252. *The Azo-group as a Chelating Group. Part III. Metallic Derivatives of Hydroxytriazens.*

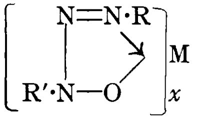
By Marjorie Elkins and Louis Hunter.

The co-ordinating function of the azo-group has been shown to extend to the hydroxytriazens, from which a series of chelate copper, nickel, cobalt, and ferric derivatives has been prepared. These metallic compounds possess greater thermal stability than the parent hydroxytriazens.

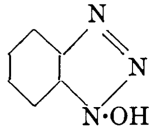
The salt-forming character of the hydroxytriazens (I) was first recognised by Bamberger and his co-workers (*Ber.*, 1896, **29**, 104; 1897, **30**, 2278), who showed them to be alkali-soluble and to give insoluble, coloured, copper salts, though only two of the latter were analysed. These and numerous other metallic derivatives have now been prepared, and shown to be typical co-ordinated compounds. There seems to be little doubt that the metal atom in such compounds replaces the hydroxyl hydrogen atom and co-ordinates with the azo-nitrogen atom to form a five-membered ring (II).

R·N=N·N(OH)R′

(I.)



(II.)

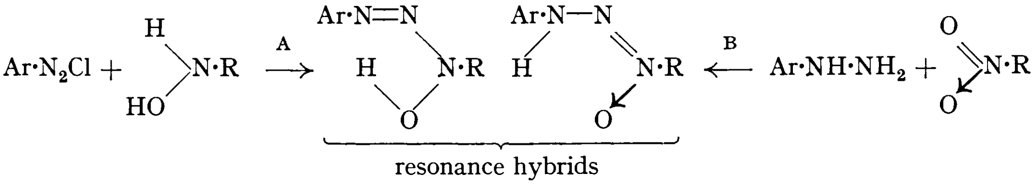


(III.)

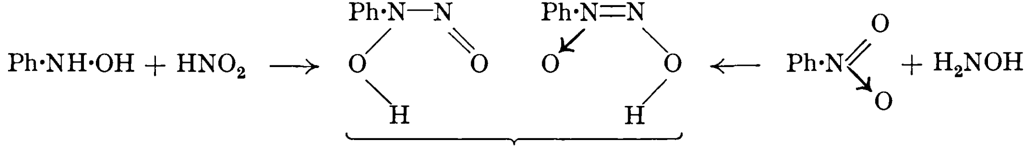
The typical dark green, blue, and black colours produced by the action of ferric chloride on hydroxytriazens (Bamberger and Renauld, *Ber.*, 1897, **30**, 2280; Gebhard and Thompson, J., 1909, **95**, 771) are now shown to be due to the formation of coloured co-ordinated ferric salts, several of which have been isolated in the pure state. In addition to these, well-defined cupric, nickel, cobaltous, and cobaltic salts have been prepared. They are highly coloured crystalline solids (the parent hydroxy-compounds are colourless or only faintly coloured), readily soluble in organic solvents, with m. p.'s which, in spite of their high molecular weights, are seldom above 200°. They dissolve readily in pyridine, with which they frequently form stable addition compounds.

By analogy with the structure assigned to these metallic derivatives, it would appear that the parent hydroxytriazens are themselves internally co-ordinated, and this is supported by their ready solubility in hydrocarbon solvents, and their low m. p.'s. Determinations of molecular weight in benzene show that, although there is some association in this solvent, it is not nearly so great as that exhibited by nitroso-compounds and oximes, to which the hydroxytriazens might be expected to show some resemblance. This diminution of the usual associating character of the hydroxyl group is interpreted as evidence of its engagement (at least in a high proportion of molecules) by chelate ring-formation. It is also of interest to compare the properties of these compounds with those of benzaziminol (III). The latter compound contains the same hydroxytriazen grouping as part of a cyclic system, the consequent *cis*-configuration precluding the possibility of internal co-ordination of the hydroxyl hydrogen atom. This compound differs completely from its open-chain analogues in being water-soluble and sufficiently strongly acidic to decompose sodium carbonate. Its metallic derivatives are true salts showing no chelate properties.

