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OXIDATION OF 3-(3- or 4-PYRIDYL)-1,5-DIPHENYL-FORMAZANS IN TETRAZOLIUM TRICHLORO-METALLATES: STRUCTURAL AND ELECTRO-CHEMICAL INVESTIGATION

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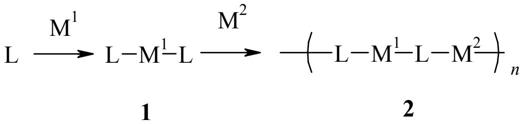
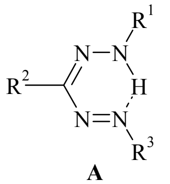
On interacting pyridine-containing formazans with cobalt(II) and copper(II) chlorides the richlorometallates of the corresponding cations are isolated, the structures of which were established by X-ray structural analysis. Using data of cyclic voltamperometry a scheme is proposed for the oxidation–reduction process of converting formazans into tetrazolium cations.

Keywords: cation radicals, tetrazolium cations, trichlorometallates, formazans, complexes, reduction, oxidation, X-ray structural analysis, cyclic voltamperometry.

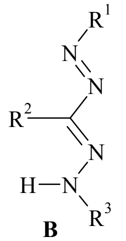
One of the most vigorously growing directions of supramolecular chemistry is the chemistry of coordination polymers, which are promising materials possessing semiconductor, optical, and magnetic properties [1, 2]. The process of forming coordination polymers **2** may consist of the preliminary preparation of a complex ligand **1** (with metal M^1) with another metal M^2. The complex ligands **1** (metalloligands or metal-organic building blocks/tectones) must possess as a minimum, two exodentate groups capable of forming additional coordination bonds [3-6].



$$L \xrightarrow{M^1} \underset{\mathbf{1}}{L{-}M^1{-}L} \xrightarrow{M^2} \underset{\mathbf{2}}{\left(L{-}M^1{-}L{-}M^2\right)_n}$$



A



B

Formazans are convenient substrates for building such metalloligands thanks to the presence of potentially chelate chromophoric groupings and the possibility of varying the substituents in positions 1, 3, and 5. It is known that formazans may exist in two forms, chelate **A** (*E,Z*) and linear **B** (*E,E*) (the *Z*-form of the azo group is usually not considered) [7].

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* Dedicated to deeply respected Academician M. G. Voronkov in connection with his birthday and as a mark of gratitude for his contribution to heterocyclic chemistry

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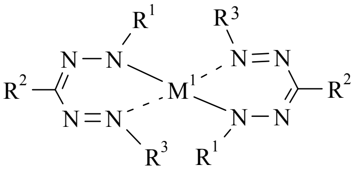
On forming complexes with metal salts the deprotonated form **A** of the formazan, in which the negative charge is delocalized along all the conjugated chain, usually reacts. As a result six-membered metallochelates are formed in which a hydrogen atom is replaced by metal [8].

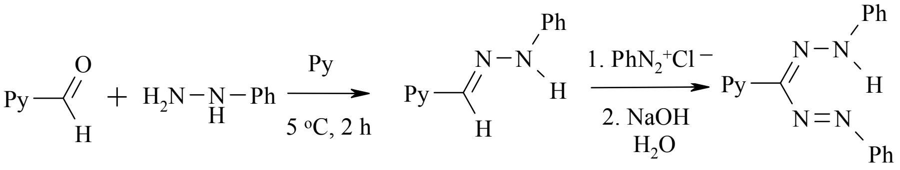


1, 1a

1 $R^1 = R^3 = Ar$, $R^2 = Ar, Alk$; **1a** $R^1 = R^3 = Ar, Het$; $R^2 = Ar, Het$;
$M^1 = Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Zn^{2+}$

Formazans coordinate the transition metals Co(II), Ni(II), Cu(II), Cd(II), Pd(II), and Zn(II) with the formation of neutral complexes with coordination unit MN_4 [9-18] (type **1**, **1a**). Formazans are known with heterocyclic substituents (benzazoles [19-24], azoles [25], pyridines [26-29], and quinolines [28-35]), however their use for obtaining metalloligands has not been considered in the literature.

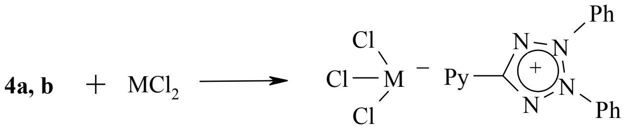
Results are given in the present paper of an investigation of the process of forming metalloligands from formazans with pyridine substituents in position **3**. The chlorides of copper(II) and cobalt(II) were chosen as sources of metal ions. Model 3-(3-pyridyl)- and 3-(4-pyridyl)-1,5-diphenylformazans (**4a,b**) were obtained by azocoupling the phenylhydrazones of the appropriate pyridinecarbaldehydes **3** with benzenediazonium chloride at 0°C by methods analogous to those described in [7, 29].



3,4 a Py = 3-Py, **b** Py = 4-Py

The synthesis of formazan **4a** is not described in the literature although it is used as a starting material for obtaining the 6-(3-pyridyl)-2,4-diphenylverdazyl radical [37]. Formazan **4b** was obtained in [26]. For compounds **4a,b**, as also for the initial phenylhydrazones of pyridinecarbaldehydes **3**, only melting points and data of elemental analysis are given in the literature. In our work compounds **3** and **4** were characterized for the first time by ^1H NMR spectroscopy. Characteristic signals were observed in the ^1H NMR spectra of hydrazones **3a,b** for the *ortho*, *meta*, *para* protons of the benzene rings, the protons of the pyridine rings of the aldehyde component, the proton of the amino group, and the proton at the double bond (see EXPERIMENTAL). In comparison with the spectra of the hydrazones the signal of the amino group proton in the ^1H NMR spectra of formazans **4** was displaced towards high field by more than 7 ppm, the *ortho*, *meta*, and *para* protons of both phenyl rings have the same chemical shifts respectively, and together with the signals of the pyridine ring protons were displaced towards high field by 0.4 ppm. These changes in the spectra are explained by the fact that as a result of rapid exchange of proton between the $N_{(1)}$ and $N_{(5)}$ atoms the phenyl rings in the formazans become equivalent in the NMR time scale.

