



Nephelauxatic Effect of Telluro Ether Complexes of Co(II), Ni(II) and Cu(II)

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(Received: 9 October 2010;

Accepted: 15 June 2011)

AJC-10044

Chalcogens are known to be good ligands. Telluroethers of molecular formula 1-(N-Me)-2-(TeC₆H₄-4'-R)-4-MeC₆H₃. (where R=H, -OCH₃ and -OC₂H₅) were prepared and they were used for complexation with Co(II), Ni(II) and Cu(II) metal ions. On the basis of IR and NMR, the ligands were found to coordinate through nitrogen and tellurium of the ligands. The 10 Dq values of Co(II) complexes were found in the range of 9,774 to 10,388 cm⁻¹, while for Ni(II) complexes the values were in the range of 9,220 to 9,290 cm⁻¹. Cu(II) complexes show 10 Dq values in the range of 14,200 to 14,700 cm⁻¹. In Co(II) complexes nephelauxatic effect, β₃₅, was the lowest (3 %) for ligand having R=H and for R= -OCH₃ and -OC₂H₅, it was very close to each other, *i.e.*, 5.35 for -OCH₃ & 4.91 for -OC₂H₅. However in Ni(II) complexes, β₃₅ was almost same for R=H & -OC₂H₅ while it was lowest for R= -OCH₃.

Key Words: Nephelauxatic effect, Racah parameter.

INTRODUCTION

The coordination chemistry of chalcogens is mainly dominated by sulphur ligands¹⁻⁶. Tellurium is the noblest metalloid has little been explored as ligand, though it is capable of acting as a Lewis acid as well as a Lewis base. Two reviews by Gysling^{7,8} followed by Singh and Shrivastava⁹ and then by Singh and Sharma¹⁰ made the ligand chemistry of tellurium popular and a versatile field for inorganic chemists. The use of tellurium compounds and organotellurium compounds as single source precursors for several semiconductors has immense interest in the ligand chemistry of tellurium. In order to focus and promote the interest in the tellurium ligand chemistry the present paper reports the synthesis of some complexes of Co(II), Ni(II) and Cu(II) with telluroether ligands of the type 1-(N-Me)-2-(TeC₆H₄-4'-R)-4-MeC₆H₃ (L₁-R=H, L₂-R= -OCH₃ and L₃-R= -OC₂H₅). This is really the extension of our work on tellurium chemistry reported earlier¹¹.

EXPERIMENTAL

All the chemicals used were of Analytical R grade. The ligand 1, 2 and 3 were prepared by the methods reported earlier¹¹. At first 1-(N-Me)-2-(Cl₂TeC₆H₄-4'-R)-4-MeC₆H₃ was prepared by refluxing 3.2 mmol (17.4 g) of *ortho* mercurated N,N-dimethyl-*p*-toluidine with equimolar amounts of phenyl tellurium trichloride *para* substituted in 100 mL of dry

chloroform for about 6 h. Thereafter the solution was cooled upto 30 °C and the precipitated HgCl₂ was filtered off. The filtrate was then concentrated whereby the pale yellow crystalline product separated out. The product was filtered and then washed with cold methanol and dried in electric oven and finally recrystallized from 30:70 benzene-chloroform mixture. Now telluroether compounds were prepared by the dechlorination of the above compounds, which was carried out by stirring the aqueous suspension of above formed compounds *i.e.* 1-(N-Me)-2-(TeCl₂C₆H₄-4'-R)-4-MeC₆H₃ with five times excess of Na₂S₂O₅ solution at 50 °C for 2 h. Dense yellow oil forms appeared, which was separated from the aqueous layer and after washing it thoroughly with water, it was extracted from hexane. The extract was dried over anhydrous sodium sulphate and hexane was removed under reduced pressure to get the telluroether compounds as yellow oil. For the preparation of complexes, 2 mmol of the ligand *i.e.* 1-(N-Me)-2-(TeC₆H₄-4'-R)-4-MeC₆H₃ was dissolved in about 50 mL of benzene and it was dropped slowly into the solution containing 1 mmol of MCl₂ [M=Co(II), Ni(II) and Cu(II)] in 50 mL of benzene or ethanol. The resulting solution was refluxed for 2-3 h. In case of Co(II) complexes, after refluxing, the solution was stirred mechanically for 0.5 h when a light pink solid separated, which was filtered and washed with benzene and then recrystallized from chloroform-benzene mixture and then it was dried over anhydrous CaCl₂ in desiccator. In case of

