

COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART VIII. COPPER AND NICKEL α -NAPHTHYLBIGUANIDINES

BY PRIYADARANJAN RÂY AND HARENDRALAL RAY

Copper and nickel α -naphthylbiguanide bases, both hydrated and anhydrous, have been prepared. The complex nickel base has been isolated in three forms, α , β and γ , differing in colour, solubility, melting point and other properties as well as in their state of hydration. Of these, α - and β -forms represent respectively the *cis*- and *trans*-isomers of the planar square nickel complex and γ , their solid solution or molecular compound. Copper α -naphthylbiguanide hydrochloride has also been isolated in two forms.

A series of complex copper naphthylbiguanide salts, *viz.*, chloride, bromide, iodide, sulphate, thiosulphate, dithionate, sulphocyanide, nitrate and carbonate have been prepared and their properties studied. In the case of nickel the only salts prepared and studied were chloride and sulphate.

In a previous paper of this series (Rây and Chakravarty, *J. Indian Chem. Soc.*, 1941, 18, 609) copper and nickel phenylbiguanidines were described. It was found that a number of copper phenylbiguanide salts could be obtained in two modifications, named α and β by the authors, differing in colour, solubility and melting point. The α -varieties were unstable and changed gradually into the β -form. This transformation was accelerated by rise of temperature and the presence of moisture. The β -variety, on the other hand, never changed back into the α -form. From a consideration of their properties the authors concluded that they represent the *cis-trans* isomers of the planar copper complex.

The same authors also succeeded in isolating three varieties of the nickel phenylbiguanide base, α , β and γ , distinguished by their difference in colour, solubility, melting point and other properties. Of these the α -form readily changed into the β -modification. The α - and β -forms were regarded by the authors as representing respectively the *cis*- and *trans*-isomers of the diamagnetic planar nickel complex, whereas the γ -variety was believed to be a solid solution or a molecular compound of the two.

In view of these findings in the case of co-ordination with an unsymmetrical molecule like phenylbiguanide, it was expected that similar isomeric copper and nickel complexes would be more readily obtained with naphthylbiguanide whose structure is more unsymmetrical than that of the phenyl derivative. With this end in view the preparation and the study of the complexes of bivalent metals with α -naphthylbiguanide were undertaken, and this forms the subject matter of the present paper.

Salts of complex copper naphthylbiguanide have not, however, been obtained in more than one modification except in the case of its chloride, which gives two varieties differing in colour. In the anhydrous state one form is chocolate-red (light red-violet when hydrated) and the other violet-blue. They, however, both dissolve in water giving light red solution. Evidences in the present case are therefore not strong enough to consider them as *cis-trans* isomers. They might as well be dimorphs or dimers.

In the case of the nickel complex, however, the nickel naphthylbiguanide base has been isolated in three different forms, α , β and γ , which differ in their state of hydration, colour when dissolved in pyridine, solubility and melting point. The α -form is a flesh-coloured substance and contains one molecule of water which it loses at 110° without any change in its colour. It is

insoluble in water, gives a red solution in pyridine and is sparingly soluble in alcohol. The β -variety forms bright yellow crystals and contains 2.5 molecules of water which it loses at 140° without changing its colour. It is insoluble in water and alcohol, but dissolves in pyridine giving a yellow solution. The γ -form is light buff in colour, contains 2 molecules of water and melts in boiling water. It gives a yellow solution in pyridine.

These observations seem to suggest that, as in the case of the corresponding nickel phenylbiguanide base, nickel α -naphthylbiguanide base can also occur in three forms: α , β and γ . Of these α and β may be regarded to represent respectively the *cis*- and *trans*-isomers of the planar square nickel complex of the penetration type and γ , their solid solution or molecular compound.

The constitution of these copper and nickel naphthylbiguanide complexes can be represented in the same way as those of the corresponding phenylbiguanide compounds.

EXPERIMENTAL

α -Naphthylbiguanide was prepared by heating for about 4 hours aqueous solutions of α -naphthylamine hydrochloride and dicyandiamide in equimolecular proportions and then treating the mixture with an excess of caustic soda solution in the cold. The white crystals of α -naphthylbiguanide separated from the solution. These were purified by recrystallisation from hot water (Cohn, *J. prakt. Chem.*, 1911, ii, 84, 394), m.p., 153.5° — 155.5° .

Copper Compounds

Copper α -Naphthylbiguanide Monohydrate.—An ammoniacal solution of copper sulphate in slight excess was added to that of naphthylbiguanide in dilute ammonia and the mixture was well shaken. The light blue-violet crystals, which separated out, were filtered after sometime and washed with water till free from sulphate. This was then dissolved in the minimum quantity of dilute hydrochloric acid and treated with an excess of caustic soda solution in the cold. Thus purified the base was washed with water till free from chloride and dried over lime to a constant weight. [Found: N, 26.16; Cu, 11.99. $[\text{Cu}(\text{Nap Big})_2]$, H_2O requires N, 26.23; Cu, 11.92 per cent; where $\text{NapBigH} = \text{C}_{12}\text{H}_{13}\text{N}_5$, a molecule of α -naphthylbiguanide].

