

STRUCTURE OF 2:1 COBALT(III) COMPLEXES DERIVED FROM ARYLAZOCITRAZINIC ACID

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¹H, ¹³C NMR and MS spectra of the 2:1 cobalt(III) complexes, the azo coupling products of 2-aminophenol or 2-aminobenzoic acid with the citrazinic acid, were measured and analysed. It was found that the cobalt atom is six-coordinated being bound to two oxygens (one from primary and one from secondary component) and the nitrogen of 2-aminophenol or 2-aminobenzoic acid. Molar magnetic susceptibility data proved the presence of Co(III). Diazotisation of 2-aminophenol or 2-aminobenzoic acid and subsequent coupling reaction with citrazinic acid and complexation of the formed azo product proceeded on standard way.

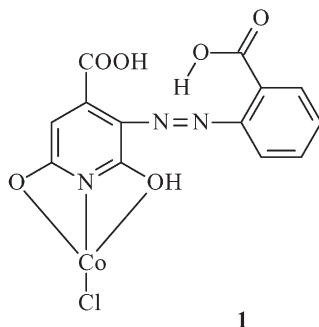
Keywords: Citrazinic acid; Complexation; Co(III) complexes; Chelates; Cobalt; NMR spectroscopy; Mass spectrometry.

Metal-complex dyes play a very important role in dyestuff technology¹⁻⁵. The complexation converts relatively cheap dyes to attractive commercial products having appropriate stability and shade. The dyes used in preparation of metal-complex dyes are usually tridentate ligands and the resulting products can have different configurations (*fac*, *mer*). It would be ideal to determine the real structure of these dyes using X-ray data. The number of existing X-ray structures is very limited (e.g. refs.^{6,7}) because of extreme difficulties in growing single crystals.

X-ray crystallography and NMR spectroscopy are in same sense complementary methods for the structure determination. NMR spectra provide information about the uniformity of metal-complex dyes, dynamic behav-

ion, position of coordination, etc., allowing, at least partially, to solve the structures of metal-complex dyes in cases where X-ray data are not available. We have successfully studied several types of metal-complex dyes derived from ligands having either hydroxy or carboxylic groups by multinuclear magnetic resonance^{8–14}.

An important group of metal-complex dyes is derived from citrazinic acid as secondary component¹⁵. Masoud et al.¹⁶ proposed the existence of structure **1** having four-membered rings as a consequence of coordination of citrazinic acid nitrogen and both oxygen atoms.

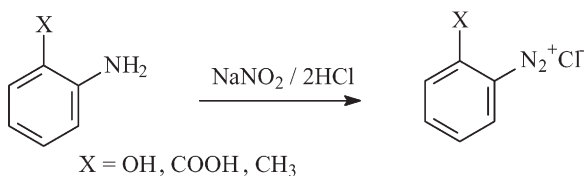


This structure differs considerably from those shown previously and also from other structures mentioned in ref.¹⁶. Since citrazinic acid and its derivatives are promising secondary components, we decided to study this type of compounds using detailed ¹H, ¹³C NMR and MS spectra.

RESULTS AND DISCUSSION

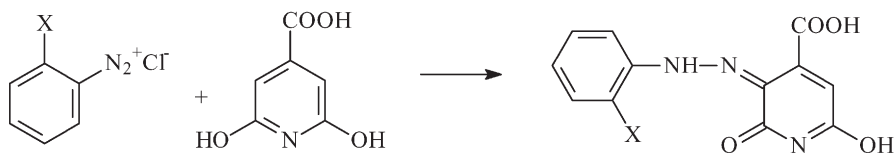
Synthesis of the Dyes

The preparation of azo dyes **2a–2c** is based on the diazotisation of primary amine (2-aminophenol, 2-aminobenzoic acid or 2-methylaniline) in dilute aqueous HCl at temperature 0–5 °C, where the reaction time is about 20–30 min (Scheme 1).



