Complexing Behaviour of 5-Amino-1,3,4-Thiazole-2-thiol. II. Complexes of Ni(II), Rh(I), Pd(II), Pt(II), Au(III) and Cu(II)

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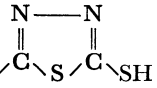
Complexes of Ni(II), Rh(I) Pd(II), Pt(II), Au(III) and Cu(II) with 5-Amino-1,3,4-thiadiazole-2-thiol have been prepared. Probable structures have been proposed for the complexes on the basis of visible and infrared spectral and magnetic susceptibility data and results of chemical analysis. Crystal field parameters have been calculated wherever possible.

In our previous communication¹⁾ we had indicated our interest in the study of metal complexes with 5-amino-1,3,4-thiadiazole-2-thiol (I).



(I)

This has been used earlier as an analytical reagent.²⁻⁴⁾ Structure elucidation of the metal complexes of this ligand have not so far been done and the present work is an attempt an investigating the structural aspects of metal complexes with this ligand. In this communication, we report the preparation and characterisation of the complexes of Ni(II), Rh(I), Pd(II), Pt(II), Au(III) and Cu(II) with the ligand in question.

Experimental

The chemicals used were all of Analar or chemically pure grade.

I *Preparation of the Ligand.* *(a) 5-Amino-1,3,4-thiadiazole-2-thiol*: This was prepared by the method given by Sandstrom.⁵⁾ The ligand is hereafter referred to as (Htta) in the abbreviated form.

(b) Deuterated form of 5-Amino-1,3,4-thiadiazole-2-thiol: About 0.1 g of (I) was dissolved in 25 ml hot D_2O and the resulting solution refluxed for 6 hr under dry nitrogen. On cooling, the deuterated ligand crystallized. The crystals were separated by centrifugation and dried in a vacuum desiccator overnight, and finally in an oven at 105°C for 4 hr.

II *Preparation of the Metal Complexes.* *(a) Bis(5-amino-1,3,4-thiadiazole-2-thiolato)diaquonickel (II)*: A solution of 1.8 g (~5 mmol) of $NiCl_2 \cdot 6H_2O$ in 25 ml water was added to a solution of 1.4 g (~10 mmol) of (I) in about 60 ml mixture of alcohol and water (1 : 1), neutralised with NH_4OH solution. A bluish green complex was immediately formed. The product was digested on a water bath for an hour, centrifuged, washed repeatedly with hot water, warm alcohol and finally with ether. The residue was dried in a vacuum desiccator about 6 hr.

(b) Chloro(5-amino-1,3,4-thiadiazole-2-thiolato)dipyridinenickel(II): About 10 ml of pyridine was added to a solution of 1.8 g (~5 mmol) of $NiCl_2 \cdot 6H_2O$ in 25 ml water. A deep blue solution resulted. This was then added to a solution of 1.4 g (~10 mmol) of (I) in about 60 ml mixture of alcohol and water (1 : 1), neutralised with NH_4OH solution. A greyish green complex was slowly formed on heating the solution on a water bath. The product was digested on the water bath for an hour, centrifuged, washed and dried as described in II(a).

(c) Chlorobis(5-amino-1,3,4-thiadiazole-2-thiol)triphenylphosphine rhodium(I): Chlorotris(triphenylphosphine)rhodium(I) was first prepared by the method given in literature.⁶⁾

A solution of 0.6 g (~0.67 mmol) of $Rh(P\text{Ø}_3)_3Cl$ in 25 ml warm benzene was added to a solution of 0.4 g (~3 mmol) of (I) in 50 ml alcohol. The resulting solution was digseted on a water bath for an hour when a reddish brown complex was formed. The product was centrifuged, washed repeatedly with hot benzene, warm alcohol and finally with ether. The residue was dried in a vacuum desiccator overnight.

(d) Bis(5-amino-1,3,4-thiadiazole-2-thiolate)palladium(II): A solution of 0.35 g (~2 mmol) of $PdCl_2$ was prepared in 50 ml warm water containing KCl. This was added to a solution of 0.35 g (~4 mmol) of (I) in a 50 ml mixture of alcohol and water (1 : 1). A chocolate red complex was immediately formed. It was digested on a water bath, centrifuged, washed and dried as described in II(a).

