Reports of the Academy of Sciences of the USSR

Physical Chemistry

1965

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 165, No. 4

UDC 541.49+541.139

Physical Chemistry

A. S. KUDRYAVTSEV, I. A. SAVICH, E. A. BYLINA,
Academician Vikt. I. SPITSYN

MAGNETIC SUSCEPTIBILITY OF INNER-COMPLEX COMPOUNDS OF NICKEL AND COPPER WITH SCHIFF BASES

In previous works ([1–3]), methods of synthesis and certain properties of inner-complex compounds (ICC) of Cu and Ni with Schiff bases were described. It seemed of interest to investigate the magnetic susceptibility of these compounds in connection with the question of their stereochemistry.

All measurements were carried out for the complexes in the solid state, by the absolute Faraday method ([4]), at a temperature of 297°K. The magnetic susceptibility of the paramagnetic ion $\chi_{Me^{2+}}$ was determined from the formula:

$$\chi_{Me^{2+}} = \chi_M + n\chi'_M + \chi^{dia}_{Me^{2+}} - n\chi_H,$$

where χ_M is the experimental molar magnetic susceptibility of the complex; χ'_M is the experimental molar magnetic susceptibility of the corresponding Schiff base ([5]), ($n = 1$ or 2); $\chi^{dia}_{Me^{2+}}$ is the diamagnetic susceptibility of the paramagnetic ion; χ_H is the correction for the magnetic susceptibility of hydrogen according to Pascal' s new scheme ([6]).

The effective magnetic moment was calculated from the formula: $\mu_{eff} = 2.839\sqrt{\chi_M \cdot T}\,\mu_B$. The results of the measurements are given in Table 1.

Although the magnetic susceptibility was studied at a single temperature, the data obtained nevertheless make it possible to express judgments about the stereochemistry of these compounds in the solid state. The divalent nickel ion in the ground state ($^3F_4$) contains eight 3*d*-electrons, two of which are unpaired:

This gives a magnetic moment equal to 2.83 Bohr magnetons (μ_B). Since unpaired electrons are mainly responsible for paramagnetism, depending on the electronic configuration of the nickel atom one may assume the formation of both paramagnetic and diamagnetic compounds. If, during complex formation, pairing of the electrons of the $3d$-shell does not occur, then it should be expected that such complexes will be paramagnetic.

In complexes with ionic or weak covalent bonds formed only by the $4s$- and $4p$-orbitals* and having a tetrahedral configuration, this magnetic moment remains unchanged, equal to $2.83\,\mu_B$. The same is also observed in nickel complexes having an octahedral configuration

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* The orbitals participating in bond formation are indicated by the arrow .

No. 2: $3d$, $4s$, $4p$, $4d$, configuration $4s4p^3 4d^2$,

where the magnetic moment is also equal to $2.83\mu_B$. Nickel complexes characterized by the octahedral configuration $3d^2 4s4p^3$

No. 3: $3d$, $4s$, $4p$, $5s$,

again have a magnetic moment equal to $2.83\mu_B$ (if the electrons are promoted to the $4d$-orbital). But if four planar–

Table 1

Results of measurements of magnetic susceptibility and μ_{eff} of nickel and copper I.C.C.
Temperature 297° K

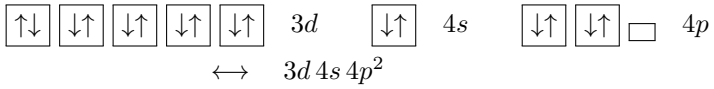
No.	Name and formula of the complex	Color of crystals	$\chi_2 \cdot 10^6$	Correction for diamagnetism $-\chi_M \cdot 10^6$	$\chi_{Me^{2+}} \cdot 10^3$	μ_{eff}, μ_B	Electronic configurations of bonds (assumed)
1	N-(2-Hydroxy-1-naphthylidene)-2-aminophenol complex — Ni^{2+}, $(C_{17}H_{11}NO_2)Ni$	Brown	3.90	102.75	1350.71	1.73	$4s\,4p^3$ or $4s\,4p^3\,4d^2$
2	N-(2-Hydroxyphenyl)-acetylacetonimine complex — Ni^{2+}, $(C_{11}H_{11}NO_2)Ni$	Brown	10.29	107.66	2659.62	2.75	Same
3	N-(3-Hydroxyphenyl)-acetylacetonimine complex — Ni^{2+}, $(C_{11}H_{11}NO_2)Ni$	Light green	0.811	102.40	303.44	0.69	Equilibrium of configurations: $3d\,4s\,4p^2 \rightleftarrows 4s\,4p^3$
4	N-(4-Hydroxyphenyl)-acetylacetonimine complex — Ni^{2+}, $(C_{11}H_{11}NO_2)Ni$	Brown	5.61	104.79	1495.45	1.83	$4s\,4p^3$ or $4s\,4p^3\,4d^2$