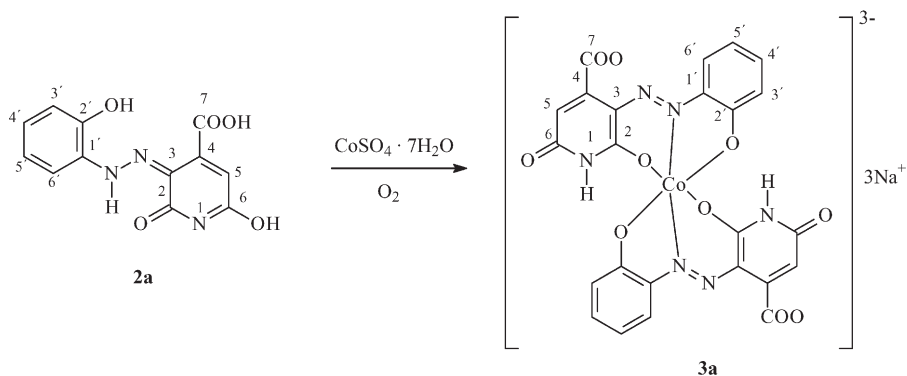
SCHEME 1

The obtained diazonium salt is coupled with aqueous solution of a mixture of citrazinic acid and its salt at pH ~ 8 , at temperature 0–5 °C; reaction time ca. 3 h (Scheme 2).



SCHEME 2

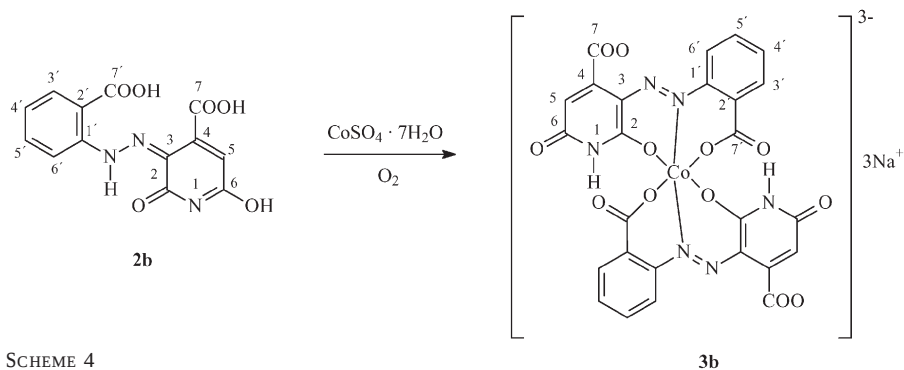
Cobalt(III) complex dyes **3a**, **3b** are prepared in water by complexation reaction of azo dyes **2a**, **2b** with cobalt(II) sulfate at pH ~ 8 –9 and reaction temperature 100 °C (reflux); reaction time ca. 3 h (Schemes 3 and 4).



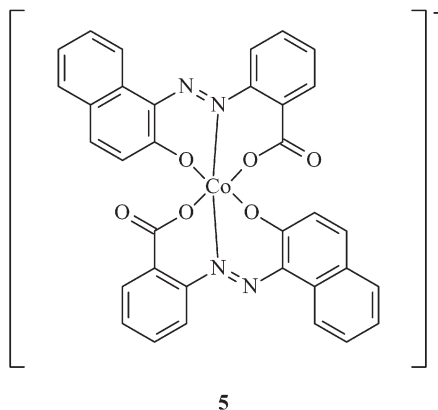
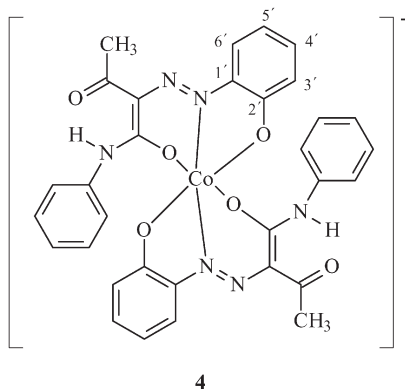
SCHEME 3

The reaction mixture is vigorously stirred to facilitate the oxidation of cobalt ($\text{Co}^{2+} \rightarrow \text{Co}^{3+}$) with air oxygen.

