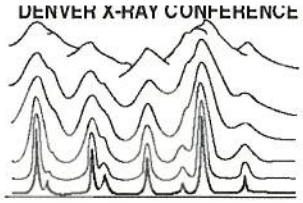
Advances in X-ray Analysis
Cumulative Title Index




# Characterization of Metal Benzotriazoles and Related Polymers

S.J. Wasson, M.C. Kerzic, J.W. Hall, M.A. Cates and J.R. Wasson, Vol. 42, pp. 555-561, (1998).

Return to Index

Go To Document

Hit Back Next Paper

# Characterization of Metal Benzotriazoles and Related Polymers

**Shirley J. Wasson [1]**
**Melissa C. Kerzic and James W. Hall [2]**
**Melanie A. Cates and John R. Wasson [3]**

*[1] MD-91, National Risk Management Research Laboratory*
*U. S. Environmental Protection Agency, Research Triangle Park, NC 27711*
*[2] Wingate University, Department of Chemistry and Physics, Wingate, NC 28174*
*[3] Advanced Materials, 865 Pea Ridge Road, New Hill, NC 27562*

## ABSTRACT

Benzotriazole (bta-H) is a well-known corrosion inhibitor for copper, copper-alloy, and other metal surfaces. Typical uses are to deactivate surfaces of computer hard drives and other internal metal computer parts, and for treatment of apparel hardware such as zippers and buttons to withstand harsh fabric washing and dyeing processes. Particles from these surface treatments will ultimately contribute to environmental indoor dust or outdoor industrial effluent, but they have not been fully characterized. Bta-H is one of a group of several organic ligands which bind to transition metals and which have similar structures. We have systematically investigated approximately 30 transition metal complexes of the general formula $ML_2$, where M = $VO^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$, and L = deprotonated benzotriazole, imidazole, benzimidazole, 2-methylimidazole, or 2-methylbenzimidazole. Where possible, these materials have been synthesized and characterized by chemical analysis, spectroscopy, and x-ray diffraction techniques. The $ML_2$ compounds are coordination polymers with metal-deprotonated nitrogen and metal-nitrogen (dative bonding) interactions. X-ray powder diffraction patterns have been determined and indexed for $Co(C_3N_2H_3)_2 \cdot H_2O$ and $Zn(C_3N_2H_3)_2 \cdot 0.5\ H_2O$ .

## INTRODUCTION

Benzotriazole (bta-H), is a well-known protective additive which reacts with copper, brass, or other metal surfaces to provide a barrier against oxygen, air pollutants [1], or attack by corrosive agents in water. Typical uses are to deactivate surfaces of computer hard drives and other internal metal computer parts, and for treatment of apparel hardware such as zippers and buttons to withstand harsh fabric washing and dyeing processes. The nature of the protective film has been probed by various procedures [2], but particles shed from these surfaces has not. Since particles from these surface treatments may ultimately contribute to environmental indoor dust or outdoor industrial or municipal effluent, we chose to investigate compounds which may be studied as particulate surrogates. Recent work on triazoles and triazolate complexes has been reviewed [3]. Reedijk et al.[4] studied the coordination compounds of several metals with both the neutral ligands (bta-H) and the deprotonated ligands ($bta^-$). They concluded that the copper (II) benzotriazole compounds which they studied were almost certainly polymeric. The search for model compounds for $Cu(bta)_2$ led them to determine the crystal structure of (benzotriazolato)thallium(I)[5]. Sotofte and Nielsen[6,7] concentrated their efforts on the

benzotriazoles and published a tetragonal-bipyramidal structure for blue polymeric $Cu(bta)_2 \cdot H_2O$. We have investigated the preparation of a series of metallic bta compounds along with simpler ligands of similar structure in the search for compounds with sufficient crystalline nature that their diffraction patterns could be determined. We investigated the preparation of six transition metals or metallic cations ($VO^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$) with the five ligands shown in Figure 1. Analysis showed that the cobalt, nickel, copper, and zinc produced the benzotriazolato, imidazolato, 2-methylimidazolato, benzimidazolato, and 2-methylbenzimidazolato polymeric complexes of the formula $ML_2$, tetrahedrally coordinated with some water involved. The vanadyl and manganese cations failed to produce the desired products with the ligands under the conditions of synthesis.

