



Photochemical characterization of Telluroether compound with some divalent Co (II), Ni (II) & Cu (II) ion

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Abstract

The synthesis and structures of acyclic and macrocyclic thio-, seleno- and telluro-ether complexes of the metallic and metalloid elements of Groups 13-16 reported since 2000 are described. The diverse structures range from discrete monomers through to infinite 1-, 2- or 3-D polymers. The coordination chemistry in this area is quite different to familiar d-block chemistry and the underlying factors are explored.

New Schiff base ($H_2 L$) ligand is prepared via condensation of o-phthaldehyde and 2-aminobenzoic acid in 1:2 ratio. Metal complexes are prepared and characterized using elemental analyses, IR, solid reflectance, magnetic moment, molar conductance, 1H NMR, ESR and thermal analysis (TGA). From the elemental analyses data, the complexes were proposed to have the general formulae $[MCl(L)(H_2 O)].2H_2 O$ (where $M = Cr(III)$ and $Fe(III)$); $[M(L)].yH_2 O$ (where $M = Mn(II), Ni(II), Cu(II)$ and $Zn(II)$, $y = 1-2$) and $[M(L)(H_2 O)_n].yH_2 O$ (where $M = Co(II)$ ($n=y=2$), $Co(II)$ ($n=y=1$), $Ni(II)$ ($n=2, y=1$)). The molar conductance data reveal that all the metal chelates were non-electrolytes. IR spectra show that $H_2 L$ is coordinated to the metal ions in a bi-negative tetradentate manner with NOON donor sites of the azomethine-N and carboxylate-O. The 1H NMR spectral data indicate that the two carboxylate protons are also displaced during

complexation. From the magnetic and solid reflectance spectra, it was found that the geometrical structure of these complexes are octahedral (Cr(III), Fe(III), Co(II) and Ni(II)), square planar (Cu(II)), trigonal bipyramidal (Co(II)) and tetrahedral (Mn(II), Ni(II) and Zn(II)). The thermal behaviour of these chelates showed that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the ligand molecule in the subsequent.

KEYWORDS: Schiff base; Transition metal complexes, Molar conductance, Thermal analysis;

1. Introduction

A large number of Schiff bases (Sonmez et al., 2003; Vaghasiya et al., 2004; Elerman and Kabak, 2002) and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, photochromic properties and complexing ability towards some toxic metals. Furthermore, complexes of Schiff bases showed promising biological activity and biological modeling applications (Khalil et al., 2005; Chantarasiri et al., 2004; Soliman, 2001; Soliman and Mohamed, 2004; Tas et al., 2004).

The Schiff base ligands with sulphur and nitrogen donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions (Kaushik and Mishra, 2003; Manav et al., 2000; Mishra et al., 2005; Abd El Wahed et al., 2004). Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhances their activities (Singh et al., 2000), as has been reported for pathogenic fungi (Patel and Parekh, 2005). There is a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they are readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes. Some of which have been shown to exhibit interesting physical and chemical properties (Tian et al., 1997) and potentially useful biological activities (Karabocek et al., 1997).

Many reports are available for the preparation and properties of model copper complexes which mimic copper-containing metalloproteins such as hemocyanine and tyrosinase. Two noticeable properties of copper proteins show an intense absorption band (Kaizer et al., 2007) near 600 nm and relatively high copper(II)/copper(I) reduction potentials (Tian et al., 1997). Attention was particularly focused on their correlation with the active site of metallo enzymes and metalloproteins containing

dinuclear metallocenters. This attention is important to elucidate the factors that determine the reversible binding and activation of O₂ in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity (Kaizer et al., 2007).

Schiff bases (Sixt and Kaim, 2000) were still regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and inexpensive determinations of different organic and inorganic substances (Estrela et al., 2003). The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

As an extension of our work on the structural characterization of Schiff base ligands and their metal complexes (Mohamed, 2006; Soliman and Mohamed, 2004; Mohamed and Sharaby, 2007), the main target of the present article is to study the coordination behaviour of a new and novel H₂L Schiff base that incorporates several binding sites towards Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) (Cl and ClO₄), Cu(II) and Zn(II) ions. Also to evaluate the relative thermal stability of the synthesized complexes and to examine their antimicrobial activity against different species of bacteria and fungi.

