Chemistry of Heterocyclic Compounds, Vol.35, No. 8, 1999

SYNTHESIS, STRUCTURE, SPECTRAL, AND ELECTROCHEMICAL PROPERTIES OF THE Au(I) COMPLEX WITH 5-METHOXY-8-(N-PICRYLAMINO)QUINOLINE

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The synthesis of a gold(I) chelate complex obtained from an autocomplex of the picryl series with a quinoline-containing donor fragment is described. The crystal structure was established by X-ray analysis, the spectral and electrochemical properties were studied. The molecules of the complex obtained have a conformation in which both o-NO_2 groups of the picryl fragment participate in intramolecular charge transfer by contact.

A study of the properties and reactivity of those organic compounds, which are charge transfer complexes (CTC) either intermolecular or intramolecular (autocomplexes), is a necessary step in the investigation of mechanisms of several biochemical processes. The idea of using CTC theory in biochemistry, expressed for the first time in [1,2], has subsequently developed significantly. The formation of charge transfer complexes is assumed in many biological conversions, particularly in processes linked with energy transformation in the living cell. The fact that the most important low molecular components of which every cell ultimately consists, *viz.* nucleotides, porphyrins, flavins, quinones, certain protein aminoacids, etc., possess a series of general properties (comparatively low electronic excitation energy, low ionization potential, and high electron affinity), indicates that all these reactive chemical groups are destined to participate in processes linked with charge transfer. The study of such processes or model systems has enabled clarification of the muscle contraction mechanisms and of the carcinogenic substances action on the cell. Charge transfer is of particular interest in connection with the possible role of donor–acceptor complexes in such vitally important phenomena as tissue respiration, photosynthesis, and the interaction of proteins with coenzymes and substrates. The formation of charge transfer complexes between flavin and nicotinamide-containing coenzymes has been established [3]. In the course of studying carcinogenesis [4], it was suggested that the first stage of the development of malignant tumors is the formation of positive charges on the DNA spiral as a result of fission of electrons by foreign acceptors. This leads to the generation of repulsive forces between the internal strands of the DNA molecule and consequently to their separation. There are data [5] according to which the energy transfer process in a cytochrome chain on respiration is linked with the formation of CTC between purines acting as electron donors and riboflavin (vitamin B2) as an electron acceptor.

The role of microelements, ions of several metals necessary for the normal activity of protein molecules, is widely known. Ions of certain metals (Cu, Mn, Mg, Zn, etc.) are located in the active centers of many enzymes. The functioning of the hemoglobin molecule, such as its ability to transfer a large amount of molecular oxygen, is determined firstly by the activity of its iron-porphyrin centers [6]. Some gold-containing complexes have been used as effective drugs in oncology or for the treatment of rheumatoid arthritis [7]. In this connection molecular

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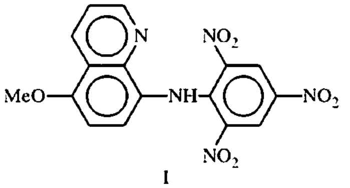
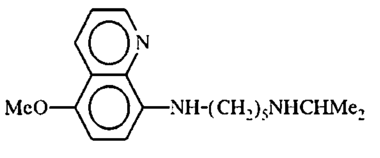
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1028-1035, August, 1999. Original article submitted May 20, 1999.

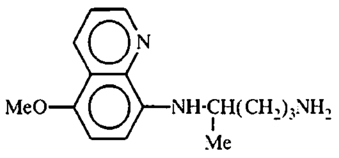
autocomplexes may be of undoubted interest as starting ligands for obtaining chelate complexes, compounds particularly promising for studying the nature of the bond in complicated multicenter donor–acceptor systems containing a metal bound in a complex.

In a series of reports [8-11] we previously described the synthesis and the results of a physico-chemical investigation of donor–acceptor interactions in several autocomplexes of the picryl type having donor fragments differing in nature and strength. The autocomplex 5-methoxy-8-(N-picrylamino)quinoline (I) with a heterocyclic quinoline-containing donor fragment was described among the compounds synthesized.

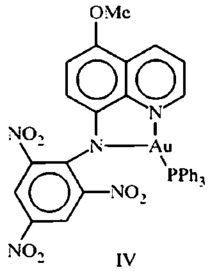

I

The same methoxyquinolinamino fragment is the basic structural synthon for a series of widely used antimalarial drugs such as pentaquine (II) and primaquine (III) [12].