To obtain metallochelates of type **1** solutions of ligand and acetates [9, 12, 38, 39] or chlorides [19, 40] of copper and cobalt are usually mixed at room temperature or on heating. To obtain complexes of type **1a** we used alcoholic solutions of cobalt and copper chlorides. On mixing a solution of formazans **4** in acetonitrile and a solution of salt in alcohol at room temperature only the complex of formazan **4a** with cobalt chloride was successfully isolated and characterized. Complex-forming reactions of formazans **4a,b** with copper(II) chloride dihydrate and **4b** with cobalt(II) chloride hexahydrate were carried out by the method of slow diffusion [5] of an alcoholic solution of salt into a solution of the ligand in methylene chloride. In the reactions of formazans **4** with cobalt chloride the color of the mixed solutions on standing changed from claret to dark blue, which serves as a sign of complex formation. The reaction of formazans **4** with copper chloride proceeded analogously. At the border separating the two phases pink needle-shaped crystals grew and the mixed solution became yellow from red.



5,6

5 a Py = 3-Py, M = Co; **b** Py = 4-Py, M = Co; **6 a** Py = 3-Py, M = Cu;
b Py = 4-Py, M = Cu

TABLE 1. Experimental X-Ray Structural Parameters

Compound	**5a**	**6b**
Formula	$C_{20}H_{17}Cl_3CoN_6$	$C_{18}H_{14}Cl_3CuN_5$
Molecular weight	506.68	470.23
Crystal size, mm	0.52 × 0.34 × 0.20	0.55 × 0.32 × 0.20
Crystal system	Monoclinic	Rhombic
Space group	$P2_1/c$	$P2_12_12_1$
a, Å	9.080(2)	10.287(2)
b, Å	12.888(3)	11.897(2)
c, Å	20.501(4)	6.976(3)
α, deg	90	90
β, deg	100.79(3)	90
γ, deg	90	90
V, Å^3	2356.7(9)	2077.6(6)
Z	4	4
d_{calc}, g·cm^{-3}	1.428	1.503
μ, mm^{-1}	1.087	1.449
F(000)	1028	948
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Temperature, K	293(2)	293(2)
Scanning region, θ	1.88-25.16	2.09-25.47
Range of reflection indices	$-10 \leq h \leq 10$	$0 \leq h \leq 12$
	$0 \leq k \leq 15$	$0 \leq k \leq 14$
	$0 \leq l \leq 24$	$0 \leq l \leq 20$
Number		2199
reflections measured	4466	
ndependent reflections (R_{int})	4212 (0.013)	2199
refinement parameters	312	244
R_1 [$I \geq 2\sigma(I)$]	0.0360	0.0242
wR_2 (all reflections)	0.1101	0.0682
Quality on F^2	0.978	0.895
Residual electron density (max/min), e.Å^{-3}	0.654 / -0.468	0.407 / -0.184

In the reactions of pyridine-containing formazans with metal chlorides at a ratio of 1 : 1, in place of the supposed complexes of type **1a** we isolated tetrazolium trichlorometallates **5a,b** and **6a,b**. For compounds **5a** and **6b** monocrystals were successfully grown and were studied by X-ray structural analysis (Tables 1-3).

In the molecular structure of complex **5a** it is possible to separate out four planar fragments, the tetrazolium ring, the pyridine ring, and the two benzene rings (Fig. 1). The first two fragments are completely coplanar, the angle between the mean-square planes is 6.3°. The two phenyl rings are twisted in different ways relative to the phenyl–tetrazole bond. The angle of turn of the phenyl ring, including atoms $C_{(7)}$ through $C_{(12)}$, was 77.0°, and for the second phenyl ring (atoms $C_{(13)}$ through $C_{(18)}$) this angle was 36.9°. The noncoplanarity of the phenyl rings with the central tetrazolium ring is linked, evidently, with the repulsion of the *o*-H atoms in the theoretically possible conformation with a coplanar disposition of these rings. The structure of the five-membered ring is analogous to data existing in the literature on the structure of tetrazolium cations [41-43] (Tables 2, 3).

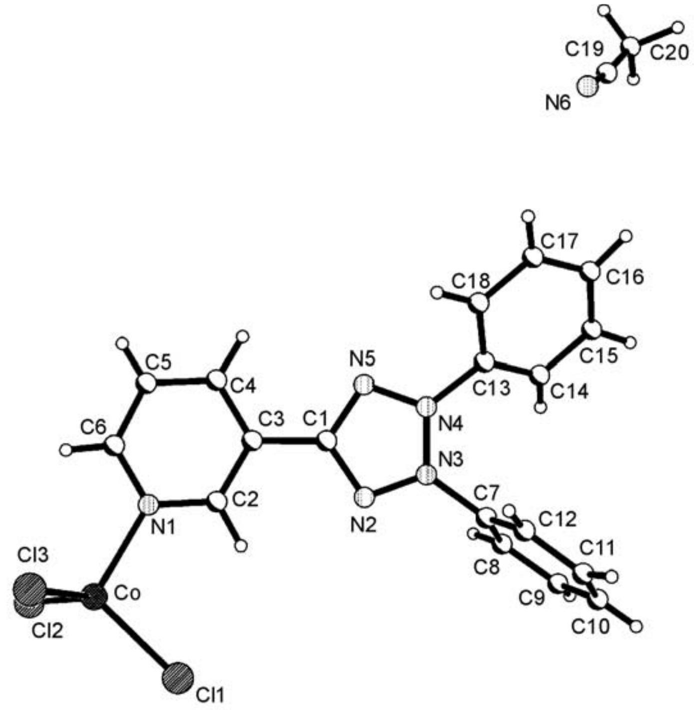


Fig. 1. Molecular structure of complex **5a**. Projection on the plane of the tetrazolium ring.

The coordination of the cobalt atom is a tetrahedron elongated lengthwise at one apex (direction Co-$N_{(1)}$) (Tables 2, 3), which is characteristic of analogous complexes of Co(II) [44-52]. The closest intermolecular contact (2.769 Å) corresponds to interaction between the $Cl_{(2)}$ atom and the H-6 atom of the centrosymmetric molecule (-x, 1-y, -z). In the asymmetric unit cell one molecule of solvated acetonitrile is found, which has no short contacts with the molecules of the complex.

It is also possible to separate out four planar fragments in the molecule of complex **6b**, analogous to those considered for compound **5a**. However in this case the pyridine ring is twisted significantly (19.8°) in relation to the central ring. The angles of turn of the phenyl rings are 46.5° and 56.8°.

