

COMPLEX COMPOUNDS OF BIGUANIDE WITH BIVALENT METALS. PART III. COPPER AND NICKEL PHENYL-BIGUANIDINES AND THEIR DIFFERENT MODIFICATIONS.

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Copper phenylbiguanide, both hydrated and anhydrous, as well as many of its salts (*viz.* chloride, bromide, iodide, sulphate, dithionate, nitrate and nitrite) have been isolated in two forms, α and β , differing in colour, m.p. and solubility. The anhydrous copper phenylbiguanidines have been proved to be monomeric by ebullioscopic measurements. The α -chloride has been found to be transformed into the β -form at 101° in presence of steam. The conditions for transformation of the two varieties for other salts have also been determined. Besides, salts such as thiosulphate, thiocyanate, sulphite, chlorate, bromate and iodate have also been prepared only in one form and their properties studied.

The two varieties of copper phenylbiguanidine, its hydrate and salts, may be regarded as dimorphs or *cis-trans* isomers, but the balance of evidences seems to support the latter view.

Of the compounds studied, the β -base, the β -chloride and the β -sulphate have been described by previous workers.

Nickel phenylbiguanidine has been isolated in three forms, namely α , β and γ , differing in colour, solubility and other properties. The γ -variety is likely to be a solid solution or molecular compound of the α and β forms, the latter two possibly representing the *cis-trans* isomerides of the planar nickel complex. The idea of polymorphism also cannot be definitely excluded without further investigations.

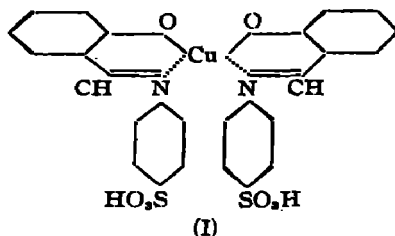
Various salts of nickel phenylbiguanide, such as the chloride, bromide, iodide, nitrate, nitrite, dithionate, sulphate, thiosulphate, sulphite, thiocyanate, chlorate, bromate and iodate have been prepared and their properties studied.

Of these nickel compounds the β -base, chloride and sulphate have been described by earlier workers.

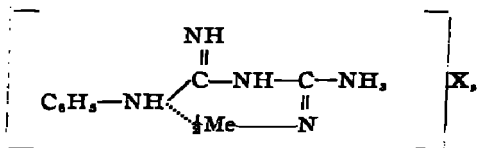
The planar configuration of the four co-ordinated inner-metallic complexes of bivalent nickel and copper has now been well established. Evidences in support of this are derived not only from the classical methods of stereochemistry but also from a substantial mass of physical data, specially relating to X-ray measurement of crystalline salts.

The occurrence of cis-trans isomerides of the nickel derivative of benzylmethylglyoxime (Sugden, *J. Chem. Soc.*, 1932, 246) is a definite illustration on the point. Cox, Wardlaw and collaborators (*ibid.*, 1935, 459, 1475) have demonstrated by means of X-ray studies the planar configuration for the 4-co-valent nickel. From the magnetic criterion of the bond type deduced from Pauling's theory (*J. Amer. Chem. Soc.*, 1931, 53, 1367) planar configuration with d-s-p² hybridisation is generally established for red and yellow nickel complexes like nickel dimethylglyoxime, nickel dicyandiamidine, potassium nickelocyanide, nickel biguanide etc., which are all diamagnetic (Rây and Bhar, *J. Indian Chem. Soc.*, 1928, 5, 499; Sugden, *J. Chem. Soc.*, 1939, 246). In the case of 4-co-valent copper complexes, however, magnetic data can offer no guidance as to their spatial configuration. All the simple and complex salts of bivalent copper possess similar paramagnetic properties. This follows directly from the electronic configuration of the cupric ion itself, which contains one unpaired electron in the fifth d-orbital. For the production of four equivalent hybrid d-s-p² bonds, giving rise to a planar configuration of the copper complex, this lone electron must be promoted to a higher level in order to make the fifth d-orbital available for bond formation; and this would make the complex paramagnetic like the cupric ion. Planar configuration for a number of copper complexes has been demonstrated by several workers with the help of X-ray measurements. Thus, cupric derivatives of β -diketones (Cox and Webster, *J. Chem. Soc.*, 1935, 731), copper phthalocyanin complex (Robertson, *ibid.*, 1935, 615), dipyridine cupric chloride (Cox, Sharatt, Wardlaw and Webster, *ibid.*, 1936, 129), cupric chloride dihydrate (Harkar, *Z. Krist.*, 1936, 98, 136) have all been found to possess planar structure. The isomorphism of 4-co-valent planar nickel complexes with the corresponding complexes of copper, e.g., nickel and copper compounds of methylethylglyoxime, is a strong indication in favour of planar configuration for the latter. Planar trans-configuration for the salicylaldoxime and picolinate of copper also has been established by X-ray studies. But a definite stereochemical evidence on the point, leading to the isolation of cis-trans isomers of a 4-co-valent copper complex, is wanting. Recently Pfeiffer and Glaser (*J. prakt. Chem.*, 1939, ii, 183, 265) have made an observation that naphthaldehyde methylimine copper, besides giving dark brown needles of metallic lustre, can be crystallised under certain conditions to form long green needles. The green crystals were transformed into brown variety on heating to 140° or on keeping under methyl alcohol at the ordinary temperature. But the colour of the solution in pyridine of both varieties was identical. Pfeiffer and Krebs (*J. prakt.*