Ni(II) complexes the refluxed solution was cooled to room temperature whereby greenish precipitate appeared, which was filtered and washed with benzene and then with alcohol. It was recrystallized from benzene-acetone mixture in 50:50 volume ratio. The solid was dried in an oven. Copper(II) complexes were obtained after stirring the refluxed solution for 1 h, when blue solid appeared, which was filtered and washed with benzene and then with acetone and recrystallized from benzene-chloroform solution mixture in 40:60 volume ratio. The complex was dried in an electric oven. The percentage of cobalt, nickel and copper in complexes was determined by usual methods while carbon, hydrogen and nitrogen were estimated on Perkin-Elmer 240C rapid elemental analyzer. The infrared spectra of compounds were recorded on a Nicolet 5 DXFT-IR spectrometer in KBr pellets. The ¹H NMR spectra were recorded at 99.55 MHz on Jeol JNM-FX-100 FT NMR spectrometer using TMS as an internal standard. The magnetic moment of the complexes was determined on Guoy-balance at room temperature using Hg[Co(SCN)₄] as calibrant. The molar conductivity of complexes was measured with a CMDWPA noble 750 conductivity meter using 0.1 mole solution in DMF. The electronic spectra were recorded on a Carry model-14 recording spectrophotometer.

RESULTS AND DISCUSSION

On the basis of elemental analysis the complexes were formulated as M(L_n)₂Cl₂ where L_n = L₁ = 1-(N-Me₂)-2-(Te-C₆H₅)-4-MeC₆H₃, L₂ = 1-(N-Me₂)-2-(Te-C₆H₄-4'-OCH₃)-4-MeC₆H₃ and L₃ = 1-(N-Me₂)-2-(Te-C₆H₄-4'-OC₂H₅)-4-MeC₆H₃. The result of elemental analysis for complexes is given in Table-1.

Infrared spectra of ligands and its complexes: All the three ligands L₁, L₂ and L₃ show a strong absorption band between 3,020-3,000 cm⁻¹ due to stretching vibration of

aromatic C-H bond¹²⁻¹⁴. The sharp bands between 2915-2900 cm⁻¹ and 2890-2860 cm⁻¹ are assigned to unsymmetrical and symmetrical C-H stretching of methyl group¹⁵⁻¹⁷. The presence of two bands in between 1615-1610 and 1505-1485 cm⁻¹ due to ν(C=C) shows the presence of Benzene ring in all the ligands. This may further be confirmed by the appearance of two bands between 724-700 and 695-680 cm⁻¹, which are specific absorption by a molecule having aromaticity due to out of plane stretching of C-H bond of Benzene ring^{12,13}. All these I.R. bands don't show any appreciable deviation in complexes. The sharp bands at 1265-1235 cm⁻¹ and medium bands at 1310-1290 cm⁻¹ are assigned to ν(N-Me) and ν(N-Arom.) stretching of the free ligand¹⁸⁻²¹. The higher wave length bands (1310-1290 cm⁻¹) appear certainly due to ν[N-C(arom.)] stretching vibration as there is little double bond character N-C(arom.) bond due to resonance as given below:

The +I effect of the 2-methyl groups attached to nitrogen atom favors the above scheme of electron shifts. In complexes the ν[N-C(me)] bonds undergo red shift by 30-40 cm⁻¹, which is indicative of coordination through nitrogen of the ligand to the metal ions Co(II), Ni(II) and Cu(II) in their complexes. However, the ν[N-C(arom.)] bands show a little blue shift in complexes, which may be attributed to +M effect of benzene ring²²⁻²⁴. The free ligands display two closely spaced doublets in far infrared regions *i.e.* at 255-265 cm⁻¹ and 280-305 cm⁻¹. These bands are assigned to ν[Te-C(arom.)] stretching. Since the two Te-C(arom.) bond vibrations belong to the same symmetry species and are very close to each other their vibrations may interact with each other producing two closely spaced bands. It is not Fermi resonance but like that²⁵⁻³⁰. These ν[Te-C(arom.)] bands undergo red shift in all the complexes showing the coordination through Te of the ligands to metal ions. The coordination through nitrogen and tellurium of the ligands is further substantiated by appearance of new bands

