Synthesis and Properties of Complexes of Copper(II), Nickel(II), Cobalt(II) and Uranyl Ions with 3-(*p*-Tolylsulphonamido)rhodanine

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Metal complexes of copper(II), nickel(II), cobalt(II), uranyl(II) with 3-(*p*-tolylsulphonamido)rhodanine (HL) have been prepared and characterized by chemical and thermal analyses, molar conductivity, magnetic susceptibility measurements, and infrared, electronic and EPR spectra. The visible and EPR spectra indicated that the Cu(II) complex has a tetragonal geometry. From EPR spectrum of the Cu(II) complex, various parameters were calculated. The crystal field parameters of Ni(II) complex were calculated and were found to agree fairly well with the values reported for known square pyramidal complexes. The infrared spectral studies showed a monobasic bidentate behaviour with the oxygen and nitrogen donor system. Thermal stabilities of the complexes are also reported.

Rhodanine plays an important role in biological reactions [1], *e.g.*, in the inhibition of mycobacterium tuberculosis [2]. Sulphonamides constitute a class of drugs, which are frequently used in pharmaceutical preparations, especially in veterinary practice. 3-Arylamidorhodanines are a class of potentially bidentate ligands [3,4]. These molecules are capable of having keto-enol tautomers, the enolic hydrogen may be replaced by a metal ion and a considerable number of various substituents can be placed on the ligand. Previously, work on solid complexes [4–6] and potentiometric studies [7,8] were used to characterize and evaluate the stability constants of the complexes formed in solid and in solution. Accordingly, in the present study we synthesized and characterized a series of Cu(II), Ni(II), Co(II) and $UO_2(II)$ complexes derived from the ligand 3-(*p*-tolylsulphonamido)rhodanine.

EXPERIMENTAL

3-(*p*-Tolylsulphonamido)rhodanine (IA) was prepared as reported earlier [4,7].

IA
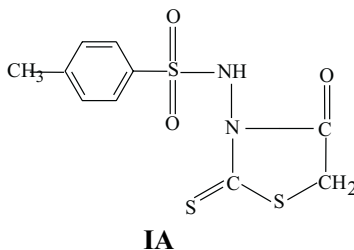
Preparation and analysis of the complexes: The complexes were prepared by mixing equimolar amounts of hydrated metal acetate and the 3-(*p*-tolylsulphonamido)rhodanine (IA) in absolute EtOH. The mixture was refluxed on a water bath for 1–2 h. The products were separated by filtration, washed several times with EtOH and Et_2O, and finally dried in a vacuum desiccator over anhydrous $CaCl_2$. All measurements were carried out as reported earlier [5,6,9].

RESULTS AND DISCUSSION

The ligand was characterized by analytical and spectral methods before using it for the preparation of complexes. The analytical data of the complexes $[CuL_2 \cdot 2X]$, $[NiLOAc \cdot X]$, $[CoL_2 \cdot 2X]$ and $[UO_2L_2 \cdot 2X]$ (where HL = bidentate monoanionic ligand, $X = H_2O$) agree well with their structure, indicating that rhodanine forms stable complexes, insoluble in common organic solvents, soluble in DMF and DMSO. The molar conductivities in DMF at room temperature showed that they are non-electrolytes.

The ligand exhibits four electronic spectral bands in DMF at 26100 cm^{-1} (CS) (n→π*), 31430 cm^{-1} (CO) (n→π*), 34150 cm^{-1} (H-bonding and association) and ≈ 38900 cm^{-1} (phenyl) (ph→ph*, π→π*) [10]. In the dioxouranium(VI) complex, the (CS) (n→π*) transition shifts slightly to lower energy and remain almost constant. The (CO) (n→π*) transition disappears with the simultaneous appearance of a new band (≈ 28600 cm^{-1}), being attributed to π→π* (CH=C) as a sequence of enolization. The band due to π→π* transition moves to lower energy at 36850 cm^{-1}. These shifts or the disappearance of the bands are indicative of coordination of the ligand to $UO_2(II)$. The dioxouranium complex exhibits a new band at 23800 cm^{-1}, which is assigned to the $^1\Sigma_g^+ \rightarrow {}^3\pi_u$ transition, typical of OUO for the symmetric stretching frequency for the first excited state. The $\nu_{as}(OUO)$ and $\nu_s(OUO)$ modes of the complex occur at 885 and 790 cm^{-1}, respectively and these are in the usual range ($\nu_{as.}$ 870–950; ν_s 780–885 cm^{-1}), as reported for the majority of dioxouranium(VI) complexes [11]. The force constant, f_{U-O} (6.51 mdynes/Å) was calculated by the method of McGlynn *et al*. [12]. The U–O bond length (1.75 Å) was calculated by $R_{U-O} = 1.08f^{-1/3} + 1.17$.

The thermogravimetric analysis reveals a progressive loss of weight. A slight inflection appears at 250°C, corresponding to the loss of one ligand molecule. As the temperature increases mass loss is progressive until a plateau is reached at 560°C, corresponding to the formation of UO_2SO_4, as intermediate stage, which on further heating decomposes finally to U_3O_8 at 600°C.