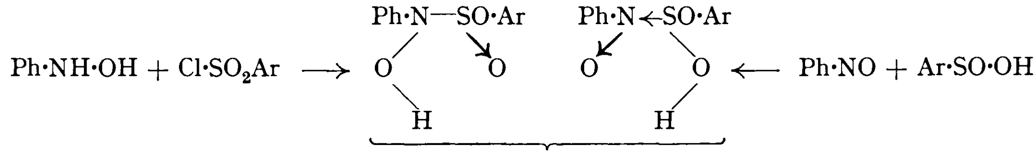
It being assumed that the co-ordination of hydrogen is a resonance phenomenon (Sidgwick, *Ann. Reports*, 1933, **30**, 112), it appears probable that the hydroxytriazens should be capable of synthesis by the two alternative routes A and B. Route A is the normal method for their preparation. The experimental realisation of route B is prevented by the strong reducing action of the arylhydrazines except in the single example of the formation of benzaziminol by the action of alkali on *o*-nitrophenylhydrazine (Nietzki and Braunschweig, *Ber.*, 1894, **27**, 3381); but the formation of hydroxytriazens by the action of phenylhydrazine on two molecular proportions of a nitroso-compound (Bamberger and Büsdorf, *Ber.*, 1896, **29**, 103; 1900, **33**, 3510; Bamberger and Stiegelmann, *ibid.*, 1899, **32**, 3554) is essentially reaction B.



Instances similar to the above, of alternative methods of preparation of chelated hydroxy-compounds are not lacking, the *o*-hydroxyazo-compounds (by diazo-coupling or by quinonehydrazone formation) and the *o*-nitrosophenols (by direct nitrosation or by quinonoxime formation) being the best known. Other hitherto obscure reactions find ready explanation by similar formulation; *e.g.*, the alternative preparations of nitrosophenylhydroxylamine



and of the arylsulphonylphenylhydroxylamines,



EXPERIMENTAL.

The parent hydroxytriazens were prepared by the method of Bamberger and Renauld (*loc. cit.*) by coupling a diazonium salt with a hydroxylamine, obtained by reduction of the corresponding nitro-compound. The crude products were impure and highly coloured, and were purified by repeated crystallisation (charcoal) from alcohol or from benzene–light petroleum. They usually explode on heating above their m. p.'s, a property which complicates their analysis; the figures for nitrogen analysis (carried out by the micro-combustion method by Drs. Weiler and Strauss, Oxford) are, as a result, frequently too low.

Metals were estimated by destroying organic matter by cautious treatment with concentrated nitric acid (frequently moderated by the addition of alcohol or acetone), followed by sulphuric acid under Kjeldahl conditions. The metals were then estimated gravimetrically by using the following organic precipitants: salicylaldoxime for copper; dimethylglyoxime for nickel; anthranilic acid for cobalt (Funk and Ditt, *Z. anal. Chem.*, 1933, **91**, 332; 1933, **93**, 241); and 5 : 7-dichloro-8-hydroxyquinoline for iron (Berg, *Z. anorg. Chem.*, 1932, **204**, 212).

1-Hydroxy-3-phenyl-1-methyltriazen, crystallised repeatedly from aqueous alcohol, and decolorised with charcoal, formed cream-white silky needles, m. p. 72—73° (Bamberger and Renauld gave m. p. 69—70°). The apparent molecular weights (Calc.: M, 151) determined cryoscopically in benzene were as follows:

G. solute/100 g. benzene	1·44	2·66	4·16	5·95	7·31
Apparent molecular weight	152	164	172	182	187

The cupric compound, obtained in theoretical yield by the dropwise addition of aqueous-alcoholic copper acetate to a warm alcoholic solution of the triazen, crystallised from alcohol as deep rust-red, shining, rhomboid platelets, m. p. 159—160° (Bamberger and Renauld gave m. p. 156°) (Found: Cu, 17·3. Calc.: Cu, 17·5%). The *nickel* compound, obtained similarly, crystallised from alcohol in small, lime-green, elongated platelets, m. p. 182° (Found: Ni, 16·3. $C_{14}H_{16}O_2N_6Ni$ requires Ni, 16·4%). By dissolving this in hot pyridine and precipitating with water, a *dipyridino*-compound was obtained as deep pink needles, m. p. *ca.* 145° after losing pyridine at about 100° (Found: Ni, 10·9. $C_{14}H_{16}O_2N_6Ni,2C_5H_5N$ requires Ni, 11·3%). It rapidly lost pyridine on standing in air, and was dried for analysis in an atmosphere of pyridine. The *ferric* compound, obtained similarly by the action of ferric acetate on the triazen, formed a coarse blue-black crystalline powder, having a violet streak, m. p. 176° (Found: Fe, 11·1. $C_{21}H_{24}O_3N_9Fe$ requires Fe, 11·0%). The *cobaltic* compound was prepared in good yield by the action of aqueous-alcoholic cobaltous acetate on a cold alcoholic solution of the triazen in the presence of hydrogen peroxide. Recrystallised from acetone containing hydrogen peroxide, it formed purple-black, shining, rectangular plates, m. p. 165° (Found: N, 24·4; Co, 11·4. $C_{21}H_{24}O_3N_9Co$ requires N, 24·7; Co, 11·6%). By excluding hydrogen peroxide from the preparation, a brown powder was obtained which contained the cobaltous compound mixed with the cobaltic compound. The *tripyridinocobaltous* compound was prepared by heating the cobaltic compound in pyridine solution for a short time and precipitating with cold water. The oil at first formed rapidly solidified, and on recrystallisation from pyridine formed bright rust-red platelets, m. p. 116—120°, losing pyridine from about 112° (Found: N, 20·8; Co, 9·6. $C_{14}H_{16}O_2N_6Co,3C_5H_5N$ requires N, 21·1; Co, 9·9%).

