ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 10, pp. 1515–1520. © Pleiades Publishing, Ltd., 2011.
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Design, Synthesis, and Spectral Parameters of Transition Metal Coordination Compounds Based on Organic Autocomplexes

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Received July 12, 2010

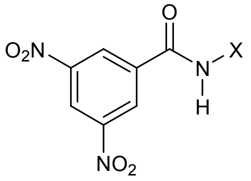
Abstract—Organic autocomplexes prepared from 3,5-dinitrobenzoyl chloride and some heterocyclic amines were used to synthesize a series of new coordination compounds with 3*d* transition metals. The new metal complexes displayed in the electronic absorption spectra charge-transfer bands typical of the initial ligands and an additional long-wave maximum in the region λ 500–625 nm.

DOI: 10.1134/S1070428011100113

In recent years, interest in studies in the field of supramolecular chemistry has increased due to the necessity of new chemical structures as building blocks capable of self-organization to form stable supramolecular assemblies. Problems of supramolecular chemistry were originally formulated by its founder J.-M. Lehn [1] as studies on structured stable non-covalently bound aggregates. As experimental data accumulated with time, the scope of supramolecular chemistry was considerably extended, and it now comprises studies on all types of interactions, from weak intermolecular to strong coordination [2, 3]. Design of molecular ensembles as supramolecular systems of new generation is based on a predetermined combination of intra- and intermolecular interactions, and the most important factors responsible for the possibility for the formation of self-organized supramolecular systems turned out to be the presence in the initial ligand molecule of three types of reactive centers, namely those ensuring hydrogen bonding, stacking interaction, and coordination with metal ions [4, 5].

On the other hand, the significance of systems based on donor–acceptor chromophores with strong electron conjugation between donor and acceptor fragments (intramolecular charge transfer, ICT) should not be excluded from consideration [6]. However, the key problem related to the role of electronic structure determined by ICT was not studied in detail, though control over ICT makes it possible to purposefully vary the degree of charge transfer and hence electron density distribution in molecule. In other words, variation of electronic parameters of a molecule ensures control over the activity of reaction centers therein. Therefore, it may be expected that organic compounds characterized by intramolecular donor–acceptor (D–A) interactions (so-called autocomplexes) could be appropriate ligands for building up supramolecular metal complex systems, in which intramolecular charge transfer is possible in addition to the three types of interactions listed above. Thus development of new methods of synthesis, diagnostics, and investigation of donor–acceptor metal complexes and studies on their electronic structure could considerably supplement known information on factors determining the possibility for formation of self-organized supramolecular systems and general relations holding therein.

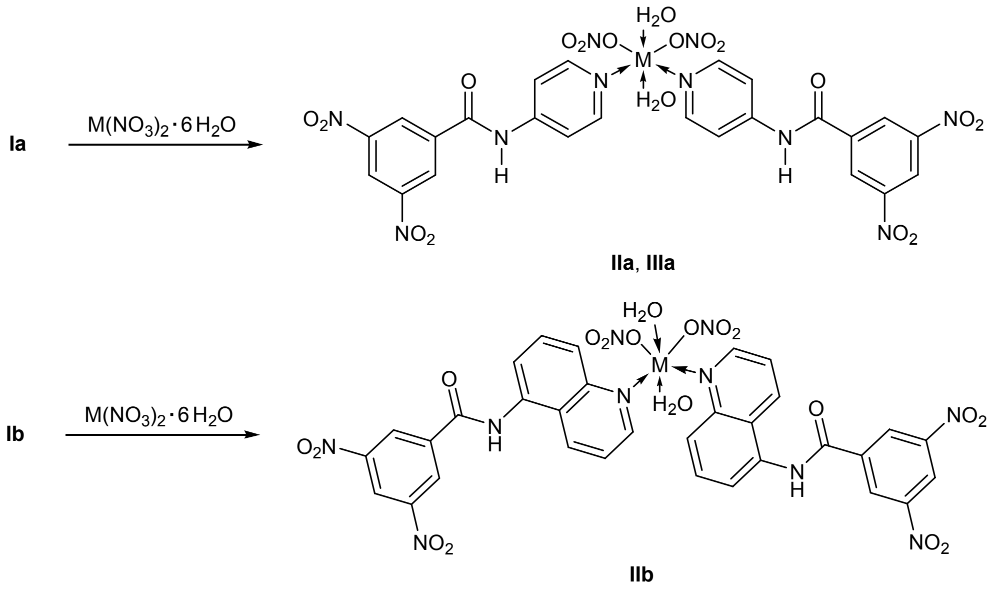
In the present work we propose possible approaches to solution of the above problem on the basis of molecular design, synthesis, and analysis of new donor–acceptor complexes of 3*d* transition metals as potential building blocks for construction of self-organized supramolecular systems. In the first step of our study we synthesized autocomplexes **Ia** and **Ib** consisting of a dinitrobenzamide acceptor fragment and a nitrogen-containing heterocycle as donor fragment.



