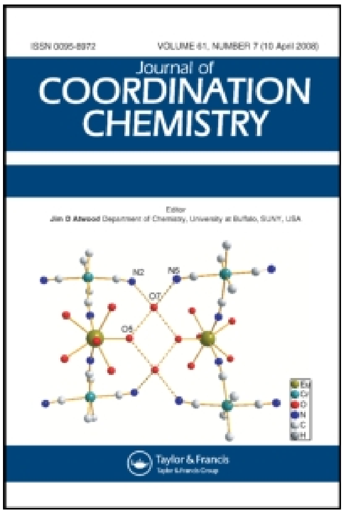

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# Synthesis, spectral, magnetic, thermal and antibacterial studies on symmetrically substituted 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines

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This article describes a simple method developed for the synthesis of symmetrically substituted 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines (M-PhproImPcs) of cobalt(II), copper(II), nickel(II) and zinc(II) by condensing 1,8,15,22-tetra amino phthalocyanines with cinnamaldehyde. The dark bluish-green colored tetraimino substituted phthalocyanine derivatives were characterized by elemental analysis, electronic spectra, IR spectra, magnetic susceptibility, powder XRD and thermogravimetric analysis (TGA) to check the structural integrity and purity. The variations of magnetic moment as a function of field strength indicated the presence of intermolecular co-operative interactions. The complexes were also evaluated for their antibacterial activities.

*Keywords*: Interactions; Magnetic; Phenylpropene; Substituted; Susceptibility

## 1. Introduction

Phthalocyanines are planar macrocyclic aromatic ligands related to porphyrins, constituted by four isoindole units consisting of an 18 $\pi$-electron cloud delocalized over an arrangement of alternating carbon and nitrogen atoms. A number of unique properties arise from this electronic delocalization, making these compounds important in different fields of material science. Phthalocyanines are the second most important class of colorants and copper phthalocyanine is the single largest volume colorant sold. Various substituted metal phthalocyanines have been extensively used in solar cells, fuel cells, electrochroism and photochroism, optical memory and data storage devices, liquid crystal displays, as dyes and pigments and in photodynamic therapy of cancer. This class of compounds has also found extensive use in many modern technologies,

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cyan dyes for inkjet printing, electro photography, as charge generation materials for laser printers and as colorants for cyano toners. Recent research has developed substituted metal phthalocyanine derivatives as catalysts [1, 2], photoconductors [3], photosensitizers [4], photovoltaics [5] and semiconductors [6]. Metallophthalocyanines also attract interest in medicine for the treatment of cancer by photodynamic therapy (PDT) [7–9] and as electric carpets with deodorizer properties for indoor air [10].

Although synthesis and characterization of metal(II) 1,8,15,22-tetraaminophthalocyanines were documented [11], no evidence is available on synthesis and structural studies of metal(II) 1,8,15,22-tetraimino phthalocyanines starting from the respective amino phthalocyanine complexes.

In the present article we report the synthesis, characterization and antibacterial activities of 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanine complexes of cobalt(II), copper(II), nickel(II) and zinc(II). The procedure available from the literature [11–13] was suitably modified for synthesis of the complexes.

## 2. Experimental

3-nitrophthalic acid was synthesized by using phthalic anhydride as reported elsewhere [11]. All other chemicals were of analytical grade. Metal(II) 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines were prepared as per scheme 1.