Thus, the compound $\text{Na}_3\mathbf{3a}$ is a Co(III) complex with 3-[(2-hydroxyphenyl)azo]citrazinic acid, $\text{Na}_3\mathbf{3b}$ is a Co(III) complex with 3-[(2-carboxyphenyl)azo]citrazinic acid. The reference anion **4** is a Co(III) complex with 2-[(2-hydroxyphenyl)hydrazono]-3-oxo-*N*-phenylbutanamide⁸ and the reference anion **5** is a Co(III) complex with 2-[(2-hydroxy-1-naphthalenyl)azo]-benzoic acid¹⁷.



SCHEME 4



Constitution of Prepared Dyes

The ^1H and ^{13}C NMR chemical shifts of starting azo dyes **2a** and **2b** and the anion **3a** were measured in $\text{DMSO-}d_6$ and the obtained data are collected in Table I.

TABLE I
 ^1H and ^{13}C NMR chemical shifts of anions **2–4** in $\text{DMSO-}d_6$

Atom	2a		2b		3a		4 (ref. ⁸)	
	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
2	–	<i>a</i>	–	<i>b</i>	–	<i>c</i>		
3	–	121.8	–	123.3	–	114.7		
4	–	146.7	–	152.1	–	<i>d</i>		
5	6.25	114.1	5.97	112.1	5.83	104.2		
6	–	<i>a</i>	–	<i>b</i>	–	<i>c</i>		
7	–	166.4	–	167.5	–	167.4		
NH–N	14.38	–	15.66	–				
1'	–	129.4	–	143.5	–	145.8	–	147.1
2'	–	146.3	–	120.1	–	168.8	–	167.7
3'	7.00	116.2	8.01	131.5	6.70	117.3	6.63	117.5
4'	7.04	126.6	7.20	123.9	7.00	128.9	6.92	127.9
5'	6.94	120.3	7.56	132.8	6.70	114.4	6.67	114.2
6'	7.47	114.7	7.86	115.3	8.03	114.6	8.23	114.9
7'	10.82	–	<i>d</i>	168.7	–	–	–	–

a 163.9 or 161.1; *b* 164.9 or 160.7; *c* 148.7 or 148.3; *d* not observed. Additional signals: **2a**: $\delta(^1\text{H})$ = 11.79 (br s, 1 H, acidic proton of NH or OH group); **3a**: $\delta(^1\text{H})$ = 11.74 (br s, 1 H, acidic proton of NH or OH group).

The ^1H and ^{13}C NMR chemical shifts were assigned using H,H-COSY, gradient-selected gs-HMQC and gs-HMBC ^{11,12} (optimised for $^1J(^{13}\text{C},\text{H})$ ca. 150 Hz and $^3J(^{13}\text{C},\text{H})$ ca. 8 Hz). Correlation of H(3') with the carbon of C-OH or COOH group in HMBC spectra was a key information for the assignment of hydrogen and carbon resonance of C1'–C7'.

Only one set of appropriate NMR signals was obtained for anion **3a**. This means that both ligands in the complex **3a** are equivalent and there is only one arrangement or a very fast exchange on the NMR time scale. The second

possibility can be theoretically examined from the measurement at low temperature. Since melting point of DMSO is +18 °C and since our complexes are insoluble in other solvents, this low temperature technique cannot be used. In addition, both ligands are spatially so far that the use of NOE or NOESY is impossible.

