In the case of 1,1-diphenylethylene the K_1 value is much lower than that for *trans*-stilbene. In this compound there is undoubtedly appreciable steric interference between rings[13] which is effective in reducing the basicity of the molecule. A complete interpretation of the K_1 and K_2 values for *trans*-stilbene and 1,1-diphenylethylene is difficult since the relative contributions of the phenyl groups and the ethylenic bonds in these molecules in forming bonds with silver ion is not known.

By the methods employed previously[1] a K_1 value for bibenzyl of 6 (twice that for toluene) would be predicted, using the assumption that there is no steric interference between the two phenyl groups of bibenzyl with respect to the coördination of silver ion.[14] A K_2 value for bibenzyl ($^1/_4 K_1$ for bibenzyl + K_2 for toluene) of 2.2 would also be predicted as compared with an observed value of 0.85. These deviations between predicted and observed values are more marked than those found for other compounds of this type. In terms of the observed K_1 value ethyl cinnamate is a weaker base even than benzene or ethyl hydrocinnamate. Thus the introduction of the carbethoxy group deactivates the styrene molecule with respect to argentation to a considerable extent. It is probable that both

(13) Coates and Sutton (*J. Chem. Soc.*, 567 (1942)) calculate on the basis of dipole moment measurements that the rings in bibenzyl are twisted 30° out of a common plane. In this configuration ortho hydrogen atoms would effectively eliminate one face of each ring as potential positions for coördination of silver ion.

(14) Jeffrey, *Nature*, **156**, 82 (1945), reports data for crystalline bibenzyl which are in harmony with this assumption.

steric and electronic effects of the carbethoxy group are responsible for this diminished reactivity. In the case of ethyl hydrocinnamate, with a K_1 value somewhat lower than that for the monoalkylbenzenes, it is probable that the diminished reactivity of the aromatic nucleus results from a steric effect of the somewhat bulky ring substituent.

Summary

In an extension of earlier work the equilibrium constants for the formation of argentation complexes of the type AgAr⁺ at 25° have been determined for several benzene derivatives. Mesitylene behaves in these reactions as a weaker base than benzene, toluene and the xylenes in contrast to its behavior in other reactions in which the aromatic nucleus is acting as an electron donor. It is possible that the methyl groups in mesitylene, through steric effects, inhibit the argentation reaction. It has been found that for a variety of monoalkylbenzenes the argentation constants are comparable to those for benzene and toluene. Styrene complexes readily with silver ion, probably with the vinyl side chain acting as the electron donor portion of the organic molecule. With *trans*-stilbene, 1,1-diphenylethylene and ethyl cinnamate a much lower reactivity is observed. In fact *trans*-stilbene and ethyl cinnamate coördinate to form AgAr⁺ less readily than do the corresponding dihydro derivatives, and 1,1-diphenylethylene shows a reactivity comparable with that of benzene.

Sexadentate Metal Complexes. II. Magnetic Studies

BY FRANCIS P. DWYER, FRANCIS LIONS AND DAVID P. MELLOR

The recent resolution of a cobalt(III) complex of 3,6-dithia-1,8-bis-(salicylideneamine)-octane[1] has been interpreted as showing that it is possible for a single molecule to attach itself to a metal atom through six atoms. Since this appears to be the first instance in which experimental evidence, other than that provided by the preparation of a compound of the appropriate composition, has been obtained indicating that a molecule is able to function in such a manner[2] it was thought worth

(1) F. P. Dwyer and F. Lions, THIS JOURNAL, **69**, 2917 (1947), and *ibid.*, in press.

(2) A sexadentate function has been proposed for ethylene diamine tetra-acetic acid (YH₄) in the compound NaCoY₄H₂O by Brintzinger, Thiele and Muller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943). Klemm, *ibid.*, **252**, 225 (1944), has shown that NaCoY₄H₂O is diamagnetic but since it is not known whether any of the four water molecules is attached to the cobalt, the sexadentate function of the chelating molecule is, to that extent, a matter of uncertainty. For more recent work on complexes of YH₄ see F. A. Long, S. S. Jones and M. Burke, *Brookhaven Conference Report, Chemistry Number*, **2**, 106 (1948).

while to obtain verification of its sexadentate character by investigating some further physical consequences of this mode of attachment.