The x-ray powder patterns of the products showed varying degrees of crystallinity. The amorphous area in the data was estimated by determining the percentage of background/total integral counts in the scan range. Most of the compounds had enough amorphous character (>50%) to seriously compromise indexing. The cobalt and zinc imidazoles, however, had sufficient crystalline character to report.

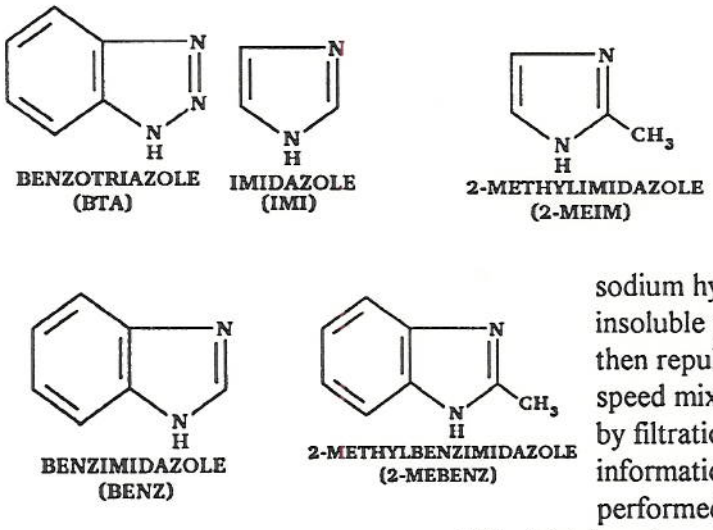



Figure 1. Ligands investigated

## EXPERIMENTAL

The $ML_2$ compounds were prepared by mixing the ligand with an aqueous solution of a stoichiometric amount of the metal chloride or nitrate salt followed by stepwise addition of sodium hydroxide with vigorous stirring. The insoluble products were isolated by filtration and then repulped with deionized water using high speed mixing. The compounds were again isolated by filtration and dried. Table 1 provides analytical information. The C, H, and N analyses were performed by Galbraith Laboratories, Knoxville, TN. Metal analyses were performed using ethylene diamine tetraacetic acid (EDTA) titrations and a Buck Scientific Model 210 atomic absorption spectrometer. Differential thermal analysis (DTA) scans were obtained using a Mini-Therm analyzer (Wagner Co., Parkesburg, PA) and an alumina reference standard. Infrared spectra were determined using a Buck Scientific Model 500 spectrometer and Nujol mulls on sodium chloride cells.

## X-RAY POWDER DATA

The samples were ground in a boron carbide mortar, put through a 325 mesh sieve, and side-drifted into a cavity in an aluminum holder. Some of the specimens were prepared by sifting onto a smear of petroleum jelly on a zero background quartz holder to sharpen the peaks. The diffraction data were collected on a Siemens D-500 diffractometer under the conditions given in

Table 2. The diffractometer was controlled by Datascan (Materials Data, Inc.) and processed using MDI Jade software. Processing the data consisted of 2θ correction by silicon NIST SRM 640b standard, and defining the background. Peaks were allowed to ride on the background, and profiles were manually fitted using the Pearson VII function[8]. The peak list thus generated was used for indexing. Initial indexing was performed on the first 12 peaks. The proposed lattice parameters were refined until the solutions converged.

