260. *The Magnetic Moments and Structures of Some* N-*Substituted Salicylideneimine Complexes of Cobalt*(II).

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The magnetic moments have been measured for nine *N*-substituted salicylideneimine complexes of cobalt(II) in the solid state and in benzene and in pyridine solution. The values of the moments suggest that the complexes have a tetrahedral configuration in the solid state and in benzene solution but take up pyridine to assume an octahedral configuration.

THE preparation of several cobalt(II) complexes with *N*-arylsalicylideneimines has been reported[1] and the compounds have been shown to be labile with respect to replacement of the metal. When the aryl ring possessed an *ortho*-substituent it was difficult to isolate complexes and steric hindrance to the formation of a tetrahedral arrangement of ligands about the cobalt ion was suggested[2] to explain this. Such "*ortho*"-substituted complexes have been isolated[3] for copper(II) and nickel(II), and *X*-ray investigations[4] have shown that a number of Schiff's base complexes of these elements have *trans*-planar configurations. The chelate rings of di-(*N*-methylsalicylideneiminato)nickel have, however, been shown[5] to be distorted from strict planarity.

The cobalt(II) complexes are slowly oxidised in solution in organic solvents by contact with air, and more rapidly by hydrogen peroxide, and tri-(*N*-arylsalicylideneiminato)-cobalt(III) complexes may be isolated.[6] *N*-Alkyl cobalt(II) compounds are much more readily oxidised than the *N*-aryl derivatives, and although cobalt(III) complexes containing these ligands have been isolated the cobalt(II) compounds are difficult to prepare. Several of these *N*-alkyl complexes have, however, been isolated by Yamada and his co-workers,[7] and their spectra have been examined. Di-(*N*-cyclohexylsalicylideneiminato)-cobalt(II) alone of all the complexes reported here is stable to air, even for several weeks. This complex has also been examined by Ciampolini *et al.*[8]

The magnetic moments have been measured for a series of cobalt(II) complexes in the solid state and in solution in benzene and in pyridine. The results are presented in Tables 1 and 2. The moments of the solid compounds are very close to those in benzene for most of the compounds, all lying in the range 4·3—4·5 B.M. There was no detectable change in the moments in benzene for an hour. Thus the cobalt compounds do not show the marked change in magnetic properties found with some *N*-alkyl- and *N*-aryl-salicylideneiminenickel(II) complexes,[9] *viz.*, spin-paired solid $\longrightarrow$ spin-free benzene solution.

The temperature-dependence of the susceptibility of one complex, di-(*N*-β-naphthylsalicylideneiminato)cobalt(II), has been examined over a wide temperature range in the solid state.* The results are given in Table 3. A plot of $1/\chi_M$ against temperature (K) gives a straight line, showing that the substance obeys a Curie–Weiss law in the range studied, with some deviation at highest and lowest temperatures. A small value of $\theta = 5°$ was found graphically.

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* The author is grateful to Dr. D. Machin for making these measurements on the temperature-controlled magnetobalance at University College, London.

[1] West, *J.*, 1952, 3115.

[2] West, *Nature*, 1954, **173**, 1187; Hocking, Robertson, and West, *ibid.*, 1955, **176**, 832.

[3] Hunter and Marriott, *J.*, 1937, 2000.

[4] Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136; Lingafelter and Stewart, *Acta Cryst.*, 1959, **12**, 842; Guare, Lessor, and Merritt, *ibid.*, 1956, **9**, 253.

[5] Frasson, Panattoni, and Sacconi, *J. Phys. Chem.*, 1959, **63**, 1908.

[6] West, *J.*, 1960, 4944.

[7] Yamada, personal communication.

[8] Ciampolini, Del Re, Maggio, and Sacconi, *J. Amer. Chem. Soc.*, 1960, **82**, 815.