Ia, **Ib**

X = pyridin-4-yl (**a**), quinolin-5-yl (**b**).

Scheme 1.



II, M = Co; **III**, M = Ni.

While performing systematic studies on the series of autocomplexes with the general formula A–Z–D [where A and D are acceptor and donor fragments, respectively, and Z is a bridging moiety (or spacer)], we previously synthesized a series of analogous amide derivatives with various donor fragments and studied in detail charge transfer in their molecules [7]. The results of spectral studies showed that these compounds should be regarded as autocomplexes with NH bridging moiety rather than structures with two-membered CO–NH spacer (as presumed initially).

We previously showed [8, 9] that autocomplexes can be used as bidentate ligands to obtain metal chelates. However, coordination compounds of metals with autocomplexes as ligands were not reported so far. We tried to use autocomplexes **Ia** and **Ib** as ligands (L) to synthesize cobalt(II) and nickel(II) complexes with the composition $ML_2(NO_3)_2(H_2O)_2$. Ligands **Ia** and **Ib** were prepared by heating equimolar amounts of 3,5-dinitrobenzoyl chloride and 4-aminopyridine or 5-aminoquinoline in acetone in the presence of an equimolar amount of triethylamine. Reactions of ligands **Ia** and **Ib** with cobalt(II) or nickel(II) nitrate hexahydrate in appropriate solvent gave metal complexes **IIa**, **IIb**, and **IIIa** (Scheme 1).

Depending on the conditions (temperature, reaction time, solvent nature) complexes $L_2(NO_3)_2M \cdot nH_2O \cdot mL''$ (**V**–**X**) with different compositions may be obtained, including adducts **VIII**–**X** containing solvent molecule L″: L = **Ia**: **V**, $n = m = 0$, M = Co; **VI**, $n = m = 0$, M = Ni; **VII**, $n = 4$, $m = 0$, M = Ni; L = **Ib**, $n = m = 1$: **VIII**, L″ = Me_2CO, M = Co; **IX**, L″ = Me_2CO, M = Ni; **X**, L″ = MeCN, M = Ni.

Unlike pyridine-containing ligand **Ia** from which the corresponding cobalt and nickel complexes **IIa** and **IIIa** can be obtained in alcohol, quinoline-containing ligand **Ib** with alcohol formed associate **IV**, and complex formation did not occur. Cobalt complex **IIb** can be obtained using a different solvent, e.g., acetonitrile. Nickel complexes were isolated as adducts with acetone or acetonitrile.

The obtained compounds were high-melting yellowish (ligands **Ia** and **Ib**) and light red or greenish–blue (metal complexes) finely crystalline substances. The complexes changed their color on heating to 100–180°C due to loss of solvate and/or hydrate shell. The structure of the products was confirmed by elemental analysis and IR and UV spectroscopy. The IR spectra (KBr) contained absorption bands in the regions 1550–1500 and 1350–1330 cm^{-1} due to antisymmetric and symmetric vibrations of nitro groups in the aromatic ring, stretching vibration band of the amide carbonyl group was observed at 1670–1710 cm^{-1}, and stretching vibrations of aromatic C–H bonds gave rise to absorption at 3095 cm^{-1}. Absorption bands due to stretching vibrations of the NH group in the initial ligands (3180–3150 cm^{-1}) were displaced to higher frequencies (3400–3300 cm^{-1}) upon complex formation.

The most valuable information on intramolecular charge transfer was obtained by analysis of the elec-

Electronic absorption spectra of autocomplexes **Ia** and **Ib** and metal complexes **IIa**, **IIb**, **IIIa**, and **X** in acetonitrile ($c = 5 \times 10^{-4}$ M) and ionization energies of donor fragments

Comp. no.	$E_\mathrm{i.}$, eV	λ_max, nm (ε, l mol^{-1} cm^{-1})			
		$\mathrm{CT}_\mathrm{K}^\mathrm{dinitro}$	$\mathrm{CT}_\mathrm{NHX}^\mathrm{CO}$	ICT-I (autocomplex)	ICT-II (metal complex)
Ia	9.26 [13]	233 (27900)	260 (14412)	–	–
IIa		228 (66280)	265 (46790)	–	518 (94)
IIIa		231 (48340)	262 (34640)	–	610 (18)
Ib	8.67 [14]	229 (39270)	294 (8005)	314 (6712)	–
IIb		226 (111830)	293 (17178)	316 (14216)	514 (65)
X$^\mathrm{a}$		227 (100000)	293 (15355)	314 (12800)	625 (22)

