[Contribution from the Department of Chemistry, Pomona College]

The Configuration of Some Cupric, Nickelous and Cobaltous Complexes by Means of Magnetic Measurements

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A large number of organo-metallic compounds, in which a transition metal is found in the quadricovalent state, have been prepared. In particular, the preparation of organic complexes of several metals was described by Zetzsche and co-workers,[1] and more recently by Pfeiffer and colleagues.[2] The compounds cupric, nickelous, and cobaltous disalicylaldehyde have been synthesized for this study, as well as the disalicylaldimine complexes of divalent copper and nickel. The magnetic susceptibilities of these complexes have been determined, and on the basis of these results alone, except in the case of the cupric compounds, the most probable configurations have been assigned to the molecules.

Experimental

Synthesis.—The cupric (I), nickelous (II), and cobaltous (III) disalicylaldehydes were prepared by treating approximately half saturated solutions of J. T. Baker Co. c. p. metal acetate salts in 50% alcohol with the stoichiometric amounts of carefully purified salicylaldehyde. The reactants were thoroughly mixed and allowed to stand at room temperature until the reactions were complete. The precipitated products were filtered, washed successively with water, alcohol and ether, and finally dried in a vacuum desiccator over concentrated sulfuric acid.

The cupric (IV) and nickelous (V) disalicylaldimines were prepared by suspending the corresponding disalicylaldehyde compounds in 10% solutions of aqueous ammonia and stirring vigorously until the reactions were completed. A definite color change indicated the completeness of the reaction in both cases. It has not been found possible to prepare the cobaltous disalicylaldimine compound by this method. The purification of the two salicylaldimine compounds was effected by the method as given above for the salicylaldehyde complexes.

Analytical Results.—Analyses for metal, carbon, hydrogen, and nitrogen, using standard electrolytic deposition methods for the metals, and standard micro and semi-micro methods for C, H, and N, gave the results listed in Table I.

All of the compounds were sparingly soluble in water, ether, and alcohol, and slightly soluble in solvents such as chloroform and carbon tetrachloride. No definite melting points were shown, but all compounds slowly decomposed when heated above 100°.

Table I

Cpd.	Metal, % Calcd.	Metal, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Color
I	20.79	20.10	55.00	55.35	3.74	3.43			Green
II[a]	17.42	17.53	49.90	49.30	4.17	4.26			Light green
III[a]	17.47	17.59	49.86	49.30	4.18	4.32			Orange
IV	20.92	21.12	55.34	55.28	3.98	3.97	9.22	9.16	Green
V	19.63	19.70	56.93	56.81	4.05	4.05	9.37	9.30	Orange

[a] Calculated percentages based on two molecules of water of crystallization.

Magnetic Measurements.—The results of magnetic measurements on the solid crystals by the Gouy method are shown in Table II. In the column listing the Bohr magnetons, the calculations have been made assuming complete quenching of the orbital contribution to the magnetic moment. In the conversion of the experimental data into Bohr magnetons, a correction has been made for the diamagnetism of the non-metal portion of the molecule.

Table II

Cpd.	$X_s \times 10^6$	$X_m \times 10^6$	Temp., °C.	Bohr magnetons Exptl.	Bohr magnetons Calcd.	Unpaired electrons present
I	4.11	1256	22	1.9	1.73	1
II	11.43	3851	23	3.1	2.83	2
III	24.26	8180	23	4.5	3.88	3
IV	4.14	1236	20	1.9	1.73	1
V	Diamagnetic					0

Discussion.—It is seen from Table II that the cupric disalicylaldehyde compound (I) exhibits a magnetic moment close to the theoretical value of 1.73 Bohr magnetons for one unpaired electron. However, from this datum it is not possible to decide whether the molecule is tetrahedral (sp^3 bonds) or coplanar (dsp^2 bonds) as the unpaired electron can occupy a 3*d* or 4*p* orbital. Cox and Webster,[3] in a study of analogous quadricovalent cupric complexes of β-diketones, have found a planar configuration by means of X-ray analysis. This result is in accord with the theoretical prediction of the greater strength of the planar bonds.[4] Accordingly, compound (I)

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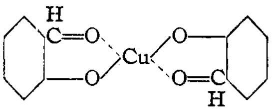
[1] Zetzsche, Silbermann and Vieli, *Helv. Chim. Acta*, **8**, 569(1925).

