

Table 1. Physicochemical characteristics of copper(II), nickel(II), and cobalt(II) complexes of isatin and *N*-methylisatin β -thiosemicarbazones

Comp. no.	Yield, %	μ_{eff} , BM (293 K)	Found, %			Formula	Calculated, %		
			Cl (Br)	M ^a	N		Cl (Br)	M ^a	N
I	69	2.04	8.87	16.14	14.09	C ₉ H ₁₅ ClCuN ₄ O ₅ S	9.09	16.39	14.34
II	80	2.13	18.89	15.24	13.20	C ₉ H ₁₃ BrCuN ₄ O ₄ S	19.18	15.35	13.43
III	75	2.18	7.93	14.52	16.01	C ₁₄ H ₁₆ ClCuN ₅ O ₃ S	8.19	14.76	16.15
IV	74	1.97	7.70	14.01	15.38	C ₁₅ H ₁₈ ClCuN ₅ O ₃ S	7.93	14.30	15.64
V	78	1.89	7.86	14.36	16.48	C ₁₅ H ₁₈ ClCuN ₅ O ₃ S	7.93	14.30	16.64
VI	79	2.11	16.49	13.18	14.47	C ₁₄ H ₁₆ BrCuN ₅ O ₃ S	16.74	13.39	14.64
VII	84	2.02	16.09	12.84	13.95	C ₁₅ H ₁₈ BrCuN ₅ O ₃ S	16.26	13.01	14.23
VIII	81	1.93	16.17	13.18	14.08	C ₁₅ H ₁₈ BrCuN ₅ O ₃ S	16.26	13.01	14.23
IX	82	1.87	6.90	13.06	16.75	C ₁₉ H ₁₉ ClCuN ₆ O ₂ S	7.18	12.94	16.99
X	74	1.82	14.63	11.95	15.29	C ₁₉ H ₁₉ BrCuN ₆ O ₂ S	14.84	11.87	15.58
XI	70	2.87	7.01	11.90	16.97	C ₁₉ H ₁₉ ClNiN ₆ O ₂ S	7.25	12.05	17.16
XII	72	4.98	7.10	11.94	17.09	C ₁₉ H ₁₉ ClCoN ₆ O ₂ S	7.25	12.05	17.16
XIII	71	1.87	7.09	12.37	16.40	C ₂₀ H ₂₁ ClCuN ₆ O ₂ S	6.98	12.59	16.52
XIV	74	3.02	6.78	12.52	16.45	C ₂₀ H ₂₁ ClNiN ₆ O ₂ S	7.05	12.71	16.68
XV	76	5.10	6.92	12.65	16.56	C ₂₀ H ₂₁ ClCoN ₆ O ₂ S	7.05	12.71	16.68

^a M is metal

molar ratio) yields complexes CuPy₂LY·H₂O [Y = Cl (**IX**), Br (**X**)]. Nickel or cobalt chlorides react in ethanol with thiosemicarbazone HL and pyridine (1:1:3) in ethanol to give complexes MPy₂LCl·H₂O [M = Ni (**XI**), Co (**XII**)]. With HL' instead of HL, compounds MPy₂L'Cl·H₂O [M = Cu (**XIII**), Ni (**XIV**), Co (**XV**)] were isolated from the reaction medium.

Complexes **I–XV** are insoluble in diethyl ether, sparingly soluble in water and alcohols, and readily soluble in DMF, DMSO, and acetonitrile. Their yields and physicochemical characteristics are given in Table 1.

A visual microscopic examination of complexes **I–XV** showed that their powders are phase homogeneous and consist of crystallites of various shapes. In view of their small sizes and the absence of single crystals, we assessed the composition and structure of these compounds by elemental and thermal analyses, molar conductivity measurements, IR spectroscopy, and magnetochemistry.

As judged from the molar conductivities of complexes **I–XV** in DMF, they all are nonelectrolytes.

Magnetochemical study (Table 1) established that cobalt and nickel complexes are paramagnetic and, judging from their effective magnetic moments, have an octahedral ligand surrounding. The magnetoche-

mical data copper complexes correspond to the spin value for one unpaired electron.

Thermolysis of compounds **I–XV** (Table 2) proceeds through the stages of dehydration (60–90°C) and deaquation (135–140°C) or deamination (160–215°C) up to complete thermooxidative decomposition (560–670°C). The temperature of complete decomposition (T_{dec}) of the complexes was found to depend on the nature of the central atom, and, at the same inner-sphere composition, it varies in the order Co \geq Ni > Cu. The decomposition temperature is also affected by the nature of inner-sphere ligands: It increases in passing from the isatin to *N*-methylisatine fragment of the ligand, from bromide to chloride ion, and from the inner-sphere water to amine. In the case of amine-containing complexes **III–XV** with the same central ion, T_{dec} increases in the order 3-CH₃C₅H₄N \geq 4-CH₃C₅H₄N > C₅H₅N.