1-*Hydroxy*-3-o-*tolyl*-1-*methyltriazen*, prepared by coupling *o*-toluenediazonium chloride with methylhydroxylamine, formed large cream-white plates from dilute alcohol, m. p. 51°, exploding above this temperature (Found: N, 23·6. $C_8H_{11}ON_3$ requires N, 25·4%). The *cupric* compound crystallised from alcohol in light brown feathery needles, m. p. 169—170° (Found: Cu, 16·3. $C_{16}H_{20}O_2N_6Cu$ requires Cu, 16·2%), and the *nickel* compound from acetone in lime-green hexagonal platelets, m. p. 208° (Found: Ni, 15·3. $C_{16}H_{20}O_2N_6Ni$ requires Ni, 15·2%). The *ferric* compound was obtained as small black needles with a golden lustre, giving a purple-black streak, m. p. 168° (Found: N, 23·7; Fe, 10·6. $C_{24}H_{30}O_3N_9Fe$ requires N, 23·0; Fe, 10·2%). The *cobaltous* compound was prepared by the action of cobaltous acetate on an alcoholic solution of the triazen in an atmosphere of hydrogen. It was quickly filtered off and dried, being stable in air, but rapidly oxidised in solution. It formed small feathery yellow-brown needles, m. p. 171° (Found: Co, 15·7. $C_{16}H_{20}O_2N_6Co$ requires Co, 15·2%). The *cobaltic* compound, prepared as before in the presence of hydrogen peroxide, formed a purple-brown amorphous powder, m. p. 136° (Found: Co, 10·7. $C_{24}H_{30}O_3N_9Co$ requires Co, 10·7%).

1-*Hydroxy*-3-m-*tolyl*-1-*methyltriazen* formed cream-white platelets or needles when precipitated rapidly by cooling in ice from benzene–light petroleum, m. p. 74°, exploding above this temperature (Found: N, 24·7. $C_8H_{11}ON_3$ requires N, 25·4%). The *cupric* compound was obtained in the form of large irregular red-brown plates with a silver lustre, m. p. 140—141° (Found: N, 21·4; Cu, 15·6. $C_{16}H_{20}O_2N_6Cu$ requires N, 21·5; Cu, 16·2%). The *nickel* compound formed lime-green rhomboidal platelets from acetone, m. p. 180° (Found: Ni, 14·9. $C_{16}H_{20}O_2N_6Ni$ requires Ni, 15·2%); when crystallised from pyridine it deposited an unstable pyridine addition compound as deep pink needles, which rapidly lost pyridine, turning yellow and ultimately leaving a residue of the original lime-green nickel compound. The ferric compound was obtained as a dark blue oil which solidified but could not be crystallised. The *cobaltous* compound, obtained as before in an atmosphere of hydrogen and rapidly dried, formed short olive-green needles, m. p. *ca.* 125° if heated rapidly, but softening at 130° and melting at 155° if heated slowly. This behaviour is due to its rapid change to the cobaltic condition on heating (Found: N, 21·8; Co, 14·6. $C_{16}H_{20}O_2N_6Co$ requires N, 21·7; Co, 15·2%). The *tripyridinocobaltous* compound formed fine light orange needles by the addition of water to a pyridine solution of the cobaltous compound. It melted between 130° and 135°, but began to lose pyridine at a lower temperature (Found: Co, 8·4. $C_{16}H_{20}O_2N_6Co,3C_5H_5N$ requires Co, 9·4%). The *cobaltic* compound, prepared as before, formed shining purple-black rhomboidal platelets from acetone, m. p. 158° (Found: Co, 10·6. $C_{24}H_{30}O_3N_9Co$ requires Co, 10·7%).

