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PHYSICAL METHODS OF INVESTIGATION

Synthesis, Characterization and Thermal Stability of Complex *cis*-[Co(bipy)$_2$(CN)$_2$] and Its Interaction with NO_2 Gas[1]

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Abstract—*cis*-[Co(bipy)$_2$(CN)$_2$] complex was successfully prepared from the reaction of [Co(CN)$_2$] with 2,2'-bipyridine in ethanol 96%. The product of complex synthesized was light brown crystal with percent yield of 75.86%. The IR spectrum of this complex showed strong characteristics vibration band at 1471.9 and 1442.75 cm^{-1} for C=N stretching, 1664.57 cm^{-1} for C=C aromatic, 1600.9 cm^{-1} 1 for HC=CH aromatic, 653.87 cm^{-1} for pyridine ring on 2,2'-bipyridine ligand, 3109.25 and 3080.32 cm^{-1} for C–H of aromatic ring. The thermogram of DTA–TG analysis showed 4 endothermic peaks at temperature of 53.4, 323.2, 444.2, and 526.4°C, where the bond breaking of the complex occurred at different temperatures. The result of moment magnet measurement of the complex showed that it was a high spin complex with moment magnet value of 3.68 BM, so it is a paramagnetic complex.

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Cobalt, a member of the first transition row element, is a unique element where it can form a variety of colour complexes when it is reacted with some specific ligands. There were many reports on the synthesis of Co complexes and their application, such as the kinetic and equilibrium studies of B_{12} coenzyme with imidazol and cyanide ligands [1], synthesis and characterization of cobalt complex with pyrimidine nucleoside (uridine) and amino acids [2], synthesis of cobalt complex with *n*-isonicotinamido-2',4'-dichlorobenzalaldimine for antifungal and antibacterial [3] and physico-chemical study of the interaction of cobalt(II) ion with ciprofloxacin [4].

Other researchers have found that in complexes of the type of $[ML_m]^{n+}$, where L is either 1,10-phenanthroline ligand or a modified phen ligand, are mainly attractive species for developing new diagnostic and theraupectic agents that can recognize and cleave DNA [5, 6]. The metals and the ligands in $[ML_m]^{n+}$ system can be varied easily in a controlled manner, so it facilitates their individual application, subsequently providing easy access for understanding details involved in DNA bonding and cleavage [7].

The substitution reaction by other ligands in complex compound can normally be done in an easy way. In this reaction, the substitution reaction of a ligand by a stronger ligand to produce other complex can be achieved by trans effect [8]. Based on this phenomena, Jian et al. have successfully prepared *cis*-[Co(phen)$_2$(CN)$_2$] complex by reacting phen ligand with Co(CN)$_2$ [9]. The complex prepared in their reaction has cis geometry. Hamza et al. [10] have also reported the similar phenomena by substituting B_{12} coenzyme in *trans*-[Co(en)$_2$(Me)H$_2$O]$^{2+}$, where the substitution occurred into H_2O by cyano and they also studied the kinetic of the substitution. Tornroos et al. [11] have studied the crystalisation of *cis* and *trans* isomer of dichlorobis(2-picolilamine)iron(II) in 1-butanol. The preparation and structural study on iron(II) complex with carbonyl cyanides by substituting CN^- by CO produced two *cis* and *trans* isomers of this complex [12].

NO_2 gas is part of nitrogen oxides (NO_x), a pollutant gas, where 10% of air pollutant annually is nitrogen oxides [13]. Besides as a pollutant, NO_2 ligand is one of quite strong ligand in the spectrochemical series, so it can substitute other weaker ligands. In this paper, we report the synthesis and characterization and thermal analysis of *cis*-[Co(bipy)$_2$(CN)$_2$] complex and study its ability to react with NO_2 gas through trans effect.

EXPERIMENTAL

Starting materials. $CoCl_2 \cdot 6H_2O$, KCN, ethanol 96% p.a., 2,2'-bipyridine p.a., copper powder, HNO_3, DMSO, were used as supplied by Sigma–Aldrich Chemical Company without further purification.

Synthesis of the complex. The complex was synthesized using the modified method done by Jian et al. [9]. In this study, the bidentate ligand used was 2,2'-bipyridine rather than 1,10-phenantroline.