By Horowitz–Metzger's method [8] with Topor's additions [9] we estimated the kinetic parameters of the dehydration, deaquation, and deamination reactions of complexes **I–XV**. The resulting data are given in Table 2 from which it follows the the activation energy E_a and preexponential factor Z are affected by the nature of the central atom, and for complexes of the same composition they vary in the order Co > Ni > Cu. The nature of the outgoing ligand (water or amine), too, affects the kinetic parameters of the process: In passing from aqua- to pyridine- or pi-

Table 2. Thermal analysis of copper(II), nickel(II), and cobalt(II) complexes of isatin and *N*-methylisatin β -thiosemicarbazones

Comp. no.	Number of the endo effect in the DTA curve	T_{dec} , °C	Weight loss			Kinetic parameters		T , °C ^a
			found, %	calculated, %	fragment lost	E_a , kJ mol ⁻¹	log Z	
I	1	70	9.5	9.2	2H ₂ O	30.6	4.7	580
	2	140	9.0	9.2	2H ₂ O	54.9	6.3	
II	1	80	4.5	4.3	H ₂ O	45.1	5.7	560
	2	135	8.5	8.6	2H ₂ O	50.2	6.0	
III	1	75	4.0	4.2	H ₂ O	35.3	5.3	610
	2	165	22.5	22.4	C ₅ H ₅ N+H ₂ O	99.4	9.2	
IV	1	80	4.3	4.0	H ₂ O	41.8	6.1	625
	2	175	24.5	24.8	C ₆ H ₇ N+H ₂ O	112.4	10.8	
V	1	90	4.1	4.0	H ₂ O	46.5	6.5	620
	2	170	25.0	24.8	C ₆ H ₇ N+H ₂ O	108.1	10.2	
VI	1	85	4.0	3.8	H ₂ O	38.1	5.2	600
	2	160	20.5	20.3	C ₅ H ₅ N+H ₂ O	90.6	8.7	
VII	1	70	3.5	3.7	H ₂ O	40.3	5.4	600
	2	165	22.5	22.6	C ₆ H ₇ N+H ₂ O	106.7	10.8	
VIII	1	90	4.0	3.7	H ₂ O	43.7	5.9	615
	2	165	22.3	22.6	C ₆ H ₇ N+H ₂ O	105.2	10.7	
IX	1	60	3.5	3.6	H ₂ O	37.9	5.4	640
	2	190	32.3	32.0	2C ₅ H ₅ N	132.8	14.3	
X	1	70	3.5	3.3	H ₂ O	35.6	5.3	625
	2	175	29.5	29.3	2C ₅ H ₅ N	125.4	13.1	
XI	1	60	3.5	3.7	H ₂ O	40.5	6.0	660
	2	205	32.5	32.3	2C ₅ H ₅ N	148.1	15.2	
XII	1	85	4.0	3.7	H ₂ O	38.6	5.5	670
	2	215	32.1	32.3	2C ₅ H ₅ N	155.0	15.9	
XIII	1	80	3.5	3.5	H ₂ O	33.9	4.9	650
	2	200	30.8	31.1	2C ₅ H ₅ N	137.4	14.5	
XIV	1	85	3.8	3.6	H ₂ O	38.9	5.5	665
	2	210	31.5	31.4	2C ₅ H ₅ N	154.1	15.8	
XV	1	80	3.5	3.6	H ₂ O	44.3	5.4	670
	2	215	31.7	31.4	2C ₅ H ₅ N	160.3	16.6	

^a Temperature of complete decomposition.

coline-containing complexes, E_a and log Z increase, in parallel with the σ -donor and π -acceptor powers of these complexes. Analysis of the calculated kinetic parameters showed that they conform with a compensation effect (see figure). Its presence, according to [10, 11], suggests that, irrespective the nature of the central atom, thiosemicarbazone (HL or HL'), and outgoing ligand (water or amine), the coordination compounds studied undergo similar thermolysis reactions. Furthermore, the activation energies and preexponential factors of amine-containing compounds **III–XV** with the same central ion vary in the order 3-CH₃C₅H₄N \geq 4-CH₃C₅H₄N > C₅H₅N. This series coincides completely with the order of the de-

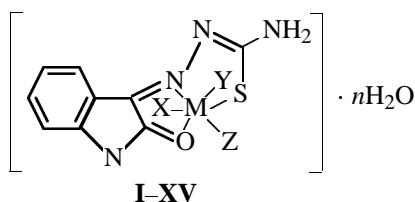
amination and complete decomposition temperatures of the complexes.