II


III

In the present investigation the previously obtained autocomplex I was used for the first time as a ligand for the synthesis on its base of chelate compound with Au(I) IV. Up to the present time organic autocomplexes have not been introduced into chelate-forming reactions.


IV

Chelate IV was synthesized by the reaction of ligand I with tris(triphenylphosphinegold)oxonium fluoroborate. The gold complex synthesized was a dark, almost black, finely crystalline substance melting with decomposition above 200°C. Its composition and structure were confirmed by data of elemental analysis and physicochemical investigations.

Important results were obtained when studying the spectral properties of complex IV compared with the spectra of the initial ligand I. The assignment of bands in the electronic spectra, as for the initial ligand [8], was carried out by the empirical method [13] based on the principle of breaking down the structure of the molecule into polar chromophoric groupings. The given method enables to determine the number of bands and their assignment in the electronic spectra of a donor–acceptor type polysubstituted benzene without quantum chemical calculations. Values of the wavelengths λ_{max} and molar absorption characteristics (ε) of the charge transfer (CT) bands for the compounds being studied are given in Table 1. Data were obtained experimentally and assignments were made by the method of [13].

TABLE 1. Electronic Spectra of the Studied Compounds in Chloroform (concn. 2×10^{-4} M)

Compound	Charge transfer bands, λ_{max}, nm (ε)			
	CT NHD^{p-NO_2}	CT NHD^{o-NO_2}	ICT by contact	
			I	II
I	290 (7700)	370 (11000)	425 (14770)	
IV	250-260 (42180)	288-290 (14060)	360-370 (11950)	485 (21090)

In the electronic spectrum of the Au complex the same three CT bands were present as in the initial ligand and must be assigned in the following manner (see Table 1). The short wave band corresponds to a transfer from the donor quinoline-containing fragment to the *p*-NO_2 group (*para* band). Then in order of reducing excitation energy the *ortho* band follows, reflecting transfer from the donor group to the *o*-NO_2 group, which in the initial ligand was linked by an intramolecular hydrogen bond with the bridge NH. Finally there is a band for the intramolecular charge transfer effected by contact (ICT-I). The latter is a consequence of the interaction of the spatially close donor fragment and the second *ortho*-nitro group. According to X-ray data this group is pulled up from the plane of the acceptor picryl ring and should lie over the donor. The observed hypsochromic shift of these bands is caused by a reduction in the strength of the quinoline-containing donor fragment due to chelate formation. Furthermore an additional long wave maximum was present in the spectrum of complex IV at 485 nm, which must also be assigned to charge transfer by contact (ICT-II) but is of a different nature. It reflects a donor–acceptor interaction between the spatially close *ortho*-nitro group, already participating in an *ortho* transfer of the complex molecule ligand portion, and the surface of a phenyl ring of the triphenylphosphine fragment (see Fig. 1).

Electrochemical Investigation. The electrochemical properties of compound I and its aurated derivative, *viz.* complex IV, were investigated in acetonitrile at a platinum electrode in Bu_4NBF_4 as base electrolyte relative to Ag/AgCl/KCl sat. by cyclic voltamperometry and a rotating disk electrode.

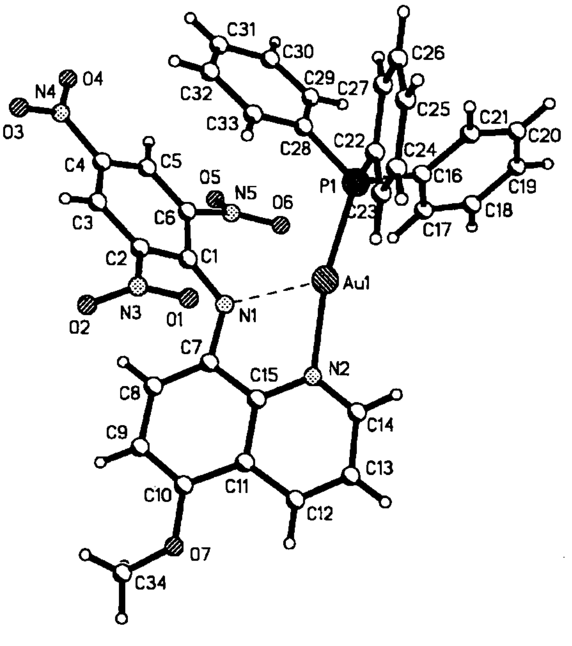
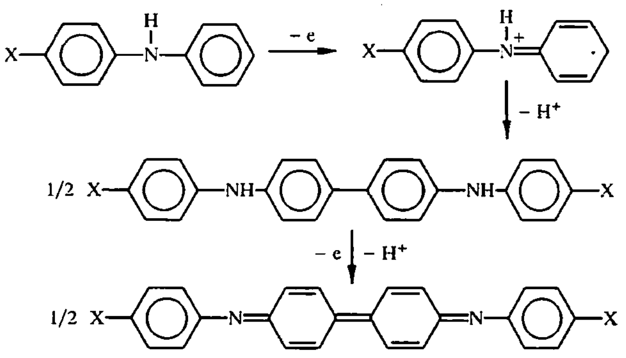