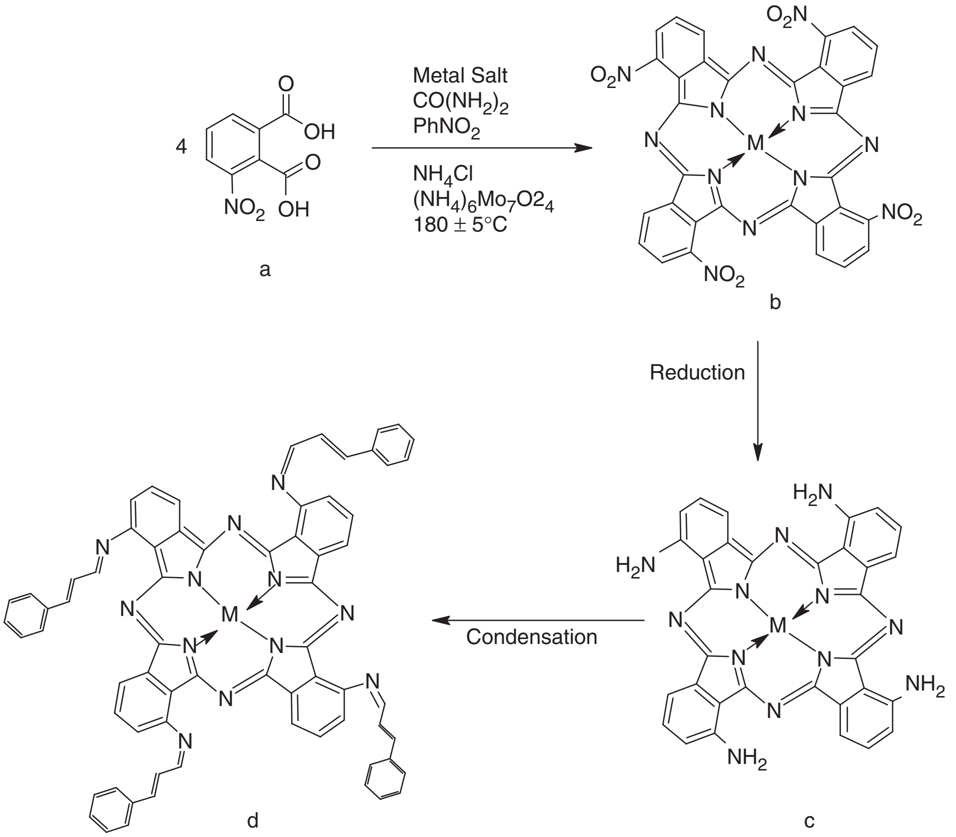
### 2.1. *Preparation of cobalt(II) 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanine complex*

The procedure for synthesis of cobalt(II) 1,8,15,22-tetranitro phthalocyanine (M-PcTN) is reported elsewhere [11]. The nitro derivative was converted into the amino derivative quantitatively by reduction using sodium sulfide nonanhydrate in aqueous medium [12]. The finely powdered cobalt(II) 1,8,15,22-tetraamino phthalocyanine (M-PcTA) (6.30 g, 0.01 M) was dissolved with stoichiometric quantity of dimethylsulfoxide (DMSO) and stirred with cinnamaldehyde (4.9 mL, 0.01 M), refluxed for 5 h in the presence of catalytic quantity of concentrated sulfuric acid and poured onto ice cold water. The settled bluish-green colored condensed imino phthalocyanine complex was washed with alcohol several times until it was free from aldehyde. The yield of the complex was about 68%.

The pigment form of the above complex was obtained by the acid pasting process, in which 1 part of the powdered sample was dissolved in 6–10 parts of concentrated sulfuric acid. The mixture was allowed to stand for 1–2 h and then poured onto 45–50 parts of crushed ice and stirred thoroughly. The pigment thus obtained was filtered off and washed with hot water. Finally, it was washed with distilled water and dried in vacuum over phosphorous pentoxide.

Metal(II) 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines of Cu(II), Ni(II) and Zn(II) were prepared by the above procedure using the respective metal amino phthalocyanines.

C, H and N elemental analyses were done by STIC, Kochi, Kerala, India. Varian Cary 5000 with 1 cm width silica cell was used for electronic absorption spectral studies.



Scheme 1. Synthesis of metal(II) 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines, (a) 3-nitrophthalic acid, (b) M-PcTN, (c) M-PcTA and (d) M-PhproImPc.

IR spectra were recorded using a Nicolet MX-FT IR spectrometer. A Philips analytical PW-1710 X-ray diffractometer was used to study the diffraction pattern of the complexes using Cu-K$\alpha$ at a voltage of 40 Kv, a current of 20 mA, a time constant of 4, a channel width of 7 mm and a chart speed of 10 mm$^{-1}$ min$^{-1}$. Magnetic susceptibility studies were made at room temperature (28°C) using a Gouy magnetic balance consisting of NP-53 type electromagnets with a DC power supply unit and a semi microbalance. Pascal's constants were used to calculate the diamagnetic corrections. A Hg[Co(SCN)$_4$] complex was used as calibrant [14]. TGA studies were carried out using a Perkin Elmer, Diamond TG/DTA thermal analyzer at a heating rate of 10° min$^{-1}$ both in the air and nitrogen atmosphere.

