				(11.2)	(5.4)	(7.5)	(21.0)	—	(13.8)	—	—	(9.4)
(**6**) $[Cr(C_3N_2H_{10})^bTeO_3(OH_2)_3]Cl.{}^1/_2NaCl.6H_2O$	grayish green	72	>230	6.8	5.3	5.3	—	24.0	9.9	—	2.1	10.3
$Na_{^1/_2}CrC_3H_{28}N_2O_{12}TeCl_{1^1/_2}$				(6.8)	(5.3)	(5.3)	—	(24.1)	(9.8)	—	(2.2)	(10.1)
(**7**) $K_3[Cr(C_2O_4)_2TeO_3].{}^1/_2C_2H_5OH$	green	98	>230	10.7	1.0	—	—	23.3	9.5	21.4	—	—
$K_3CrC_5H_3O_{11^1/_2}Te$				(11.0)	(0.6)			(23.5)	(9.6)	(21.6)		
(**8**) $Na_2K[Cr(C_2O_4)_2SeO_3].{}^1/_2H_2O$	green	69.5	>230	10.7	trace	—	17.5	—	11.4	8.7	10.2	—
$Na_2KCrC_4HO_{11^1/_2}Se$				(10.7)	(0.2)		(17.6)		(11.6)	(8.7)	(10.2)	
(**9**) $Na_2K[Cr(C_2O_4)_2(HSeO_3)_2].C_2H_5OH$	olive green	71	>230	12.2	2.0	—	25.6	—	8.8	6.4	7.4	—
$Na_2KCrC_6H_8O_{15}Se_2$				(11.7)	(1.3)		(25.7)		(8.5)	(6.4)	(7.5)	

[a] 1,2-pn.

[b] 1,3-pn.

[c] Changed to gray at 190°C.

[d] Changed to gray at 200°C.

[e] Changed to dark green at 170°C and decomposed at 200°C.

using a Shimadzu UV-Visible spectrophotometer 1601. Electronic spectra of aqueous solutions (10^{-3} M) of the complexes which were soluble in water were recorded on a JASCO V550 spectrophotometer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Product, Model No. MKI magnetic susceptibility balance. Diamagnetic corrections were calculated from Pascal's constants. Molar conductances of the aqueous solutions of the complexes (10^{-3} M) were measured on the Corning conductivity meter NY 14831 mode 1441 (USA).

Microanalysis of carbon, hydrogen, nitrogen, halogen, and alkali metals were carried out at the Microanalytical Centre, Cairo University, Giza, Egypt. Chromium(III) was estimated by EDTA titrations. Tellurium(IV) was reduced to elemental tellurium by potassium sulfite and the precipitated tellurium was filtered, washed with water then air-dried and weighed. The chemical analyses of Cr(III) complexes together with their uncorrected melting points are listed in Table I.

RESULTS AND DISCUSSION

New tellurito, selenito, and hydrogenselenito complexes of Cr(III), with different diamine and oxalate ligands, where the inorganic ligands act either as monodentate or bidentate chelate ligands. The obtained complexes were formed by the replacement of the chloride ions or water molecules, coordinated to the central Cr(III) cation in the parent complexes, by either one or two inorganic anions. Only one SeO_3^{2-} or TeO_3^{2-} anion and two $HSeO_3^-$ anions, were coordinated to the central Cr(III) ion in the octahedral products, Figure 1. It is also worth mentioning that in the reactions of the SeO_3^{2-} and TeO_3^{2-} ions, with either dichloro bis(1,2-pn) or bis(1,3-pn) Cr(III) complexes, one of the coordinated diamine molecules was replaced by two coordinated water molecules. This was interpreted as due to the bulkiness of both the entering inorganic anions and the leaving diamine groups. However, this was not the case with ethylenediamine, probably because it is less bulky than the other two diamine compounds.

