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# MIXED LIGAND TRANSITION METAL COMPLEXES OF TRIDENTATE SCHIFF BASE WITH THIOCYANATE

***M Saidul Islam*, M Akhter Farooque and M A K Bodruddoza***

*Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh*

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A tridentate Schiff base $C_{13}H_{20}N_2O$ having ONN donor sequence has been synthesised from the condensation of 1.6-diaminohexane with salicylaldehyde. Several new thiocyanato complexes of Cu (II), Pd (II), Ti (III) and V(IV) containing the above ligand have been synthesised and characterized by elemental analyses, conductivity, magnetic measurements, IR and NMR spectra and electronic spectroscopic studies. Magnetic and spectral data support the octahedral geometries for Ti (III) and V(IV) complexes, whereas Cu(II) and Pd(II) complexes are square-planar in nature.

***Key words*****:** Thiocyanato complexes of Schiff base, Mixed ligand, Transition metal.

## Introduction

There is considerable interest in coordination chemistry of thiocyanato complexes of transition metals as such a study reveals some fundamental aspects of metal ions. (Ahrland *et al* 1958; Pearson 1963; Basolo *et al* 1964; Destefano and Burmeister 1971; Meelpolder and Burmeister 1972; Laner *et al* 1972; Gelbman and Westland 1975; Makhija and Westland 1977; Westland and Tarafder 1983; Tarafder and Fatema 1988). Thiocyanato complexes of transition metals are the key compounds in this area and we have a programme to synthesize new complexes of this kind to understand the bonding and structures of these complexes. Several thiocyanato complexes containing unidentate and bidentate auxiliary ligands have been reported. (Basolo *et al* 1964; Lauer *et al* 1972; Tarafder and Fatema 1988; Trafder *et al* 1988). We report here the synthesis and characterisation of thiocyanato complexes of Cu(II). Pd(11), Ti(III) and V(IV) containing the tridentate ONN ligand derived from the condensation of 1,6-diaminohexane with salicylaldehyde.

## Experimental

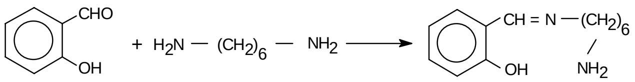
*Physical measurements.* The IR spectra (KBr disc) were recorded on Shimadzu IR-470 and Perkin Elmer IR-400 spectrophotometer. $^1H$ NMR in DMSO-$d_6$ were obtained with Bruker DRX-400 (400.13 MHz) NMR spectrophotometer. Conductivities of $10^{-3}$ M solutions of the complexes in DMSO were measured at room temperature using a WPA CM 35 conductivity meter and a dip-type cell with platinized electrodes. Magnetic measurements have been carried out in a Jhonson Mathey magnetic susceptibility balance at room temperature. Electronic spectra were obtained on a LKB-Ultrospec K4053 spectrophotometer. Melting point and decomposition point of complexes have been taken in an electrothermal melting point apparatus. The molecular weights of the complexes were determined in nitrobenzene by the cryoscopic method.

Palladium, vanadium and titanium were estimated gravimetrically using standard procedure (Vogel 1978). Copper was estimated complexometrically using EDTA (Vogel 1961).

Microanalyses for carbon, hydrogen and nitrogen were performed by the microanalytical services of the Department of Chemistry, University of St. Andrews, Scotland.

*Reagents and chemicals.* All chemicals used were of AR grade and used as supplied by E Merck and BDH Ltd. Ethanol was purified by refluxing the crude 99% product with iodine and magnesium turnings.

*Preparation of Schiff base* $C_{13}H_{19}N_2OH$ *(HONN).* Salicylaldehyde (0.61g, 0.005 mol) in absolute ethanol (20 ml) was added to an ethanolic (25ml) solution of 1.6-diaminohexane (0.58g, 0.005 mol). The mixture was heated on a water-bath to reduce the volume of the solution to ca. 20ml. The solution was then cooled to room temperature when yellow crystals were formed. These were separated and washed throughly with ethanol and dried in vacuo over $P_4O_{10}$.



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*Author for correspondence

*General method for the preparation of [M ($C_{13}H_{19}N_2$ O) (SCN)] [M = Cu (II) and Pd (II)].* An appropriate solution of $CuCl_2.H_2O$ or $PdCl_2$ (0.005 mol) in absolute ethanol (25 ml) was added to an ethanolic (30 ml) solution of potassium thiocyanate (0.005 mol). The solution was filtered and the ethanolic solution of $C_{13}H_{19}N_2OH$ [(0.005 mol) (80 ml)] was added to filtrate. The resulting mixture was heated on a water bath for 5 min and cooled. The complexes were separated, washed with hot ethanol and dried in vacuo over $P_4O_{10}$.

