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Complexing Behaviour of 2*H*-1,2,4-Triazole-3-thiol Complexes of Co(II), Ni(II), Cu(II), Ru(II), Rh(III), Pd(II), Pt(II), and Au(I)

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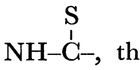
Complexes of Co(II), Ni(II), Cu(II), Ru(II), Rh(III), Pd(II), Pt(II), and Au(I) with 2*H*-1,2,4-triazole-3-thiol have been prepared. Probable structures have been proposed for the complexes on the basis of visible and infrared spectra, magnetic susceptibility, and chemical analysis. Crystal field parameters have been calculated wherever possible.

In the course of studies on metal complexes derived from the ligands having the skeletal unit  $\mathrm{NH{-}\overset{\overset{S}{\|}}{C}{-}}$, the ligand 2*H*-1,2,4-triazole-3-thiol, whose *N*-substituted derivatives are of great biochemical interest,[1–3] has been found to be a good complexing agent. The isolation and characterization of complexes with the metal having d^{10} configuration have been described.[4] In this paper, the synthesis and structural studies of the complexes of Co(II), Ni(II), Cu(I/II), Ru(II), Rh(III), Pd(II), Pt(II), and Au(I) are reported.

Experimental

All the chemicals were or Analar or chemically pure grade.

Preparation of the Ligand. *(a) 2*H*-1,2,4-Triazole-3-thiol (I)*: The ligand in the H form and its sodium salt were prepared by the method given in literature.[4,5]

*(b) Deuterated form of 2*H*-1,2,4-Triazole-3-thiol*: About 0.1 g of the ligand was dissolved in 25 ml D_2O. The resulting solution was refluxed for *ca.* 4 h, heated to dryness, and kept overnight in a desiccator.

General Method of Preparation of Complexes. Conditions for preparation and analytical data of the complexex are given in Table 1. All the complexes were prepared by mixing an aqueous solution of an appropriate metal salt (sulfate or chloride) with an alcoholic solution of the ligand. The mixed solutions were heated on a water bath or refluxed, whereby the complexes of all the metal ions were precipitated out. The complexes were separated by centrifuging the slurry and were washed with methanol or ethanol and ether, and dried in a vaccum desiccator.

Analyses. Sulfur, chloride (wherever present), and metal ions were analysed by the standard methods[6–8] after fusion in a Parr-bomb by Na_2O_2 and KNO_3. Analyses of carbon, hydrogen, and nitrogen were carried out in the Microanalytical Section of the Indian Institute of Technology, Kanpur, India.

Magnetic Susceptibility. Magnetic susceptibility was determined at room temperature with a Gouy balance. Mercurytetrathiocyanatocobaltate(II) was used as a magnetic

TABLE 1. CONDITIONS FOR PREPARATION AND ANALYTICAL DATA OF THE COMPLEXES

Complex[a)]	Reaction[b)] condition (M : L)	Heating[c)] time (h)		Analysis (%) C	H	N	S	M	Colour[d)]
$CoL_2(H_2O)_3$	A (1 : 2)	5 (R)	Calcd	15.3	3.2	26.8	20.4	18.8	g
			Found	15.5	3.0	26.3	20.3	18.6	
$CoL'(H_2O)_3$	B (1 : 2)	5 (R)		11.2	3.7	19.7	15.0	27.7	p
				11.1	3.5	19.5	14.9	27.5	
$NiL_2(H_2O)_3$	A + 1 ml of pyridine (1 : 2)	2 Room temp		15.3	3.2	26.8	20.5	18.8	g
				15.2	3.0	26.6	20.3	18.5	
$Cu_2L_x(LH)_y(H_2O)_4$ ($x+y=2$)	C (1 : 2)	No heating		12.0	3.0	21.0	16.0	31.8	bl
				12.2	3.0	21.3	16.2	31.5	
$RhL_2(LH)$	B (1 : 3)	2 (W)		18.0	1.5	31.4	23.9	25.2	bl
				18.2	1.7	31.7	23.7	—	
$RhL_2(H_2O)_2$	C (1 : 1)	2 (W)		16.4	2.3	28.6	21.8	23.4	bl
				16.7	2.6	28.7	21.6	—	
PdL_2	D (1 : 2)	2 (W)		15.7	1.5	27.4	20.9	34.7	o
				15.6	1.2	27.8	20.9	34.5	
$Pt(LH)_4Cl_2$[e)]	E (1 : 5)	2 (R)		14.5	1.9	25.0	19.0	29.2	y
				14.0	1.6	24.7	18.8	—	
AuL	C (1 : 2)	3 (W)		8.1	0.7	14.1	10.8	66.3	y
				8.6	0.9	14.4	10.5	—	