(e) Bis(5-amino-1,3,4-thiadiazole-2-thiolate)platinum(II): K_2PtCl_4 was first prepared by the method given in the literature.⁷⁾

A solution of 0.4 g (~1 mmol) of K_2PtCl_4 in 20 ml water was added to a solution of 0.30 g (~2 mmol) of I in 25 ml alcohol. A rose red complex was formed when the solution was heated on a water bath. The rest of the procedure was the same as that described in II(a).

(f) Tris(5-amino-1,3,4-thiadiazole-2-thiolate)gold(III): A solution of 0.45 g (~1 mmol) $AuCl_3$ in about 10 ml water was added to a solution of 0.4 g (~3 mmol) of (I) in 30 ml alcohol. A pale yellow complex was immediately formed. The product was digested on a water bath for an hour, centrifuged, washed and dried as described in II(a).

(g) Bis(5-amino-1,3,4-thiadiazole-2-thiolato)copper(II): A solution of 0.8 g iodine in 50 ml alcohol was added to a solution of 1.2 g (~6 mmol) of $CuCl_2$ $2H_2O$ in 30 ml alcohol. The resulting solution was then added to a solution of 1.6 g (~12 mmol) of (I) in 100 ml alcohol. A green complex was immediately formed on mixing. The product was digested on a water bath, centrifuged, washed and dried as described in II(a).

Analyses. The sulphur, phosphorus and chloride (wherever present) in the ligand and the complexes were estimated by standard method.⁸,⁹⁾ The analyses of the metal ions in the complexes were carried out by the methods given in literature.⁹,¹⁰⁾

Carbon, hydrogen and nitrogen were analysed by the microanalytical section of the Indian Institute of Technology, Kanpur.

The results of all the analyses are given in Table 1.

Magnetic Susceptibilities. Magnetic susceptibilities of the complexes were determined at room temperature with a Guoy balance. Mercurytetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard. Diamagnetic

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corrections were calculated by the method given in literature.11) The values of the magnetic moments are given in Table 1.

Spectra. *(i) Visible and Ultraviolet*: The absorption spectra of the ligand and the complex were recorded with a Cary-14 recording spectrophotometer in alcoholic solution and nujol mull respectively in the range 1600—300 nm. The absorption bands are given in Table 2.

(ii) Infrared: The infrared spectra of the ligand and the complexes were taken with the help of a Perkin-Elmer 521 Grating Infrared Spectrophotometer in the range 4000—250 cm^{-1}, using KBr pellets of the samples. The major infrared bands are given in Table 3.

Results and Discussion

Magnetic moments. *(i) Complexes of Ni(II)*: The experimental values of the magnetic moments of $Ni(tta)_2(H_2O)_2$ and $Ni(py)_2(tta)Cl$ as given in Table 1 are close to those reported in literature for other octahedral Ni(II) complexes.

(ii) Complexes of Rh(I), Pd(II), Pt(II), and Au(III): All these complexes are found to be diamagnetic. The diamagnetism of these complexes supports the square planar arrangement of the ligand molecules around the central metal ion.

(iii) Cu(II) Complexes: This complex is diamagnetic. Only in a few Cu(II) complexes, the paramagnetism equivalent to one unpaired electron is completely quenched ($\mu_{eff}=0$) at room temperature,12,13) as against partial quenching observed in the case of several Cu(II) complexes.14–16)

Since the complex is prepared in the presence of stoichiometric amounts of I_2, reduction of Cu^{2+} to Cu^+ and hereby the diamagnetic behaviour of the complex appears to be highly unlikely. Also the complex of Cu(I), prepared (and reported elsewhere)17) by reducing Cu^{2+} ions with SO_2 solution followed by treatment with the ligand, has totally different physical porperties and stoichiometry in contrast to the Cu(II) complex.

With a view to knowing the oxidation state of the metal ion in the Cu(II) complex, the authors dissolved the Cu(II) complex in pyridine and determined the magnetic susceptibility of the solution, when the complex showed a magnetic moment of 1.77 B.M. Since pyridine is not an oxidising agent is it unlikely that the Cu^+ ions, if present at all, in the complex, could have been oxidised to Cu^{2+} to account for the observed paramagnetism in pyridine solution.