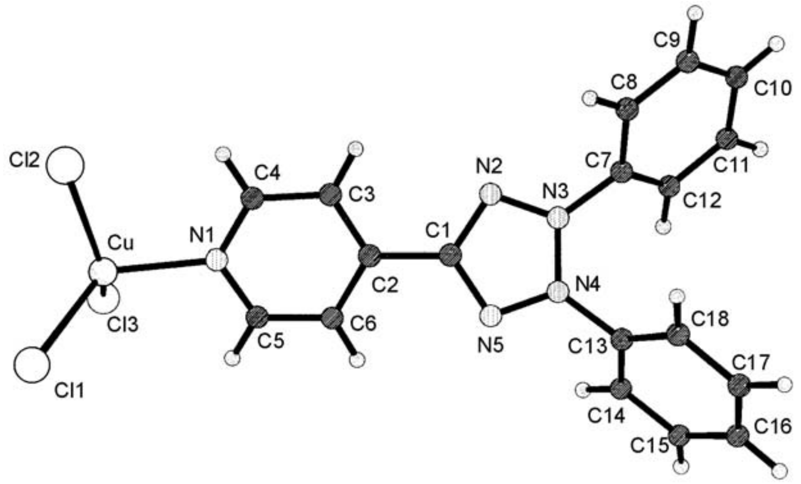


Fig. 2. Molecular structure of complex **6b**. Projection on the plane of the tetrazolium ring.

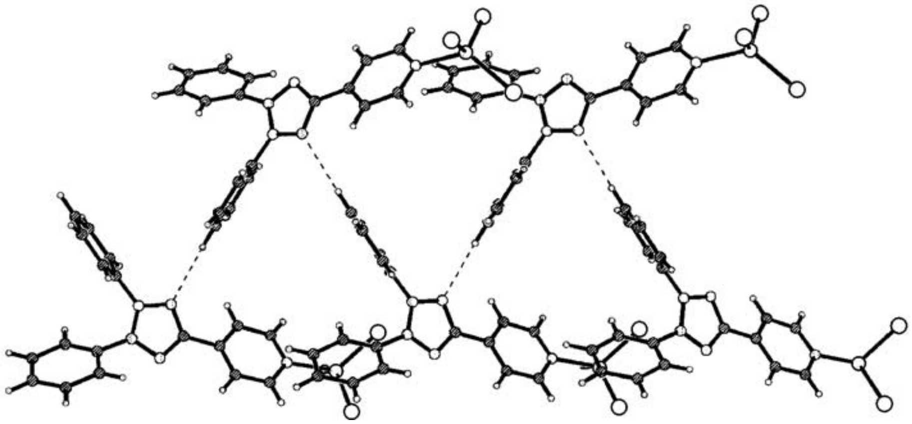


Fig. 3. Fragment of the crystal structure of complex **6b**.
The $N_{(5)}$…H-16 hydrogen bond is shown by dotted lines.

The coordination polyhedron of the copper atom is a heavily distorted tetrahedron (Tables 2 and 3), which is characteristic of analogous complexes of copper(II) [53-56]. In difference to the structure of complex **5a** short intermolecular contacts (2.583 Å) were observed in the crystal of the copper analog **6b** between the tetrazolium $N_{(5)}$ atom and the *para* hydrogen atom (H-16) of one of the phenyl rings of a neighboring molecule

TABLE 2. Some Bond Lengths (*l*) in Complexes **5a** and **6b**

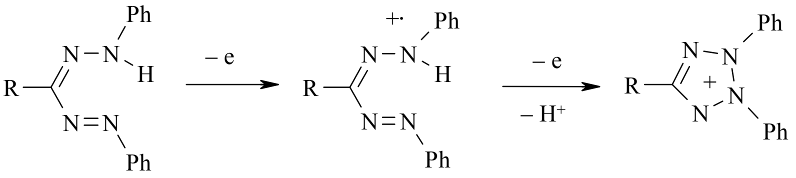
Bond	*l*, Å	
	5a, M = Co	**6b**, M = Cu
$C_{(1)}$–$N_{(2)}$	1.3404(3)	1.3310(2)
$N_{(2)}$–$N_{(3)}$	1.3040(3)	1.3036(2)
$N_{(3)}$–$N_{(4)}$	1.3331(3)	1.3424(2)
$N_{(4)}$–$N_{(5)}$	1.3093(3)	1.3029(2)
$N_{(5)}$–$C_{(1)}$	1.3319(3)	1.3290(2)
$N_{(1)}$–M	2.0551(4)	2.0317(3)
M–$Cl_{(1)}$	2.2585(5)	2.2139(3)
M–$Cl_{(2)}$	2.2453(5)	2.2328(4)
M–$Cl_{(3)}$	2.2316(5)	2.2131(3)

TABLE 3. Some Valence Angles (ω) in Complexes **5a** and **6b**

Angle	ω, deg	
	5a, M = Co	**6b**, M = Cu
$C_{(1)}–N_{(2)}–N_{(3)}$	103.73(2)	103.73(2)
$N_{(2)}–N_{(3)}–N_{(4)}$	110.08(2)	110.08(2)
$N_{(3)}–N_{(4)}–N_{(5)}$	109.70(2)	109.70(2)
$N_{(4)}–N_{(5)}–C_{(1)}$	103.95(2)	103.95(2)
$N_{(5)}–C_{(1)}–N_{(2)}$	112.52(2)	112.52(2)
$N_{(1)}–M–Cl_{(1)}$	104.01(2)	124.34(2)
$N_{(1)}–M–Cl_{(2)}$	108.78(2)	99.33(1)
$N_{(1)}–M–Cl_{(3)}$	102.56(2)	97.45(1)
$Cl_{(1)}–M–Cl_{(2)}$	114.88(2)	103.90(1)
$Cl_{(2)}–M–Cl_{(3)}$	112.09(2)	130.91(2)
$Cl_{(3)}–M–Cl_{(1)}$	113.93(2)	103.71(1)

(-0.5 + *x*; 1.5 – *y*; -*z*). In its turn atom H-16 of the first molecule is linked to the $N_{(5)}$ atom of another neighboring molecule (0.5 + *x*; 1.5 – *y*; -*z*). As a result endless chains of **6b** molecules are formed in the crystal (Fig. 3), disposed along the crystallographic *a* axis. Neighboring chains are linked by weak interactions (2.765 Å) between the $Cl_{(3)}$ and H-6 atoms.