The IR spectra of the complexes showed six vibration bands in the range 470–850 cm^{-1}. It was previously observed that the vibrational frequencies of the SeO_3^{2-} and TeO_3^{2-} anions lie in the same region[2,12] despite the differences of the atomic weights of selenium and tellurium and its consequent effect on the force constants of both the Se—O and Te—O bonds. However, they differ from the vibrational frequencies of the SO_3 group which usually occur in the region 500–1200 cm^{-1}.[9] The appearance of six bands in their IR spectra indicate[3] the lowering of

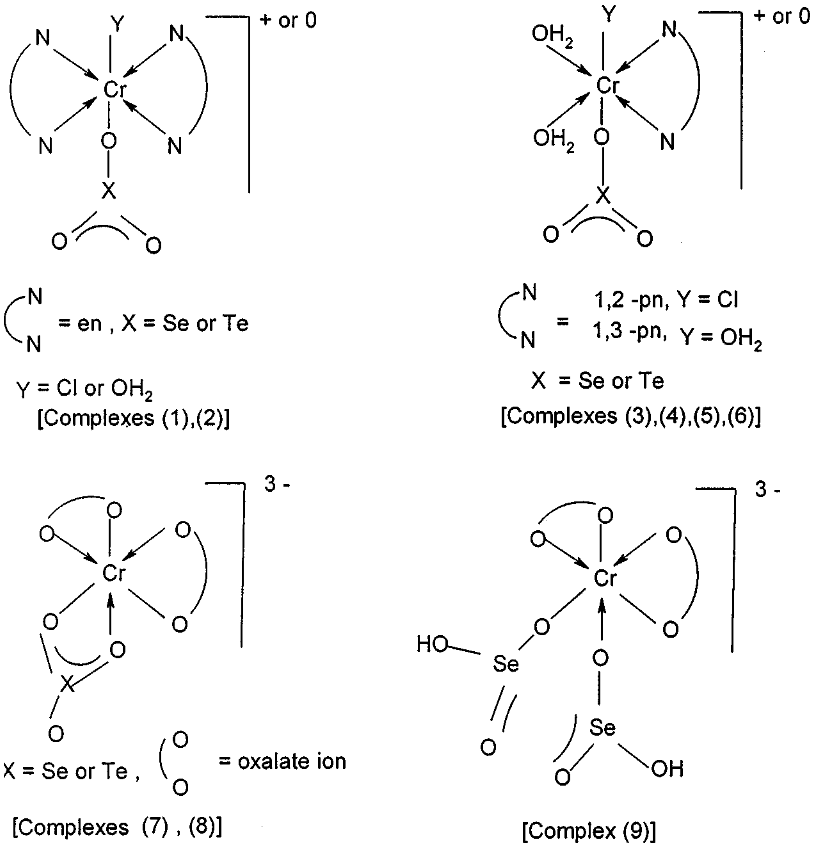

FIGURE 1 Suggested structures of the complexes (for numbering of complexes, see also Table I).

the symmetry of the inorganic anions from C_{3v}, in their ionic state, to C_s, in their coordinated compounds. It also indicates that the oxygen atoms, rather than the selenium and tellurium atoms, are involved in coordinating the central Cr(III) ion.

The IR spectra of the ethylenediamine-selenito or tellurito complexes are shown in Figure 2 as representative compounds of the mixed diamine-selenito or tellurito complexes prepared in this study. Besides the above mentioned vibrations characteristic of the SeO_3^{2-} and TeO_3^{2-} groups, the following vibrations were also observed. The asymmetrical and symmetrical stretching vibrations of the coordinated NH_2 groups appeared at 3250–3280 and 3215–3220 cm^{-1}, respectively. The latter two bands may be fused together and appear as a single broad band at 3250–3270 cm^{-1}. The stretching vibrations of the O—H bond