[9] Mellor and Willis, *J. Amer. Chem. Soc.*, 1947, **69**, 1237; Clark and Odell, *J.*, 1955, 3431; Holm and McKinney, *J. Amer. Chem. Soc.*, 1960, **82**, 5506; Holm, Proc. Sixth Internat. Conference on Coordination Chemistry, Macmillan, New York, 1961, p. 341.

The complexes have moments showing the presence of three unpaired electrons, with an orbital contribution added to the spin-only value of 3·88 B.M. A tetrahedral complex of a d^7-ion such as cobalt(II) should, if there is no mixing-in of upper states, show a spin-only value for the magnetic moment, since the ground state of the ion is a singlet and no orbital momentum is associated with a singlet level.[10] However, the moments of tetrahedral cobalt(II) complexes are observed to be higher than 3·88 B.M. owing to spin–orbit coupling which produces some mixing of the next highest triplet level with the lower singlet. The range of moments[10] for known or presumed tetrahedral cobalt(II) compounds is 4·26—5·00 B.M., and the complexes reported here all have moments in the lower portion of this range. The presumption is strong that they have a tetrahedral configuration in the solid state and in benzene. The moments are comparable with those reported by Gill and Nyholm[11] for CoX_2,py_2 compounds (4·42—4·50 B.M. for solids, 4·52—4·49 B.M. for solutions in nitrobenzene). Some of these compounds have been shown by *X*-ray analysis to have a tetrahedral configuration.[12]

TABLE 1.

Magnetic moments of some solid *N*-substituted salicylideneiminatocobalt(II) complexes.

R	Temp. (K)	$10^6\chi_g$	$10^6\chi_M$	$\mu_{eff.}$ (B.M.)
Ph	296·0°	17·55	8147	4·41
m-C_6H_4Me	298·1	16·43	8124	4·42
p-C_6H_4Me	296·4	16·07	7951	4·36
o-$MeO{\cdot}C_6H_4$	299·0	15·80	8338	4·48
p-$MeO{\cdot}C_6H_4$	296·4	14·86	7859	4·34
p-C_6H_4Cl	295·3°	16·09	8625	4·53
p-C_6H_4Br	297·2	12·43	7846	4·34
β-$C_{10}H_7$	297·2	14·04	8026	4·39
Cyclohexyl	297·2	17·26	8264	4·45

TABLE 2.

Magnetic moments of some *N*-substituted salicylideneiminatocobalt(II) complexes in benzene and pyridine.

	Benzene			Pyridine		
R	Temp. (K)	concn. (mmolal)	$\mu_{eff.}$	Temp. (K)	concn. (mmolal)	$\mu_{eff.}$
Ph	298·5°	35·5	4·50	299·0°	14·6	4·97
m-C_6H_4Me	293·9	17·97	4·46	294·0	33·95	4·86
p-C_6H_4Me	294·2	39·13	4·32	293·3	40·24	4·84
o-$MeO{\cdot}C_6H_4$		(insol.)		293·5	20·39	4·54
p-$MeO{\cdot}C_6H_4$	294·1	16·18	4·33	294·8	15·29	4·84
p-C_6H_4Cl	294·8	4·52	4·22	295·4	18·58	4·91
p-C_6H_4Br	296·2	3·22	4·56	295·0	13·06	4·74
β-$C_{10}H_7$	294·4	15·45	4·34	295·4	14·09	4·81
Cyclohexyl	294·1	33·98	4·43	300·4	23·15	4·72

TABLE 3.

Temperature-dependence of χ_M for di-(*N*-β-naphthylsalicylideneiminato)cobalt(II).

Temp. (K)	$10^6\chi_M$	$\mu_{eff.}$ [a]
302·9	7932	4·44
278·2	8569	4·43
253·3	9312	4·40
229·7	10,224	4·40
206·4	11,207	4·37
182·8	12,657	4·38
160·3	14,357	4·38
137·6	16,637	4·38
121·6	18,667	4·37
104·5	21,687	4·38
94·0	24,017	4·38
79·8	28,377	4·41

[a] Calc. from the expression, $\mu_{eff.} = 2{\cdot}84\,[\chi_M(T + \theta)]^{\frac{1}{2}}$ with $\theta = 5°$ as determined from the plot of $1/\chi_M$ against temp. (K).