*Preparation of K [Ti ($C_{13}$ $H_{19}$ $N_2$ O) $(SCN)_3$].* The complex was prepared by adding an ethanolic (15ml) solution of $TiCl_3$ (0.005 mol) to a solution of potassium thiocyanate (0.015 mol) in the same solvent (45 ml). The solution was filtered and the ethanolic solution of $C_{13}H_{19}N_2OH$ [(0.005 mol) (60 ml)] was added to the filtrate. The resulting mixture was boiled on a water-bath for 5 minutes and cooled. The complex was separated, washed with hot ethanol and dried in vacuo over $P_4O_{10}$.

*Preparation of K [V (O) ($C_{13}$ $H_{19}$ $N_2$ O) $(SCN)_2$].* An ethanolic (25 ml) solution of vanadylsulphate pentahydrate (0.005 mol) was added to a solution of potassium thiocyanate (0.01 mol) in the same solvent (40 ml). The solution was filtered and to the filtrate the ethanolic solution of $C_{13}H_{19}N_2OH$ [(0.005 mol) (70 ml)] was added. The complex was separated and washed successively with ethanol and ether and dried as above.

## Results and Discussion

*Elemental analysis and conductivity.* The analytical and physical data of the complexes are presented in Table 1. All the complexes are soluble in DMSO but insoluble in common solvents. The molar conductance values (Table 1) indicate that the complexes (no. 1&2) are all 1:1 electrolytes while the other complexes (no.3&4) are 2:1 electrolytes. (Geary 1971; Tarafder *et al* 1989).

*I.R.studies.* The Schiff base, $C_{13}H_{19}N_2OH$ is potentially tridentate, the available coordination sites being the amino nitrogen, methine nitrogen and the oxo anion. The free ligand $C_{13}H_{19}N_2OH$ shows characteristic bands at 3500 (νOH), 3420, 3480 (ν$NH_2$) and 1613 $cm^{-1}$, (νC=N). In all of the complexes, a broad band appears at 3300-3600 $cm^{-1}$, in which ν ($NH_2$) bands of the complexes are probably hidden. The $NH_2$ complexation is afforded from the appearance of ν ( M-N) modes at 400-470 $cm^{-1}$ in the complexes (Nakamoto 1963; Tarafder and Akbar Ali 1978; Tarafder *et al* 1981). We believe that the ligand deprotonates at the OH end providing an oxo coordination, as is evident from the ν (M-O) bands at 435-520 $cm^{-1}$ in the complexes. The ν(C=N) band observed at 1613 $cm^{-1}$ in the free ligand is shifted to 1600-1608 $cm^{-1}$ indicating coordination by the methine nitrogen.

The ambidentate thiocyanate ligand can coordinate either through the nitrogen or through the sulfur depending on the size of the metal ions. In general, the ν(CN) modes appear at lower frequencies in M-N=C=S complexes than those in M-S-C ≡ N complexes (Basolo *et al* 1964; Destefano and Burmeister 1971; Tarafder and Fatema 1988; Tarafder and Nath 1988; Trafder and Bodruddoza 1991).

The complexes also display ν(CN) at 2053-2080 $cm^{-1}$ characteristic of S-bonded thiocyanato moieties (Lewis *et al* 1961; Basolo *et al* 1964; Destefano and Burmeister 1971).

In pearson's terminology, these are soft acids. The ν(CS) modes appear at lower frequencies in the M-S-C ≡ (N com-

**Table 1**

Analytical data of the complexes

| S. No. | Compound | M. Point (°C) | Mol. wt. found (calc.) | Found (Calc.)% M | C | H | N | Molar conductance (ohm$^{-1}$cm$^{2}$ mol$^{-1}$) | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|---|---|---|---|
| 1. | $[Cu(C_{13}H_{19}N_2O)(SCN)]$ | 64 | 358<br>(340.5) | 17.74<br>(18.65) | 46.93<br>(49.34) | 5.31<br>(5.58) | 11.73<br>(12.33) | 30 | 1.93 |
| 2. | $[Pd(C_{13}H_{19}N_2O)(SCN)]$ | 144 | 402<br>(383.42) | 26.47<br>(27.76) | 41.79<br>(43.82) | 4.73<br>(4.96) | 10.45<br>(10.95) | 35 | Dia. |
| 3. | $K[Ti(C_{13}H_{19}N_2O)(SCN)_3]$ | 181 | 450<br>(479.67) | 10.59<br>(9.94) | 42.67<br>(40.03) | 4.22<br>(3.96) | 15.56<br>(14.59) | 60 | 1.87 |
| 4. | $[V(O)(C_{13}H_{19}N_2O)(SCN)_2]$ | 116 | 458<br>(440.94) | 11.12<br>(11.55) | 39.30<br>(40.83) | 4.15<br>(4.31) | 12.23<br>(12.70) | 65 | 1.42 |

plexes than those in the M-N=C=S complexes. (Basolo *et al* 1964; Destefano and Burmeister 1971; Tarafder and Fatema 1988; Tarafder and Nath 1988; Trafder and Bodruddoza 1991). Complexes (**1-4**) exhibit $\nu$(CS) at 738-762 cm$^{-1}$ characteristic of M-S-C ≡ N bonding sequence. This is further apparent from the $\nu$(M-S) modes at 350-425 cm$^{-1}$ in the far IR spectra of the complexes (Tarafder and Akbar Ali 1978; Trafder *et al* 1981; Ali *et al* 1986).

