

Unique Coordination of Copper in Hexacyanometallates

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Within divalent transition metals hexacyanometallates (III) the copper (2+) salts show unique features. To the copper (2+) salts correspond the shortest unit cell edges, the highest $\nu(\text{CN})$ vibration frequencies, the lowest hydration degree and dehydration temperatures, the lowest Mössbauer isomer shift value, and the strongest magnetic exchange interaction (J) between the metal centers. Such unique features were attributed to a particularly strong bond of the copper atom to the N ends of the CN groups. The driving force for such behaviour was ascribed to a combined effect where the copper (2+) shows a high ability to receive electrons in its $3d$ hole favouring an electronic configuration close to $3d^{10}$ and the CN group complements such ability donating electrons through its 5σ orbital which has certain anti-bonding character. This hypothesis is supported by the obtained structural and spectroscopic data. The occurrence of a cooperative Jahn–Teller effect in this family of materials was discarded. In the pseudo-octahedral coordination for the copper (2+) atom the e_g orbital degeneration is initially removed. The collected EPR spectra are characteristic of a cubic environment (isotropic g -values). Analogue evidence was obtained from high resolution X-ray powder patterns recorded in the 12–300 K temperature range. All the patterns correspond to a cubic unit cell.

1. Introduction

Hexacyanometallates or Prussian blue (PB) analogues form an interesting family of molecular materials. Within their most interesting features are those related to the porous structure and the relatively high hydrogen adsorption [1–3], the strong charge overlapping among the metals linked at the C and N ends of

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