Table 1.Results of Elemental and Physical Analyses

| Compound | | %C | %H | %N | C/N Ratio | Color | Percent Amorphous |
|---|---|---|---|---|---|---|---|
| $Co(im)_2 \cdot H_2O$ | Calc | 34.14 | 3.82 | 26.54 | 1.286 | ------ | ------ |
| | Found | 33.91 | 3.74 | 26.63 | 1.273 | Purple | 37 |
| $Zn\ (im)_2 \cdot 0.5\ H_2O$ | Calc | 34.56 | 3.38 | 26.87 | 1.286 | ------ | ------ |
| | Found | 34.69 | 3.39 | 26.86 | 1.292 | White | 25 |

Table 2: Experimental Parameters

| Parameter | Setting or Condition |
|---|---|
| Radiation: CuKα | 1.5418Å |
| Monochromator | Graphite |
| Detector | Scintillation |
| Divergence Slits (fixed) | 1° |
| Receiving Slits | 0.15° |
| Soller Slit | Present, 2 °, diffracted beam |
| Resolution | Quartz, $H_1/H_2 = 1.59$ |
| Range of 2θ | 5 to 85° |
| Internal 2θ standard | Silicon, NIST SRM 640b |
| 2θ calibration correction | Less than 0.01° 2θ |
| Step size/dwell time | 0.04°/5 s |
| Voltage/Current | 45 kV/40 mA |
| Diameter of Measuring Circle | 401 mm |

## DISCUSSION

$Co(C_3N_2H_3)_2 \cdot H_2O$ and $Zn\ (C_3N_2H_3)_2 \cdot 0.5\ H_2O$ are both tetragonal, but they are not isomorphous. Diffraction data are given in Tables 3 and 4, and the spectra are shown in Figures 2 and 3, respectively. The cobalt imidazolate crystallizes in the space group $I4_1/acd$, while the zinc imidazolate belongs to the space group $I4_1cd$. The crystal data reported by Lehnert and Seel [9] confirm our reported data for the zinc complex including the tetragonal symmetry, the space group, and the cell parameters. They did not report any water in the crystal lattice, however. Sturm et al. [10] reported crystal data for anhydrous $Co(C_3N_2H_3)_2$. They found tetragonal symmetry, but a space group of $I4_1$ ,and slightly different cell parameters than we report.

## CONCLUSIONS

Previously unreported diffraction data are reported for two crystalline polymeric complexes of the type $ML_2 \cdot x\ H_2O$ where M = cobalt and zinc, and L = deprotonated imidazole. Our work confirms that of Lehnert and Seel for the zinc compound, although they did not report the presence of water. The cell parameters and space group reported by Sturm et al. for the anhydrous cobalt compound are different from the data we report for the complex with one water.

Table 3.
Diffraction Data for $Co(C_3N_2H_3)_2 \cdot H_2O$
Tetragonal (I-Center), I41/acd (142), <origin at -4>,
a = 23.467 Å, c = 12.464 Å, V = 6864.0 Å$^3$,
$d_{calc}$ = 1.634 g/cm$^3$ from formula $Co(C_3N_2H_3)_2 \cdot H_2O$, Z = 32,
$F_{20}$ = 100.1 (0.0074, 27), $F_{30}$ = 57.2 (0.0099,53)