Copper(II) complex gave a magnetic moment (1.93 BM), corresponding to one unpaired spin [13]. Irrespective of stereochemistry involved, bivalent copper(II) complexes exhibit exchange interaction between copper pairs, leading to lower magnetic moments or even diamagnetism [14].

The absorption spectra of six-coordinate copper(II) complexes are analyzed assuming D_4 or C_{4v} symmetry, the e_g and t_{2g} levels of the ^2D free ion term are further split into B_{1g}, A_{1g}, B_{2g} and E_g levels, respectively. Thus, three spin allowed transitions are expected in the visible and near IR region of copper(II) and such bands are resolved by Gaussian analysis and analyzed by single crystal polarization studies and

are assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}(d_{z^2} \leftarrow d_{x^2-y^2})$; $^2B_{1g} \rightarrow {}^2B_{2g} (d_{xy} \leftarrow d_{x^2-y^2})$ and $^2B_{1g} \rightarrow {}^2B_g(d_{xz}, d_{yz} \leftarrow d_{x^2-y^2})$ transitions in order of increasing energy. The energy level sequence will depend on the amount of distortion, due to ligand field and Jahn-Teller effect [15]. The electronic spectrum of the present complex displays a sharp band ($^2B_{1g} \rightarrow {}^2E_g$) (13100 cm^{-1}) and a well defined shoulder ($^2B_{1g} \rightarrow {}^2A_{1g}$)(15150 cm^{-1}). Because of the low intensity of $^2B_{1g} \rightarrow {}^2B_{2g}$ this band is usually not observed as a separate band in tetragonally distorted complexes. The anisotropic EPR spectrum is characteristic of a tetragonal copper(II) complex. The g-tensor has been calculated by Kneubuhl [16], El-Sonbati and El-Bindary [17] method and the results are presented in Table 1.

Table 1. EPR data of the copper(II) polycrystalline complex at room temperature.

Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av.}$	G	$A_{\parallel}$(cm^{-1})	α^2
Cu(II)	2. 235	2.056	2.122	> 4	85.51×10^{-4}	0.55

The g-tensor copper(II) complexes can be used to derive the ground state [18]. In an elongated octahedral geometry, the unpaired 3d electron for Cu^{2+} ion lies in $d_{x^2-y^2}$ orbital ($^2B_1$ as ground state). The g-values are then given by $g_{\parallel} = 2[1 - (4\lambda/\Delta_1)]$ and $g_{\perp} = 2[1 - (\lambda/\Delta_2)]$. In a compressed octahedral, on the other hand, the unpaired 3d electron lies in d_{z^2} orbital ($^2A_1$ ground state) and so gives the g-value expressions: $g_{\parallel} = 2$ and $g_{\perp} = [1 - (3\lambda/\Delta_3)]$. Here, Δ_1, Δ_2 and Δ_3 are $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ excitation energies, respectively. From the g-values it is evident, that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital with the possibility of some d_{z^2} character, being mixed with it because of low symmetry. A parameter G has been calculated by $g = (g_{\parallel} - 2)/(g_{\perp} - 2)$. A value of G larger than four indicates that considerable exchange interaction is absent. $g_{\parallel} > g_{\perp} > 2$ indicates that the unpaired electron is located mainly in the $d_{x^2-y^2}$ orbital. We have reported [17] that $g_{\parallel}$ in a Cu(II) complex can be used as a measure of the covalent character of the metal–ligand bond. Approximate metal–ligand δ-bond coefficients (α^2), which are defined as the fraction of unpaired electron density located on the copper ion, for this complex were calculated, neglecting the π-bonding, from the solid state optical absorption data [17]. The α^2 value for copper(II) complex indicates a considerable covalency in the bonding between the Cu(II) ion and the ligand, comparable to that obtained by us [17]. The super-exchange splitting constant $A_{\parallel}$ was obtained semi-empirically, according to Pryce [19]. The small $g_{\parallel}$ can be attributed to the large covalent interaction. This reduction may be due to the orientation of the SO$_2$-Ph-(*p*-CH$_3$) group, such as to increase the separation between successive planes.

In the thermogram of the copper(II) complex no weight changes are observed until 150°C, where an initial weight loss is observed, due to the loss of both water molecules. The plateau registered in the 300–480°C interval corresponds to copper sulphate with formation of CuO above 900°C.

The magnetic moment of nickel complex is 2.78 BM at room temperature, being within the range known for five coordinate complexes. The slight lowering may be

attributed to distortion of the molecule from idealised symmetry, however, the value indicates that metal–metal interaction is absent.