2. Experimental

2.1. Materials and reagents

All chemicals used were of the analytical reagent grade (AR). They included o-phthaldehyde (Sigma); 2-aminobenzoic acid (Sigma); copper(II) chloride dihydrate (Prolabo); cobalt(II) and nickel(II) chlorides hexahydrates (BDH); cobalt(II) and nickel(II) perchlorates hexahydrates (Sigma); zinc(II) chloride dihydrate (Ubichem), chromium(III) chloride hexahydrate (Sigma); manganese(II) chloride and ferric(III) chloride hexahydrate (Prolabo). Zinc oxide, EDTA (AnalaR), ammonium solution (33% v/v) and ammonium chloride were supplied from El-Nasr Pharm. Chem. Co., Egypt. Organic solvents used included absolute ethyl alcohol, diethyl ether, and dimethyl-formamide (DMF). These solvents were spectroscopic pure from BDH. Hydrogen peroxide, hydrochloric and nitric acids (MERCK) were used. De-ionized water collected from all glass equipments was usually used in all preparations.

2.2. Instruments

The molar conductance of solid complexes in DMF (10^{-3} M) was measured using Sybron–Barnstead conductometer (Meter-PM.6, E= 3406). Elemental microanalyses of the separated solid chelates for C, H, N and S were performed in the Micro-analytical Center, Cairo University. The analyses were re-peated twice to check the accuracy of the data. Infrared spectra were recorded on a Perkin–Elmer FT-IR type 1650 spectrophotometer in the region 4000–400 cm^{-1} as KBr discs. The solid ESR spectra of the complexes were recorded with ELEXSYS E500 Bruker spectrometer in 3 mm Pyrex tubes at 298 K. Diphenylpicrylhydrazide (DPPH) was used as a marker for the calibration of the spectra. The ^1H NMR spectra were recorded with a JEOL EX-270 MHz in d_6 -DMSO as solvent, where the chemical shifts were determined relative to the solvent peaks. The solid reflectance spectra were measured on a Shimadzu 3101 pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. The magnetic data for the background of the sample holder were corrected. The thermogravimetric analysis (TGA and DSC) was carried out in dynamic nitrogen atmosphere (20 ml min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ using Shimadzu TGA-50H thermal analyzers.

2.3. Synthesis of the Schiff base (H_2L)

Hot solution (60°C) of 2-aminobenzoic acid (2.74 g, 20 mmol) was mixed with hot solution (60°C) of o-phthalaldehyde (1.34 g) 10 mmol in 50 ml ethanol. The resulting mixture was left under reflux for 4 h and the solvent was evaporated till deep yellow oil product is separated. This oil is poured on ice cold dilute HCl whereupon the yellow crystalline product is separated. The formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethylether and dried in a vacuum over anhydrous calcium chloride. The yellow product is produced in 86% yield.

2.4. Synthesis of metal complexes.

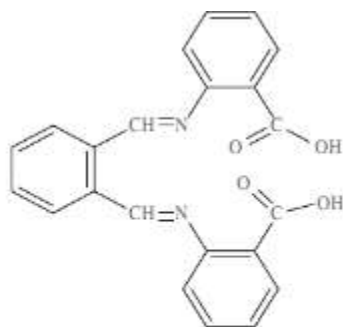
The metal complexes were prepared by the addition of hot solution (60°C) of the appropriate metal chloride or perchlorate (1 mmol) in an ethanol–water mixture (1:1, 25 ml) to the hot solution (60°C) of the Schiff base (0.372 g, 1 mmol) in the same solvent (25 ml). The resulting mixture was stirred under reflux for one hour