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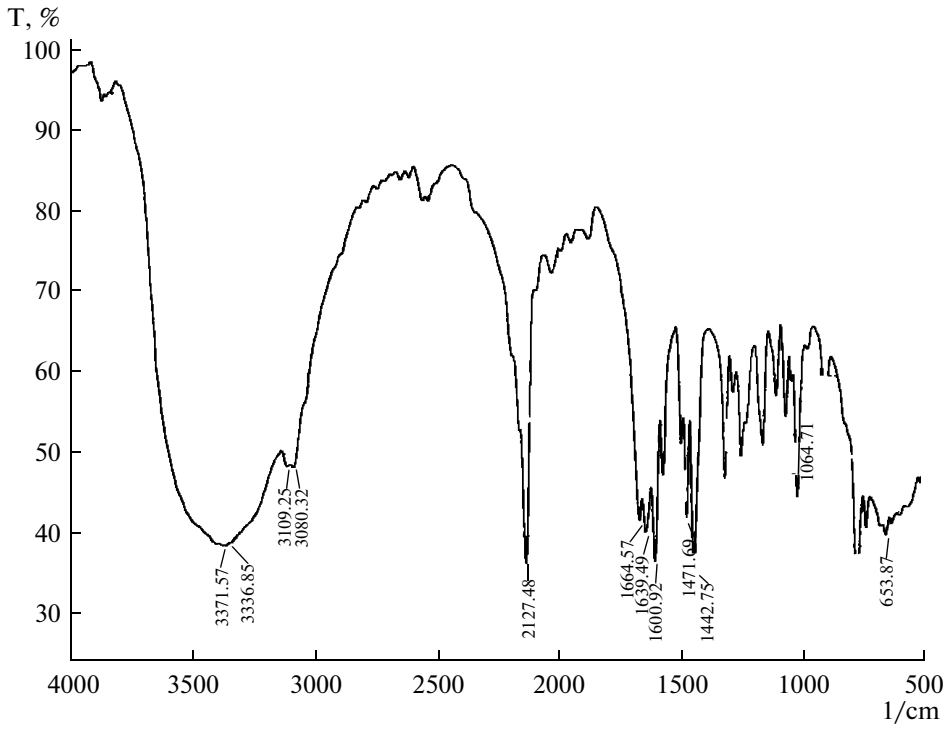

Fig. 1. The IR spectrum of $[Co(bipy)_2(CN)_2]$.

Synthesis of $[Co(CN)_2]$. $[Co(CN)_2]$ was synthesized by mixing the solution of 1.1897 g (0.005 mol; 1.25 M) $CoCl_2 \cdot 6H_2O$ in 4 mL aquabidest and a solution containing 0.6512 g (0.01 mol; 3.3 M) KCN in 3 mL warm aquabidest. The mixtures were then stirred until they were homogen. The solid produced was then filtered off and washed with aquabidest and wind dry till ready for further reaction [9].

Synthesis of $[Co(bipy)_2(CN)_2]$ complex. 1.0052 g (0.005 mol) solid $[Co(CN)_2]$ was added stepwise to solution containing 2,2'-bipyridine (1.8719 g; 0.012 mol) in 70 mL of ethanol 96%. The mixture was then stirred for 2 h. This mixture was then evaporated at room temperature for 4–5 days until the crystal was obtained [9]. The crystal obtained was then washed with ethanol 50% three times to get the pure crystal. The crystal was then placed in a disk and left it to dry at room temperature.

The characterization of the complexes. Determination of the UV-vis spectra: 0.125 g of the complex is dissolved in 25 mL of the solvent used (aquabidest for $[Co(CN)_2]$, DMSO for $[Co(bipy)_2(CN)_2]$ and the product of reaction between $[Co(bipy)_2(CN)_2]$ and NO_2 gas) and then scan in the wave length of 200–400 nm for $[Co(CN)_2]$ and 400–700 nm for $[Co(bipy)_2(CN)_2]$) to find the λ_{max}.

Determination of functional groups of the complexes. The determination of the functional groups of the complexes was done with IR spectra.

Determination of thermal decomposition. Determination of thermal decomposition of the complexes was done with Differential Thermal Analysis and Thermogravimetric (DTA–TG) methods. This method is one of the ways to find whether the $[Co(bipy)_2(CN)_2]$ complex has geomethrical isomer *cis* or *trans*.