The vanadium complex (no.4) displays $\nu$(V=O) modes (Nakamoto 1978; Mia *et al* 1994) at 938 cm$^{-1}$.

*Magnetic moment and electronic spectra.* The Cu (II), Ti (III) and V (IV) complexes are paramagnetic and show magnetic moment (1.42 - 1.93 B.M) corresponding to one unpaired electron. The palladium (II) complex is diamagnetic in nature.

Three bands were observed at 15350, 19450 and 22172 cm$^{-1}$, corresponding to the transitions, $^2B_{1g}\rightarrow(^2A_{1g}$, $^2B_{1g}\rightarrow(^2Eg$ and charge transfer respectively for Cu(II) complex. There bands are consistent with square-planar geometry (Figgis 1966).

The spectra of the Pd(II) complex in DMSO show three spin allowed d-d transitions and two charge transfer transitions. The bands were obtained at 22000, 28700, 30030, 35087 and 40000 cm$^{-1}$, corresponding to the transitions $^1A_{1g}\rightarrow(^1A_{2g}$, $^1A_{1g},\rightarrow{}^1B_{1g}$, $^1A_{1g}\rightarrow{}^1Eg$, $^1A_{1g},\rightarrow{}^1A_{2u}$ and $^1A_{1g}\rightarrow{}^1E_u$ respectively which indicate square planar stereochemistry (Lover 1964).

The titanium (III) complex exhibits only one band at 19450 cm$^{-1}$. This band corresponds to the transition $^2T_{2g}\rightarrow{}^2E_g$, characteristic for $O_h$ symmetry (Islam *et al* 1990).

The vanadium (IV) complex show four bands at 19801, 22500, 31746 and 39215 cm$^{-1}$. The first two bands correspond to the transitions $^2B_2\rightarrow{}^2B_1$ and $^2B_2\rightarrow{}^2A_1$ respectively where as, the last two absorptions are caused by metal to ligand charge transfer. All these bands are characteristic for octahedral vanadium (IV) complex (Figgis and Lewis 1964; Selbin 1965; Islam and Israt Jahan 1981).

*$^1$H NMR spectra.* The $^1$H NMR spectra of the ligand $C_{13}H_{19}N_2OH$ and its complex (no. 2) were recorded in DMSO-$d_6$ solution at room temperature. The spectra of the ligand ($C_{13}H_{19}N_2OH$) showed resonances corresponding to-$CH_2$-, -$NH_2$, -CH = N and -OH protons, respectively.

A singlet at 3.52 ppm corresponds to the twelve protons of the six -$CH_2$ - groups in diaminohexane in identical enviornments. The CH = N - proton resonance of the ligand ($C_{13}H_{19}N_2OH$) gave a singlet at 8.48 ppm. For the-$NH_2$ and -OH group showed resonance as singlet at 6.82 and at 13.10 ppm, respectively.

Complex (no. 2) showed a downfield shift of the CH=N-azomethine hydrogen signal at 8.85 ppm compared to the free ligand ($C_{13}H_{19}N_2OH$) which supports the coordination of the azomethine to Pd (II) centre. For the -$NH_2$ protons resonance of this complex (no.2) occurred at low field at 7.01 ppm which also supports the coordination of -$NH_2$ group nitrogen to the Pd (II). This type of phenomena is consistent with those observed for other N-coordinated amino complex. Coordination of the oxy ($O^-$) anion to the Pd (II) centre is suggest in the complex (no.2) on the basis of disappearance of -OH proton signal. So we assumed that the disappearance of -OH proton resonance signal in the complex (no. 2), which clearly indicates the coordination of oxy (O-) anion to Pd (II) centre. This result also supports the IR data.

The $^1$H NMR of other complexes can shows peak for six -$CH_2$,- $NH_2$,-CH=N-protons.

From the given IR,$^1$H NMR evidences and references envisage us to construct a probable structure which is given in the Fig 1.1.

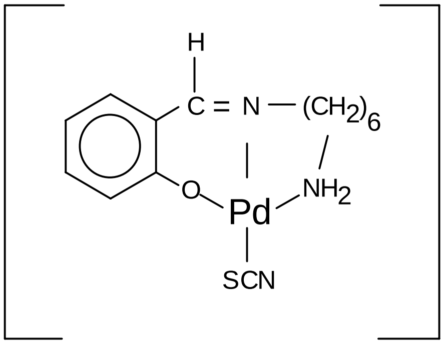

**Fig 1.1** Proposed structure of complex no.2: [Pd ($C_{13}H_{19}N_2O$) (SCN)].

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