whereupon the complexes precipitated. They were collected by filtration, washed with a 1:1 ethanol:water mixture and diethylether. The microanalysis data for C, H and N were repeated twice. 2.5. Biological activity A filter paper sterilized disc saturated with measured quantity of the sample (10 μ l, 20 mg/ml) is placed on plate containing solid bacterial medium (nutrient agar broth) or fungal medium (Dox s medium) which has been heavily seeded with spore suspension of the tested organism. The assay plates which incubated at 28 $^{\circ}$ C for 2 days for yeasts and at 37 $^{\circ}$ C for 1 day for bacteria. After inoculation, the diameter of the clear zone of inhibition surrounding the sample is taken as a measure of the inhibitory power of the sample against the particular test organism (Grayer and Harbone, 1994; Irob et al., 1996). The organisms used included Gram-positive (*Staphylococcus aureus*), Gram-negative (*Escherichia coli*) bacteria and Fungi (*Candida albicans* and *Aspergillus flavus*).

3. Results and discussion

3.1. Schiff base characterization

The Schiff base, H₂ L, is subjected to elemental analyses. The results of elemental analyses (C, H and N) with molecular formula and the melting points are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula. The melting points are sharp indicating the purity of the prepared Schiff base. The scheme of the Schiff base preparation is given by Fig. 1. The structure of this Schiff base is also confirmed by IR and ¹H NMR spectra, which will be discussed in detailed manner together with its metal complexes later. It takes the following structural formula and IUPAC name:



3.2. Composition and structures of Schiff base complexes

The isolated solid complexes of Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) (chlorides and perchlorates), Cu(II) and Zn(II) ions with the Schiff base H₂L ligand were subjected to elemental analyses (C, H, N and metal content), IR, magnetic studies, molar conductance and thermal analysis (TGA), to identify

Table 1 Analytical and physical data of H₂L ligand and its metal complexes.

Compound	m.p. (°C)	Colour (% yield)	% Found (Calcd.)				μ_{eff} (B.M.)	$\Omega_m \Omega^{-1} \text{mol}^{-1} \text{cm}^{-2}$
			C	H	N	M		
H ₂ L (C ₂₂ H ₁₆ N ₂ O ₄)	100	Yellow (86)	70.27 (70.47)	5.07 (5.30)	7.14 (7.53)	—	—	—
[CrCl(L)(H ₂ O)]·2H ₂ O C ₂₂ H ₂₀ ClCrN ₂ O ₇	> 300	Green (70)	51.33 (51.61)	4.11 (3.91)	5.17 (5.47)	9.86 (10.17)	4.05	10.26
[Mn(L)]·H ₂ O C ₂₂ H ₁₆ MnN ₂ O ₅	> 300	Brown (72)	60.07 (59.73)	3.63 (3.62)	6.64 (6.33)	12.45 (12.22)	4.72	10.11
[FeCl(L)(H ₂ O)]·2H ₂ O C ₂₂ H ₂₀ ClFeN ₂ O ₇	> 300	Yellowish Brown (63)	50.83 (51.21)	3.76 (3.88)	5.56 (5.43)	11.08 (10.86)	5.39	9.75
[Co(L)(H ₂ O)] ₂ ·2H ₂ O C ₂₂ H ₂₂ Co ₂ N ₂ O ₈	> 300	Reddish brown (59)	52.38 (52.69)	4.31 (4.39)	5.95 (5.59)	12.89 (12.69)	5.62	11.25
[Co(L)(H ₂ O)]·H ₂ O C ₂₂ H ₁₈ CoN ₂ O ₆	> 300	Brown (66)	56.68 (56.77)	4.02 (3.87)	6.35 (6.02)	12.56 (12.69)	5.25	12.30
[Ni(L)]·2H ₂ O C ₂₂ H ₁₈ NiN ₂ O ₆	> 300	Green (60)	56.94 (56.77)	3.58 (3.87)	6.43 (6.02)	12.92 (12.69)	4.64	6.75
[Ni(L)(H ₂ O) ₂]·H ₂ O C ₂₂ H ₂₀ NiN ₂ O ₇	> 300	Yellow (68)	54.39 (54.66)	3.86 (4.14)	5.42 (5.78)	12.56 (12.22)	3.67	8.45
[Cu(L)]·1.5H ₂ O C ₂₂ H ₁₇ CuN ₂ O _{5.5}	> 300	Green (70)	57.43 (57.33)	3.47 (3.69)	5.74 (6.08)	13.43 (13.79)	1.93	15.65
[Zn(L)]·H ₂ O C ₂₂ H ₁₆ N ₂ O ₅ Zn	> 300	Yellow (58)	58.07 (58.28)	3.69 (3.53)	6.37 (6.18)	14.05 (14.35)	diam.	13.64