The agar diffusion cup plate method was followed for antibacterial assay as described in Indian Pharmacopia [15]. Inoculum was prepared from 24 h old culture in nutrient broth. The 500 ppm solutions of each M-PhproImPc complex were prepared by dissolving the required quantity of complexes in DMF. The corresponding tetraamino phthalocyanine complexes were also dissolved in DMF to prepare 500 ppm solution and antibacterial studies were carried out under similar conditions for comparison. The above solutions were further diluted with DMF to prepare 200 ppm, 100 ppm and 50 ppm solutions. With the help of a stainless steel well cutter (6 mm), cups were cut out and into each of these cups 100 µL of each solution of different concentration and control (DMF) were placed separately under aseptic conditions with the help of a sterile micropipette. The plates were then maintained at room temperature (26°C) for 1 h to allow diffusion of the solutions into medium and then incubated at 37°C for *Xanthomonas citri* and *Xanthomonas compstris*.

## 3. Results and discussion

The procedure adopted for the synthesis of M-PhproImPc's yielded dark bluish-green pure complexes. These complexes give clear solution in concentrated sulfuric acid, DMSO, DMF and pyridine and are sparingly soluble in alcohol. Elemental analyses for carbon, hydrogen and nitrogen and metals (table 1) are in good agreement with the calculated values and consistent with the proposed structures.

### 3.1. *Electronic spectra*

Electronic spectra of M-PhproImPc's were recorded in DMF in the concentration range 1.0–1.5 × $10^{-5}$ M; a summary of the results are presented in table 2 and figure 1. The observed deep bluish-green color of the complexes may be due to $a_{2u} \rightarrow e_g$ and $b_{2u} \rightarrow e_g$ transitions [8]. For all the complexes absorption bands were observed in the wavelength 746–769 nm, which are considerably higher than the corresponding parent metal phthalocyanine [8]. This observed red shift was attributed to increase in conjugation of the $\pi$-electron of the phthalocyanine with those of peripheral substituted aromatic

Table 1. Elemental analysis and magnetic susceptibility data of the metal phthalocyanines.

| Complex (Color) (Yield) | Empirical formulae (Molecular weight) | Field strength K Gauss | Magnetic susceptibility ($\chi_m \times 10^{-6}$ cgs unit) | Magnetic moments $\mu_{eff}$ (B.M.) | Elemental analysis Found (Calc.) |
|---|---|---|---|---|---|
| Co-PhproImPc (Bluish-green) (68%) | $C_{68}H_{44}N_{12}Co$ (1086.93) | 2.20 | +3599.20 | 2.97 | C: 74.86; (75.13) |
| | | 2.66 | +3439.03 | 2.88 | H: 3.88; (4.02) |
| | | 3.10 | +3127.39 | 2.75 | N: 15.21; (15.44) |
| | | 3.58 | +2983.82 | 2.68 | Co: 5.23; (5.33) |
| | | 4.01 | +2778.52 | 2.59 | |
| Cu-PhproImPc (Bluish-green) (64%) | $C_{68}H_{44}N_{12}Cu$ (1091.53) | 2.20 | +3522.75 | 2.93 | C: 74.54; (74.79) |
| | | 2.66 | +3390.05 | 2.81 | H: 3.90; (4.03) |
| | | 3.10 | +3135.61 | 2.76 | N: 15.44; (15.39) |
| | | 3.58 | +2975.12 | 2.69 | Cu: 5.45; (5.76) |
| | | 4.01 | +2582.05 | 2.51 | |
| Ni-PhproImPc (Bluish-green) (67%) | $C_{68}H_{44}N_{12}Ni$ (1086.69) | 2.66 | −655.22 | – | C: 74.98; (75.13)<br>H: 3.86; (4.05)<br>N: 15.32; (15.47)<br>Ni: 5.28; (5.36) |
| Zn-PhproImPc (Bluish-green) (59%) | $C_{68}H_{44}N_{12}Zn$ (1093.39) | 2.66 | −725.65 | – | C: 74.36; (74.65)<br>H: 3.95; (4.02)<br>N: 15.34; (15.37)<br>Zn: 5.79; (5.91) |

