The Ligand Chemistry of 2-(4-Ethoxyphenyltelluro)benzoate

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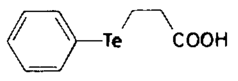
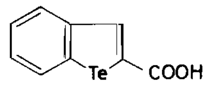
Abstract

Complexes of the ligand 2-(4-ethoxytelluro)-benzoate (ETB$^-$) with Tl(I), Ag(I), Co(II), Ni(II), Cu(II), Cr(III) and Fe(III) are prepared. Only in the complexes with thallium, silver and nickel is it possible to invoke the ligation of tellurium. Generally, the ligand behaves as a simple carboxylate giving examples of bidentate (Tl, Ag, Co, Ni, Cr, Fe), monodentate (Ni), and bridging (Cu) coordination. In two cases (Cr, Fe), the presence of the free acid in the complex was noted. Many of the complexes show antiferromagnetic coupling of the metal ions.



I



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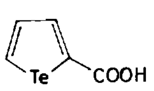

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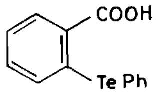

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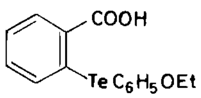

V

Introduction

There is a discernable growth in current interest in the chemistry of ligands containing tellurium as a coordinating atom [1, 2], yet relatively few papers have been published describing the chemistry of bidentate tellurium ligands. It has been our experience [3] that tellurium ligands favour strongly those ligands which are designated Class B in the Arhland, Chatt, Davies classification [4]. We reasoned that extensions of tellurium ligand chemistry should be possible if we synthesised ligands in which another donor atom which was 'hard' in the Pearson classification [5] was also present. To that end we have synthesised new Te, N ligands [6, 7] and also Te, O ligands, one of which, 2-(4-ethoxyphenyltelluro)-benzoic acid is described in this paper. This ligand could behave as a simple carboxylate in the presence of metals, or as a simple telluride ligand, or as a bidentate Te, O ligand. In this paper we seek to establish the choices made with some first row transition elements.

Piette and Renson [8, 9] have prepared compounds **I** and **II** and Fringuelli and Taticchi [10] have reported **III**. Subsequently Piette *et al.* reported **IV** [11], which is similar to **V** reported here. No coordination chemistry of **I**–**IV** was described, but synthetic routes to such ligands are clearly available. One of the few studies of complex formation with a tellurocarboxylate was by Liang and Pettit [12] who studied the formation constants for some bivalent first row transition metal ions, together with silver(I), with bis(3-carboxylpropanyl)telluride. No solid compounds were isolated.

Experimental and Results

Syntheses

2-(4-Ethoxyphenyltelluro)benzoic acid

2-Aminobenzoic acid (27.5 g, 0.2 mol) in conc. HCl (25 cm^3) and distilled water (100 cm^3) was diazotised at 0–5 °C with $NaNO_2$ (13.8 g) in distilled water (25 cm^3). The medium was rendered basic with the minimum of sodium carbonate solution. The cold solution thus obtained was shaken rapidly with a warm (30 °C) solution of sodium 4-ethoxyphenyltelluride, obtained from reduction under dinitrogen of a warm solution of bis(4-ethoxyphenyl)ditelluride (25 g, 0.05 mol) in a mixture of ethanol (50 cm^3) and tetrahydrofuran (100 cm^3) with the minimum amount of basic sodium tetrahydroborate (2.5 g in 35 cm^3 1 M NaOH). On completion of the evolution of dinitrogen, the solution was warmed and then extracted with benzene from which some regenerated ditelluride was recovered. The aqueous layer was chilled with ice and the precipitate so formed was filtered, washed with benzene, then dissolved in acetone and reprecipitated

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by addition of petroleum ether (60–80 °C) to give a white crystalline sodium salt (49%) which had a melting point (m.p.) of 257–260 °C. *Anal.* Found: C, 40.1; H, 4.50. Calc. for $C_{15}H_{13}NaO_3Te{\cdot}3H_2O$: C, 40.4; H, 4.29%.

The acid was then prepared by adding hydrochloric acid (1 M) to a solution of the sodium salt in ethanol/water (1:3). The white acid was dried over P_4O_{10} to m.p. 194–196 °C. *Anal.* Found: C, 48.5; H, 3.50. Calc. for $C_{15}H_{14}O_3Te$: C, 48.7; H, 3.79%.

Metal complexes

A standard procedure was developed; thus, sodium 2-(4-ethoxyphenyltelluro)benzoate (0.002 mol) in water (50 cm^3; hot (Tl) or warm (others)) was treated with the metal salt (0.001 mol of Tl_2SO_4, $AgClO_4$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $(NH_4)_2Fe(SO_4)_2{\cdot}12H_2O$, $Cr(NO_3)_3$). The complex precipitated and was filtered, washed with water and air dried. Where possible recrystallisation was from chloroform (Co, Ni) or 1:5 DMSO/CH_3CN (Tl, Ag). Analytical and other data are given in Table 1.