Magnetic susceptibility measurements of compounds of the transition elements can, in certain favorable instances, be used not only to determine the oxidation state but also the number, character and configuration of the chemical bonds formed by these elements.

With such information it is then possible to discover whether a multidentate molecule in a complex of known composition, utilises all of its available coördinating groups in attaching itself to a metal atom.[3] It has been abundantly proved[4] that octahedrally (d²sp³) coördinated complexes of Co(III) are invariably diamagnetic. We should therefore expect a sexadentate cobalt

(3) D. P. Mellor, *Aust. J. Science*, **3**, 120 (1941); F. P. Dwyer and D. P. Mellor, THIS JOURNAL, **63**, 81 (1941).

(4) F. Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).

TABLE I

Compound	Mass susceptibility $\chi \times 10^6$	Molar susceptibility $\chi_M \times 10^6$	Temp., °K.	Atomic susceptibility of metal $\chi_A \times 10^6$	Magnetic moment of metal in Bohr magnetons	Number of unpaired electrons
SH$_2$(Metal-free sexadentate)^a	−0.511	−198	297	..	..	..
Co(III)S$^+$I	−0.240	−137	297	114	0	0
NH$_2$(Metal-free sexadentate)^b	−0.589	−259	297	..	..	..
Co(III)N$^+$Br^{-c}	0.239	138	297	432	∼0	0
Co(II)S 3H$_2$O	15.1	7535	290	7733	4.25	3
Ni(II)S	8.1	3600	293	3798	3.00	2
Fe(II)S	10.2	4510	291	4708	3.32	2
Cu(II)S	3.09	1390	288	1588	1.92	1

^{a} SH$_2$ = 3,6-dithia-1,8-bis-(salicylideneamino)-octane = C$_{20}$H$_{24}$N$_2$O$_2$S$_2$. ^{b} NH$_2$ = 3,6-dithia-1,8-bis(β-hydroxy-α-naphthylideneamino)-octane = C$_{24}$H$_{28}$N$_2$O$_2$S$_2$. ^{c} Cobalt(III) complexes of several other related sexadentate molecules (to be described later) have also been measured. With the exception of the naphthylidene compounds described above they are all diamagnetic. The atomic susceptibilities assumed for I$^-$ and Br$^-$ were −53 and −35 × 10^{-6} c. g. s. units, respectively.

(III) complex to exhibit diamagnetism. Experiment does in fact show this to be true. This communication reports the results of magnetic susceptibility measurements made on the Co(III), Co(II), Ni(II) and Fe(II) complexes of 3,6-dithia-1,8-bis-(salicylideneamino)-octane and the Co(III) complex of corresponding β-hydroxy-α-naphthylidene compound. These sexadentate molecules will be designated SH$_2$ and NH$_2$ respectively and their internal complexes with a bivalent metal as [MeS] and [MeN].

Experimental

Susceptibility measurements were carried out by means of the Gouy method, weighings being made with a Sartorius microbalance. Tubes were calibrated with C. P. benzene whose susceptibility was assumed to be −0.702 × 10^{-6} c. g. s. unit.

Moments were calculated by means of the equation $\mu_{eff} = 2.839 \sqrt{\chi_A T}$, a relationship which holds only approximately. For this reason the values of the moments, though quoted to two decimal places, are probably reliable only to one.

The substances used and their method of preparation have already been described.[1] Where compounds were readily oxidized in the presence of moisture, they were specially prepared for the work and used immediately. Because of its sensitivity in this respect, extreme care had to be taken with the preparation of the Co(II) complex. Measurements on repeatedly recrystallized specimens of [FeS] revealed that the susceptibility gradually decreased. Some lighter colored oxidation product was formed but no attempt was made to isolate it and measure its susceptibility.

