The Crystal and Molecular Structure of Chloro(bis-{2-[(2-pyridylmethyl)amino]ethyl}disulphide)nickel(II) Perchlorate

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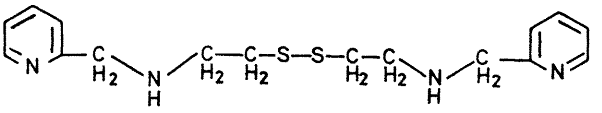
Summary A single-crystal *X*-ray diffraction study of $[Ni(C_{16}H_{22}N_4S_2)Cl]ClO_4$ shows that one sulphur atom of a disulphide group in an aliphatic chain is co-ordinated at an octahedral Ni^{II} site with an Ni^{II}–S bond-length of 2.47 Å, approximately equal to the sum of the Pauling covalent radii.

RED solutions of the Ni^{II} complex of the tridentate ligand 2-[(2-pyridylmethyl)amino]ethanethiol can be oxidized by air[1] or H_2O_2 in Me_2CO–EtOH[2] to give a blue octahedral Ni^{II} complex[1] which is readily crystallized. The existence of the ligand (I) was suggested,[2] and the possibility of disulphide co-ordination, as had been demonstrated for Cu^{II}–cystine systems in solution,[3] existed. Conductivity measurements in solvents of widely varying polarity indicate anomalously that two such ligands and two Ni^{II} ions form a dimeric cation.[2]

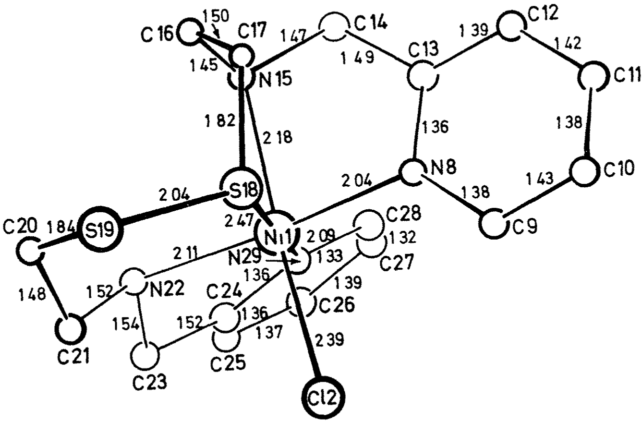


(I)

Crystals formed as deep blue rectangular prisms with the following crystal data $[Ni(C_{16}H_{22}N_4S_2)Cl]ClO_4$, orthorhombic, *Pbca* $a = 24.031(3)$, $b = 14.698(2)$, $c = 12.461(2)$ Å, $D_m = 1.587$, $D_c = 1.594$, $Z = 8$.

Data representing 90% of the Cu ($\lambda = 1.5418$ Å) sphere of reflection were collected using equi-inclination Weissenberg film methods and were estimated visually. The 4473 unique observations were corrected for several effects including spot shape and absorption ($\mu = 56.3$). The positions of the five largest atoms in the asymmetric unit were determined by both Patterson and direct methods, and Fourier refinement revealed the positions of all non-hydrogen atoms except for two perchlorate oxygens. Full-matrix least-squares refinement of positional and isotropic thermal parameters has led to the present *R* of 0.19. Standard deviations in heavy-atom bond lengths are <0.03 Å.

A single pentadentate ligand is associated with each Ni^{II} to form a monomeric complexed cation (see Figure).



FIGURE

Although this complex is asymmetric, two enantiomorphs, related by an inversion centre, are found. One sulphur atom of the disulphide group occupies an octahedral site at the Ni^{II}, approaching it with a co-ordinate covalent bond of 2.47 Å, in approximate agreement with the sum of the Pauling covalent radii,[4] 2.43 Å. A chloride ion co-ordinates the sixth Ni^{II} site. The two pyridine rings are *cis*, the two amino-groups are *cis* and the chloride and the co-ordinating sulphur are *cis*. The octahedral angles are all within 10° of right angles, and the largest deviations can be explained by strain in the ligand. The S–S and S–C single bond lengths are normal, apparently unaffected by the sulphur co-ordination. The perchlorate ion is able to participate in one hydrogen bond to each of the two *cis* amino-groups of a single complexed cation. Replacing chloride by bromide, or both chloride and perchlorate by iodide ions, yields an isomorphous structure

We thank Dr Ruth L Gavino for supplying the crystals, and John R Ruble and Linda L Y Chun for their assistance

(*Received, November 16th,* 1970, *Com* 1970)

[1] R L Gavino and J W Wrathall Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, April, 1968.

[2] R L Gavino and J W Wrathall Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis April, 1969

[3] C J Hawkins and D D Perrin *Inorg Chem* , 1963 **2**, 843

[4] L Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1960