The spin-pairing in the complex may be explained by the overlap of the d_{z^2} or $d_{z^2-y^2}$ orbitals of the Cu^{2+} ions resulting in σ or δ bond formation,18–20) or by super-exchange mechanism.21) In complexes with ligands containing sulphur as donor atom, bonding of the metal ion with the easily polarizable sulphur atom of the ligand may result in a large transfer of electron density from sulphur to the metal ions with the consequent increase in the overlap of the metal orbitals.22) Hence a direct metal-metal bond is preferred for the quenching of the paramagnetism over super exchange mechanism. However, it is only tentative.

Electronic Spectra. *(i) Complexes of Ni(II)*: The visible spectrum of $Ni(tta)_2(H_2O)_2$ shows three bands whose positions are characteristic of those found for other octahedral complexes of Ni(II). In the spectrum of $Ni(py)_2(tta)Cl$, only two bands are seen. The third band, expected around 27000 cm^{-1}, may be masked by the intense charge transfer band due to pyridine molecule. The positions of these bands together with their assignments are given in Table 2. These are taken as evidence in support of the octahedral geometry of the ligand molecules around the central metal ion.

Besides these bands, a shoulder appears at 875 nm

Table 1. Analytical data, magnetic moments and solubilities of the ligand and the complexes

	Compound		C	H (or D)	N	S	Cl	P	M	Magnetic moment	Solubility
I(a)	Ligand	Calcd	18.0	2.26	31.6	48.1	—	—	—	—	s in water
	$C_2H_3N_3S_2$	Found	17.8	2.40	31.8	47.7	—	—	—		S in alcohol
(b)	Ligand(deuterated)	Calcd	17.7	4.41	30.9	47.1	—	—	—	—	s in water
	$C_2D_3N_3S_2$	Found	17.9	2.7	31.3	46.9	—	—	—		S in alcohol
II(a)	$Ni(C_2H_2N_3S_2)_2(H_2O)_2$	Calcd	13.4	2.23	23.4	35.7	—	—	16.4	3.01 BM	I
		Found	13.1	2.00	23.3	35.2	—	—	16.1		
(b)	$Ni(C_5H_5N)_2(C_2H_2N_3S_2)Cl$	Calcd	37.5	3.13	18.2	16.7	9.2	—	15.3	2.97 BM	I
		Found	37.8	3.40	18.0	16.2	8.5	—	15.1		
(c)	$Rh(P(C_6H_5)_3)(C_2H_3N_3S_2)Cl$	Calcd	39.6	3.06	12.6	19.3	5.2	4.7	15.5	D	s in alcohol
		Found	39.6	3.00	12.7	19.0	4.5	4.0	15.0		
(d)	$Pd(C_2H_2N_3S_2)_2$	Calcd	13.0	1.08	22.7	34.6	—	—	28.7	D	I
		Found	12.8	1.50	23.1	34.2	—	—	28.6		
(e)	$Pt(C_2H_2N_3S_2)_2$	Calcd	10.5	0.87	18.3	27.9	—	—	42.5	D	I
		Found	10.2	1.01	18.0	28.0	—	—	41.7		
(f)	$Au(C_2H_2N_3S_2)_3$	Calcd	12.1	1.01	21.2	32.4	—	—	33.2	D	I
		Found	11.9	1.00	20.5	31.2	—	—	32.0		
(g)	$Cu(C_2H_2N_3S_2)_2$	Calcd	14.7	1.22	25.7	39.1	—	—	19.4	D	I
		Found	14.3	1.09	25.4	38.6	—	—	19.1		

s=slightly soluble; S=soluble; D=diamagnetic; I=insoluble in water and other common non-coordinating organic solvents.

TABLE 2. ELECTRONIC SPECTRAL BANDS, THEIR ASSIGNMENTS AND CRYSTAL FIELD PARAMETERS[a)]