An electrochemical investigation by cyclic voltamperometry has been carried out to study the reactions forming complexes **5** and **6** in more detail (Table 4). As is seen from Table 4, formazans **4** are oxidized in two steps and reduced in one. The presence of a system of four nitrogen atoms and one carbon atom conjugated with three aromatic rings leads to ready electrochemical formation of stable anionic and cationic particles. The mechanism of oxidation of compounds of this class may be described by a fairly simple scheme [57].



Reduction of the tetrazolium cation occurs at -0.30 V according to [57]. Consequently, as is seen from Fig. 4, a quasireversible peak is observed at potential -0.30 V after oxidation in a reversible cathodic scan.

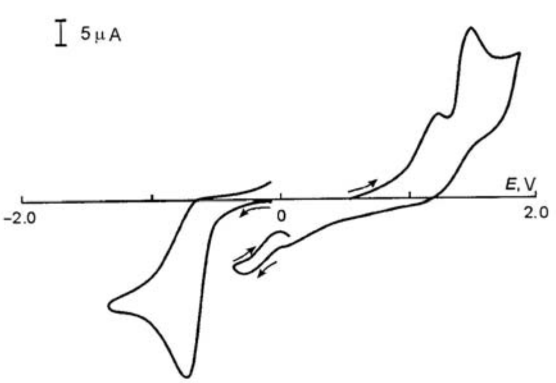


Fig. 4. Cyclic voltamperogram of formazan **4b**.

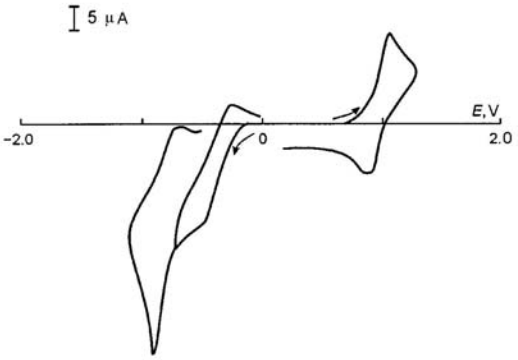


Fig. 5. Cyclic voltamperogram of the tetrazolium salt.

For comparison we synthesized 2,3,5-triphenyltetrazolium chloride (**7**) [28] from 1,3,5-tetraphenylformazan (**4c**).

On the electrochemical curves for salt **7** (Fig. 5) three peaks were observed, an anodic peak corresponding to oxidation of chloride ion (E_p^{ox} = 1.05 V), and two quasireversible reduction peaks (E_{p1}^{red} = -0.49; E_{p1}^{ox} = -0.28), (E_{p2}^{red} = -0.87; E_{p2}^{ox} = -0.70 V).

TABLE 4. Oxidation and Reduction Potentials of Formazans and Their Complexes according to Data of Cyclic Voltamperograms*

Compounds	Oxidation		Reduction	
	$E_{1/2}^{ox}$, B**	E_p^{ox}, B***	$-E_{1/2}^{red}$, B**	$-E_p^{red}$, B***
4a		0.93; 1.20 (1.14)		0.82 (0.76)
4b	1.08 (0.5)	1.19; 1.46 (1.32)	0.71 (1.85)	0.78 (0.73); 1.90
4c	0.94 (0.6)	0.87; 1.05 (0.86)	0.78 (1.3)	0.79 (0.68)
5a		1.25 (0.33)		0.33 (0.20); 0.74 (0.64)
5b		1.23		0.30 (0.20); 0.84 (0.66)
6a	0.57 (0.3); 1.45 (0.48)	0.65 (0.52); 1.06 (0.94); 1.50	0.33 (0.48); 0.74 (1.04)	0.37 (0.28); 0.79; 1.11 (1.18)
6b	0.58 (0.4); 1.44 (0.4)	0.64 (0.52); 1.06 (0.94); 1.49	0.30 (0.22); 0.75 (0.58)	0.37 (0.23); 0.76 (0.68); 1.21 (1.12)
7	1.00 (0.5)	1.05 (0.91)	0.46 (0.7); 1.02 (1.04)	0.49 (0.28); 0.87 (0.70)
4a + $CoCl_3$		1.06; 1.18 (1.03)		0.36 (0.15); 0.72 (0.60); 1.03
4b + $CoCl_3$		0.83; 1.03 (0.89); 1.36		0.37 (0.18); 0.71 (0.60); 1.00
4a + $CuCl_2$		1.03 (0.96); 1.61 (1.20)		0.32 (0.21); 0.75 (0.61); 1.27 (1.17)
4b + $CuCl_2$		1.06 (0.97); 1.51 (1.27)		0.31 (0.23); 0.68 (0.51); 1.22

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* Solvent was DMF with added tetrabutylammonium tetrafluoraborate, standard was saturated Ag/AgCl/KCl, platinum electrode.

** Number of electrons is given in parentheses.

*** Reversible peaks are given in parentheses.

In the anodic region of the second peaks of the oxidation of the formazans, where oxidation of the appropriate radical to tetrazolium cation occurs, no electrochemical processes were observed, except a peak for the oxidation of chloride ion. In the cathodic region the previous cathodic peak was observed at a potential close to -0.3 V. On reducing formazans, probably an anion radical is formed the negative charge on which is distributed along all four nitrogen atoms.

The complexes of ligands **4** with cobalt(II) and copper(II) chlorides also demonstrate fairly simple electrochemical curves (Figs. 6 and 7).

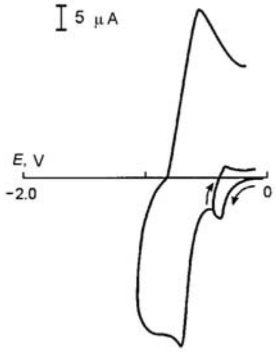


Fig. 6. Cyclic voltamperogram of complex **5a**.

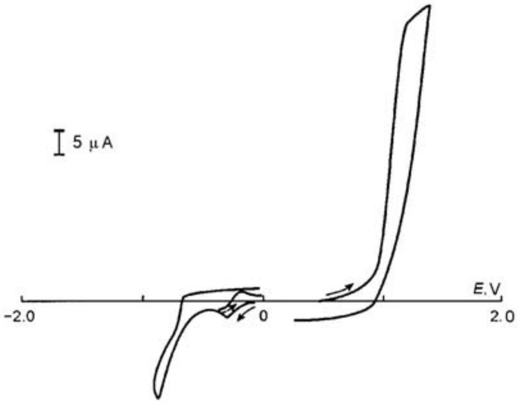
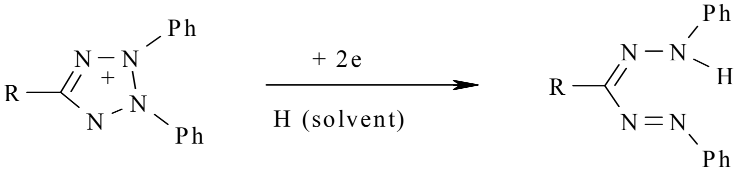


Fig. 7. Cyclic voltamperpgram of complex **5b**.

