Sir:

Chloramphenicol having the possible three metal-binding sites, an amide and two hydroxy groups, is a well known antibiotic, but its reaction schemes with metal ions were not fully established, although the importance of metal interactions with antibiotics in relation to their subsequent actions has been discussed\(^1\). MEDVEDOVSKII et al proposed the structure I in Fig. 1 to the purple complex in reaction of Cu (II) with chloramphenicol in alkaline aqueous solution\(^2\). On the other hand, a green Cu (II)-chloramphenicol complex was isolated from methanol by FAZAKERLEY et al\(^3\), who were unable to characterize the coordination mode in this complex. In a recent communication, JEREMIC et al concluded that the amide group was not involved in coordination in the purple complex suggesting the structure II in Fig. 1\(^4\).

In this paper we propose structures for the two kinds of complexes colored green and purple, which were formed in the reaction of Cu (II) and chloramphenicol under different pH conditions. A characterization of these complexes in metha-
to Cu (II) by the molar ratio method, corresponding well with the result of JEREMIC et al.4). The two complexes showed unique and almost the same CD spectra with each other with the sign (— + —) above 400 nm and the purple complex gave a larger magnitude than the green one.

Involvement of the two nitrogen atoms as the metal-binding sites in the green and purple 1:2 Cu (II)-chloramphenicol was unequivocally demonstrated by ESR detection of the ligand hyperfine splittings (5 lines) due to the equivalent nitrogen atoms (14N, I=1) (Fig. 2). The presence of the deprotonated amide nitrogen bound to Cu (II) in both complexes was further corroborated by monitoring the frequencies of carbonyl groups with the IR spectra measured in methanol (Fig. 3). The band at 1593 cm⁻¹ in both complexes is assigned to the carbonyl group of the amides which involve deprotonated amide nitrogens bound to Cu (II)⁵,⁶.

From these data, we propose that Cu (II)-chloramphenicol green complex has two coordination sites with Cu (II), the deprotonated amide nitrogen and oxygen attached to C1 or C3 forming a tetracoordinated square planar configuration. The purple one has three sites, the deprotonated amide nitrogen and two oxygen attached to C1 and C3 forming a hexacoordinated octahedral configuration (Fig. 4). At present we can not answer which oxygen atom attached to C1 or C3 is used to form the chelation in the green complex.

Further investigations are under way to establish this point.

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