| $2\theta_{obs}$ ° | $2\theta_{calc}$ ° | $d_{obs}$ (Å) | $I/I_0$ | hkl | $2\theta_{obs}$ ° | $2\theta_{calc}$ ° | $d_{obs}$ (Å) | $I/I_0$ | hkl |
|---|---|---|---|---|---|---|---|---|---|
| 7.519 | 7.527 | 11.748 | 2.1 | 200 | 34.100 | 34.138 | 2.6271 | 0.5 | 840 |
| 10.642 | 10.652 | 8.3066 | 1.4 | 220 | 34.600 | 34.615 | 2.5903 | 0.5 | 822 |
| 11.003 | 11.010 | 8.0342 | 1.1 | 211 | 35.201 | 35.202 | 2.5474 | 2.5 | 723 |
| 15.097 | 15.086 | 5.8636 | 100 | 400 | 35.964 | 35.974 | 2.4951 | 3.3 | 921 |
| 15.354 | 15.342 | 5.7660 | 22.2 | 321 | 36.861 | 36.842 | 2.4364 | 1.9 | 604 |
| 16.088 | 16.087 | 5.5045 | 8.4 | 202 | 37.699 | 37.695 | 2.3842 | 1.6 | 743 |
| 16.875 | 16.879 | 5.2495 | 1.5 | 420 | 38.638 | 38.637 | 2.3283 | 1.2 | 325 |
| 17.108 | 17.109 | 5.1785 | 13.7 | 411 | 39.134 | 39.140 | 2.3000 | 2.2 | 932 |
| 18.571 | 18.573 | 4.7738 | 14.9 | 312 | 39.633 | 39.634 | 2.2722 | 2.3 | 714 |
| 20.197 | 20.196 | 4.3930 | 5.2 | 431 | 40.700 | 40.679 | 2.2150 | 0.7 | 772 |
| 20.778 | 20.773 | 4.2716 | 20.6 | 402 | 41.038 | 41.056 | 2.1975 | 2.0 | 862 |
| 21.558 | 21.581 | 4.1188 | 7.4 | 521 | 41.552 | 41.566 | 2.1715 | 2.4 | 923 |
| 22.100 | 22.123 | 4.0189 | 0.6 | 422 | 42.238 | 42.238 | 2.1379 | 1.4 | 961 |
| 22.703 | 22.712 | 3.9135 | 3.0 | 600 | 43.718 | 43.718 | 2.0689 | 3.2 | 664 |
| 23.014 | 22.999 | 3.8613 | 1.8 | 213 | 45.011 | 45.003 | 2.0124 | 1.6 | 1060 |
| 24.014 | 24.013 | 3.7027 | 8.9 | 512 | 45.388 | 45.476 | 1.9965 | 0.7 | 914 |
| 25.316 | 25.304 | 3.5151 | 5.1 | 541 | 46.034 | 45.976 | 1.9700 | 0.7 | 725 |
| 26.335 | 26.334 | 3.3814 | 2.6 | 532 | 46.423 | 46.414 | 1.9544 | 1.4 | 972 |
| 26.534 | 26.535 | 3.3565 | 4.8 | 413 | 47.151 | 47.153 | 1.9259 | 2.5 | 981 |
| 26.884 | 26.885 | 3.3136 | 6.3 | 602 | 48.038 | 48.000 | 1.8924 | 0.8 | 516 |
| 27.964 | 27.957 | 3.1880 | 1.2 | 622 | 48.557 | 48.544 | 1.8734 | 1.5 | 1053 |
| 28.562 | 28.573 | 3.1194 | 6.8 | 721 | 49.314 | 49.317 | 1.8464 | 2.2 | 835 |
| 29.685 | 29.678 | 3.0070 | 4.8 | 523 | | | | | |
| 30.469 | 30.485 | 2.9314 | 5.6 | 712 | | | | | |
| 31.073 | 31.097 | 2.8758 | 1.6 | 314 | | | | | |
| 31.532 | 31.531 | 2.835 | 7.4 | 811 | | | | | |
| 32.489 | 32.502 | 2.7536 | 5.7 | 404 | | | | | |
| 33.380 | 33.371 | 2.6821 | 3.5 | 831 | | | | | |

Table 4.
Diffraction Data for $Zn(C_3N_2H_3)_2 \cdot 0.5H_2O$
Tetragonal (I-Center), I41cd (110),
a = 23.505 Å, c = 12.451 Å, V = 6879.3 Å$^3$,
$d_{calc}$ = 1.611 g/cm$^3$ from formula $Zn(C_3N_2H_3)_2 \cdot 0.5H_2O$, Z = 32,
$F_{20}$ = 62.5(0.0119,27), $F_{30}$ =44.1(0.0126,54)