We compared the ^1H and ^{13}C chemical shifts measured for anion **3a** with those for anion **4** for which we undoubtedly proved⁸ that cobalt atom is six-coordinated via two oxygen and nitrogen atoms from starting 2-aminophenol. A comparison of ^1H and ^{13}C chemical shifts in complexes **3a** and **4** convincingly shows that the NMR data for comparable structures in both molecules are practically the same. Consequently, the bonding arrangement around cobalt atom in both complexes is also quite the same.

To provide chemical evidence for the importance of the hydroxy group presence in the ligand molecule, we prepared compound **2c** in which hydroxy group was replaced with methyl group having similar steric requirement as OH group. In accord with our expectation, no complexation of **2c** with cobalt(III) cation was observed.

Moreover, in structure **1**, proposed by Masoud et al.¹⁶, it could be expected that both the hydroxy groups and even the phenylazo substituent are not of decisive importance for a formation of cobalt(III) complex. Thus, we tested the complexation of unsubstituted citrazinic acid but, again, no complexation was observed.

Schetty and Kuster¹⁷ observed the three components having considerably different shades in cobalt(III) complex **5**. We proved¹³ that all the anions **3a**, **3b**, **4** and **5** contain six-coordinated cobalt atom and the difference consists in different mutual orientation of two ligands. All three components, however, are separable, after standing of each isomer in DMSO solution, which results in the formation of the starting equilibrium.

We measured ^1H and ^{13}C NMR spectra of anion **3b** and observed a mixture of four components. The ^1H NMR spectrum consists of a strongly overlapped signals ($\delta(^1\text{H})$ 7.25–8.28) and four separated signals resonating at 6.34, 6.20, 6.14 and 6.07 ppm, having approximately the same intensities. The latter ^1H NMR resonances resemble those for H-3' protons¹³ in the compound. An attempt to separate these isomers chromatographically was not completely successful since the tendency to establish an equilibrium during evaporation of solvent is stronger in **3b** than that in **5**.

The fact that the ligand **2b** was bound to cobalt(III) ion (forming **3b**) was also convincingly proved using mass spectrometry. The value of m/z of **3b** was found to be 661 (negative mode of electrospray ionisation) and 663

(positive mode of electrospray ionisation) for each chromatographic fraction.

We studied the cobalt oxidation state by measuring specific susceptibility of compound $\text{Na}_3\mathbf{3a}$. The experimental value χ_g was $(0.85 \pm 0.02) \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$. Calculating molar magnetic susceptibility $\chi_M = 570 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ and correcting this value for diamagnetic contribution $358 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$, we obtained corrected molar magnetic susceptibility $\chi_M = 928 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$.

Anion $\mathbf{3a}$ exists predominantly as a diamagnetic complex with Co(III) in the low-spin state (t_{2g}^6) (high-spin state has been observed so far exclusively in hexafluorocobaltate(III) complexes in which their magnetic properties are determined by four unpaired electrons with nonquenched orbital angular momentum and observed magnetic moments 6.5–9.5 BM¹⁹). A small contribution of a Co(II) impurity in the high-spin state with the configuration (t_{2g}^5)(e_g^2) having three unpaired electrons cannot be excluded taking experimental data into account. Complexes of this type give magnetic moments μ_{eff} in the range from 4.3 to 5.2 BM¹⁹ which correspond to the values of corrected molar magnetic susceptibility in the range of 9760×10^{-11} – $14268 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ using the expression $\mu_{\text{eff}} = 797.5 \times (\chi_M T)^{1/2}$. Provided this assumption is correct, the Co(II) complex content could be estimated to be 6–9% using the experimental value of $\chi_M = 876 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$.

The results of electrospray ionisation (ESI) mass spectrometry measurements both in the positive- and negative-ion modes for compounds $\mathbf{2a}$ – $\mathbf{2c}$ and Na^+ salts $\mathbf{3a}$, $\mathbf{3b}$ are summarised in Experimental and they are in agreement with their molecular weights and the structures. Ions presenting in the full-scan positive- and negative-ion mass spectra strongly depend on the Na^+ concentration in the solution which is related to the character of measured compounds. The presence of carboxylic group of ligands is confirmed by the fragment ions observed in the full-scan negative-ion mass spectra for compounds $\mathbf{2a}$, $\mathbf{2b}$, $\mathbf{2c}$ and $\text{Na}_3\mathbf{3b}$ and tandem mass spectra for compound $\text{Na}_3\mathbf{3a}$.