Physical Measurements

Conductivity measurements were taken with a Mullard bridge and immersion type bright platinum electrodes. Infrared spectra (4000–200 cm^{-1}) were obtained with a Perkin-Elmer 599B spectrometer. UV and visible spectra were taken on Pye-Unicam SP800 B and SP 8 100 instruments. Magnetic measurements were by the Gouy method at room temperature and mass spectra were determined with an AEI MS9 instrument. A ^{57}Fe Mössbauer measurement was carried out on the Fe(III) complex. Physical data are incorporated into Tables 1 and 2.

Discussion

The new ligand gave satisfactory elemental analysis and the free acid showed the molecular ion in the 70 eV mass spectrum. It was convenient to use the sodium salt in the preparations when the sparingly soluble metal complexes precipitated.

Infrared Data

With the exception of the thallium complex, all the new compounds show strong, broad and ill resolved bands in the OH region of the spectrum. Analytical data may be fitted by invoking the presence of lattice water, but in some cases alternative explanations of the OH bands must be sought. Curtis [13] has shown that for acetato complexes it is possible to distinguish ionic, unidentate, bidentate or bridging acetato-groups from the separation of the asymmetric and symmetric (COO) stretching modes. Thus [14], Δ(COO) will be greater for the monodentate group than for the free ion, whereas for the bidentate group Δ(COO) is generally less than for the free ion. For a bridging group, the value of Δ(COO) is comparable to that for the free ion. On the reasonable assumption that these arguments may be transferred to the present system,

TABLE 1. Analytical[a] and Physical Data for New Complexes of the 2-(4-Ethoxyphenyltelluro)benzoate Ligand

Compound	C(%)	H(%)	μ_{eff} (BM)	^{57}Fe Mössbauer		
				Λ_M (ohm^{-1} cm^2 mol^{-1})	δ* (mm s^{-1})	Δ* (mm s^{-1})
1 $C_{15}H_{13}NaO_3Te{\cdot}3H_2O$	40.1 (40.4)	4.50 (4.29)				
2 $(C_{15}H_{13}O_3Te)Tl$	31.2 (31.4)	2.30 (2.28)		15 DMSO		
3 $(C_{15}H_{13}O_3Te)Ag{\cdot}H_2O$	36.5 (36.4)	2.85 (3.05)		3.5 DMSO		
4 $(C_{15}H_{13}O_3Te)_2Co{\cdot}2H_2O$	43.3 (43.3)	3.30 (3.63)	5.52	2.2 acetone		
5 $(C_{15}H_{13}O_3Te)_2Ni{\cdot}H_2O$	44.2 (44.2)	3.30 (3.47)	2.83			
6 $(C_{15}H_{13}O_3Te)_2Cu{\cdot}H_2O$	44.1 (44.0)	3.50 (3.44)	1.55			
7 $(C_{15}H_{13}O_3Te)_3Cr{\cdot}H_2O$	45.8 (45.9)	3.20 (3.51)	2.48			
8 $(C_{15}H_{13}O_3Te)_3Fe{\cdot}H_2O$	45.9 (45.8)	3.40 (3.50)	2.80	7.6 DMF	0.37 +0.03	0.61 +0.05

[a] Calculated values are given in parentheses.

TABLE 2. Infrared and UV–Vis Spectroscopic Data on New Complexes

Compound number	Infrared data (cm^{-1})			UV–Vis spectra (nm) (l mol^{-1} cm^{-1})
	ν_{as}(COO)	ν_s(COO)	Δ	
1	1660s	1270s	390	
1 (Na salt)	1572s	1395s	177	
2	1512s	1318s	132	
3	1532s	1388 1375	~150	
4	<1600	1395		624(94), 589(110), 540(89), 354 (13200), 324(10000)
5	1650s			750(6), 679(6), 324(7600)
	1525sh	1390s	135	
6	1590s	1395s	195	764(58), 347(5000), 320(8250)
7	1658s	1263s	395	800(26), 575(61)
	1525sh	1410s	115	357(14000), 324(6000)[a]
8	1660s	1265s	395	480(770), 354(14000)
	1515s	1410s	105	315(10000)[a]

[a] Partially obscrured.

it is noted that Δ(COO) for the free acid is 390 cm^{-1} and for the sodium salt 177 cm^{-1} (Table 2). Hence the presence of bidentate carboxylate groups is indicated for compounds **2**, **3**, **4**, **5**, **7** and **8** (Table 1). The data for the Cu(II) complex (**6**) suggest a bridging carboxylate group to be present. For compounds **7** and **8** there is clear evidence that some free acid is present, thus the formulations must be revised to [M(ETB)$_2$(ETBH)(OH)] (M = Cr, Fe). (ETBH is 2-(4-ethoxyphenyltelluro)benzoic acid.)