To determine the modes of ligand coordination to the central ions, we performed a comparative analysis of the IR spectra of synthesized complexes **I–XV** and starting thiosemicarbazones HL and HL', as well as published spectra of transition metal complexes with similar Schiff bases [1–3, 7]. Azomethines HL and HL' were found to behave in the compounds in study as tridentate monodeprotonated *O,N,S*-ligands that coordinate to the central atom via the carbonyl oxygen atom of the isatin fragment, the nitrogen atom of the C=N bond, and the sulfur atom to give two five-

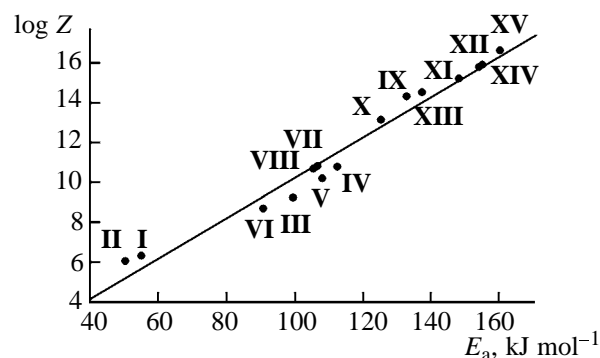
membered metal cycles. Evidence for this conclusion comes the fact that the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ absorption bands to the low-frequency region by $25\text{--}20\text{ cm}^{-1}$ the compared to respective bands of the starting thiosemicarbazones (these bands in the spectra of HL and HL' appear at $1710\text{--}1700$ and $1620\text{--}1610\text{ cm}^{-1}$). Evidence for the involvement of the sulfur atoms in the HL and HL' ligands of the deprotonated thioenol forms in coordination with the central atoms is provided by the disappearance of the $\nu(\text{C}=\text{S})$ bands at $760\text{--}750$ and the $\nu(\text{NH})$ bands at $3210\text{--}3200$ and $3170\text{--}3150\text{ cm}^{-1}$ from the IR spectra of compounds **I–XV**. Further evidence is provided by the appearance of a new absorption band at $605\text{--}585\text{ cm}^{-1}$, which, according to [12], belongs to $\nu(\text{C}-\text{S})$, as well as by the splitting of the $\nu(\text{C}=\text{N})$ band at $1595\text{--}1590\text{ cm}^{-1}$ into two components. The proposed coordination of thiosemicarbazones HL and HL' is also supported by the observation in the IR spectra of all the complexes of a number of new bands at $550\text{--}400\text{ cm}^{-1}$, assignable to $\nu(\text{M}-\text{N})$ ($525\text{--}510$ and $420\text{--}405\text{ cm}^{-1}$), $\nu(\text{M}-\text{O})$ ($490\text{--}470\text{ cm}^{-1}$), and $\nu(\text{M}-\text{S})$ ($460\text{--}445\text{ cm}^{-1}$).

The involvement of other functional groups of Schiff bases HL and HL' in the coordination with metal ions is excluded, since their characteristic absorption bands appear in the sameregions as in the starting thiosemicarbazones. The presence of coordinated water and amine molecules in complexes **I–XV** is proved by the observation of the corresponding absorption bands in their IR spectra [aqua complexes **I–VIII**: $\nu(\text{H}_2\text{O})$ $3590\text{--}3580$, $\delta(\text{H}_2\text{O})$ $1580\text{--}1575$, and $\gamma(\text{H}_2\text{O})$ $925\text{--}920\text{ cm}^{-1}$; amine-containing compounds **III–XV**: $\nu(\text{CC}) + \nu(\text{CN}) + \delta(\text{CCH})$ $1640\text{--}1635$, $1530\text{--}1525$, $\nu(\text{CN})$ $1310\text{--}1305$, $\delta(\text{CCH})$ $1230\text{--}1225$, $\delta(\text{CCH}) + \nu(\text{CC}) + \delta(\text{CNC})$ $1060\text{--}1055$, $1030\text{--}1025$, $\gamma(\text{CCC}) + \gamma(\text{CNC})$ $730\text{--}725$, and $\rho(\text{CH})$ $830\text{--}825\text{ cm}^{-1}$].