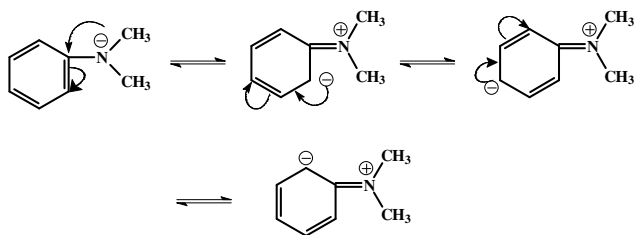
TABLE-1

S. N.	Compounds	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)					
				M	C	H	N	Te	Cl
1	1-(N-Me ₂)-2-(Te-C ₆ H ₅)-4-MeC ₆ H ₃ (L ₁)	Yellow Oil(Dense Viscous)	70	-	53.20 (53.60)	4.98 (5.02)	4.05 (4.13)	37.26 (37.68)	-
2	1-(N-Me ₂)-2-(Te-C ₆ H ₄ -4'-OCH ₃)-4-MeC ₆ H ₃ (L ₂)	Pale Yellow	74	-	51.94 (52.08)	4.98 (5.15)	3.65 (3.79)	34.59 (34.62)	-
3	1-(N-Me ₂)-2-(Te-C ₆ H ₄ -4'-OC ₂ H ₅)-4-MeC ₆ H ₃ (L ₃)	Pale Yellow	99	-	53.18 (53.32)	5.34 (5.49)	3.49 (3.66)	33.21 (33.35)	-
4	Co(L ₁) ₂ Cl ₂	Pink	165	7.20 (7.30)	44.72 (44.55)	4.15 (4.21)	3.38 (3.46)	31.59 (31.68)	8.53 (8.79)
5	Co(L ₂) ₂ Cl ₂	Light Pink	170	6.63 (6.79)	44.54 (44.24)	4.19 (4.38)	3.10 (3.23)	29.32 (29.49)	8.00 (8.18)
6	Co(L ₃) ₂ Cl ₂	Light Pink	171	6.46 (6.58)	45.88 (45.53)	4.59 (4.69)	3.00 (3.13)	28.42 (28.57)	7.81 (7.92)
7	Ni(L ₁) ₂ Cl ₂	Light Green	169	7.11 (7.27)	44.79 (44.57)	4.00 (4.21)	3.29 (3.47)	31.51 (31.69)	8.58 (8.79)
8	Ni(L ₂) ₂ Cl ₂	Bluish Green	171	6.63 (6.76)	44.48 (44.25)	4.28 (4.38)	3.16 (3.23)	29.45 (29.50)	8.00 (8.18)
9	Ni(L ₃) ₂ Cl ₂	Deep Green	171.5	6.47 (6.55)	45.69 (45.55)	4.42 (4.69)	3.00 (3.17)	28.49 (28.58)	7.84 (7.93)
10	Cu(L ₁) ₂ Cl ₂	Blue	175	7.72 (7.82)	44.54 (44.30)	4.05 (4.18)	3.31 (3.44)	31.41 (31.50)	8.62 (8.74)
11	Cu(L ₂) ₂ Cl ₂	Yellowish Green	178	7.12 (7.28)	44.28 (44.00)	4.30 (4.36)	3.12 (3.20)	29.25 (29.34)	8.06 (8.16)
12	Cu(L ₃) ₂ Cl ₂	Blue	179	7.00 (7.06)	45.52 (45.31)	4.58 (4.66)	3.08 (3.11)	28.31 (28.43)	7.72 (7.88)

in far infrared region in the spectra of complexes *i.e.* at 210-200 and 420-390 cm^{-1} , which are assigned to $\nu(\text{M-Te})$ and $\nu(\text{M-N})$ stretching respectively³¹⁻³³. Out of cumbersome IR data some important bands and their assignments are given in Table-2.

Complexes	$\nu[\text{N-C}(\text{me})]$	$\nu[\text{N-C}(\text{arom.})]$	$\nu(\text{Te-C})$	$\nu(\text{M-Te})$	$\nu(\text{M-N})$
L ₁	1235	1290	255290	-	-
L ₂	1240	1300	260290	-	-
L ₃	1265	1310	265305	-	-
Co(L ₁) ₂ Cl ₂	1200	1300	235272	205	415
Co(L ₂) ₂ Cl ₂	1200	1310	240275	208	420
Co(L ₃) ₂ Cl ₂	1205	1308	245275	210	420
Ni(L ₁) ₂ Cl ₂	1190	1305	238268	200	405
Ni(L ₂) ₂ Cl ₂	1170	1320	245270	210	400
Ni(L ₃) ₂ Cl ₂	1180	1315	248270	215	408
Cu(L ₁) ₂ Cl ₂	1200	1315	240272	205	390
Cu(L ₂) ₂ Cl ₂	1210	1320	245275	210	400
Cu(L ₃) ₂ Cl ₂	1220	1305	250275	210	405