CONCLUSIONS

^1H , ^{13}C NMR and MS data, suitable model experiments and taking into account some data from literature, we proved that 2:1 cobalt(III) complexes $\mathbf{3a}$ and $\mathbf{3b}$ derived from azo coupling products of 2-aminophenol or 2-aminobenzoic acid with citrazinic acid have the same structure as the complexes prepared by coupling of 2-aminophenol or 2-aminobenzoic acid with other secondary components and subsequent complexation. Anion $\mathbf{3a}$

is a less flexible complex with new five- and six-membered rings, which are more flexible and, thus, several isomers existing in an equilibrium can be formed. Molar magnetic susceptibility data proved the existence the Co(III) oxidation state in the complexes.

EXPERIMENTAL

General

Acetonitrile and methanol for HPLC were purchased from Sigma–Aldrich (Prague, Czech Republic). Water was purified using the Milli-Q® plus water purification system (Millipore, USA). Ammonium acetate was purchased from Lach-Ner (Czech Republic). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer (500.13 MHz for ^1H and 125.76 MHz for ^{13}C) in $\text{DMSO}-d_6$. The ^1H and ^{13}C NMR chemical shifts were referenced to internal TMS. All 2D experiments (gradient-selected gs-COSY, gs-HMQC, gs-HMBC) were performed using manufacturer's software. Magnetic susceptibility was measured at room temperature (25 °C) using a Variable Temperature Gouy Balance apparatus (Newport Instruments, UK) and $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. The values of magnetic molar susceptibility were corrected by the Pascal constants¹⁹. Positive- and negative-ion electrospray ionisation (ESI) mass spectra were measured on an ion trap analyser (Esquire 3000, Bruker Daltonics, Germany). The full-scan mass spectra were measured in the range m/z 50–1000. The samples were dissolved in a water/acetonitrile (1:1) mixture and analysed by direct infusion at the flow rate $5\ \mu\text{l min}^{-1}$. The ion source temperature was 300 °C, the flow rate and the pressure of nitrogen were $4\ \text{l min}^{-1}$ and 10 Pa, respectively.

Diazotisation of 2-Aminophenol

2-Aminophenol (0.02 mol, 2.18 g; Aldrich) was mixed with water (20 ml) and concentrated HCl (5 ml, 35%). The obtained fine suspension was externally cooled under intensive stirring to 0–5 °C and 5 M aqueous NaNO_2 (5 ml) was slowly added. The cooling was stopped and the suspension was stirred at ambient temperature (ca. 22 °C) for 20–30 min until a yellow-brown solution of the diazonium compound was produced. The solution was used for subsequent coupling reaction.

Preparation of 3-[(2-Hydroxyphenyl)azo]citrazinic Acid (**2a**)

