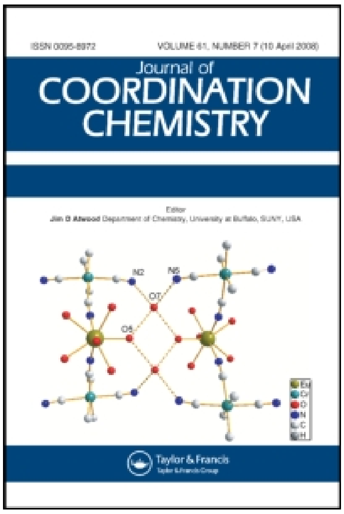

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COMPLEXES OF DI- AND TERVALENT COBALT, MONO- AND DIVALENT COPPER WITH 2-(2-ARYLTELLUROETHYL) PYRIDINES: SYNTHESIS AND SPECTRA

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Complexes of 2-(2-phenyltelluroethyl)pyridine (L^1) and 2-{2-(4-methoxyphenyl}telluro) ethylpyridine (L^2) with Co(II and III) and Cu(I and II) having compositions [$Co(L)Br_2$] (**1**, **2**), [$Co(L)_2$]BPh_4 (**3**, **4**), [$Cu(L)Br]_2$ (**5**) and [$Cu(L)_2Br]_2(BPh_4)_2$ (**6**) have been synthesized and characterized by molecular weight, molar conductance, ESR, IR, ^{1}H and ^{125}Te{^{1}H} NMR and electronic spectra in conjunction with magnetic susceptibility measurements and ESCA (in case of Cu (II)). The species **6** is diamagnetic and ESR silent because the odd electron of each copper is paired as two basal coordination planes are coplanar. The μ_{eff} values of **1** and **2** (3.5–3.7 BM) indicate the existence of the equilibrium

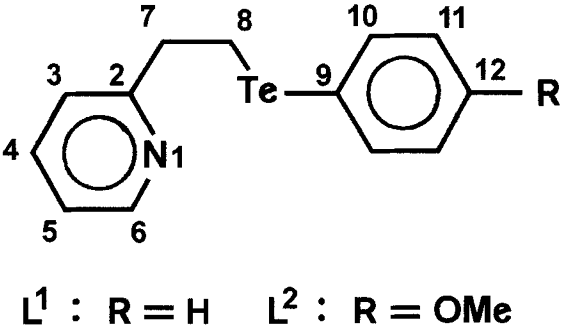
$$2[Co(L)Br_2 \rightleftharpoons [Co(L)_2][CoBr_4]$$

which is supported by molecular weight and Λ_M values. The ν(Cu—Br) stretch at 181 cm^{-1} in the IR spectrum of **5** indicates that it is a bromine bridged dimer. The ^{125}Te{^{1}H} NMR signal of L^2 undergoes an upfield shift (141 ppm) on coordination with Cu(I). Deshielding of up to 1 ppm of the CH_2Te signal in ^{1}H NMR spectra of **3** to **6** indicates that L^1/L^2 coordinates with Cu/Co *via* tellurium, a fact which is supported by the deshielding of the ^{125}Te NMR signal (167–200 ppm) on formation of **4** and **6**. The pyridine proton *ortho* to nitrogen also undergoes significant deshielding (0.5 ppm) on formation of **5**. Cu(I) species appear to be tetrahedral and Cu(II) ones square planar. Co(II) and Co(III) complexes seem to have octahedral geometry with two bromine atoms in **3** and **4** *trans* to each other.

Keywords: cobalt; copper; tellurium; 2-(2-aryltelluroethyl)pyridine; synthesis

INTRODUCTION

Tellurium ligands behave as soft donors[1–3] and therefore their complexes with copper(II) and cobalt(III) reported so far are scanty.[4–6] By using hybrid telluroether ligands, such complexes may be synthesized with support of hard-metal donor bonds.