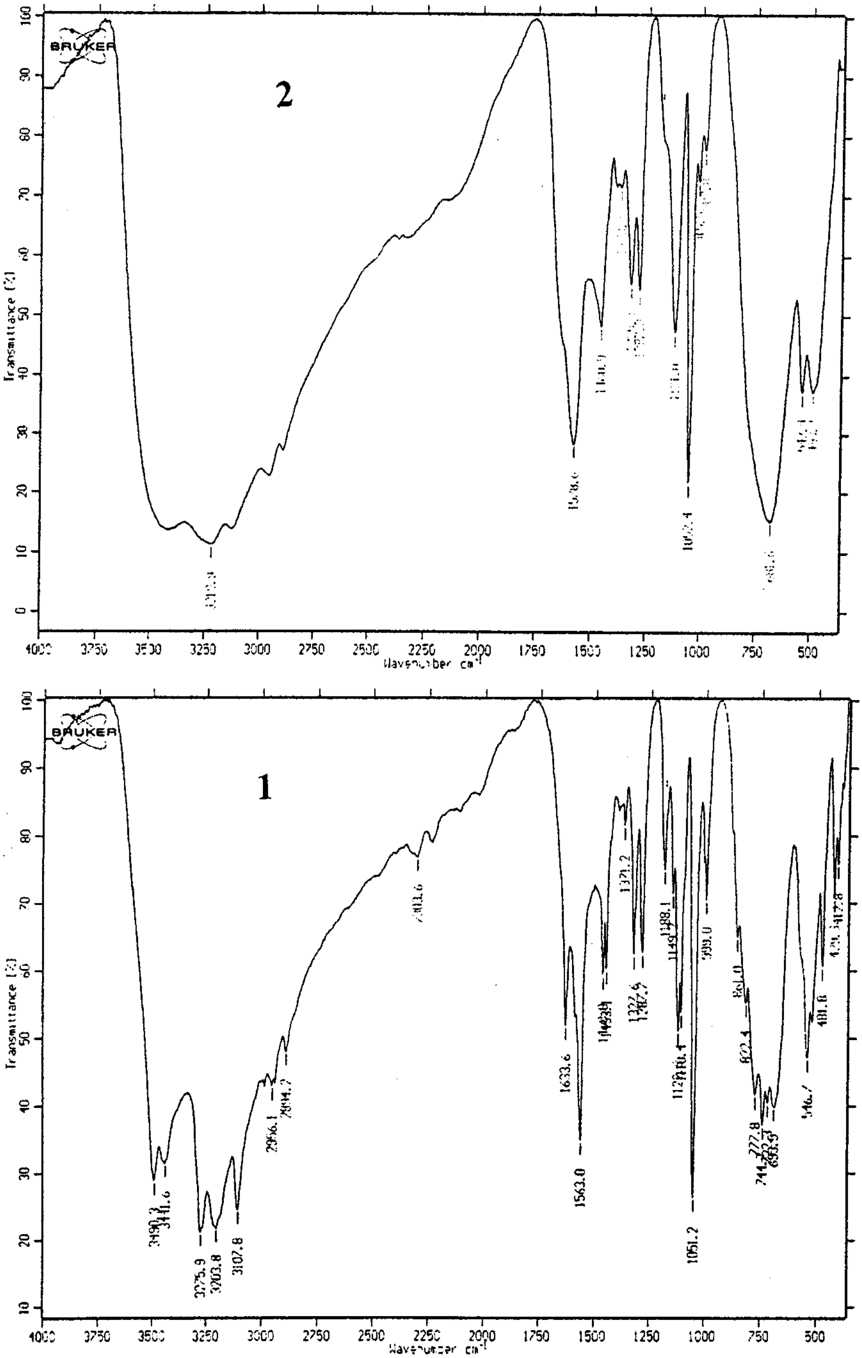

FIGURE 2 IR spectra of (1) complex (**1**) and (2) complex (**2**).

of either the hydrated water or methanol molecules appeared at 3490 and 3446 cm^{-1}. The latter two bands may also be fused together and appear as a single broad band at 3425–3430 cm^{-1}. Another band appeared at 3105–3140 cm^{-1} either as a sharp or broad band which may be attributed to the H-bonded OH group of the hydrated water or methanol molecules. The bending vibrations of the OH and NH bonds appeared at 1625–1630 and 1565–1585 cm^{-1}, respectively. The stretching vibration of the Cr—N bond appeared at ~430 cm^{-1} and that of the Cr—O bond appeared at ~410 cm^{-1}.[20]