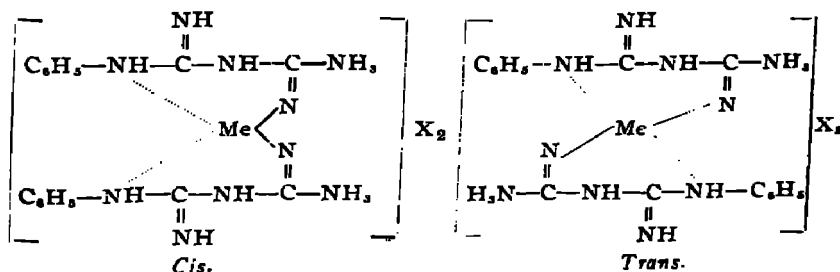
Chem., 1940, ii, 155, 77) also obtained two forms of sodium and barium salts of the acid (I), differing in their solubility in glycol or glycerine. Whether these represented real cases of *cis-trans* isomerism or dimorphism could not be decided by the authors.



Of the various 4-co-valent copper compounds so far studied only the *trans*-modifications could be isolated. All attempts to prepare the *cis*-form ended in failure. With a view to study the subject further, preparation of copper and nickel complexes with long-chain co-ordinating molecules was undertaken. Phenylbiguanide was selected as a suitable bidentate molecule for the purpose. Simple and substituted biguanides have been found by Rây and co-workers (*J. Indian Chem. Soc.*, 1937, 14, 670; 1938, 15, 353) to give fairly stable, well-defined, characteristic complexes with trivalent and bivalent metals like Cr, Co, Ni, Cu, etc. The constitution of the biguanide complexes with bivalent metals can be represented according to Rây and Saha (*loc. cit.*) by the following formula :



where X is a monovalent anion. This structure suggests the existence of two isomeric *cis* and *trans* forms :



We have been able to obtain a number of copper phenylbiguanide complexes in two modifications, *viz.* chloride, bromide, iodide, sulphate, nitrate, nitrite, dithionate and the free base. These might be called α - and β -forms. The α -form in each case differs considerably from the β -variety in solubility, melting point, colour (both in the hydrated and the anhydrous state) and rate of hydrolysis. Temperature and moisture accelerate the transformation of α - into β -variety.

The α -chloride is changed into the β -form at 101° in presence of steam, or when kept for a long time in contact with water, or by boiling. It crystallises with 6 molecules of water in the form of bluish violet crystals and when dehydrated retains the same colour. The β -chloride, which is prepared from slightly acidic solution at the boiling temperature, gives rise to light brick-red crystals and contains 3 molecules of water, the colour remaining unchanged on dehydration. The anhydrous α -chloride melts at 170° and the anhydrous β -chloride at 210° . The freshly prepared aqueous solution of the α -variety is violet-blue in colour and that of β -variety is reddish violet. The α -chloride is more soluble than the β -form. The α - and β -varieties of other salts and of complex base (both hydrated and anhydrous) also differ from each other in a similar way.

The two varieties may be regarded as *cis* and *trans* isomers of the planar copper complex, or as dimorphs or polymers. But the balance of evidences supports the first view.

Each variety (hydrated or anhydrous) retains its melting point and other properties unchanged on repeated crystallisation from water under the same condition. The α -variety changes into the β -form as stated above, but the β -form has never been found to change into the α -modification.

In aqueous solution they are all monomeric as indicated by cryoscopic and conductivity measurements. The α -chloride is much less dissociated at 0° than the β -chloride.