Complex		Band position nm	Band position cm^{-1}	Assignment	A_q^A cm^{-1}	D_q^E cm^{-1}	D_t cm^{-1}	B cm^{-1}	β	Δ_1 cm^{-1}	Δ_2 cm^{-1}	C cm^{-1}
1		2	3	4	5	6	7	8	9	10	11	12
1. $Ni(tta)_2(H_2O)_2$	ν_1	1050	9524	$^3B_{1g} \rightarrow {}^3B_{2g}$								
	ν_1'	875	11430	$^3B_{1g} \rightarrow {}^3E_g$								
	ν_2	625	16000	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	775	1143	218	762	0.75			
	ν_2'	—	—	—								
	ν_3	400	25000	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$								
2. $Ni(Py)_2(tta)Cl$	ν_1	1050	9524	$^3B_{1g} \rightarrow {}^3E_g$								
	ν_1	970	10310	$^3B_{1g} \rightarrow {}^3B_{2g}$								
	ν_2	600	16667	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	1010 (Py)	952 (Cl+tta)	−90	866	0.85			
	ν_2	625 sh	16000	due to departure from O_h symmetry								
	ν_3	—	—	—								
3. $Rh(PØ_3)(Htta)_2Cl$		Charge transfer band only										
4. $Pd(tta)_2$	ν_1	500	18200	$^1A_{1g} \rightarrow {}^3E_g$				750		20820	4852	2620
	ν_2	480	21000	$^1A_{1g} \rightarrow {}^1A_{2g}$								
5. $Pt(tta)_2$	ν_1	740	13500	$^1A_{1g} \rightarrow {}^3A_{2g}$				750		25200	9250	3900
	ν_2	625	16000	$^1A_{1g} \rightarrow {}^2E_g$								
	ν_3	470	21300	$^1A_{1g} \rightarrow {}^1A_{2g}$								
6. $Au(tta)_3$	ν_1	600	16667	$^1A_{1g} \rightarrow {}^3A_{2g}$				750		25116	7995	2816
	ν_2	520	19230	$^1A_{1g} \rightarrow {}^3E_g$								
	ν_3	445	22300	$^1A_{1g} \rightarrow {}^1A_{2g}$								
7. $Cu(tta)_2$	ν_1	700	14285	$d_{xy} \rightarrow d_{z^2}$								
	ν_2	620	16130	$d_{xy} \rightarrow d_{x^2-y^2}$								

a) Calculations based on expressions given in Ref. 23 (pp. 310 and 338) for Ni and Ref. 28 (p. 69) for others.

TABLE 3. MAJOR INFRARED SPECTRAL BANDS AND THEIR ASSIGNMENTS IN THE CASE OF LIGAND AND THE COMPLEXES

Ligand cm^{-1}	Ligand (Deuterated) cm^{-1}	Ni(II) Complexes cm^{-1}	Rh(I) Complex cm^{-1}	Au(III) Complex cm^{-1}	Other Complexes cm^{-1}	Assignments
		$3500^{a)}$ m				$\nu_{(O-H)}$
		$3400^{b)}$ m				Characteristic of Py
2900— $3400^{c)}$ s	3000— $3400^{d)}$ m	3160— 3400 mb	2900— 3380 mb	3080— 3380 mb	3080— 3280 mb	$\nu_{(N-H)}$
2570 m	—	—	2570 w	—	—	$\nu_{(S-H)}$
—	2300—2450 m	—	—	—	—	$\nu_{(N-D)}$
—	1750 w	—	—	—	—	$\nu_{(S-D)}$
1600 s	1580 sh	1605±5 s	1600 s	1634 s	1630±10 s	
1535 s	1550 s			1590 sh	$1590^{e)}$±10 s	Thioamide band I[g)]
1500 s	1530 s	1525±5 s	1515 s	1500 s	$1525^{f)}$	
	1460 m				1490±10 s	
1365 s	1365 s	1400±10 m	1335—1370 mb	1420 w	1390±5 m	
1335 m	1335 s	1350±10 m		1390 m	1310±10 w	Thioamide band II[h)]
				1320 w		
1080 sh	1030—80 sb	1050±5 sb	1050 m	1060 mb	1040±10 m	
1070 sh				1040 wb		Thioamide band III[i)]
1060 s						
750 m	—	750 w	750 m	740—700 mb	690±10 m	$\tau_{(N-H)}$
—	730 sh	—	—	—	—	$\tau_{(N-D)}$
735 m	720 m	635±5 w	700 s	630 w	630±10 m	Thioamide band IV[j)]
		450—350 w (two bands)	400 w	450—350 w (two bands)	450—350 w (two bands)	$\nu_{(M-N)}$ $\nu_{(M-S)}$

a) present in $Ni(tta)_2(H_2O)_2$. b) present in $Ni(Py)_2(tta)Cl$. c) multiple bands well resolved. d) perhaps due to some protons remaining over unexchanged with deuterium. e) present in Pt(II) and Cu(II) complexes. f) present in Pd(II) complex. g) due to $\delta_{(NH)}$ (major contribution)+$\nu_{(CN)}$ (minor contribution. h) due to $\delta_{(HH)}$ (minor contribution)+$\nu_{(C=N)}$ (major contribution). i) due to $\nu_{(C-N)}$; j) due to $\nu_{(C=S)}$.
s=strong. m=medium, mb=medium broad, w=weak, shoulder.