Recently, several hybrid telluroether ligands have been designed.[2-3, 7-9] Of these, those containing the pyridyl group are worth exploring for this purpose, in view of ligational properties of the nitrogen atom of the pyridine ring. In the present paper, the synthesis of copper (I and II) and cobalt(II and III) complexes of 2-(2-aryltelluroethyl)pyridine (L^1 and L^2) and their characteristics are reported.

EXPERIMENTAL

Published methods[7] were used to synthesize the 2-(2-aryltelluroethyl)pyridines, L^1 and L^2. Magnetic susceptibility measurements at room temperature (25°C) were carried out on a CAHN 2000 magnetic balance using $Hg[Co(SCN)_4]$ as calibration standard. ESR spectra were recorded on a JEOL-JES-3XG ESR spectrometer using 10 mW X-band microwave radiation (ν 9.03 GHz). The photoelectron spectrum was recorded using a PHI-ESCA (model 1800), equipped with a dual anode (Al/Mg) X-ray source and double pass cylindrical analyzer. An X-ray beam of nearly 6 mm^2 was used for obtaining spectra at room temperature with a base pressure of 2×10^{-9} torr. IR spectra in the range 200–4000 cm^{-1} were recorded on a Nicolet 5 DX FT-IR spectrophotometer in KBr/CsI pellets and far-lR spectra in the range 700-30cm^{-1} were recorded in polyethylene on a Perkin Elmer 1700X FT-IR instrument. Electronic spectra were recorded in chloroform on a Hitachi 330 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ on a JEOL FX100 FT spectrometer at 99.5 Hz. ^{125}Te NMR spectra were recorded in $CHCl_3$ at 126 MHz on a Bruker AMX 400 FT spectrometer using $(CH_3)_2Te$ as external standard. Conductance measurements were made on *Ca* 1 mM solutions in CH_3CN using a Metrohm 660 conductometer. A Knauer vapour pressure osmometer was used to determine molecular weights in $CHCl_3$/ CH_3CN. Elemental analyses were performed on a Perkin Elmer 240C instrument.

Anhydrous CuBr and $CoBr_2$ were prepared by the literature method.[10a] To estimate halogen the complex was fused with Na_2CO_3 and its halogen content was titrimetrically determined by Volhard's method.[10b] Tellurium was also estimated titrimetrically.[10c] The metal content of the complexes was estimated by atomic absorption. The melting points determined in open capillary are reported as such.

$[Co(L)Br_2]$ (1–2)

Anhydrous cobalt(II) bromide (0.5 g, 2.3 mmol) was dissolved in 7 cm^3 of nitromethane under an oxygen-free nitrogen atmosphere. L^1 or L^2 (2.3 mmol) dissolved in nitromethane (5 cm^3) was added to it and the resulting mixture stirred for 1 h. The dark green solution was filtered through celite and evaporated to dryness under reduced pressure. The residue was redissolved in chloroform, filtered through celite and evaporated to dryness. The green residue was stored under dry condition.

$[Co(L^1)Br_2]$ (**1**) : Yield 78%, M.P. 82°C (d). Analyses: found (calc.): C, 30.14 (31.53); H, 2.31(2.45); N, 2.51(2.57); Br, 28.89(28.59); Te, 21.30(22.80); Co, 10.98 (10.05)%; IR (cm^{-1}): 480 (ν(Te—C(alkyl)). 426 (δ(C—N)), 318 (ν(Co—Te)), 250 (ν(Co—N(py)), 245 (ν(Co—Br)).

$[Co(L^2)Br_2]$ (**2**): Yield: 71%, M.P. 86°C (d). Analyses: found (calc.): C, 30.53 (30.02); H, 2.93 (2.68); N, 2.70 (2.68); Br, 28.89 (28.59); Te, 22.30 (22.80); Co, 10.01 (10.54)%; IR (cm^{-1}): 481 (ν(Te—C (alkyl))), 427 (δ(C—N)), 316(ν(Co—Te)), 250 (ν(Co—(py)), 240 (ν(Co—Br)).