The aqueous solution of the α -chloride is quite stable and does not suffer any appreciable change by keeping at the room temperature for some days. The β -chloride, when dissolved in water, readily gives rise to the formation of a number of colloidal aggregates in solution as could be detected by ultramicroscope. Even after ultrafiltration of a solution of the β -chloride the filtrate is found to develop again a number of colloidal particles in a day or two. The absorption spectra of the aqueous solutions of the two chlorides after ultrafiltration were, however, found to be identical. An X-ray study of their crystals, therefore, would help to make a definite conclusion on the point.

As the β -variety appears to be more stable, since it is formed from slightly acid solution as well as by rise of temperature from the α -variety in presence of steam, it may reasonably be regarded to represent the *trans* modification, the α -form having the *cis* configuration.

In the case of nickel phenylbiguanide complexes only the base has been isolated in more than one form. These differ in their colour, solubility and decomposition temperature.

The α -nickel base is brick-red in colour and contains only $\frac{1}{2}$ molecule of water which is lost at 110° . It is insoluble in water, but soluble in alcohol and acetone changing rapidly into the yellow variety (γ). The same change occurs on keeping it in contact or on heating with water.

The β -nickel base is anhydrous and light yellow in colour. It is insoluble in water and all common organic solvents. On heating it decomposes at 265° , while the decomposition of the α -base occurs at 257° . On account of its greater stability it may be represented by the *trans* configuration. The α -form, therefore, represents the *cis* modification.

Besides these a third (γ) variety of yellow colour has also been prepared. This is very likely a molecular compound or mixed crystals of the α - and β -forms.

As none of the nickel phenylbiguanide salts, however, have been obtained in more than one form, no definite conclusion can be arrived at without further investigation, and the above representation regarding the different forms of the base as *cis-trans* isomers should be viewed as a tentative one. For they might as well be dimorphs or polymers.

A number of complex copper and nickel phenylbiguanide salts have been prepared and their properties studied. Generally, the solubility of nickel complex was found to be much less than that of their corresponding copper compounds. The sulphate, iodate, bromate, chlorate and dithionate of nickel compounds were found to be very sparingly soluble in water at the ordinary temperature.

The following compounds have been prepared and described in this paper.

Copper. The free base, hydrated and anhydrous in two forms— α and β ; the chloride, bromide, iodide, nitrite, nitrate, sulphate and dithionate in α - and β -forms, besides the thiosulphate, thiocyanate, chlorate, bromate, iodate and sulphate.

Of these, the dark rose base (β), the red chloride (β), the rose-coloured sulphate (β) and the chromate have been described by previous workers (Smolka and Friedrich, *Monatsh*, 1888, 9, 227).

Nickel. The free base in three forms (α , β and γ), the chloride, bromide iodide, sulphate, iodate, nitrate, nitrite and sulphocyanide. Of these the free base (β), chloride and sulphate have already been described before (Smolka and Friedrich, *loc. cit.*).

E X P E R I M E N T A L.

I. *Copper Compounds.*

α Copper Phenylbiguanidine and its Hydrate.—The hydrate was precipitated in the form of light pink, finely divided crystals by adding a concentrated solution of caustic soda in excess to a cold concentrated solution of α -copper phenylbiguanide hydrochloride. This was rapidly filtered by suction, washed with cold water and dried on a porous plate. On keeping in contact with water at the ordinary temperature it changes into the rose-red β -form. It liberates ammonia from hot ammonium chloride solution. {Found: N, 31.20; Cu, 14.05. $[\text{Cu}(\text{PhBigH}^+)]_2(\text{OH})_2$ requires N, 31.0; Cu, 14.06; H_2O , 7.97}. $\text{PhBigH} = \text{C}_8\text{N}_3\text{H}_{11}$ = one molecule of phenyl biguanide.

The substance loses 7.9% of its weight at 100°–110°. {Found: Cu, 15.10. $\text{Cu}(\text{PhBig})_2$ requires Cu, 15.28 per cent}.

The anhydrous base possesses the same colour as the hydrated variety. The substance is soluble in methyl and ethyl alcohol and also in acetone, but is insoluble in chloroform or benzene. M. p. (decompos.) 155°.

The molecular weight of the anhydrous substance determined by the boiling-point method in methyl alcoholic solution, gave a value of 382.3 showing its monomeric nature. Calc. M. W. = 415.5.