The substance forms light blue-violet crystals insoluble in cold water. On boiling with water it melts and slowly dissolves. It is insoluble in cold or hot alkali but is decomposed by mineral acids. In organic solvents like acetone, pyridine, alcohol and ether it dissolves to a pink solution. It behaves as a fairly strong base and liberates ammonia from ammonium chloride. When heated at 90° for about 10 hours it lost whole of its water (3.41%; calc. 3.37%). The anhydro-base gave on analysis Cu, 12.35. $[\text{Cu}(\text{C}_{12}\text{H}_{12}\text{N}_5)_2]$ requires Cu, 12.34%. The anhydro-base has the same colour and other properties as the hydrated variety.

Copper α -Naphthylbiguanidinium Chloride.—An excess of copper chloride solution was added to that of naphthylbiguanide in water. Solid ammonium chloride was then added to the mixture to salt out the complex chloride. The light red-violet crystals separated from the solution. These were washed several times with cold water and dried to a constant weight in air. It is soluble in hot water as well as in pyridine and alcohol, giving a light red solution. [Found: N, 22.70; Cu, 10.35; Cl, 11.57; H_2O (by loss at 115°), 4.41. $[\text{Cu}(\text{NapBigH}^+)]_2 \text{Cl}_2$, $1.5\text{H}_2\text{O}$ requires N, 22.74; Cu, 10.33; Cl, 11.53; H_2O , 4.39 per cent].

The colour of the anhydrous chloride is chocolate-red. When a solution of the above compound in absolute alcohol was left exposed to air for sometime, blue-violet crystals of the same composition gradually separated from it. These, however, dissolve in water giving a light red solution as the previous compound. {Found: N, 23'93; Cl, 12'16; Cu, 10'89. [Cu(NapBigH⁺)₂] Cl₂ requires N, 23'79; Cl, 12'06; Cu 10'81 per cent}.

The bromide.—An excess of copper chloride solution was added to that of α -naphthylbiguanide in water. A strong solution of potassium bromide was then added to the mixture. Pale red crystals of the complex bromide separated at once. These were washed and dried as before. The substance dissolves in alcohol and hot water giving a red solution. {Found: Br, 22'96; Cu, 9'08. [Cu(NapBigH⁺)₂] Br₂, H₂O requires Br, 23'0; Cu, 9'14 per cent}.

The iodide was prepared by adding an excess of concentrated potassium iodide solution to that of freshly prepared complex chloride in the cold. The mixture was thoroughly stirred and allowed to rest. The sparingly soluble chocolate-brown crystals were washed with cold water, dried first over a porous plate and then to a constant weight in air. The substance dissolves in pyridine to a red solution. {Found: I, 32'91; Cu, 8'21. [Cu(NapBigH⁺)₂] I₂ requires I, 32'92; Cu, 8'24 per cent}.

The nitrate.—A strong solution of ammonium nitrate was added to a mixture of naphthylbiguanide and excess of copper chloride in water. The complex nitrate was obtained in the form of sparingly soluble rose-red crystals. These were washed and dried as usual. It dissolves in pyridine giving a violet solution and also in many other organic solvents like alcohol acetone, ether, toluene, etc. {Found: Cu, 9'85; NO₃, 19'20. [Cu(NapBigH⁺)₂](NO₃)₂ requires Cu, 9'91; NO₃, 19'32 per cent}.

The Sulphate.—A solution of copper chloride in excess was mixed with that of naphthylbiguanide. From the resulting red coloured solution sparingly soluble light violet crystals of the sulphate were precipitated by adding a concentrated solution of ammonium sulphate. It is soluble in many organic solvents giving a light violet solution. {Found: Cu, 8'60; SO₄, 12'99. [Cu(NapBigH⁺)₂] SO₄, 7 H₂O requires Cu, 8'60; SO₄, 12'98 per cent}.

The thiosulphate.—Pale violet crystals of the thiosulphate were obtained by adding a concentrated solution of sodium thiosulphate to that of the freshly prepared complex chloride. The substance is almost insoluble in water, but dissolves slightly in many organic solvents. {Found: Cu, 9'55; S₂O₃, 33'60. [Cu(NapBigH⁺)₂] S₂O₃, 2H₂O requires Cu, 9'55; S₂O₃, 33'64 per cent}.