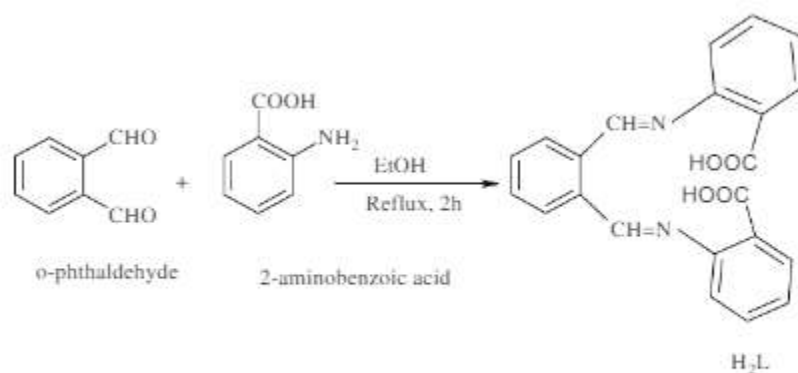


Figure 1 Preparation scheme of H₂L ligand.

their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses listed in Table 1 suggest the formulae [MCl(L)(H₂O)]·2H₂O (where M = Cr(III) and Fe(III)); [M(L)]·yH₂O (where M = Mn(II), Ni(II), Cu(II) and Zn(II), y = 1–2) and [M(L)(H₂O)_n]·yH₂O (where M = Co(II) (n = y = 2), Co(II) (n = y = 1), Ni(II) (n = 2, y = 1)).

3.2. Molar conductivity measurements

The chelates were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at 25 °C were measured. Table 1 shows the molar conductance values of the complexes. The molar conductance values of the complexes fall in the range 6.75–15.65 mol⁻¹ cm² indicating that these chelates are non-electrolytes.

3.3. IR spectral studies

The IR data of the spectra of H₂ L Schiff base and its complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may involve in chelation. The position and/or the intensities of these peaks are expected to be changed upon chelation. New peaks are also guide peaks as well as water in chelation. These guide peaks are listed in Table 2.

Table 2 IR spectra (4000–400 cm⁻¹) of the H₂L ligand and its metal complexes.

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{COO})$ (asym)	$\nu(\text{COO})$ (sym.)	$\nu(\text{CH}=\text{N})$	$\nu(\text{H}_2\text{O})$ (coord.)	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
H ₂ L	1682br	1587s	1393sh	1603m	—	—	—
[CrCl(L)(H ₂ O)]·2H ₂ O	1679m	1544s	1403sh	1588m	812w, 758sh	534m	450w
[Mn(L)]·H ₂ O	1678sh	1503sh	1401sh	1587sh	815s, 757sh	526m	426w
[FeCl(L)(H ₂ O)]·2H ₂ O	1677sh	1503sh	1400sh	1587sh	870s, 758sh	530s	475s
[Co(L)(H ₂ O)]·2H ₂ O	1716sh	1556m	1454s	1599sh	823s, 757sh	528w	460s
[Co(L)(H ₂ O)]·H ₂ O	1675sh	1504m	1403m	1590sh	812s, 758sh	535w	486w
[Ni(L)]·2H ₂ O	1678sh	1503sh	1405sh	1591sh	810s, 757sh	530w	464w
[Ni(L)(H ₂ O)]·H ₂ O	1676sh	1503sh	1401sh	1590sh	811m, 757sh	484w	420w
[Cu(L)]·1.5H ₂ O	1675sh	1502sh	1404m	1589sh	842m, 758sh	533s	488s
[Zn(L)]·H ₂ O	1679m	1508m	1401m	1595sh	812m, 758sh	530w	474s

sh = sharp, m = medium, s = small, w = weak, br = broad.

