959. *Complexes of Tervalent Cobalt with* N-*Substituted Salicylideneimines.*

By B. O. West.

The preparation of cobalt(III) complexes with seven *N*-substituted salicylideneimines is reported. The complexes have the general formula $Co(O{\cdot}C_6H_4{\cdot}CH{:}NR)_3$ and are crystalline compounds soluble in organic solvents. Geometric isomers may exist for such compounds but a separation has not been achieved. A preference for the *trans*-form is indicated on steric grounds. The C:N link is more resistant to acid hydrolysis when the Schiff's base is combined with a cobalt ion, cobalt(III) being more effective than cobalt(II).

SCHIFF's bases derived from salicylaldehyde and primary amines react with bivalent metal ions to form complexes $M(O{\cdot}C_6H_4{\cdot}CH{:}NR)_2$. Such compounds have been isolated for nickel,[1] copper,[1,2] and cobalt,[3] and the magnetic properties,[4,5] absorption spectra,[5] and dipole moments [6] of a number of such complexes have been studied. The only complex

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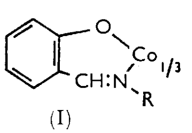
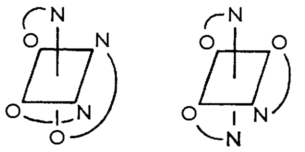
[1] Hunter and Marriott, *J.*, 1937, 2000.
[2] Verter and Frost, *J. Amer. Chem. Soc.*, 1960, **82**, 85.
[3] West, *Nature*, 1954, **173**, 1187; *J.*, 1952, 3115.
[4] Clark and Odell, *J.*, 1955, 3431.
[5] Sacconi, Paoletti, and Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.
[6] Sacconi, Ciampolini, Maggio, and Re, *J. Amer. Chem. Soc.*, 1960, **82**, 815.

previously known between a tervalent metal ion and such ligands was tris(salicylideneimino)iron(III) prepared by Klemm and Raddatz.[7]

Cobalt(III) complexes (I) may be easily prepared by the oxidation of a cobalt(II) complex in the presence of excess of Schiff's base with hydrogen peroxide in aqueous ethanol. The complexes are highly crystalline and generally appear black in reflected light but when crushed are brown-yellow or yellow-green. Their solutions in organic solvents vary from yellow-brown when R is an aryl substituent to yellow-green when R is alkyl or cyclohexyl. These colours are in marked contrast to the yellow-orange of solutions of cobalt(II) complexes with similar ligands. Slow oxidation of cobalt(II) complexes is shown by the visible colour change when solutions are exposed to the air for several days. The organic peroxides formed in various organic solvents as impurities will also cause oxidation of cobalt(II) complexes with salicylideneimines, and the rapid colour change can be used as a simple test for the presence of such impurities. The compounds are diamagnetic as is expected for spin-paired cobalt(III) complexes.



(I)



cis *trans*

(II)

(R = Et, cyclohexyl, CH_2Ph, Ph, p-C_6H_4Me, p-$C_6H_4{\cdot}OMe$, p-C_6H_4Cl)

Isomerism.—The presence of two different kinds of co-ordinating atom on each ligand, *viz.*, oxygen and nitrogen, allows the existence of structural isomers for the cobalt(III) complexes with the configurations shown in (II). Attempts to isolate the two forms of any of the complexes prepared have failed. Molecular models [Stuart and Briegleb components (Leybolds Nachfolger)] suggest that a molecule bearing the *cis*-configuration would be under very great steric strain because of the nearness of the nitrogen atoms. So much congestion arises between neighbouring alkyl or aryl substituents that models having the *cis*-configuration could not be assembled. Models of the *trans*-form still show considerable, but much less, strain, and it is tentatively concluded that the complexes are isolated mainly in the *trans*-form. Most of the cobalt(III) complexes prepared show some tendency to be reduced to the 4-co-ordinate cobalt(II) state when solutions containing these complexes are refluxed or evaporated, and this would support the concept of steric strain in the 6-co-ordinate cobalt(III) form since reduction would lead to a great decrease of strain in the cobalt(II) complex that would be formed. Ley and Winkler [8] isolated two geometrical isomers of tris(glycino)cobalt(II) which would also have the *cis–trans*-configurations of (II), and the absolute configuration of each separated isomer has been suggested on the basis of spectral data.[9]

There is also the possibility of positional isomerism among salicylideneimine complexes containing aryl substituents attached to the nitrogen atom, depending upon whether the substituents are in the *ortho*-, *meta*-, or *para*-position. Thus three possible forms of tris(salicylidenetoluidinato)cobalt(III) could exist depending on the position of the methyl group, and with two possible structural isomers for each form a total of six isomers could exist. Such " constitutional isomers " as they may be termed have been isolated for the bivalent complexes of nickel,[1] copper,[3] and cobalt(II),[3] but all attempts to isolate cobalt(III) complexes bearing *ortho*- or *meta*-substituents have so far been unsuccessful: the reaction products obtained are dark tars or amorphous solids of indefinite composition. A similar

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[7] Klemm and Raddatz, *Z. anorg. Chem.*, 1942, **250**, 207.