$[Co(L)_2Br_2]BPh_4$ (3–4)

Anhydrous cobalt(II) bromide (0.22 g, 1 mmol), L^1/L^2 (1 mmol) and sodium tetraphenylborate (1 mmol) were added to nitromethane (50 cm^3) in succession under an oxygen-free nitrogen atmosphere and the mixture was stirred for 30 min. The nitrogen inlet was replaced with a calcium chloride tube to allow access of dry air into the mixture, which was stirred overnight. Thereafter the colour of the reaction mixture changed to brown. It was filtered through celite and the solvent was removed under reduced pressure. The residue was dissolved in chloroform (10 cm^3) and the complex was precipitated with hexane (3–4 cm^3). The brown precipitate was filtered washed with hexane and dried *in vacuo*.

$[Co(L^1)_2Br_2]BPh_4$ (**3**): Yield, 75%; M.P. 132°C. Analyses: found (calc.): C, 50.91 (50.32); H, 3.68 (3.86); N, 2.30 (2.35); Br 12.87 (13.42); Te, 20.83 (21.41); Co, 4.56 (4.95); NMR (^1H, $CDCl_3$, 25°C) : δ, 3.20–3.60(t, 2H, H_7): 4.01–4.20(t, 2H, H_8), 6.81–8.18 (m, 8H ArH + pyH), 8.59 (d, 1H, H6); 1R (cm^{-1}): 460 (ν(Te—C(alkyll))), 415 (δ(C—N)), 350 (ν(Co—Te)), 250 (ν(Co—N (py)), 213 (ν(Co—Br)).

$[Co(L^2)_2Br_2]BPh_4$ (**4**): Yield 71%, M.P. 132°C (d). Analyses: found (calc.): C, 51.14 (51.18); H, 3.94 (4.10); 2.23 (2.29); Br, 12.89 (13.70); Te, 19.91 (20.87); Co, 4.66 (4.82) %; NMR (^1H, $CDCl_3$, 25°C): δ 2.90–3.70(m, 7H, H_7 + H_8 + OCH_3), 6.73–8.17 (m, 8H, ArH + pyH); 8.57 (d, 1H, H_6); ^{125}Te {^{1}H}, $CHCl_3$, 25°C) δ : 680 (L^2 : δ, 480); IR (cm^{-1}): 461 (ν(Te—C (alkyl))), 417 (ν(C—N)), 348 (ν(Co—Te)), 249 (ν(Co—(py))), 212 (ν(Co—Br)).

$[Cu(L^2)Br]_2$ (5)

Anhydrous cuprous bromide (0.144 g, 1 mmol) and L^2 (0.34 g 1 mmol) were taken up in nitromethane (10 cm^3) and the mixture stirred for 30 min under an oxygen-free nitrogen atmosphere. It was filtered through celite and solvent removed under reduced pressure. The residue was dissolved in 10 cm^3 of chloroform and hexane (3–4 cm^3) was added. The precipitate was filtered washed with hexane, dried *in vacuo* and stored in a strictly oxygen and moisture-free atmosphere. Yield 85%, M.P. 64°C (d). Analyses: found (calc.) : C, 34.19 (34.09); H, 2.92 (3.09); N, 3.10 (2.99); Br 16.40 (17.09); Te, 25.98 (26.36); Co, 12.86 (13.12) %; NMR (^{1}H, $CDCl_3$, 25°C); δ: 3.00–3.50 (t, 2H, H_7); 3.85–4.05 (t, 2H, H8 + OMe); 6.71–8.25 (m, 8 H, ArH + pyH); 9.35 (d, 1H, H_6); (^{125}Te{^{1}H}, $CHCl_3$, 25°C): δ 340; IR (cm^{-1}): 481 (ν(Te—C(alkyl))), 424 (δ(C—N)), 400/340 (ν(Cu—Te)), 273 (ν(Cu—(py))), 171 (ν(Cu—Br).