β -Copper Phenylbiguanide and its Hydrate.—The β -hydrate was prepared by adding a concentrated solution of caustic soda to a hot solution of α -copper phenylbiguanide hydrochloride. The mixture was allowed to cool and the precipitated base was filtered and washed with water. The product was dried over caustic soda. {Found: N, 31.1; Cu, 14.0. $[\text{Cu}(\text{PhBigH}^+)]_2(\text{OH})_2$ requires N, 31.0; Cu, 14.06; H_2O , 7.97 per cent}.

Loss at 118° = 7.9 per cent. {Found: Cu, 15.20; $\text{Cu}(\text{PhBig})_2$ requires Cu, 15.28%}.

Both hydrated and the anhydrous base form finely divided dark red crystals, insoluble in water. The anhydrous base melts at 165°. It appears to be more soluble than the α -variety in alcohol and acetone.

Molecular weight of the anhydrous base by ebullioscopic method in methyl alcoholic solution was found to be 386.2, showing that it is monomeric. Calc. M. W. = 415.5.

α -Copper Phenylbiguanidinium Chloride.

The compound can be prepared in several ways.

(i) By treating an aqueous solution of phenylbiguanide base with a solution of cupric chloride.

(ii) By treating a hot solution of phenylbiguanide hydrochloride with an ammoniacal cupric chloride solution.

(iii) By heating a solution of ammonium chloride with α -copper phenylbiguanide until the evolution of ammonia ceases.

(iv) By digesting freshly precipitated copper hydroxide with a solution of phenylbiguanide hydrochloride on water-bath. This method was usually adopted for the preparation of the substance.

On concentrating and cooling the filtrate from copper hydroxide (method, *iv*) blue-violet crystals of copper phenylbiguanide hydrochloride separated out. The product was purified by recrystallisation at 60-70° and dried in air. {Found: N, 23·37; Cl, 11·86; Cu, 10·70. [Cu(PhBigH⁺)₂]Cl₂·6H₂O requires N, 23·50; Cl, 11·90; Cu, 10·66 per cent}.

Loss of water at 110° = 18·04%. Calc.: H₂O, 18·10%.

The anhydrous chloride retains the colour of the original hydrated substance. (Found: Cu, 13·0. Calc.: Cu, 13·02 per cent).

Solubility at 28° = 2·1088 g. of the hydrated chloride per 100 g. of the solution. M p. (anhydrous salt), 170° (decomp.).

The hydrated chloride also melts at 170° on slowly heating. But on rapid heating or sudden immersion in a hot bath at 100°, the hydrate first forms a frothy mass, then solidifies with rise of temperature and finally melts at 210°, which is the melting point of β -copper phenylbiguanide hydrochloride. This suggests the transformation of α -form into the β -variety under the conditions of the experiment, *i.e.*, rise of temperature and presence of steam. On the other hand, if the α -hydrated chloride is gradually heated to make it anhydrous, it does not change into β -variety on further rise of temperature. Rise of temperature in presence of steam is, therefore, a necessary condition for its transformation into the anhydrous β -variety. This can be demonstrated by actual experiment and the transition temperature thus determined was found to lie between 102° and 103°. Even at the ordinary temperature the α chloride changes slowly into the β -form on keeping in contact with water for several days.

Equivalent conductivity at 28°.

v (dilution in litres) ...	32	64	128	256	512	1024
λ_v ...	89·1	102·2	105·7	109·04	112·2	115·4
λ_∞ (mean) ...	117·9 from Walden's formula $\lambda_\infty = \lambda_v(1 + 11 \cdot 7 \cdot 10^6 v^{-1})$					

where n_1 and n_2 are the valencies of the cation and anion respectively (Walden. "Leitvormögen der Lösungen," 1924, V, 53). The mobility of $\text{Cu}(\text{PhBigH}^+)_2 = 117.9 - 79.5 = 38.4$, the ionic mobility of chlorine at 28° being 79.5 .

Cryoscopic measurement.

Substance in 100 g. water (on the anhydrous basis).	Depression in $^\circ\text{C}$. Δ .	M.W. (found) m .	Vant Hoff's factor $i = \frac{M \text{ (calc.)}}{m}$	Degree of dissociation $\alpha = \frac{i-1}{n-1}$ ($n=3$).
1.3080 g.	0.12	202.7	2.40	0.70

The β -Chloride.—A concentrated solution of the α -chloride was heated to boiling and acidified distinctly with hydrochloric acid. The solution was then almost neutralised with caustic soda solution and boiled further for about 1 minute. It was then filtered hot and the filtrate heated once more and then allowed to cool. On keeping overnight, the β -chloride separated out in the form of red crystals. These were purified by recrystallisation and dried in air. {Found ; N, 25.83 ; Cl, 12.90 ; Cu, 11.75 ; H_2O (loss at 110°), 9.60. [$\text{Cu}(\text{PhBigH}^+)_2$] $\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ requires N, 25.80 ; Cl, 13.08 ; Cu, 11.72 ; H_2O , 9.95 per cent}.