¹H NMR: In the ¹H NMR spectra of the free ligand shows the methyl protons flip at $\delta = 268$ ppm, while in complexes they flip at higher δ *i.e.* at lower field ($\delta = 274$ -280 ppm). It confirms the coordination through nitrogen. The decrease in the field strength at which methyl protons flip may be attributed to the fact that after donation of lone pair from nitrogen the N-Me bonding pair slightly shifts towards nitrogen causing the methyl hydrogen more deshielded and hence they flip at lower field. The hydrogen atom at *ortho*-position to tellurium in the two benzene rings flips at $\delta = 6.48$ ppm. In complexes this proton flips at higher δ value ($\delta = 6.62$ -6.78 ppm) *i.e.* at lower field. This is because the *ortho*-hydrogen is more shielded in free ligands due to lone pair of electrons on tellurium. In complex tellurium donates its lone pair of electrons to metal ions and thus the *ortho*-hydrogen gets deshielded and hence flip at lower field³⁴⁻³⁶.



Magnetic moment and electronic spectra

Co(II) complexes: The magnetic moment of Co(II) complexes and their electronic spectral bands are given in Table-3.

Complexes	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\mu_{\text{eff}}(\text{BM})$
Co(L ₁) ₂ Cl ₂	8690	17300	22300	4.90
Co(L ₂) ₂ Cl ₂	8740	17200	22100	5.20
Co(L ₃) ₂ Cl ₂	8800	17400	22400	5.00

The μ_{eff} values of Co(II) complexes are in the range of 4.90 to 5.20 BM. The values are higher than expected for three unpaired electron ($\mu_s = 3.88$ BM) in high spin Oh complexes of Co(II) d^7 system. The higher value may be attributed to the appreciable orbital contribution from the triply degenerate ligand field term ${}^4T_{1g}$ ³⁷⁻⁴⁰. These values are in good agreement with the reported μ_{eff} value for high spin octahedral complexes of Co(II). The three bands displayed by Co(II) complexes in their electronic spectra may be assigned to 1. $\nu_1 = {}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$, 2. $\nu_2 = {}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}$ and 3. $\nu_3 = {}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ the various crystal field parameters were calculated as below:

$$1. \text{Co(L}_1\text{)}_2\text{Cl}_2: \nu_3/\nu_1 = 22300/8690 = 2.56$$

In Tanabe-Sugano diagram this ratio corresponds to $Dq/B = 0.9$. At $Dq/B = 0.9$, ν_1/B comes to be 8. So $8690/B = 8$, $\therefore B = 8,690/8 = 1086 \text{ cm}^{-1}$. Since $Dq/B = 0.9$, So $Dq = 0.9(1086) = 977.4 \text{ cm}^{-1}$, $\therefore 10 Dq = 9774 \text{ cm}^{-1}$.

The B_0 for free Co(II) ion is 1120 cm^{-1} . Hence nephelauxatic ratio (β) = $B/B_0 = 1086/1120 = 0.9$. So $\beta_{35} = (B_0 - B)/B_0 \times 100 = (1120 - 1086)/1120 \times 100 = 3400/1120 = 3.1\%$. In the similar way the nephelauxatic ratio for Co(L₂)₂Cl₂ and Co(L₃)₂Cl₂ have also been calculated and values have been given in Table -4.

Complexes	ν_3/ν_1	$10Dq(\text{cm}^{-1})$	$B(\text{cm}^{-1})$	β	$\beta_{35}(\%)$
Co(L ₁) ₂ Cl ₂	2.56	9774	1086	0.97	3.10
Co(L ₂) ₂ Cl ₂	2.528	10224	1065	0.95	5.36
Co(L ₃) ₂ Cl ₂	2.545	10338	1060	0.94	5.35

Thus, nephelauxatic effect increases in the order of $L_1 < L_2 \sim L_3$ and the covalence in M-L bond is in the order of $\text{Co(L}_1\text{)}_2\text{Cl}_2 < \text{Co(L}_2\text{)}_2\text{Cl}_2 \sim \text{Co(L}_3\text{)}_2\text{Cl}_2$.