The spectrum bands are consistent with those predicted for five coordinated nickel complexes. It is interesting, however, that for a similar set of donor atoms in a regular trigonal bipyramidal geometry only one is expected in the near IR region at *ca*. 7000 cm^{-1}, while two are expected for a regular square-pyramidal structure, one at 7500 cm^{-1} and the other at 10800 cm^{-1} [20]. The spectrum of the present complex is consistent with a five-coordinate square-pyramidal [21]. Thus, it seems reasonable to consider the structure to be distorted square-pyramidal. The various bands can be assigned to $^3B_1 \rightarrow ^3B_2$ (8300), $^3B_1 \rightarrow ^3E^a$ ($\approx$10000), $^2B_1 \rightarrow ^3A_2$ ($\approx$ 13550) and $^3B_1 \rightarrow ^3E^b$ ($\approx$22350 cm^{-1}) [22], assuming the effective symmetry to be C_{4v} based on the argument, that the description for D_{4h} complexes applies equally well to square-pyramidal C_{4v} complex utilizing various energy transitions; the values of ligand field parameters Dq_{xy} (1041) and Dq_z (600) have been evaluated [22], indicating that the equatorial ligand field is much stronger than the field produced by the anions.

For nickel complex no weight changes are observed until 135°C, where a weight loss occurs due to the elimination of one water molecule. The mass loss at 220°C corresponds approximately to loss of the acetic acid, although the elimination took place more slowly in this case with temperature increase. The mass loss is progressive until a plateau is reached at 560°C, corresponding to the formation of nickel sulphate. A new plateau at 700°C corresponds to the formation of nickel oxide. The behaviour of the nickel complex in these last stages of the thermogram is analogous to that found in the nickel sulphate thermogram [23].

The electronic spectrum of cobalt complex shows three bands at 8200 [$^4T_{1g} \rightarrow ^4T_{2g}$](F), 18610 [$^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$] and 21310 cm^{-1} [$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$], similar to those reported in octahedral structures [17]. The magnetic moment of the cobalt complex is 4.6 BM.

The thermogram of the cobalt complex shows no weight changes until 155°C, where an initial weight loss is produced, corresponding to the elimination of both water molecules. The plateau registered between 300–500°C corresponds to cobalt sulphate. The formation of CoO takes place above 650°C.

The NMR spectrum of the ligand in DMSO-d_6 exhibits two signals δ(NH) (11.4) and δ(CH$_2$) (4.8) ppm. The observation of the NH signal at large values downfield of TMS suggests a strong hydrogen bonding. This bond occurs between NH and carbonyl oxygen of rhodanine, IA.

(IA)   **(IB)**
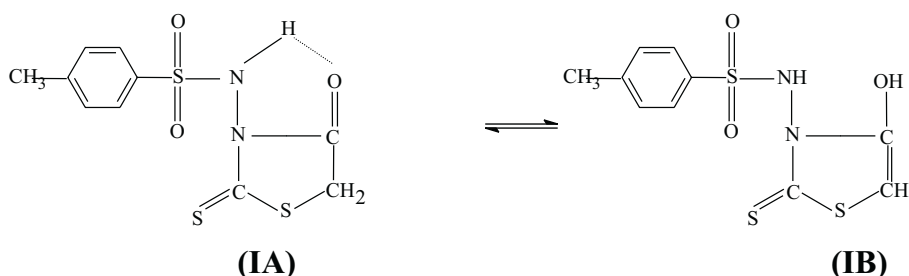
In the uranyl complex the NH signal is shifted to a lower value 10.2 ppm upfield of TMS. This indicates the destruction of the hydrogen bond as well as the coordination through the NH group. The disappearance of the CH_2 signal with the simultaneous appearance of a new signal at 7.2 ppm are attributed to the proton of the CH=C group, **II**.

II

R= -SO_2-Ph-(p-CH_3)
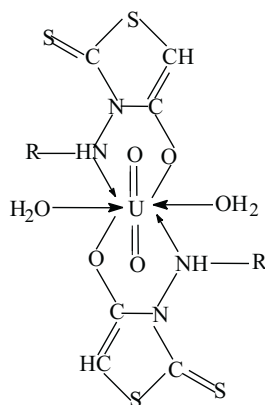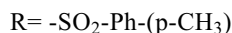
The absence of any peak attributable to the N–H..O moiety implies that in solution the ligand remains predominantly in form IA. However, in solution and in the presence of nickel, cobalt, copper and uranyl ions these compounds exist in a tautomeric equilibrium [24] IA ⇔ IB. The tautomeric form IB reacts with metal ions by loss of phenolic proton as mononegative chelating agents producing of (CO)/(OH) mode of the free ligand. New bands for (C=C) (1585) and ν(C–O) (1180 cm^{-1}) [19] in the IR spectra of the complexes indicate the coordination to that metal ions *via* deprotonation. NMR spectrum of the uranyl complex does not contain a signal, due to the –OH proton of the free ligand, suggesting that the ligand is deprotonated during complexation. The strong band at 1770 cm^{-1} and a shoulder at 1780 cm^{-1} are both assigned to the free and hydrogen bonded carbonyl oxygen of the rhodanine moiety. The ν(N–H) band is observed in all complexes in 3220–3060 cm^{-1} regions, the same wavenumber as in the free ligand. These data agree with the conclusion that the ligand is bonded to the metallic cation without deprotonation of the N–H group.

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