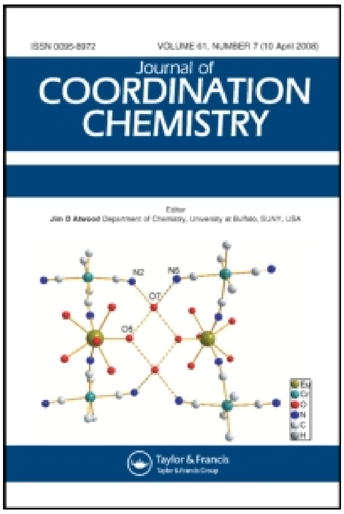


Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

BINDING OF 2-(2-ARYLTELLUROETHYL)PYRIDINES WITH Cu AND Co

Bishan L. Khandelwal[a]; Abu Khalid[a]; A. K. Singh[a]
[a] Department of Chemistry, Indian Institute of Technology, New Delhi, India

To cite this Article Khandelwal, Bishan L. , Khalid, Abu and Singh, A. K.(1995) 'BINDING OF 2-(2-ARYLTELLUROETHYL)PYRIDINES WITH Cu AND Co', Journal of Coordination Chemistry, 36: 3, 207 — 214

To link to this Article: DOI: 10.1080/00958979508022562

URL: http://dx.doi.org/10.1080/00958979508022562

J. Coord. Chem., 1995, Vol 36, pp. 207–214
Reprints available directly from the publisher
Photocopying permitted by license only

BINDING OF 2-(2-ARYLTELLUROETHYL) PYRIDINES WITH Cu AND Co

BISHAN L. KHANDELWAL,* ABU KHALID and A.K. SINGH

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

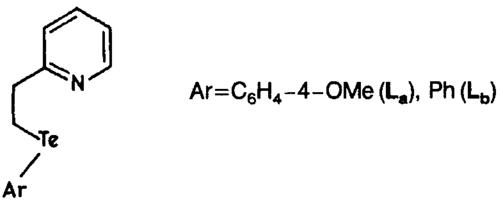
(Received March 28, 1995)

2-(2-Aryltelluroethyl)pyridine(L) complexes of copper(I) and cobalt(II), $[Cu(L)(\mu\text{-}Br)_2Cu(L)]$ and $[CoBr_2(L)]$, have been synthesized by reaction of the ligand with anhydrous metal bromides in nitromethane under a dinitrogen atmosphere. The same reaction in the presence of $NaBPh_4$, excess ligand and air led to the oxidation of metals and formation of the complexes $[Cu(L)(\mu\text{-}Br)_2Cu(L)](BPh_4)_2$ and $[CoBr_2(L)_2](BPh_4)$. All complexes have been characterized by elemental analyses, molecular weight and molar conductance measurements, magnetic moments and spectroscopy (IR, electronic, ^1H and ^{125}Te NMR).

KEYWORDS: tellurium ligands, bidentates, copper, cobalt

INTRODUCTION

Tellurium, being 'soft' in nature, has little ability to coordinate with relatively 'hard' 3d-transition metals in medium and high oxidation states. If a 'hard' donor atom in conjunction with tellurium is present in the chelating ligand, it may force interaction of tellurium with 'hard' metals. There are some reports in which the coordination chemistry of such ligands with 3d-transition metals has been described.[1–3] We have recently described the synthesis of 2-(2-aryltelluroethyl)pyridines(L) [where aryl = 4-methoxyphenyl (L_a) and phenyl (L_b)] and their palladium(II) and platinum(II) complexes.[4] This ligand, having 'hard' and 'soft' donor atoms, is exploited to coordinate with 'hard' as well as 'soft' metals.



Copper and cobalt in medium and high oxidation states behave as 'hard' acids and are worth exploring for this purpose. In this paper the ligation of (L) with Cu

---

* Author for correspondence.

(I and II) and Co (II and III) has been described. The synthesized complexes have been characterized by multinuclear (^{1}H, ^{128}Te{^{1}H}) NMR, IR, and electronic spectroscopic methods, magnetic moments and ESCA measurements.