For the anhydrous salt (Found : Cu, 12.95. Calc. : Cu, 13.02%).

Smolka and Friedrich (*loc. cit.*) described a carmine-red chloride containing $1\frac{1}{2} \text{H}_2\text{O}$ only.

The solubility of the β -chloride (hydrated) at 28° is considerably less than that of the α -chloride and is equal to 1.6055 g. per 100 g. of solution. The anhydrous compound retains the colour of the original hydrate ; m.p. (both hydrated and anhydrous), 210° .

A freshly prepared solution of the β chloride is red-violet and is found to contain a number of colloidal aggregates when examined under the microscope. After ultrafiltration the colour of the solution becomes identical (blue-violet) with that of the α -chloride, but turns red-violet again in a day or two. The phenomenon is possibly connected with its increased tendency to hydrolysis.

Equivalent conductivity at 28° .

v (litres)	...	32	64	128	256	512	1024
λ_v	...	92.98	94.84	100.9	107.2	110.9	114.8
λ_∞ (mean) =		117.5					

Cryoscopic measurement.

Substance in 100 g. water (on the anhydrous basis).	Depression in °C. Δ .	M. W. (found) <i>m</i> .	Van't Hoff's factor $i = \frac{M(\text{calc.})}{m}$	Degree of dissociation $\alpha = i - 1/n - 1$ ($n=3$).
0.9830 g.	0.105	174.1	2.80	.90

The degree of dissociation is much higher than that of the α -variety (0.74).

The α -*Bromide*.—This was prepared by adding a concentrated solution of potassium bromide to a cold concentrated solution of the complex α -chloride. This was filtered, washed with water and dried on a porous plate. It forms finely divided, light pink coloured crystals. {Found : N, 22.89; Br, 26.20; Cu, 10.28. $[\text{Cu}(\text{PhBigH}^+)_2]\text{Br}_2, 2\text{H}_2\text{O}$ requires N, 22.80; Br, 26.08; Cu, 10.30 per cent}. Solubility at 28° = 1.71 g. per 100 g. of the solution.

When the α -bromide was kept in contact with its solution at the ordinary temperature, it gradually changed into the deep rose-coloured β -bromide. The same transformation occurs on keeping the moist α -bromide for some days.

The β -*Bromide*.—When the α -bromide was kept in contact with its solution in a beaker for 3-4 days, it completely changed into the deep rose-red β -variety. This was washed with water and dried in air. {Found : Br, 26.21; Cu, 10.20. $[\text{Cu}(\text{PhBigH}^+)_2]\text{Br}_2, 2\text{H}_2\text{O}$ requires Br, 26.08; Cu, 10.30 per cent}. Solubility at 28° = 1.55 g. in 100 g. of the solution.

The α -*Iodide* was precipitated in the form of finely divided, light pink crystals by adding a concentrated solution of potassium iodide in excess to that of the α -chloride in the cold. The precipitate was washed with water and dried on a porous plate. On boiling with water it changes into the brown β -form. {Found : N, 19.77; I, 35.90; Cu, 9.01. $[\text{Cu}(\text{PhBigH}^+)_2]\text{I}_2, 2\text{H}_2\text{O}$ requires N, 19.79; I, 35.88; Cu, 8.97 per cent}.

The β -*iodide* was prepared by heating the α -iodide with water to 100° and then keeping the mixture overnight. The product was washed with water and dried in air. It forms brown coloured crystals, difficultly soluble in water. {Found : I, 35.60; Cu, 8.90. $[\text{Cu}(\text{PhBigH}^+)_2]\text{I}_2, 2\text{H}_2\text{O}$ requires I, 35.88; Cu, 8.97 per cent}.

The α -*nitrate* was obtained as a violet coloured, crystalline precipitate by adding a cold concentrated solution of potassium nitrate to that of α -chloride, cooled in ice. The precipitate was washed with cold water, dried first on a porous plate and then over concentrated H_2SO_4 . {Found : Cu, 11.70; NO_2 , 22.60. $[\text{Cu}(\text{PhBigH}^+)_2](\text{NO}_2)_2$ requires Cu, 11.72; NO_2 , 22.89 per cent}. Solubility at 28° = 0.4988 g. in 100 g. of the solution.