imino groups. The splitting of the Q-band was observed in all the complexes in the range 446–475 nm. The origin of the Q-band was attributed to $a_{1u} \rightarrow e_g$ transition of the phthalocyanine molecule. A sharp and intense B-band was observed for all the complexes in the range 331–355 nm.

Table 2. Spectral data of metal(II) 1,8,15,22-tetra-phenylpropene-1-imino phthalocyanines.

| Complex | UV-Visible wavelength $\lambda$ nm(log $\varepsilon$) in DMF | IR spectral data (cm$^{-1}$) | Powder XRD data $2\theta$ angle (dÅ) | Powder XRD Relative intensity % |
|---|---|---|---|---|
| Co-PhproImPc | 336 (3.98)<br>478 (3.53)<br>768 (4.19) | 607, 752, 1123,<br>1316, 1491,<br>1635, 3418 | 26.12 (3.28)<br>25.74 (3.58)<br>38.33 (2.35) | 100.00<br>64.12<br>24.25 |
| Cu-PhproImPc | 335 (3.99)<br>431 (3.00)<br>766 (4.09) | 690, 747, 1098,<br>1310, 1497,<br>1631, 3428 | 26.25 (3.48)<br>28.54 (3.18)<br>40.50 (2.10) | 100.00<br>59.59<br>24.00 |
| Ni-PhproImPc | 328 (4.60)<br>454 (4.10)<br>765 (4.53) | 648, 750, 1098,<br>1338, 1491,<br>1638, 3436 | 25.90 (3.35)<br>29.75 (3.25)<br>40.31 (2.10) | 100.00<br>55.26<br>25.45 |
| Zn-PhproImPc | 338 (4.89)<br>475 (4.45)<br>744 (4.82) | 700, 742, 1093,<br>1341, 1486,<br>1637, 3430 | 26.66 (3.56)<br>28.85 (3.21)<br>45.75 (2.54) | 100.00<br>62.45<br>30.25 |

Pc – Phthalocyanine.

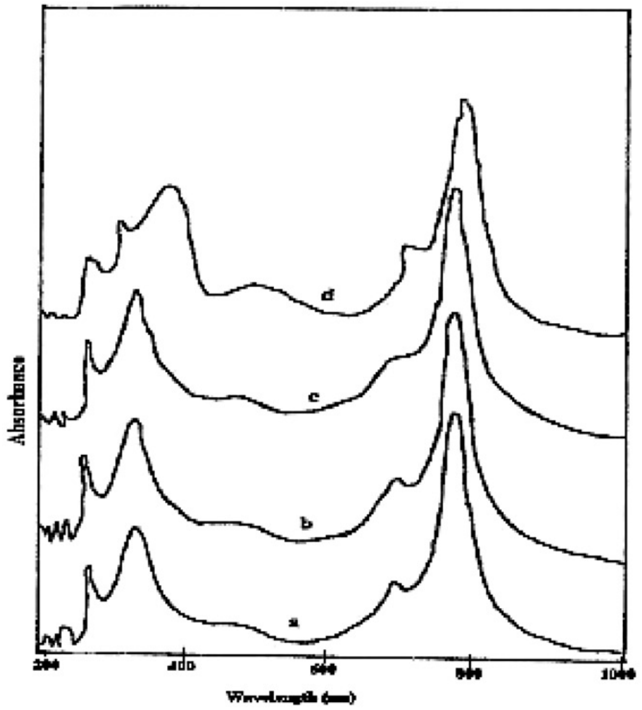


Figure 1. Electronic spectra of (a) Co–PhproImPc, (b) Cu–PhproImPc, (c) Ni–PhproImPc and (d) Zn–PhproImPc recorded in DMF.