On the electrochemical curves for cobalt complexes **5a,b** at the single anodic stage, oxidation probably occurs at the Co-Cl bond (the potential of the oxidation peaks of complexes **5a,b** lie in the region for oxidation of chloride ions). The potentials of the second reduction peaks of **5a,b** coincide almost exactly with the potentials of the sole reduction peak of the corresponding ligand. Formazans **4** are therefore generated after transfer of the first electron to complexes **5a,b**. Reduction of of the cation occurs at the very first cathodic stage at low cathodic potentials with the addition of a hydrogen atom from the solvent to it.



For a detailed study of the process of forming complexes we carried out experiments with the aim of obtaining complexes **5** and **6** in the electrochemical cell. Solutions of the appropriate ligands in DMF were poured in with cobalt(II) and copper(II) chloride and maintained for 5 h at room temperature. The formation of the corresponding complex was therefore noted by the appearance of a reduction peak for the tetrazolium cation at -0.3 V. It has been established that tetrazolium cations are formed on interaction of compound **4** with copper chloride (Fig. 8) and are not formed on interaction with cobalt chloride. This is evidently linked with the lower oxidative ability of Co(II) (E_p^{red} = -0.90 V) in comparison with Cu(II) (E_p^{red} = 0.54 V).

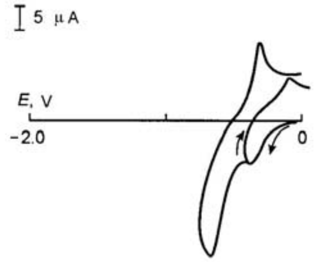
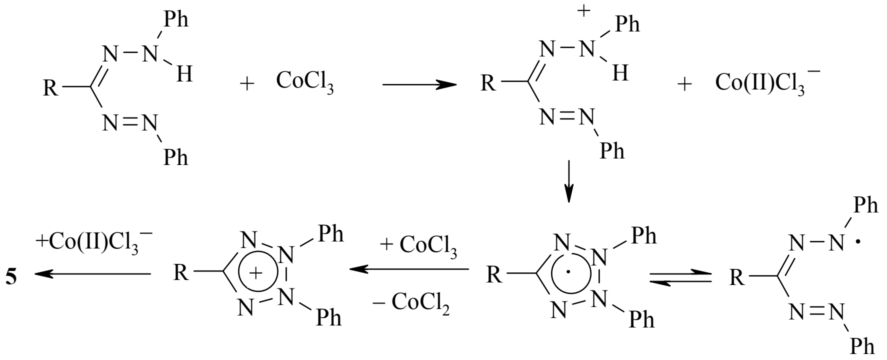


Fig. 8. Cyclic voltamperogram of complex **6a**.

The desired peak at -0.30 V was not observed on the first reduction curve of a mixture of formazans 4 with cobalt(II) chloride. However, after the first cathodic record the potential in the anodic region is scanned and then the cathodic once again, it is possible to observe a reduction peak at -0.40 V on the reduction curves. This peak is observed both at a reverse potential after 0.3 V and also at a reverse in current at the point of 0.8 V. This peak emerging once again may be attributed to reduction of the tetrazolium cation, reduction of Co^{3+} (originating on oxidation of metallic cobalt deposited on the surface of the platinum electrode, E_p^{ox} = 0.1 V), or reduction of complex **5a**, which may be formed on reaction of ligand **4a** with Co^{3+} (see below). The available data are unable to choose unequivocally any of the proposed variants.



On replacing cobalt(II) chloride by cobalt(III) chloride in the electrochemical cell tetrazolium cation is formed at once (E_p^{red} = -0.30 V) when pouring in a solution of salt and a solution of ligand. In this case the strength of $CoCl_3$ as an oxidizing agent proved to be sufficient so that oxidation of formazans occurred on mixing solutions of the appropriate ligands and $CoCl_3$ salts. It should be mentioned that the cobalt salt itself is reduced at this potential. However the presence of the opposite oxidation peak (at -0.18 V), the absence of the anodic desorption peak for the oxidation of the cobalt film on the surface of the platinum electrode, and the fact that the reverse pair of peaks are absent on treating the Co(III) salt of compounds **5a,b**, confirm our conclusion on the formation of complexes **5** according to the following mechanism.

An analogous mechanism also describes the formation of metallocomplexes on reaction with copper(II) chloride. But in this case the oxidation of formazan occurs initially on reduction of Cu(II) to Cu(I). The Cu(I) ion formed is then oxidized to Cu(II) by oxidation of the air or electrochemically.

Compound **4c**, containing no pyridine, does not react with cobalt(II) salt nor with $CoCl_3$. This indicates that the important step of the reaction forming tetrazolium salts is the step of complex-formation of metal with the pyridine nitrogen atom.

On the basis of the data presented it is possible to draw the conclusion that the principal step of forming tetrazolium cations is the one-electron oxidation of formazans by a suitable oxidizing agent. Metal ions [Cu(II) or Co(II)] or an electrode surface may act in this way. Participation of air oxygen, oxidizing Co(II) to Co(III) and Cu(I) to Cu(II), is a necessay step in carrying out this process in the chemical reaction.

EXPERIMENTAL

A check on the progress of reactions and the homogeneity of the compounds obtained was effected by TLC on a bound silica gel layer (Silufol). The ^1H NMR spectra were recorded on a Bruker-Avance (400 MHz) instrument in $CDCl_3$ (compounds **3a,b** and **4a,b**) and acetone-d_6 (compound **7**). The residual protons in deuterochloroform were used as internal standard. Measurement of electrochemical oxidation and reduction potentials was carried out with the aid of a PI-50-1.1 potentiostat, switched to program PR-8. Recording of cyclic voltamperograms and waves at the rotating disk electrode was carried out on an automatic two-dimensional recorder. Tetrabutylammonium perchlorate (highest purity, 99.8%, Fluka) served as base electrolyte. Electrolyte concentration = 0.05 M.