in the case of the aquo complex and 970 nm in the case of the pyridine complex. These could be assigned to departure from O_h towards D_{4h} symmetry, on the assumption that the water or the pyridine molecules are *trans* to each other in the respective complexes. In the D_{4h} symmetry, all the three bands should split. But the spectrum of the aquo complex does not show any such splitting of the bands at 625 nm and 400 nm. This may be because both the terms $^3T_{1g}(F)$ and $^3T_{1g}(P)$ yield $^3A_{2g}$ and ^3E_g terms in D_{4h} symmetry. In the strong fields the components of the $^3T_{1g}(F)$ level lies in the sequence $^3A_{2g}<^3E_g$, while those of the $^3T_{1g}(P)$ level are inverted ($^3E_g<^3A_{2g}$). Thus, when configurational interactions are taken into consideration, the splittings tend to cancel out[23] and it would be difficult to resolve the bands due to these transitions. The amount of splitting in the 1050 nm band may be taken as a measure of the degree of distortion.[24,25]

The values of D_q^E, D_q^A and D_t have been calculated using the expressions given in the literature[23] (Table 2). In these calculations the field strengths due to water and pyridine have been assumed respectively to be less than and greater than that due to ligand.

It may be noted that the values of B and β are quite low. This puts the ligand towards the strong end of the nephelauxetic series. As was pointed out by Schaffer[26] and later on by Jørgensen[27] the low value of β independently suggests bonding through sulphur.

(ii) Complexes of Rh(I), Pd(II), Pt(II) and Au(III): Metal ions of d^8 system exhibit square planar structure in most of their complexes.[28] In D_{4h} symmetry of the field, the d orbitals split into four levels, *viz.*, b_{1g}, b_{2g}, a_{1g}, and e_g. The ground state for the low spin d^8 system is $^1A_{1g}$ $(=a_{1g}^2 \cdot e_g^4 \cdot b_{2g}^2)$.[28] The ligand field excited states are $^3A_{2g}$, $^1A_{2g}$ $(b_{2g}\rightarrow b_{1g})$, ^3E_g, $^1E_g(e_g\rightarrow b_{1g})$ and $^3B_{1g}$, $^1B_{1g}$ $(a_{1g}\rightarrow b_{1g})$. Therefore, one should expect three spin allowed and three spin forbidden transitions in these cases. In the electronic spectra of the Rh(I), Pd(II), Pt(II) and Au(III) complexes, the bands obtained together with their probable assignments are given in Table 2. Owing to the forbidden nature of the singlet→triplet transitions, it is quite probable that they may not appear at all in the electronic spectra some of the complexes in nujol mull.

The low intensity bands arising out of transition, $a_{1g}\rightarrow b_{1g}$ could not be assigned unambiguously, since the intense charge transfer bands (L→M) masks the forbidden d–d transition bands. The shift of the intense charge transfer bands in the spectra of some of the complexes is in accordance with the optical electronegativity values,[29] with the result that all the d–d transition bands in the case of Rh(I) complex are masked by the charge transfer bands. The metal ions with next higher optical electronegativity values are Pt(II) and Au(III). Charge transfer bands in the case of complexes of these metal ions start from 450 nm, with the result that the d–d transition bands in these cases appear only as shoulders. The spectrum of Pd(II) ion having highest value of the optical electronegativity exhibits bands due to d–d transition in the visible region.

Assuming the value of B to be 750 cm^{-1}, the values of C, Δ_1 and Δ_2 were calculated on the basis of the assignments given in Table 2. These values compare quite well with those cited in literature for other complexes of these metal ions. This suggests that the field around the metal ion should be tetragonal (D_{4h}-symmetry). This is also in conformity with the preferred orientation of the ligand molecules in the complexes of these metal ions.[30]

It is interesting to note that the value of Δ_1 is much larger than that of Δ_2. This means that similar to other σ or π donor molecules, the ligand molecules cause a marked destabilization of the b_{1g} level ($d_{x^2-y^2}$ orbital) as compared to other d orbitals. This is what one should expect in the square planar geometry.