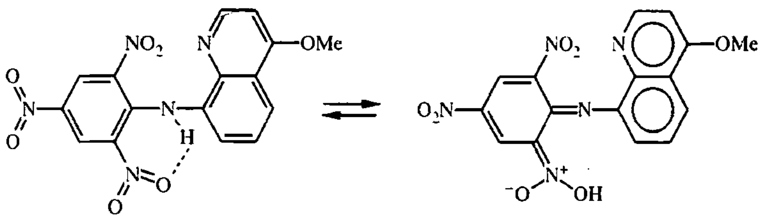
Fig. 1. Molecular structure of [5-methoxy-8-(N-picrylamino)quinolinato](triphenylphosphine)gold (I).

Compounds I and IV were oxidized in two one-electron irreversible stages (1.35 and 2.11 V for I and 1.19 and 1.89 V for IV). It is known from the literature [15], that the oxidation of *para*-mono-substituted secondary aromatic amines leads to the formation of N,N'-diarylbenzidines which are oxidized to N,N'-diaryldiphenylquinone diimines.



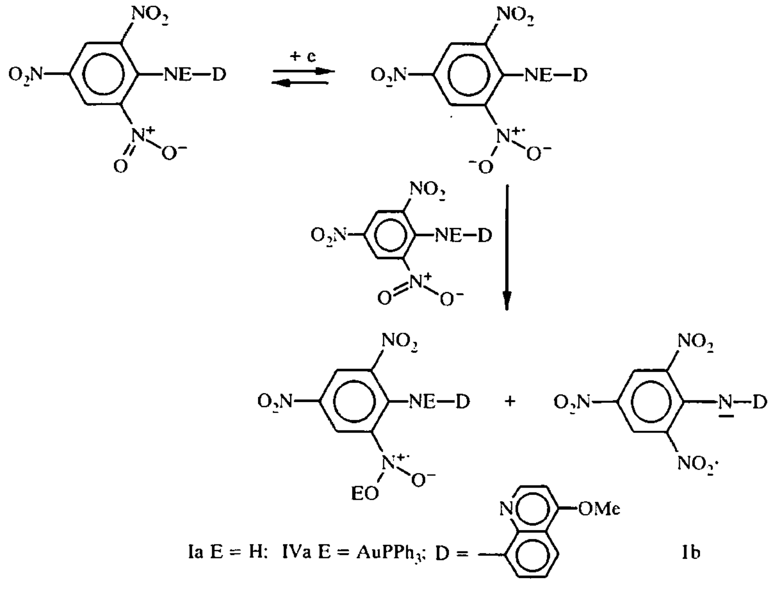
A similar mechanism may also be suggested for the oxidation of compounds I and IV, the difference between which is only that after transfer of the second electron in compound I fission of the NH group proton occurs, and in complex IV fission of the AuPPh$_3$ group occurs. The presence in compound IV of the Au(I) atom instead of proton must show up in the values of E^{ox1} and particularly in E^{ox2}. Consequently, according to our data, transfer of the first electron to compound IV compared with transfer of an electron to compound I is eased by 170 mV, and the second electron by 220 mV which may serve as an indirect confirmation of the proposed oxidation mechanism.

It was interesting to carry out the reduction of these compounds. For both compounds the first reduction stage potentials lie in the region of the reduction potentials for picramide, *viz.* -0.50 V for I and -0.56 V for IV (according to our data the reduction potential of picramide is -0.50 V). However the reduction of compounds I and IV, unlike that of picramide, is an electrochemically irreversible process (the number of transferable electrons in the first electrochemical stage was 0.4-0.6). Previously [10] we reported the reversible one-electron reduction and oxidation of ligand I. According to our data compounds of this type are capable of existing in several crystalline modifications differing markedly in crystalline form and color (from yellow to dark red). We assume that this effect is connected with the existence of the molecule in benzenoid and quinonoid forms.