The above physicochemical data allow the following distribution of chemical bonds to be proposed for compounds **I–XV**:



M = Cu (**I–X**, **XIII**), Ni (**XI**, **XIV**), Co (**XII**, **XV**); R = H (**I–XII**), CH_3 (**XII–XV**); Y = Cl (**I**, **III–V**, **IX**, **XI–XV**), Br (**II**, **VI–VIII**, **X**); X = H_2O (**I–VIII**), $\text{C}_5\text{H}_5\text{N}$ (**IX–XV**); Z = H_2O (**I**, **II**), $\text{C}_5\text{H}_5\text{N}$ (**III**, **VI**, **IX–XV**), $3\text{-CH}_3\text{C}_5\text{H}_4\text{N}$ (**IV**, **VII**), $4\text{-CH}_3\text{C}_5\text{H}_4\text{N}$ (**V**, **VIII**); $n = 1$ (**II–XV**), 2 (**I**).



Compensation effect in deaquation and deamination of complexes **I–XV**.

EXPERIMENTAL

The resistance of solutions of complexes **I–XV** in DMF (20°C , c 0.001 M) was measured with an R-38 slidewire bridge. The IR spectra were obtained on a Specord M-80 spectrophotometer in suspensions in Vaseline and fluorinated oils; the samples were preliminary dried to constant weight in a drying oven at 105°C . The effective magnetic moments were measured by the Gouy method. The molar magnetic susceptibility corrected for diamagnetism were calculated from theoretical magnetic susceptibilities of organic compounds. The thermoanalytical curves of complexes **I–XV** were recorded on a Paulik–Paulik–Erdey derivatograph in the range $20\text{--}1000^\circ\text{C}$ in air (reference Al_2O_3 , corundum crucible).

The starting β -thiosemicarbazones of isatin (HL) and *N*-methylisatin (HL') were prepared by the procedure described in [1].

Diaquachloro(isatin β -thiosemicarbazone)copper dihydrate (I). A hot ($50\text{--}55^\circ\text{C}$) ethanol solution of 10 mmol of isatin β -thiosemicarbazone was mixed with an aqueous solution of 10 mmol of copper(II) chloride dihydrate. Alcoholic KOH was then added to pH $7\text{--}7.5$, and the resulting mixture was heated ($50\text{--}55^\circ\text{C}$) for $50\text{--}60\text{ min}$ with continuous stirring. After cooling, a greenish brown precipitate formed and was filtered off, washed with ethanol, diethyl ether, and dried in air.

Complex **II** was synthesized in a similar way from copper(II) bromide and thiosemicarbazone HL at a $1:1$ molar ratio. Complexes **III–VIII** were prepared by the above procedure by the reaction of copper(II), nickel(II), or cobalt(II) halides hydrates with Schiff base HL and pyridine (or 3- or 4-picoline) at a $1:1:1$ molar ratio, and the same reaction at a $1:1:3$ reactant molar ratio gave complexes **IX–XII**. Complexes

XIII–XV were synthesized by the same reaction using thiosemicarbazone HL' instead of HL.

REFERENCES

1. Zhungietu, G.I. and Rekhter, M.A., *Izatin i ego proizvodnye* (Isatin and Its Derivatives), Kishinev: Shtiintsa, 1977.
2. Paul, R.Gh. and Chandra, S.L., *J. Inorg. Nucl. Chem.*, 1969, vol. 31, no. 9, p. 2753.
3. Neamtu, M. and Grecu, I., *Rev. Chim. Miner.*, 1971, vol. 8, no. 5, p.761.
4. Kraf, M.Ya., *Zh. Vses. Khim. O–va*, 1965, vol. 10, no. 4, p. 630.
5. Gupta, R.P. and Srivastova, A.K., *Rev. Rom. Chim.*, 1982, vol. 27, no. 3, p. 393.
6. Ioffe, I.S., Tomchin, A.B., Dobrego, V.A., and Etev-tsian, L.N., *Khim.-Farm. Zh.*, 1973, vol. 7, no. 8, p. 2.
7. Pollikoff, R., Lieberman, M., Lem, N.E., and Foley, E.J., *J. Immunol.*, 1965, vol. 94, no. 3, p. 794.
8. Horowitz, H.H. and Metzger, G.A., *Anal. Chem.*, 1963, vol. 35, no. 10, p. 1464.
9. Topor, N.D., *Vestnik Mosk. Gos. Univ., Ser. Geol.*, 1967, no. 1, p. 84.
10. Logvinenko, V.A., *Termicheskiy analiz koordinatsionnykh soedinenii i klatratov* (Thermal Analysis of Coordination Compounds and Clathrates), Novosibirsk: Nauka, 1982.
11. Nikolaev, A.V., Logvinenko, V.A., Shestak, Ya., and Shkvara, V., *Dokl. Akad. Nauk SSSR*, 1976, vol. 231, no. 1, p. 146.
12. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York: McGraw-Hill, 1986.