3-Pyridinecarbaldehyde Phenylhydrazone (3a). 3-Pyridinecarbaldehyde (3.0 g, 28.0 mmol) was added dropwise to a solution of phenylhydrazine (2.80 g, 25.9 mmol) in pyridine (15 ml) with ice-cooling at such a rate that the temperature of the mixture did not exceed 10°C. The mixture was then stirred at the same temperature for a further 2 h. The mixture was evaporated to dryness in vacuum until disappearance of the odor of pyridine. The dry residue was recrystallized from alcohol and dried in the air. Phenylhydrazone **3a** (3.45 g, 61%) was obtained as yellow crystals of mp 162.5°C (from ethanol). ^1H NMR spectrum, δ, ppm (J, Hz): 8.79 (1H, s, H-α' Py); 8.53 (1H, d, $J = 4.3$, H-α Py); 8.07 (1H, d, $J = 8.0$, H-γ Py); 7.85 (1H, s, NH); 7.68 (1H, s, CH=); 7.29-7,35 (3H, m, H-β Py, H-*m* Ph); 7.12 (2H, d, $J = 7.7$, H-*o* Ph); 6.93 (1H, t, $J = 7.3$, H-*p* Ph). Found, %: C 72.84; H 5.53; N 21.17. $C_{12}H_{12}N_3$. Calculated, %: C 73.10; H 5.58; N 21.32.

4-Pyridinecarbaldehyde Phenylhydrazone (3b) was synthesized by a procedure analogous to that for obtaining compound **3a**, from phenylhydrazine (1.88 g, 17.4 mmol) and 4-pyridinecarbaldehyde (2.00 g, 18.7 mmol) with a yield of 2.95 g (76%). Yellow powder of mp 179°C (from ethanol). ^1H NMR spectrum, δ, ppm (J, Hz): 8.59 (2H, d, $J = 3.0$, H-α' Py); 8.13 (1H, br s, NH); 7.63 (1H, s, CH=); 7.53 (2H, d, $J = 3.3$, H-β Py); 7.33 (2H, t, $J = 7.9$, H-*m* Ph); 7.17 (2H, d, J = 8.4, H-*o* Ph); 6.93 (1H, t, J = 7.4, H-*p* Ph). Found, %: C 73.16; H 5.36; N 21.38. $C_{12}H_{12}N_3$. Calculated, %: C 73.10; H 5.58; N 21.32.

1,5-Diphenyl-3-(3-pyridyl)formazan (4a). A diazonium salt solution was obtained first. For this ice (0.5 g) was added to a solution of aniline (0.47 g, 5.08 mmol) in conc. HCl (1 ml) and the mixture was diazotized at <5°C by adding dropwise a solution of $NaNO_2$ (0.35 g, 5.1 mmol) in water (1 ml). Acetic acid (1 ml) was added to a solution of hydrazone **3a** (1.00 g, 5.1 mmol) in pyridine (8 ml) and methanol (4 ml) and the solution of diazonium salt was added dropwise with vigorous stirring and cooling at such a rate that the temperature did not exceed 5°C. Constant foaming was observed during the reaction. After the end of adding diazonium salt the mixture was stirred at 5°C for a further 30 min. The mixture was then heated at 50-60°C for a short time and cooled to room temperature. Water (10 ml) was added to the mixture and 2 M NaOH solution was added dropwise with constant stirring to pH 9. The resulting claret-colored viscous solid was filtered off, suspended in water (10 ml), and filtered off once again. The operation was repeated a further 2 times. After drying in vacuum the solid was recrystallized from ether. Formazan **4a** (0.78 g, 51%) was obtained as a dark claret powder of mp 169°C (from ether). ^1H NMR spectrum, δ, ppm (*J*, Hz): 15.66 (1H, s, NH); 9.40 (1H, s, H-α' Py); 8.62 (1H, d, *J* = 4.6, H-α Py); 8.39 (1H, dd, *J* = 8.3, *J* = 1.4, H-γ Py); 7.80 (4H, d t, *J* = 8.0. *J* = 1.1, H-*o* Ph); 7.55 (4H, tt, *J* = 7.5, *J* = 1.2, H-*m* Ph); 7.36-7.45 (1H, m, H-β Py); 7.33 (2H, t t, *J* = 7.8. *J* = 1.6, H-*p* Ph). Found, %: C 71.46; H 4.86; N 23.41. $C_{18}H_{15}N_5$. Calculated, %: C 71.76; H 4.98; N 23.26.

1,5-Diphenyl-3-(4-pyridyl)formazan (4b) was obtained analogously to the previous compound **4a** from hydrazone **3b** (1.72 g, 8.73 mmol) and aniline (0.81 g, 9.00 mmol) as a dark claret powder. Yield was 1.00 g (38%) of mp 192°C (from ether) (lit. mp 185-187°C [26]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 15.80 (1H, s, NH); 8.66 (2H, d, *J* = 4.5, H-α Py); 8.03 (2H, d, *J* = 4.6, H-β Py); 7.72 (4H, d, *J* = 8.0, H-*o* Ph); 7.49 (4H, t, *J* = 7.8, H-*m* Ph); 7.34 (2H, t, *J* = 7.3, H-*p* Ph). Found, %: C 71.76; H 4.86; N 23.70. $C_{18}H_{15}N_5$. Calculated, %: C 71.76; H 4.98; N 23.26,

1,3,5-Triphenylformazan (4c) was obtained analogously from benzaldehyde phenylhydrazone (1.72 g, 8.73 mmol) and aniline (0.81 g, 9.00 mmol) as a dark claret powder. Yield was 1.32 g (50%) of mp 176°C (from ether) (lit. mp 175-176°C [58]).

2,3-Diphenyl-5-(3-pyridyl)tetrazolium Trichlorocobaltate(II).MeCN (5a). A solution of cobalt chloride hexahydrate (24 mg, 0.100 mmol) in ethanol (4 ml) was slowly poured into a solution of formazan **4a** (30 mg, 0.100 mmol) in acetonitrile (4 ml). After keeping in a closed vessel for 20 days dark blue crystals of complex **5a** separated from the blue solution. The crystals were washed with ether and air dried. Complex **5a** (21 mg, 91%) was obtained having mp 293°C. Found, %: C 47.30; H 3.25; N 16.51. $C_{20}H_{17}Cl_3CoN_6$. Calculated, %: C 47.38; 3.36; N 16.58.