a) L, ($C_2H_2N_3S$); (LH), ($C_2H_3N_3S$); L′, (C_2HN_3S). b) Number in parentheses indicates the molar ratio (metal : ligand) in 25 ml of solvents; A, metal salt dissolved in water and ligand in ethanol; B, both metal and ligand dissolved in ethanol; C, metal salt and sodium salt of ligand dissolved in water; D, metal salt in water and ligand in ethanol; E, H_2PtCl_6 in 5 ml ethanol and ligand in 10 ml ethanol. c) R, refluxed; W, water bath. d) g, green; p, pink; bl, black; o, orange; y, yellow. e) In $Pt(LH)_4Cl_2$ the chloride was found to be 10.4% (Calcd value, 10.6%).

Table 2. Electronic spectral bands and their assignments

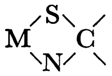
Complex	Band position (nm)	Assignment	Magnetic moment (BM)	Solubility
$NiL_2(H_2O)_3$	950	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$	3.2	I
	640	$^3A_{2g}\rightarrow{}^3T_{2g}$		
	380	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$		
$CoL_2(H_2O)_3$	585	$^4T_{2g}\rightarrow{}^4A_{2g}$	4.5	s
	540	$^4T_{2g}\rightarrow{}^2T_{1g}(P)$		
PdL_2	735	$^1A_{1g}\rightarrow{}^3A_{2g}$	D	I
	530	$^1A_{1g}\rightarrow{}^3E_g$		
	490	$^1A_{1g}\rightarrow{}^1A_{2g}$		
	370	$^1A_{1g}\rightarrow{}^3B_{1g}$		
	330	$^1A_{1g}\rightarrow{}^1E_g$		
PtL_4Cl_2	650	$^1A_{1g}\rightarrow{}^3A_{2g}$	D	S
	480	$^1A_{1g}\rightarrow{}^3E_g$		
	455	$^1A_{1g}\rightarrow{}^1A_{2g}$		
	435	$^1A_{1g}\rightarrow{}^3B_{1g}$		
$Cu_2L_x(LH)_y(H_2O)_4$ $(x+y=2)$	800—450(br)	—	0.9	I
	440(sh)	Cu(I)-Cu(II) charge transfer		

Abbreviations: br, broad band; D, diamagnetic; I, insoluble; S, soluble in water and alcohol; s, slightly soluble in water; sh, shoulder.

susceptibility standard. Diamagnetic corrections were made by the method given in literature.[9] Electronic spectral bands and their assignments are given in Table 2.

Spectra. Visible and ultraviolet spectra were recorded in Nujol mulls with a Cary-14 spectrophotometer in the range 1600—300 nm. Infrared spectra were taken with a Perkin-Elmer 521 Grating Spectrophotometer in the range 4000—250 cm^{-1}, using Nujol mulls and KBr pellets. The major infrared bands are given in Table 3.

Results and Discussion

The ligand in solution exists in either thiol or thioxo form, behaving as a weak dibasic acid. In either form it has four bonding sites (three N's and one S). It can thus behave as a mono, bi, tri, or tetradentate towards one or more metal ions. However, a chelate ion is difficult to envisage, because of a four membered  ring, where C and N belong to a five membered heterocycles. We, thus, expect bridge configurations through the ligands which are bonded to two or more metal atoms. The formation of polymeric complexes is more likely to occur. This is also suggested by poor solubility of the complexes (except that of Pt(II)) in water or in organic solvents. Methods like NMR, molecular weight or conductivity measurements could not be used for their structural studies.