| $2\theta_{obs}$ ° | $2\theta_{calc}$ ° | $d_{obs}$ (Å) | $I/I_0$ | hkl | $2\theta_{obs}$ ° | $2\theta_{calc}$ ° | $d_{obs}$ (Å) | $I/I_0$ | hkl |
|---|---|---|---|---|---|---|---|---|---|
| 7.489 | 7.516 | 11.793 | 1.3 | 200 | 37.686 | 37.674 | 2.3850 | 1.4 | 743 |
| 10.622 | 10.637 | 8.3214 | 1.1 | 220 | 38.663 | 38.673 | 2.3269 | 1.4 | 325 |
| 11.000 | 11.006 | 8.0367 | 0.6 | 211 | 39.102 | 39.097 | 2.3018 | 1.7 | 932 |
| 11.940 | 11.897 | 7.4062 | 0.2 | 310 | 39.628 | 39.633 | 2.2724 | 1.8 | 714 |
| 15.102 | 15.064 | 5.8616 | 100 | 400 | 40.690 | 40.092 | 2.2156 | 0.5 | 1031 |
| 15.332 | 15.329 | 5.7743 | 65.6 | 321 | 41.021 | 41.010 | 2.1984 | 1.7 | 1002 |
| 16.093 | 16.097 | 5.5029 | 5.6 | 202 | 41.538 | 41.535 | 2.1723 | 2.1 | 923 |
| 16.857 | 16.855 | 5.2553 | 2.5 | 420 | 42.154 | 42.179 | 2.1419 | 1.2 | 961 |
| 17.102 | 17.092 | 5.1804 | 12.1 | 411 | 43.714 | 43.716 | 2.0690 | 2.8 | 943 |
| 18.570 | 18.575 | 4.7741 | 13.7 | 312 | 43.964 | 43.392 | 2.0578 | 1.3 | 116 |
| 19.236 | 19.238 | 4.6104 | 0.6 | 510 | 44.388 | 44.424 | 2.0392 | 0.8 | 1013 |
| 20.171 | 20.174 | 4.3986 | 4.8 | 431 | 44.962 | 44.981 | 2.0144 | 1.3 | 1102 |
| 20.760 | 20.769 | 4.2751 | 14.1 | 402 | 45.343 | 45.334 | 1.9984 | 0.7 | 316 |
| 21.555 | 21.556 | 4.1192 | 3.8 | 521 | 45.991 | 45.988 | 1.9717 | 0.6 | 725 |
| 22.095 | 22.116 | 4.0197 | 0.4 | 422 | 46.372 | 46.363 | 1.9564 | 1.4 | 406 |
| 22.684 | 22.679 | 3.9167 | 2.6 | 600 | 47.142 | 47.171 | 1.9262 | 2.1 | 963 |
| 22.990 | 23.019 | 3.8653 | 1.0 | 213 | 48.035 | 48.040 | 1.8925 | 0.8 | 516 |
| 23.998 | 24.001 | 3.7052 | 7.5 | 512 | 48.500 | 48.499 | 1.8754 | 1.2 | 1123 |
| 25.278 | 25.273 | 3.5203 | 3.8 | 541 | 49.306 | 49.318 | 1.8467 | 1.9 | 835 |
| 26.323 | 26.317 | 3.3829 | 2.8 | 532 | 49.730 | 49.674 | 1.8319 | 0.6 | 606 |
| 26.540 | 26.543 | 3.3557 | 4.8 | 413 | | | | | |
| 26.867 | 26.867 | 3.3157 | 4.9 | 602 | | | | | |
| 27.907 | 27.936 | 3.1944 | 0.7 | 622 | | | | | |
| 28.577 | 28.537 | 3.1210 | 6.1 | 721 | | | | | |
| 29.674 | 29.678 | 3.0081 | 4.7 | 523 | | | | | |
| 30.459 | 30.459 | 2.9323 | 4.3 | 552 | | | | | |
| 31.143 | 31.123 | 2.8695 | 1.4 | 314 | | | | | |
| 31.496 | 31.490 | 2.8381 | 5.8 | 741 | | | | | |
| 32.500 | 32.524 | 2.7527 | 5.2 | 404 | | | | | |
| 33.342 | 33.327 | 2.6851 | 3.0 | 831 | | | | | |
| 34.102 | 34.089 | 2.6270 | 0.3 | 840 | | | | | |
| 35.222 | 35.187 | 2.5459 | 2.0 | 723 | | | | | |
| 35.978 | 36.021 | 2.4942 | 2.9 | 444 | | | | | |
| 36.847 | 36.850 | 2.4373 | 1.5 | 604 | | | | | |