[8] Ley and Winkler, *Ber.*, 1909, **42**, 3894.

[9] Basolo, Ballhausen, and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810.

difficulty has been reported in the preparation of cobalt(II) complexes with salicylidenearylimines bearing substituents in the aryl ring *ortho* to the imino-nitrogen:[3] compounds can be readily prepared from bases containing *meta*- or *para*-substituents, and complexes of copper or nickel can be prepared with all three kinds of substituent present. In order to explain this behaviour it has been suggested that cobalt(II) complexes of this kind prefer a tetrahedral arrangement of ligands, and *ortho*-substituents in the arylimine ring system, for steric reasons, prevent the most stable configuration from being adopted, so that crystalline products cannot be isolated.[3,10] Nickel and copper complexes exist preferentially in a planar configuration and such compounds show a greatly reduced steric hindrance to chelation. The development of brown-yellow colours after oxidation of reaction mixtures of cobalt(II) and either *ortho*- or *meta*-substituted salicylidenearylimines indicates that co-ordination of some kind does occur in solution even though pure products could not be isolated. Models of such complexes show considerable steric hindrance to the arrangement of six co-ordinating groups about the metal when substituents are *ortho* to the nitrogen atom. However, there appears to be little added steric strain when *meta*-substituents are present beyond that due to the ring system itself. Such complexes may well be prepared by some alternative synthetic method.

The C:N *Bond*.—A qualitative study has been made of the effect of chelation on the resistance to hydrolysis of the C:N band in the particular compound salicylidene-*p*-toluidine. This was done by measuring the amount of free base or complex remaining in acetone solution after the addition of aqueous perchloric acid of different concentrations. The results (see Table) indicate that co-ordination of the Schiff's base with cobalt ions increases the resistance of the C:N link to hydrolysis, while cobalt(III) has a greater effect than cobalt(II) in " protecting " the double bond. Similar stabilisation of the C:N bond to acid attack has been reported for copper and nickel complexes with *NN'*-di(1-methyl-3-oxobutylidene)ethylenediamine[11] and for the copper derivative of salicylideneglycine.[12]

The following reactions are considered to occur. The Schiff's base will be hydrolysed to its constituents (1)

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_3 + H_2O \xrightarrow{H^+} HO{\cdot}C_6H_4{\cdot}CHO + NH_2{\cdot}C_6H_4{\cdot}CH_3} \quad . \quad . \quad . \quad (1)$$

while the complexes will be dissociated (2):

$$\mathrm{Co(O{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_3)}_x + x\mathrm{H^+} \longrightarrow \mathrm{Co}^{x+} + x\mathrm{HO{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CH_3} \quad . \quad . \quad . \quad (2)$$

followed by hydrolysis of the liberated base. Although the mechanism of acid hydrolysis of Schiff's bases has not been extensively studied, it is reasonable to assume that a hydronium ion must attach itself to the nitrogen atom as a first step in the reaction. In a metal complex, since the nitrogen atom is already bound to a metal ion, a hydronium ion must compete with the metal ion and hydrolysis becomes more difficult. The greater resistance to attack shown by the cobalt(III) complex than by the cobalt(II) may be explained by the greater bond strength of the Co–N link in the tervalent than in the bivalent complex,

*The acid-hydrolysis of salicylidene-*p*-toluidine complexes of cobalt in aqueous acetone at 20°.*

$HClO_4$ (10^3M)	Free base [a]	Co(II) complex [a]	Co(III) complex [b]	$HClO_4$ (10^3M)	Free base [a]	Co(II) complex [a]	Co(III) complex [b]
0·0	100	100	100	1·6	—	—	100
0·5	34	91	—	2·0	0	12	
0·8	—	—	100	4·0	—	—	100

Results are expressed as the percentage of the compound remaining undissociated in solution as determined by the optical densities of the solutions. Concentrations in the reaction mixtures were: free base, $1{\cdot}9 \times 10^{-3}$M; Co(II) complex, $1{\cdot}2 \times 10^{-3}$M; Co(III) complex, $0{\cdot}51 \times 10^{-3}$M. The concentrations represent approximately the same " concentration " of C:N bonds in each solution examined.

[a] 50% Aqueous acetone after mixing. [b] 40% Aqueous acetone after mixing.

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[10] West, Robertson, and Hocking, *Nature*, 1955, **176**, 832.

[11] McCarthy, Hovey, Ueno, and Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.

[12] Eichhorn and Marchand, *J. Amer. Chem. Soc.*, 1956, **78**, 2688.

making it more difficult for an attacking hydronium ion or proton to gain a share in the nitrogen electrons.