The following method was used: the complex was measured with DTA–TG is N_2 gas (80 mL/min) and

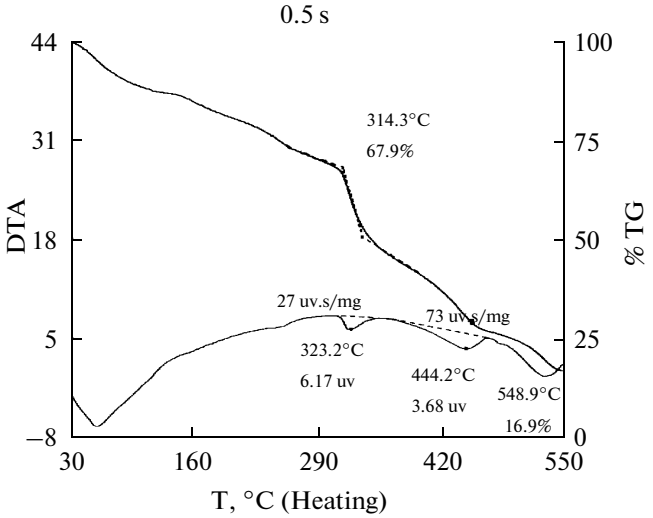

Fig. 2. The DTA–TG curve of $[Co(bipy)_2(CN)_2]$ complex.

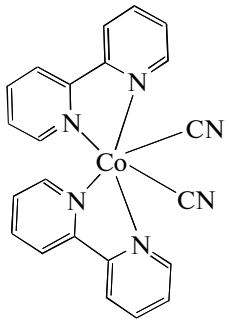

Fig. 3. The structure of *cis*-$[Co(bipy)_2(CN)_2]$ complex.

heated at temperature of 30–550°C with heating rate of 10°C/min. The scanning result between ΔT as function of T is indication of energy lost and the mass changed of the sample is observed.

Determination of magnetic moment of the complex. Determination of magnetic moment of the complex was done with Magnetic Susceptibility Balance (MSB). The measurement was done at room temperature (298 K). The empty, clean and dry MSB tube is weighted out and the magnetic susceptibility is measured, the crystal is then placed in the MSB tube with the height of 1.5–2.5 cm, to obtain the weight of the sample and tube [14, 15].

Study of reaction between *cis*-$[Co(bipy)_2(CN)_2]$ and NO_2 gas. 0.45 g of the solid *cis*-$[Co(bipy)_2(CN)_2]$ is reacted with NO_2 gas in a closed-tube. NO_2 gas is produced from the reaction of 0.25 g powder copper with 2.5 mL of conc. HNO_3. The reaction was done for 2–3 h till the colour change of the complex was observed.

RESULTS AND DISCUSSION

Determination of functional groups of the complexes. The IR spectrum of the $[Co(bipy)_2(CN)_2]$ is shown in Fig. 1. From this figure, it is clear that the complex showed some strong characteristic bonds at the region of 1471.69 and 1442.75 cm^{-1} for C=N vibration stretch, 1664.57 cm^{-1} for C=C aromatic stretch, 1600.9 cm^{-1} (HC=CH aromatic stretch), 653.87 cm^{-1} for pyridine ring on 2,2'-bipyridine ligand, 3109.25 and 3080.32 cm^{-1} for C–H in aromatic ring. The stretch at 2127.48 cm^{-1} showed characteristic stretch for C≡N and at 3336.85 cm^{-1} showed the present of O–H from hydrated water molecule as well as at 1639.49 cm^{-1} characteristic for O–H of crystallized water molecule. By the presence of O–H bond from hydrated and crystallized water molecules, it can be assumed that the compound synthesized is a hydrated complex and similar to complex previously reported [9].

Determination of thermal decomposition. Determination of decomposition thermal was done by heating the sample in the amount of 6.8 mg at the temperature range of 30–550°C with the rate of 10°C/min. By the use of DTA–TG, the heat and mass contents due to the heating (change of temperature) against the compound used was measured. This method is valuable in determining the formula of thermal decomposition. The thermogram of the $[Co(bipy)_2(CN)_2]$ complex (Fig. 2). The thermogram DTA–TG in Fig. 2 showed four transition peaks of crystalline phase at temperature of 53.4, 323.2, 444.2, and 526.4°C shown by the endothermic peaks. These peaks represent the physical change of the compound analyzed and the peaks found represent the crystal change by the melting process.