Citrazinic acid (0.02 mol, 3.20 g; Aldrich) was mixed with water (15 ml) and 5 M aqueous NaOH (13 ml) and the temperature was maintained at 0–5 °C (external cooling). The solution of the diazonium compound was gradually added under intensive stirring. pH was adjusted to ca. 8 by the addition of 5 M aqueous NaOH. When the coupling reaction was completed (after ca. 3 h), pH was adjusted to 4 by the addition of concentrated HCl (35%) and the precipitated monoazo dye was filtered off and dried at 90–110 °C. The yield of crude dye **2a** was 5.84 g (98%). The purity of the dye was determined by TLC (Alugram SIL G/UV₂₅₄, Macherey–Nagel, Germany; mobile phase: propan-2-ol/propan-1-ol/ethyl acetate/water 2:4:1:3 (v/v/v/v)). According to TLC, **2a** was pure (R_F 0.8). $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_5$ (275): ESI^+ , m/z : 320.0 $[\text{M} + 2\ \text{Na} - \text{H}]^+$, 100%; 301.9 $[\text{M} + 2\ \text{Na} - \text{H} - \text{H}_2\text{O}]^+$; 276.0 $[\text{M} + \text{H}]^+$. ESI^- , m/z : 295.8 $[\text{M} - 2\ \text{H} + \text{Na}]^-$; 273.8 $[\text{M} - \text{H}]^-$; 255.8 $[\text{M} - \text{H} - \text{H}_2\text{O}]^-$; 229.8 $[\text{M} - \text{H} - \text{CO}_2]^-$, 100%.

Preparation of 3-[(2-Carboxyphenyl)azo]citrazinic Acid (**2b**)

Preparation was analogous to the preparation of compound **2a**. According to TLC, **2b** was pure (R_F 0.75). $C_{13}H_9N_3O_6$ (303): ESI^- , m/z : 301.8 $[M - H]^-$, 100%; 257.8 $[M - H - CO_2]^-$; 213.8 $[M - H - 2 CO_2]^-$.

Preparation of Complex $Na_3\mathbf{3a}$

The monoazo dye **2a** (0.02 mol, 5.94 g) was dissolved in water (50 ml) and pH was adjusted to 8–9 by the addition of 5 M aqueous NaOH. Then $CoSO_4 \cdot 7H_2O$ (2.80 g, 0.01 mol) was added and the reaction mixture was vigorously stirred at 100 °C (reflux) for ca. 3 h. When the reaction was completed, compound $Na_3\mathbf{3a}$ was precipitated by addition of NaCl, filtered off and dried. The yield of compound $Na_3\mathbf{3a}$ was ca. 78% (based on **2a**). The purity of the dye $Na_3\mathbf{3a}$ was determined by TLC (Alugram SIL G/UV₂₅₄, Macherey–Nagel, Germany; mobile phase: propan-2-ol/propan-1-ol/ethyl acetate/water 2:4:1:3 (v/v/v/v)). According to TLC, **3a** was pure (R_F 0.69). $Na_3[Co(C_{12}H_6N_3O_5)_2]$; $C_{24}H_{12}CoN_6Na_3O_{10}$ (672): ESI^+ , m/z : 651.0 $[M - Na + 2 H]^+$, 100%. ESI^- , m/z : 605.1 $[M - 3 Na + 2 H]^-$, 100%. MS/MS, m/z : 605; 560.9 $[M - 3 Na + 2 H - CO_2]^-$; 517.0 $[M - 3 Na + 2 H - 2 CO_2]^-$.

Preparation of Complex $Na_3\mathbf{3b}$

Preparation was analogous to the preparation of complex $Na_3\mathbf{3a}$. According to TLC, **3b** was pure (R_F 0.71). $Na_3[Co(C_{13}H_6N_3O_6)_2]$; $C_{26}H_{12}CoN_6Na_3O_{12}$ (728): ESI^+ , m/z : 684.9 $[M - 2 Na + 3 H]^+$; 663.0 $[M - 3 Na + 4 H]^+$, 100%. ESI^- , m/z : 661.0 $[M - 3 Na + 2 H]^-$, 100%; 616.9 $[M - 3 Na + 2 H - CO_2]^-$; 572.9 $[M - 3 Na + 2 H - 2 CO_2]^-$.

Preparation of 3-[(2-Methylphenyl)azo]citrazinic Acid (**2c**)

Preparation was analogous to the preparation of compound **2a**. According to TLC, **2c** was pure (R_F 0.84). $C_{13}H_{11}N_3O_4$ (273): ESI^- , m/z : 271.8 $[M - H]^-$; 227.8 $[M - H - CO_2]^-$, 100%.

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