EXPERIMENTAL

Published methods were used to synthesize 2-(2-aryltelluroethyl)pyridines.[4] Anhydrous Cu(1) and Co(II) bromides were prepared by standard methods.[5] IR spectra in the range 4000–200 cm^{-1} were recorded on a Nocolet 5DX FT spectrophotometer in KBr/CsI pellets and far IR spectra in the range 700–300 cm^{-1} were recorded in polyethylene on a Perkin Elmer 1700 X FT instrument. Electronic spectra of the complexes were obtained on a Hitachi 330 spectrophotometer. ^{1}H NMR spectra were obtained on a Jeol FX 100 FT instrument at 99.5 MHz and the ^{125}Te{^{1}H}NMR spectra on a Bruker AMX 400 FT spectrometer at 126 MHz using Me_2Te as external reference. Conductance measurements were made on 1 mM solutions in acetonitrile or nitromethane using a Metrohm 660 conductometer and molecular weights were determined in chloroform and acetonitrile using a Knauer vapour pressure osmometer. Elemental analyses were performed on a Perkin Elmer 240C analyser. Solvents were dried and distilled before use.

Synthesis of [Cu(L$_a$)Br]$_2$ (1) [Co(L$_a$)Br$_2$] (2) and [Co(L$_b$)Br$_2$] (3)

Anhydrous Cu(1) or Co(II) bromide (1 mmol) and the ligand $\mathbf{L_a}$ or $\mathbf{L_b}$ (1 mmol) were added in succession under an oxygen-free dinitrogen atmosphere to nitromethane (10 cm^3) and the mixture was stirred for 30 min. It was filtered through celite and concentrated under reduced pressure to obtain solid product. This was dissolved in chloroform, reprecipitated with hexane, filtered, dried in vacuum and stored under absolutely dry conditions.

Synthesis of [Cu(L$_a$)$_2$Br]$_2$(BPh$_4$)$_2$ (4), [Co(L$_a$)$_2$Br$_2$](BPh$_4$) (5) and [Co(L$_b$)$_2$Br$_2$](BPh$_4$) (6)

Anhydrous Cu(1) or Co(II) bromide (1 mmol), the ligand $\mathbf{L_a}$ or $\mathbf{L_b}$ (2 mmol) and sodium tetraphenylborate (0.65 g, 0.5 mmol) were added in succession under an oxygen-free dinitrogen atmosphere to nitromethane (50 cm^3) and the mixture stirred for 30 min. The nitrogen inlet was replaced with a calcium chloride guard tube to allow access of dry air and the mixture was stirred overnight during which the colour of the solution changed from pale yellow to brownish red. The solution was then concentrated *in vacuo* to obtain solid product, which, after washing with hexane, was extracted into chloroform. The chloroform extract was evaporated to drysness under vacuum.

RESULTS AND DISCUSSION

2-(2-Aryltelluroethyl)pyridines react with anhydrous copper(I) and cobalt(II) bromides in nitromethane under dinitrogen atmosphere to form complexes with 1:1 molar ratios. However, these reactions, when carried out in the presence of $NaBH_4$, excess ligand (L_a/L_b) and air, result in oxidation of metals and formation of complexes having a ligand to metal ratio of 2:1.

These ligands, when reacted with metal chlorides, form complexes which readily decompose, probably because chloride increases the hard nature of metal and the bonds formed between metal and tellurium ligand are too weak. Complexes of metals in medium oxidation states, *i.e.*, Cu(I) and Co(II) (**1-3**) are less stable as compared to those in which the metals are in higher oxidation states, *i.e*, Cu(II) and Co(III) (4–6). The Cu(I) complex (**1**) is rather unstable on exposure to air as is apparent from its colour change from off-white to greenish brown, probably due to slow air oxidation of the metal in the complex as evidenced by magnetic measurements (slight paramagnetism). This greenish brown material was found to be insoluble in common organic solvents. Freshly prepared Co(II) complexes (2 and 3) were found to be soluble in common organic solvents but after few days became insoluble (probably due to polymerization). The green colour of the complex solution slowly fades in few days with deposition of an off-white material which is insoluble in organic solvents. Stoichiometries of the complexes have been authenticated by elemental analyses (Table 1). The complex stoichiometries do not alter on changing the metal to ligand ratio during synthesis. Spectroscopic and other characteristics of the complexes are discussed below.