Crystals of **5a** were grown from an acetonitrile–ethanol mixture.

2,3-Diphenyl-5-(4-pyridyl)tetrazolium Trichlorocobaltate(II) (5b). Ethanol (2 ml) was added slowly to a solution of formazan **4b** (30 mg: 0.100 mmole) in methylene chloride (4 ml) in such a way that the ethanol formed a uniform layer above the layer of formazan solution. A solution of cobalt chloride hexahydrate (24 mg, 0.100 mmol) in ethanol (3 ml) was added to the ethanol layer and the whole was left for 14 days. On mixing the solutions dark red needles with a green iridescence were precipitated. The needles were washed with ether and dried in the air. Complex **5b** (20 mg, 87%) was obtained with mp 315°C. Found, %: C 46.46; H 2.63; N 15.02. $C_{18}H_{14}Cl_3CoN_5$. Calculated, %: C 46.40; H 3.01; N 15.04.

2,3-Diphenyl-5-(3-pyridyl)tetrazolium Trichlorocuprate(II) (6a). Ethanol (3 ml) was added slowly to a solution of formazan **4a** (50 mg, 0.166 mmol) in methylene chloride (5 ml) in such a way that the ethanol formed a uniform layer above the layer of formazan solution. A solution of copper chloride dihydrate (28 mg, 0.166 mmol) in ethanol (4 ml) was added to the ethanol layer. After 7 days pink crystals grew at the separation boundary of the solutions and the red solution of formazan changed to yellow. The crystals were filtered off, washed with water, and dried in the air. Complex **6a** (35 mg, 92%) was obtained as orange needles with mp 250-251°C. Found, %: C 45.46; H 2.63; N 14.79. $C_{16}H_{14}Cl_3CuN_5$. Calculated, %: C 45.96; H 2.98; N 14.89.

2,3-Diphenyl-5-(4-pyridyl)tetrazolium Trichlorocuprate(II) (6b). Ethanol (3 ml) was added slowly to a solution of formazan **4b** (50 mg, 0.166 mmol) in methylene chloride (5 ml) in such a way that the ethanol formed a uniform layer above the layer of formazan solution. A solution of copper chloride dihydrate (28 mg, 0.166 mmol) in ethanol (4 ml) was added to the ethanol layer and after 7 days pink crystals grew at the separation boundary of the solutions and the formazan solution changed from red to yellow. The crystals were filtered off, washed with ether, and dried in the air. Complex **6b** (33 mg, 84%) was obtained of mp 267-268°C. Found, %: C 46.05; H 2.99; N 14.80. $C_{18}H_{14}Cl_3CuN_5$. Calculated, %: C 45.96; H 2.98; N 14.89. On evaporating the mother liquor in the air yellow monocrystals suitable for X-ray structural analysis were obtained. Crystals of compound **6b** were grown from a methylene chloride–ethanol mixture.

2,3,5-Triphenyltetrazolium Chloride (7). Isoamyl nitrite (110 mg, 0.927 mmol) was added dropwise to formazan **4c** (100 mg, 0.333 mmol) in absolute chloroform (10 ml). A stream of dry gaseous HCl was passed through the solution stirring constantly until the color of the solution did not change first from claret to blue-green and then to reddish brown. The mixture was left to stand for several hours, after which HCl gas was passed for a further short time. The solution was evacuated in vacuum, the oily residue was dissolved in a little amount of ethanol and two volumes of a chloroform-diethyl ether 1 : 1 mixture were added. A white flaky solid was precipitated, which was filtered off, and dried in the air. Product **7** (44 mg, 40%) was obtained with mp 251-253°C (lit. mp 242-243°C [40]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.35 (2H, d, *J* = 6.9, H-*o* $Ph_{(C)}$); 8.24 (4H, d, *J* = 7.9, H-*o* $Ph_{(N)}$); 7.86 (2H, d, *J* = 7.1, H-*m* $Ph_{(C)}$); 7.70-7.82 (7H, *m*, H-*p* $Ph_{(C)}$, H-*m* $Ph_{(N)}$, H-*p* $Ph_{(N)}$).

REFERENCES

1. J.-M. Lehn, *Supramolecular Chemistry: Concepts and Prospects* [Russian translation], Izdanie, Novosibirsk (1995).
2. C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2781 (2003).
3. V. Yu. Kukushkin and A. J. L. Pombeiro, *Chem. Rev.*, **102**, 1771 (2002).
4. M. N. Kopylovich, A. J. L. Pombeiro, A. Fischer, L. Kloo, and V. Yu. Kukushkin, *Inorg. Chem.*, **42**, 7239 (2003).
5. V. D. Vreshch, A. N. Chernega, J. A. K. Howard, J. Sieler, and K. V. Domasevitch. *J. Chem. Soc., Dalton Trans.*, 1707 (2003).
6. V. Yu. Kukushkin and A. J. L. Pombeiro, *Inorg. Chim. Acta*, **358**, 1 (2005).
7. I. Hausser, D. Jerehel, and R. Kuhn, *Chem. Ber.*, **82**, 515 (1949).
8. B. I. Buzykin, G. N. Lipunova, L. P. Sysoeva, and L. I. Rusinova, *Chemistry of Formazans* [in Russian], Nauka, Moscow (1992).
9. L. Hunter and C. Roberts, *J. Chem. Soc.*, 820 (1941).
10. L. Hunter and C. Roberts, *J. Chem. Soc.*, 823 (1941).
11. A. Siedle and L. Pignolet, *Inorg. Chem.*, **19**, 2052 (1980).
12. Kh. M. Severo, B. E. Zaitsev, V. I. Ivlieva, G. V. Avramenko, T. S. Kolodina, and B. I. Stepanov, *Zh Neorg. Khim.*, **29**, 2314 (1984).
13. A. S. Batsanov, Yu. T. Struchkov, Kh. M. Severo, B. E. Zaitsev, and V. I. Ivlieva, *Zh. Neorg. Khim.*, **32**, 93 (1987).
14. H. Irving, J. B. Gill, and W. R. Cross, *J. Chem. Soc.*, 2087 (1960).
15. D. J. Dale, *J. Chem. Soc., A*, 278 (1967).
16. I. N. Polyakova, Z. A. Starikova, O. P. Sulim, and G. N. Lipunova, *Kristallogr.*, **37**, 653 (1992).
17. C. Banciu, *Rev. Roum. Chim.*, **44**, 3 (1999).
18. K. Ohashi, K. Kurosawa, and K. Yamamoto, *Bunseki Kagaku*, **32**, E361 (1983).
19. G. N. Lipunova, E. I. Krylov, N. P. Bednyagina, and V. A. Sharov, *Zh. Obshch. Khim.*, **39**, 1293 (1969).
20. I. I. Shevelina, L. P. Sidorova, V. N. Podchainova, and N. P. Bednyagina, *Zh. Obshch. Khim.*, **42**, 2546 (1972).
21. R. I. Ogloblina, N. P. Bednyagina, and A. D. Garnovskii, *Zh. Obshch. Khim.*, **40**, 367 (1970).
22. N. N. Gumileva, L. F. Lipatova, G. N. Lipunova, and N. P. Bednyagina, *Khim. Geterotsikl. Soedin.*, 774 (1974). [*Chem. Heterocycl. Comp.*, **10**, 671 (1974)].
23. N. N. Gumelina, G. N. Lipunova, N. P. Bednyagina, and S. L. Mertsalov, *Zh. Org. Khim.*, **5**, 1108 (1977).
24. N. P. Bedyagina and G. N. Lipunova, *Khim. Geterotsikl. Soedin.*, 877 (1969). [*Chem. Heterocycl. Comp.*, **5**, 652 (1969)].
25. A. D. Garnovskii, N. P. Bednyagina, L. I. Kuznetsova, V. T. Panyushkin, O. A. Osipov, R. I. Ogloblina, and A. P. Novikova, *Zh. Neorg. Khim.*, **14**, 1576 (1969).
26. H. J. Cottrell, D. L. Pain, and R. Slack, *J. Chem. Soc.*, 2968 (1954).
27. E. Suenaga, *Yakugaku Zasshi*, **79**, 803 (1959); *Chem. Abs.*, 21938 (1959).
28. W. Ried and H. Gick, *Ann. Chimie (Paris)*, **581**, 16 (1951).
29. J. N. Ashley, B. M. Davis, A. W. Nineham, and R. Slack, *J. Chem. Soc.*, 3881 (1953).