Several of the compounds studied by Cotton and Holm,[13] for which tetrahedral configuration has been suggested by spectral measurements, also have similar low moments, *e.g.*, $[Me_3PO]_4Co(ClO_4)_2$ 4·34; $K_2Co(CNS)_4$ 4·43; CoO in a ZnO lattice 4·26 B.M.; but the tetrahalogenocobaltate(II) complexes[10] and many other presumed

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[10] Figgis and Nyholm, *J.*, 1954, 12; 1959, 338; Cotton and Holm, *J. Chem. Phys.*, 1959, **31**, 788.
[11] Gill and Nyholm, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.
[12] Malinovski, *Kristallografiya*, 1957, **2**, 734; Porai-Koshits, *Zhur. neorg. Khim.*, 1959, **4**, 730.
[13] Cotton and Holm, *J. Chem. Phys.*, 1960, **32**, 1168.

tetrahedral phosphine and phosphine oxide cobalt complexes examined by Cotton *et al.*[14] have higher moments, in the range 4·50—5·00 B.M.

Some additional evidence for the tetrahedral nature of the di-(*N*-arylsalicylideneiminato)cobalt(II) complexes comes from the dipole moment of the *N*-cyclohexyl complex measured by Ciampolini *et al.*[8] who found a large value for the difference between the total polarisation and the electric polarisation of a benzene solution of the complex, *viz.*, 503 c.c., of the order expected for a tetrahedral complex. Complexes of nickel, copper, and palladium where planar configurations are believed to exist gave values less than 100 c.c. Yamada and his co-workers [7] examined the visible spectra of a number of these cobalt(II) complexes and concluded that the complexes have tetrahedral configurations. Although the evidence supports the earlier prediction of tetrahedral structures made on the basis of what appeared to be steric hindrance,[2] di-(*N*-*o*-tolylsalicylideneiminato)cobalt(II) has now been prepared, together with a complex which appears to contain a hydroxide group, namely, (*N*-*o*-tolylsalicylideneiminato)cobalt(II) hydroxide.[15] This "*ortho*"-effect is being investigated.

In pyridine solution, with one exception, the complexes all show paramagnetism greater than in the solid state or in benzene. The values lie between 4·7 and 4·97 B.M., *i.e.*, at the lower end of the range generally found for octahedrally co-ordinated, spin-free compounds of cobalt(II).[10] This implies that pyridine can interact with the complexes and in support of this view unstable dipyridine solvates were isolated from solutions of the *m*-tolyl and *p*-tolyl complexes in pyridine. These readily lost their co-ordinated solvent on exposure to air and reverted to the original complexes. The co-ordination of pyridine to similar nickel complexes [9,16] has been shown to bring about an increase in the magnetic moments of the complexes to the values expected for octahedral compounds and several dipyridine solvates have been isolated.[9,16]

The *o*-methoxyphenyl complex does not show a marked increase in moment in pyridine solution and can be recovered from solution without any associated molecules of solvent. The latter observation may mean only that the solvate is extremely unstable, but the fact that the solution moment is only slightly different from that of the solid suggests that solvent interaction is extremely weak. This complex was the only "*ortho*"-substituted complex which could be readily prepared [2] and it was suggested that co-ordination between the methoxyl group and cobalt may stabilise the molecule, leading to a distorted octahedral configuration overall. The magnetic moment of the solid does not support this view. However, the apparent resistance to solvation by pyridine may indicate some form of steric effect whereby the methoxyl groups can prevent the close approach of solvent molecules to the metal ion.

EXPERIMENTAL

Preparation of the Complexes.—Although the complexes described are relatively easily oxidised to cobalt(III) compounds, the method described by Calvin and Bailes [17] for preparing oxygen-carrying complexes has been found suitable for their synthesis. The yields were 55—85%, based on cobalt acetate; higher yields could certainly be obtained by addition of aqueous alkali to the reaction mixtures once the reagents had been mixed.