### 3.2. *IR spectra*

IR spectral data were recorded in KBr pellets, and selected bands of the functional groups are summarized in table 2 and shown in Supplementary Material. The sharp peaks of M-PhproImPc's at 1631–1638 $cm^{-1}$ are attributed to C=N of aromatic imino and peaks in the range 1486–1497 $cm^{-1}$ are due to C–N aromatic stretching. The peaks in the range 1310–1341 $cm^{-1}$ are due to C–H symmetric bending. All the remaining bands observed in the range 742–752 and 607–700 $cm^{-1}$ may be assigned to various skeletal vibrations of the phthalocyanine ring [8].

### 3.3. *Powder XRD*

The powder X-ray diffraction patterns of M-PhproImPc's taken through a range of $2\theta$ angles from 6–70° showed identical peaks with relatively poor crystallinity (table 2, Supplementary Material). The observed patterns are similar to that of unsubstituted parent phthalocyanines except for broadening of the peaks with diffused intensity. The broadening may be due to the substituents at the periphery of the molecule, which provide hindrance for effective stacking of the molecule and thus poor crystallinity of the complexes.

### 3.4. *Magnetic susceptibility*

Magnetic susceptibility studies were carried out at ambient temperature and results are in table 1 (magnetic moment values reported in the table are the average of three independent determinations). The magnetic susceptibility studies revealed that Co-PhproImPc and Cu-PhproImPc are paramagnetic, whereas Ni-PhproImPc and Zn-PhproImPc are diamagnetic. The measured magnetic moments for Co-PhproImPc and Cu-PhproImPc are higher than the spin only value corresponding to one unpaired electron (1.73 BM), due to mixing of ground state orbitals with higher energy degenerate states and intermolecular co-operative effect [14]. This effect decreases with increase in field strength and $\mu_{eff}$ value approaches spin only value at higher field strength. The observed higher $\mu_{eff}$ value at lower field strength is attributed to intermolecular magnetic interaction coupled with magnetic anisotropy of phthalocyanine $\pi$-current [16]. Crystallographic studies reveal that the metal phthalocyanines of Co, Cu, Ni and Zn are square planar structure with $D_{4h}$ symmetry and are isomorphous [17]. The molecular plane is approximately normal to the a-b plane and molecules are stacked along the short b-axis. The molecular planes are inclined to the a–c axis at an angle of 45°. Thus, the complexes stack in columns with N-atom above and below every metal atom (figure 2). Hence, the nearest neighboring molecule along the b-axis contributes a nitrogen atom at the interplanar distance 3.4 Å [18].

### 3.5. *Thermogravimetric and kinetic studies*

Thermogravimetric data of imino substituted metal phthalocyanine complexes are summarized in the table 3. Decomposition of the complexes in air generally occurs in two steps. The first step from 128–360°C may be accounted for by loss of four imino groups. The major weight loss was observed in the last step for all the complexes in the

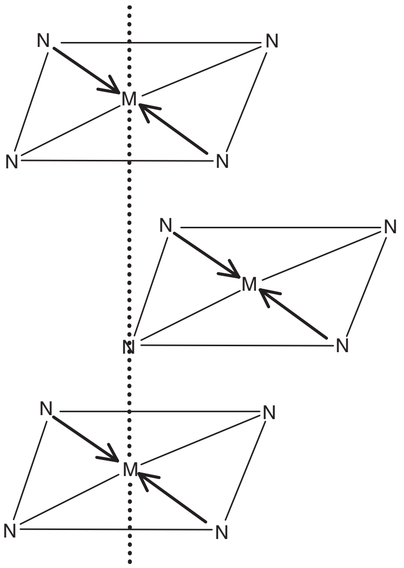


Figure 2. Probable molecular stacking of metal phthalocyanines. M = Cu, Co, Ni and Zn, N = azamethine atom of phthalocyanine.