When kept in contact with its solution it gradually changed into the red β -form in 3 to 4 days.

Equivalent conductivity at 28°.

v (litres)	...	64	128	256	512	1024
λ_v	...	92.21	98.5	100.9	103.6	108.9
λ_∞ (mean)	...	110.5				

The β -nitrate was prepared from the α -variety by keeping it in contact with water for 7 days when a complete change into the red β -form occurs. {Found: Cu, 11.39; NO₃, 21.77. [Cu(PhBigH⁺)₂](NO₃)₂, H₂O requires Cu, 11.36; NO₃, 22.16 per cent}. Solubility at 28° = 0.2923 g. in 100 g. of the solution.

The α -sulphate was obtained as a sparingly soluble, pink coloured crystalline precipitate by adding a concentrated solution of potassium sulphate in excess to that of the α -chloride, washed and dried as usual. When heated with water it changes into the violet-red β -form. {Found: Cu, 10.92; SO₄, 16.71. [Cu(PhBigH⁺)₂SO₄], 4H₂O requires Cu, 10.84; SO₄, 16.40 per cent}.

The β -sulphate was prepared by heating the α -sulphate with water to 100° and keeping the product overnight. It forms sparingly soluble, violetred crystals. {Found: N, 23.11; Cu, 10.45; SO₄, 16.20. [Cu(PhBigH⁺)₂]SO₄, 5H₂O requires N, 23.19; Cu, 10.53; SO₄, 15.9 per cent}.

Smolka and Friedrich (*loc. cit.*) have described a rose-red sulphate with $1\frac{1}{2}$ H₂O.

The α -nitrite was prepared by adding a cold concentrated solution of sodium nitrite to that of the α -chloride, cooled in ice. The red-violet precipitate was allowed to settle, filtered by suction, washed with ice-cold water and dried on a porous plate. It is very unstable in the moist state and changes rapidly at the room temperature into the β -form. {Found: Cu, 12.05; NO₂, 17.30. [Cu(PhBigH⁺)₂](NO₂)₂, H₂O requires Cu, 12.05; NO₂, 17.44 per cent}. Solubility at 28° = 0.096 g. per 100 g. of the solution.

The β -nitrite was prepared by keeping the α -nitrite in contact with water for a day or two till complete transformation occurs. It forms dark violet crystals, sparingly soluble in water. It is nearly 50% less soluble than the α -form. {Found: Cu, 12.44; NO₂, 18.05. [Cu(PhBigH⁺)₂](NO₂)₂ requires Cu, 12.47; NO₂, 18.05 per cent}. Solubility at 28° = 0.0457 g. per 100 g. of the solution.

The α -dithionate was obtained from a concentrated solution of sodium dithionate and that of the α -chloride. The light pink-coloured precipitate was washed with water, dried first on a porous plate and then in a desiccator over H_2SO_4 . When heated with water it changes into the red β -form. {Found: Cu, 11'0; S_2O_6 , 28'0. $[Cu(PhBigH^+)_2]_2S_2O_6$ requires, Cu, 10'99; S_2O_6 , 27'70 per cent}.

The β -dithionate was prepared by heating the α -variety with a little water and keeping the product overnight. This was washed with water and dried in air. The substance forms red crystals, sparingly soluble in water. {Found: Cu, 10'68; S_2O_6 , 27'0. $[Cu(PhBigH^+)_2]_2S_2O_6$, H_2O requires Cu, 10'66; S_2O_6 , 26'88 per cent}.

Copper phenylbiguanidinium sulphite was obtained as a dark violet crystalline precipitate by adding a concentrated solution of the α -chloride to that of sodium sulphite. The product was washed with water and dried in air. {Found: N, 23'55; Cu, 10'70; SO_3 , 14'05. $[Cu(PhBigH^+)_2]SO_3$, $5H_2O$ requires N, 23'80; Cu, 10'80; SO_3 , 13'60 per cent}.

The thiosulphate was prepared by adding a concentrated solution of sodium thiosulphate to that of the complex α -chloride. The light blue, crystalline precipitate was washed with water and dried in air. {Found: N, 24'80; Cu, 11'20; S_2O_3 , 19'95. $[Cu(PhBigH^+)_2]S_2O_3$, $2H_2O$ requires N, 24'75; Cu, 11'24; S_2O_3 , 19'80 per cent}.