The dithionate was prepared by adding a concentrated solution of sodium dithionate to that of a freshly prepared complex chloride. The substance forms pale violet crystals, slightly soluble in hot water and alcohol. {Found: Cu, 8'94; S₂O₆, 44'80. [Cu(NapBigH⁺)₂] S₂O₆, 2H₂O requires Cu, 8'91; S₂O₆, 44'85 per cent}.

The sulphocyanide was prepared from a concentrated solution of ammonium sulphocyanide and that of the freshly prepared complex chloride. The pink crystals of the precipitated sulphocyanide were filtered and washed, and then dissolved in absolute alcohol. The solution was filtered and allowed to evaporate in air when pure crystals of the substance were obtained. These were dried in air. {Found: Cu, 10'09; SCN, 18'10. [Cu(NapBigH⁺)₂](SCN)₂ requires Cu, 10'04; SCN, 18'10 per cent}.

The carbonate was prepared from a concentrated solution of sodium carbonate and that of a freshly prepared complex chloride. The precipitated carbonate was filtered and washed several times with water. Dried first over a porous plate and then in air to a constant weight. {Found :

C, 51'80; H, 4'52; Cu, 11'0. $[\text{Cu}(\text{NapBigH}^+)_2] \text{CO}_3$ requires C, 51'93; H, 4'50; Cu, 11'01 per cent}.

The substance forms light violet crystals, insoluble in cold water, but dissolves slightly in acetone and alcohol. In pyridine it forms a red solution.

Nickel Compounds

Nickel α -Naphthylbiguanide and its Hydrate. (a) α -Variety.—An ammoniacal solution of nickel sulphate in slight excess was added to that of naphthylbiguanide in hot dilute ammonia. After some time the precipitate was filtered and washed several times with water till free from sulphate. The product was dried first on a porous plate and then over alkali to a constant weight. {Found: N, 26'61; Ni, 11'13. $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_3)_2]$, H_2O requires N, 26'48; Ni, 11'10 per cent}.

The substance forms flesh-coloured crystals, insoluble in water. It can displace ammonia from boiling ammonium chloride solution. It is sparingly soluble in alcohol, but dissolves in pyridine giving a red solution. When heated at 110° for about 12 hours it lost the whole of its water (3'40%, calc. 3'41%) and formed the anhydro-base without any change of colour. {Found: Ni, 11'50. $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_3)_2]$ requires Ni, 11'49 per cent}.

(b) β -Variety was obtained as insoluble yellow crystals by adding a large excess of naphthylbiguanide solution drop by drop to that of nickel chloride at the boiling temperature. The crystals were washed several times with hot water and dried as before. The substance dissolves in pyridine and warm alcohol to a yellow solution. {Found: N, 25'0; Ni, 10'59. $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_3)_2]$, $2\frac{1}{2}\text{H}_2\text{O}$ requires N, 25'20; Ni, 10'56 per cent}.

On heating the substance at 140° for about 12 hours it lost all its water and formed the anhydro-base without any change of colour. {Found: H_2O , 8'0. Calc. H_2O , 8'09 per cent}.

(c) γ -Variety was obtained by dissolving the hydrated α -form in the minimum quantity of cold hydrochloric acid and then adding an excess of cold caustic soda solution. The light buff coloured crystalline precipitate was filtered, washed with cold water free from chloride and then dried as before. {Found: N, 25'70; Ni, 10'71. $[\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_3)_2]$, $2\text{H}_2\text{O}$ requires N, 25'61; Ni, 10'74 per cent}.

The substance melts when boiled with water. It is sparingly soluble in alcohol, but dissolves in pyridine giving a yellow solution.

Nickel α -Naphthylbiguanidinium Sulphate was obtained as a buff coloured crystalline precipitate by adding a solution of nickel sulphate in slight excess to that of α -naphthyl biguanide. The substance is sparingly soluble in pyridine, acetone and alcohol. {Found: Ni, 9'37; SO_4 , 15'30. $[\text{Ni}(\text{NapBigH}^+)_2] \text{SO}_4 \cdot \text{H}_2\text{O}$ requires Ni, 9'36; SO_4 , 15'32 per cent}.

Nickel α -Naphthylbiguanidinium Chloride.—A solution of naphthylbiguanide was added to a hot solution of nickel chloride in calculated amount. The mixture was filtered from any precipitated β -base. The filtrate, on cooling, gave light yellow crystals of the complex chloride. The substance dissolves completely in hot water as well as in pyridine, acetone and warm alcohol. {Found: N, 22'58; Ni, 9'50; Cl, 11'48. $[\text{Ni}(\text{NapBigH}^+)_2] \text{Cl}_2 \cdot 2\text{H}_2\text{O}$ requires N, 22'59; Ni, 9'47; Cl, 11'46 per cent}.