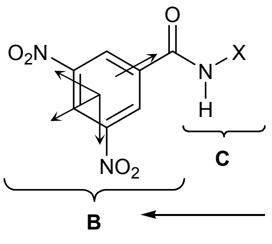
[a] Nickel complex **X** is an adduct with acetonitrile.

tronic absorption spectra of coordination compounds **IIa**, **IIb**, **IIIa**, and **X** in comparison with the spectra of initial ligands **Ia** and **Ib**. The electronic absorption spectra of these compounds contained four maxima with different intensities in the λ range from 230 to 625 nm (see table). The bands were assigned by empirical procedure [10] based on decomposition of a molecule into polar chromophores. This procedure was developed for polysubstituted benzenes of donor–acceptor type, and it makes it possible to determine the number of absorption bands and their origin without resorting to quantum-chemical calculations. The procedure was validated by us previously [7–9, 11, 12] using a large number of both autocomplexes and metal chelates based thereon.

The compounds under study were arbitrarily represented as a model system which, in keeping with the quasi-autonomous model [15], was divided into donor–acceptor type components; theoretically possible charge transfer bands and direction of their polarization were determined, and the bands of the components were summed.

According to the data of [16], the electronic spectra of counter-polarized quasi-autonomous donor–acceptor systems like **B**–**C** contain an additional broad band which is absent in the total absorption of the components that are simpler compounds including only acceptor or donor fragment. This band originates from intramolecular interaction of chromophore systems **B** and **C** as a result of electron transfer from the donor fragment to acceptor along the conjugation chain. As applied to ligands **Ia** and **Ib**, the corresponding band arises from charge transfer from the donor amino group (NH–X) to acceptor carbonyl group ($\mathrm{CT}_\mathrm{NHX}^\mathrm{CO}$) with a contribution of $^1\mathrm{L_B}$ type transition in the aromatic chromophore.

Like initial autocomplexes **Ia** and **Ib**, the electronic absorption spectra of their coordination compounds with metals contained charge transfer bands belonging mainly to electron transitions in the ligand. According to the empirical procedure described in [10] and the data of [7], these bands should be assigned as follows (see table). The short-wave band at λ 230 nm corresponds to charge transfer from the aromatic ring to nitro group (nitrobenzene band $\mathrm{CT}_\mathrm{K}^\mathrm{dinitro}$) which is the vector sum of transitions from the ring to each *meta*-nitro group ($\mathrm{CT}_\mathrm{K}^\mathrm{nitro}$). The blue shift of that band relative to the corresponding band of nitrobenzene (λ_max 250 nm, ε 8900 [17]) may be rationalized in terms of reduced donor power of the aromatic ring due to opposite transition from the ring to the acceptor carbonyl group ($\mathrm{CT}_\mathrm{K}^\mathrm{CO}$). Next follows (in order of decreasing excitation energy) a band which, according to [16], results from intramolecular interaction of chromophores **B** and **C**, involving electron density transfer from the donor fragment to acceptor along the conjugation chain. This band originates from charge transfer from the substituted amino group (donor fragment NH–X) to the acceptor carbonyl group ($\mathrm{CT}_\mathrm{NHX}^\mathrm{CO}$) with a contribution of $^1\mathrm{L_B}$ electron transition in the aromatic chromophore. The maximum at a longer wavelength (λ ~300 nm) reflects intramolecular charge transfer (ICT-I) in a conformation ensuring spatial proximity of the donor and acceptor components, and the transition occurs in the contact mode through space.



Apart from the above ligand bands, the metal complexes displayed in the electronic absorption spectra an additional low-intense long-wave maximum (ICT-II) in the region λ 500–625 nm, which characterizes bond configuration at the central metal ion.

Thus the presence of a long-wave absorption band (ICT-II) which is absent in the electronic absorption spectra of the initial ligands and increased (by a factor of 1.5–2) intensity of the other absorption bands due to doubling of interacting fragments may be regarded as evidences in support of complex formation.