1-*Hydroxy*-3-p-*tolyl*-1-*methyltriazen*, precipitated by rapidly cooling a benzene–light petroleum solution, formed cream-white needles, m. p. 115—116° and exploding above this temperature (Found: N, 24·8. $C_8H_{11}ON_3$ requires N, 25·4%). The *cupric* compound formed light red-brown platelets with a silver lustre, m. p. 187° (Found: Cu, 16·2. $C_{16}H_{20}O_2N_6Cu$ requires Cu, 16·2%). The *nickel* compound was a dull yellow crystalline powder, m. p. 227° (Found: N, 21·4; Ni, 15·0. $C_{16}H_{20}O_2N_6Ni$ requires N, 21·7; Ni, 15·2%); a pyridine addition compound was formed as pink-buff needles which lost pyridine during filtration and rapidly reverted to the original dull yellow nickel compound. The *ferric* compound formed blue-black rectangular platelets from acetone, m. p. 176° (Found: Fe, 10·1. $C_{24}H_{30}O_3N_9Fe$ requires Fe, 10·2%). The *cobaltous* compound formed a coarse crystalline powder, orange from alcohol, rust-red from acetone, m. p. 184—186° (Found: Co, 15·3. $C_{16}H_{20}O_2N_6Co$ requires Co, 15·2%). It was stable in air, and only oxidised in solution after standing for several hours. By dissolving it in cold pyridine and adding water, a pyridine addition compound was precipitated as bright scarlet needles which rapidly lost pyridine in air, reverting to the rust-red cobaltous compound. The *cobaltic* compound was obtained as small, mauve, feathery needles from acetone, m. p. 156° (Found: Co, 10·9. $C_{24}H_{30}O_3N_9Co$ requires Co, 10·7%). On heating a concentrated solution in pyridine for 15 minutes and cooling, the scarlet cobaltous pyridine compound was deposited.

1-*Hydroxy*-3-β-*naphthyl*-1-*methyltriazen* was obtained by repeated crystallisation from a benzene–light petroleum mixture as cream platelets, m. p. 143—144°, exploding above this temperature (Found: N, 21·1. $C_{11}H_{11}ON_3$ requires N, 20·9%). It slowly darkened on exposure to light. The apparent molecular weights (Calc.: *M*, 201) determined cryoscopically in benzene were as follows:

G. solute/100 g. of benzene	1·01	1·52	2·08	2·44
Apparent molecular weight	192	199	208	212

The *cupric* compound formed a pale buff microcrystalline powder, m. p. 212° (Found: Cu, 13·4. $C_{22}H_{20}O_2N_6Cu$ requires Cu, 13·7%). The *nickel* compound formed feathery orange needles from alcohol; it was purified by heating the pyridine addition compound at 120° to constant weight, forming a deep ochre-yellow crystalline powder, m. p. 216° (Found: N, 18·2; Ni, 12·5. $C_{22}H_{20}O_2N_6Ni$ requires N, 18·3; Ni, 12·8%). Addition of water to a pyridine solution precipitated a *dipyridino*-compound as a pink-brown crystalline powder, losing pyridine on heating to about 90° (Found: Ni, 9·6; loss on heating, 26·7. $C_{22}H_{20}O_2N_6Ni,2C_5H_5N$ requires Ni, 9·6; loss for $2C_5H_5N$, 25·6%). The *ferric* compound formed a very finely divided amorphous purple-blue powder, m. p. 155°, the analysis of which showed it to be somewhat impure (Found: N, 17·5; Fe, 10·5. $C_{33}H_{30}O_3N_9Fe$ requires N, 19·2; Fe, 8·5%). The cobaltous compound was obtained in an impure condition as a light brown powder, giving a brown oily pyridine addition compound which could not be obtained crystalline. The *cobaltic* compound formed purple-grey feathery needles from acetone, m. p. 170° (Found: N, 18·5; Co, 8·5. $C_{33}H_{30}O_3N_9Co$ requires N, 19·1; Co, 8·9%).