Magnetic Moments. The magnetic moments of Ni(II) and Co(II) (green) complexes (Table 2) are close to those of other octahedral complexes.[10] The value of Co(II) (pink) complex was slightly lower than the normal octahedral complexes but somewhat higher than the distorted tetrahedral complexes.[10,11] The distortion in the octahedral arrangement in the latter may thus be comparable to that of green complex.[11]

The complexes of Au(I), Rh(III), and Pd(II) are dia-

Table 3. Assignments of the major infrared bands of the ligand and complexes (cm^{-1})

Ligand		Complexes[a]			
Hydrogen form	Deuterated from	Ni(II), Co(II), Cu(II), Pd(II), Rh(III), Au(I)	Pt(II)	Cu(II)/(I) and Co(II) (pink)*	Assignment
3050(s)		3000	3160, 3140		νNH
—	2180 2250 (s)	—	—	—	νND
1580(s)	1550 1530 (w)	1570	1575, 1550	—	Thioamide band I[b]
1480(s)	1470(s)	1500(s)	1500, 1495	1475	νCN+δNH+νNN
1320(ms)	1310(ms)	1335(m)	1365	1330	
1275(m)	—	1290(m)	1270, 1280	1280	Thioamide band II[c]
1200(s)	1200(s)	1200	1220, 1210	1200	δCH
	1160	—	—	—	Mainly due to δND
1080(s)	1085(ms)	1075	1085, 1065 (1015)	1070	Due to νCN+νC=S
—	965	—	—	—	Mainly due to δND
960	960(m)	980	965, 975	970	νCN+νCS
690(m)	—	695	680, 685	—	τNH
650(m)	680(m)	640	650, 635	635 540	Thioamide band IV
550(m)	550(m)	530	500(br)		
—	520(mw)	—	—	—	τND
—	—	300—400	280—325	300—400	May be due to νMS and/or νMN

a) All those having water have bands due to νOH and δOH around 3300 and 1650 cm^{-1}. b) Mainly due to δNH+νCN. c) Due to δNH+νCN+δOH+νCN; * broad bands.

magnetic. This is what would be expected if they assume linear, octahedral, and square planar configurations, respectively.

The diamagnetism of the ruthenium complex is rather unexpected since $RuCl_3 \cdot xH_2O$ was used as the starting material for its synthesis. This could be due to either the presence of ruthenium in +2 oxidation state or spin pairing through NCS group. The former seems to be more probable since Ru(III) is a relatively powerful oxidizing agent and might be reduced to Ru(II) by the ligand during the course of the reaction.

Platinum complex was also found to be diamagnetic indicating the presence of platinum of +2 or +4 state. It is probable that platinum(IV) is reduced by the ligand to +2 state during the course of preparation.[12]

The magnetic moment of copper complex (0.9 B.M.) was found to be lower than that expected for one electron. Possibly Cu(II) ions were partially reduced to +1 state during the course of preparation, so that the complex obtained contains copper both in +2 and +1 states. This is also suggested by the black coloration of the complex where the charge transfer between Cu(I) and Cu(II) may be taking place through NCS group of the ligand. When the complex was decomposed in pyridine in N_2 atmosphere, the pyridine complex of Cu(II) of the type $Cu(py)_xL_y$ where $x<4$ was formed in solution, indicating at least a part of copper to be present in +2 state in the complex. Although a similar anomalous magnetic moment of Cu(II) in some copper complexes was interpreted in terms of antiferromagnetic interactions, either by forming σ or δ bond between two copper ions or by superexchange phenomenon through NCS group, a consideration of the reducing power of the ligand and the oxidizing power of the Cu^{2+} suggest that the partical quenching of paramagnetism in the complex is not due to such effects.

Visible Spectra. The visible spectra of all the complexes showed bands around 410 and 390 nm. The bands were also observed, slightly on the higher wave number side, in the spectrum of the ligand. They are thus due to ligand molecule (possibly arising from transition $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ of NCS group).

The positions of the bands in the spectrum of $NiL_2 \cdot 3H_2O$ (Table 2) are characteristic of those found for octahedral complexes of Ni(II)[11] which supports the octahedral structure of the complex. The bands at 950 and 640 nm are unsymmetrical, possibly owing to a slight distortion[12] from the O_h symmetry towards a rhombic or tetragonal one. From the positions of these bands the values of $10Dq$, B, β, and the position of the band due to $^3A_{2g} \rightarrow {}^3T_{1g}$ were calculated[13] to be 10160 cm^{-1}, 870 cm^{-1}, 0.85, and 10160 cm^{-1}, respectively, assuming O_h symmetry (approximately). The calculated value (10160 cm^{-1}) is quite close to that found experimentally (10530 cm^{-1}) which supports assignments. The value of β (0.85) indicates that the bonds between the ligand and the metal ion are essentially ionic having a small degree of covalence.[14]