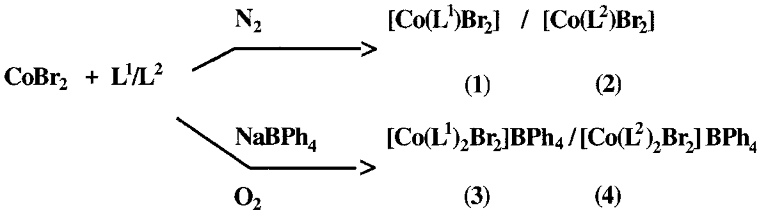
$[Cu(L^2)_2Br]_2(BPh_4)_2$ (6)

Anhydrous cuprous bromide (0.144 g, 1 mmol), L^2 (0.68 g, 2 mmol) and $NaBPh_4$ (1.0 mmol) were mixed in nitromethane (50 cm^3) under oxygen-free nitrogen and stirred for 30 min. The nitrogen inlet was replaced with a $CaCl_2$ tube to allow access of dry air and the mixture was further stirred over night or until its colour changed from pale yellow to brownish red. The solution was then concentrated *in vacuo*. The resulting precipitate was filtered, washed with hexane and extracted into chloroform. The solid complex was recovered after removing $CHCl_3$ under reduced pressure and dried *in vacuo*.

Yield, 70%, M.P. 110°C (d). Analysis: found (calc.) C, 55.03 (55.30); H, 4.03 (4.30); N, 2.39 (2.39); Br, 7.11 (6.96); Te 21.58 (22.58); Cu 4.91 (5.53) %: NMR (^{1}H, $CDCl_3$, 25°C): δ, 2.17–4.15(m 7H, H_7 + H_8 + OCH_3); 6.63–7.93 (m, 7H, ArH + pyH) 8.52(d, 1H, H_6); (^{125}Te{^{1}H}, $CDCl_3$, 25°C): δ 648; IR (cm^{-1}): 462 (ν(Te—C (alkyl))), 407 (δ(C—N)), 350 (ν(Cu—Te)), 270(ν(Cu—(py))), 181 (ν(Co—Br)).

RESULTS AND DISCUSSION

The following reactions in nitromethane have resulted in complexes of Cu(I/II) and Co(II/III) with L^1/L^2 = L.



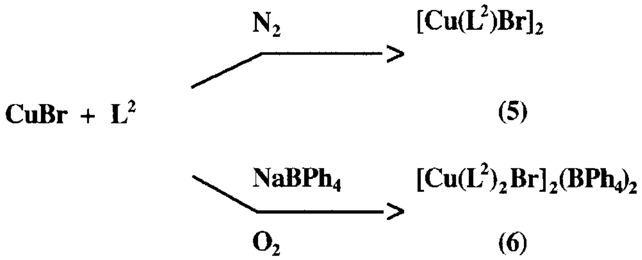
$$\mathrm{CoBr_2} + \mathrm{L^1/L^2} \xrightarrow{\mathrm{N_2}} [\mathrm{Co(L^1)Br_2}] \; / \; [\mathrm{Co(L^2)Br_2}]$$

(1) (2)

$$\mathrm{CoBr_2} + \mathrm{L^1/L^2} \xrightarrow[\mathrm{O_2}]{\mathrm{NaBPh_4}} [\mathrm{Co(L^1)_2Br_2}]\mathrm{BPh_4} \; / \; [\mathrm{Co(L^2)_2Br_2}]\mathrm{BPh_4}$$

(3) (4)

(*1*)



$$\mathrm{CuBr} + \mathrm{L^2} \xrightarrow{\mathrm{N_2}} [\mathrm{Cu(L^2)Br}]_2$$

(5)

$$\mathrm{CuBr} + \mathrm{L^2} \xrightarrow[\mathrm{O_2}]{\mathrm{NaBPh_4}} [\mathrm{Cu(L^2)_2Br}]_2(\mathrm{BPh_4})_2$$

(6)

(*2*)

The analogous chloro derivatives of these complexes readily decompose because in the presence of chloride the 'hard' nature of the metal increases and this in turn makes the metal-tellurium bond too weak. Complexes of Cu(I) and Co(II) have been found to be less stable than those of Cu(II) and Co(III). The Cu(I) complex becomes green on exposure to air due to aerial oxidation whereas the Co(II) complex becomes insoluble in common organic solvents within 2–3 days, probably due to polymerization.