1-Hydroxy-1 : 3-diphenyltriazen was obtained as pale yellow needles, m. p. 127—128° (Bamberger and Büsdorf, *loc. cit.*, gave 126—127°), darkening on exposure to light. Apparent molecular weights (Calc.: *M*, 213) determined cryoscopically in benzene were as follows:

G. solute/100 g. of benzene	0·56	1·23	1·92	2·78
Apparent molecular weight	191	201	206	217

The *cupric* compound was obtained by precipitation from chloroform solution with light petroleum as light copper-coloured needles having a strong metallic lustre, m. p. 190—192° (Found: Cu, 12·9. $C_{24}H_{20}O_2N_6Cu$ requires Cu, 13·0%). The *nickel* compound formed a bright yellow microcrystalline powder from acetone, m. p. 211° (Found: Ni, 11·9. $C_{24}H_{20}O_2N_6Ni$ requires Ni, 12·1%). Precipitation of a pyridine solution by the addition of water yielded an olive-green crystalline *dipyridino*-compound, which was unstable in air, and was dried for analysis in an atmosphere of pyridine vapour (Found: loss on heating, 25·8. $C_{24}H_{20}O_2N_6Ni,2C_5H_5N$ requires $2C_5H_5N$, 24·7%). An impure *ferric* compound was obtained from pyridine as a shining, jet-black, crystalline powder, m. p. 156° (Found : N, 16·7; Fe, 11·8. $C_{36}H_{30}O_3N_9Fe$ requires N, 18·2; Fe, 8·1%). The *cobaltous* compound was obtained from acetone as a khaki-coloured powder consisting of micro-needles, m. p. 175° (Found : Co, 12·1. $C_{24}H_{20}O_2N_6Co$ requires Co, 12·2%). It was stable in air, and oxidised only slowly in solution. It gave a *dipyridino*-addition compound, which formed a red-brown crystalline powder having a yellow streak, m. p. 120—125° after losing pyridine at *ca.* 115° (Found : Co, 8·9. $C_{24}H_{20}O_2N_6Co,2C_5H_5N$ requires Co, 9·2%). The *cobaltic* compound was obtained as a dark greenish-brown amorphous powder, m. p. 108—109° (Found : Co, 8·6. $C_{36}H_{30}O_3N_9Co$ requires Co, 8·5%).

1-*Hydroxy*-3-p-*tolyl*-1-*phenyltriazen*, prepared by coupling diazotised *p*-toluidine with a solution containing phenylhydroxylamine freshly prepared from nitrobenzene, formed large lemon-yellow needles from alcohol, m. p. 131°, and exploding above this temperature (Found : C, 69·1; H, 5·8; N, 18·2. $C_{13}H_{13}ON_3$ requires C, 68·7; H, 5·7; N, 18·5%). The *cupric* compound formed a buff amorphous powder from acetone, m. p. 191° (Found : Cu, 12·7. $C_{26}H_{24}O_2N_6Cu$ requires Cu, 12·3%). The *nickel* compound was obtained from alcohol as a deep yellow powder, which was purified by heating the pyridine addition compound at 140° to constant weight. It formed deep gold, square platelets, m. p. 222° (Found : Ni, 11·2. $C_{26}H_{24}O_2N_6Ni$ requires Ni, 11·5%). By precipitating a warm pyridine solution with water a *dipyridino*-compound was obtained as a coarse, golden-brown, crystalline powder which lost pyridine on heating (Found : Ni, 8·7. $C_{26}H_{24}O_2N_6Ni,2C_5H_5N$ requires Ni, 8·8%). The *ferric* compound formed a jet-black amorphous powder, m. p. 155° (Found : Fe, 7·7. $C_{39}H_{36}O_3N_9Fe$ requires Fe, 7·6%). The *cobaltous* compound formed minute light brown needles from acetone, m. p. 184° (Found : Co, 11·3. $C_{26}H_{24}O_2N_6Co$ requires Co, 11·5%); it was stable in air, and oxidised only slowly in solution. By crystallisation from pyridine, a red-purple crystalline pyridine addition compound was obtained which lost pyridine explosively on heating. The *cobaltic* compound formed a dark greenish-brown amorphous powder, m. p. 117° after softening at 105° (Found : N, 16·8; Co, 8·4. $C_{39}H_{36}O_3N_9Co$ requires N, 17·1; Co, 8·0%). The substance decomposed in hot solvents, and all attempts at recrystallisation resulted in the formation of low-m. p. tars.

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