Upon comparison it was found that the azomethine(C,N) stretching vibration is found in the free ligand at 1603 cm⁻¹. This band is shifted to lower wavenumbers (1587–1599 cm⁻¹) in the complexes indicating the participation of the azomethine nitrogen in coordination (Mohamed and Sharaby, 2007). The $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{asym}(\text{COO}))$ and $\nu(\text{sym}(\text{COO}))$ stretching vibrations are observed at 3300–3400 (broad band), 1682, 1587 and 1393 cm⁻¹ for H₂ L. The existence of water of hydration and/or water of coordination in the spectra of the complexes render it difficult to get conclusion from the OH group of the H₂ L ligand, which will be overlapped by those of the water molecules. The participation of the OH group is further confirmed by clarifying the effect of chelation on the asymmetric and symmetric carboxylic stretching vibrations. The participation of the carboxylate-O atom in the complex formation was evidenced from the shift in position of these

bands to 3275–3309, 1675–1716, 1502–1556 and 1400–1454 cm^{-1} in the metal complexes (Soliman and Mohamed, 2004). New bands are found in the spectra of the complexes in the regions 484–535 cm^{-1} , which are assigned to $\nu(\text{M}-\text{O})$ stretching vibrations (Mohamed, 2006; Mohamed and Sha-raby, 2007). The bands at 420–488 cm^{-1} have been assigned to $\nu(\text{M}-\text{N})$ mode (Mohamed, 2006; Mohamed and Sharaby, 2007). Therefore, from the IR spectra, it is concluded that H_2L ligand behaves as a bi-negative tetradentate ligand coordinating

Table 3 ^1H NMR spectral data of H_2L and its $\text{Zn}(\text{II})$ complex.

Compound	δ (ppm)	Assignments
H_2L	11.641	(s, 2H, $-\text{COOH}$)
	8.538	(s, 2H, $-\text{CH}=\text{N}$)
	6.50–7.96	(m, 12H, ArH)
$[\text{Zn}(\text{L})]\cdot\text{H}_2\text{O}$	8.477	(s, 2H, $-\text{CH}=\text{N}$)
	6.419–8.008	(m, 12H, ArH)
	4.15	(br, 2H, H_2O)

to the metal ions via the azomethine N and deprotonated carboxylate O.

3.5 ^1H NMR spectra

The chemical shifts of the different types of protons in the ^1H NMR spectra of the H_2L ligand and its diamagnetic $\text{Zn}(\text{II})$ complex are listed in Table 3. Upon comparison, the COOH signal is found at 11.641 ppm in the spectrum of H_2L ligand. This signal is completely disappeared in case of $[\text{Zn}(\text{L})]\cdot\text{H}_2\text{O}$ complex indicating the participation of the COOH group in chelation with proton displacement. Also the signal observed at 4.15 ppm with an integration corresponding to two protons in case of $\text{Zn}(\text{II})$ complex, is assigned to one water molecule.

3.6. Magnetic susceptibility and electronic spectral measurements

For the hexa-coordinated $\text{Cr}(\text{III})$ complex, there are three spin allowed transitions i.e., $\nu_1: {}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, $\nu_2: {}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, $\nu_3: {}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{P})$ Estrela et al., 2003. The diffused reflectance spectrum of the $\text{Cr}(\text{III})$ chelate shows three absorption bands at 19,275 (ν_1), 26,940 (ν_2), and 28,960 cm^{-1} (ν_3). The electronic spectrum of the chelate reported here is in reasonable agreement with those in the literature (Cotton et al., 1999). The magnetic moment at room temperature is 4.05 B.M. which corresponds to the expected value for octahedral $\text{Cr}(\text{III})$ complexes (Cotton et al., 1999). From the diffused reflectance spectrum it is observed that, the