The thermogram of $[Co(bipy)_2(CN)_2]$ complex showed three weight loss. The first stage loss was at temperature range of 100–160°C where the weight loss was 13.6%. This percent loss is equal to the loss of four hydrated water molecules (calculated 14.55%). The second loss was at temperature range of 200–323°C where the weight loss was 6%. This loss is attributed to the loss of N_2 (calcd. 5.65%). The third loss was at temperature range of 323–548.5°C, where the weight loss was 63.5%, and it is equal with the loss of two bipy group (calcd. 63.05%). At temperature of 548.5°C the residual weight of the complex was 1.15 mg (16.9%) which is equal to one molecule of CoC_2 (calcd. 16.75%). The melting point of $[Co(bipy)_2(CN)_2]$ complex is predicted more than 550°C. The release of two subsequent N atom and followed by the loss of two bipy group might be assumed that the complex has formula of *cis*-$[Co(bipy)_2(CN)_2] \cdot 4H_2O$ (Fig. 3). This result is similar by previous result reported by Jian et al. for *cis*-$[Co(fen)_2(CN)_2] \cdot EtOH \cdot 2H_2O$ compound [9].

Determination of magnetic moment of *cis*-$[Co(bipy)_2(CN)_2] \cdot 4H_2O$ complex. Based on the measurement of magnetic moment with magnetic susceptibility balance, *cis*-$[Co(bipy)_2(CN)_2] \cdot 4H_2O$ complex has magnetic moment of 3.68 BM. Thus this complex is paramagnetic. The result of measurement has been corrected against the diamagnetic susceptibility as in the magnetic moment measurement, the value observed was combined values of paramagnetic and diamagnetic susceptibilities of the complex measured.

Characterization of product obtained from interaction of *cis*-$[Co(bipy)_2(CN)_2]$ with gas NO_2. The solid complex of *cis*-$[Co(bipy)_2(CN)_2]$ is light brown, after being bubbled with NO_2 gas for 3 hours, the color of the solid turn orange. This color change is an indication of the substitution reaction has occurred into *cis*-$[Co(bipy)_2(CN)_2]$ complex. NO_2 acts as stronger ligand than bipy although it is weaker than CN, than the substitution might occur to bipy. The Uv spectrum of *cis*-$[Co(bipy)_2(CN)_2]$ complex showed a λ_{max} at 484.5 nm with absorbance of 0.303, while the spectrum of complex from the interaction of *cis*-$[Co(bipy)_2(CN)_2]$ with NO_2 gas has λ_{max} at 692.5 nm

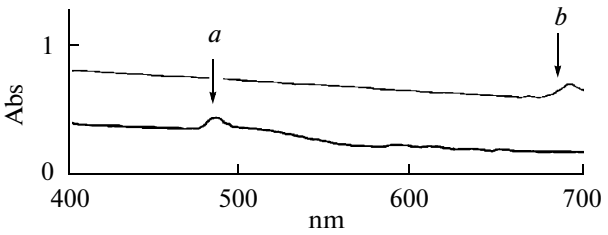

Fig. 4. The UV-vis spectra of *cis*-$[Co(bipy)_2(CN)_2]$ (*a*); *cis*-$[Co(bipy)(NO_2)_2(CN)_2]$ (*b*).

with absorbance of 0.337 (Fig. 4). There was a long shifting before and after interaction (208 nm) which showed the batochromic shifting has occurred to the new complex. This shifting might occur due to the presence of free electron pair in N atom of NO_2 ligand which can shift to the longer λ_{max}. This is because NO_2 is one of auxochrome which chromofore substituent that can shift to the red shift (batochromic). This auxochorme can intensify the color of a complex compound which can be observed visually by the change of the colour where in this reaction this occur from light brown to orange.

The IR spectrum of the complex obtained from interaction between *cis*-$[Co(bipy)_2(CN)_2]$ and NO_2, showed characteristic of M–NO_2 bond at 1386.82 cm^{-1} and 1761.01 cm^{-1} , this is an indication that the Co metal ion is directly attached to NO_2 ligand. This result agreed to the report by Feltham [16] that the absorption of asymmetric NO_2 was observed at 1390 cm^{-1}, while for the symmetric NO_2 was observed at 1320 cm^{-1}, in which N acts as electron pair donor in M–NO_2 structure.

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