Comparison of the electronic absorption spectra of ligands **Ia** and **Ib** and metal complexes based thereon (see table) shows that the intensity of the $\mathrm{CT}^{\mathrm{CO}}_{\mathrm{NHX}}$ band of the complexes with ligand **Ia** is considerably higher than the intensity of the corresponding band of the complexes with ligand **Ib**. On the other hand, unlike ligand **Ib**, the intensity of the ICT-I band in the spectra of ligand **Ia** and its complexes is reduced so strongly that it becomes almost indistinguishable at λ ~ 300 nm. It may be presumed that the conformation of pyridine-containing derivatives excludes ICT through space. As a result, intramolecular interaction of chromophore systems **B** and **C** in compound **Ia** and its complexes involves mainly charge transfer along the conjugation chain, and the intensity of the corresponding band considerably increases. Although autocomplex **Ib** contains a stronger donor fragment, some blue shift of the nitrobenzene band in its electronic absorption spectrum may be attributed to a large contribution of electron density transfer from the donor fragment in the contact mode.

EXPERIMENTAL

The electronic absorption spectra were measured on a Thermo Evolution-300 BB spectrophotometer from solutions in acetonitrile with a concentration of 5×10^{-4} M (cell path length 0.1 or 1 cm). The IR spectra were recorded on a Thermo-Nicolet IR 200 spectrometer with Fourier transform; in some cases, attenuated total reflectance spectra were recorded to avoid undesirable absorption in the region of 3400 cm^{-1} (OH stretching vibrations). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using toluene–acetone (1 : 1) as eluent. The mass spectra (MALDI, positive and negative ion detection) were obtained on a Bruker Autoflex II instrument (FWHM resolution 18000); samples were applied onto a polished steel support. The ^{1}H NMR spectra were recorded from solutions in CD_3OD on a Bruker Avance DPX 400 spectrometer (400 MHz) using TMS as internal reference.

Commercially available pyridin-4-amine, quinolin-5-amine, 3,5-dinitrobenzoic acid, and cobalt(II) and nickel(II) nitrate hexahydrates were used without additional purification. 3,5-Dinitrobenzoyl chloride was synthesized by heating 3,5-dinitrobenzoic acid in boiling thionyl chloride containing 2–3 drops of dimethylformamide; the crude product was crystallized from a minimal amount of hot toluene and dried [18].

Autocomplexes Ia and Ib (*general procedure***).** A solution of 5 mmol of 3,5-dinitrobenzoyl chloride, 5 mmol of pyridin-4-amine or quinolin-5-amine, and 5 mmol of triethylamine in 30 ml of acetone containing 5 ml of ethanol (to avoid crystallization of triethylamine hydrochloride) was heated for 40 min under reflux. The mixture was cooled and left overnight in a refrigerator. The precipitate was filtered through a glass filter and washed with cold alcohol, the filtrate was evaporated, and the residue was combined with the main portion of the product, recrystallized from aqueous acetone, and dried in air.

3,5-Dinitro-*N*-(pyridin-4-yl)benzamide (Ia). Yield 75%, light brown crystals, mp 240–250°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 7.91 d (2H, pyridine), 8.52 d (2H, pyridine), 9.25 s (1H, H_{arom}), 9.33 s (2H, H_{arom}). Mass spectrum: *m*/*z* (I_{rel}, %): 289 (100) $[M + H]^+$, 288 (46) $[M]^-$. Found, %: C 50.21; H 2.69; N 19.28. $C_{12}H_{18}N_4O_5$. Calculated, %: C 50.01; H 2.80; N 19.44. *M* 288.22

3,5-Dinitro-*N*-(quinolin-5-yl)benzamide (Ib). Yield 85%, light brown needles (from acetone or acetonitrile), mp 245°C. ^{1}H NMR spectrum, δ, ppm: 7.63 d.d (1H), 7.86 d.t (2H), 8.08 d (1H), 8.58 d (1H), and 8.94 d (1H) (quinoline); 9.25 s (1H) and 9.33 s (2H) (C_6H_2). Mass spectrum: *m*/*z* (I_{rel}, %): 339 (100) $[M + H]^+$, 338 (20) $[M]^-$. Found, %: C 56.72; H 2.82; N 16.45. $C_{16}H_{10}N_4O_5$. Calculated, %: C 56.81; H 2.98; N 16.56. *M* 338.28.

Metal complexes (*general procedure***).** The corresponding transition metal salt, 1 mol, was added to a hot solution of 2 mol of compound **Ia** or **Ib** in alcohol, acetone, or acetonitrile, and the resulting homogeneous solution was heated for 5 h under reflux, cooled, and left to stand on exposure to air for slow evaporation. The precipitate was filtered off, washed with several portions of the corresponding cold solvent, and dried in air.