No.	Name and formula of the complex	Color of crystals	$\chi_2 \cdot 10^6$	Correction for diamagnetism $-\chi_M \cdot 10^6$	$\chi_{Me^{2+}} \cdot 10^3$	μ_{eff}, μ_B	Electronic configurations of bonds (assumed)
5	N-Phenylacetylacetonimine complex — Ni^{2+}, $(C_{11}H_{12}NO)_2Ni$	Light green	1.21	203.38	695.96	1.09	Equilibrium of configurations: $3d\,4s\,4p^2 \rightarrow 4s\,4p^3$; $3d\,4s\,4p^3\,4d^2$; $3d\,4s\,4p^3$
6	N,N′-Ethanobisacetylacetonimine complex — Ni^{2+}, $(C_{12}H_{18}N_2O_2)Ni$	Dark cherry	−0.331	—	—	Dia 0	$3d\,4s\,4p^2$
7	2-(2′-Aminobenzylimino)-phenol complex — Ni^{2+}, $(C_{13}H_{11}N_2O_2)Ni$	Brownish red	−0.802	—	—	Dia 0	$3d\,4s\,4p^2$
8	N-Phenylacetylacetonimine complex — Cu^{2+}, $(C_{11}H_{12}NO)_2Cu$	Greenish brown	3.88	204.39	1802.72	1.95	Same

No.	Name and formula of the complex	Color of crystals	$\chi_2 \cdot 10^6$	Correction for diamagnetism $-\chi_M \cdot 10^6$	$\chi_{Me^{2+}} \cdot 10^3$	μ_{eff}, μ_B	Electronic configurations of bonds (assumed)
9	N,N′-Ethanobisacetylacetonimine complex — Cu^{2+}, $(C_{12}H_{18}N_2O_2)Cu$	Violet	4.23	113.76	1322.86	1.70	» »
10	N-(2-Hydroxyphenyl)-acetylacetonimine complex — Cu^{2+}, $(C_{11}H_{11}NO_2)Cu$	Green	3.76	101.66	1051.36	1.51	» »
11	N-(3-Hydroxyphenyl)-acetylacetonimine complex — Cu^{2+}, $(C_{11}H_{11}NO_2)Cu$	Dark brown	3.49	103.40	985.46	1.45	» »
12	N-(4-Hydroxyphenyl)-acetylacetonimine complex — Cu^{2+}, $(C_{11}H_{11}NO_2)Cu$	Brownish black	3.64	99.79	1019.76	1.48	» »

No.	Name and formula of the complex	Color of crystals	$\chi_2 \cdot 10^6$	Correction for diamagnetism $-\chi_M \cdot 10^6$	$\chi_{Me^{2+}} \cdot 10^3$	μ_{eff}, μ_B	Electronic configurations of bonds (assumed)
13	N-(2-Hydroxy-1-naphthylidene)-2-aminophenol complex – Cu^{2+}, $(C_{17}H_{11}NO_2)Cu$	Green	2.72	107.75	991.31	1.46	» »
14	2-(2′-Aminobenzyl-imino)-phenol complex – Cu^{2+}, $(C_{13}H_{11}N_2O_2)Cu$	Brownish red	1.71	183.79	1016.92	1.41	» »

···such $3d4s4p^2$ bonds

No. 5 

then only four $3d$-orbitals remain for accommodating the eight electrons. Therefore nickel complexes having a planar, square configuration are diamagnetic and their magnetic moment is equal to zero ($\mu_B = 0$).

The value μ_{eff}, equal to $2.83\mu_B$, is observed for divalent nickel ions in the case when the magnetic moments have only a "spin" origin. The effective magnetic moments measured experimentally sometimes exceed the calculated "spin" value. This is explained by a certain contribution of the orbital component to the effective magnetic moment. The magnitude of this contribution depends chiefly on the crystal field surrounding the given paramagnetic ion, i.e., on the nature of the ligands.

