3-Methyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IIb). Yield 76%. Mp 278–278.5° C (long colorless needles from ethanol). Found, %: C 43.22; H 3.06. Calculated for $C_7H_6N_4O_3$, %: C 43.30; H 3.11.

1-Methyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IIc). Yield 83%. Mp 358–360° C (fine yellow needles from dimethylformamide). Found, %: C 43.28; H 3.02. Calculated for $C_7H_6N_4O_3$, %: C 43.30; H 3.11.

1, 3-Dimethyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IId). Yield 80%. Mp 230.5–231.5° C (long pale yellow needles from ethanol). Found, %: C 46.30; H 4.21. Calculated for $C_8H_8N_4O_3$, %: C 46.15; H 3.87.

3-Methyl-2, 6-dinitropyridine. Yield 95%. Mp 199–200° C (long bright yellow rods from acetone). Found, %: N 28.20. Calculated for $C_6H_6N_4O_4$, %: N 28.27.

2-Amino-3-methyl-6-nitropyridine (III). Yield 43%. Mp 234–236° C (rhombic orange crystals from dioxane). Found, %: C 42.65; H 4.51. Calculated for $C_6H_8N_4O_2$, %: C 42.86; H 4.79.

REFERENCES

1. R. M. Bystrova and Yu. M. Yutilov, KhGS [Chemistry of Heterocyclic Compounds], **4**, 953, 1968.

2. H. J. den Hertog and C. Jouwersma, Rec. trav. chim., **72**, 125, 1953.

3. J. Bernstein, B. Stearns, E. Schaw, and W. A. Lott, J. Am. Chem. Soc., **69**, 1151, 1947.

4. Yu. M. Yutilov and R. M. Bystrova, KhGS [Chemistry of Heterocyclic Compounds], **4**, 954, 1968.

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MAGNETIC SUSCEPTIBILITY AND EFFECTIVE MAGNETIC MOMENTS OF METALLOATRANE-3, 7, 10-TRIONES

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In the course of a study of internally complexed alkoscides and inorganic esters of triethanolamine and its C-substituted derivatives—the metalloatranes $\overline{\underset{|}{\underset{\downarrow}{N}}(CH_2CH_2O)_3M}$ (where M is a tervalent metal or a group of atoms containing a multivalent metal) [1, 2]—it appeared to us to be of interest to study the internally complexed salts and mixed inorganic anhydrides of aminotriacetic acid $\overline{\underset{|}{\underset{\downarrow}{N}}(CH_2COO)_3M}$, with apparently analogous structures, which we have formally named metalloatrane-3, 7, 10-triones. It might have been expected that the appearance of three carbonyl groups in the atrane skeleton would lead to an anomalous change in the physicochemical properties of these compounds due to the increased polarity of the M—O bond, to the change in the strength of the M←N bond, and to the nature of the intermolecular interaction.

With this object, we have determined the effective magnetic moments of a number of metalloatranetriones, mainly in the form of the hydrates $\overline{\underset{|}{\underset{\downarrow}{N}}(OCOCH_2)_3M} \cdot nH_2O$. A comparison of the values of μ_{eff} obtained with the calculated moments for "pure spin" paramagnetism determined by the total number of unpaired electrons [3] is given in the table.

In all cases, the experimental figures obtained (μ_{exp}) are of the same order as the calculated figures (μ_{calc}). The fact that the values of μ_{exp} are greater than μ_{calc} for the compounds of cobalt, iron, and manganese is explained by the contribution of the spin-orbital coupling, which is characteristic for the formation of complexes [3]. In the case of intermolecular interaction in the crystal lattice of the metalloatrane-3, 7, 10-triones due to the carbonyl groups, a deviation of μ_{exp} from μ_{calc} is possible—in particular, a lowering in μ_{exp} as a consequence of the exchange interaction, as has been observed for copper complexes [4]. As was to be expected, the lanthanum compound is diamagnetic. A comparison of the experimental magnetic susceptibility with the value calculated by Pascal's new scheme ($\chi_{calc} = -0.2335 \cdot 10^{-6}$) [5]

Magnetic Susceptibilities and Effective Magnetic Moments of the Metalloatrane-3, 7, 10-triones $\overline{\underset{|}{\underset{\downarrow}{N}}(CH_2COO)_3M} \cdot nH_2O$

M	n	T°, K	$\chi_g \cdot 10^{-6}$	$\chi_{mol} \cdot 10^{-6}$	μ_{exp}	μ_{calc}
La	3	298	−0.1599			
Cr	3	299	20.42	6094	3.83	3.88
Mn	0	296	32.60	8013	4.37	4.90
Mn	1	296	32.20	10844	5.09	4.90
Fe	1	299	62.17	16375	6.28	5.92
Co	3	298	40.95	12418	5.46	4.90
Ni	3	298	20.25	6182	3.82	3.88

shows the presence of polarization paramagnetism, which is probably due to the closure of the ring in complex-formation.

Thus, the presence of carbonyl groups in the ring has no substantial influence on the physicochemical properties of the compounds studied, which makes it possible to draw an analogy between the structure of the metalloatrane-3,7,10-triones and the metalloatranes.

The magnetic susceptibilities were determined by Gouy's method.

REFERENCES

1. M. G. Voronkov, Vestn. AN SSSR, **38**, 48, 1968; Pure Appl. Chem., **13**, 35, 1966; z. chem., **8**, 214, 1968.

2. M. G. Voronkov, O. A. Osipov, V. A. Kogan, V. A. Chetverikova, and A. F. Lapsin, KhGS [Chemistry of Heterocyclic Compounds], **3**, 35, 1967.

3. J. Lewis and R. G. Wilkins, editors, Modern Coordination Chemistry [Russian translation], IL, Moscow, 1963.

4. M. Kato, H. B. Jonasson, and J. C. Fannig, Chem. Rev., **64**, 99, 1964.

5. Ya. G. Dorfman, Diamagnetism and the Chemical Bond [in Russian], Izd-vo fiz.-mat. liter., Moscow, 1961.

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