Di-(N-m-*tolylsalicylideneiminato*)*cobalt*(II). The Schiff's base was preformed by treating salicylaldehyde (7·3 g.) with *m*-toluidine (6·4 g.) in ethanol (250 ml.) and warming the solution on the water-bath until the yellow colour of the base was fully developed (10 min.). The flask containing the solution was evacuated at the pump until the warm ethanol boiled, driving out the bulk of the air in the vessel. The flask was then closed and a filtered solution of cobalt acetate tetrahydrate (7·5 g.) in water (100 ml.) was added through a separatory funnel attached to the flask. The mixture was shaken and the flask re-evacuated until boiling commenced. The flask was again closed and the solution allowed to cool slowly, yielding the *complex* as dark

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[14] Cotton, Faut, Goodgame, and Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 1780.

[15] Diamantis, Weigold, and West, unpublished work.

[16] Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663.

[17] Bailes and Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

red prisms that recrystallised from bromobenzene (the occasional formation of red oils instead of crystals in this or other preparations was overcome by addition of more ethanol and re-heating) (Found: C, 70·0; H, 5·2; N, 5·65. $C_{28}H_{24}CoN_2O_2$ requires C, 70·1; H, 5·05; N, 5·9%).

The following were similarly prepared:

Di-(N-p-*tolylsalicylideneiminato*)*cobalt*(II), dark red needles from ethanol (Found: C, 70·3; H, 4·8; N, 5·7%).

Di-(N-p-*chlorophenylsalicylideneiminato*)*cobalt*(II), pale red prisms from chlorobenzene (Found: C, 60·2; H, 3·5; N, 5·3. $C_{26}H_{18}Cl_2CoN_2O_2$ requires C, 60·0; H, 3·5; N, 5·4%).

Di-(N-p-*bromophenylsalicylideneiminato*)*cobalt*(II), pale orange-red prisms from bromobenzene (Found: C, 51·5; H, 3·0; N, 4·6. $C_{26}H_{18}Br_2CoN_2O_2$ requires C, 51·3; H, 3·0; N, 4·6%).

Di-(N-o-*methoxyphenylsalicylideneiminato*)*cobalt*(II), dark crimson prisms from bromobenzene (Found: C, 66·0; H, 4·9; N, 5·5. $C_{28}H_{24}CoN_2O_4$ requires C, 65·7; H, 4·7; N, 5·5%).

Di-(N-p-*methoxyphenylsalicylideneiminato*)*cobalt*(II), purple-red crystals from chlorobenzene (Found: C, 65·7; H, 4·9; N, 5·6%).

Di-(N-*phenylsalicylideneiminato*)*cobalt*(II), dark red needles from ethanol (Found: C, 69·8; H, 4·6; N, 6·1. $C_{26}H_{20}CoN_2O_2$ requires C, 69·2; H, 4·6; N, 6·2%).

Di-(N-β-*naphthylsalicylideneiminato*)*cobalt*(II), pale red rhombs from ethanol (Found: C, 74·2; H, 4·4; N, 5·0. $C_{34}H_{24}CoN_2O_2$ requires C, 74·0; H, 4·4; N, 5·1%).

Di-(N-*cyclohexylsalicylideneiminato*)*cobalt*(II), dark red prisms from ethanol (Found: C, 67·6; H, 7·1; N, 5·8. $C_{26}H_{32}CoN_2O_2$ requires C, 67·4; H, 7·0; N, 6·1%).

Solubility.—The complexes are all readily soluble in pyridine. The *o*-methoxyphenyl complex is almost insoluble, the *p*-chlorophenyl and *p*-bromophenyl complexes are only sparingly soluble, and the remaining compounds readily soluble in benzene. The phenyl, *m*- and *p*-tolyl, β-naphthyl, and cyclohexyl complexes are soluble in ethanol, methanol, and acetone on prolonged boiling, the remaining complexes but slightly soluble. All the compounds are easily soluble in bromo- or chloro-benzene.