A sample of **5**, fresh and preserved in a nitrogen atmosphere exhibits diamagnetic behaviour. The compound **6** has also been found to be diamagnetic and ESR silent in the solid state as well as in chloroform solution. The binding energy value of **6** determined by ESCA, is –933.6 eV which is characteristic of a $\mathrm{Cu^{2+}}$ ion.[11] The diamagnetic behaviour of the complex suggests that two copper basal coordination planes are coplanar and this results in pairing of odd electrons in the dx^2-y^2 orbital of each copper atom. The green coloured species **1** and **2** are paramagnetic with μeff = 3.5–3.7BM. It appears that these complexes adopt the formulation $[\mathrm{Co(L)_2}]$ $[\mathrm{CoBr_4}]$.[14–16] On subtracting magnetic moment values for $[\mathrm{CoBr_4}]^{2-}$ (4.69 BM) from the observed μeff value of **1** and **2**, the μeff of $[\mathrm{Co(L)_2}]^{2+}$ (2.7 BM) is consistent with the planer Co (II) ion.[17] Both complexes **1** and **2** are ESR silent at room and liquid nitrogen temperatures. The species **3** and **4** are diamagnetic and ESR silent in solid/solution. The molecular weight of **5** was found to be 1810, nearly double the calculated value 968. This suggests its non-ionic and dimeric nature, which is consistent with Λ_M, 60 ohm^{-1} cm^2 mol^{-1} in $\mathrm{CH_3CN}$. The molecular weight of **6** has been found to be 401 (calc. value 1149) which is consistent with the formulation given in equation (*2*) and supported by its Λ_M value of 270 ohm^{-1} cm^2 mol^{-1}

(in CH_3CN). The molecular weight of **1/2** has been found to be 630/705 which is between monomeric and dimeric formulations and indicates the existence of following equilibrium in solution.

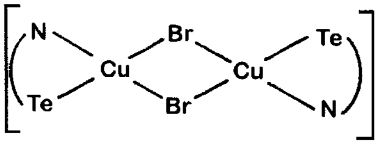
$$2[Co(L)Br_2] \rightleftharpoons [Co(L)_2][CoBr_4]$$

Molar conductances of **1** and **2** are 105 and 110 ohm^{-1} cm^2 mol^{-1}, respectively, which are lower than those expected for divalent electrolytes [20] and consistent with the above equilibrium. Λ_M values of **3** and **4** are 170 and 175 ohm^{-1} cm^2 mol^{-1}, respectively. Their molecular weights have been found to be 603 and 675, respectively (calc. 1191 and 1224). Both observations concur with 1:1 electrolyte formulation adopted in equation (*1*) for **3** and **4**.

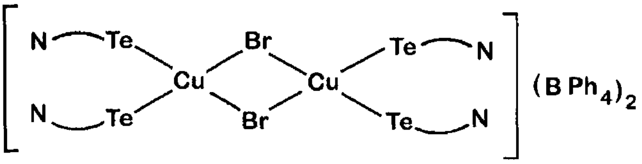
In the IR spectrum of **5** δ(C-N) appears at higher frequency (15 cm^{-1}) in comparison to that of L^2. The ν(Te—C (alkyl)) mode does not exhibit any shift. New bands at 273 and 340/400 cm^{-1} may be assigned to ν(Cu-(pyridine)) and ν(Cu—Te) vibrations, respectively. The appearance of ν(Cu—Br) at 181 cm^{-1} indicates that **5** most probably is a bromine bridged dimer. The electronic spectrum of **5** has bands at 25, 38 and 40 kK. The first may be taken as evidence for a binuclear system involving cuprous ions,[21] each of which has tetrahedral geometry. The other two arise from intraligand transitions. In the ^1H NMR spectrum of **5** H_6 appears down field (0.85 ppm) with respect to L^2 (^1H NMR : δ 3.2 (m, 4H, $H_7 + H_8$), 3.75 (s, 3H, OMe) 6.70–7.70 (m, 7H, ArH + pyH), 8.5 (d, 1H, H_6)). Similarly, deshielding of 0.7 ppm has been observed for the CH_2Te signal in comparison to free ligand. This in conjunction with IR data suggests that in **5**, L^2 coordinates through pyridine nitrogen and tellurium atoms. As crystals of **5** suitable for X-ray diffraction could not be grown, the following structure for **5** seems to be most plausible.