If both the forms indicated exist separately in solution and convert from one to the other fairly slowly, then the electrochemical behavior observed on dissolving crystals of different color will also be different. A separate communication will be devoted to the problem of the connection between electrochemical behavior and crystalline form.

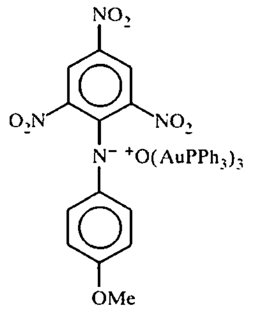
It is known [16-20] that if a heteroatom–proton bond is found in a molecule together with an electron-accepting group as strong as NO$_2$, then fission of such bonds as N–H, O–H, and S–H occurs with evolution of hydrogen and the process becomes electrochemically irreversible. The same probably occurs in the reduction of compounds I and IV.



Ia E = H: IVa E = AuPPh$_3$; D =

Ib

In order to confirm the fact that reduction leads to anion Ib we studied the electrochemical behavior of salt V, which was synthesized specially.



V

This salt, the synthesis of which will be reported later, was oxidized under our conditions in a one-electron step, chemically reversible, electrochemically quasireversible ($E_{pa} - E_{pc}$ = 140 mV, $i^a/i^c = 1$) at a potential of 0.57 V. If the direction of polarization is changed to anodic after the first reduction peak of compound I, an oxidation peak at a potential of 0.56 V is observed on the cyclic voltamperometric curve, close to the oxidation potential of compound V (0.40 V for compound IV).

After the first peak for compounds I and IV a further two reduction peaks were observed at more cathodic potentials, which were practically independent of the nature of the group E at -1.34 and -1.81 V for I and -1.33 and -1.78 V for IV. Probably the second cathodic wave corresponds to further reduction of Ia or IVa.

At significantly more cathodic potentials of the third wave, probably the reduction of the quinoline fragment occurs, since the reduction of quinoline under conditions close to the conditions of our experiments (MeCN, Et_4NBF_4) proceeds at a potential of -1.60 V [21].

X-Ray Structural Investigation. An X-ray structural investigation of compound IV was carried out in order to establish its structure (details will be published separately).

The molecular structure of compound IV is shown in Fig. 1. In difference to the proton in the initial organic molecule forming a chemical bond with the amino nitrogen atom, the gold(I) atom of the cationic fragment AuPPh3 forms a chemical bond with the quinoline $N_{(2)}$ nitrogen atom and not with the amino $N_{(1)}$ atom. The gold(I) atom has the usual T-shaped coordination. The main bond lengths $Au_{(1)}-N_{(2)}$ 2.122(8) Å and $Au_{(1)}-P_{(1)}$ 2.231(3) Å have the usual values. The distance between $Au_{(1)}$ and the amino $N_{(1)}$ atom of 2.620(8) corresponds to a weak interaction (secondary bond). Almost the same distance [2.627(9) Å], also corresponding to a secondary Au–N_{qu} bond, was observed previously in (8-S_{qu})$AuPPh_3$ (8-Squ is 8-mercaptoquinolinate) [22]. The valence angle $N_{(2)}$–$Au_{(1)}$–$P_{(1)}$ was equal to 168.4(2)°, and the $Au_{(1)}$–$P_{(1)}$ bond is bent away from the $N_{(2)}$ atom. This indicates a small rehybridization of the gold atom bond under the influence of the secondary $Au_{(1)}$...$N_{(1)}$ bond.