Isolation of Pyridine Solvates.—(a) m-*Tolyl complex*. Water was added drop by drop to a stirred solution of di-(*N*-*m*-tolylsalicylideneiminato)cobalt(II) in pyridine; cinnamon-brown crystals were precipitated. The solid began to evolve pyridine as soon as it was separated from the solution, so it was dried as completely as possible between filter paper and then a weighed sample was heated under vacuum for 2 hr. at 80° and the weight loss determined. The compound lost pyridine completely in several days at room temperature, the original compound being re-formed. Addition of acetone to crystals of the solvate also brought about immediate dissociation and the parent complex was re-formed.

0·1102 g. of solvate lost 0·029 g. when heated under a vacuum, *i.e.*, 26·3% (loss of 2 mol. requires 24·8%).

(b) p-*Tolyl complex*. A light brown crystalline compound was similarly precipitated from a pyridine solution of di-(*N*-*p*-tolylsalicylideneiminato)cobalt(II) and had properties similar to those of the *m*-tolyl derivative (0·1775 g. lost 0·0439 g. under a vacuum for 2 hr. at 80°, *i.e.*, 25%. Loss of 2 mol. requires 24·8%).

(c) o-*Methoxyphenyl complex*. Water reprecipitated the dark crimson complex from pyridine solution (0·0874 g. under a vacuum at 120° for 3 hr. lost 2·6 mg., *i.e.*, 3%).

Magnetic Measurements.—These were made by the Gouy method. The specimen tube used for measurements with solids was standardised with $HgCo(CNS)_4$, $\chi_g = 16{\cdot}44 \times 10^{-6}$ c.g.s.[18] Solution measurements were carried out in a Pyrex-glass tube having a sample volume of 10 ml. The tube was standardised against distilled water, previously boiled and cooled under nitrogen ($\chi_g = -0{\cdot}720 \times 10^{-6}$ at 20°).[19] Susceptibilities of the solvents used were measured for each batch purified, because some variation of the gram-susceptibility was observed from batch to batch. The appropriate value was then used in calculating the moments of complexes for the batch of solvent used in making up a particular solution.

Values obtained were: Pyridine (i) $-0{\cdot}6158 \times 10^{-6}$, (ii) $-0{\cdot}643 \times 10^{-6}$, (iii) $-0{\cdot}639 \times 10^{-6}$, (iv) lit.,[20] $-0{\cdot}623 \times 10^{-6}$. Benzene (i) $-0{\cdot}737 \times 10^{-6}$, (ii) $-0{\cdot}694 \times 10^{-6}$, (iii) lit.,[20] $-0{\cdot}712 \times 10^{-6}$.

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[18] Figgis and Nyholm, *J.*, 1958, 4190.

[19] Figgis and Lewis, " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960.

[20] Internat. Crit. Tables, 1929, Vol. VI, p. 361.

Measurements for solutions were made at intervals during 1 hr. to see if the susceptibility varied with time. No special precautions were taken to guard against oxidation of the complexes in solution beyond provision of a ground-glass cap for the Gouy tube: separate experiments showed that oxidation was negligible for an hr. under the conditions used. The accuracy of the measurements for solids is considered to be ±1·5%; those for solutions are less accurate (±2%) owing to the high dilution. Diamagnetic corrections were made to the molar susceptibilities by the use of atomic and constitutive corrections [19] and include a factor for the diamagnetism of the metal ion. Effective magnetic moments were calculated from the formula $\mu_{\text{eff.}} = 2{\cdot}84\ (\chi_M T)^{\frac{1}{2}}$.

Pyridine was dried and fractionally distilled over barium oxide. Benzene was dried with B.D.H. molecular sieves, grade 4A, and was distilled before use. Both were of C.P. grade.

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