The IR spectra of the mixed oxalato–tellurito or selenito or hydrogenselenito Cr(III) complexes are shown in Figure 3. In addition to the observed vibrations of the inorganic ligands, other vibrations are characterized for the oxalate ligand and the hydrated water or ethanol molecules. The asymmetrical and symmetrical stretching and bending vibrations of the oxalate anion appeared at 1715–1720, 1675–1685, ~1400, ~1310, ~1265, ~900 cm^{-1}. The other lower vibrations may be overlapped by the stretching and bending vibrations of the inorganic anions. The corresponding $K_3[Cr(OX)_3].3H_2O$ showed 10 stretching, bending and ring deformation vibrations.[20] The stretching O—H vibrations appeared as a broad band and a shoulder at 3440–3450 cm^{-1} and ~3220 cm^{-1} respectively. The bending vibration of the O—H bond was overlapped by the oxalate vibrations and thus was not exactly characterized. The Cr—O stretching band appeared at ~410 cm^{-1}. No characteristic stretching and bending vibrations due to the $HSeO_3^-$ anion which were expected to occur at 2400–2430 and 1137–1256 cm^{-1}[16] were observed in the hydrogenselenite complex (**9**) prepared in this work. This may be due to the lack of H—bonding between the $HSeO_3^-$ anions in the present complex as compared with the previously prepared Cu(II) and Ni(II) complexes which only contain the selenite ligands.[16]

The electronic spectra of the complexes are shown in Table II. The spectra of the solids showed two transitions, the first one was due to the transition $^4A_{2g} \rightarrow {}^4T_{2g}$ and occurred at 16100–18730 cm^{-1} and the second one was due to the transition $^4A_{2g} \rightarrow {}^4T_{1g}$ and occurred at 22880–24240 cm^{-1}. The third transition $^4A_{2g} \rightarrow {}^4T_{1g}$ (P), which usually occurs at a higher energy region ~37000 cm^{-1}, would be overlapped with ligand transitions. Other transitions in the range 25280–32570 cm^{-1}, were also observed which would be due to ligand transitions. In addition, other bands appeared at 14090, 15040, and 15750–15760 cm^{-1} in the spectra of some complexes which may be due to spin-forbidden transition from $^4A_{2g}$ ground state to the doublet states arising from the ^2G state of the free ion. These latter transitions appeared as sharp lines of lower intensity. The electronic spectra of the aqueous solutions of complexes, which were soluble in water, were also determined. The bands

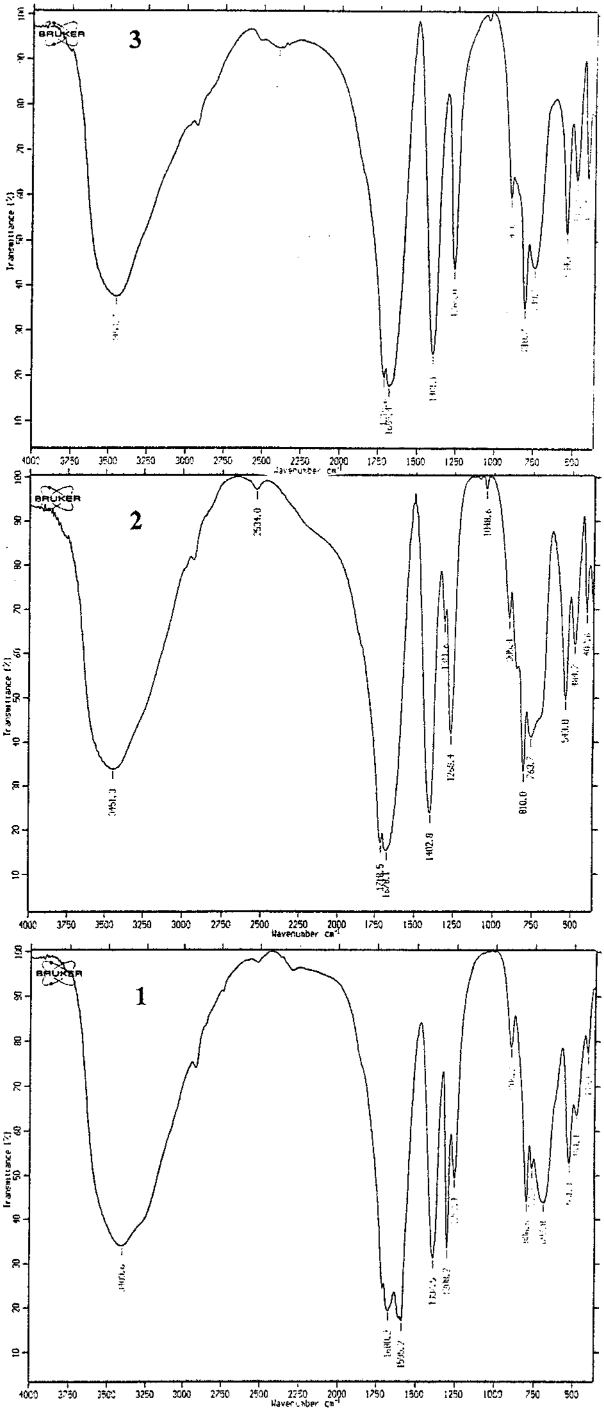

FIGURE 3 IR Spectra of (1) complex (**7**), (2) complex (**8**), and (3) complex (**9**).