Discussion of Results

Table I summarizes the results obtained. The susceptibility of [CoS]$^+$I$^-$ and [CoN]$^+$Br$^-$ shows that in each compound the oxidation number of the cobalt atom is +3 and that it forms six strong, octahedrally directed, covalent (d^{2}sp^3) bonds. There is therefore no possibility that the optical activity of [CoS]$^+$I$^-$, reported earlier, arises from a molecular configuration in which cobalt is attached to the chelating molecule through four atoms only since, if cobalt were so attached, a moment of 4.9 Bohr magnetons would be expected. There is however the possibility that all six bonds are not formed between cobalt and a single chelating molecule. In Part I it was shown that the ra-

tio of chelating molecule to metal is 1 : 1 and that no water molecules are involved. Furthermore, measurements of molecular weight and electrolytic conduction revealed that substances of the type [CoS]$^+$I$^-$ behave as binary electrolytes.[1] Taken altogether the evidence leaves little or no doubt that 3,6-dithia-1,8-bis-(salicylideneamino)-octane and the corresponding β-hydroxy-α-naphthylidene moieties function as sexadentate chelate molecules. Although d^{2}sp^3 bonded Co(II) complexes are very rare, it was thought that a complex of this kind might well be formed by coördination with a sexadentate molecule. Theory predicts[5] a magnetic moment of 1.73 Bohr magnetons in such a case. Surprisingly enough the observed moment of the compound [CoS] proved to be a great deal larger—4.25 Bohr magnetons—from which it may be inferred that Co(II) in this complex contains three unpaired electrons. This implies that Co(II) is bound to the sexadentate molecule by weak covalent bonds but no conclusion can be drawn as to whether four or six such bonds are involved.[6] The Co(II) complex is extremely readily oxidized in the presence of moisture. Even on standing closely packed in a tube, the magnetic susceptibility of the Co(II) complex gradually diminishes—a result to be expected if the complex is undergoing slow oxidation.

Complexes in which Fe(II) is bound by six strong, octahedrally disposed, covalent (d^{2}sp^3) bonds are diamagnetic. It is clear from Table I that iron is not bound in this manner in the compound [FeS]. The observed moment of 3.22 Bohr magnetons is unusual—in fact, unique. It indicates that, when due allowance is made for unquenched orbital moment, Fe(II) contains two unpaired electrons, the number of unpaired electrons predicted by theory for square coördinated Fe(II). It seems unlikely that Fe(II) is bound in

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 94.

(6) It is no longer considered that the magnetic criterion distinguishes between essentially covalent and essentially ionic bonds "but between strong covalent bonds using good hybrid bond orbitals and with the possibility of unsynchronised ionic-covalent resonance and weak covalent bonds using poor bond orbitals. . . ." (L. Pauling, Liversidge Lecture, J. Chem. Soc., 1461 (1948)).

this way in [FeS]. A more likely possibility is that we have here a parallel of the behavior of Fe(III) in ferriheme hydroxide. In this compound Fe(III) appears, on the basis of magnetic measurements, to be square bonded.

Pauling and Coryell[7] have suggested that in ferriheme hydroxide Fe(III) is linked by four bonds which resonate among six positions. A similar resonance in [FeS] would explain the observed moment. It is interesting to note that, as judged by the magnetic criterion, the modes of attachment of Co(II) and Fe(II) to the sexadentate are quite different.

The moment of [CuS] lies within the range of values found for other complexes of Cu(II). Its value reveals little or nothing about the constitution of the substance. On the basis of the known structures of Cu(II) complexes as revealed by X-ray crystal analysis[8] it is suggested that Cu in [CuS] is attached to the sexadentate molecule by four strong square (dsp^2) bonds and two longer, weaker bonds in the 1,6-octahedral positions.