In the assignment of the bands of $CoL_2 \cdot 3H_2O$ (assuming approximately octahedral symmetry) (Table 2), fitting the positions of the bonds give Dq, B and β as 860, 750 cm^{-1}, and 0.74 and places the $^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$ absorption band at 6480 cm^{-1} (near IR region) which could not be observed in our spectrum. Some splitting was found in the bands at 540 and 585 nm. This indicates that the orbital degenerate terms T_{1g} and T_{2g} are split because of the lowering of the symmetry of the complex from O_h.

The spectrum of $CoL \cdot 3H_2O$ showed a very broad weak band at 500 nm with shoulders at 530, 490, 470. The intensities of these shoulder bands were found to be nearly equal to each other as indicated by their respective optical densities. Apparently there is practically no symmetry in the complex, the degenerate terms *e.g.*, T_{1g} and T_{2g}, being split completely into non-degenerate ones. The evidence in support of the lowering of symmetry also comes from the magnetic moment values (4.5 B.M.), which is too low for an octahedral Co(II) ion.

The spectrum of copper complex showed a continuous absorption from 800 nm down to 450 nm followed by three, bands at 440, 410, and 395 nm. If copper in the complex is present in +2 state, we should expect one, three, and four bands in O_h, D_{4h}, and D_{2h} symmetry respectively. The continuous absorption and the presence of 440 nm band together with the magnetic evidence supports the view that copper in the complex exists in two mixed valence states. The band at 440 nm may then be assigned to mixed valence state band similar to that present in other mixed valence state copper complex.[15] It is the origin of the very dark coloration of this complex (dark brown to black) which is also characteristic of a mixed valence complex.

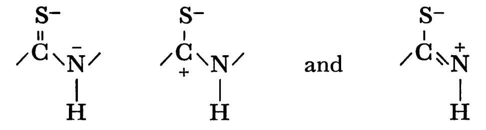
The spectrum of gold complex showed no band except the ligand bands at 410 and 395 nm. This suggests the oxidation state of gold as +1, which is also indicated by the formulla AuL where one of the two protons of NH groups is deprotonated.

The spectrum of ruthenium complex is similar to that of copper with ligand bands at 410 and 390 nm, no d-d band appearing in the visible region owing to intense absorption.

The bands at 650 and 480 nm in the spectrum of PtL_4Cl_2, and at 735 and 530 nm in the PdL_2 spectra were found to be much weaker than the other bands. In a d^8 system, we expect six transitions in D_{4h} symmetry (three spin allowed and three weak spin forbidden bands)[16] (Table 2). The values of parameters calculated from the positions of these bands are as follows: PdL_2: $\Delta_1=23800$ cm^{-1}, $\Delta_2=7200$ cm^{-1}, $\Delta_3=2900$ cm^{-1}, $B=200$ cm^{-1}, $C=3300$ cm^{-1}; PtL_4Cl_2: $\Delta_1=25300$ cm^{-1}, $C=3300$ cm^{-1}. In the case of Pd, the calculated frequency for the band due to $^1A_{1g} \rightarrow {}^1B_{1g}$ was found to be 29700 cm^{-1} which is close to the value found experimentally (30000 cm^{-1}), supporting our assignments. In case of Pt, owing to the lack of data, some of the parameters have not been calculated.

The spectrum of Rh complex showed no band except at 410 and 395 nm. However, there was a continuous strong absorption whose intensity decreased gradually from 650 to 400 nm. The weak d-d bands are possibly obscured by the intense charge transfer band (L→M) present in the visible region. No information regarding the structure of the complex has been obtained from the visible spectral studies.

Infrared Spectra. The ligand is best described as a resonance hydrid of the structures:



(I) (II) (III)

Metal coordination through sulfur will lead to a decrease in the thiocarbonyl stretching force constant and an increase in CN force constant. Coordination to nitrogen, on the other hand, would increase the contribution of structure I to the ground state of the complexes and cause an increase in the thiocarbonyl frequencies and decrease in CN and NH stretching frequencies.[17,18]

In order to determine the coordination sites in the complexes, we have classified the spectra of the complexes into the following four groups (A to D):

(A) Spectra of Ni(II), Co(II), Cu(II), Pd(II), Rh(III), and Au(I).