Thallium and Silver Complexes

The thallium complex is partially ionised in DMSO, but the silver compound is essentially a non-electrolyte in this solvent (Table 1). If the carboxylate group is bidentate, steric requirements of the ligand would dictate that either the tellurium atom is not involved in coordination, or it engages in some intermolecular interaction with a neighbouring metal atom. Attempts to verify this for the thallium complex via a single crystal X-ray study were frustrated by the failure of the data to refine [15]. 2-Mercaptobenzoic acid is said to coordinate to thallium via both carboxylate and sulfur [16] and the crystal structure of D,L-cysteinatothallium(I) shows the complex to be dimeric and that the metal atom is bonded to two O and two S atoms [17]. Thus precedent within the literature would favour a Tl–Te interaction. In the case of silver(I), a study of the formation constants of complexes with bis(3-carboxylpropanyl)chalcogenides [12] indicated stronger complexes with the Te ligand, again supporting the view that coordination of the tellurium atom in the present silver complex is likely: but the data do not justify further speculation.

Cobalt and Nickel Complexes

The violet cobalt(II) complex is hygroscopic, turning pink when left in moist air thus care was taken during spectroscopic and magnetic measurements. The infrared data are consistent with the presence of bidentate carboxylate groups and both the magnetic data and the visible spectra suggest a six-coordinate environment for the cobalt(II). It is probable that the environment is distorted octahedral (see visible spectra, Table 2) arising from the small 'bite' of the two carboxylate ligands; the remaining coordination positions are then taken by water molecules. The implied monomeric structure is consistent with the non-electrolyte behaviour in acetone (Table 1). The data available do not require the postulate of Co–Te interactions for their interpretation and this is in contrast to the nickel(II) data. Thus the infrared spectra suggest that there are two types of carboxylate in the nickel(II) complex, one monodentate ($\nu_{as} > 1600$ cm^3) and one bidentate ($\nu_{as} < 1600$ cm^3). The visible spectrum is consistent with an octahedral environment, albeit distorted, and the magnetic moment (Table 1), with virtually no orbital contribution supports this view. Thus the simplest model for the structure of the complex is that one EAB$^-$ ligand is bidentate via the carboxylate group and that the other is bidentate via a carboxylate oxygen and tellurium. A water molecule can enter the primary coordination sphere but the stoicheiometry implies that there must be further association in the solid, probably involving the second oxygen of the monomeric carboxylate, or alternatively the uncoordinated tellurium atom of the bidentate carboxylate. It is interesting to note that the study of bis(3-carboxypropanyl)chalcogenides [12] revealed for nickel(II) an order of stability: Te > Se < S > O.

Copper Complex

The infrared data suggest the carboxylate group to be bridging copper ions and this is a common phenomenon in copper carboxylate chemistry, thus in addition to the classical copper(II) acetate monohydrate [18], copper(II) benzoate also contains bridging carboxylate groups [19]. The presence of bridging carboxylate groups is usually accompanied by the observation of a magnetic moment which is below the spin only value (copper(II) benzoate is an exception with μ_{eff} = 1.87 BM [20], despite a Cu–Cu distance of 3.15 Å [19]). In this case the observed moment is 1.55 BM, implying antiferromagnetic coupling between copper ions in a non-monomeric structure. The visible spectrum of the complex (Table 2) consists of a broad band at 764 nm which would be consistent with a tetragonal microenvironment for the copper(II) ions. A well resolved room temperature ESR powder spectrum was obtained with $g_{\parallel} = 2.254$ and $g_{\perp} = 2.069$ which is consistent with local tetragonal symmetry. Calculation of $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ gives a value of 3.68. This, being <4, implies that there is exchange coupling present [21], a result which is consistent with the bulk magnetic measurement. The implied structure is therefore one in which the carboxylate groups bridge copper(II) in a symmetrical fashion, the local tetragonal environment is then completed with a water molecule and by bridging to a carboxylate oxygen from another polymeric layer. There is no compelling need to invoke the coordination of tellurium.

Chromium and Iron Complexes

The elemental analyses can be fitted to a variety of stoicheiometries, but the infrared data clearly indicate the presence of the acid ETBH as well as of ETB$^-$. It is likely that these complexes are isostructural. Both complexes show a new medium intensity band at close to 520 cm^{-1} which has been assigned to a Cr(OH)Cr grouping [22] in other chromium(III) complexes. Both complexes show magnetic moments (Table 1) which are well below the spin only values for three (Cr) or five (Fe) unpaired electrons. This antiferromagnetism could certainly arise through hydroxo-bridges. Indeed, at 2.80 BM, the value for the iron complex could almost be consistent with low spin iron(III). However the Mössbauer data (Table 1) confirm that the individual iron atoms are high spin and that, consequently, they must be antiferromagnetically coupled. The visible spectrum for the chromium complex is consistent with a distorted six-coordinate local environment; that of the iron(III) complex seems dominated by charge transfer bands. Thus the conclusion is reached that these complexes are to be formulated $[(ETBH)(ETB)_2M(OH)_2M(ETB)_2(ETBH)]$ (M = Cr, Fe). The precise role (if any) played by ETBH in determining the primary coordination shell cannot be extracted from the limited data; however it does not seem necessary to invoke a role for the tellurium atom.

Of the first row transition metals considered, only in the case of nickel(II) was any evidence obtained for the coordination of tellurium, thus providing further confirmation that tellurium has a poor affinity for hard Lewis acids.

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