(7) L. Pauling and C. D. Coryell, This Journal, **59**, 633 (1937).

(8) A. F. Wells, Acta Crystallographica, **2**, 175 (1949); see also "The Nature of the Chemical Bond," L. Pauling, Cornell University Press, Ithaca, N. Y., 1940, p. 105.

The moment of 3.00 Bohr magnetons found for the compound [NiS] is consistent with the view that the chelating molecule is bound by six covalent bonds. Other structural possibilities are however not excluded since the same magnetic moment may occur with tetrahedrally bound Ni(II).

Summary

The susceptibility of the Co(III) complex of 3,6-dithia-1,8-bis-(salicylideneamino)-octane and the corresponding β-hydroxy-α-naphthylidene complex confirms the fact, established earlier by a resolution into optical antipodes, that these chelate molecules function as sexadentates. Magnetic susceptibilities of the Co(II), Ni(II) and Fe(II) complexes of 3,6-dithia-1,8-bis-(salicylideneamino)-octane are also reported. The Fe(II) complex is unique in having two unpaired electrons which is interpreted as meaning that Fe(II) is bound to the sexadentate in the same manner as Fe(III) in ferriheme hydroxide—by four bonds resonating among six positions.

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The Osmium Tetroxide Catalyzed Oxidation of Fumaric and Maleic Acids[1]

By Murray Zelikoff and H. Austin Taylor

The oxidation of fumaric and maleic acids to racemic and mesotartaric acids by aqueous osmium tetroxide–potassium chlorate solution was first studied by Hoffmann[2] who suggested that the reaction mechanism involves a complex of the osmium tetroxide and potassium chlorate. In a more extended study Milas[3] checked the stoichiometry of the reaction, showed that potassium chloride was the principal reduction product of the chlorate, there being only traces of chlorite and hypochlorite, and suggested as a mechanism alternate reduction of the tetroxide by the maleic acid and oxidation by the chlorate. Criegee[4] in a general study of the influence of osmium tetroxide on the conversion of various olefins to their corresponding glycols observed the formation of a precipitate on the addition of the tetroxide to the olefin in an anhydrous medium. Analysis of the precipitate showed it to contain one atom of osmium for each molecule of olefin. As a mechanism of the over-all reaction he suggested the formation of this compound as a first step succeeded by its hydrolysis to the

(1) Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, February, 1950.

(2) Hoffmann, Ber., **46**, 1657 (1913).

(3) Milas, This Journal, **47**, 1413 (1925).

(4) Criegee, Ann., **522**, 75 (1936).

glycol and a partially reduced oxide of osmium which is subsequently reoxidized. The present work was undertaken to check this mechanism by a rate study and thus to determine the rate-controlling step.

Experimental

Reagents.—Maleic and fumaric acids were recrystallized from hot water several times until the melting points checked the literature values of 130.5° and 287°. The potassium chlorate was C. P. grade, free of chloride and the purity was checked by the procedure used in the analysis. Lithium chlorate was prepared from equimolar amounts of lithium sulfate and barium chlorate solutions, the barium sulfate precipitate was filtered and the remaining solution evaporated slowly to dryness and finally under vacuum. The composition was checked by analysis. The osmium tetroxide, C. P. grade, was found to melt between 39 and 39.5°, the latter being the reported melting point. Dioxane was purified from a commercial sample by refluxing with metallic sodium for one week followed by distillation. A fraction boiling between 101.2 and 101.8° was used.

Procedure.—For a run the desired amounts of standard fumaric or maleic acid and standard potassium chlorate were mixed in a glass-stoppered bottle and placed in a thermostat at 25 ± 0.05° for about an hour. During this time no detectable reaction occurred. In fact no reaction occurred under these conditions in two weeks. Zero time for a run was noted at the instant of addition of the osmium tetroxide solution. At the higher temperatures the three solutions were preheated separately and then rapidly mixed. Aliquot samples were removed and analyzed for chlorate at various time intervals.