Cu(I) Complex [Cu(L_a)Br]$_2$ (1)

The molecular weight of complex **1** is found to be almost double the calculated value for its empirical formula [Cu(L_a)Br], a fact which suggested dimeric behaviour of the complex in solution. The molar conductance value (λ_m) in acetonitrile is found to be much lower than expected for a 1:1 electrolyte. In the IR spectrum of (**1**) (Table 2) the δ(C-N) vibration undergoes a shift to higher frequency (~15 cm) with respect to that of the free ligand, suggesting coordination of the pyridine ring nitrogen with the metal. This is also supported by the appearance of new band at 273 cm^{-1} assignable to ν(Cu-N).[6] Although there is no apparent shift in ν(Te-C) in the complex with respect to the free ligand, appearance of new bands at 340 and

Table 1 Analytical and physical data for the complexes

Complex	Analysis %: Found (calcd)							
	C	H	N	Br	Te	Cu/Co	λ_m in CH_3CN (ohm^{-1} cm^2 mol^{-1})	MW
1	34.19	2.92	3.10	16.10	25.28	12.36	60	905
	(34.09)	(3.09)	(2.99)	(17.09)	(26.36)	(13.12)		(968)
4	55.30	4.30	2.39	7.11	20.58	4.91	270	401
	(55.30)	(4.30)	(2.39)	(6.96)	(22.58)	(5.53)		(1149)
2	30.14	2.31	2.51	28.89	21.30	12.98	105	630
	(31.53)	(2.45)	(2.57)	(28.59)	(22.80)	(10.05)		(1087)
3	31.53	2.93	2.70	27.89	21.30	10.02	110	705
	(30.02)	(2.68)	(2.68)	(28.59)	(22.80)	(10.54)		(1119)
6	51.91	3.68	2.30	12.57	20.33	4.56	170	603
	(50.32)	(3.86)	(2.35)	(13.42)	(21.41)	(4.95)		(1191)
5	51.14	3.94	2.23	11.89	19.41	4.66	175	675
	(51.18)	(4.10)	(2.29)	(13.70)	(20.87)	(4.82)		(1224)

Table 2 Important IR bands (cm^{-1}) in the copper and cobalt complexes.

Complex	δ(C-N)	ν(Te-C) (aliphatic)	ν(Cu/Co-N)	ν(Cu/Co-Br)	ν(Te-Cu/Co)
1	424	481	273	171	340,400
2	426	480	250	245	318
3	427	481	250	240	316
4	407	462	-	181	250
5	417	461	249	212	248
6	415	460	250	213	250
L_a	409	479			
L_b	409	479			

400 cm^{-1} assignable to ν(Cu-Te) (Table 2) suggests coordination of Te with the metal atom. The appearance of one band in the far -IR spectrum of **1** at 171 cm^{-1} assignable to ν(Cu-Br) suggests that the dimer is bridged through bromine.

The electronic spectrum of **1** exhibits three bands at 25, 38 and 40 kK. The first may be due to binuclear Cu(1) ion. The remaining bands in the UV region are due to intra-ligand and or charge transfer transitions.

Chemical shifts observed in the ^1H NMR spectrum of **1** along with their assignments are given in Table 3. In the spectrum of the complex, the pyridine ring proton *ortho* to nitrogen (H_6) shifts downfield (0.85 ppm) with respect to the free ligand, indicating coordination of pyridine ring nitrogen with Cu(1). The downfield shift (0.5 ppm) of the CH_2Te signal with respect to the free ligand suggests coordination of tellurium with the metal. In the $^{125}Te\{^1H\}$ NMR spectrum (Table 3) of the complex an upfield shift of the tellurium signal (as compared with the free ligand) rather than a downfield shift, as usually observed when a ligand coordinates through tellurium, is observed. This suggests that π bonding is strong as compared to sigma bonding in the complex.