The formation of a main bond by the gold atom with the quinoline nitrogen atom is the most interesting result of auration of the corresponding organic compound showing the difference in behavior of the isoelectronic and seemingly isolobal particles -H^+ and $AuPPh_3^+$. The structure IV found leads to a significant redistribution of bonds in both the trinitroaniline and in the quinoline fragments compared with the corresponding fragments of the initial ligand I. According to the data of the Cambridge Structural Data Bank (CSDB, winter 1999 version) [23] in trinitroaniline derivatives the N_{amine}–C_{ar} bond length is 1.32-1.41 Å, the lengths of two C–C bonds at the key carbon atom carrying an amino group are 1.39-1.44 Å, the valence angle at the key carbon atom is 111-117°, with average values equal to 1.36, 1.42 Å, and 114° respectively. In the structure of compound IV the $N_{(1)}$–$C_{(1)}$ bond of 1.30(1) Å is significantly shorter, but the $C_{(1)}$–$C_{(2)}$ and $C_{(1)}$–$C_{(6)}$ bonds (both 1.47 Å) are significantly longer than the corresponding values in organic trinitroaniline derivatives. In addition in the molecule IV the $C_{(2)}$–$C_{(3)}$ [1.37(1) Å] and $C_{(5)}$–$C_{(6)}$ (1.35 Å) bonds in the benzene ring are significantly shorter than the $C_{(3)}$–$C_{(4)}$ and $C_{(4)}$–$C_{(5)}$ bonds [both 1.39(1) Å]. Such a bond distribution corresponds to a contribution of a *para*-quinonoid structure. It is also characteristic of substituted trinitroanilines (CSDB data). However in compound IV the contribution of a quinonoid structure is significantly more distinct. The deepening of the color (transition from dark red to practically black) occurring on auration of the initial ligand I is probably determined by this.

Both nitro groups in the positions *ortho* to the amino group are significantly bent out from the plane of the benzene ring (43.4 and 38.1°) due to steric interactions with the aurated quinoline fragment. The nitro group in the *para* position is coplanar with the plane of the benzene ring (178.0°).

Conjugation of the formal double bond ($N_{(1)}$–$C_{(1)}$) and the benzene ring leads to the fact that in the $C_{(2)}C_{(1)}N_{(1)}C_{(7)}$ fragment no over-large torsion was observed relative to its central bond (27.0°). In addition the torsion angle $C_{(1)}$–$N_{(1)}$–$C_{(7)}$–$C_{(8)}$ (41.7°) indicates that the unshared electron pair of the $N_{(1)}$ nitrogen atom is effectively removed from conjugation with the quinoline fragment. As a result the observed $N_{(1)}$–$C_{(7)}$ bond length of 1.44 Å proved to be greater than the length of the corresponding bond in amino-quinoline derivatives cited in the CSDB, where it varies within the limits 1.36-1.43 Å with a mean value of 1.388 Å. The remaining bond lengths in the quinoline fragment of complex IV underwent certain changes (compared with those in quinoline derivatives), caused by both the absence of conjugation of the amino nitrogen atom with the quinoline fragment and by the presence of gold on the quinoline nitrogen atom. However the main tendency of bond distribution in the quinoline nucleus is retained in the molecule of IV, though there is some localization of double bonds between $C_{(7)}$–$C_{(8)}$ and $C_{(9)}$–$C_{(10)}$, and $C_{(12)}$–$C_{(13)}$ and $C_{(14)}$–$N_{(2)}$. The most significant difference in the N-aurated quinoline is the $C_{(14)}$–$N_{(2)}$–$C_{(15)}$ valence angle, which in (IV) is significantly greater [121.4(8)°] than in the corresponding organic derivatives, where it varies within the limits 117-119° with an average value of 117.7°.

EXPERIMENTAL

The UV spectra were measured on a Cary 219 spectro-photometer in chloroform at solution concentrations of 2×10^{-4} M.

[5-Methoxy-8-(N-picrylamino)quinolinato](triphenylphosphine)gold (IV). Water (5 drops) and potassium carbonate (0.1 g) were added to a solution of 5-methoxy-8-(N-picrylamino)quinoline (0.13 g, 0.34 mmol) in THF (5 ml) purified from peroxides. After 5 min tris-(triphenylphosphinegold)oxonium fluoroborate (0.17 g, 0.11 mmol) and THF (3 ml) were added to the reaction mixture. After 15 min the bright solid oxonium salt had dissolved and a dark precipitate separated from the reaction mixture. The reaction mixture was dried by adding potassium carbonate, the solid was filtered off, and washed on the filter with THF and ether until extracts were colorless. The solid was dissolved in chloroform, the solution filtered, and precipitated with petroleum ether. Fine, almost black crystals (0.16 g) were obtained. Additional substance (0.07 g) was isolated from the filtrate and the organic extracts. Total yield was 0.23 g (79%); mp 210°C (with decomposition). The compound dissolved readily in $CHCl_3$, THF, poorly in ether, alcohol, and hexane. Crystals were grown for X-ray analysis from a mixture of $CHCl_3$–ether–hexane, 1:1:5. Found, %: C 48.19; H 2.91; N 8.31. $C_{34}H_{25}AuN_5O_7P$. Calculated, %: C 48.41; H 2.98; N 8.30.