Ni(II) complexes: The magnetic moment of Ni(II) complexes is 3.04 to 3.30 BM at room temperature. The values are greater than expected from two unpaired electrons ($\mu_s = 2.828$ BM). Ni(II) is a d^8 system for which the ground state term is 3F . For d^8 system the term 3F splits in Oh crystal field with ${}^3A_{2g}$ as ground state crystal field term. As ${}^3A_{2g}$ is a singly degenerate it doesn't contribute significantly to the magnetic moment of Ni(II) Oh complexes. However due to spin orbit coupling the magnetic moment of such systems is given by- $\mu_{\text{eff}} = \mu_o(1 - 4\lambda/10 Dq)$. Since λ which is spin-orbit coupling constant is negative for d^8 system the μ_{eff} becomes greater than μ_s values⁴¹⁻⁴⁵.

The above values of μ_{eff} are also in good agreement with the reported values for octahedral complexes of Ni(II)⁴⁶⁻⁵⁰. Ni(II) complexes exhibit three bands in their electronic spectra. These bands in their assignment are given in Table-5.

Complexes	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\mu_{\text{eff}}(\text{BM})$
Ni(L ₁) ₂ Cl ₂	9220	16300	24600	3.10
Ni(L ₂) ₂ Cl ₂	9270	16500	24650	3.04
Ni(L ₃) ₂ Cl ₂	9290	16400	24680	3.30

The Nephelauxatic effect of these complexes have been determine as below:

$$\text{Ni(L}_1\text{)}_2\text{Cl}_2: \nu_1 = 10 Dq = 9220 \text{ cm}^{-1}$$

$$\nu_2/\nu_1 = 16300/9220 = 1.77.$$

$$\Rightarrow \nu_3 + \nu_2 - 3\nu_1 = 15B.$$

$$\text{or, } 24600 + 16300 - 3 \times 9220 = 15B.$$

$$\text{or, } 40900 - 27660 = 15B.$$

$$\text{or, } B = 13,240/15 = 882.67 \text{ cm}^{-1}.$$

The Bo value for free Ni(II) ion is 1040 cm^{-1} so nephelauxetic effect $\beta = B/Bo = 882.67/1040 = 0.848$.

$$\text{And } \beta_{35} = (Bo-B)/Bo \times 100.$$

$$= (1040-882.67)/1040 \times 100.$$

$$= 15.127 \text{ \%}.$$

Similarly the values for $\text{Ni}(\text{L}_2)_2\text{Cl}_2$ and $\text{Ni}(\text{L}_3)_2\text{Cl}_2$ have been calculated and presented in Table-6.

TABLE-6

Complexes	10Dq (cm^{-1})	B(cm^{-1})	β	β_{35} (%)
$\text{Ni}(\text{L}_1)_2\text{Cl}_2$	9220	882.67	0.848	15.127
$\text{Ni}(\text{L}_2)_2\text{Cl}_2$	9270	889.00	0.854	14.519
$\text{Ni}(\text{L}_3)_2\text{Cl}_2$	9290	880.67	0.846	15.320

Here nephelauxetic effect is almost same for all the three ligands while maximum co-valency is found in $\text{Ni}(\text{L}_3)_2\text{Cl}_2$. The values of 10 Dq, B, β and β_{35} for all the three Ni(II) complexes are in good agreement with reported values for Oh Ni(II) complexes⁴⁷⁻⁵².

Cu(II) complexes: The magnetic moment values at room temperature and the electronic spectral bands have been given in Table -7.

TABLE-7
ELECTRONIC SPECTRAL BANDS AND μ_{eff} VALUES.

Complexes	$\nu(\text{cm}^{-1})$	μ_{eff} (BM)
$\text{Cu}(\text{L}_1)_2\text{Cl}_2$	14200	2.00
$\text{Cu}(\text{L}_2)_2\text{Cl}_2$	14500	1.99
$\text{Cu}(\text{L}_3)_2\text{Cl}_2$	14700	1.96

The magnetic moment values of Cu(II) complexes are found between 1.96-2.00 BM, which show the nonomeric nature of Cu(II) complexes with one unpaired electron (5355). All the three complexes display a broad band centered at $14200 - 14700 \text{ cm}^{-1}$ in their electronic spectra. The band may safely be assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition.

The values are in good agreement with reported values for Oh Cu(II) complexes⁵⁰⁻⁵⁴.

ACKNOWLEDGEMENTS

One of the authors, Amit K. Singh is thankful to U.G.C. for awarding him J.R.F.

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