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X-RAY STUDIES ON BIS-(1-ACETYL-2 PHENYL-2 [4′-1′-PHENYL-3′- METHYL-2′ PYRAZOLIN-5′ONE-4′-y1]-1-CARBOXY Cu(II), Ni(II), Zn(II) AND Co(II) COMPOUNDS

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Complex compounds of Cu(II), Ni(II), Zn(II) and Co(II) with pyrazolones as chelating ligands has been synthesized and X-ray diffraction studies have been carried out. All the four complexes have been found to have isomorphous structure and the radial distribution studies indicate that there is a slight change in the bond distances.

INTRODUCTION

Complex compounds of cobalt (II), nickel (II), zinc (II) and copper with pyrazolones as chelating agents have been synthesized in the laboratory and have been found to be strong fungicidal agents. X-ray diffraction studies have been carried out to obtain structural information about the complexes. In the absence of good single crystals, detailed crystal structure analysis is not possible. However radial distribution analysis of the X-ray powder diffraction data give information about the inter atomic bond distances in the molecule and the method has been applied for studying the structure of minerals [1] and polymeric compounds [2]. Hence in the present case an r.d.f. study of the X-ray diffraction data has been carried out.

EXPERIMENTAL

Synthesis of the complexes :

The metal complexes were synthesized following standard procedure. All the metal ions were taken in the +2 oxidation state. Thiocynate, nitrate, chloride, bromide and acetate served as their anion counterpart. The ligand used for complexation was 1-Acetyl-2-phenyl (or its ortho or paraderivatives)-2[4′-1′-phenyl-3′-methyl-2′ Pyrazolin-5′one-4′-y1]-1-carboxy ethyl ethane. The above ethylacetoacetate derivative was synthesized in solid crystal form by simply adding 1-phenyl-3-methol-4-medium and subsequent treatment with water. Alcoholic solution of the metal salt and the pyrasolone aceto acetic ester was then refluxed on water both when the complex compounds crystallized out in solid state on cooling. The cobalt (II) and nickel (II) complexes were coloured greenish white and that of copper (II) were blue and zinc (II) faint yellow. The melting points for all the complexes were above 360°C.

X-ray measurements :

X-ray diffraction patterns for the samples were recorded on strip chart with the help of a Norelco diffractometer using monochromatised CuK_{α} radiation at a scanning rate of 1° per minute. The recorded intensities were corrected for polarization and absorption using the procedure described by Kaelble [3]. Tabulated values of the atomic scattering factor [4] and the incoherent scattering factors [5] were used for obtaining the independent scattering curves. The corrected intensities were scaled to electron units first by the high angle method and then by the method due to Kroughmoe [6]. Contribution of the flat faced diffractometer sample in the small angle region and that due to multiple scattering were subtracted by following the method described by Warren [7].

Following the method described by Kaelble [3], the radial electronic distribution function for poly atomic samples is given by

$$4\pi r^2 \rho e(r) = 4\pi r^2 \rho_0 e + \frac{2r}{n}\int_0^{\infty} s.i(s).m_1(s),\ m_2(s)\, m_3(s)\, snisr.ds$$

where $s = \dfrac{4\pi sn\theta}{\lambda}$

$$i(s) = \frac{loles}{K} - (\Sigma_i\, x_i f_i^2(s) + \Sigma_i\, x_i I_{inc})$$

x_i = mole fraction of atom of type *i*

$f_i(s)$ = atomic scattering factor of atom of type *i*

I_{inc} = incoherently scattered intensities

ρ_{oe} = mean electron density and is given by $\rho_o [\Sigma x_i f_i(o)]^2$

$M_i(s)$ = a suitable sharpening function = $\dfrac{[\sum x_i f_i(o)}{[\sum x_i f_i^2(s)}$

$M_2(s)$ = $\exp(-bs^2)$

= an artificial temperature factor introduced to suppress ripples due to series termination.

$M_3(s)$ = a strip function = 1 up to s_{max} and 0 beyond s_{max}

Results and discussion

The interplanar distances (*d*) have been calculated from the diffractograms. Some of the prominent d_{hkl} values for the four samples have been tabulated in Table-1. It has been observed that all the five complexes have nearly the same *d*-values. This indicates that the structures of the four complexes are almost same except for the metallic ions.

The radial distribution function $4\pi r^2 \rho_e (r)\, dr$ gives the number of electrons in a shell of radius r and $r + dr$ with respect to the atom placed at the origin. For a fully amorphous sample the function is expected to increase monotonously. Because of the presence of the local order in the structures peaks are observed at different positions corresponding to the atomic positions. In the present case the r.d.f. has been calculated in the range 1Å to 5Å and the obtained interatomic vector values have been shown in Table-2. It is observed that the C—N, C—O and C—C bond lengths are of the order of 1.32, 1.36, 1.52 respectively. A prominent

peak is observed in the r.d.f. function curve at a distance of about 1.90 Å. This value is usually the bond distance for metal-oxides. Hence it can be inferred that the metal atoms are attached to the oxygen atom in the middle of the molecules.

Table-1. Prominent Interplanar Distances ("d" values) for the four complexes in A Units

Cu(II)	Co(II)	Ni(II)	Zn(II)
8.80	-	8.81	8.80
7.45	7.45	7.45	7.45
5.61	5.38	5.34	5.56
4.05	4.05	4.05	4.05
3.63	3.67	3.63	3.63
2.82	2.80	2.82	2.82
2.23	2.20	2.26	2.18

Table-2. Interatomic Vectors (in Å) as calculated from the R.D.F. Analysis

	Cu(II)	Co(II)	Ni(II)	Zn(II)
C-N	1.32	1.35	1.33	1.33
C-O	1.36	1.38	1.37	1.37
C-C	1.53	1.51	1.52	1.51
Metal-O	1.96	1.88	1.92	1.85
–	2.78	2.69	2.70	2.72
–	3.46	3.51	3.52	3.50
–	4.17	4.25	4.20	4.26

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