30. A. Eibner and K. Hofmann, *Chem. Ber.*, 3011 (1904).
31. W. Ried, *Angew. Chem.*, **64**, 391 (1952).
32. M. Seyhan, *Chem. Ber.*, 646 (1955).
33. L. Mester, *J. Am. Chem. Soc.*, 4301 (1955).
34. S. V. Shinkorenko, G. T. Pilyugin, and G. B. Finkel', *Zh. Obshch. Khim.*, **42**, 2551 (1972).
35. M. Seyhan and W. C. Fernelius, *J. Am. Chem. Soc.*, 217 (1957),
36. E. S. Karavaeva, N. P. Bednyagina, T. A. Sharkova, and I. I. Mudretsova, *Khim. Geterotsikl. Soedin.*, 1420 (1975). [*Chem. Heterocycl. Comp.*, **11**, 1208 (1975)].
37. K. Mukai, M. Matsubara, H. Hisatou, Y. Hosokoshi, K. Inoue, and N. Azuma, *J. Phys. Chem.(B),* **106**, 8632 (2002).
38. M. Kishita, Y. Mito, and M. Kubo, *Aust. J. Chem.*, **11**, 309 (1958).
39. M. I. Ermakova, E. I. Krylov, and I. Ya. Postovskii, *Zh. Obshch. Khim.*, **30**, 849 (1960).
40. R. Price, *J. Chem. Soc. A*, 3378 (1971).
41. M. Predota, V. Petricek, Z. Zak, T. Glowiak, and J. Novotny, *Acta Crystallogr,*. **C47**, 738 (1991).
42. R. Luboradzki, W. Kozminski, and L. Stefaniak, *J. Crystallogr. Spectrosc. Res.*, **23**, 133 (1993).
43. R. Luboradzki, J. Lipkowski, W. Kozminski, and L. Stefaniak, *J. Chem. Crystallogr.*, **25**, 29 (1995).
44. V. M. Divjakovic, V. M. Leovac, B. Ribar, G. Argay, and A. Kalman, *Acta Crystallogr. B*, **38**, 1738 (1982).
45. G. A. Bogdanovic, V. B. Medakovic, L. S. Vojinovic, V. I. Cesljevic, V. M. Leovac, A. Spasojevic-de Bire, and S. D. Zaric, *Polyhedron*, **20**, 2231 (2001).
46. M. Bloy, M. Kretschmann, S. Scholz, M. Teichert, and U. Diefenbach*, Z. Anorg. Allg. Chem.*, **626**, 1946 (2000).
47. Hao Xu, Jinyu Ji, Zhongzhi Wu, Jianzhong Zou, Zheng Xu, and Xiaozeng You, *Polyhedron*, **12**, 2261 (1993).
48. Tian-Tian Pan and Duan-Jun Xu, *Acta Crystallogr.,* **E60**, m56 (2004).
49. C. M. Armstrong. P. V. Bernhardt, Piao Chin, and D. R. Richardson, *Eur. J. Inorg. Chem.*, 1145 (2003).
50. F. E. Hahn, D. Scharn, and T. Lugger, *Z. Kristallogr.-New Cryst. Struct.*, **212**, 472 (1997).
51. A. Skorska, B. J. Oleksyn, and J. Sliwinski, *Enantiomer*, **7**, 295 (2002).
52. P. Pytel, B. J. Oleksyn, and J. Sliwinski, *Enantiomer*, **6**, 201 (2001).
53. P. C. Healy, C. Pakawatchai, and A. H. White, *Aust. J. Chem.*, **38**, 669 (1985).
54. J. M. Savariault, J. Galy, J. M. Gutierrez-Zorilla, and P. Roman, *J. Mol. Struct.*, **176**, 313 (1988).
55. R. Clerac, F. A. Cotton, S. P. Jeffery, C. A. Murillo, and Xiaoping Wang, *Dalton Trans.*, 3022 (2003).
56. A. V. Navlyuk, V. N. Davydov, and M. G. Mys'kiv, *Koordin. Khim.*, **27**, 917 (2001).
57. M. Lacan, I. Tabakovic, and Z. Cecovic, *Tetrahedron*, **30**, 2991 (1974).
58. A. M. Mattson, C. O. Jensen, and R. A. Duther, *J. Am. Chem. Soc.*, **70**, 1284 (1948).