In ^{125}Te NMR spectrum of **5** the signal is shielded (141 ppm) with respect to L^2 (481 ppm). For a d^{10} system, such an observation has been reported earlier. [6]

Comparison of the IR spectrum of **6** with that of L^2 does not give much information about structure. The band at 181 cm^{-1} observed in this spectrum may be assigned to bridging ν(Cu-Br). [22] The electronic spectrum of **6** exhibits bands at 14.3, 27, 38 and 40 kK, the first two of which are characteristic of a binuclear system with square planar Cu(II) ions. In ^1H NMR spectrum of **6**, the H_6 signal of pyridine does not undergo any significant shift with respect to that of $L.^2$ H_7 and



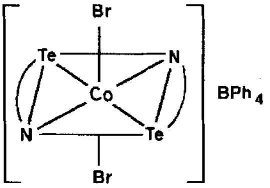
5



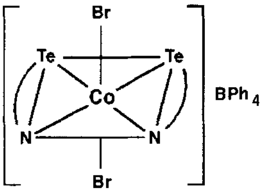
6

H_8 signals exhibit 1 ppm deshielding with respect to free ligand, which indicates coordination through tellurium. The downfield shift (168 ppm) observed in the ^{125}Te {^{1}H} NMR spectrum of **6** with respect to L^2 supports this conclusion. Thus the following structure may be proposed for **6**. Attempts to grow crystals did not succeed. The two copper atoms interact, resulting in pairing of electron and thus its diamagnetic character.

The δ(C—N) band in IR spectra of **1** and **2** exhibits a blue shift (18 cm^{-1}) with respect to that of L^1/L^2. The shift in ν(Te—C(alkyl)) is not apparent but the new band appearing at 320 cm^{-1} may be due ν(Co—Te). A broad band at 245 cm^{-1} in the far-IR spectrum of **1**/**2** indicates the presence of the $[CuBr_4]^{2-}$ unit, supported by a band between 13–16 kK in the reflectance spectra.[24] In the IR spectra of **3** and **4**, δ(C—N) exhibits a small blue shift (≈7 cm^{-1}) relative to L^1/L^2 whereas ν(Te—C(alkyl)) undergoes a red shift (17 cm^{-1}) on complexation, with respect to the free ligands. The new band at 348/350 cm^{-1} in these spectra may be assigned to ν(Te—Co) whereas the presence of an unsplit band at 213 cm^{-1} is due to ν(Co—Br) and suggests that the two bromine atoms are *trans* to each other in the octahedral array of ligands around cobalt. [22] This is supported by bands at 23 and 16 kK observed in the electronic spectra (recorded in $CHCl_3$) due to $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions, respectively. In ^{1}H NMR spectra of **3** and **4**, H_7 and H_8 signals appear downfield (≈1 ppm) with respect to those of L^1/L^2 [^{1}H NMR of L^1 : δ, 3.2(m, 4H, $H_7 + H_8$) 7.00 – 7.60 (m, 8H, ArH + pyH) 8.56 (d, 1H, H_6)], thus indicating the formation of a Co—Te bond, which is supported by the ≈ 200 ppm downfield signal in the ^{125}Te{^{1}H} NMR spectrum of **4** with respect to the free ligand. Deshielding of H_6 on formation of the complex was small (0.05 ppm). However, the signals in the aliphatic region appear somewhat broad, probably due to interconversion of *trans* and *gauche* forms. The following two structures are possible for **3** and **4**.



trans



cis

Acknowledgments

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