Acetonitrile was purified by sequential treatment with CaH_2, a mixture of H_2SO_4/KNO_3, and P_2O_5. Electrochemical investigations of complexes were carried out in acetonitrile in the presence of Bu_4NF_4 (0.05 M) at a platinum electrode. Potential was measured relative to a silver chloride electrode. Cyclic voltamperometry was used with a rotating disk electrode. A PI-50 1.1 potentiostat was used for the electrochemical investigations. All measurements were carried out in an atmosphere of argon.

The authors are grateful to the Russian Fund for Fundamental Investigations for financial support of the present study (Project Nos. 98-03-33142 and 97-03-32920a).

REFERENCES

1. A. Sent-D'erd'i, *Bioenergetics* [in Russian], Fizmatgiz., Moscow (1960), 155 pp.
2. A. Sent-D'erd'i, *Introduction to Submolecular Biology* [in Russian], Nauka, Moscow (1964), 138 pp.
3. G. Radda and M. Calvin, *Biochemistry*, **3**, 384 (1964).
4. A. Pullman and B. Pullman, *Adv. Cancer Res.*, **3**, 117 (1955).
5. L. A. Blyumenfel'd, *Problems of Biological Physics* [in Russian], Nauka, Moscow (1977), 336 pp.
6. M. Weissbluth, *Structure and Bonds* [Russian translation], Mir, Moscow (1969), p. 11.
7. T. M. Simon, D. H. Kunishima, G. J. Vilbert, and A. Lorber, *Cancer*, **44**, 1965 (1979).
8. I. G. Il'ina, O. V. Mikhalev, and V. M. Potapov, *Organic Semiconductor Materials* [in Russian], Perm State University, Perm (1984), Part 9, p. 102.
9. I. G. Il'ina, E. V. Ivanova, O. V. Mikhalev, and V. M. Potapov, *Electronics of Organic Materials* [in Russian], Nauka, Moscow (1985), p. 228.
10. K. P. Butin, I. G. Il'ina, A. A. Moiseeva, and O. A. Reutov, *Zh. Obshch. Khim.*, **62**, 188 (1992).
11. I. G. Il'ina, E. V. Ivanova, L. D. Ashkinadze, S. V. Zabaznova, and K. P. Butin, *Izv. Russ. Akad. Nauk, Ser. Khim.*, No. 5, 1188 (1996).
12. M. Goodman and F. Morehouse, *Organic Molecules in Action*, Gordon and Breach, New York (1972).
13. E. E. Milliaresi, V. E. Ruchkin, T. I. Orlova, and V. V. Efremov, *Dokl. Akad. Nauk SSSR*, **205**, 353 (1972).
14. G. V. Gridunova, V. N. Petrov, Yu. T. Struchkov, I. G. Il'ina, and O. V. Mikhalev, *Kristallografiya*, **35**, 54 (1990).
15. D. Serve, *Electrochim. Acta*, **21**, 1171 (1976).
16. S. G. Mairanovskii, I. M. Sosonkin, and T. K. Ponomareva, *Elektrokhimiya*, **14**, 567 (1978).
17. S. G. Mairanovskii, *Catalytic and Kinetic Waves in Polarography* [in Russian], Nauka, Moscow (1966), p. 113.
18. J. W. A. M. Janssen and C. R. Kruse, *Heterocycles*, **10**, 1055 (1973).
19. J. J. Gallo and C. R. Pasqualucci, *J. Org. Chem.*, **29**, 862 (1964).
20. L. I. Bagal and M. S. Pevzner, *Khim. Geterotsikl. Soedin.*, No. 4, 558 (1970).
21. C. Parkanyi and R. Zahradnic, *Bull. Soc. Chim. Belg.*, **73**, 57 (1964).
22. L. G. Kuz'mina, N. V. Dvortsova, O. Yu. Burtseva, M. A. Porai-Koshits, E. I. Smyslova, and K. I. Grandberg, *Metalloorg. Khim.*, **3**, 364 (1990).
23. F. H. Allen and O. Kennard, *Chem. Design Autom. News*, **8**, 11 (1993).