On the basis of the data, it can be proposed that the complex is the bromo-bridged dimer with psuedo-tetrahedral geometry around Cu(1), ion as shown below.

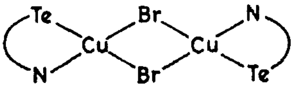
(Co(L_a)Br_2] (2) and [Co(L_b)Br_2] (3)

The green coloured Co(II) complexes (**2** and **3**) are paramagnetic with μ_{eff}~3.5–3.7 BM. Since the magnetic moment value of the tetrahedral cobaltate ion is ~4.7 BM,

Table 3 Chemical shifts (δ, ppm) in ^1H and $^{125}Te\{^1H\}$ NMR spectra of the copper and cobalt complexes in $CDCl_3$.

Complex	^1H				$^{125}Te\{^1H\}$
	H_6 (d)	Aryl and pyridyl protons (m)	H_7 & H_8 (m)	OCH_3	
1	9.35	6.71-8.25	3.10-3.90	*	340
4	8.52	6.63-7.93	2.17-4.15	*	648
5	8.57	6.73–8.17	2.90-3.70	*	
6	8.59	6.81-8.18	2.57-4.09		680
L_a	8.50	6.70-7.70	3.2	3.75	480
L_b	8.56	7.00-7.60	3.2		

Merged with H_7 and H_8 signal; d = doublet, m = multiplet.



the magnetic moments of the present Co(II) complexes **2** and **3** indicate that the assumption that these complexes adopt the $[Cu(L)_2][CoBr_4]$ formulation is logical.[8–10] On substracting the moment of $[CoBr_4]^{2-}$ (4.69 BM) from the observed magnetic moments of **2** and **3**, a μ_{eff} value of ~ 2.7 BM for $[Co(L)_2]^{2+}$ is obtained and which is consistent with the planar Co(II) ion.[12] Probably, the complex is present in the $[Co(L)_2]$ $[CoBr_4]$ form in the solid state due to favourable lattice energy factors. These complexes in solution are found to be ESR silent both at room and liquid nitrogen temperatures. This is most probably due to the dimeric nature of the complex in solution.[13,14] The presence of tetrabromocobaltate(II) ion in **2** and **3** is also supported by appearance of highly structured absorption band between 13–16 kK in the reflectance spectra of these complex.[15] The transition at 11 kK may be a d-d transition.

The presence of a broad band at 245 cm^{-1} in the far-IR of these complexes further supports the presence of tetrabromocobaltate(II) ion[11]. The δ(C-N) band in these complexes is shifted to higher frequency (by 18 cm^{-1}) with respect to the free ligand, again suggesting the coordination of pyridyne ring nitrogen with the metal. No apparent shift in ν(Te-C) is observed in these spectra but the presence of new band at 320 cm^{-1} may be due to ν(Co-Te) (Table 2).

The molecular weights of **2** and **3** were found to be higher than those calculated from their molecular formula but less than the dimeric formulations. This suggests that the complexes in solution are in equilibrium mixture of monomeric and dimeric forms. The molar conductance values (λ_m) in acetonitrile (~ 105 ohm^{-1} cm^2 mol^{-1}) of **2** and **3** are lower than expected for di-divalent electrolytes. This suggests that dissolution is accompanied by an isomeric conversion as shown below

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

and the equilibrium is shifted completely to the left in the solid.

^{1}H NMR spectra of these complexes were very broad and unresolved, as expected, due to their paramagnetic nature. Besides this, the instability of the complexes restricted exploration of their properties in the solid state as well as in the solution.

IR, molecular weight, conductance and magnetic moment data are insufficient to draw any firm conclusion on these complexes. It seems that complexes exist as $[Co(L)_2][CoBr_4]$ in the solid state but in solution they undergo conversion to other isomeric forms.