The thiocyanate was obtained from a concentrated solution of ammonium thiocyanate and that of the α -chloride. The pink coloured crystalline precipitate was washed and dried as usual. {Found: N, 30'40; S, 11'71; Cu, 11'50. $[Cu(PhBigH^+)_2](SCN)_2 \cdot H_2O$ requires N, 30'40; S, 11'60; Cu, 11'53 per cent}.

The chlorate was prepared from a concentrated solution of potassium chlorate and that of the complex chloride. The pink coloured crystalline precipitate was washed with water and dried over H_2SO_4 in a desiccator. The dry salt explodes on rubbing in a mortar. {Found: Cu, 10'85; ClO_3 , 28'20. $[Cu(PhBigH^+)_2](ClO_3)_2$ requires Cu, 10'85; ClO_3 , 28'56 per cent}.

The bromate was obtained from potassium bromate and the α -chloride as in the previous case. It forms pink coloured crystals and explodes like the chlorate when ground in a mortar. {Found: Cu, 9'48; BrO_3 , 37'87. $[CuPhBigH^+)_2](BrO_3)_2$ requires Cu, 9'43; BrO_3 , 38'0 per cent}.

The iodate was obtained as violet crystals from potassium iodate and the complex chloride. This was washed and dried as in the previous case. {Found: Cu, 8'22; IO_3 , 44'79. $[Cu(PhBigH^+)_2](IO_3)_2$ requires Cu, 8'27; IO_3 , 45'60 per cent}.

Nickel Compounds.

α-Nickel Phenylbiguanidine and its Hydrate.—To a cold (8°-10°) concentrated solution of nickel phenylbiguanide hydrochloride a cold concentrated solution of caustic soda was rapidly added in excess. The red precipitate was immediately washed with ice-cold water, dried first on a porous plate and then over caustic potash. {Found: N, 33'09; Ni, 13'88 Ni(PhBig)₂. $\frac{1}{3}$ H₂O requires N, 33'36; Ni, 13'99 per cent}.

When heated to 110° for 2 hours it lost 2% of its weight without any change of colour. Calc. H₂O, 2'14 per cent.

[Found for anhydrous product: Ni, 14'11. Calc.: Ni, 14'22 per cent].

The substance is soluble in methyl alcohol, ethyl alcohol and also in acetone forming an orange-red solution, but rapidly separates out in the form of a yellow powder (*β*-variety). The same change is also observed to occur in the moist state. It decomposed at 255° without melting.

β-Nickel phenylbiguanidine was precipitated as a light yellow, crystalline powder by adding a concentrated solution of caustic soda to a warm solution of the hydrochloride. This was washed with water and dried over caustic soda. {Found: N, 33'73; Ni, 14'12. Ni(PhBig)₂ requires N, 34'09; Ni, 14'22 per cent}.

The substance is insoluble in alcohol, acetone or water, and decomposes, without melting at about 265°. The compound has also been described by Smolka and Friedrich (*loc. cit.*).

γ-Nickel Phenylbiguanidine and its Hydrate.—This was prepared by keeping the moist *α*-variety at the room temperature, when after 2 to 3 days the mass changed completely into a deep yellow product. This was dried over caustic soda. {Found: N, 33'10; Ni, 13'93; H₂O (by loss at 110°) 2'04. Ni(PhBig)₂, $\frac{1}{3}$ H₂O requires N, 33'36; Ni, 13'99; H₂O, 2'14 per cent}.

There was no change of colour on dehydration.

The anhydrous product gave Ni, 14'17; Calc. 14'22 per cent. The substance is insoluble in alcohol, acetone or water and decomposes without melting at 263°. This is likely to be a molecular compound or solid solution of *α*- and *β*-variety.

Nickel phenylbiguanidinium chloride can be prepared by any of the following methods.

(a) By the action of phenylbiguanide hydroxide on a solution of nickel chloride.

(b) By adding a solution of ammoniacal nickel chloride to that of phenylbiguanide hydrochloride.

(c) It was, however, prepared by digesting a solution of phenylbiguanide hydrochloride with excess of freshly prepared nickel hydroxide. The mixture was filtered hot. The filtrate on concentration and cooling deposited golden yellow crystals of nickel phenylbiguanidinium chloride. These were purified by recrystallisation either from water or from absolute alcohol and dried in air. {Found: N, 26'30; Cl, 13'20; Ni, 11'08; H₂O (by loss at 110°), 8'43. [Ni (PhBigH⁺)₂]Cl₂, 2½H₂O requires N, 26'50; Cl, 13'43; Ni, 11'12; H₂O, 8'52 per cent}.

The anhydrous chloride gives Ni, 12'11; Calc. Ni, 12'14 per cent.