Values of the magnetic moments smaller than $2.83\mu_B$ are probably associated with polymerization of the molecules, especially if oxygen participates in it, which naturally decreases the effective magnetic moment. It is of interest to compare with one another nickel IACS having μ_{eff} equal to 2.75, 1.83, and $0.69\mu_B$. These compounds differ from one another only in that in their ligands the OH group is located, respectively, in the ortho-, para-, and meta-positions. Thus, the structure of the addends has a noticeable influence on the magnitude of the magnetic susceptibility of a complex with identical central atoms (cations).

The complex N-(2-hydroxyphenyl)-acetylacetonimine-Ni^{2+}, having a magnetic moment equal to $2.75\mu_B$, can probably be assigned a tetrahedral $4s4p^3$ or octahedral $4s4p^34d^2$ configuration. In the case of the complex N-(4-hydroxyphenyl)-acetylacetonimine-Ni^{2+}, the decrease of the magnetic moment to $1.83\mu_B$ should be attributed to dimerization. The magnetic moment for the complex N-(3-hydroxyphenyl)-acetylacetonimine-Ni^{2+}, close to zero ($0.69\mu_B$), can be explained by an equilibrium between a planar structure, for which $\mu_{eff} = 0$, and a tetrahedron, for which $\mu_{eff} = 2.83\mu_B$, i.e., $3d4s4p^2 \rightleftarrows 4s4p^3$; furthermore, the formation of a polymeric structure with participation of oxygen is possible. For the complex N-(2-hydroxy-1-naphthylidene)-2-aminophenol-Ni^{2+}, the magnetic moment, equal to $1.73\mu_B$, is also probably due to a polymeric structure.

In the complex N-phenyl-acetylacetonimine-Ni^{2+}, evidently, an equilibrium of configurations

$$\begin{array}{rcl} 3d\,4s\,4p^2 & \leftarrow & 4s\,4p^3 \\ & & \text{(tetrahedral)} \\ & \leftarrow & 4s\,4p^3\,4d^2 \\ \text{(planar square)} & & \text{(octahedral)} \end{array}$$

leads to $\mu_{eff} = 1.09\mu_B$.

For copper IACS, as is evident from the data of Table 1, values of the effective magnetic moments from 1.95 to $1.41\mu_B$ were obtained. It is known that the magnetic moment of copper(II), having only a "spin" origin, is equal to $1.73\mu_B$. The excess observed in the complex N-phenylacetylacetonimine-Cu^{2+} ($\mu_{eff} = 1.95\mu_B$) can be explained by a certain contribution of the orbital component to the effective magnetic moment. This compound should naturally be assigned a planar structure with one unpaired electron:

For the compound N,N′-ethano-bis-acetylacetonimine-Cu^{2+}, the experimentally found magnetic moment is 1.70 μ_B, which apparently corresponds to a rigid, planar configuration.

It is interesting to note the compounds N-(2-oxyphenyl)-acetylacetonimine-Cu^{2+}, N-(3-oxyphenyl)-acetylacetonimine-Cu^{2+}, and N-(4-oxyphenyl)-acetylacetonimine-Cu^{2+}, in which the structure of the ligands differs

only in the position of the hydroxyl group in the benzene ring. These complexes have magnetic moments from 1.51 to 1.45 μ_B. Their reduced value should probably be attributed to polymerization. The same phenomenon apparently can also explain the decrease in the magnetic moment in the complexes N-(2-oxy-1-naphthylidene)-2-aminophenol-Cu^{2+} (1.46 μ_B) and 2-(2′-aminobenzaliminophenol)-Cu^{2+} (1.41 μ_B).

Thus, the study of magnetic susceptibility makes it possible, with some degree of certainty, to make statements about the type of bonding and the stereochemistry of intracomplex compounds of Ni and Cu.

However, in order to establish definitively the structure of the described intracomplex compounds, it is necessary to combine the results of magnetic and X-ray structural measurements. Research in this direction is continuing.

Moscow State University
named after M. V. Lomonosov

Received
17 V 1965

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Note: Figure translations are in progress. See original paper for figures.