Crystal Structural Studies of Bis(biguanide)nickel(II) Chloride

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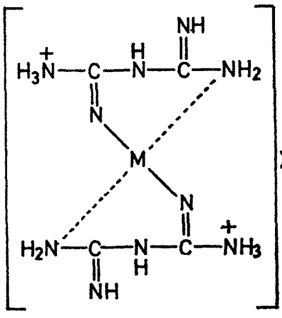
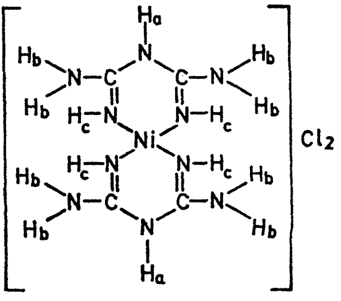
Summary Evidence is presented for a new structure for bis(biguanide)nickel(II) chloride.

THE structure of four-co-ordinated metal biguanide complexes has long been a topic of controversy among several research groups. Ray and Saha[1] have considered a variety of structures for the biguanide complexes and have cited evidence in support of structure (I). Kunchur and Mathew[2] have reported a single crystal X-ray diffraction study in which they state that they have confirmed the structure suggested by Ray and Saha for a substituted biguanide complex, ethylenebis(biguanide)copper(II) chloride monohydrate. We report a single crystal X-ray diffraction study of bis(biguanide)nickel(II) chloride dihydrate and a ^{1}H n.m.r. study of anhydrous bis(biguanide)nickel(II) chloride, which provide the first definite evidence favouring the alternative structure (II) for a complex of this type.

The structure of bis(biguanide)nickel(II) chloride dihydrate has been solved by single-crystal X-ray diffraction techniques with visually estimated Weissenberg intensity data for 848 diffraction maxima. The data were refined by a block diagonal isotropic least-square procedure to a conventional R-factor of 12·3%. Crystals of the complex are triclinic, space group $P\bar{1}$, a = 6·85 ± 0·02, b = 9·48 ± 0·03, c = 12·50 ± 0·03 Å; α = 112·8 ± 0·3, β = 100·5 ± 0·3, γ = 100·2 ± 0·3°; D_m = 1·71 ± 0·02g./cm.^{3}, D_c = 1·73 g./cm.^{3} (for two formula units per unit cell). The structure is made up of essentially planar bis(biguanide)-nickel(II) ions stacked approximately along the a axis and held together by electrostatic attraction to the chloride ions and by hydrogen bonding to the water molecules. The biguanide molecules act as bidentate ligands giving the Ni^{II} ion square-planar co-ordination. Bond distances and bond

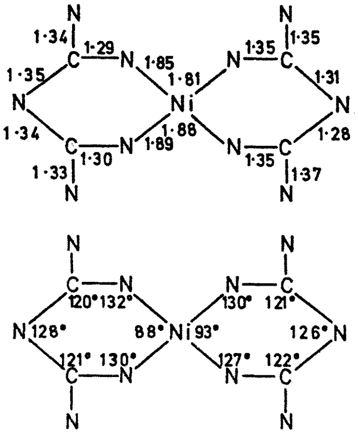


(I)



(II)

angles for the bis(biguanide)nickel(II) ion are shown in the Figure. The standard deviation in the Ni–N bond distances is 0·03 Å; for C–N it is 0·04 Å. The C–N bond distances are all of the same length within the accuracy of this structural determination and do not differ significantly from those found in ethylenebis(biguanide)copper(II) chloride by Kunchur and Mathew.[2] Although structure (II) requires different bond orders for the various C–N bonds, it is not surprising that their lengths do not differ significantly in view of the fact that all of the nitrogens have p_π-orbitals with electrons in them, such that considerable delocalization of the π-system must occur. In 2-cyanoguanidine, Z. V. Zvonkova *et al.*[3] have shown that the three nitrogens bonded to the trigonal carbon are all at the same distance from the carbon, within experimental error. It was not possible to locate the hydrogen atoms by the *X*-ray analysis.



FIGURE

The ^1H n.m.r. spectrum† of anhydrous bis(biguanide)nickel(II) chloride in $(CD_3)_2SO$ shows three peaks: τ 0·12 (very broad), 3·40 (broad), and 5·35 (narrow), with respective intensities of 1 : 4 : 2. These ^1H n.m.r. data are consistent with the expected 14 protons and indicate three sets of 2, 8, and 4 equivalent protons. These data are not consistent with structure (I), in which there would be four sets of 2, 2, 4, and 6 equivalent protons, but are consistent with our suggested structure (II). The set of 2 equivalent protons can be assigned to the 2 H_a protons. Their downfield chemical shift can easily be explained by the "ring current effect"[4] arising from the π-cloud formed by the p_π ligand orbitals and the d_π metal orbitals. In a somewhat similar system, pyrrole, the N–H proton exhibits a chemical shift of τ 2·00[5] due to the "ring current effect." The set of 8 equivalent protons can then be assigned to the 8 H_b protons. Their chemical shift might be ascribed to the electron-attracting C=NH group which withdraws electron density from the amino-nitrogen and in turn from the protons. An analogy can be drawn to amides in which the NH_2 protons have a chemical shift in a range from τ 1·5—5·0.[4] The last set of 4 equivalent protons is due to the 4 H_c protons. Their high-field position in relation to the other two peaks is due to shielding by the filled d_{xy} orbitals of the diamagnetic d^8 Ni^{2+} metal ion.

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† A Varian T-60 was used to record the ^1H n.m.r. spectrum using reagent grade $(CD_3)_2SO$ containing Me_4Si as a reference.

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[4] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, NewYork, 1967, p. 116.
[5] H. A. Szymanski and R. E. Yelin, "NMR Band Handbook," Plenum, New York, 1968, p. 375.