$[Cu(L_a)_2Br]_2(BPh_4)_2$(4)

The molecular weight determined for **4** in acetonitrile is found to be 1/3 of the value calculated on the basis of its dimeric structure. This is supported by its conductance value (λ_m = 270 ohm^{-1} cm^2 mol^{-1} in acetonitrile) which suggests it to be a 1:1 electrolyte.[17]

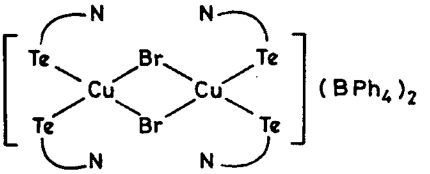
Complex (**4**) shows intriguing behaviour in that it is diamagnetic and thus ESR silent in the solid state as well as in chloroform solution. A binding energy determined by ESCA of −933.6 eV is characteristic of Cu^{2+} ion.[18] The diamagnetic behaviour of the complex suggests that the two copper basal planes are coplanar which results in complete pairing of unpaired electrons in the $d_{x^2-y^2}$ orbital of each copper atom,[19,20] at least in the solid state.

The electronic spectrum of **4** exhibits a broad band at 14.3 kK which may be assigned to d-d transitions. The other band at 27 kK seems to be a characteristic of a binucler copper(II) complex[16] whereas bands at 38 and 40 kK may be assigned to intraligand transitions.

In the IR spectrum of **4** (Table 2), no apparent shift δ(C-N) with respect to the free ligand is observed. This indicates that nitrogen is not involved in coordination, a suggestion supported by the absence of ν(Cu-N) in the IR spectrum of this complex. The presence of one band in the far-IR spectrum of the complex at 181 cm^{-1} assignable to ν(Cu-Br) vibration suggests that in the dimer the two metal centres are bridged through bromine.

In the ^1H NMR spectrum of **4**, the pyridine ring proton *ortho* to nitrogen (H_6) does not undergo any significant shift with respect to that of free ligand, again suggesting non-involvement of nitrogen in the coordination. The methylene protons (H_7 & H_8) experience significant deshielding effect (~1 ppm) when L_a ligates with Cu(II), indicating coordination of ligand through tellurium, which is also supported by a downfield shift of 168 ppm observed in the $^{125}Te\{^1H\}$ NMR spectrum of the complex with respect to the free ligand (L_a).

Based on molecular weight, conductance magnetic moment and ESCA data, it can be concluded that in the diamagnetic bromo-bridged dimeric complex **4** ligand L_a coordinates through tellurium alone and two metal centres have almost planar geometry as shown below.



There is also an interaction between two copper centres which pairs gives the diamagnetic properties observed experimentally.

[Co(L$_a$)$_2$Br$_2$](BPh$_4$) (*5*) *and* *[Co(L$_b$)$_2$Br$_2$](BPh$_4$)* (*6*)

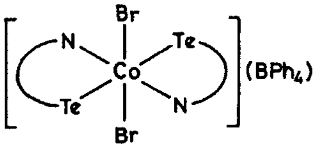
The Co(III) complexes **5** and **6** are diamagnetic, monomeric and behave as 1:1 electrolytes in the acetonitrile solution (λ_m = 170 ohm^{-1} cm^2 mol^{-1}).[17] This is also supported by their molecular weight measurements which are half the expected values.

The electronic spectra of both the complexes **5** and **6** exhibit bands around 16 and 23 kK. These probably originate from $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1T_{2g}$ transitions respectively.[16]

In the IR spectra of **5** and **6**, δ(C-N) undergoes a high frequency shift (~ 7 cm^{-1}) relative to the free ligand. This suggests coordination of the pyridine nitrogen with the metal in these complexes. This is supported by the appearance of a ν(Co-N) band at 250 cm^{-1}. The red shift (17 cm^{-1}) in ν(Te-C) in these complexes with respect to the free ligand, suggests that tellurium also coordinates with Co(III). This is also supported by the appearance of a new band at 248 cm^{-1}, which may be assigned to ν(Co-Te). The presence of one band at 213 cm^{-1} assignable to ν(Co-Br) in these complexes suggests that the two bromine atoms are *trans* to each other in the octahedral cobalt coordination sphere.