[2] Pfeiffer, *et al.*, *Ann.*, **84**, 503 (1933).

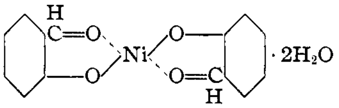
[3] Cox and Webster, *J. Chem. Soc.*, 731 (1935).

[4] Pauling, "The Nature of the Chemical Bond," Cornell University Press., Ithaca, New York, 1939, p. 100.

is considered to have a planar configuration, and the formula is written as

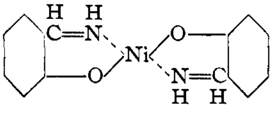


From Table II it is seen that the nickelous disalicylaldehyde compound (II) has a magnetic moment corresponding approximately to that given by two unpaired electrons. The twenty-six electrons of the nickel are in the $1s2s2p^3$ $3s3p^33d^3$ orbitals as completed pairs, while the two remaining $3d$ orbitals each contain an unpaired electron to account for the observed magnetic moment. The quadricovalent bonding should therefore occur in the $4s$ and three $4p$ orbitals, with the formation of the tetrahedral configuration. Thus, tetrahedral nickelous disalicylaldehyde (II) is written



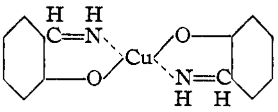
The formation of a planar configuration for this compound is also a reasonable interpretation of the data. It is possible that an unpaired electron might occupy a $4p$ in place of a $3d$ orbital, as previously noted in the copper compound. There would then be available a $3d$, $4s$, and two $4p$ orbitals for bond formation, and the planar configuration is seen to be possible.

The nickelous disalicylaldimine compound (V) is found to be diamagnetic, indicating the formation of the planar (dsp^2 bonds) configuration. It is assumed that the electrons in the two $3d$ orbitals have paired, leaving one $3d$ orbital available for bond formation together with the $4s$ and two of the $4p$ orbitals. Thus, the planar compound (V) is written

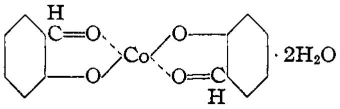


It is interesting to note that in the case of the nickelous compounds, the formation of the disalicylaldimine from the disalicylaldehyde results in the change of the probable tetrahedral configuration of the aldehyde complex to a planar structure in the aldimine compound. A marked color change also is noted, as shown in Table I.

The same reasoning is applied to cupric salicylaldimine (IV) as in the case of cupric salicylaldehyde (I). A magnetic moment corresponding to one unpaired electron is also given by (IV), so that until evidence to the contrary is obtained, the configuration of this molecule is to be considered as planar. The structural formula is



It is assumed that the twenty-five electrons in the cobalt of the cobaltous disalicylaldehyde have the electronic configuration of electron pairs in the $1s2s2p^33s3p^33d^2$ orbitals, and one unpaired electron in each of the three remaining $3d$ orbitals. The quadricovalent bonding of the cobalt would then use the $4s$ and three $4p$ orbitals, resulting in a tetrahedral configuration. Thus cobaltous disalicylaldehyde is considered to be tetrahedral, and the formula is written as



The possibility of this compound having a planar configuration must be considered as in the case of the nickel disalicylaldehyde discussed previously.

An attempt is currently being made to correlate the colors shown by these compounds, together with additional complexes of the transitional elements to be obtained, with the configuration of the molecules.[5]

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Summary

From magnetic measurements made on the salicylaldehyde complexes of copper, nickel and cobalt, and the salicylaldimine complexes of copper and nickel (the synthesis and analysis of which have been given), it has been possible to assign the following configurations to the compounds: (1) cobaltous and nickelous disalicylaldehyde probably have tetrahedral configurations; (2) nickelous disalicylaldimine has a planar configuration; (3) cupric disalicylaldehyde and cupric disalicylaldimine are probably both planar in configuration.

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(5) Lifschitz, *et al.*, *Z. anorg. allgem. Chem.*, **242**, Part 2, 97 (1939).