Table 3. TGA data for the complexes.

| Compound | Decomposition Temp °C | Mass loss % Found | Mass loss % Calculated | Probable mode of decomposition and fragments lost |
|---|---|---|---|---|
| Co-PhproImPc | 100–340 | 46.66 | 45.84 | 4 Imino groups |
|  | 350–510 | 45.58 | 46.99 | Pc Moiety |
| Cu-PhproImPc | 100–350 | 47.13 | 45.23 | 4 Imino groups |
|  | 350–470 | 44.25 | 45.65 | Pc Moiety |
| Ni-PhproImPc | 100–360 | 45.62 | 45.03 | 4 Imino groups |
|  | 360–480 | 45.61 | 46.99 | Pc Moiety |
| Zn-PhproImPc | 100–340 | 45.44 | 45.16 | 4 Imino groups |
|  | 340–580 | 44.22 | 45.56 | Pc Moiety |

temperature region 360–580°C, corresponding to oxidative degradation of phthalocyanine. The residues after thermal decomposition were the corresponding metal oxides [19]. The thermal decomposition of these imino substituted complexes in nitrogen appears to be very slow. For Co-PhproImPc, 65% of the complex decomposed at 700°C. For Cu-PhproImPc, Ni-PhproImPc and Zn-PhproImPc about 62%, 58% and 52% loss of mass was observed even at 700°C. The above trend confirms the relatively higher stability of these complexes in nitrogen atmosphere than that in air. Even though all four functional groups seem to be lost during the first step, a dimer or a polymer is suspected to be formed via the nitrogen atoms of the peripheral end groups before the second step of decomposition starts [20]. DTA results revealed that all degradation steps are exothermic. Kinetic and thermodynamic parameters of the title complexes have been evaluated by Broido's method [21]. Plots of ln $(\ln 1/y)$ *versus* 1/T (where $y$ is the fraction of the complex undecomposed) were developed for the decomposition

Table 4. Zones of inhibition for metal(II) 1,8,15,22-tetra-tetra-phenylpropene-1-imino phthalocyanines.

| Compound | Conc. (in ppm) | *Xanthomonas compstris* Zone of inhibition (in mm) | *Xanthomonas citri* Zone of inhibition (in mm) |
|---|---|---|---|
| Control (DMF) | | 02 | 03 |
| Co-PhproImPc | 50 | 04(03) | 05(03) |
| | 100 | 07(05) | 08(05) |
| | 200 | 12(06) | 13(08) |
| | 500 | 18(08) | 19(10) |
| Cu-PhproImPc | 50 | 05(04) | 06(03) |
| | 100 | 08(07) | 09(05) |
| | 200 | 13(09) | 14(07) |
| | 500 | 19(10) | 19(11) |
| Ni-PhproImPc | 50 | 05(04) | 04(03) |
| | 100 | 07(06) | 07(05) |
| | 200 | 14(08) | 13(07) |
| | 500 | 18(11) | 19(10) |
| Zn-PhproImPc | 50 | 06(04) | 05(04) |
| | 100 | 09(05) | 09(07) |
| | 200 | 14(07) | 15(09) |
| | 500 | 22(10) | 21(11) |

The values in the bracket correspond to the parent metal(II) amino phthalocyanines.

segment, where loss of functional groups occur. From the plots, energy of activation (Ea), frequency factor (ln A), enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of the title complexes have been computed by using standard equations (Supplementary Material).

### 3.6. *Antibacterial activity*

Bacterial strains of *Xanthomonas* were procured from the Department of Biotechnology, Sahyadri Science College, Shimoga.

The imino phthalocyanine complexes were tested against pathogenic bacteria *Xanthomonas citri* and *Xanthomonas compstris*.

Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 h [22–25]. Maximum inhibition was observed in Zn-PhproImPc with tested organism and the least inhibition was observed in Co-PhproImPc. This indicates that metal substitution affects antibacterial activity. Different group substitutions, amino and imino, show that imino group substitution has potent antibacterial effect, whereas amino group substitution has less antibacterial property. The data of zones of inhibition are given in table 4.

## 4. Conclusions

The synthetic route adopted was simple and gave good yield. The red shift of the complexes compared to the parent phthalocyanine was due to increase in conjugation of

$\pi$-electrons with the $\pi$-electron cloud of peripheral substituted imino groups. The magnetic susceptibility studies clearly revealed structural information of the complexes. The peripheral substituted phenylpropene-1-imino groups enhance the solubility of phthalocyanine complexes. Positive results of antibacterial activity add more value to the work.

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