EXPERIMENTAL

Microanalyses were by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

Tris(salicylideneanilinato)cobalt(III).—Cobalt acetate tetrahydrate (5·0 g., 0·02 mole) was dissolved in water (50 ml.), and the solution filtered and added to a solution of salicylideneaniline (11·8 g., 0·06 mole) in ethanol (300 ml.). To the resulting dark red solution was added dropwise a slight excess of hydrogen peroxide (100-vol.) with vigorous stirring (*ca.* 1·5 ml., 0·013 mole). The dark yellow-brown solution was kept until crystallization was complete (11·7 g., 91% based on cobalt salt). The product was recrystallized from alcohol and obtained as black needles which crushed to an olive-green powder, m. p. 194° (Found: C, 72·4; H, 4·7; N, 6·4. $C_{39}H_{30}CoN_3O_3$ requires C, 72·4; H, 4·6; N, 6·5%).

Similar procedures were used to prepare the following compounds. *Tris(salicylidene-*p-*toluidinato)cobalt*(III), black prisms, m. p. 193° (Found: C, 73·2; H, 5·3; N, 6·0. $C_{42}H_{36}CoN_3O_3$ requires C, 73·1; H, 5·3; N, 6·1%). *Tris(salicylidene-*p-*chloroanilinato)cobalt*(III), black prisms, m. p. 214°, somewhat unstable and reverting to the cobalt(II) complex on continued boiling in solvents (Found: C, 62·7; H, 3·4; N, 5·5. $C_{39}H_{27}Cl_3CoN_3O_3$ requires C, 62·4; H, 3·6; N, 5·6%). *Tris(salicylidene-*p-*anisidinato)cobalt*(III), black prisms, m. p. 193° (Found: C, 68·6; H, 5·05; N, 5·9. $C_{42}H_{36}CoN_3O_6$ requires C, 68·4; H, 4·9; N, 5·7%).

Tris(salicylidenebenzyliminato)cobalt(III).—The Schiff's base was prepared by warming salicylaldehyde (7·3 g., 0·06 mole) and benzylamine (6·4 g., 0·06 mole) in ethanol (400 ml.) at 70°. To this was added a filtered solution of cobalt acetate tetrahydrate (5 g., 0·02 mole) in water (60 ml.). Excess of 100-vol. hydrogen peroxide (2 ml., 0·018 mole) was added dropwise to the mixture with constant stirring. Fine, dark green needles were formed on cooling; this complex had m. p. 221° (Found: C, 73·7; H, 5·5; N, 6·1. $C_{42}H_{36}CoN_3O_3$ requires C, 73·1; H, 5·3; N, 6·1%).

Tris(salicylidenecyclohexyliminato)cobalt(III), dark green prisms, m. p. 187° (Found: C, 69·8; H, 7·8; N, 6·1. $C_{39}H_{48}CoN_3O_3$ requires C, 70·2; H, 7·3; N, 6·3%), was prepared similarly.

Tris(salicylidene-ethyliminato)cobalt(III).—The Schiff's base was prepared from salicylaldehyde and the amine hydrochloride in the presence of sodium hydroxide. Cobalt acetate and hydrogen peroxide were then added and the mixture was kept on the water-bath until reaction was complete; the *product* formed dark green prisms, m. p. 216° (Found: C, 64·3; H, 6·3; N, 8·1. $C_{27}H_{30}CoN_3O_3$ requires C, 64·5; H, 6·1; N, 8·4%).

Salicylidene-*p*-toluidine was prepared by heating salicylaldehyde and *p*-toluidine in ethanol on a water-bath and allowing the product to crystallize; yellow needles from ethanol, m. p. 94°, were obtained (Found: C, 79·3; H, 6·2. Calc. for $C_{14}H_{13}NO$: C, 79·6; H, 6·2%).

Bis(salicylidene-*p*-toluidinato)cobalt(II) was prepared by West's method,[3] forming dark red prisms (from ethanol), m. p. 180° (decomp.) (Found: C, 69·8; H, 5·0; N, 5·6. Calc. for $C_{28}H_{24}CoN_2O_2$: C, 70·1; H, 5·05; N, 5·9%).

Hydrolysis Experiments.—Standard solutions of the base and complexes in acetone were prepared by direct weighing. Standard aqueous perchloric acid solutions were prepared by dilution of a stock, standard solution. Reaction mixtures were prepared by mixing equal volumes (2 ml.) of the reagents. A sample was quickly transferred to a spectrophotometer cell, and the optical density of the solution determined immediately at a suitable wavelength, *viz.*, salicylidene-*p*-toluidine, 4300 Å; cobalt(II) complex, 4900 Å; cobalt(III) complex, 4000 Å. For the reactions of the cobalt(III) complex additional acetone (1 ml.) was added to the reaction mixture to delay precipitation of the complex until a reading could be made. Precipitation commenced after 3—4 min. The optical densities of mixtures prepared by using distilled water in place of acid were considered as standards representing no hydrolysis in the solutions. A Unicam S.P. 500 spectrophotometer was used in the experiments.

Magnetic Measurements.—Diamagnetism was detected by Gouy's method.

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