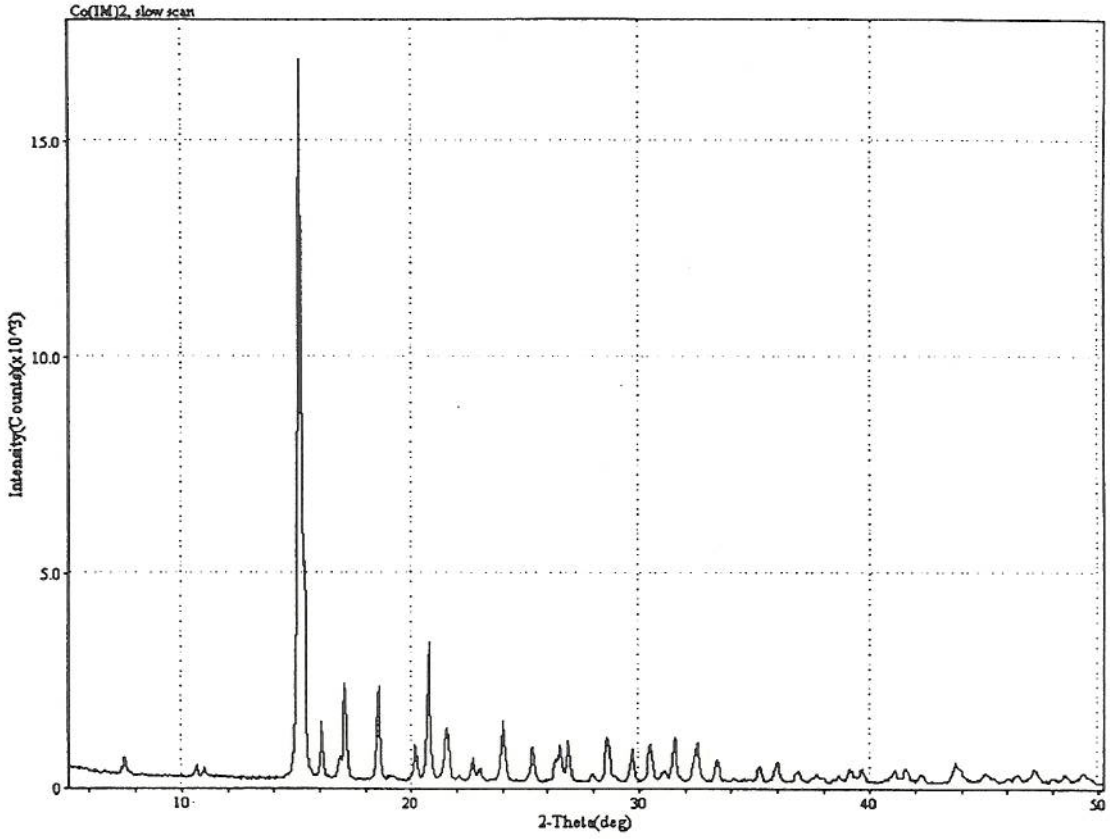



Figure 2. Diffraction pattern for cobalt imidazolate

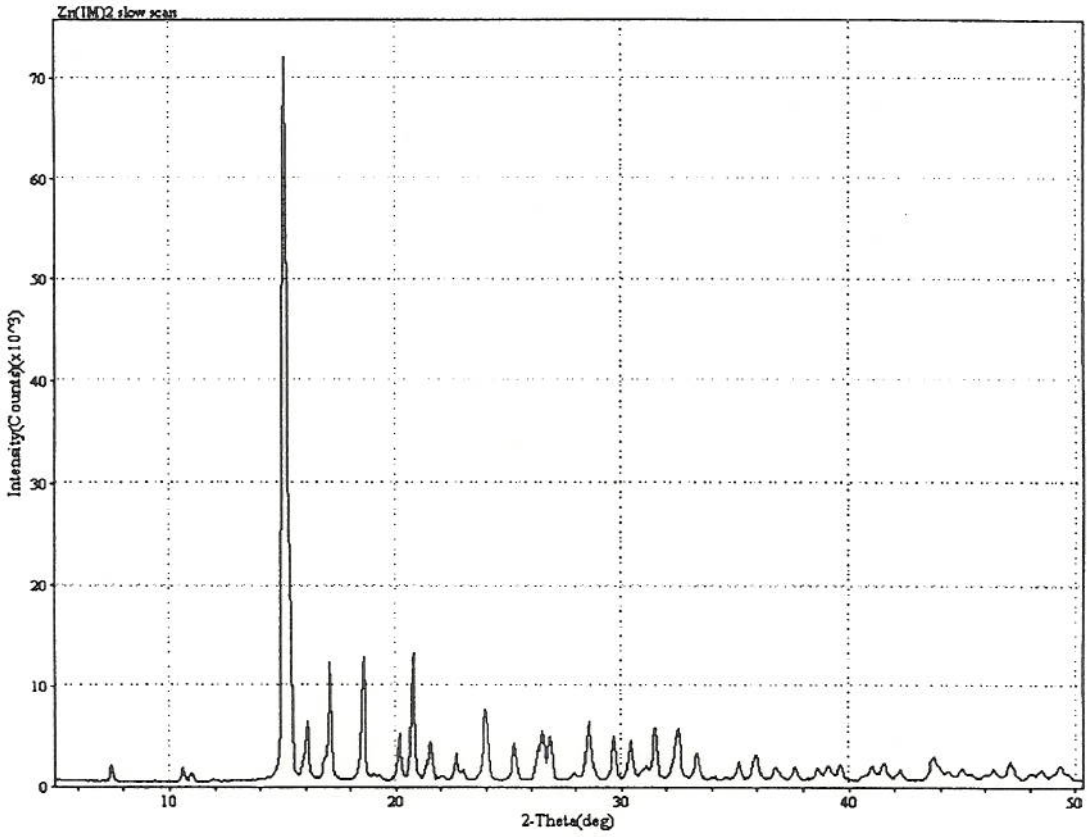



Figure 3. Diffraction pattern for zinc imidazolate

## REFERENCES

[1] R. R. Thomas, V. A. Brusic, and B. M. Rush, *J. Electrochem. Soc.*, **139** (1992) 678-685
[2] R. Walker, *Corrosion (NACE)*, **32** (1976) 414
[3] D.S. Moore and S.D. Robinson, *Advances in Inorganic Chemistry*, **32** (1988) 171-239
[4] J. Reedijk, A. R. Siedle, R. A. Velapoldi, and J. A. M. Van Hest, *Inorg. Chim. Acta* **74** (1983) 109
[5] J. Reedijk, G. Roelofsen, A. R. Siedle, and A. L. Spek, *Inorg. Chem.*,**18** (1979) 1947
[6] I. Sotofte and K. Nielsen, *Acta Chem. Scand.*, **35A** (1981) 733
[7] Ibid. **38A** (1984) 253
[8] A. Brown and S. Linde, "Powder Diffraction Profiles and the Pearson VII", *Adv. X-ray Anal.*, **30** (1985) 343-350
[9] R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem.* (1980) **464** 187-194
[10] M. Sturm, F. Brandel, D. Engel, and W. Hoppe, *Acta Crystallogr.*, **B31** 2369 (1976)