In the ^1H NMR spectra of **5** and **6**, the methylene protons (H_7 and H_8) undergo significant downfield shifts (1 ppm) with respect to those of the free ligand, thus also suggesting that the ligand coordinates through tellurium with Co(III). The signal in the $^{125}Te\{^1H\}$ NMR spectrum of **5** shows a downfield shift (200 ppm) with respect to the free ligand. This further supports the coordination of the ligand through tellurium. Rather insignificant deshielding of the pyridine ring proton (H_6) in the complexes with respect to that of the free ligand does not unambiguously prove coordination of pyridine ring nitrogen to the metal. However, broad signals in the aliphatic region of the ^1H NMR spectra of **5** and **6** are observed. This may arise from the fact that the chelate ring formed by the coordination of both nitrogen and tellurium with the metal to give interconverting *trans* and *gauche* conformations in solution which would impart broadening in the ^1H NMR.

On the basis of electronic, IR, NMR and conductance data it is proposed that the octahedral complexes **5** and **6** have the structure shown below:



Acknowledgement

The authors thank DST and UGC (India) for financial support and IISc, Bangalore for providing facilities for recording ^{125}Te NMR spectra on the Bruker AMX 400 NMR National Facility.

References

1. J.L. Brown, T. Kemmitt and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1513 (1990).
2. N.I. Al-Salim, A.A. West, W.R. McWhinnie and T.A. Hamor, *J. Chem. Soc., Dalton Trans.*, 2363 (1987).
3. B.L. Khandelwal and K. Uppal, *Indian J. Chem.*, **32A**, 39 (1993).
4. A. Khalid, B.L. Khandelwal, A.K. Singh, B. Padmanabham and T.P. Singh, *J. Coord. Chem.*, **31**, 19 (1994).
5. G. Brauer, *Hand Book of Preparative Inorganic Chemistry*, Vol 2, (Academic Press, New York, 1965).
6. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., (John Wiley and Sons, New York, 1986).
7. D. Adams, *Metal-Ligand and Related Vibrations*, (E. Arnold Ltd., London, 1967), p. 57.
8. W. Levason and C.A. McAuliffe, *Inorg. Chim. Acta*, **14**, 127 (1975).
9. L. Sindellari, B. Zarli, S. Sitran and E. Celon, *Inorg. Chim. Acta*, **64**, L79 (1982).
10. W. Levason, C.A. McAuliffe and S.G. Murray, *Inorg. Chim. Acta*, **24**, 63 (1977).

11. J.H. Canterford and R. Colton, *Halides of First Row Transition Metals,* (Wiley, 1969), Chap. 17 and references therein.
12. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.,* **12** (1954).
13. M. Abkowitz and A.R. Monahan, *J. Chem. Phys.,* **58**, 2281 (1973).
14. E.R. Milaeva, Z. Szeverenyi and L.I. Simandi, *Inorg. Chim. Acta,* **167**, 139 1990),
15. F.A. Cotton, M.F. Goodgame and M. Goodgame, *J. Am. Chem. Soc.,* **83**, 4690 (1961).
16. A.B.P. Lever, *Inorganic Electronic Spectroscopy,* (Elsevier, Amsterdam, 1984).
17. W.J. Geary, *Coord. Chem. Rev.,* **7**, 81 (1971).
18. H. Windawi and F.F.L. Ho, *Applied Electronic Spectroscopy for Chemical Analysis,* Eds., P.J. Elving, J.D. Windefordner and I.M. Kolthoff, (Wiley-Interscience, New York, 1982).
19. A. Bencini and Midollini, *Coord. Chem. Rev.,* **120,** 87 (1992).
20. O. Kahn, *Inorg. Chim. Acta,* **62**, 3 (1982).