Bis[3,5-dinitro-*N*-(pyridin-4-yl)benzamide]-cobalt(II) dinitrate dihydrate (IIa). Yield 80%, light red crystals, mp >160°C (decomp.). Found, %: C 36.43; H 2.84; N 17.45. $C_{24}H_{20}CoN_{10}O_{18}$. Calculated, %: C 36.24; H 2.53; N 17.61.

Bis[3,5-dinitro-*N*-(quinolin-5-yl)benzamide]-cobalt(II) dinitrate dihydrate (IIb) was synthesized using acetonitrile as solvent. Yield 89%, light red crystalline powder, mp >225°C (decomp.). Found, %: C 43.20; H 2.48; N 15.59. $C_{32}H_{24}CoN_{10}O_{18}$. Calculated, %: C 42.92; H 2.70; N 15.64.

Bis[3,5-dinitro-*N*-(quinolin-5-yl)benzamide]-nickel(II) dinitrate dihydrate (IIIa) was synthesized by prolonged (10–20 days) keeping of a solution of anhydrous complex **VI** in alcohol at room temperature. Yield quantitative, grayish–green crystals, mp >170°C (decomp.). Found, %: C 36.29; H 2.60; N 17.59. $C_{24}H_{20}N_{10}NiO_{18}$. Calculated, %: C 36.24; H 2.54; N 17.62.

3,5-Dinitro-*N*-(quinolin-5-yl)benzamide–ethanol (1/1) (IV) was isolated by recrystallization of autocomplex **Ib** from ethanol. Yield quantitative, light yellow plates, mp 245°C. Found, %: C 56.62; H 4.25; N 14.61. $C_{18}H_{16}N_4O_6$. Calculated, %: C 56.25; H 4.20; N 14.58.

Bis[3,5-dinitro-*N*-(pyridin-4-yl)benzamide]-cobalt(II) dinitrate (V) was obtained by heating complex **IIa** at 110–115°C under reduced pressure. Yield quantitative, light violet finely crystalline powder, mp >160°C (decomp.). On exposure to atmospheric moisture complex **V** was converted back into dihydrate **IIa**.

Bis[3,5-dinitro-*N*-(pyridin-4-yl)benzamide]-nickel(II) dinitrate (VI). A solution of **Ia** and Ni(II) salt in alcohol was heated for 24 h under reflux. The mixture was then cooled to 3–4°C. Yield 85%, large bluish–green crystals, mp >240–290°C (decomp.). Found, %: C 41.75; H 2.25; N 18.56. $C_{24}H_{16}N_{10}NiO_{16}$. Calculated, %: C 37.97; H 2.12; N 18.45.

Bis[3,5-dinitro-*N*-(pyridin-4-yl)benzamide]-nickel(II) dinitrate tetrahydrate (VII). A solution of the initial reactants in alcohol was allowed to slowly cool down to room temperature. Yield 85%, yellow–brown crystalline powder, mp >170°C (decomp.). Found, %: C 34.85; H 2.91; N 16.86. $C_{24}H_{24}N_{10}NiO_{20}$. Calculated, %: C 34.68; H 2.98; N 16.85.

Bis[3,5-dinitro-*N*-(quinolin-5-yl)benzamide]-cobalt(II)–nitrate–acetone–water (1/1/1/1) (VIII) was obtained using acetone as solvent. Yield 90%, light–red crystalline powder, mp >160°C (decomp.). Found, %: C 45.12; H 2.75; N 15.39. $C_{35}H_{28}CoN_{10}O_{18}$. Calculated, %: C 44.93; H 3.02; N 14.97.

Bis[3,5-dinitro-*N*-(quinolin-5-yl)benzamide]-nickel(II)–nitrate–acetone–water (1/1/1/1) (IX) was obtained using acetone as solvent. Yield 87%, greenish finely crystalline powder, mp >300°C (decomp.). Found, %: C 45.24; H 2.31; N 15.86. $C_{35}H_{28}N_{10}NiO_{18}$. Calculated, %: C 44.94; H 3.02; N 14.98.

Bis[3,5-dinitro-*N*-(quinolin-5-yl)benzamide]-nickel(II)–nitrate–acetonitrile–water (1/1/1/1) (X) was obtained using acetonitrile as solvent. Yield 90%, large greenish–blue crystals, mp >225°C (decomp.). Found, %: C 44.27; H 2.55; N 16.35. $C_{34}H_{25}N_{11}NiO_{17}$. Calculated, %: C 44.47; H 2.74; N 16.78.

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