Smolka and Friedrich (*loc. cit.*) have also described the anhydrous chloride.

The *bromide* was obtained as a bright yellow crystalline precipitate by adding a hot concentrated solution of potassium bromide to that of the complex chloride. This was washed with water and dried in air. {Found: N, 22'80; Br, 26'20; Ni, 9'80. [Ni(PhBigH⁺)₂]Br₂, 2H₂O requires N, 23'0, Br, 26'28; Ni, 9'64 per cent}.

The *iodide* was prepared from potassium iodide and the complex chloride as described above. The sparingly soluble, yellow crystals of the iodide were washed and dried as usual. {Found: N, 20'30; I, 37'0; Ni, 8'59. [Ni(PhBigH⁺)₂]I₂, H₂O requires N, 20'44; I, 37'09; Ni, 8'57 per cent}.

The *dithionate* was obtained from concentrated solutions of sodium dithionate and the complex chloride. On cooling, the dithionate separated in the form of yellow crystals. {Found: N, 24'40; Ni, 10'23; S₂O₆, 28'13. [Ni (PhBigH⁺)₂] S₂O₆ requires N, 24'48; Ni, 10'25; S₂O₆, 27'95 per cent}.

The *thiosulphate* was obtained from an excess of a concentrated solution of sodium thiosulphate and that of the complex chloride. The yellow crystalline precipitate was washed and dried as usual. {Found: N, 26'50; Ni, 11'17; S₂O₃, 21'53. [Ni(PhBigH⁺)₂] S₂O₃ requires N, 26'68; Ni, 11'18; S₂O₃, 21'33 per cent}.

The *nitrate* separated in the form of finely divided, bright yellow crystals on cooling a mixture of concentrated solutions of potassium nitrate and the complex chloride. {Found: Ni, 10'50; NO₃, 22'50. [Ni(PhBigH⁺)₂] (NO₃)₂, H₂O requires Ni, 10'58; NO₃, 22'35 per cent}.

The *sulphate* was obtained as yellow crystals by precipitating a concentrated solution of the complex chloride with that of potassium sulphate. {Found: Ni, 10'70; SO₄, 17'70. [Ni(PhBigH⁺)₂]SO₄, 2H₂O requires Ni, 10'77; SO₄, 17'61 per cent}.

The sulphate has also been described by Smolka and Friedrich (*loc. cit.*), which, however, contains 1½ H₂O only.

The sulphite.—A concentrated solution of sodium sulphite in excess was added to a hot concentrated solution of the complex chloride. On cooling, the yellow crystals of the sulphite gradually separated out. {Found: Ni, 11'53; SO₃, 15'75. [Ni(PhBigH⁺)₂]SO₃, H₂O requires Ni, 11'50; SO₃, 15'65 per cent}.

The chlorate was obtained as a light yellow, crystalline precipitate by adding an excess of a concentrated solution of potassium chlorate to that of the complex chloride. {Found: Ni, 10'10; ClO₃, 28'20. [Ni(PhBigH⁺)₂](ClO₃)₂ requires Ni, 10'14; ClO₃, 28'8 per cent}.

The bromate was obtained as sparingly soluble, orange coloured crystals from a concentrated solution of potassium bromate and a hot concentrated solution of the complex chloride. {Found: Ni, 8'72; BrO₃, 37'92. [Ni(PhBigH⁺)₂](BrO₃)₂ requires Ni, 8'77; BrO₃, 38'27 per cent}.

The iodate was obtained as orange-red, crystalline precipitate by adding a concentrated solution of potassium iodate to that of the complex chloride. {Found: Ni, 7'31; IO₃, 43'54. [Ni(PhBigH⁺)₂](IO₃)₂, 2H₂O requires Ni, 7'34; IO₃, 43'82 per cent}.

The thiocyanate was prepared as a yellow crystalline precipitate by adding a concentrated solution of potassium thiocyanate to that of the complex chloride. {Found: N, 32'22; S, 12'21; Ni, 11'05. [Ni(PhBigH⁺)₂](SCN)₂ requires N, 31'78; S, 12'10; Ni, 11'10 per cent}.

The nitrite was obtained from a concentrated solution of sodium nitrite and that of the complex chloride. It forms sparingly soluble, orange-yellow crystals. {Found: Ni, 11'15; $\frac{1}{2}$ NO₂, 18'0. [Ni(PhBigH⁺)₂](NO₂)₂, H₂O requires Ni, 11'23; NO₂, 17'60 per cent}.