The value of Δ_1 depends on the relative energy of $b_{1g}(d_{y^2-x^2})\sigma^*$ and $b_{2g}(d_{xy})\pi^*$ levels and therefore, both σ and π bonding are the contributing factors (π acceptor ligands cause destabilization of the b_{1g} level, keeping the b_{2g} level essentially non-bonding). Table 2 also shows Δ_1 value of the Pd(II) complex to be less than the Δ_1 value of Pt(II) complex. The increase in the value of Δ_1 for Pt(II) complex may be due to the increasing σ-bond strength in the order $4d\sigma<5d\sigma$. This result is quite in conformity with existing results. Also the values of Δ_1 for Pt(II) and Au(III) complexes are nearly the same. This reslt is also in agreement with the results of molecular orbital calculations.[31]

(iii) Cu(II) Complex: As already discussed, the Cu(II) complex is diamagnetic. Harris, *et al.*[32] have proposed a structure for the diamagnetic Cu(II) complex of diazoaminobenzene in which there is metal-metal interaction and the Cu^{2+} ion has squareplanar geometry. The electronic spectrum of this complex shows two bands at 670 nm and 530 nm. These were assigned by them tentatively to $d_{xy}\rightarrow d_{z^2}$ and $d_{xy}\rightarrow d_{x^2-y^2}$ transitions. Tsuchida *et al.*[33,34] have observed a band around 375 nm in all the diamagnetic carboxylate complexes of Cu(II). They have suggested that these bands are characteristic of metal-metal interaction.

The Cu(II) complex reported here has in its electronic spectrum, a shoulder at 700 nm, a weak and broad band at 620 nm and a well defined band at 425 nm. Assuming a square planar arrangement of the ligand molecules around Cu^{2+} ion, these bands are assigned to $d_{xy}\rightarrow d_{z^2}$, $d_{xy}\rightarrow d_{x^2-y^2}$ and metal-metal bond respectively. The assignments, however, are tentative.

Infrared Spectra. From the analytical, electronic spectral and magnetic susceptibility data given in Tables 1 and 2, it appears that the ligand is acting as bidentate in most of the complexes reported here. This is quite in keeping with the preferred geometries the metal ions would take in their complexes.

In solution the ligand can exist either in the thiol form or in the thione form or both. It is believed that it exists as tautomers. Infrared spectral studies were made, with a view to ascertaining the existence of tautomerism and to know the mode of linkage with metal ions in the complexes.

In order to confirm our assignments, the IR spectrum of the deuterated ligand was also studied. Since shifts due to isotopic effect could be expected in the positions of only those bands which arise due to fundamental modes of vibration of the NH and the SH groups, comparison of these two spectra confirms not only the assignment but also the existence of the ligand in the thiol form (Table 3).

A close look at the infrared spectra of the complexes suggests that the complexes can be classified into groups on the basis of the direction of shifts in the positions of the major bands in their spectra. The spectra of all the complexes in any group are similar so far as the direction of shifts in the band positions is concerned. It is reasonable to expect the bonding scheme in these complexes to be the same. The following is a brief groupwise discussion regarding the shifts in the positions of the major bands in the spectra of the complexes.

(i) Complexes of Ni(II). The major shifts in the positions of bands were found to be similar to those of cobalt(II)[1] and therefore, the mode of bonding in nickel complex (Fig. 1) should be the same as that of cobalt complex.[1]

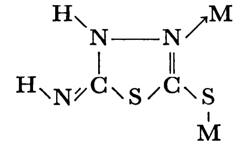


Fig. 1.

(ii) Complexes of Pd(II), Pt(II), and Cu(II). In the spectra of this group of complexes, the shifts in the position of the bands are similar to those found in the spectra of the complexes of Ru(III), Rh(III), Ir(III), Pd(IV).[1] Thereby the mode of linkage in these complexes as shown in Fig. 2 should be identical with those in Rh(III), Ru(III), Ir(III) and Pd(IV) complexes.[1]

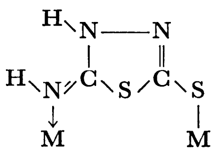


Fig. 2.

(iii) Rh(I) Complexes. (a) The band at 2750 cm^{-1} in the spectrum of the ligand is also seen in that of the complex. (b) Bands due to $\nu_{(N-H)}$, $\delta_{(N-H)}$ and $\tau_{(N-H)}$ appear in the spectrum of the complex at about the same positions as in the spectrum of the ligand. (c) Thioamide band II shifts slightly towards higher wave number side. (d) Thioamide band III remains practically unchanged. (e) Thioamide band IV shifts towards lower wave number side. (f) New bands appear in the region of 400 cm^{-1}. (g) All bands due to triphenylphosphene molecule appear in the spectrum of the complex with slight shifts in their positions.