Fe(III) chelate exhibit a band at $21,249 \text{ cm}^{-1}$, which may be assigned to the ${}^6A_{1g} \rightarrow T_{2g}(G)$ transition in octahedral geometry of the complexes (Mohamed and Sharaby, 2007; Cotton et al., 1999). The $A_{1g} \rightarrow T_{1g}g$ transition appears to be split into two bands at $16,746$ and $14,975 \text{ cm}^{-1}$. The observed magnetic moment of Fe(III) complex is 5.39 B.M. Thus, the complexes formed have the octahedral geometry (Mohamed and Sharaby, 2007; Cotton et al., 1999). The spectrum shows also a band at $28,431 \text{ cm}^{-1}$ which may attribute to ligand-metal charge transfer. The diffused reflectance spectrum of the Mn(II) complex shows three bands at $16,445$, $22,965$ and $27,265 \text{ cm}^{-1}$, which are assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ transitions, respectively (Cotton et al., 1999). The magnetic moment value is 4.72 B.M. which indicates the presence of Mn(II) complex in tetrahedral structure.

The electronic spectrum of the Co(II) complex; $[\text{Co(L)}-(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, gives three bands at $15,076$, $18,674$ and $22,330 \text{ cm}^{-1}$. The bands observed are assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) (\nu_1)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) (\nu_2)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P) (\nu_1)$, respectively, suggesting that there is an octahedral geometry around Co(II) ion (Mohamed and Sharaby, 2007; Cotton et al., 1999). The magnetic susceptibility measurements lie at 5.62 B.M. (normal range for octahedral Co(II) complexes is 4.3–5.2 B.M.), is an indicative of octahedral geometry. The band at $25,390 \text{ cm}^{-1}$ refers to the charge transfer band.

The Ni(II) complex; $[\text{Ni(L)}] \cdot 2\text{H}_2\text{O}$, has a lower magnetic susceptibility than expected for a tetrahedral complex (West et al., 1999) due to the tetradentate H2L ligand coordinating as a planar ligand. The diffused reflectance spectrum shows two bands at 6990 and $17,730 \text{ cm}^{-1}$ which are assigned to ${}^3T_{1g} \rightarrow {}^3A_1$ and ${}^3T_{1g} \rightarrow {}^3T_1(p)$ transitions, respectively, confirming tetrahedral structure of Ni complex (West et al., 1999). The leff value of the Cu(II) complex of 1.93 B.M. indicates a square planar geometry. In confirmation of this structure only one band is seen in the spectrum around $14,250 \text{ cm}^{-1}$ with two shoulders on either sides at $18,450$ and $11,205 \text{ cm}^{-1}$. These are assigned to ${}^2B_{1g} \rightarrow {}^3A_1$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}$ transitions, respectively (Shukla et al., 1983).

4. Conclusion

Since almost all scientists working in the field of research for new antitumours depend basically on the line of antibiotics affecting Gram-negative bacteria (Nikaido and Nakae, 1979; Brown, 1975; Hodnett et al., 1987; Hickman, 1987; El-Sharief et al., 1984), and since there are certain organisms which have proved difficult to treat and most of them are Gram-negative rods. It is therefore believed that all the complexes which are biologically active against both the Gram-negative strains may has something to do with the barrier function of the envelope of these Gram-negative strains activity, acting in a way similar to that described by Nikaido and Nakae (1979), and Brown (1975). Therefore, it is claimed here that the synthesis of these complexes might be recommended and/or established a new line for search to new antitumour particularly when one knows that many workers studied the possible antitumour action of many synthetic and semisynthetic compounds e.g., Hodnett et al. (1987) and Hickman (1987). Such compounds may have a possible antitumour effect since Gram-negative bacteria are considered a quantitative microbiological method testing beneficial and important drugs in both clinical and experimental tumour chemotherapy (El-Sharief et al., 1984).

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