TABLE II Observed IR Frequencies of the Selenite/Hydrogenselenite or Tellurite Groups, Electronic Spectra, Magnetic Moments, and Conductance of the Complexes

	Absorption frequences (cm^{-1})						Electronic spectra^{a} (cm^{-1})				
Complexes	$\nu_1(A')$	$\nu_2(A')$	$\nu_3(A')$	$\nu_4(A')$	$\nu_5(A'')$	$\nu_6(A'')$	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}$	Other peaks	μ_{eff} B.M.	Conductance^{b} Ohm^{-1} cm^2 mol^{-1}
(**1**)	843	738	593	458	700	482	18730	24210	14400, 15630, 27780, 30910	4.56	136
							18800 (36)	**25000** (45)			
(**2**)	814	771	593	541	685	496	17410, 18180 (sh)^{c}	23070	14090, 15550, 28050, 28500, 32570	4.28	126
							18520 (83)	**25710** (107)			
(**3**)	800	747	643	543	685	471	17090, 16390 (sh)	24240	15760, 30440	3.37	—
(**4**)	829	779	609	550	690	508	16350, 17170 (sh)	23070	15760	3.59	—
(**5**)	814	750	636	526	703	481	16100, 16960 (sh)	22880	15760	3.52	96
(**6**)	814	743	616	541	667	481	16100, 17320 (sh)	22680	15750, 25280, 28250	3.35	375
(**7**)	805	757	614	533	694	483	16100	23420	14090, 15040, 15750 (sh), 26040, 29850, 31060	3.63	—
							16810 (26)	**23580** (48)	**27030** (85)		—
(**8**)	804	747	643	539	697	477	16230, 17240 (sh)	23070	14180, 15760, 25280, 30440	3.64	340
							17080 (77)	**24130** (154)	**26000** (163)		
(**9**)	809	748	657	544	714	483	16450, 17240 (sh)	23090	14090, 15760	4.00	279
							17510 (56)	**23870** (117)			

[a] Reflectance spectra of the solid complexes are indicated in ordinary letters and electronic spectra of 10^{-3} M aqueous solutions of the complexes are shown in bold letters; ε values (M^{-1} cm^{-1}) are written between brackets.

[b] 10^{-3} aqueous solutions of the complexes.

[c] sh = shoulder.

appearing in these spectra are shown in bold numbers together with their extinction coefficients. The differences which may be encountered in their values as compared with those of the solid spectra would be due to the solvent effects.

The magnetic moments of the complexes (Table II) were in the range 3.35–4.56 B.M. It is expected that the magnetic moments of Cr(III) complexes are slightly below the spin-only value of 3.88 b.m. However, complexes (**1**), (**2**), and (**9**) showed higher values than those expected, may be due a certain extent of orbital contribution.

The molar conductances of the aqueous solutions (10^{-3} M) of the complexes which dissolved in water showed variable values. Complexes (**1**), (**2**), and (**5**), Table II, showed values in the range 96–136 ohm^{-1} cm^{-2} mmol^{-1} and indicate the presence of 1:1 electrolytes. Complex (**1**) showed conductance, although the complex is a neutral one, due to the presence of a NaCl molecule coprecipitated with each molecule of the complex compound. Complexes (**2**) and (**5**) are 1:1 electrolytes as the chloride ion is in the ionic form. Complex (**6**) showed a high value of molar conductance 375 ohm^{-1} cm^{-2} mmol^{-1} due the ionic nature of the complex besides the coprecipitation of a half NaCl molecule with each complex molecule. Complexes (**8**) and (**9**) were 1:3 electrolytes and showed molar conductance in the range 279–340 Ohm^{-1} cm^{-2} mol^{-1}.

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