These results can be explained if the mode of bonding is as shown in Fig. 3.

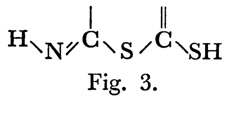


Fig. 3.

From this type of bonding it is evident that the positions of the bands due to (a) $\nu_{(S-H)}$ should not disappear and (b) $\nu_{(N-H)}$, $\delta_{(N-H)}$ and $\tau_{(N-H)}$ should not shift. The bond order of (C=N) should increase, while that of (C=S) should decrease and $\nu_{(M-N)}$ coupled with other bending modes of vibration of the ligand molecule should appear.

(iv) Au(III) Complex. The infrared spectrum of this complex is quite complicated because most of the bands are either split or broadened. In the spectrum of the Au(III) complex, the positions of most of the major bands are the same as those present in the spectra of Pd(II) and Ni(II) complexes (except those of water or pyridine in the latter complex). This behaviour is not quite unexpected because three ligand molecules as required by stoichiometry can be arranged in a square planar geometry around the metal ion (as determined from magnetic and visible spectral data) only in one way and that is two of the ligand molecules act as monodentate whereas the third one, as bidentate as shown in Fig. 4.

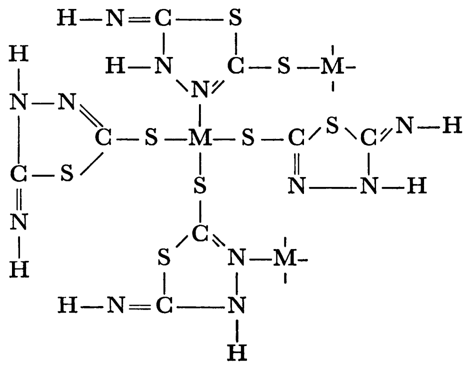


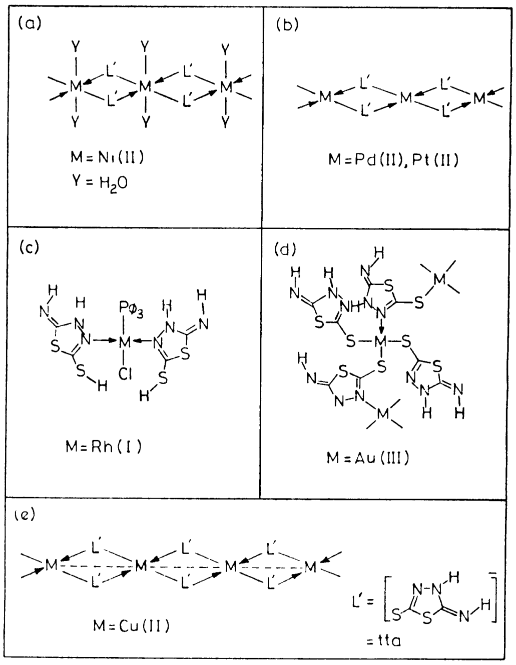
Fig. 4.

It is evident from this mode of bonding that the bond orders of (C=N) of the bonded N=C–SH and the unbonded H–N–C=N–H groups in the mono and bidentate ligand molecules should be different (next page).

It is reasonable to expect that the fundamental modes of vibrations of (C=N) bonds with different bond orders in the same ligand molecule interact strongly while those in different ligand molecules would interact rather weakly. As a result of these interactions, thioamide band II would appear considerably split bands should appear at higher wave number, one at slightly higher wave number and one at lower wave number. The appearance of bands at 1420, 1390, and 1320 cm^{-1}, assigned to thioamide band II is in keeping with the results expected. Besides, the shift of thioamide band IV towards lower wave number side lends support to the bonding scheme proposed. (next page)

With the exception of Rh(I) complex which is very slightly soluble in alcohol, all the other complexes reported here are insoluble in water and other common non-coordinating organic solvents. This suggest that they are polymeric in nature.

Therefore, on the basis of the analytical, magnetic and spectral data as well as the preferred geometries the metal ions would take in their complexes, the following plausible polymeric structures are proposed for the complexes.



Scheme.

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