(1) The positions of those bands having contributions from νCN (1480, 1320, 1275 cm^{-1}) shifted towards higher wave number (+20 cm^{-1}) suggesting the increase in CN bond order.

(2) The shifts in the positions of bands at 1080 and 960 cm^{-1} were small ($\pm$10 cm^{-1}). There also appeared a band around 1020 cm^{-1} which may be due to two different types of νCN.

(3) The positions of the bands arising mainly from νCS, *viz.*, 650 and 550 cm^{-1} shifted to lower wave numbers ($-$20 cm^{-1}).

(4) The positions of the bands arising from νNH, δNH and τNH remained practically constant, their relative intensities decreasing.

(5) In the spectra of Ni(II), Co(II), Cu(II), and Rh(II) the characteristic bands due to νOH and δOH were present around 3400 cm^{-1} (broad) and 1650 cm^{-1} (medium) respectively.

All the above shifts can be explained by the assumption that the metal ion is coordinated to one of the NH groups after deprotonation and the thiocarbonyl sulfur with relatively strong interaction.

(B) Spectra of Pt(II).

(1) All the bands having contributions from νNH, δ NH and τNH were split with the separation $\pm$10 cm^{-1} around the positions found in the spectrum of the ligand.

(2) The positions of νCN bands shifted to higher wave numbers and were split (10—20 cm^{-1}).

(3) The positions of the νCS bands shifted to lower wave number. The band at 500 cm^{-1} was broad while that of 525 cm^{-1} was split.

These observations can be explained if the platinum ion in the complex is assumed to be bonded separately with four thiocarbonyl sulfur atoms of the four ligand molecule arranged in a square planar arrangement to form an ionic complex [PtL$_4$]Cl$_2$.

In such a bonding scheme we should expect the interaction between νCN bands and δNH bands in one ligand molecule to give asymmetric and symmetric modes of vibration.

(C) Spectrum of Ru(II). The spectrum of ruthenium is quite complicated, but the positions and shifts of the bands appear to be similar to those of the combined spectra of Group A (*e.g.*, Ni(II) or Co(II)) and Group B (Pt(II)) complexes, with the bands at 3000, 3150, 1570, 1550, 1500, 1335, 1360, 1290(br), 1200(br), 1075, 1060, 980, 970, 695, and 680 cm^{-1}). It is therefore assumed that two of the three ligand molecules are linked with thiocarbonyl sulfur and nitrogen after deprotonation, while the third ligand molecule is linked with thiocarbonyl sulfur strongly and nitrogen without deprotonation weakly. This is in line with the charge balance in the complex where ruthenium atom is assumed to be in +2 oxidation state.

(D) Spectra of Cu(II/I) and Co(II) (pink). Since it is improbable for cobalt to be reduced in +1 state by the ligand, the formula indicates that both the NH groups of the ligand are deprotonated. Owing to the presence of broad bands due to water molecule around 3300 and 1600 cm^{-1}, the band due to νNH could not be confirmed. However, no band at 690 cm^{-1} assigned to τNH appeared in the spectrum of the complex, suggesting the possibility of complete deprotonation. Further in the finger print region bands were rather broad and no definite conclusion regarding their structure could be drawn. The general pattern in the shifts of the band positions are similar to those of Group A, suggesting at least a linkage of the ligand through nitrogen and thiocarbonyl sulfur.

On the basis of these data the following structures were assigned:

(i) NiL$_2$(H$_2$O)$_3$, CoL$_2$(H$_2$O)$_3$, CoL(H$_2$O)$_3$, RhL$_3$(H$_2$O)$_2$, RuL$_3$, CuL(H$_2$O)$_2$: Octahedron with bonding through thiocarbonyl sulfur and –NH nitrogen, the latter after deprotonation. Except for Rh and Ru complexes water molecules are also coordinated.

(ii) PdL$_2$: Square planar with bonding through thiocarbonyl sulfur and –NH nitrogen, the latter after deprotonation.

(iii) PtL$_4$Cl$_2$: Square planar with bonding through thiocarbonyl sulfur.

(iv) AuL: Linear with bonding through thiocarbonyl sulfur and –NH nitrogen, the latter after deprotonation.

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